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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS: CRITICAL ASSESSMENT REVIEW PAPERS

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NOTICE

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

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PREFACE

The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers public review draft, is a technical review document in two volumes, prepared and released for a 90-day period of public technical comment. The Environmental Protection Agency will develop an interpretive summary, The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document, based upon the content of the Review Papers and the public comments.

The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers was requested by the Clean Air Scientific Advisory Committee (CASAC) of EPA's Science Advisory Board and will be reviewed by that committee. The CASAC is comprised of independent scientists who are quite knowledgeable in matters pertaining to atmospheric pollution and its effects. These scientists will evaluate the scientific adequacy of the Critical Assessment Document. As part of this evaluation, the CASAC considers the comments and criticisms of the general public and scientific community as they pertain to scientific issues and questions. (Although the science of an issue may obviously have implications for policy decisions, matters of policy per se are not in the province of the document.) This review process is essential to developing a scientifically unimpeachable assessment.

The document's original charge was to prepare '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.' It was the decision of the editors to provide the following guidelines to the authors writing the Critical Assessment Review Papers to meet this overall objective of the document:

1. Contributions are 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_x Criteria Document is to be minimized.

6. Potential vs known processes/effects is to be clearly noted to avoid misinterpretation.

7. The certainty of our knowledge should be quantified, when possible.

8. Conclusions are to be drawn on fact only.

9. Extrapolation beyond the available data is to 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 reader, to avoid possible misinterpretation of the information presented, is advised to consider and understand these directives before reading.

Again, the document has been designed to address our present status of knowledge relative to the acidic deposition phenomenon and its effects. It is not a Criteria Document; it is not designed to set standards and no connections to regulations should be inferred. The literature is reviewed and conclusions are drawn based on the best evidence available. It is an authored document, and as such, the conclusions are those of the authors after their review of the literature.

The success of the Critical Assessment Review Papers has depended on the coordinated efforts of many individuals. The document involved the participation of over 54 scientists contributing material on their special areas of expertise under the broad headings of either atmospheric processes or effects. Coordination within these two areas has been the responsibility of A. Paul Altshuller and Rick A. Linthurst, the atmospheric and effects section editors, respectively. Overall coordination of the project for EPA is under David A. Bennett's direction. Dr. Altshuller is an atmospheric chemist, past recipient of the American Chemical Society Award in Pollution Control, and recently retired director of EPA's Environmental Sciences Research Laboratory; Dr. Linthurst is an ecologist and serves as Program Coordinator for the Acid Precipitation Program at North Carolina State University. Dr. Bennett is the Director of the Acid Deposition Assessment Staff in EPA's Office of Research and Development and provides liaison between the section editors/contributors and CASAC scientific reviewers.

The United States and Canada in 1980 signed a Memorandum of Intent to seek agreement on transboundary air pollution issues. A number of working groups are compiling technical information to support the negotiations called for by the Memorandum. Although the Critical Assessment Document and the U.S.-Canada working group reports come from different origins, and are intended for different purposes, there is likely to be some overlap in their areas of coverage.

The written materials to follow are contributions from one to eight authors per chapter, integrated by the editors. Approximately 75 scientists, with expertise in the fields being addressed, have participated in reviewing earlier drafts of the chapters. In addition, 200 individuals participated in a public workshop held for the review of these materials in November of 1982. Numerous changes resulted from these reviews, and this document reflects those comments. This is the final public review draft and comments are welcome. However, several guidelines and forms should be used to submit formal comments. Please consult the last section of the volume for details.

ACKNOWLEDGMENTS FROM NORTH CAROLINA STATE UNIVERSITY

The editorial staff wishes to extend special thanks to all the authors of this document. They have been patient and tolerant of our changes, recommendations, and deadlines, leading to this fourth version of the document. These dedicated persons are to be commended for their efforts.

We also wish to acknowledge our Steering Committee, who has been patient with our errors and deadline delays. These people have made major contributions to this product, and actively assisted us with their recommendations on producing this document. Their objectivity, concern for technical accuracy, and support is appreciated. Dr. J. Michael Davis of EPA deserves special thanks, as he directed the initial draft of the document in December of 1981. His concern for clarity of thought and writing in the interest of communicating our scientific knowledge was most helpful. Dr. David Bennett of EPA is specifically recognized for his role as a scientific reviewer, and an EPA staff member who buffered the editorial staff and the authors from the public and policy concerns associated with this document. Dr. Bennett's tolerance, patience, and understanding are also appreciated.

All the reviewers, too numerous to list, are gratefully acknowledged for helping us improve the quality and accuracy of this document. These people were from private, State, Federal, and special-interest organizations. Their concern for the truth, as we know it now, is a compliment to all the individuals and organizations who were willing to deal objectively with this most important topic. It has been a pleasure to see all groups, independent of their personal philosophies, work together in the interest of producing a technically accurate document.

Dr. Arthur Stern is acknowledged for his contribution as a technical editor of the atmospheric sciences early in the document's preparation. He has made an important contribution to the final product.

Finally, EPA is acknowledged for its willingness to give the scientists an opportunity to prepare this document. Its interest, as expressed through the staff and authors, in having this document be an authored document to assist in research planning, is most appreciated. Rarely does a group of scientists have such a free hand in contributing independently to such an important issue and in such a visible way.

THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS:
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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS:
CRITICAL ASSESSMENT REVIEW PAPERS

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Acronym and Abbreviation List

ADI (acceptable daily intake) E-6

AL (Aeronomy Laboratory, NOAA)

δ-ALA (δ-aminolevulinic acid) E-6

ANC (acid neutralizing capacity) E-4

ARL (Air Resources Lab, NOAA)

ARS (Agricultural Research Service, DOA)

BCF (bioconcentration factor) E-6

BLM (Bureau of Land Management, DOI)

BLMS (boundary layer models) A-9

BM (Bureau of Mines, DOI)

BNC (base neutralizing capacity) E-4

BNC aq (aqueous base neutralizing capacity) E-4

BOD (biologic oxygen demand)

BS (base saturation) E-4

BSC (base saturation capacity) E-4

BUREC (Bureau of Reclamation, DOI)

BWCA (Boundary Water Canoe Area)

CANSAP (Canadian Sampling Network for Acid Precipitation)

C_B (base cation level) E-4

CDR (cation denudation rate) E-4

CEC (cation exchange capacity) E-2

CEQ (Council on Environmental Quality)

CSI (calcite saturation index) E-4

CSRS (Cooperative State Research Service, DOA)

DOA (Department of Agriculture)

DOC (dissolved organic carbon) E-4

DOD (Department of Defense)

DOE (Departrment of Energy)

DOI (Department of Interior)

DOS (Department of State)

ELA (experimental lakes area) E-4

ENAMAP (Eastern North America Model of Air Pollutants)

EPA (Environmental Protection Agency)

EPRI (Electric Power Research Institute)

ERDA (Energy Research and Development Agency (defunct)

ESRL (Environmental Sciences Research Laboratory, EPA)

FA (fulvic acid) E-4

FDA (flourescein diacetate) E-2

FEP (free erythrocyte protoporphyrin) E-6

FGD (Flue Gas Desulfurization)

FS (Forest Service, DOA)

FWS (Fish and Wildlife Service, DOI)

GTN (Global Trends Network)

HHS (Department of Health and Human Services)

ILWAS (Integrated Lake Watershed Acidification Study) E-4

LAI (leaf area index) A-7

LIMB (Limestone Injection/Multistage Burner)

LRTAP (Long-Range Transboundary Air Pollution)

LSI (Langelier Saturation Index) E-6

MAP3S (Multi-State Atmospheric Power Production Pollution Study)

MCPS (Mesoscale convective precipitation systems)	A-3
MOI (Memorandum of Intent, U.S.-Canada)	
NADP (National Atmospheric Deposition Program)	
NASA (National Aeronautics and Space Administration)	
NATO (North Atlantic Treaty Organization)	
NBS (National Bureau of Standards, DOC)	
NCAR (National Center for Atmospheric Research)	
NECRMP (Northeast Corridor Regional Modeling Program)	A-2
NOAA (National Oceanic and Atmosperic Administration, DOC)	
NPS (National Park Service, DOI)	
NSF (National Science Foundation)	
NSPS (New Source Performance Standards)	
NTN (National Trends Network)	
NWS (National Weather Service, NOAA)	
OECD (Organization for Economic Cooperation and Development)	
OMB (Office of Management and Budget)	
ORNL (Oak Ridge National Laboratory)	
OSM (Office of Surface Mining, DOI)	
PAN (peroxyacetyl nitrate)	E-3, A-5
PBCF (practical bioconcentration factor)	E-6
PBL (planetary boundary layer)	A-4
PGF (pressure gradient force)	A-3
PHS (Public Health Service)	
RSN (Research Support Network)	
SAC (SO_4 adsorption capacity)	E-4
SEAREX	

SAES (State Agricultural Experiment Station, DOA)

SCS (Soil Conservation Service, DOA)

SURE (Sulfate Regional Experiment, EPRI)

TFE (total fixed endpoint alkalinity) E-4

TIP (total inflection point alkalinity) E-4

TVA (Tennessee Valley Authority)

USGS (United States Geological Survey, DOI)

VOC (Volatile Organic Compounds)

WMO (World Meteorological Organization)

THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-1. INTRODUCTION

(R. A. Linthurst)

1.1 OBJECTIVES

The basic and applied scientific knowledge that can be gained through the study of the acidic deposition phenomenon will undoubtedly advance our understanding of emissions, transport, scavenging, and deposition interactions. This knowledge is essential for a more complete understanding of the causes of acidic deposition and for defining the loadings of acidic and acidifying substances that ultimately interact with the ecosystem. However, it is the perception that acidic deposition may be harming our natural and managed environment that has stimulated world-wide interest. As a result, the effects and/or the potential effects of acidic deposition are the primary motivation for public concern and research activities now designed to learn more about this phenomenon.

The objectives of the effects portion of this document are to define the logic behind the concerns of potential effects, present the support, or lack of support, for these concerns and draw conclusions relative to the effects of acidic deposition based on the best available evidence. Special attention is given to quantitative information on the magnitude and extent of effects. However, it will become evident that placing statistical confidence limits on the data presently available is difficult, and in most instances, impossible. A lack of quantitative cause and effect data, in itself, defines the state of knowledge in many of the research areas.

1.2 APPROACH

An ecosystem approach to the acidic deposition effects issues has been used. Figure 1-1 diagramatically presents a conceptual flow of wet and dry deposition through a forested system. As most of the terrestrial landscape is covered by vegetation, most acidic inputs to a system pass through the canopy or down the stems of plants, to the soil; and finally, over or through the soil to aquatic systems, lakes and/or streams, or into the ground water system. At any point along this pathway, the chemistry of precipitation can be significantly altered. As a result, the complexities of quantifying effects in relation to a chemical dose becomes increasingly difficult.

Direct deposition of acidic and acidifying substances to soils and aquatic systems also occurs. The size of the receiving system of interest, in relation to the size of any other ecosystem component which may alter the deposition chemistry prior to contact, becomes important.

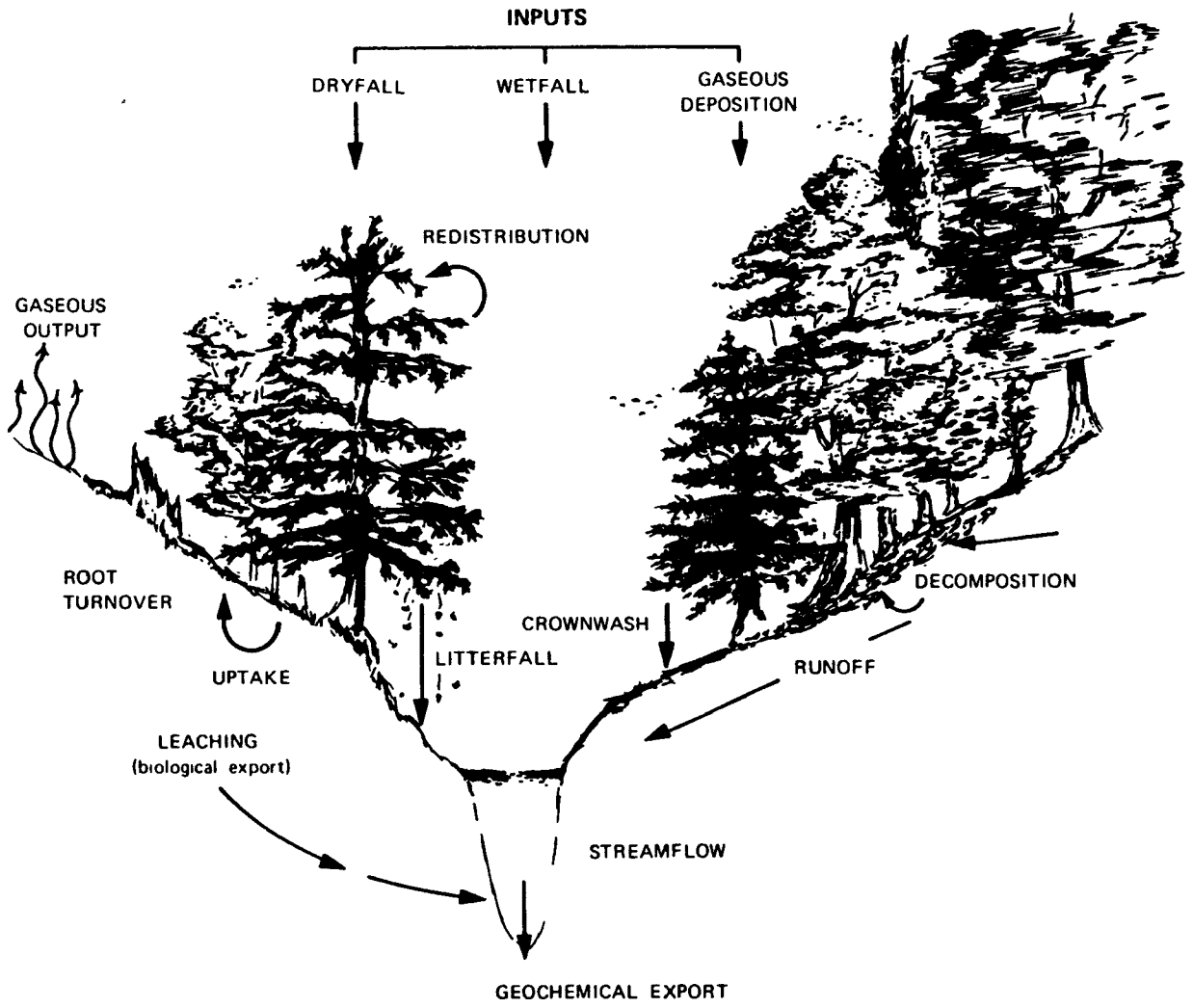

Figure 1-1. Conceptual diagram of wet and dry deposition pathways in an ecosystem context (from Johnson et al. 1982. The effects of acid rain in forest nutrient status. Water Res. Research 18(3):449-461)

A common example of this concept is lake and watershed interactions. Small lakes surrounded by large watersheds are more greatly influenced by those waters which pass through the terrestrial landscape prior to entering the lake; since most of the water received is from the terrestrial pathway. Thus, the effect of the terrestrial system on precipitation/deposition chemistry becomes a variable which ultimately defines the chemistry of the water entering the aquatic systems via this path. If a lake is large in relation to the area it drains, direct deposition to the lake surface becomes increasingly important and the terrestrial component of the system plays a less important role.

Having defined a representative flow path through a system from a chemical perspective, one must recognize that any part of the system which alters the chemistry of precipitation can be affected. Thus, the vegetation, the soil, and the waters may be altered by incoming wet and dry deposition. In addition to these direct alterations of the system components, indirect effects can also occur. Soils, for example, if chemically altered, ultimately affect vegetation responses; soils being the medium in which plants grow. If water chemistry is affected, the biota in those waters are then subject to change. Subsequently, these changes can be of significance to human health since both vegetation and aquatic organisms are part of the human food chain.

This ecosystem perspective, with all its complexities and linkages, should be kept in mind throughout the reading of the chapters. The concept of acidic deposition effects can only be fully understood with this perspective in mind. However, for convenience of presentation, each major ecosystem component has been somewhat artificially separated from the others and subsequently discussed in partial isolation from the holistic approach.

1.3 CHAPTER ORGANIZATION AND GENERAL CONTENT

Because soils affect both vegetation and water, the effects of acidic deposition on soils are discussed first. Secondly, vegetation effects are evaluated from a more direct influence perspective, capitalizing on the knowledge of soils/nutrient cycling, i.e., the potential indirect effects. Next, the water chemistry component of the system is reviewed from a watershed perspective, continuing to rebuild the ecosystem perspective. Having defined the effects of acidic deposition on water chemistry, a discussion of aquatic organism responses to changing water chemistry follows.

Indirect effects on human health and a discussion of acidic deposition on materials, man's structures of art and shelter, are also presented. Although manmade structures are not part of the 'natural ecosystem' concept, they are certainly a part of our landscape and any effects of acidic deposition on them are of concern.

The general content of the chapters is presented briefly below; in the interest of establishing a general sense of what will be found in more detail in the chapters to follow.

1.3.1 Effects on Soil Systems

Soils are natural integrators of ecosystem structure and function. They provide a pathway for water delivered to aquatic systems or for uptake by vegetation. Therefore, in this chapter, emphasis is placed on the natural processes that contribute to acidification, nutrient status, and metal movement in soils. The effects of acidic and acidifying substances on these natural processes is then superimposed as an additive factor, and their contribution to these processes is examined. Natural and managed systems are discussed separately. Reversibility concepts are presented and predictions of changes over time are made after making several assumptions. These sections of the chapter are chemically oriented and some basic soil chemistry is also included.

Nutrient cycling aspects of acidic deposition influences on soils is the primary emphasis of the chapter. Both the chemical and biological components of this process are discussed in detail. The importance of changing nutrient/metal mobilization activity in soils is discussed as it relates to both vegetation response and water chemistry. The soil organisms, their role in nutrient cycling, and the potential and measured effects of acidic deposition are also discussed.

Soils are chemically and biologically complex systems. The effect that acidic deposition will have on such systems is dependent on numerous variables. Because of this complexity and the expectation that potential effects may be long-term, the definitive conclusions one can draw are not as numerous as some might expect.

1.3.2 Effects on Vegetation

Most of the terrestrial landscape is covered by vegetation. Because vegetation collectively includes the primary producers in the food web, its importance to man is without question. Thus, any change in plant productivity, whether it be an increase or decrease, can have significant implications for man's food and fiber system.

The material presented in the vegetation section discusses a diverse range of acidic deposition/plant interactions. These include direct effects on the smallest scale; i.e. physiological and cell/leaf response, to the gross scale of forest and crop productivity. The potential effects of acidic deposition, plant, and environmental condition interactions, leading to quantification of plant response, are presented. Special attention is given to the concept of cumulative effects on forests over time and the lack of data in this field of acidic deposition effects at the present time. The effects of vegetation on deposition chemistry, as it passes through/over vegetation to soils, is not discussed in detail.

Plants are subject to more environmental stress factors than any other component of the system. Their fixed position in the system causes them to be exposed regularly to changes in air quality, precipitation chemistry, soil physiochemical characteristics, disease

influence, and climate, to which their limited avoidance/tolerance mechanisms may or may not be able to respond. This immobility and dependence on air, soil, and water regimes of high variability makes it difficult to isolate single causes of response, whether they be beneficial or detrimental. At the present level of understanding of plant response as influenced by general stress factors, the direct and indirect effects of acidic deposition that can be definitely stated are extremely limited.

1.3.3 Effects on Aquatic Chemistry

Most of the present concern for the potential effects of acidic deposition, and the significance of these effects, has been derived from the aquatics literature. As already noted, lakes and streams in an ecosystem are not isolated units. They are directly subject to acidic deposition inputs, but they are also dependent on the terrestrial system buffering, or lack of buffering, of these inputs. Unlike the longer term, chronic changes in soils and vegetative productivity, evidence suggests that aquatic systems are responsive to both episodic shocks of acidity (e.g., during snow melt) and chronic inputs of acidic and acidifying substances over time.

The discussion of aquatic chemistry is designed to deal with the complexity of processes that influence water quality and the relative importance of these processes/events. Because considerable emphasis has been placed on aquatic resources in the study of acidic deposition, rather lengthy discussions of methodology and historical trends are relevant to drawing conclusions regarding impacts of acidic deposition and are included. These topics have been an important source of controversy and are therefore dealt with in detail in this section. Predictive models, sensitive regions, significance of metals, and mitigative strategies are also discussed extensively.

The data base for defining historical changes in aquatic chemistry as a result of acidic deposition is among the strongest for the ecosystem components discussed in this document. Like any of the other system components, however, predictions of water quality require an understanding of a large number of other influencing variables, e.g., soils. Unfortunately, at this time, our ability to predict changes expected from acidic deposition is limited since predictive models have yet to be adequately validated.

1.3.4 Effects on Aquatic Biology

The emphasis of the aquatic biology chapter is placed on the response of aquatic organisms to acidification. For the most part, these discussions do not attempt to link the acidic deposition phenomenon to observed biological changes, but rather, define the link between biological response and acidification, whatever the cause.

The chapter discusses the biota found in naturally acidic systems, recognizing that such systems have and will always exist. Such

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information proves useful for comparing naturally vs artificially acidified systems and the biota that are found in both. The components of the food chain in oligotrophic water systems most susceptible to change are discussed relative to their importance and response to acidity. Benthos, macrophytes, plankton and fish are included. Organisms which are dependent on aquatic systems, for at least a portion of their life cycle, are also discussed. Mechanisms of response, field and laboratory evidence for changes in aquatic biota resources, and biological mitigation options are also presented and evaluated.

Although predictions of species survival as a function of water quality are feasible, the limited resource inventory and lack of predictive chemistry models inhibits quantification of the magnitude and extent of acidic deposition impacts on aquatic resources. Quantification of direct impacts of acidification is most likely for the higher trophic levels, e.g., fish, especially as better resource inventories become available. However, the effects of acidification on the interactions between trophic levels remain unclear at this time.

1.3.5 Indirect Effects on Health

Limited data is available on the potential and known effects of acidic deposition on human health. Food chain dynamics are discussed in a bioaccumulation context. Particular emphasis is placed on aquatic organisms of importance to man, and drinking water from ground, surface, or cistern systems. Those metals suspected as being influenced by acidity are highlighted. These include mercury, lead, and aluminum.

Although the acidic deposition oriented 'toxicity data base', is somewhat limited, the authors have capitalized on the extensive toxicity literature and research in other fields of science. Superimposed on these concepts is the effect of acidification, and conclusions are drawn.

1.3.6 Effects on Materials

Like the natural ecosystem, materials, both natural and manmade, are subject to many environmental influences. Among them are the effects of acidic and acidifying substances. This chapter of the document reviews the rather limited data available on the specific topic of acidic deposition effects, as defined in this document, and discusses the major building and construction materials that might be affected by acidic deposition. Mechanisms of damage, economic implications, and mitigative measures are presented and evaluated. The importance of dry deposition over wet deposition is highlighted.

1.4 ACIDIC DEPOSITION

The previous sections refer to acidic deposition without definition. Volume I, Chapter A-1 defines this term for technical use in the atmospheric/deposition sciences. However, from an effects point of view, the chemical quality of precipitation is as, if not more, important than the pH. Deposition, both wet and dry, contains both

essential and nonessential substances needed by ecosystems as part of their natural nutrient cycle. Therefore, the materials presented in the effects chapters concentrate on the generic concept of acidification and the importance of sulfate and nitrate loadings to the ecosystem. Whether these substances are deposited in dry or wet form is not differentiated. Because the inputs of sulfur and nitrogen can be acidic upon delivery, or can become acidifying as they cycle through the system, these substances are the critical elements for discussion. Because the data bases were not sufficient to conclusively define input limits for 'protection' of biological resources, there was no need to deal with a separation of wet and dry forms of deposition. When simulated treatments are involved, differentiation of deposition forms is noted as necessary; e.g., in the crop productivity discussion. Although an effort to separate the components of deposition was not undertaken, this does not minimize the potential for differential effects of wet vs dry deposition exposures.

Therefore, reference to acidic deposition will refer to total deposition of acidic or acidifying substances. Differentiation is made only as deemed appropriate by the authors on an issue-by-issue basis.

1.5 LINKAGE TO ATMOSPHERIC SCIENCES

Every effort to use information from the atmospheric chapters of the document was made. Reference to deposition changes over time, emissions levels, natural vs anthropogenic sources of sulfur and nitrogen, and/or sulfur and nitrogen loadings are consistent with those presented in Volume I. Any conclusion which would have been drawn using data not consistent with the atmospheric/deposition chapters was modified or removed. Therefore, Volume I appropriately sets the stage for the levels of acidity/deposition, the 'cause', that was considered in the development of the effects presentations. References to chapters in Volume I are made, as necessary.

1.6 SENSITIVITY

In addition to problems of interpreting the meaning of the acidic deposition concept, other terminology is equally subject to misinterpretation. In particular, the term 'sensitivity' lends itself to varied interpretations. Sensitivity, as used in the effects chapters, refers to the relative potential for changes to occur within an ecosystem or one of its components. A highly sensitive portion of an ecosystem will change more noticeably, or rapidly, to acidic inputs than will one that is generally classified as having moderate, low, or no sensitivity. However, the reader must be cautious in many of the effects areas to be certain the reference to sensitivity is clear. For example, reference to a sensitive soil is not meaningful. Acidic deposition effects must be considered with respect to a specific physiochemical property of the soil. Soil-metal mobility or pH, for example, can be classified as 'sensitive' to change. Likewise, particular tree species, aquatic organisms, processes, and/or materials can be sensitive to change due to acidic deposition. However,

developing sensitivity classifications for larger units of the ecosystem can be misleading, and comparing dissimilar ecosystem components, e.g., soils and fish, is inappropriate. In addition, quantification of 'sensitivity' is defined in the aquatic chemistry chapter but only qualitative relative usage of the word appears in discussions of other ecosystem components.

1.7 PRESENTATION LIMITATIONS

A phenomenon as complex as acidic deposition cannot be presented with respect to every environmental factor that might influence ecosystem response. In the discussions that follow, it is recognized that acidic deposition is treated as if it were isolated from other pollutants with which it might interact. Thus, not every possible link between the ecosystem and influencing variables has been considered. What is presented is the authors'/editors' perspective of key issues. This does not infer that other issues are unimportant. Rather, an absence of discussion suggests that the issue has not, as yet, been recognized as essential to our understanding or that data to support any relevant comments were lacking.

THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-2. EFFECTS ON SOIL SYSTEMS

(W. W. McFee, F. Adams, C. S. Cronan, M. K. Firestone, C. D. Foy, R. D. Harter, and D. W. Johnson)[1]

2.1 INTRODUCTION

Soil plays a key role in ecosystems. It is one of their most stable components and, when combined with climate, defines a terrestrial ecosystem's productivity limits. Moreover, because much of the water entering streams and lakes directly contacts soil, soil properties also exert important influences on aquatic systems.

Because of soil's importance to most ecosystems, the impact of acidic deposition on soils assumes prominence in our discussion. Defining soil sensitivity to acid inputs depends on understanding soil properties and chemistry, which are discussed early in this chapter. Thereafter, we can locate vulnerable soils and determine expected and potential effects on various soil components. Types and rates of changes can be determined, and the effects of soil changes on aquatic and terrestrial ecosystems can be considered. Specifically, questions concern impacts on soil fertility; nutrient, toxic substance, and organic acid availability; plant vitality; and water quality. Both short and long-term implications must be considered in relation to numerous soil components, to soil-plant relationships, and to soil-water relationships.

2.1.1 Importance of Soils to Aquatic Systems

Aquatic systems receive diverse outputs from terrestrial ecosystems. Influences of acidic deposition on transfers from terrestrial to aquatic systems may be direct, when material deposited from the atmosphere passes over or through the soil with little interaction, or they may be indirect, when deposited materials cause changes in soil processes, such as weathering, leaching, and organic matter decomposition. Thoroughly assessing effects of atmospheric deposition on any element transferred from a terrestrial to an aquatic system requires extensive measurements of inputs, internal processes, and outflows (Gorham and McFee 1980). These authors note that our understanding of the processes is rather incomplete.

2.1.1.1 Soils Buffer Precipitation Enroute to Aquatic Systems--Soil systems are generally strongly buffered against changes in pH. They are usually thousands of times more resistant than water to pH shifts (Brady

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[1]All of these authors have contributed to this chapter. Because of subsequent integration of the material, these authors are not identified by section.

1974). Therefore, pH of deposited precipitation tends to shift toward that of the soil if the water comes into intimate contact with the soil. The cation exchange capacity (CEC) of the soil and the extent of its saturation with basic cations (e.g., Ca^{2+}, Mg^{2+}, K^{+}) determine the soil buffering capacity in moderately acid soils (see Section 2.2). Strongly acid soils may be buffered by the soil minerals. In general, soils with high clay content, especially smectite clays, and with high organic matter content are strongly buffered. These soils tend to deliver water that has come in intimate contact with the soil matrix to aquatic systems at or near the soil pH. In areas with alkaline, neutral, or slightly acid soils, the soil buffer system removes much of the acidity in acidic deposition. Where the soils are near the acidity of the incoming precipitation, they may not change the pH of water as it passes through, especially if the soil solution remains rather dilute.

2.1.1.2 Soil as a Source of Acidity for Aquatic Systems--Many of the soils in the world's humid regions have been acid for very long periods. Bailey (1933) pointed out that podzol soils (soil order Spodosol) were generally the most acidic, followed by lateritic (Oxisols and Ultisols) and podzolic (Ultisols and Alfisols) soils. He did not consider organic soils (Histosols), many of which are quite acid. For example, all of those designated "Dysic" at the family level of classification have a pH less than 4.5, and some have a much lower pH (Soil Survey Staff 1975). Drainage waters from such acid soils may be equally acidic as the soil and essentially control the pH of receiving lakes or streams. In many cases, however, after percolating water passes through acid soil, it interacts with more basic materials underneath before reaching a stream. Thus, a lake may be surrounded with surface soil considerably more acid than the water. Such is the case around many lakes in the Adirondack mountains where most of the soils are strongly acid (Galloway et al. 1980).

2.1.2 Soil's Importance as a Medium for Plant Growth

All of the other roles of soil fade into insignificance when compared to its importance as a medium for plants. Soil provides the physical support, 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. Soil properties set limits on the productivity of terrestrial ecosystems. Even though soils tend to resist rapid change, any significant reduction in their ability to support plants, such as the increased Al toxicity cited by Ulrich et al. (1980) and A. H. Johnson et al. (1981), is a serious matter.

2.1.3 Important Soil Properties

Any changes deleterious to the soil's role as a plant growth medium or that alter its output to aquatic systems are causes for concern. These include chemical changes, such as in acidity, nutrient supply, cation exchange capacity, leaching rates of nutrients, or mobilization of toxic substances; physical changes, such as accelerated weathering

rates or changes in aggregation; or biological changes, such as reductions in nitrification or other processes.

2.1.3.1 Soil Physical Properties--Soil physical properties are never independent of chemical and biological properties; however, water movement, water retention/storage capacity, and soil aeration are determined primarily by physical properties. Controlling water flow is the most important influence of soil physical properties on interaction of soil with acid rain. Soils that have high surface runoff rates, such as those on steep slopes or with low porosities, tend to transmit water rapidly without changing its composition. Likewise, if the soil has many coarse pores and is well drained, as are many sands and loamy sands, water passing through may be changed only slightly. Therefore, if the primary consideration is protection of a body of water by the soil's buffering capacity, the two situations described are "sensitive." On the other hand, if changes in the soil itself are the concern, these soils are not particularly sensitive from the physical standpoint.

2.1.3.2 Soil Chemical Properties--Resistance of soil chemical properties to the effects of acidic deposition is measured in terms of the buffering capacity, initial pH, sulfate adsorption capacity, and amount and type of weatherable minerals. Soils with high buffering capacities due to high CEC and high base status will be very slow to respond to acid inputs of the magnitude acidic deposition introduces. Weatherable minerals containing carbonates are common in lower horizons of the younger soils in many regions and will effectively neutralize acids from all sources. Details of these relations are discussed in later sections.

2.1.3.3 Soil Microbiology--Biological processes in soils may be influenced by acid precipitation and, at the same time, provide some of the means of resistance and/or recovery. If important soil biochemical processes, such as N fixation, nitrification, organic matter decay, and nutrient release are changed by acid precipitation, the impact could be significant. Studies of relationships of soil acidity to biochemical activity are plentiful. However, most have doubtful applications to the acid rain problem because they were studies of natural pH differences, not of shifts due to acid inputs. A few recent studies indicate alteration in microbial activity near the soil surface due to simulated acid rain (Strayer and Alexander 1981, Strayer et al. 1981). The capacity of most soils to buffer acid inputs as well as the diversity and adaptability of microbe in the soil contribute to resistance to acid rain effects. A more complete discussion of soil biology and acidic deposition follows in Section 2.4.

2.1.4 Flow of deposited materials through soil systems

A generalized depiction of the flow of deposited materials through a terrestrial ecosystem is shown in Figure 2-1. In a forested ecosystem (to a lesser degree on cropland, also), a major portion of the precipitation is intercepted by foliage. The chemical properties of the resultant throughfall and stemflow can be substantially altered from the

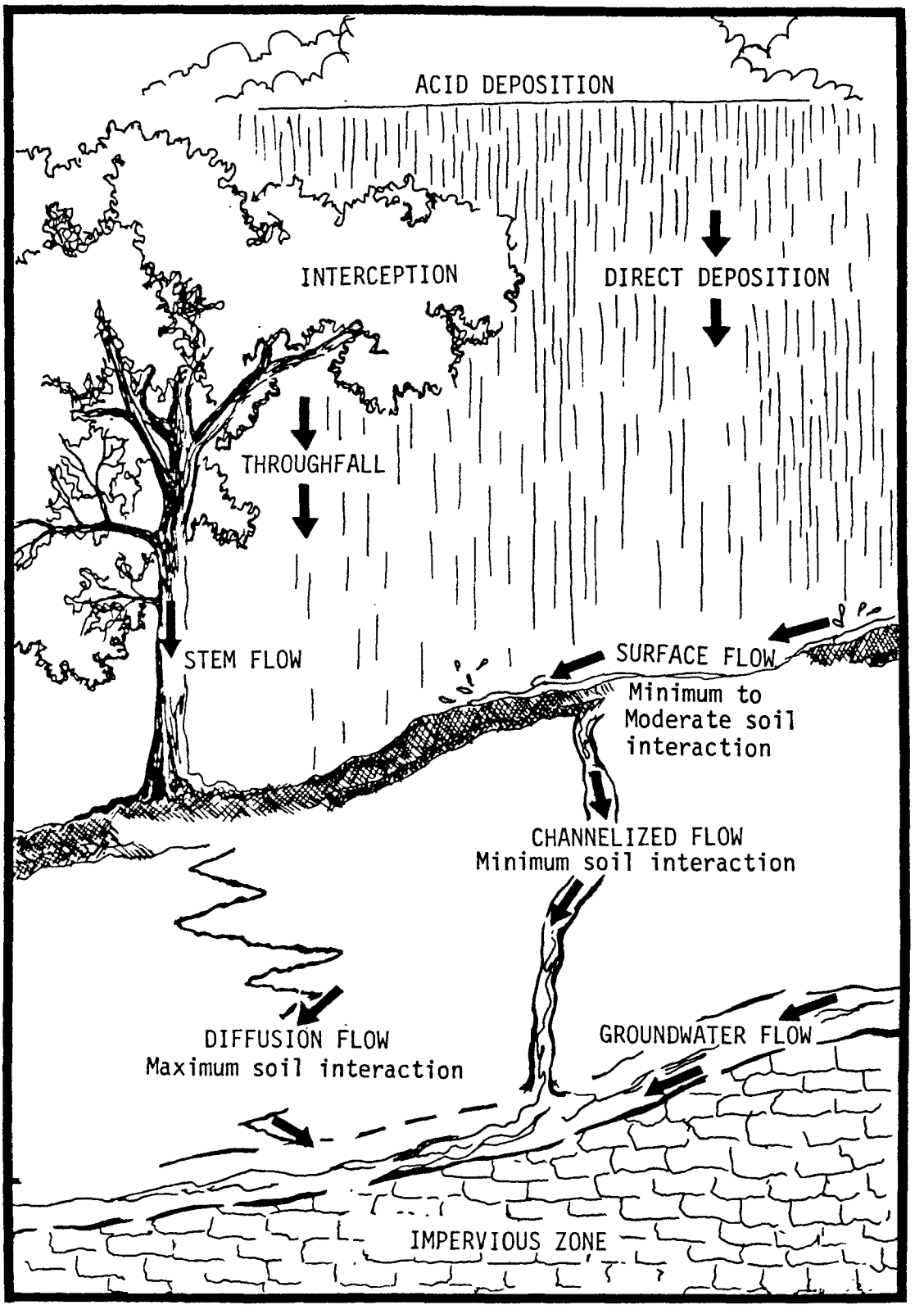

Figure 2-1. Flow paths of precipitation through a terrestrial system.

incipient precipitation (see Section 3.2.1.2). While this alternation may be of no importance in constructing the total system input-output balance, it has a big impact on the nature of reactions expected at the soil surface.

Upon striking the surface, the water may infiltrate the soil or move laterally as surface flow. In a forested ecosystem, surface flow will usually not be visible on the forest floor but will flow through the surface organic layers. This provides opportunity for water to react chemically with surficial materials to a greater extent than does surface flow in cultivated areas. The amount of interaction will be proportional to path length and flow rate.

In uncultivated areas, many large channels are established by burrowing animals and decomposing roots. These are frequently open to the surface and provide open conduits for flow of drainage water. These channels may carry nearly all drainage water during saturated flow, and may be dominant conduits during all rainfall events. Little opportunity for soil interaction is provided, and the precipitation may be conducted through the soil with little or no alteration.

Water movement by unsaturated flow will usually be through the capillary pores where maximum opportunity exists for interaction with the soil. This is the major source of water to plants. Flow through fine pores is necessary in many deeper soil layers that have limited macropore space. The various flow paths are depicted in Figure 2-1.

2.2 CHEMISTRY OF ACID SOILS

A brief discussion of important concepts in the chemistry of acid soils is presented here as background for understanding the sections that follow. Those already familiar with these concepts may wish to proceed to Section 2.3.

Although little is known about the impact of acidic deposition per se on soils, much is known about acid soils in general. The factors which determine the natural acidification of soils are important to the development of an adequate comprehension of recent and/or future acidic deposition impacts. There are many acid soils in the United States, and it is appropriate to capitalize on our understanding of these systems.

2.2.1 Development of Acid Soils

The eastern half of the United States has a climate in which rainfall exceeds the combined losses of water by runoff, evaporation, and transpiration from the soil. The excess water leaches through the soil, carrying with it basic cations and other soluble materials. If leaching removes basic cations faster than they are replenished by natural processes or human activities, the soil profile becomes increasingly acid and impoverished of nutrients (Pearson and Adams 1967). However, a prerequisite for leaching to cause soil acidity is the addition of H^+ ions to the system (Bache 1980, Ulrich 1980) along with mobile anions. The H^+ ions can be donated from a variety of sources.

2.2.1.1 Biological Sources of H^+ Ions--Although H^+ ions may be generated by chemical weathering of minerals through hydrolytic reactions, the significant sources of H^+ production in soils are all based on biological reactions.

Oxidation of sulfur and sulfides can be important natural sources of acidity. Much of the sulfur in soils is present in a highly reduced state. This includes combined S in soil organic matter and such common minerals as pyrite, FeS_2. The release of sulfur from organic-matter in aerobic soils is followed by the H^+-producing oxidation reaction

$$S + 3/2\ O_2 + H_2O = SO_4^{2-} + 2H^+.$$

Elemental S is sometimes used in agriculture for disease control and as a fertilizer material. Its contribution to soil acidity is readily calculable from the equation above, i.e., 16 kg of S per hectare is equivalent to one hundred cm of pH 4.0 precipitation, 1 keq H^+ ha^{-1}.

When sulfide minerals, e.g., pyrite, are exposed to atmospheric oxygen, oxidation of these minerals results in significant H^+ production, according to the reaction

$$2FeS_2 + 7H_2O + 7\ 1/2\ O_2 = 2\ Fe(OH)_3 + 4SO_4^{2-} + 8H^+.$$

Significant quantities of sulfide minerals are found only in recently exposed soil materials or those that have been maintained in anaerobic conditions, e.g., coastal marshes. Therefore, their influence is important in only very limited areas.

Acidity from nitrification is an important contribution in most soils of the humid regions. Nitrogen is one of the most abundant elements in plants and in soil organic matter and is present mostly in a highly reduced state. It is released from organic matter as NH_3, which hydrolyzes to NH_4^+ in soil solution. Much of the NH_4^+ is oxidized to nitrate by bacteria, according to the reaction

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O.$$

By this reaction, 9 kg NH_4^+ ha^{-1} could produce 1 keq H^+ ha^{-1}. The theoretical maximum acidity from nitrification is never realized in soils because concurrent or subsequent reactions involving N neutralize a portion of the H^+ produced.

2.2.1.2 Acidity from Dissolved Carbon Dioxide--Atmospheric CO_2 contributes some acid to soils, however, the respiratory activities of plant roots and soil microbes result in soil air containing considerably more CO_2 than atmospheric air. Soil air commonly contains up to 1 percent CO_2, in comparison to the 0.033 percent of a normal atmosphere (Patrick 1977). This CO_2 lowers the pH of pure water according to the equation below, which can be derived from the relationships among CO_2 content of air, dissolved H_2CO_3, and H^+ activity.

$$(H^+) = [1.50 \times 10^{-10} \times \% CO_2]^{1/2}.$$

If atmospheric CO_2 is 0.033 percent, then H^+ activity of rainwater is 2.2 X 10^{-6}M (moles per liter) or pH 5.65. If soil air contains 1.0 percent CO_2, then H^+ activity is 1.2 X 10^{-5}M or pH 4.91. Thus, biologically generated CO_2 is a source of H^+ ions in soils but has very little influence below a pH of about 5.0.

The dominant source of H^+ in many soils used in nonleguminous agricultural production in the United States is from the use of ammoniacal fertilizers, e.g., NH_3, NH_4NO_3, $(NH_2)_2CO$, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$. Because nitrogen is often used at rates of 100 to 200 kg ha^{-1}, fertilizers alone may generate H^+ in soils at rates of 3.6 to 21.6 keq H^+ ha^{-1}. It should be noted that the net acidification from ammoniacal N is frequently less than the theoretical due to direct uptake of NH_4^+ by plants and H^+ consuming reactions in soils. Although these calculations are based on fertilizer application to agricultural lands, these same relationships are applicable for determining the acidification impact on soils from atmospheric N sources. Nitrogen additions contribute to acidification by increasing basic cation removal in plants harvested and by furnishing a mobile anion, NO_3^-, for leaching losses.

Acidity is also added from soil organic matter. The microbial process by which plant residues are converted into soil humus generates many carboxyl ligands, RCOOH, on the humus. The protons of such ligands partially dissociate, adding H^+ to the soil solution. This source of H^+ production becomes increasingly important when large amounts of soil humus are present.

Roots can absorb unequal amounts of anions and cations because the uptake mechanisms are relatively independent of each other. The electroneutrality of the soil solution is maintained by plant release of H^+ or HCO_3^- during the uptake process. Plants with N-fixing rhizobia absorb more cations than anions from the soil when N is obtained almost entirely from N_2. High yielding legumes may produce H^+ equivalent to several hundred kg $CaCO_3$ per hectare (several keq H^+ ha^{-1}).

2.2.1.3 Leaching of Basic Cations--Production of H^+ resulting from the various mechanisms does not produce acid soils unless it is accompanied by leaching. In the absence of leaching (arid and semi-arid regions), HCO_3^- tends to accumulate in soil solution, leading to H^+ neutralization and precipitation reactions with Ca. In the presence of leaching, H^+ in the soil solution replaces some of the adsorbed basic cations (Ca, Mg, K) on the exchange surfaces of soil particles. As the excess soil solution moves downward through the soil profile, it carries basic cations equivalent to its anionic content. Meanwhile, the adsorbed H^+ remains in place with the soil particles, causing the soil to become more acid.

2.2.2 Soil Cation Exchange Capacity

Many differences in the sensitivity of soils to acidic inputs can be traced to the extent of base saturation and to differences in cation exchange capacity (CEC), the sum of the exchangeable cations, expressed in chemical equivalents, in a given quantity of soil. It is the major characteristic of soils that prevents them from becoming rapidly impoverished when leached. This section is presented to explain the source of CEC and some of the variables which affect it.

2.2.2.1 Source of Cation Exchange Capacity in Soils--To have a CEC, soil particles must have a net negative charge. Soil clay particles may have a negative charge due to isomorphous substitution of Al^{3+} for Si^{4+} in tetrahedral layers and of Mg^{2+} or Fe^{2+} for Al^{3+} in octahedral layers of the clay structure. This charge is termed a "permanent charge" (Coleman and Thomas 1967). A second mechanism is the result of the terminal metal atom's reaction with water to complete its coordination with either OH^- or H_2O. At low pH, the coordinating ligand tends to be H_2O, which results in a site with a positive charge; at high pH, the coordinating ligand tends to be OH^-, which results in a negatively charged site. Minerals with this kind of negative charge as their primary source of CEC are referred to as having a "pH-dependent charge." Therefore, these soil particles change CEC as the pH changes.

In most soils, a significant component of the CEC comes from organic matter. The major portion of soil humus is associated with the clay fraction, except in extremely sandy soils (Schnitzer and Kodama 1977). Its pH-dependent CEC is a major component of the CEC of surface soils and may be almost the sole source of CEC in sandy soils. Soil humus has many ligands from which protons dissociate, such as carboxyl (-COOH), phenol (-OH), and imide (-NH). In acidic soils, however, only the carboxyl ligand ionizes enough to affect pH, i.e., $R\text{-}COOH \rightarrow R\text{-}COO^- + H^+$, creating a negatively charged exchange site. The fraction of H^+ that ionizes from carboxyl ligands increases with increasing pH, thereby increasing soil CEC.

The CEC of surface soils is determined by their clay and organic matter contents. In the highly weathered Ultisol soils common to the Southeast, surface-soil clays are usually kaolinite and hydroxy-Al intergrade vermiculite. These soils contain a high percentage of sand and low contents of clay and organic matter, and commonly have a CEC of about 5 meq 100 g^{-1}. In soils with a more temperate climate in the eastern half of the United States, soil organic matter is usually higher and smectite clays are sometimes more abundant, hence the CEC is normally higher, about 15 meq 100 g^{-1} (Coleman and Thomas 1967).

2.2.2.2 Exchangeable Bases and Base Saturation--The exchangeable cations in acid soils consist primarily of Ca, Mg, K, Al, H, and Mn. The basic cations are Ca, Mg, and K, while Al and H are measures of soil acidity. The fraction of the CEC that is satisfied by basic cations is defined as "base saturation." For a particular soil and CEC method, a

well-defined, positive correlation between pH and base saturation exists. Unfortunately, the CEC reported in the literature is method dependent. The most common methods of determining CEC are (1) sum of exchangeable cations by neutral salt extraction, (2) NH_4^+ adsorption at pH 7.0, (3) Na^+ adsorption at pH 8.2, and (4) sum of exchangeable cations by neutral salt extraction plus titratable acidity by triethanolamine at pH 8.0. The most commonly used method is probably 1.0 N NH_4OAc extraction at pH 7.0, method (2) above. For soils with similar characteristics, pH can be used as a reasonable estimate of base saturation. For example, the "soil pH" - "base saturation" relationship of Ultisols in Alabama is similar to the combined relationship of Alfisols, Inceptisols, and Spodosols in New York (Figure 2-2).

Analogous to the base-saturation concept, quantities of individual exchangeable cations can be expressed in terms of saturation of the CEC. This concept is particularly useful in defining the relative availability of cations. The cation-saturation concept is also useful in predicting probable toxic levels of Al. Although Al phytotoxicity is a function of soil-solution Al activity, it is more convenient to measure exchangeable Al.

2.2.3 Exchangeable and Solution Aluminum in Soils

Aluminum mobility is a key area of concern for both aquatic impacts and terrestrial vegetative response relative to acidic deposition. The soluble Al in soils is a product of acid weathering of clay minerals. As H^+ concentration increases in soil solution, the stability of clay minerals decreases, resulting in the release of Al^{3+} ions from their surface structure. Measurable amounts of soluble Al are found only at a pH less than 5.5. Only a small portion of the dissolved Al resides in the soil solution. Most becomes exchangeable, since cation-exchange sites in soils have a strong affinity for Al^{3+} ions.

Even though Al saturation of strongly acid soils (pH < 5.0) will normally exceed 50 percent of the CEC, the concentration of Al in soil solution is usually < 1 ppm. The significance of exchangeable Al is two-fold: (1) it is the major component of exchangeable acidity in soils (i.e., acidity displaced by a neutral-salt solution), and (2) it is the source for the immediate increase of Al into soil-solution from an acid soil when replaced by other cations on the exchange sites.

Soil-solution Al concentration is determined by the pH dependent solubility of Al-containing clay minerals. For example, kaolinite dissolves according to the reaction

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2Si(OH)_4 + H_2O.$$

Thus, soil-solution Al concentration will be determined by the activities of H^+, $Si(OH)_4$, or other products of weathering reactions.

Aluminum oxides are common in acid soils, and it is frequently assumed that solution Al is controlled by $Al(OH)_3$ solubility. In that

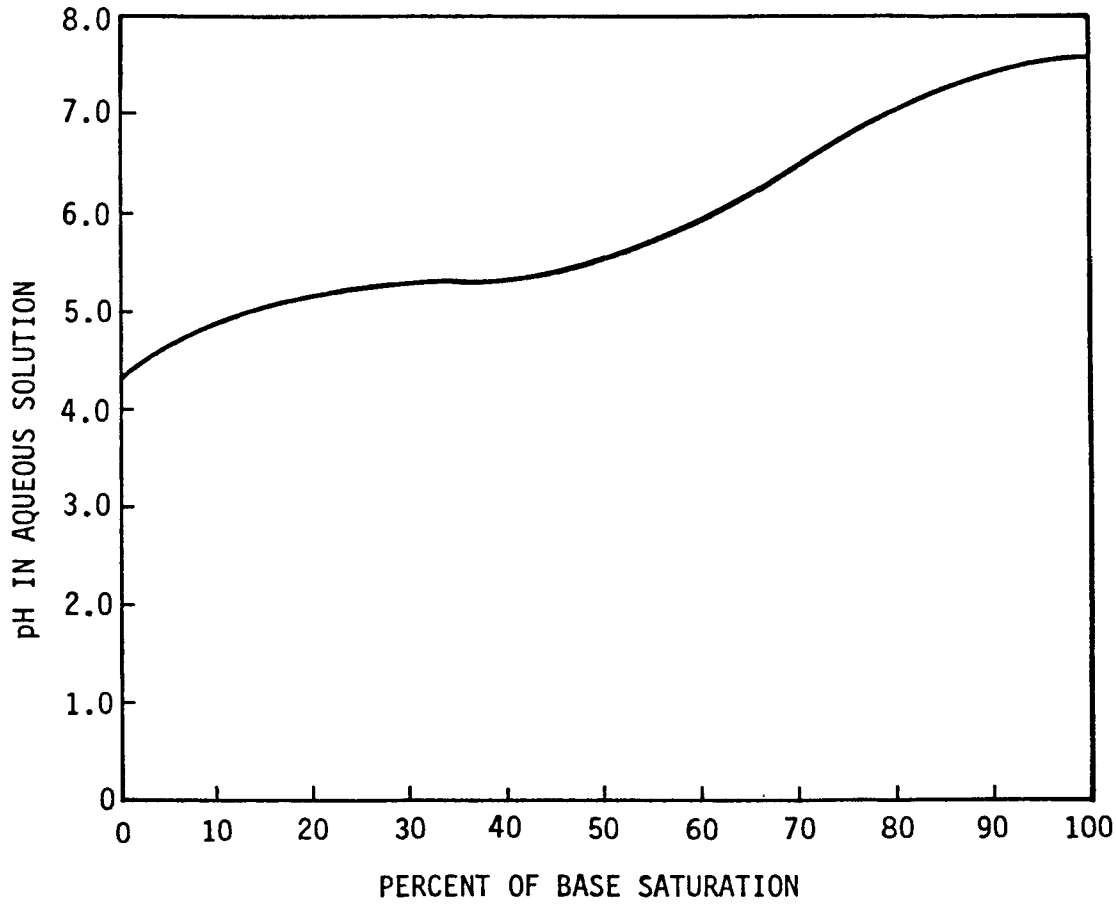

Figure 2-2. Typical relationship of soil pH to the percent base saturation. Adapted from Lathwell and Peech (1969).

case, Al^{3+} activity in soil solution is a function only of pH because of the reaction

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O.$$

The equilibrium log K for this reaction, log Al^{3+} - 3 log H^+, varies from 9.7 for the amorphous oxide to 8.0 for crystalline gibbsite. At pH 5.0, for example, Al^{3+} activity would vary from 20 μM for the more-soluble amorphous oxide to 0.1 μM for gibbsite at equilibrium with the soil solution.

In most acid soils of the United States, clays are primarily aluminosilicates, and solution Al is controlled by soil-solution Si as well as pH. When both Al and Si are present in soil solution, their activities frequently depend upon a solid-phase component with the general composition of $Al_2Si_2O_5(OH)_4$. Its solubility in acid soils is expressed by the equation

$$1/2Al_2Si_2O_5(OH)_4 + 3H^+ = Al^{3+} + Si(OH)_4 + 1/2H_2O.$$

The equilibrium log K for this reaction, log Al^{3+} + log Si(OH) - 3 log H^+, varies from 5.6 for amorphous halloysite to 3.25 for crystalline kaolinite. If $Si(OH)_4$ in soil solution is 0.2 mM (a reasonable value for acid soils), then Al^{3+} activity at pH 5.0 would range from 2 μM for amorphous halloysite to 0.01 μM for crystalline kaolinite at equilibrium with the soil solution.

The relative solubilities of Al oxides and aluminosilicates in soils show that soil-solution Al^{3+} activity, at the same pH, varies according to the solubility of the Al-controlling mineral as follows: amorphous Al oxide > amorphous halloysite > gibbsite > kaolinite > smectite. Consequently, the level of soil-solution Al, and its phytotoxic effect on plants or its transport to aquatic systems, varies among soils at the same pH, depending upon which mineral is controlling solution Al.

Under nonagricultural ecosystems, soils generally contain too little solution phosphorus (P) to affect soluble Al. However, fertilizer P is an effective agent for lowering solution Al by forming such insoluble precipitates as variscite, $Al(OH)_2H_2PO_4$. Dilute, acid solutions of Al react with sulfate to form insoluble compounds but these compounds will be the controlling factor very infrequently. The influence of Al and Mn on plant nutrition is discussed in Section 2.3.3.3.

In the presence of organic ligands, the solubility of aluminum can be greatly enhanced (Lind and Hem 1975). Numerous reports emphasize the importance of polyphenols and other components of soil organic matter in the transport of Al within soils (Bloomfield 1955, Davies et al. 1964, Malcolm and McCracken 1968). In many cases, organic-aluminum complexes are the major form of mobile Al. Cronan (1980b,c) points out the importance of organic substances in Al leaching and discusses the changes likely when strong acid anions such as sulfate are present.

Inorganic aluminum is present in acid soil solutions primarily as monomeric ions, the most common ones being Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3^{o}$, $AlSO_4^{+}$ and $AlH_2PO_4^{2+}$. In most acid soils, $Al(OH)_2^{+}$ is the most abundant solution ion.

Since about 1920 soluble Al has been recognized as an important factor limiting plant growth in acid soils (Adams and Pearson 1967). Because of the pH-dependent solubility of Al, phytotoxic levels of solution Al can be expected in most mineral soils when soil pH is < 5.0 to 5.5. Only a fraction of a ppm is needed for sensitive species to exhibit symptoms (see Section 2.3.3.3.2.1).

2.2.4 Exchangeable and Solution Manganese in Soils

Another result of acidification is associated with the mobility of manganese. Manganese occurs in soils in three valency states. Since divalent Mn (Mn^{2+}) is the most soluble form, Mn availability depends upon the redox potential of the system. The equilibrium between Mn oxides and solution Mn^{2+} is subject to rapid shifts in the soil.

In most soils with significant levels of easily reducible Mn, toxic levels of Mn^{2+} in soil solution can be expected when soil pH is < 5.5. The lower the pH, the more likely phytotoxicity will occur. Lower redox potentials favor Mn-oxide dissolution. In turn, lower redox potentials are favored by waterlogged conditions, particularly when accompanied by the rapid decomposition of organic matter. Consequently, over the short-term, toxic levels of Mn are more likely under poorly aerated conditions. A long-term consequence of poor aeration, however, is the depletion of easily reducible Mn and soluble Mn to quite low levels through leaching.

It is normal for Mn and Al phytotoxic symptoms to occur concurrently in many acid soils because the pH-dependent solubility of Mn oxides and the Al-containing soil minerals release toxic levels of Mn and Al at about the same pH level, i.e., < pH 5.0 to 5.5. Whereas Al phytotoxic symtoms are not generally evident on aerial plant parts, symptoms of Mn phytotoxicity are quite severe before plant growth is affected significantly.

2.2.5 Practical Effects of Low pH

Low soil pH influences most chemical and biological reactions. It accelerates mineral weathering and the release of phytotoxic ions to the soil solution; it affects the downward migration of clay and organic-matter particles in the soil-profile development process, and it affects the level and availability of most plant nutrients in the soil-solution.

The solubility of soil minerals at low pH is important to plant growth and transport of ions to aquatic systems. The common Al minerals or compounds in acid soils are the aluminosilicates, hydrated oxides,

phosphates, and hydroxy-sulfates. The relationship of low pH to Al and Mn solubility was covered in Sections 2.2.3 and 2.2.4, and their influence on plant nutrition is covered in Section 2.3.3.3.

Low soil pH affects the availability of all macronutrients (N, P, S, Ca, Mg, K) to some extent (Adams and Pearson 1967; Adams 1978; Rorison 1980). These effects, however, are seldom great enough to influence plant yields. Nitrogen availability is affected because low pH decreases the rate at which organic matter decomposes and releases N to the soil solution. Phosphorus availability is affected primarily via chemical solubilities. At low pH (< pH 5.5), P is made increasingly less available because of its reaction with Al and Fe. Sulfate availability is determined by both organic-matter decomposition and by inorganic reactions with Al and Fe. The result of these effects is that sulfate becomes progressively less available as pH decreases below 6.0.

Cation (Ca, Mg, K) availability is not readily expressed as a function of soil pH. The relative availability of these nutrients as a function of pH is of no practical consequence in most cases, except that most soils become acid only after depletion of these cations. In strongly acid soils, however, toxic levels of solution Al render vegetation less able to utilize the Ca and Mg.

Low soil pH affects the availability of all micronutrients (B, Cl, Cu, Fe, Mn, Mo, Zn) except chloride (Adams and Pearson 1967; Rorison 1980). The availability of Cu, Fe, Mn, and Zn is significantly increased by lower soil pH in the range 6.5 to 5.0. Boron availability increases only slightly with decreasing pH. Molybdenum availability decreases with decreasing pH because of decreased solubility of molybdate forms. Additional information on soil acidity and plant nutrition is given in Section 2.3.

2.2.6 Neutralization of Soil Acidity

In unamended soils, the natural forces that neutralize acidity are weathering of neutral or basic minerals, the addition of basic materials from the atmosphere or floods, and the deposition of basic cations by vegetation recycling. In humid temperate regions outside of floodplains, the uptake of basic cations by plant roots and their deposition on the soil surface and weathering are the important neutralizing forces. These forces do not normally reverse the natural acidification trends, but modify the rate and distribution of acidification within the soil profile.

The effectiveness with which soil acidity can be neutralized by liming depends upon the purity and particle size of the lime, the amount of lime applied, the soil pH, the cation exchange capacity, the uniformity with which the lime is spread, and the extent of soil-lime mixing (Barber 1967). Liming materials are restricted to the Ca and Mg salts of carbonate, silicate, and hydroxide. The bulk of agricultural lime comes from ground limestone.

The net reaction that causes lime to neutralize soil acidity is the result of two separate reactions. One is the cation-exchange reaction that releases Al^{3+} and H^+ to the soil solution from exchange sites; the other is lime dissolution and the hydrolysis of CO_3^{2-}. When exchangeable Al^{3+} is displaced by Ca^{2+} from dissolving lime, it undergoes stepwise hydrolysis to form a precipitate of $Al(OH)_3$ and solution H^+ ions. The overall exchange-hydrolytic reaction is expressed by the equation

$$2\ \text{Al-soil} + 3\ CaCO_3 + 3\ H_2O = 3\ \text{Ca-soil} + 2\ Al(OH)_3 + 3\ CO_2.$$

With thorough mixing of small lime particles with an acid soil, the neutralization reaction is quite efficient in raising soil pH to about 6.0. Lime becomes increasingly less effective in dissolving and raising soil pH beyond this value.

2.2.7 Measuring Soil pH

The term "soil pH" as it is commonly used refers to the pH of the solution in contact with the soil. Soil pH is one of the most useful measurements made on soils (Adams 1978). It is used to predict the likelihood of excessive toxic ions, the need for liming a soil, a variety of soil microbial activities, and the relative availability of several inorganic nutrients.

The usual method of measuring soil pH is to immerse a glass-electrode, reference-electrode assembly into a soil-water suspension and measure the electromotive force (emf) of the cell. Part of the measured emf is due to a junction potential at the salt-bridge, test-solution interface. A basic premise of soil pH measurements is that the junction potential between the salt bridge and the test solution (or soil suspension) is the same as with the standard solution. This equality is realized only where test solutions and standard solutions are similar in ionic compositions. Soil suspensions hardly meet this requirement, but they approximate it if the reference electrode is placed in the supernatant while the glass electrode is immersed in the settled suspension.

Because soil pH is an empirical value, the method of measurement must be standardized. Samples should be either air-dried or oven-dried at low temperature (< 50 C); oven drying at 105 C produces meaningless pH values. When soil solution is separated from solid-phase soil, its pH seldom matches that of the soil suspension. One reason for the discrepancy is the loss or dilution of CO_2 in the soil solution upon drying of the soil sample and the subsequent addition of water.

Soil pH is influenced by the soil-water ratio and the salt concentration of the water used. There is no universal agreement on what the ratio should be. Soil to water ratios of 1:1 up to 5:1 are commonly used. Since most soils are highly buffered, the differences obtained due to variations in soil:water ratio are not of practical importance as long as the procedure is consistent and stated with the results.

In acid soils, soil pH generally decreases temporarily with the addition of fertilizer or other salts and increases with the dissipation of fertilizer, either by crop removal or by leaching. In poorly buffered soils, this pH change may be as much as 0.5 to 1.0 pH unit for normal fertilizer rates. These changes in soil pH are not due to changes in total soil acidity but are due to shifts of Al and H ions from exchange sites to soil solution because of cation-exchange reactions. Some of this variation can be overcome by use of a 0.01M $CaCl_2$ solution instead of water when measuring pH.

If soil acidity of an area is to be monitored over years, time of sampling should be consistent with annual inputs of fertilizers, natural vegetative cycles, and weather cycles. The most consistent values will be obtained if samples are taken when salt content is at a minimum.

Spatial variation of soil pH within a field, both vertically and horizontally, requires careful sampling to obtain a sample that represents the area of interest. The area to be represented should be reasonably uniform in appearance within one soil series and uniform in history. Several identical soil cores should be composited and thoroughly mixed before a subsample of the composite for pH measurement is taken.

2.2.8 Sulfate Adsorption

As pointed out in Section 2.2.1.3, the presence of mobile anions is necessary for the leaching of cations to occur. The dominant anion in the atmospheric deposition in North America is sulfate (SO_4^{2-}). Therefore, the reaction of sulfate, especially its adsorption or free movement, is an important soil characteristic.

Soils containing large quantities of amorphous Fe and Al oxides or hydroxides have a capacity of adsorb SO_4^{2-}. Sulfate adsorption results in the displacement of OH^0 or OH_2^+ from iron or aluminum hydroxide surfaces (Rajan 1978). This results in an increased negative charge on the hydroxide surface which accounts for the simultaneous retention of sulfate and associated cations in soil. Sulfate adsorption is strongly affected by pH since deprotonization of amphoteric adsorption sites can make them negatively-charged and cause repulsions of anions. Sulfate adsorption is also affected by the cations present on exchange sites, with the presence of polyvalent cations causing more adsorption than monovalent ions. Soil pH is a more important factor than cation type, however (Chao et al. 1963). Recently, it was shown that organic matter has a decidedly negative influence on sulfate adsorption, even when free Fe and Al oxide content is high (Johnson et al. 1979, 1980, Couto et al. 1979). This effect is thought to be due to the blockage of adsorption sites by organic liquids.

The question of reversibility of sulfate adsorption is crucial to the long-term effects of acidic deposition on soil leaching. If sulfate is irreversibly adsorbed, sulfate adsorption can be viewed as increasing

the soil's capacity to accept acidic deposition before significant leaching of cations begins. If sulfate is reversibly adsorbed, however, its effects on reducing leaching are only short-term, since desorption of sulfate will result in equivalent losses of sulfate and cations from the soil.

The reversibility of sulfate adsorption varies with soil properties and the desorbing solution used. In some cases, H_2O recovers all adsorbed sulfate whereas in other cases, full recovery is achieved only with phosphate or acetate extractions. Reasons for the better recovery with phosphate or acetate include the greater affinity of these anions for adsorption sites and, in the case of acetate, the increase in pH as well. Pre-treatment of soils with phosphate (such as by fertilization in the field) is known to reduce sulfate adsorption capacity since sulfate does not displace phosphate from adsorption sites. However, phosphate does not always displace all adsorbed sulfate, as shown by Bornemisza and Llanos (1967) for highly-weathered tropical soils rich in Fe and Al oxides.

There is evidence that "aging" or prolonged contact between soil and solution reduces the recovery of sulfate (Barrow and Shaw 1977). This effect is attributed to slow reactions and occurs with other adsorbed anions as well. Some soils are known to adsorb sulfate irreversibly (against H_2O) under field conditions but not in laboratory conditions (Johnson and Henderson 1979), a phenomenon likely related to slow reactions. Microbial immobilization may be a factor in the "aging" phenomenon as well.

Sulfate adsorption is concentration-dependent, i.e., sulfate adsorption increases with solution sulfate concentration (Chao et al. 1963). Thus, for any given input concentration, sulfate will adsorb on to soil sesquioxide surfaces until the corresponding soil adsorbed sulfate value is reached on the sulfate adsorption isotherm. When that point is reached, the soil should be in steady-state with outputs equalling inputs. In the case where sulfuric acid inputs increase, concentrations increase, thereby activating "new" sulfate adsorption sites and causing a net sulfate retention in the soil. With continued inputs, a new steady-state condition would eventually be reached. This is schematically depicted in Figure 2-3 (Johnson and Cole 1980).

This concentration-dependent relationship will result in a "front" moving downward through a sulfate adsorbing soil when a new, higher level of sulfate concentration is introduced, and continually applied to the soil. Soil above (or behind) the front will have a new higher level of sulfate on the soil in response to the higher solution levels. Soil solution samples taken behind the front might indicate signficant movement of cations and sulfate, while samples at a lower depth indicate essentially no leaching of cations and sulfate. Thus, the sulfate adsorbing soil delays cation leaching effects of dilute sulfuric acid inputs until the adsorbing capacity (dependent on input concentration) is satisfied down through the soil zones of interest.

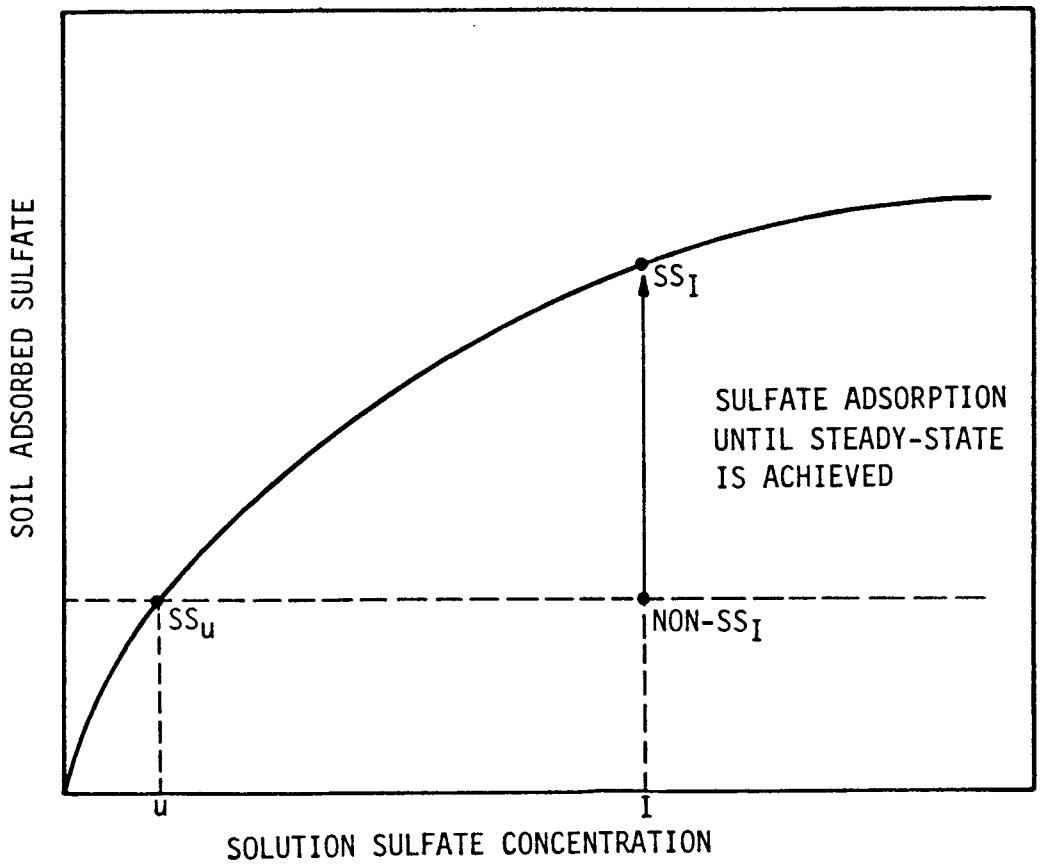

Figure 2-3. Schematic representation of a soil sulfate adsorption isotherm. U = undisturbed soil conditions, I = soil conditions following increased H_2SO_4 input, SS and NON-SS refer to steady-state and non-steady-state conditions, respectively. Adapted from Johnson and Cole (1980).

In the case where sulfuric acid inputs decrease, sulfate will desorb from the soil, unless it is irreversibly adsorbed, to a point on the isotherm at which the equilibrium sulfate concentration equals input concentrations. At this point, inputs and outputs are equal. Prior to this point, outputs exceed inputs during sulfate desorption and the sulfate and cations previously retained during adsorption are leached from the soil.

Sulfate adsorption capacity of soils is not routinely determined; therefore, the extent of soils with significant capacity to adsorb sulfate has not been established. Some adsorption is a common property of many Ultisols, Oxisols, some Alfisols, and is reported for other soils (Singh et al. 1980). The work of Johnson and Todd (1983) shows sulfate adsorption is low in Spodosols. The distribution of these soil orders within the U.S. is depicted in Figure 2-4 (Section 2.3.5).

2.2.9 Soil Chemistry Summary

Acid soils are a natural consequence of long exposure to a climate of excess rainfall because of the leaching action of natural inputs of acidic ions. Unleached soils do not become acid. The rate at which leached soils become acid depends upon soil characteristics, including buffer capacity, and the rate of H^+ input and the accompanying anion. Natural H^+ inputs come from CO_2, organic matter, nitrification, and sulfur oxidation. The buffer capacity of soils partially neutralizes H^+ input by reactions with carbonates (> pH 7.0), with exchangeable bases (pH 5.5 to 7.0), and with clay minerals (< pH 5.5). Soil-mediated injury to vegetation from H^+ inputs occurs only when pH is low enough to cause significant dissolution of Al- or Mn-containing clay minerals (< pH 5.0 to 5.5).

The amount of H^+ required to lower pH of an acid soil depends upon the CEC of that soil. For example, a loamy sand Ultisol with the rather low CEC of 2.0 meq 100 g^{-1} requires about 1.1 meq H^+ 100 g^{-1} to lower pH from 6.0 (65 percent base saturated) to 4.5 (10 percent base saturated). That would be about 22 keq H^+ ha^{-1} to effect the change to a depth of 15 cm. A finer textured Ultisol with a CEC of 10 meq 100 g^{-1} requires about five times that amount. Soils high in smectites (expandible clays) or organic matter require considerably more H^+ for a comparable pH change.

The weathering of alumino-silicate clays will produce strong buffering in soils that are already acid (5.5 or below) such that calculations of pH changes, based on changes in basic cation removal by H^+ additions, grossly underestimate the amount of acid required to cause the changes in these soils. The presence of sulfate adsorption capacity (see Section 2.2.8) increases their capacity to absorb dilute H_2SO_4 inputs before significant change in pH or base status occurs.

2.3 EFFECTS OF ACIDIC DEPOSITION ON SOIL CHEMISTRY AND PLANT NUTRITION

It is not always clear what deposition is acidic or acidifying. From the standpoint of the effects on neutral to acid soils, the following depositional materials could be expected to have acidifying effects: H_2SO_4, HNO_3, H_2SO_3, SO_2, S, NH_3, NH_4SO_4, whereas the following sulfate salts are essentially neutral or slightly basic in effects on long-term soil pH: $CaSO_4$, K_2SO_4, Na_2SO_4, $MgSO_4$. Carbonates of calcium and magnesium would raise the pH.

To alter the soil chemically, precipitation must bathe the soil particles. Runoff water will minimally impact soil due to its brief contact with soil particles. As Tamm (1977) has noted, water percolating through soil is not necessarily at equilibrium with the soil solution but may move directly through old root channels, animal burrows, and large pores at ped surfaces. Soils percolating similar quantities of water may differ in the extent of their reaction with the water. Under unsaturated conditions, water tends to move through the small pores of soil aggregates and has the best opportunity to attain chemical equilibrium with the soil. During a rainfall, the flow velocity in the small pores within aggregates becomes negligible relative to that in the large pores between aggregates. Drainage water, therefore, only reacts with the soil to the extent that dissolved constituents diffuse between the small and large pores (Bolt 1979). This effect can be demonstrated by comparing soil solution chemistry, obtained by porous ceramic cups, with that of free leachate water. Using this system, Shaffer et al. (1979) demonstrated that solutions applied to a saturated soil can pass through the soil rapidly and nearly unchanged.

2.3.1 Effects on Soil pH

In considering the effects of acidic deposition, it is essential to realize that acids are produced naturally within soils (Reuss 1977, Rosenqvist 1977, Rosenqvist et al. 1980; also see Section 2.2.1). Atmospheric acidic inputs must be viewed as an addition to natural, continual acidification and leaching processes due to carbonic acid formation, organic acid formation, vegetative cation uptake, and a variety of management practices (Reuss 1977, Johnson et al. 1977, Andersson et al. 1980, Sollins et al. 1980). In Table 2-1 several values are given for potential acidifying or neutralizing effects of lime, N fertilizer, acidic precipitation, and internal acid production in soils. Even though most of the values are only approximate, it is clear that a year of rather heavy acidic deposition has potential acidifying effects that are small compared to common agricultural amendments. For that reason, it is generally concluded (McFee et al. 1977, Reuss 1977) that acidic deposition will not have a measurable effect on the pH of soils that are under normal cultivation practices.

The values for internal acidity production (see Table 2-5 in Section 2.3.3.1) span a wide range. If the lower values occur, then acidic deposition is potentially as influential as natural processes,

TABLE 2-1. RELATIVE ACIDIFYING AND NEUTRALIZING POWER OF MATERIALS ADDED TO SOILS

Source	Potential acid or base effect	
Agricultural liming operation 5000 kg $CaCO_3$ ha^{-1}	Neutralizing or basic effect 100 keq ha^{-1}	10 eq m^{-2}
Nitrogen fertilization with reduced form of N, such as urea or NH_4 70 kg N ha^{-1}	Acidifying effect[a] 10 keq ha^{-1}	1 eq m^{-2}
Atmospheric deposition 1 year (100 cm) pH 4.0 rain	Acidifying effect 1 keq ha^{-1}	0.1 eq m^{-2}
16 kg S ha^{-1} dry deposition	Acidifying effect 1 keq ha^{-1}	0.1 eq m^{-2}
Internal acid production in soils due to carbonic and organic acids in one year from Table 2.5	Acidifying effect .23-22.7 keq ha^{-1}	.023-2.27 eq m^{-2}

[a]N fertilization usually has somewhat less actual acidifying effect. This is the maximum assuming complete nitrification of the N fertilizer.

but in other cases it would be quite small and of little consequence in natural ecosystems. Unfortunately, the data base for including natural acid formation in assessments of impact on soils is extremely limited. Thus, current schemes, by default, often assume that atmospheric inputs add significantly to internal acid production, an assumption that is not universally accepted (e.g., Rosenqvist 1977, Rosenqvist et al. 1980). Carbonic acid is a major leaching agent in some forest soils (McColl and Cole 1968, Nye and Greenland 1980), yet it does not produce low pH (i.e., < 5.0) solutions under normal conditions (McColl and Cole 1968; Johnson et al. 1975, 1977). Organic acids may contribute substantially to elemental leaching in forest soils undergoing podzolization (Johnson et al. 1977) and can produce low pH (i.e., < 5.0) in unpolluted natural waters as well (Johnson et al. 1977, Rosenqvist 1977, Johnson 1981).

Experiments that directly indicate a change in pH due to acidic deposition inputs (Tamm 1977, Abrahamsen 1980b, Farrell et al. 1980, Wainwright 1980, Stuanes 1980, Bjor and Teigen 1980) either used accelerated application rates far exceding natural precipitation or applied concentrated acid. Both create situations unlikely to exist in nature because they do not allow for normal influences of weathering, and nutrient recycling. It is also clear that soils exposed to concentrated acids over short periods will undergo reactions and changes that would never occur with more dilute acid over longer periods. Therefore, the effects of acidic deposition on soil pH are often predicted from known soil chemical relationships, using input values similar to those measured in recent years and without the benefit of long-term experiments under simulated natural conditions.

McFee et al. (1976) calculated theoretical reductions in both soil pH and base saturation from atmospheric H^+ inputs, assuming no concurrent inputs of basic cations. They concluded that most soils resist pH change and that there is only a "small likelihood of rapid soil degradation due to acid precipitation." However, they also suggest that long-term (e.g., 100 years) soil acidification trends could have an impact on non-agricultural soils and that these trends are very difficult to evaluate in short-term experiments. Models of soil acidification processes range from complex ecosystem budget approaches (Andersson et al. 1980, Sollins et al. 1980) to process-oriented soil leaching models (Reuss 1978). Their quantitative applicability on a wide range of sites has not been tested, but they can add to our understanding of the concepts involved and may be applied to many terrestrial ecosystems.

Despite uncertainties in estimating potential acidification rates, the authors of this chapter provide some illustrations in Table 2-2. The data illustrate that large differences in potential acidification rates can be expected due to CEC alone, even without considering such other soil properties as anion adsorption capacity or hydrologic characteristics. It also illustrates how the assumptions concerning accompanying cations, H^+ replacement efficiency, and weathering rates change estimates of acidification rates.

Several considerations embodied in Table 2-2 must be understood if the data are to be used correctly.

1) The input rates of acidic deposition are considerably higher than those now reported for the United States.

2) Most natural ecosystems within humid regions have acid soils. Soils with neutral to slightly-acid pH and with very low CEC, 3 to 6 meq 100 g^{-1}, are uncommon in the humid regions.

3) A 50 percent decrease in base saturation in many mineral soils could lower pH from the slightly acid (6.6 to 6.8) range to strongly acid (5.0 to 5.5) range.

4) These estimates ignore anion adsorption capabilities and natural acidifying processes.

5) Assumptions under scenario 1 are not realized in nature. Those under 2 and 3 are realistic for many soils and many deposition situations, but cannot be considered universally applicable.

If we consider a soil with a low CEC of only 3 meq 100 g^{-1} and assume a soil bulk density of 1.3 g cc^{-1}, this soil would have a total of 60 keq cation exchange capacity per hectare in the top 15 cm (third soil in Table 2-2). A significant pH change could be accomplished by reducing the percent base saturation by 50 percent. This would seem to be theoretically possible in 15 years: 15 yr x 2 keq ha^{-1} yr^{-1} = 30 keq ha^{-1}. However, all of the acid input would have to replace and leach an equivalence of bases (Assumption 1 in Table 2-2). This is highly unlikely. Wiklander (1974) indicates a replacement efficiency considerably less than 1.0 in acid soils, pH 5.5 to 6.5. Further, accompanying salts of Ca, Mg, and K also reduce the acid efficiency in lowering pH (Assumption 2). Such rapid change also assumes no H^+ consumption by weathering and no recycling of bases to the surface soil whereas Abrahamsen (1980b) indicated weathering rates were keeping pace with acid inputs in treatments with pH above 4.0. Moreover, vegetation may deposit significant quantities of basic nutrient ions on the surface. A more reasonable estimate of the years required to lower the soil pH significantly, even in this very poorly buffered example, is 22 to 90 years. If a value of 9 meq CEC or higher is assumed (a more common value for most surface soils in the United States) then the minimum time is 67 years without weathering and much longer, or infinity, with normal weathering.

The magnitude of soil resistance to pH changes is illustrated by the small pH changes that have resulted from natural acid inputs of 0.23 to 2.27 keq ha^{-1} yr^{-1} generated by N-fixation-metabolism, organic matter decay and CO_2 from respiration (Table 2-1). These inputs have not caused rapid pH changes and it is unlikely that an additional 2 keq ha^{-1} yr^{-1} or less from acidic deposition will cause a significant change in many soils.

TABLE 2-2. ESTIMATES OF TIME REQUIRED TO EFFECT A 50% CHANGE IN BASE SATURATION IN THE TOP 15 CM OF SOIL. TIME REQUIRED FOR SIGNIFICANT ACIDIFICATION OF UNCULTIVATED SOILS THAT ARE SLIGHTLY ACID OR NEARLY NEUTRAL UNDER HIGH RATES OF ACIDIC DEPOSITION--100 CM OF PH 4.0 PRECIPITATION PLUS 16 KG S HA^{-1} YR^{-1} IN DRY DEPOSITION (TOTAL ACID INPUT OF 2 KEQ H^+ HA^{-1} YR^{-1})

Soil	CEC meq 100 g^{-1}	Assumption 1	2	3
		years		
Midwestern Alfisol	15	75	110	220 ∞
Southeastern Ultisol	9	45	67	125 ∞
Quartzipsamnent with low organic matter	3	15	22	45-90

Assumption 1. All incoming H^+ exchanges for (replaces) basic cations on the soil exchange complex. There are no accompanying basic cations and no weathering or other input of basic cations. This is the "worst case" situation and cannot exist in nature.

Assumption 2. The incoming H^+ is accompanied by 0.3-0.5 keq ha^{-1} yr^{-1} of basic cations Ca, Mg, K (Cole and Rapp 1981), and the replacing efficiency of H^+ for basic cations drops below 1.0 as the base saturation of the soil drops (Wiklander 1975).

Assumption 3. Same as under 2 except that acidification is further slowed by release of basic cations from weathering 1 keq ha^{-1} yr^{-1} (for example, 20 kg Ca ha^{-1} of 15 kg Ca plus 3 kg Mg ha^{-1} yr^{-1} within range calculated for Hubbard Brook (Likens et al. 1977) and the cycling of basic cations back to soil surface by plants.

The evidence for acidification of soils by the present rate of acidic deposition is not strong. If significant acidification is to occur within a few decades, it will be in the limited soil areas that combine the following characteristics: the soil is not renewed by fresh soil deposits; it is low in cation exchange capacity, i.e., low in clay and organic matter; it is low in sulfate adsorption capacity; it receives high inputs of acidic deposition without significant basic cation deposition; it is relatively high in present pH (neutral to slightly acid) and free of easily weatherable materials to one meter depth (see Section 2.3.5.2.1).

As Section 2.3.3.1 discusses, acid precipitation cannot leach nutrient cations unless the associated sulfate or nitrate anions in the soil are mobile. Evidence indicates that sulfate is not always mobile (Section 2.2.8) particularly as soils become more acid (Johnson and Cole 1977, Johnson et al. 1979, Abrahamsen 1980b, Singh et al. 1980).

It is also possible for a soil to be leached of cations without concurrent acidification, if acidic inputs stimulate the weathering of cations from primary minerals. Therefore, it is important to make a distinction between cation leaching and the process of soil acidification. It is unrealistic to assume either a steady-state condition for soil exchangeable cations or a condition where weathering is zero and cations are depleted from exchange sites in proportion to H^+ inputs. These common assumptions made in predictive models seriously limit the models' applicability to natural systems. Another important factor which models do not consider is the acidification caused by natural processes. As noted in Section 2.2.1, atmospheric acid inputs must be viewed as an addition to the natural acidification processes of cation uptake by plants, nitrification, and soil leaching by organic and carbonic acids (Johnson et al. 1977, Reuss 1977, Cronan et al. 1978, Rosenqvist et al. 1980).

Section 2.1.3, on leaching is closely related because long-term pH changes require leaching of basic cations as well as acidic inputs.

2.3.2 Effects on Nutrient Supply of Cultivated Crops

This section deals with the significance of atmospheric additions of S and N to crop requirements. Few detrimental effects of acidic deposition are expected on nutrient supply to cultivated crops (see Section 2.3.1) because by comparison agricultural practices have a massive effect.

Input of nutrients to plant systems from rainfall has been documented since the mid-19th century (Way 1855). Calculations made in a number of U.S. regions have estimated the seasonal atmospheric deposition of nutrient species, particularly sulfate and nitrate, to agricultural and natural systems and the implications of this deposition on plant nutrient status. Estimates by Hoeft et al. (1972) of 30 kg S ha^{-1} yr^{-1} and 20 kg N ha^{-1} yr^{-1} deposited in precipitation in

Wisconsin indicates the importance of atmospheric sources of these elements. These values, however, are higher than those usually reported in the United States (see Chapter A-8). Jones et al. (1979) reported that atmospheric S is a major contribution to the agronomic and horticultural crop needs for S as a plant nutrient in South Carolina.

The amount of annual S deposition at selected sites is presented in Table 2-3. Amounts of S recorded for 1953-55 in rural areas along the Gulf and southern Atlantic coasts were usually less than 6 kg S ha^{-1} yr^{-1}. In northern Alabama, Kentucky, Tennessee, and Virginia the levels were much higher (10 to 30 kg ha^{-1} yr^{-1}) (Jordan et al. 1959). These can be compared with the recent NADP data for wet deposition of S (Chapter A-8).

These amounts of S represent a significant portion of that required by crops. The amounts of S absorbed by crops are summarized in Table 2-4. Terman (1978) estimates an average crop removal of 18.5 kg S ha^{-1} yr^{-1} and concludes that if current rates of atmospheric S deposition are greatly reduced, the need for applying fertilizer S for satisfactory crop yield will increase.

The atmospheric deposition of N is usually lower than deposition of S, but crop requirements are much higher. Therefore, it is generally accepted that atmospheric N deposition plays a small or insignificant role in nutrition of cultivated crops (see Chapter E-3, Section 3.4.2).

It is well known that foliar applications of plant nutrients can stimulate plant growth (Garcia and Hanway 1976). It is possible, but unproven, that repeated exposure of plants to small amounts of atmospheric deposition may be more effective in stimulating plant growth than a comparable amount applied to soils (see Chapter E-3, Section 3.4).

2.3.3 Effects on Nutrient Supply to Forests

Nutrient supply may be influenced by acidic deposition effects on leaching of cations or by pH induced changes in mineral solubility, microbial processes, or weathering rates in addition to the direct influence of additions of N and S in deposition. Microbial processes are discussed in Section 2.4. Solubility (availability) and weathering reactions are discussed in Section 2.2.

Acid rain has created a major concern because of the potential for accelerated cation leaching from forest soils and eventual losses of productivity (Engstrom et al. 1971). This concern was the driving force for numerous empirical studies of acid rain effects on forest nutrient status in general and cation leaching in particular (reviewed by Johnson et al. 1982).

Perhaps because of the negative implications of the term "acid rain," initial speculations about acid rain's effects on forest

TABLE 2-3. AMOUNTS OF SULFUR FOUND IN PRECIPITATION IN VARIOUS STATES

State	Location in state	Sites	Years	Major source	Average kg S ha^{-1} yr^{-1}
Southern States					
Alabama	Prattville	1	1954-55	General	3.7
	Muscle Shoals	19	1954	General	5.4
	Muscle Shoals	20	1955	Steam Plant	11.9
	Muscle Shoals	23	1956	Steam Plant	11.0
Arkansas	NW and SE	2	1954-56	General	3.7
Florida	Gainesville	1	1953-55	Urban	8.8
	Others	5	1953-55	General	3.2
Kentucky	Various	6	1954-55	General	13.1
Louisiana	Various	5	1954-55	General	9.0
Mississippi	Various	7	1953-55	General	5.0
North Carolina	Statesville	1	1953-55	Industry	15.5
	Others	15	1953-55	General	6.0
Oklahoma	Stillwater	1	1927-42	General	9.7
Tennessee	Various	7	1955	General	14.2
	Various	5	1971-72	General	17.1
Texas	Beaumont	1	1954-55	Industry	12.1
	Others	4	1954-55	General	5.7
Virginia	Norfolk	1	1954-55	Industry	35.2
	Various	16	1953-56	General	21.4

TABLE 2-3. CONTINUED

State	Location in state	Sites	Years	Major source	Average kg S ha^{-1} yr^{-1}
Northern States					
Indiana	Gary	1	1946-47	Industry	142.2
	Others	10	1946-47	General	30.0
Michigan	Various	5	1959-60	Industry	11.3
Nebraska	Various	7	1953-54	General	7.2
New York	Ithaca	1	1931-49	Urban & Industry	54.9
Wisconsin	Industrial Site	1	1969-71	Industry	168.0
	Urban	9	1969-71	Urban	42.0
	Rural	13	1969-71	General	16.0

Adapted from Terman (1978). See original for data sources.

TABLE 2-4. SULFUR CONTENT OF CROPS

Crops	Yield tons ha^{-1}	Total S Content kg ha^{-1}
Grain and oil crops		
Barley (*Hordeum vulgare* L.)	5.4	22
Corn (*Zea Mays* L.)	11.2	34
Grain sorghum (*Sorghum bicolor* L. Moench)	9.0	43
Oats (*Avena sativa* L.)	3.6	22
Rice (*Oryza sativa* L.)	7.8	13
Wheat (*Triticum aestivum* L.)	5.4	22
Peanuts (*Arachis hypogaea* L.)	4.5	24
Soybeans (*Glycine max* Merr.)	4.0	28
Hay Crops		
Alfalfa (*Medicago sativa* L.)	17.9	45
Clover-grass	13.4	34
Bermuda-grass (*Cynodon dactylon* L.)		
Common	9.0	17
Coastal	22.4	50
Orchardgrass (*Dactylis glomerata* L.)	13.4	39
Timothy (*Phleum pratense* L.)	9.0	18
Cotton and tobacco		
Cotton (lint + seed) (*Gossypium hirsutum* L.)	4.3	34
Tobacco (*Nicotiana tabacum* L.)		
Burley	4.5	21
Flue-cured	3.4	50
Fruit, sugar, and vegetable crops		
Beets		
Sugar (*Beta saccharifera*)	67	50
Table (*Beta vulgaris* L.)	56	46
Cabbage (*Brassica oleracea*)	78	72
Irish potatoes (*Solanum tuverosum* L.)	56	27
Oranges (*Citrus* sp.)	52	31
Pineapple (*Ananas comosus*)	40	16

Estimates by Potash/Phosphate Institute of North America. Adapted from Terman (1978).

productivity devoted little or no attention to concurrent sulfate and nitrate deposition on forests deficient in S or N. Only recently has it been recognized that acid rain can cause increases as well as decreases in forest productivity (Abrahamsen 1980b, Cowling and Dochinger 1980). The net effect of acid rain on forest growth depends upon a number of site-specific factors such as nutrient status and amount of atmospheric acid input. (See also Chapter E-3, Section 3.4.1.)

It is also very important to consider that ions such as SO_4^{2-} and NO_3^- are already in the ecosystem and that H^+ is generated naturally by the plant community (Ulrich 1980). Thus, the question is one of relating inputs to natural levels; e.g., does atmospheric H^+ input significantly add to or exceed natural H^+ production within the soil? Do the detrimental effects of H^+ deposition offset the benefits of NO_3^- deposition in an N-deficient ecosystem or the benefits of SO_4^{2-} deposition in an S-deficient ecosystem? In short, the problem of assessing the effects of acid rain on forest nutrient status is largely a matter of quantification and requires a nutrient cycling approach.

2.3.3.1 Effects on Cation Nutrient Status--Cation leaching is important to soil properties because it may lead to a loss of plant nutrients and depressed soil pH. It is important in hydrology because cations leached from soils may be deposited in aquatic systems.

The basic cation status of a soil depends on the net effect of leaching and other losses versus weathering and other inputs (Abrahamsen 1980a, Ulrich et al. 1980). Weathering is stimulated by additional H^+ input, offsetting leaching to some extent. However, most acid irrigation studies (Abrahamsen 1980b) and one study under ambient conditions (Ulrich et al. 1980) indicate a net decline in exchangeable basic cations with time. There is little doubt that acid rain can accelerate cation leaching rates, but the magnitudes of these increases must be evaluated within the context of natural, internal leaching processes. The magnitude is quite variable, depending upon the amount of acid input, the rate of soil leaching by natural processes (Cole and Johnson 1977, Cronan et al. 1978), and the degree to which soils are buffered against leaching (e.g., by anion adsorption; Johnson and Cole 1977). Furthermore, the ultimate effects of accelerated cation leaching on cation nutrient status depend upon a number of variables, most notably exchangeable cation capital, primary mineral weathering rate (Stuanes 1980), forest cation nutrient requirement, and management practices such as harvesting.

A comparison of the effects of some of these factors on cation nutrient status is given in Table 2-5. Various schemes for evaluating internal acid production have been proposed (Reuss 1977, Sollins et al. 1980, Ulrich 1980), but in this case, only the values reported by various investigators for soil leaching (usually by carbonic acid) are considered. It is obvious that atmospheric acid inputs vary not only in absolute magnitude, but also in their importance relative to internal leaching processes and effects of harvesting.

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TABLE 2-5. ATMOSPHERIC H^+ INPUTS VS CATION REMOVAL BY INTERNAL H^+ PRODUCTION (CARBONIC AND ORGANIC ACIDS) AND POTENTIAL NET ANNUAL CATION REMOVAL IN BOLE ONLY AND WHOLE-TREE HARVESTING (WTH) IN SELECTED FOREST ECOSYSTEMS (ADAPTED FROM EVANS ET AL. 1981)

Site	Species	Age (yr)	Precipitation H^+ input[a]	Cation leaching by internal acid production[b]	Cation removal by harvesting[c]	
					Bole	WTH
			(eq ha^{-1} yr^{-1})			
Thompson, Washington	Pseudotsuga menziesii	42	240[d] (4.8)	420[d] (5.9)	380[e]	660[e]
Solling, W. Germany	Fagus sylvatica	59	900[g]	1950[g]	220[g]	370[e]
Jadrass, Sweden	Pinus sylvestris	-	190[g]	226[g]	-	-
Findley, Washington	Abies amabilis, Tsuga mertensiana	175	90[h] (5.6)	1410[h] (4.5)	272[e]	460[e]
H.J. Andrews, Oregon	Pseudotsuga menziesii	450	28[g]	22700[g]	60[e]	106[e]

[a]Weighted average $[H^+]$ times precipitation amount; weighted average $[H^+]$ as pH appears in parenthesis where available.

[b]Calculated from net increase in weighted average HCO_3^- or organic anion concentration (the latter estimated by anion deficit) times water amount. Weighted average $[H^+]$ as pH for solutions appears in parentheses where available.

[c]Nutrient content divided by age; WTH = whole tree harvest, removal of all aboveground biomass.

[d]From Cole and Johnson (1977).

[e]From Cole and Rapp (1981).

[f]From Lindberg et al. (1979).

[g]From Andersson et al. (1980). For comparison in this table, only H_2CO_3 production values are included.

At the unpolluted site in Findley Lake, it is not surprising that internal leaching processes and harvesting effects exceed atmospheric H^+ inputs. However, even in the beech stand at Solling, West Germany, values for H_2CO_3 production reported by Andersson et al. (1980) exceed atmospheric H^+ inputs as measured by open-bucket collectors. In this case, the comparison is misleading, however, since dry deposition to the forest canopy at Solling is known to be exceedingly high (Ulrich et al. 1980), and, consequently, H^+ inputs to the forest floor substantially exceed those deposited above the canopy. It is also noteworthy that Ulrich et al. believe that while internal H^+ producing processes are important at Solling, acid rain is having serious, deleterious effects on forests there.

Studies of basic cation leaching due to acidic inputs sometimes give inconsistent results. Under ambient conditions, Mayer and Ulrich (1977) noted a net loss of Ca, Mg, K, and Na from the soils under a beech forest. Except for Na, however, the loss was equal to or less than nutrient accumulation in the trees. Roberts et al. (1980) reported that acidic precipitation on Delamere forest (pine) of central England may produce small changes in litter decomposition, but they found no effect on Ca, Mg, K, or Na leaching rate. Cole and Johnson (1977) found no detectable effect of acid precipitation on the soil solution of a Douglas-fir ecosystem. On the other hand, Andersson et al. (1980) noted a net output of Ca from both a pine forest soil in Sweden and a beech forest soil in West Germany; both soils accumulated N but not sulfate. Cronan (1980a) reported net losses of Ca, Mg, K, and Na from subalpine soil in New Hampshire, attributing losses to acidic precipitation. Studies by Mollitor and Raynal (1982) suggest that leaching of K may be the most serious problem of cation leaching in Adirondack forest soils.

Nitrate is sometimes associated with acidic deposition and differs considerably from sulfate in that it is very poorly adsorbed to most soils (Johnson and Cole 1977). However, biological processes in N-limited ecosystems quickly immobilize nitrate, and since N limitations are common in forested regions of the world, nitrate is rarely mobile (Abrahamsen 1980b). On the other hand, nitrogen-rich ecosystems (where biological immobilization of NO_3^- is minimal) are susceptible to leaching by HNO_3.

With regard to North American forests, cation deficiencies are very rare although they are known to occur in red pine (Pinus resinosa) on some sandy soils in New York State (Stone and Kszystyniak 1977, Heiberg and White 1951, Hart et al. 1969). Acid rain accelerated leaching could, in theory, exacerbate this situation, but this possibility has not been investigated. It should be noted, however, that these ecosystems are exceedingly conservative with regard to potassium (Stone and Kszystyniak 1977), and biological cycling and conservation may play major roles in resisting effects of acid rain on K^+ leaching (e.g., other cations may be leached while K^+ is conserved).

2.3.3.2 Effects on S and N Status--Deficiencies of S have been indicated in forests remote from pollutant inputs in eastern Australia

(Humphreys et al. 1975) and the northwestern United States (Youngberg and Dyrness 1965, Will and Youngberg 1978). Humphreys et al. (1975) suggest that pollutant inputs from power plants benefit S-deficient Australian forests, particularly when the soils have little SO_4^{2-} adsorption capacity. In these situations continual input of moderate amounts of H_2SO_4 as acid rain may be a source of fertilizer.

At the other extreme, continual atmospheric S inputs may help alleviate sub-optimal sulfate availability in sulfate "fixing" soils that are rich in hydrated Fe and Al oxides. Although adsorbed insoluble sulfate is thought to be available to plants in the long run, the intensity or rate of supply to the soil solution can be less than that required by plants, effecting an S limitation (Hasan et al. 1970).

Research has shown that N fertilization, a practice in some forested regions of the world, results in rapid use of ecosystem S supplies, possibly leading to S limitations (Humphreys et al. 1975, Turner et al. 1980). It has been suggested that forest N and S status must be evaluated because of the closely related roles of these elements in protein synthesis (Kelly and Lambert 1972, Turner and Lambert 1980, Turner et al. 1980). In relatively unpolluted regions of the northwestern United States, evidence indicates that lack of growth response to N by Douglas-fir is due to marginal S status (Turner et al. 1977, 1979). Thus, it seems evident that moderate amounts of S in deposition could benefit forests undergoing N fertilization. In the United States this currently involves a total of about 1,000,000 ha of forest lands, primarily in the Northwest and Southeast (Bengston 1979).

Amounts of atmospheric S input sufficient to satisfy forest S requirements are much smaller than many crop requirements. In general, S inputs of 5 kg ha^{-1} yr^{-1} are sufficient to satisfy S requirements in most forest ecosystems (Humphreys et al. 1975, Evans et al. 1981, Johnson et al. 1982). Inputs of SO_4^{2-} in acid rain affected regions frequently exceed this value (often by a factor of 2 to 4), implying that S is currently being deposited in excess of forest requirements (Table 2.3).

Several studies have shown that excess S cycles within vegetation and accumulates in soils as SO_4^{2-} without any apparent harm (Kelly and Lambert 1972, Turner et al. 1980, Turner 1980). The plateau between S sufficiency and toxicity in forest ecosystems appears to be quite broad. Inputs of S usually constitute a more significant increment to the natural sulfur flux within forest ecosystems than do equivalent inputs of H^+ to the natural flux of H^+. Therefore, it would appear that further emphasis ought to be given to effects from the SO_4^{2-} component of acidic deposition. Similarly, further emphasis ought to be given to the effects of N inputs, since they appear to be increasing (Abrahamsen 1980b) and N is commonly the limiting nutrient in forest ecosystems.

Nitrogen deficiencies are common in forests throughout the world (Abrahamsen 1980b). Inputs of NO_3^- (as well as NH_4^+ and other forms of N) are likely to improve forest nutrient status and productivity in many cases. Nearly all forest ecosystems for which nutrient budgets are available appear to accumulate NO_3^- as well as other forms of N (i.e., inputs > outputs; Abrahamsen 1980b). Since NO_3^- is very poorly adsorbed to most soils (Vitousek et al. 1979), this accumulation is undoubtedly due to biological uptake. The inhibiting effect of NO_3^- immobilization on the leaching potential of HNO_3 is the same as that of SO_4^{2-} immobilization on the leaching potential of H_2SO_4 even though the mechanisms of immobilization for those two anions are different.

Because forest N requirements are relatively high compared to S requirements, instances of atmospheric N inputs in excess of forest N requirements seldom occur. An apparent exception is the Solling site in West Germany, where atmospheric inputs of N, S, and H^+ are high (Ulrich et al. 1980).

If atmospheric N inputs increase to the point where N deficiencies are alleviated and excess N is available in soils, nitrification may be stimulated. Nitrification pulses are thought to be responsible for a large percentage of leaching at the heavily-impacted Solling site in West Germany, for example (Ulrich et al. 1980). Thus, nitrogen "saturation" of forest ecosystems could result in significant increases in cation leaching and, under extreme circumstances, soil acidification. Such "saturation" would occur most readily in forests with low N demand (i.e., boreal coniferous forests; Cole and Rapp 1981) or in forests with adequate or excessive N supplied (such as by N-fixing species). Indeed, the naturally acidifying effects of red alder, an N-fixing species indigenous to the northwestern United States, have been noted by several investigators. However, there is not evidence of widespread, imminent nitrogen saturation of forests since N deficiencies are still quite common and most ecosystems are still accumulating N (Abrahamsen 1980, Johnson et al. 1982).

Acidic deposition may indirectly affect N availability in forest soils. Tamm (1976) predicted short-term increases in N availability (due to increased decomposition and microbiological N immobilization) and tree growth due to acidic precipitation. However, long-term declines in both N status and tree growth could occur due to net N losses from the ecosystem. With regard to decomposition, empirical results have been variable (see Section 2.5). Whether this increase in N availability is due to changes in microbial activity or to the acid-catalyzed hydrolysis of labile soil N is unknown. In either event, the results of the Norwegian studies, in which both N availability and nitrate leaching were stimulated by H_2SO_4 inputs, strongly suggest that, contrary to earlier predictions that nitrification would be inhibited by acidic inputs (Tamm 1976), nitrification can be stimulated by acidic inputs.

2.3.3.3 Acidification Effects on Plant Nutrition--It is unlikely that many soils will be significantly acidified by acid rain at current input levels in the United States (see Section 2.3.1). Should soil acidification occur, however (e.g., in restricted areas with high acid inputs and very poorly buffered soils), a great deal of information is available about plant responses. Also, recent results from the heavily-impacted Solling site in West Germany suggest that slight changes in soil pH due to the combined effects of acid rain and internal processes are causing serious negative effects on forests there (Ulrich et al. 1980).

2.3.3.3.1 Nutrient deficiencies. In general, only those acidic soils that are highly leached (sandy and/or low CEC) are likely to be sufficiently low in Ca to affect growth of higher plants. That is, if Al and other toxic ions are not present in excess, most acidic soils will have adequate Ca for good growth of most plants (Foy 1964, Foy 1974a). The evidence suggests that many, if not all, of the Ca deficiencies reported on acidic soils in the field are due to Al-Ca antagonisms rather than low Ca per se. For a fuller treatment of the Ca-deficiency Al-toxicity argument, see earlier reviews (Kamprath and Foy 1972; Foy 1974a,b; Foy 1981). Similarly, magnesium deficiencies observed in plants grown on acid soils are often due to Al-Mg antagonisms rather than low total soil Mg levels.

Phosphorus deficiency is a common problem in crops and forests grown on acidic soils because such soils are often low in total P and because native P, as well as fertilizer P is combined with Al and Fe in forms that are only sparingly soluble (Adams and Pearson 1967, Kamprath and Foy 1972, Graham 1978, Pritchett and Smith 1972).

Unlike other micronutrients, Mo is less available in strongly acid soils (Kamprath and Foy 1972). Molybdenum deficiencies such as those reported on the Eastern Seaboard, in the Great Lakes states, and on the Pacific coast of the United States generally occur on such soils (Kubota 1978).

2.3.3.3.2 Metal ion toxicities. Any metal can be toxic if soluble in sufficient quantities. In near-neutral soils, heavy metals occur as inorganic compounds or in bound forms with organic matter, clays, or hydrous oxides of Fe, Mn, and Al. However, a decrease in soil pH can create metal toxicity problems for vegetation. Zinc, Cu, and Ni toxicities have occurred frequently in a variety of acid soils. Iron toxicity occurs only under flooded conditions where Fe occurs as the reduced, soluble Fe^{2+} form (Foy et al. 1978). Toxicities of Pb, Co, Be, As, and Cd occur only under very unusual conditions. Lead and Cd are of particular interest because they move into the food chain and affect human and animal health. For further details, see a recent review (Foy et al. 1978).

Aluminum and Mn toxicities are the most prominent growth-limiting factors in many, if not most, acidic soils (Foy 1973, 1974b, 1981;

Tanaka and Hayakawa 1974). Hence, this review will emphasize the harmful effects of these two elements on plants. The chemistry of Al and Mn in soils was discussed in Sections 2.2.3 and 2.2.4.

2.3.3.3.2.1 Aluminum toxicity. Because Al is a structural constituent of soil clay mineral particles, Al toxicity is theoretically possible in most, if not all, soils. The primary condition required to produce solubility of excess Al is a low pH. As Section 2.2.3 pointed out, aluminum may become soluble enough to be of concern when the soil pH is in the range 5.0 to 5.5 or below.

Aluminum toxicity is believed to be a primary factor in limiting plant root development (depth and branching) in many acidic subsoils of the southeastern United States (Foy 1981). For example, Kokorina (1977) noted that acid soil toxicity was more harmful in dry years. This dry season phenomenon in concert with acidic deposition may also be a factor in Ulrich's (1980) recent reports on forest growth reduction in West Germany.

On the basis of some complex theories of ecosystem acidification processes on and after a decade of monitoring at the Solling site, scientists at the University of Gottingen in West Germany state that the forests of Solling (as well as others like it in Germany) are being seriously impacted by acid rain (Ulrich 1980). Most significantly, at the Solling site Al concentrations in soil solutions have increased twofold (from 1-2 mg ℓ^{-1} to 2-5 mg ℓ^{-1}) beneath the beech stand and ~ tenfold (from 1-2 mg ℓ^{-1} to 15-18 mg ℓ^{-1}) beneath the spruce stand over the last decade (Matzner and Ulrich 1981). It is hypothesized that Al concentrations are reaching toxic levels, thereby damaging or killing tree roots and causing serious consequences to the maintenance of these forest ecosystems. An important question relative to toxicity of Al levels concerns the form of Al in soil solution. It would be important to know the extent of chelation by organic materials.

Atmospheric H^+ inputs must be viewed as additions to natural, internal acid generation (Ulrich 1980). One very important internal H^+ generating process at Solling is nitrification in mineral soil layers during warm, dry years. Nitrification during these periods (thought to be caused by decomposition of previously accumulated N-rich root residues) causes a pulse of acid production. According to Ulrich et al. (1980), systems that have been acidified by acid precipitation are unable to withstand such pulses because their buffering capacities are much reduced. Thus, Al is mobilized at such times, creating toxic conditions for roots.

Undoubtedly, acid inputs to the Solling site are very high. Inputs of H^+ measured with open-bucket collectors are not themselves excessively high, being approximately 700 eq ha^{-1} yr^{-1}; comparatively, H^+ input values of this magnitude are not uncommon in forests of the United States (Evans et al. 1981). However, at Solling

H^+ flux in throughfall is 2 to 5 times greater than in open precipitation due to dry deposition in the forest canopy.

In contrast to results and hypotheses at Gottingen, scientists with the Norwegian SNSF Project demonstrated the ability of forest ecosystems to tolerate acid inputs and Al levels exceeding those reported at Solling. This ability is shown by results of an intensive series of irrigation studies involving inputs of H_2SO_4 ranging from current background levels (approximately 0.8 keq ha^{-1} yr^{-1}) up to approximately 30 times that amount (26 keq ha^{-1} yr^{-1}). Although Al concentrations in soil solutions and in tree foliage increased substantially, no indications of Al toxicity were noted and growth effects were small (slight growth increases occurred in some species, slight decreases in other species, and no effects in some species; Abrahamsen 1980a,b; Tveite 1980a,b). It is also noteworthy that large nitrification pulses occurred in most acid treatments (Abrahamsen 1980a). Finally, greenhouse studies involving acid irrigation and liming of Norway spruce showed that this species (which occurs also at the Solling site) is extremely tolerant of high acid inputs and foliar Al concentrations.

Plant species and cultivars differ widely in their tolerances to excess Al in the growth medium. Published references to such differences are too numerous to cite individually, but access to the older literature is provided in review papers (Foy 1974b, 1981). Aluminum tolerance has been associated with pH changes in root zones, Al trapping in non-metabolic sites within plants, P uptake efficiency, Ca and Mg uptake and transport, root cation exchange capacity, root phosphatase activity, internal concentrations of Si, NH_4^+ - NO_3^- tolerance or preference, organic acid contents, Fe uptake efficiency and resistance to drought. For citations from the earlier literature, see review papers (Foy 1974b 1981, Foy and Fleming 1978, Foy et al. 1978).

2.3.3.3.2.2 Manganese toxicity. Manganese toxicity frequently occurs in soils with pH values of 5.5 or below, if the soil parent materials are sufficiently high in easily reducible Mn content. However, some soils do not contain sufficient total Mn to produce toxicity, even at pH 5.0 or below. Soils of the Atlantic Coastal Plain of the United States are lower in total Mn than those of the Gulf Coastal Plain (Adams and Pearson 1967). However, within any area, soils vary widely in Mn contents (Sedberry et al. 1978). In that study, the DTPA extractable Mn varied more with parent material and clay than with pH and organic matter. Reducing environments induced by poorly aerated conditions in soils increase Mn availability and potential for toxicity.

2.3.4 Reversibility of Effects on Soil Chemistry

Changes in soil chemistry caused by acidic deposition in unmanaged terrestrial ecosystems must, in general, be considered irreversible, but there are exceptions. Nutrients lost are not readily regained. However, exchangeable basic cations in surface soils may be replaced

gradually by weathering, by recycling by deep rooted species, and by dust inputs if the acidic inputs are reduced. Since basic cation depletion is the normal, long-term trend in humid regions, the trend toward increased acidity would probably not be reversed in such environments even if inputs stopped.

Since microbial activity in soils responds quickly to changing environments, important soil processes it moderates can be expected to return to former levels when the environment changes as a result of reductions in deposition.

Leaching of Al to aquatic systems in response to acidic inputs would likely lessen with reduced acidic deposition.

2.3.5 Predicting Which Soils will be Affected Most

2.3.5.1 Soils Under Cultivation--It is unlikely that acidic precipitation will adversely affect cultivated soils. Not only do many management practices result in acid production greater than that expected to be derived from acidic deposition, but good management also requires controlling pH at a level most conducive to plant growth (see Section 2.2.6). For example, NH_4^+ is an important source of fertilizer N to soils. This form rapidly oxidizes to NO_3^- in soil, resulting in significant acid production (see Section 2.2.1). Routine additions of N fertilizers may result in the release of between one and two orders of magnitude more H^+ than will be annually derived from acidic deposition (McFee et al. 1976).

2.3.5.2 Uncultivated, Unamended Soils--As indicated in the soil chemistry section, 2.2.1.3, arid or semi-arid region soils that are not normally leached do not naturally acidify, and adding acidic deposition will not change that nor cause any foreseeable ill effects.

The soils that might be affected are those of the humid regions, which are not normally amended with lime and/or fertilizers. This area includes most of the forested land of the eastern United States, the Pacific Northwest and some high altitude areas of the west. It is important to identify which soils in these regions are likely to be adversely affected by acidic deposition.

Various schemes for assessing site sensitivity to acidic deposition effects have been proposed. Those directed toward aquatic effects have emphasized bedrock geology (Hendry et al. 1980, Norton 1980), while those concerned with terrestrial effects have emphasized cation exchange capacity and base saturation (McFee 1980, Klopatek et al. 1980). For the reasons previously discussed, sulfate adsorption capacity should be included in the sensitivity criteria for both aquatic and terrestrial impacts (Johnson 1980), but unfortunately, the data base for the latter is limited. In considering soil sensitivity to adverse effects of acidic deposition, it is helpful to separate the effects into two

Figure 2-4. Generalized soil map of the United States (SCS USDA, 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

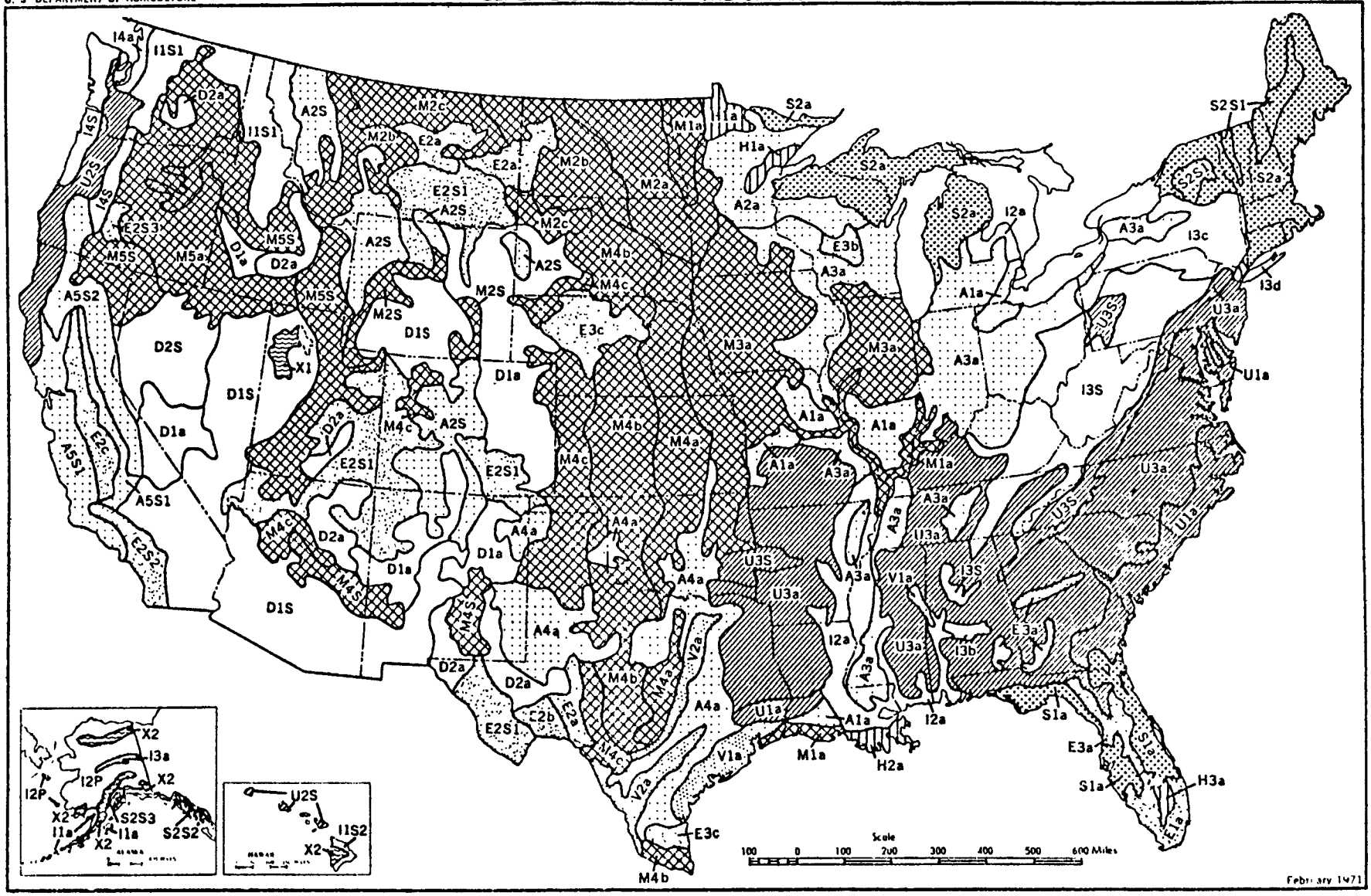
Ultisols
- U1 Aquults
- U2 Humults
- U3 Udults

Vertisols
- V1 Uderts
- V2 Usterts

U. S DEPARTMENT OF AGRICULTURE

GENERAL SOIL MAP OF THE UNITED STATES

SOIL CONSERVATION SERVICE



categories: (1) changes related to soil pH-basic cation changes, which would include any direct losses of nutrients and changes in processes or availability related to pH; (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 aluminum concentration in solution.

McFee (1980) has suggested that cation exchange capacity (CEC) be used as the primary criterion for determining soil sensitivity to acidic deposition. The suggested classification considers soils with CEC greater than 15.4 meq 100 g^{-1}, those subject to frequent flooding, or those with free carbonates in the upper 25 cm of the solum to be insensitive. Non-calcareous, non-alluvial soils with CEC between 6.2 and 15.4 meq 100 g^{-1} are classed as slightly sensitive, and those with CEC less than 6.2 meq 100 g^{-1} are classified as sensitive.

Wiklander (1974, 1980b) proposed a more complex classification system, which considers soil buffering capacity as well as the ability of H^+ to compete for exchange sites in low pH, low base saturated soils. Buffering capacity will, of course, be directly affected by CEC as well as by pH, base saturation, and the presence of carbonates and ferromagnesium minerals. Considering base saturation separately recognizes that H^+ competes best with base ions on pH-dependent charge sites (Snyder et al. 1969, McLean and Bittencourt 1973). As base saturation decreases and a larger proportion of the pH-dependent charge sites are filled with acidic ions, H^+ inputs become less effective in removing basic cations.

Wiklander's classification scheme still does not include all known factors that moderate effects of acidic deposition. For example, Wiklander (1975, 1980a,b) demonstrated that the presence of neutral salts, either in the precipitation or in the soil, significantly moderates the effect of acidic precipitation on soil. Sulfate adsorption capacity of the soil should also be considered because mobile sulfate serves as a counter ion for cation leaching (Cronan et al. 1978, Johnson 1980). Many acid soils have an anion retentive capacity which can be related to both the presence of hydrated Fe and Al oxides and to charge of the soil with decreased pH (Wiklander 1980a). High sulfate adsorption capacity will decrease soil sensitivity to cation removal.

Comparisons of above systems indicate weakness in all, but a tendency to agree when viewed on a national scale. The regions dominated by Ultisols, Spodosols and some of the Inceptisols (Figure 2-4) encompass most of the areas predicted to be sensitive to acidic deposition. All mapping efforts at any level above the most detailed (county soil maps for example) will of necessity include a wide range of conditions within any map unit. For that reason, all of the efforts published thus far should be used with some caution.

2.3.5.2.1 Basic cation-pH changes in forested soils. Based on the sensitivity criteria proposed by McFee (1980), Wiklander (1980b), and

Johnson (1980), it is clear that soils likely to undergo significant changes in basic cation content or change in pH have these characteristics:

(1) they are not renewed by flooding or other processes;

(2) they are free of carbonates to considerable depth (1.0 meter or more);

(3) they have low CEC but pH of at least 5.5 to 6.0; and

(4) they have a low sulfate adsorption capacity.

Because soils with low CEC (< 6.0 meq 100 g^{-1}, McFee 1980, Klopatek et al. 1980) in humid climates tend to become acid naturally over time, few soils meet criteria 3 above. So few have, in fact, that by the time we apply the other criteria, it is clear that accelerated loss of basic cations and lowered soil pH as a result of acidic deposition are unlikely to be extensive problems. Maps prepared by Olsen et al. (1982) show areas of low CEC and moderately high pH that are extensive enough to appear on a national map, only in the central portion of the United States. In that area, however, most soils do not meet criteria 2 and do not currently receive significant acidic deposition.

2.3.5.2.2 Changes in aluminum or other metal concentration in soil solution in forested soils. Based on the discussion of soil chemistry in Section 2.2.3, it is clear that soils most likely to have increased Al in solution or in leachate due to acidic deposition are already acid, (< pH 5.5), and meet criteria 1, 2, and 4 above. Cation exchange capacity is not as important in this case, but effects will be most pronounced where CEC is low. In such soils, the buffer capacity is largely controlled by Al-mineral chemistry. Increased acidic inputs may increase the rate of Al release and increase its concentration in soil solution or leachate from the soil. This is most likely to occur where total quantity of the controlling Al compounds exposed to chemical action is small, e.g., in a coarse-textured acid soil.

2.4 EFFECTS OF ACIDIC DEPOSITION ON SOIL BIOLOGY

2.4.1 Soil Biology Components and Functional Significance

The biological component of soil is of primary importance in the functioning of the complete ecosystem. In this section, the soil biota will be briefly described in terms of functional significance. For general reference, see Alexander (1980a), Richards (1974), or Gray and Williams (1971).

2.4.1.1 Soil Animals--The most significant roles played by the invertebrate soil fauna pertain to turnover of organic material and soil physical characteristics. Many members of this group, such as earthworms, mites, ants, and termites are involved in mixing the organic

and inorganic soil constituents. The quantity of organic material actually assimilated by these organisms is small, generally less than 10 percent, but the relatively large quantity of material consumed is frequently altered chemically by enzymes or microorganisms present in the animal's gut. Thus, by maceration and mixing, these organisms play an important role in the conversion of plant material to soil humus.

2.4.1.2 Algae--Chlorophyta (green algae), Cyanobacteria (blue-green algae) and Chrysophyta (diatoms) are common inhabitants of the soil surface. Since algae are dominantly photoautotrophic organisms (using light as an energy source and CO_2 as a carbon source) they can colonize environments lacking the organic carbon required by many life forms. In areas where higher life forms are largely absent, such as fresh volcanic deposits, beach sands, eroded areas, and freshly burned areas, algae commonly appear as the pioneering species, frequently supplying the organic material required for subsequent colonization by other life forms. Some blue-green algae (bacteria) can convert atmospheric N_2 to organic compounds. In many environments, such as flooded paddy fields, this ability to fix nitrogen provides a critical input of nitrogen to the system. Lichens, an intimate association between certain algae and fungi, are also important pioneering species, and some have the ability to fix nitrogen. Ubiquitous on rock surfaces and other extremely harsh environments, lichens are instrumental in the long-term breakdown and dissolution of rocks ultimately to form soil.

2.4.1.3 Fungi--Soil fungi are involved in degrading a wide range of organic compounds, from simple sugars to complex organic polymers. Many members of this group possess the enzymatic capacity to attack the major plant constituents, such as cellulose, hemicellulose, and lignin. Fungi are normally the dominant initial colonizers of plant debris and are ultimately responsible for many of the steps occurring during the conversion of plant material to soil organic matter. The complex network of fungal hyphae which totally permeates the fabric of soil constitutes a major portion of the soil biomass as well as binding together soil particles to form aggregates. Products of fungal metabolism in soil, such as carbohydrates, can act as glues for primary soil particles.

Certain types of soil fungi can play direct roles in nutrient availability to plants by forming mycorrhizal associations with plant roots. The fungal hyphae greatly expand the volume of soil from which plant roots can effectively draw nutrients. In deficient soils, the fungal partner can substantially improve phosphorus, copper, zinc, and possibly nitrogen (ammonium) availability to plants. In addition, the mycorrhizal association may enhance water availability, increase salt tolerance, enhance heavy metal resistance, and affect plant growth via hormone production. Although relationships are not yet well understood, each of these effects is currently under investigation.

2.4.1.4 Bacteria--The procaryotic microflora of soils are also extremely important in the decomposition of plant litter and the

synthesis and breakdown of soil organic matter. Bacteria are primarily responsible for making organic forms of N, S, and P available to plants by mineralizing organic matter. For substantial plant uptake to occur, S must be as SO_4^{2-} and N as either NO_3^- or NH_4^+. Oxidation of NH_4^+ to NO_3^- (nitrification) is dominantly catalyzed by autotrophic soil bacteria. Nitrogen is lost from the soil through anaerobic bacterial reduction of NO_3^- to the gaseous species N_2 and N_2O (denitrification). Most nitrogen enters ecosystems through bacterial reduction of atmospheric N_2 to NH_4^+ (N_2-fixation). Fixation by bacteria living symbiotically with plants can contribute significant amounts of nitrogen to both agricultural and forest systems. Nitrogen nutrition of many leguminous plants is enhanced through N_2-fixation by bacteria of the genus Rhizobium. Fixation by actinomycetes, such as Frankia, in association with woody species may contribute critical amounts of nitrogen to some forest systems. The oxidation and reduction of S roughly parallel that of N. In addition to bearing primary responsibility for the availability of N and S to plants, soil microbes also strongly influence the availability of phosphorus, iron, and manganese through organic mineralizations and redox reactions.

The distribution of microbial activity in soil generally reflects the fact that many of these microbes are heterotrophs, that is, they require preformed organic compounds. Soil microbial activity is generally greatest in regions of high organic carbon availability. While most types of microbial activity do occur to some extent throughout the soil profile, recognizing that maximal activity commonly occurs in somewhat discrete areas of the soil is important to understanding potential effects of acidic deposition. Microbial attack on plant debris takes place largely in the surface litter layer. Production and breakdown of soil humus occur dominantly in the upper portion of the soil profile, reflecting the site of initial leaf, stem, and root material deposition. Heterotrophic microbial activity is also high in soil near plant roots, where root-derived material provides carbon for soil bacteria and fungi.

2.4.2 Direct Effects of Acidic Deposition on Soil Biology

The effects of acidic deposition should be expected to vary tremendously, depending on the type of organism and the characteristics of the soil which it inhabits. While soil acidification does affect many biological processes, it is often impossible to distinguish direct effects of acidification from secondary effects resulting from acid-induced changes in the soil solution. The following section documents some effects which have been attributed to soil acidification resulting from acid inputs.

2.4.2.1 Soil Animals--Many classes of soil animals, such as earthworms (Lumbricidae), millipedes (Myriapoda), and nematodes (Nematoda), are known to be less abundant in acid soils than in neutral soils. However, high populations of other soil animals, such as springtails (Collembola)

and potworms (Enchytraeidae), are common in acid soils high in organic matter (Richards 1974).

Effects of simulated acid precipitation on soil fauna vary markedly according to the species observed. Studies by Baath et al. (1980), in which soils were treated with 50 or 150 kg ha^{-1} H_2SO_4 for 6 years, showed that the numbers of Collembola increased, Enchytraeidae decreased, but mites (Acarina) were generally unaffected by both application rates. In a two-year exposure to simulated rain of pH 2.5 to 6.0 (25 or 50 mm per month), Collembola, Acarina, and Enchytraeidae were generally unaffected or increased in number with the acid treatments. However, a few species of Acarina and the dominant Enchytraeid were significantly reduced by the more extreme acidification (Hagvar 1978, Abrahamsen et al. 1980). It should be noted that the soils studied by these two groups were naturally very acidic; hence the indigenous soil fauna may have been relatively acid tolerant. In less acid deciduous woodland soils (Kilham and Wainwright 1981), the native population of soil animals appeared to be much more sensitive to acid rain (pH 3.0) localized near a coking works, but these results also reflect the presence of substantial dry deposition on the litter.

2.4.2.2 Terrestrial Algae--While green algae (Chlorophyta) readily colonize relatively acid soils, blue-green algae (Cyanobacteria) have been reported to be particularly sensitive to soil acidity (Dooley and Houghton 1973, Wilson and Alexander 1979). While there is little experimental verification in soil systems, the general sensitivity of free-living Cyanobacteria to acidity suggests they may be susceptible to acidic deposition. The sensitivity of blue-green algae to acid precipitation has been demonstrated in a lichen symbiosis. Simulated acidic deposition of pH 4.0 or less substantially reduced N_2-fixation by the dominant N_2-fixing lichen in a deciduous forest (Denison et al. 1977).

2.4.2.3 Fungi--Fungi become increasingly important in acid soils as compared to neutral-alkaline soils (Gray and Williams 1971). The commonly observed dominance of fungi over bacteria in acid soils may, in part, result from a greater sensitivity of heterotrophic bacteria to H^+ concentration and the consequent reduction in competition (Alexander 1980a).

The relative tolerance of fungi to acid precipitation was demonstrated by Wainwright (1979), who isolated fewer heterotrophic bacteria but more fungi from soils exposed to acid rain and heavy atmospheric pollution than from similar but unaffected soils. The presence of nitrifying fungi in acid soils lacking autotrophic nitrifiers (Remacle 1977, Johnsrud 1978) also appears to indicate the relative resistance of fungi to soil acidity.

Most investigations of the effects of acidic deposition on soil fungi, however, have used traditional plate count methods, which do not

necessarily reflect viable fungal biomass. Baath et al. (1980) found that FDA (fluorescein diacetate) active fungal biomass decreased significantly under the two acid regimes described earlier (Section 2.4.2.1) while total fungal mycelia (the sum of viable and non-viable hyphae) increased.

To date, little information available concerns the response of mycorrhizal associations to acidic deposition. Sobotka (1974) reported a reduction in the fungal mantle of spruce mycorrhizae receiving heavy atmospheric pollution, including acid rain. In a short-term experiment, Haines and Best (1975) found no visible damage to endomycorrhizae of sweetgum exposed to pH 3.0 treatments. To explain deviations in nutrient flux data, these researchers suggested that cation carriers of mycorrhizal roots may be more susceptible to inhibition by H^+ than are non-mycorrhizal roots.

2.4.2.4 Bacteria--The discussion in this section pertains largely to soil bacteria. In many soil microbial processes, however, it is impossible or meaningless to isolate bacterial functions from soil fungal and faunal processes with which they are inherently integrated. For example, leaf litter decomposition requires fungal, bacterial, and faunal attack.

Bacteria are generally considered to be less acid tolerant than fungi. Some bacteria, however, are extremely acid tolerant. For example, species of the chemoautotrophic thiobacilli can survive at pH 0.6 and thrive at pH 2.0 (Butlin and Postgate 1954).

Acidic deposition may affect heterotrophic bacteria in soil by causing changes in total numbers and/or species composition. Francis et al. (1980) reported that the total number of bacteria and actinomycetes generally declined in soil acidified from pH 4.6 to 3.0 with an addition of H_2SO_4, although the magnitude of these effects was not reported. In soils transferred to a site receiving pH 3.0 rain and dry deposition, Wainwright (1980) found that over a one-year period bacterial numbers did not change significantly, even though the soil pH fell from 4.2 to 3.7. Baath et al. (1980) noted a shift towards spore-forming bacteria in soils receiving H_2SO_4 inputs for six years as compared to control soils, suggesting a response to adverse conditions. In the same experimental series, total bacterial numbers (by plate counts) did not change, but bacterial biomass and FDA-active bacteria did decrease with increasing severity of treatment (Baath et al. 1979, 1980).

2.4.2.5 General Biological Processes--Net heterotrophic activity (bacterial, fungal, and faunal) and the rate of organic matter decomposition are commonly determined by measuring CO_2 evolution. The rate of glucose mineralization was reduced in surface soils receiving 100 cm of simulated rain (pH 3.2 and 4.1), continually or intermittently, over a 7-week period (Strayer and Alexander 1981). However, the 7-week treatments caused less significant effects than did the continuous exposure, and the reductions were less severe in soils of

greater natural acidity. The authors therefore suggested that some microbial adaptation was occurring over time.

Respiration in soils transferred to a site receiving pH 3.0 rain was reduced by 50 percent after a one-year exposure (Wainwright 1980). Similar effects of simulated acid precipitation have also been reported by Tamm et al. (1977). Observed effects of simulated acid precipitation on litter decomposition are summarized in Section 2.5.

Several reports now indicate that acid inputs can slightly accelerate mineralization of organic nitrogen (Wainwright 1980, Strayer et al. 1981) Tamm et al. (1977) similarly found increased accumulation of NH_4^+ in acid-treated humus samples, but they interpreted this to mean that immobilization was more retarded than mineralization (a hypothesis for which no substantiating data existed). Conversely, Francis et al. (1980) found lower NH_4^+ production in a soil that had received an addition of H_2SO_4. For all of this work, the treatment periods were relatively short (from 1 hour to 1 year); longer exposures may yield more consistent results. The data, however, are compatible with the fact that "natural" soil acidity does not have a uniform effect on N-mineralization (Alexander 1980b).

Since nitrification is generally believed to be catalyzed by relatively autotrophic nitrifiers (known to be acid-sensitive on laboratory media), researchers have predicted that this process should be one of the microbial processes most sensitive to acid precipitation (Tamm 1976, Alexander 1980b). While evidence indicates that acid inputs to soil inhibit autotrophic nitrification, the overall effects on NH_4^+ oxidation to NO_3^- are neither uniform nor easily interpreted. Francis et al. (1980) could detect little nitrifying activity in the naturally acid forest soil studies (pH 4.6) or in the soil sample that had received an addition of H_2SO_4, but they concluded that further acidification of an acid forest soil would lead to a significant reduction in nitrification. Wainwright (1980) found essentially no effect on nitrifying activity in a soil exposed to acid rain (pH 3.0) from a coking works. Strayer et al. (1981) examined the effects of acute acidification on nitrification in surface soil from soil columns and found interesting but somewhat complex results. When high NH_4^+ amendments (100 ppm-N) were added to the nitrification assay, all acid treatments tested (pH 3.3 to 4.1) caused substantial reductions in nitrification rates. However, when NH_4^+ was not added to the soil, the acid treatments caused no detectable effect, or in some cases, caused a slight stimulation in NO_3^- production. Since forest soils would be expected to have relatively low natural concentrations of NH_4^+, the authors conclude that short-term exposures to acid rain should not substantially affect nitrification in forest soils. The results reported by Strayer et al. (1981) are consistent with the occurrence of heterotrophic nitrifying organisms in naturally acidic forest soils; these heterotrophic nitrifiers are considered much less sensitive to acidity than are autotrophic nitrifiers (Remacle 1977, Johnsrud 1978).

Little published data concern effects of acidic deposition on soil denitrification. While slight soil acidification may not alter the overall rate of this process, it should be expected to increase N_2O production relative to N_2 (Firestone et al. 1980).

A substantial amount of work on the sensitivity of N_2-fixation by legume-Rhizobium associations to soil acidity has been published. In some cases, the bacterial symbiont appears to be sensitive to acidity (Bromfield and Jones 1980, Lowendorf et al. 1981); in other cases, the nodule formation or activity are affected (Evans et al. 1980, Munns et al. 1981). However, work on the effects of acidic deposition on N_2-fixation by legumes is scant. Shriner and Johnston (1981) reported that simulated rain of pH 3.2 applied for 1 to 9 weeks caused decreased nodulation in kidney beans. The authors suggest that similar effects would be unlikely to occur under normal agricultural management practices but might be expected to occur in natural, unmanaged ecosystems (Shriner and Johnston 1981). No data are available concerning effects of acid rain on the associations of actinomycetes with woody plants.

2.4.3 Metals--Mobilization Effects on Soil Biology

Two questions concerning mobilization of metals and effects on soil biology must be addressed. First, the input of acidity to soil can cause mobilization of Al and Mn from mineral forms indigenous to the soil. Can mobilization of Al and Mn by acid inputs be expected to have toxic effects on the soil biota? Second, acidic deposition is sometimes accompanied by atmospheric deposition of various heavy metals. Does the acidity of the rain increase the potential toxicity of these metals? While few data available directly or realistically address these potential effects of acidic deposition, a small body of pertinent background literature exists.

The toxicity of available Al to soil microbial activity has been reported by Mutatkar and Pritchett (1966), who found that additions of Al to soils with pH maintained below 4.0 significantly reduced the rate of soil respiration. Ko and Hora (1972) have identified Al^{3+} ions as being fungitoxic in acid soil extracts. These workers found germination of ascospores to be totally inhibited by aqueous solutions (pH 4.8) containing as little as 0.65 ppm Al. They did not identify Mn as toxic to the fungi tested, but the concentrations of this metal in the soil extracts examined were low compared to Al concentrations. In studies dealing with the growth of the Rhizobium-bean symbiosis in acid tropical soils, Dobereiner (1966) found that additions of 40 ppm Mn to acid soils reduced either N_2-fixation efficiency or nodule numbers. Since preliminary evidence suggests that the threshold concentrations for toxicity of mobilized aluminum are relatively low, such an indirect consequence of acid input to soil may be a possibility. However, acid rain, within current pH limits, has not been shown to mobilize these metals in quantities toxic to soil biota.

Soils in the vicinity of metal-smelting and coal-burning are likely to be subject to atmospheric deposition of heavy metals (Little and Martin 1972, Freedman and Hutchinson 1980) in addition to acidic deposition. The input of heavy metals to these soils is significant because metal solubilization and biological toxicity are pH dependent. Numerous pure culture studies demonstrate increasing metal toxicity with decreasing pH of solution (e.g., Babich and Stotzky 1979). However, many of these studies should not be extrapolated to soils because of the complexity of the metal cation interactions with soil constituents. Babich and Stotzky (1977) found that Cd toxicity to microbes in soil was a function of soil pH; however, this may have been an anomaly, since toxicity increased with increasing soil pH.

Metals vary in potential toxicity; work by Somers (1961) indicated that the microbial toxicity of heavy metals is highly correlated with the electronegativity of the metal. When attempting to assess the potential effects of acidic deposition in association with metal deposition, one must consider several factors: 1) the toxicity potential of the metal, 2) the quantities and speciation of metals deposited and degree of association with acid inputs, and 3) the pH dependence of metal toxicity in the recipient soil environment. Mobilization of metal ions in soils receiving acid inputs, and subsequent toxicity of these metals, may be a mechanism by which acidic deposition affects soil biological activity, but experimental evidence is lacking.

Apparently certain plant-microbial associations are able to protect plants from metal toxicity. Bradley et al. (1981) found that mycorrhizal infection of an ericaceous, Calluna species reduced heavy metal uptake by the plant. The authors suggested that protection by the fungal symbiont allowed this species to colonize heathland soils in which the low pH increases availability of metal cations to levels which are toxic to many non-ericaceous species.

2.4.4 Effects of Changes in Microbial Activity on Aquatic Systems

Because our current understanding of the effects of acidic deposition on microbial activity in terrestrial ecosystems is limited, extrapolations to possible secondary effects on aquatic systems are tenuous at best. It is important to recognize, however, that even a small change in microbial activity in soil may cause profound changes in aquatic systems, into which much of the soil water will ultimately drain.

2.4.5 Soil Biology Summary

The following statements represent simplifications of complex and sometimes contradictory trends in the existing data. They reflect both the complexity of microbial processes and the variability in experimental protocols. The extreme variability in pH and ionic

composition of simulated rain, as well as differences in important soil characteristics, makes comparing data difficult. Treatment durations in the experiments reported ranged from 1 hour to 6 years. Short-term "accelerated" treatments may not only overlook potential long-term effects, but also may yield misleading predictions. The shortcomings of long-duration experiments involving infrequent sampling should also be recognized. Acid rain rarely occurs in isolation, rather it occurs in association with other pollutants such as heavy metals and the gaseous precursors of acid species. The potential synergisms among these pollutants should not be overlooked. The following statements summarize or interpret the limited data available and should be read with the above-mentioned limitations in mind.

Acidic deposition will not substantially affect soil biological activity in cultivated soils because of the much greater influence of soil amendments.

The following statements pertain to uncultivated soil systems:

- The effects of acidic deposition on animals in strongly acid soilsare not significant. In less acid soils, pH 3.0 simulated rain significant changes in litter animals.

- Certain types of soil microbial activity are more sensitive to soil acidity than are others. Soil fungi are probably the components of the soil biota least sensitive to acid inputs; but little is known about effects on mycorrhizal symbionts.

- Preliminary evidence indicates that N_2-fixation by lichens is inhibited by rain of pH less than 4.0. The evidence for acidic deposition influences on Rhizobium or actinomycete symbiotic N-fixation is insufficient for a conclusion.

- Autotrophic nitrification in surface soils is reduced by artificial acid inputs; however, no evidence exists to prove that acidic deposition at the rates currently common in the United States will cause such a decrease. Net nitrification may not be similarly decreased because of the acid tolerance of heterotrophic nitrifiers.

- Slight increases and decreases in N-mineralization rates result from treatments of short duration, but little direct evidence concerning long-term responses to realistic inputs exists.

2.5 EFFECTS OF ACIDIC DEPOSITION ON ORGANIC MATTER DECOMPOSITION

One of the long-standing hypotheses regarding the environmental effects of acidic deposition has been that increased acid loading to

forest soils will result in decreased decomposition rates for organic matter. This hypothesis has been addressed by a number of investigators (Tamm et al. 1977; Abrahamsen et al. 1976, 1980; Abrahamsen and Dollard 1978; Alexander 1980a,b; Baath et al. 1980; Cronan 1980a,b; Hovland et al. 1980; Francis et al. 1980; Lohm 1980; Roberts et al. 1980; Hovland 1981; Kilham and Wainwright 1981; Strayer and Alexander 1981; and Strayer et al. 1981). Unfortunately the results from these studies have appeared mixed and inconsistent (Table 2-6). However, if one screens the published studies and selectively excludes the results from those investigations that represent extremely acute treatments, then the following summary statements emerge.

(1) Most decomposition studies related to acidic deposition have been conducted with coniferous litter materials.

(2) Results suggest that it is important to interpret data from decomposition studies in relation to H^+ loading and not simply with respect to the pH of the artificial rain treatments.

(3) It is important to distinguish between the physical-chemical and the biological components of organic decomposition. Based upon shorter-term studies (2 to 4 months or less), it has been shown that increased H^+ loading generally will increase leaching of cations and organic constituents from forest litter. This response may help to explain why acidic precipitation treatments increase the initial rate of weight loss in some experiments. Over the longer term (> 4 months), it appears that the biologically-mediated mineralization of organic matter in forest soils will be only slightly inhibited by acidic deposition (< 1 to 2 percentdecrease in decomposition rate).

(4) Overall, unless average precipitation inputs were to drop to pH 3.0 or below, one would not expect significant impacts of acidic deposition on litter decomposition.

2.6 EFFECTS OF SOILS ON THE CHEMISTRY OF AQUATIC ECOSYSTEMS

Much of the evidence for atmospheric depositions' contribution to surface water acidification, while convincing in many cases (e.g., N. M. Johnson 1979), is circumstantial. Only recently have efforts been made to establish the mechanisms by which atmospheric acid inputs are transferred to aquatic ecosystems (Abrahamsen et al. 1979, Seip 1980, N. M. Johnson et al. 1981). If acidic precipitation passes through soil prior to entering an aquatic ecosystem, it will usually be strongly influenced by the chemical nature of the soil. Even barren rock has some influence on the chemistry of runoff water (Abrahamsen et al. 1979). The pH of water leaving the soil is not necessarily the same as the soil solution pH in intimate contact with the soil.

TABLE 2-6. REVIEW OF STUDIES CONCERNED WITH THE IMPACT OF ACIDIC DEPOSITION ON ORGANIC DECOMPOSITION

Author	Soil Type	Duration of Experiment	Treatments	Results
1. Abrahamsen et al. 1980	Lodgepole pine needles	75-90 days	Needles from field experiments at pH 5.6 and 3.0 were incubated in moist condition and weighed.	Acid treatment increased decomposition-29% greater at pH 3 than 5.6
	Norway spruce needles	3-9 mos.	Spruce needles in lysimeters were watered 2x weekly with pH 5.6, 3, or 2 water at a rate of 100 mm $mo.^{-1}$ or 200 mm $mo.^{-1}$.	Relatively small effects from acid treatments. No significance at 100 mm $mo.^{-1}$. At 200 mm $mo.^{-1}$, the pH 3 and 2 treatments decreased decomposition by < 5% Increased leaching of K, Mg, Mn, Ca.
	Raw coniferous humus	unspecified	Raw humus in litterbags exposed to pH 5.3, 4.3, and 3.5 treatments.	pH 4.3 treatment caused 8% decrease in decomposition rate, while pH 3.5 caused 10% decrease.
2. Abrahamsen and Dollard 1978	General Review	----	----	Decomposition of organic matter in acidic coniferous forest soils is apparently only slightly sensitive to acidification. Decomposition of fresh litter and cellulose is influenced only at pH $\leq$ 3.
3. Abrahamsen et al. 1976	Lodgepole pine needles	90 days	Needles moistened with dilute H_2SO_4 solutions.	Decomposition was depressed at pH 1.8 as compared to 3.5. No difference between pH 3.5 and 4.0
	Cellulose/Wood	Unspecified	Unspecified acid treatments	No consistent trends.

TABLE 2-6. CONTINUED

Author	Soil Type	Duration of Experiment	Treatments	Results
4. Alexander 1980a Strayer and Alexander 1981	Honeoye silt loam (pH 7.1)	2+ wk.	Soils were exposed to pH 4.1 and 3.2 acid rain treatments and were incubated with C^{14} glucose.	pH 4.1 treatment had no effect on glucose mineralization pH 3.2 treatment decreased glucose mineralization rate by 30-66%.
5. Alexander 1980b	Spodosols from the central Adirondacks	14-61 days	Soils were exposed to 100 cm of pH 3.5 and 5.6 artificial rain for 14 consecutive or 35 intermittent days.	In 14 day consecutive rain, the rate of total organic carbon (TOC) leaching was initially greater at pH 3.5 than 5.6. This later reversed. In 35 day intermittent treatment: pH 3.5 leached more TOC than pH 5.6. CO_2 evolution response varied with soil pH -- inhibition in more acid soils, but stimulation by pH 3.5 rain in less acid soil.
6. Baath et al. 1980.	Coniferous iron Podzol	12 mo.	Litterbags were placed in field plots exposed to H_2SO_4 treatments @ 50 and 150 kg ha^{-1}.	No significant difference compared to controls for Scots pine needle litter. Root litter exposed to 150 kg ha^{-1} had 21% decrease in decomposition rate.
7. Cronan 1980a.	Coniferous forest floor	4 mo.	Forest floor microcosms were exposed to pH 5.7, 4.0 and 3.5 artificial rains.	Increased rainfall acidity caused increased leaching of Ca, Mg, K, and NH_4^+. Compared to the pH 4 treatment, the pH 3.5 rain caused 50-150% more K, Ca, and Mg leaching.

TABLE 2-6. CONTINUED

Author	Soil Type	Duration of Experiment	Treatments	Results
8. Cronan 1980b	Coniferous and hardwood forest floors	3 mo.	Forest floor microcosms were subjected to weekly 3.5 cm simulated rains at pH 5.7 and 4.0	Hardwood forest floors showed 60% more Ca leaching and 65% more Mg leaching at pH 4.0. Coniferous forest floors showed 40% more Ca and 25% more Mg leaching at pH 4 compared to pH 5.7. In general, cation fluxes from the hardwood litter were much greater than from coniferous litter.
9. Hovland 1981	Norway spruce needle litter	5 yr.	Field plots were exposed to pH 6.1, 4.0, 3.0, and 2.5 rains over 5 yr. Litter collected from these plots was assayed.	Acid rain treatments produced very little effect on biological activity in litter as measured by respiration and cellulose activity.
10. Hovland et al. 1980	Norway spruce needles	16-38 wk.	Lysimeters containing spruce needles were exposed to pH 5.6, 3.0 and 2.0 solutions at 100 and 200 mm mo^{-1}.	Small effects on decomposition. Treatments at pH 3 and 2 initially increased the decomposition rate at 100 mm mo^{-1}. After 38 wk., decomposition had decreased relative to controls in pH 3 and 2 treatments at 200 mm mo^{-1}. Effect of acid treatments on monosaccharide content was not consistent. However, there was an indication of reduced lignin decomposition at 200 mm mo^{-1} for pH 3 and 2. Acid treatments caused increased leaching of Mg, Mn, and Ca. Initially, acid rains decreased P leaching; later, this reversed.

TABLE 2-6. CONTINUED

Author	Soil Type	Duration of Experiment	Treatments	Results
11. Francis et al. 1980	Oak-pine sandy loam (pH 4.6)	5 mo.	Soils were adjusted with acid or base to give a soil pH of 3.0 or 7.0, and were then incubated with controls.	The acidified soil showed 6-52% less CO_2 production, depending upon amendments.
12. Lohm 1980	Coniferous iron Podzol	6 yr.	Plots were exposed to 0, 50, and 150 kg ha^{-1} H_2SO_4 per yr. Litter bags were exposed for 2 yr.	Acid treatments lowered the decomposition rate by 5-7%.
13. Roberts et al. 1980	Coniferous Podzol	5 mo.	Field plots were subjected to biweekly 5 mm applications of pH 3.1 and 2.7 acid rain.	No significant effect of acid treatments on respirtion. Litterbags showed significant increase in weight loss (15%) with increased acidity.
14. Tamm et al. 1976	Coniferous Podzol	5-6 yr.	Field plots received 0, 50, and 100 kg ha^{-1} yr^{-1} applications of H_2SO_4.	Found decreased CO_2 respiration with increased H_2SO_4.

Rosenqvist (1977, 1978, Rosenqvist et al. 1980) has argued that the influence of soil and bedrock on the chemistry of waters is overwhelming and that the pH of runoff water would be the same whether snowmelt was acid or neutralized by a suitable base. Seip et al. (1980) carried out an experiment to test Rosenqvist's hypothesis by applying NaOH to one of the mini-catchment watersheds in Norway; results showed that, indeed, the neutralization of snow with NaOH had little effect on runoff pH. The investigators attributed the lack of effect, to differences in weather conditions, and Na content of the deposition.

Seip (1980) presented a hypothesis for surface water acidification which has met with agreement among soil scientists as to its mechanism but not necessarily to its magnitude. This has been termed the "mobile anion mechanism." In essence, it states that the introduction of a mobile anion into an acid soil will cause the pH of a soil solution to drop. This is because of the requirement for cation-anion balance in solution and because most exchangeable cations in acid soils are H^+ and Al^{3+}. Thus, due to cation exchange processes and the requirement for cation-anion balance, increased anion concentration in an acid soil solution causes increased H^+ and Al^{3+} concentrations, regardless of whether the anion is introduced as a salt or an acid. This mechanism has been known to soil scientists for decades as the "salt effect," wherein soil pH is usually more acid in $CaCl_2$ solutions than in H_2O (Yuan 1963). Field studies have confirmed that this mechanism is valid (Abrahamsen et al. 1979; Seip et al. 1979a,b, 1980; Abrahamsen and Stuanes 1980). However, doubt remains as to whether the magnitude of pH change this mechanism can produce could cause the pH changes reported for acidified surface waters (Abrahamsen and Stuanes 1980; Johnson 1981; Rosenqvist 1981, pers. comm.). It is clear, however, that neutral salts can, when added to an acid soil, cause a flux of Al in a low-pH solution to streams.

Natural acid production, changes in land use patterns, and management practices such as harvesting, burning, and fertilizing are suggested alternative sources for surface water acidification (Rosenqvist 1977, 1978; Patrick et al. 1981). These possibilities have been explored to some extent in southern Norway, but we have no concrete evidence that changes due to harvesting and land use have caused surface water acidification (Drabløs et al. 1980) although the debate continues. Evidence suggests, however, that fish kills associated with acidic pulses have been occurring in at least one place in southern Norway (Roynelandsvann) since the 1890's (Torgenson 1934). In this instance, liming was successful as a mitigative measure for short-term effects on fish populations (Abrahamsen, pers. comm.). The causes of these acid pulses are unknown, but presumably acid rain effects were much smaller nearly a century ago.

Some attention has been given to neutralization processes affecting acid rain as it passes through terrestrial to aquatic ecosystems. N. M. Johnson et al. (1981) found a two-stage process operative in the Hubbard

Brook, NH ecosystem in which H^+ in acid rain is initially neutralized by dissolution of reactive alumina in the soil before both H^+ and Al^{3+} are neutralized by chemical weathering of alkali and alkaline earth minerals in bedrock. Because stage 2 proceeds more slowly than stage 1, first- and second-order streams may contain H^+ and Al^{3+}, but neutralization is usually complete before surface waters reach third-order streams.

Kilham (1982) reports a case in which deposition appears to have caused an increase in lake alkalinity. Alkalinity in Weber Lake, Michigan, has increased twofold over the last thirty years, and theoretical considerations of acid-base budgets lead to the hypothesis that this alkalization has resulted from plant nitrate uptake, bacterial sulfate reduction, and carbonate mineral weathering, all enhanced by acid precipitation. This effect, while no more desirable than acidification, contradicts the assumption that acid rain always causes surface water acidification and is ample testimony to the complexity of terrestrial-aquatic interactions. Kilham (1982) indicates that alkalization is likely only in lakes of high alkalinity with abundant carbonates in the watershed.

In view of the lack of understanding of terrestrial-aquatic transport processes, assigning "sensitivity" ratings to acid deposition on a regional scale is premature. Nonetheless, agencies alarmed by reports of ecological effects of acid precipitation insist upon knowing something about the geographical magnitude of the acid rain "problem," and scientists must make their best guesses as to appropriate criteria, even though the mechanisms are not completely understood. This situation reflects a gap in understanding and a critical research need that encompasses not only soil and bedrock chemical reactions but also hydrological processes. Recent studies have shown the important contribution of variable source areas (i.e., portions of watershed landscapes that contribute to streamflow during storm events) to surface waters and their chemical composition during stormflow (Henderson et al. 1977, Huff et al. 1977, Johnson and Henderson 1979).

Similarly, water flow through soil macropores (See Figure 2-1) can be a very important component of soil water flux during periods of saturated flow (Luxmoore 1981). Both variable source areas and macropore flow reduce the amount of contact between soils or bedrock and waters passing through terrestrial ecosystems. Integrated studies of terrestrial-aquatic transport processes involving both hydrological and chemical components are essential to an understanding of the effects of acid rain on aquatic ecosystems.

2.7 CONCLUSIONS

Effects of acidic deposition related to soils are in these general categories: soil acidification, nutrient supply, metal mobility, and microbial activity. The following conclusions, relative to these general categories, can be drawn from Chapter E-2:

- Soils amended in agricultural practice will not be harmed by acidic deposition (Section 2.3.5).

- Soil acidification is a natural process in humid regions. It is obvious that acidic deposition contributes to this process; however, at current levels, it is a minor contribution (Section 2.3.5).

- Most soils that were easily acidified are already acid; therefore, soils likely to become perceptibly more acid due to deposition are limited. They are the soils that have low buffering capacity, a relatively high pH (slightly acid, pH 5.5 to 6.5), low sulfate adsorption capacity, no carbonates, and no basic inputs (Section 2.3.5).

- The availability of sulfur and nitrogen to plants will be enhanced by their presence in the deposition. Because nitrogen limitations are so common and cation limitations are so rare in forests of the United States, it seems likely that HNO_3 inputs generally will be beneficial. Exceptions may occur on sites with adequate or excessive N supplies. Benefits of H_2SO_4 deposition are probably minimal, because S deficiencies are rare and probably easily satisfied with moderate atmospheric S inputs (Section 2.3.2).

- The long-term effect (i.e., over decades or centuries) of acidic deposition can be expected to remove cations from forest soils, but it is not clear whether this will reduce available cations and enhance acidification of soils. For example, cation leaching rates, although increased by acid precipitation, may remain insignificant relative to total soil supplies and forest growth requirements; furthermore, exchangeable cations may be replaced by weathering from primary minerals at rates sufficient to maintain their current status partially as a result of acid precipitation inputs (Section 2.3.3).

- Assessing acidic deposition effects on forest nutrient status involves quantifying amounts of inputs involved and the S, N, and cation nutrient status of specific sites. It cannot be stated that forest ecosystems, in general, respond to acidic deposition in a single predictable way. Indeed, the contrasting behavior of Norway spruce in Germany and in Norway exemplifies the variable response that can be expected from different sites (Section 2.3.3).

- The most likely damage to forest productivity, and the one for which some evidence exists, would result from Al toxicity. This may occur on already acid soils where acidic deposition plus natural acidifying processes increase acidity enough to cause a significant rise in Al availability. If soil pH is low enough (< pH 5.0 to 5.5) in mineral soils to cause the

dissolution of Al- and Mn-containing clay minerals, any H^+ input will increase solution of Al and Mn concentration (Section 2.3.3).

- The increased mobility of Al in uncultivated, acid soils is probably the most significant effect of acidic deposition on soils as they influence terrestrial plant growth and aquatic systems (Section 2.3.3).

- Based upon shorter term studies, we can expect that increased H^+ loading will generally cause increased loss of cation and organic components from forest litter. Over the longer term, it appears that the biologically-mediated mineralization of organic matter in forest soils will be only slightly inhibited by acidic deposition (< 1 to 2 percent decrease in decomposition rate). In general, experimental data suggest that decomposition processes are relatively unaffected by simulated precipitation pH's above 3.0. Thus, unless average precipitation inputs were to drop to pH 3.0 or below, significant impacts of acidic deposition or litter decomposition in natural systems are not expected (Section 2.3.3).

- Soil microbial activity may be significantly influenced near the surface if inputs are great enough to affect pH or nutrient availability. Evidence for effects of acidic deposition Rhizobium or actinomycete is reduced by artificial acid inputs, but no evidence exists that current rates common in the United States will cause such a decrease. Slight decreases and increases in N mineralization rates result from short-term acid inputs, but long-term responses are not documented. Possible effects of acidic deposition as soil microbial activity in natural systems have not been ruled out, but important effects under field conditions have not been clearly demonstrated (Section 2.4).

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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-3. EFFECTS ON VEGETATION

3.1 INTRODUCTION

3.1.1 Overview

This chapter examines diverse plant-pollutant relationships to assess potential and recognized effects of acidic deposition as described in the extant literature. Vegetation responses discussed include morphological and physiological responses, species/varieties and life-stage susceptibilities, disease and insect stresses, indirect effects of nutrient cycle alterations, and crop and forest productivity.

Since the close relationship between soils and plants bears examination in terms of how soil acidification affects productivity. It is important to recall from the previous chapter the following points:

- soils amended in agricultural practice will not likely be negatively impacted by acidic deposition;
- soil acidification is a natural process in humid regions, so most soils that are easily acidified are already acid; and
- soils with low buffering capacity, relatively high pH, low sulfate adsorption capacity, no carbonates, and no basic inputs are susceptible to increased acidification rates from atmospheric inputs of acidic and acidifying substances.

Keeping these points in mind, Chapter E-3 will deal more with the direct effects of acidic deposition on plant response, and to interactive effects of acidic deposition with other factors, such as other pollutants, insects, pathogens, and pesticides.

Given the uncertainty still surrounding effects on plant productivity, however, this document does not attempt to make economic assessments of recognized or potential damage to vegetation; nor does it consider mitigative measures to counter acidic deposition inputs to plant systems. Discussions of nutrient cycling and forest productivity are included in both this chapter and the soils chapter, from slightly different perspectives. Both chapters should be read carefully to gain a more complete understanding of the issues.

3.1.2 Background (P. M. Irving and S. B. McLaughlin)

The observation that both gaseous and rain-borne pollutants affect vegetative growth is not limited to recent years. Robert Angus Smith (1872) in his manuscript, "Air and Rain: The Beginnings of a Chemical Climatology," included a section on "Effect of Acid Gases on Vegetation and Capability of Plants to Resist Acid Fumes." As early as 1866 the Norwegian playwrite Ibsen (1866) referred to the phenomenon in the drama "Brand":

> "... A sickening fog of smoke from British coal
> Drops in a grimy pool upon the land,
> Befouls the vernal green and chokes to death
> Each lovely shoot, ..."

Of course the fog of smoke referred to by Ibsen was from imported British coal and not from the long-range transport of pollutant gases. An intensive effort to study the effect of acidic deposition was not initiated until the Norwegian SNSF (Sur Nedbørs Virkning Pa Skog Og Fisk--"Acid Rain Effects on Forests and Fish") Project was established in 1972. The phenomenon was first widely recognized in North America at the First International Symposium on Acid Precipitation and the Forest Ecosystem in Ohio (USDA 1976), and at the NATO Conference on Effects of Acid Precipitation on Vegetation and Soils (Toronto 1978). At the Ohio conference, Tamm and Cowling (1976) speculated upon the potential effects of acidic deposition, but few existing studies directly supported their hypotheses of damaging effects.

As the acid rain phenomenon gained increasing attention and its occurrence was reported over large areas of North America, economic damage to vegetation was predicted and a number of research programs to investigate the effects were initiated in the mid-1970's.

Anthropogenic and natural air contaminants are usually inventoried on a separate basis (e.g., chemical speciation) when information is sought as to sources, dispersion, or induced effects (see Chapters A-2 and A-5). Categorically, the National Ambient Air Quality Standards (NAAQS) for criteria pollutants (ozone, sulfur oxides, hydrocarbons, nitrogen dioxides, carbon monoxide, and particulate matter) have been established to protect human health and welfare. Comprehensive documents that describe vegetation effects of the major phototoxic air pollutants are available (U.S. EPA 1978, 1982). As distances from pollutant sources increase, chances for combinations to occur also increase, or, as in the case of large metropolitan/industrial areas, pollutant combinations are the rule rather than the exception.

The wet deposition of acidic pollutants may consist of a number of variables affecting vegetation (i.e., hydrogen, sulfur, and nitrogen doses). The influence of predominant gaseous pollutants that may be present within the defined isopaths of acidic precipitation must also be

taken into account. If results of such interaction studies are not available or understood, effects may be attributed to acidic depositions but instead be due to gaseous pollutants alone, or as combined with the influence of acidic depositions. Because of the potential for interactions with biotic and abiotic entities, factorial research designs and multivariate analyses may be necessary to gain a more complete understanding of vegetative response to acidic deposition.

In the United States, the eastern half of the country is the geographical area of major concern for impacts of air pollution (both gaseous pollutants and acid rainfall) on crop and forest productivity. The combination of a high density of fossil-fuel combustion plants, a high frequency of air stagnation episodes, and elevated levels of both photochemical oxidants and rainfall acidity over widespread areas of the eastern United States have resulted in exposure of large acreages of forests to increased deposition of atmospheric pollutants (McLaughlin 1981). An overlay of isopleths of air stagnation frequency (a measure of the potential of pollutants to accumulate during periods of limited atmospheric dispersion), isopleths of rainfall acidity, and forest zones of the United States is shown in Figure 3-1. This overlay highlights this juxtaposition of stress potential and forest types. While air stagnation episodes are not in themselves a measure of air pollution stress, they do provide an indication of the potential for pollutants from multiple sources to be concentrated within regional air masses. The eastern half of the United States, with approximately 80 percent of the total fossil-fueled electric power plants, thus has both the emissions and the atmospheric conditions to create regional scale elevation of air pollutants (see Chapter A-2). Comparable conditions also appear to exist in coastal California, where severe air stagnation has led to very high levels of photochemical oxidants. The acidity of rainfall in much of the Northeast quadrant of the United States (Figure 3-1) averages about pH 4.1 to 4.3 annually--about 30 to 40 times as acid as the hypothetical carbonate-equilibrated natural rainfall with a pH of 5.6 (Likens and Butler 1981). Vegetation in the high-altitude boreal forests of New England experiences even greater inputs, being exposed to hundreds of hours during the growing season to clouds with pH values in the range of 3.5 to 3.7 (Johnson and Siccama 1983). Photochemical oxidants, principally ozone, which are formed both naturally in reactions involving ultraviolet radiation and from biogenic and anthropogenic hydrocarbon and nitrogen oxide precursors, occur at potentially phytotoxic levels over the entire eastern region (Westburg et al. 1976). Forest productivity losses from this pollutant have not been quantified except in southern California, where extreme urban pollution from the Los Angeles Basin and poor air dispersion have combined to produce the highest oxidant concentrations in the United States and widespread mortality and decline of forests in the nearby San Bernadino Mountains (Miller et al. 1977).

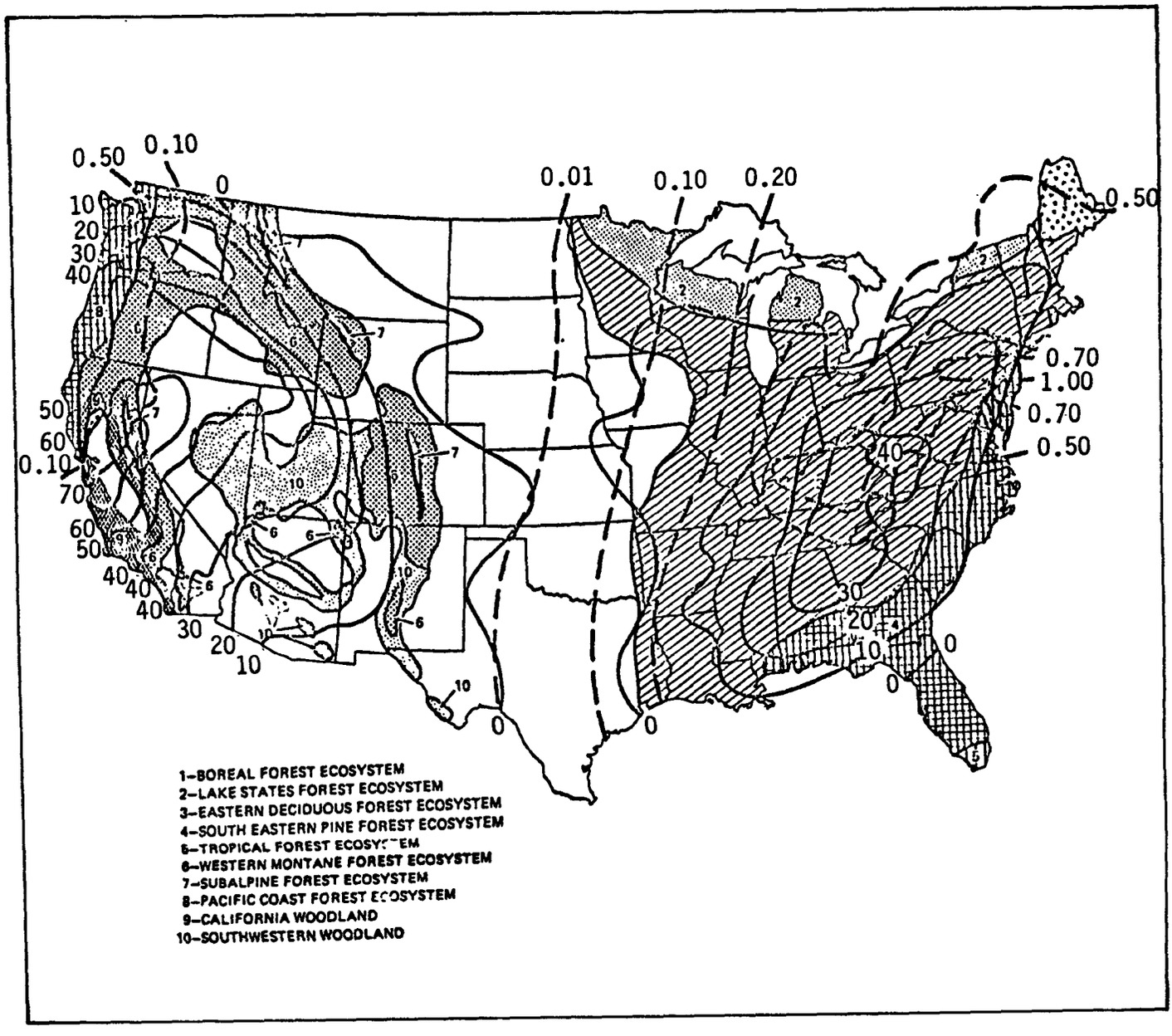

Figure 3-1. Distribution of frequency isopleths for total number of forecast days with high meteorological potential for air pollution over a 5-year period. Isopleths are shown in relation to major forest types of the United States (adapted from Miller and McBride 1975) and in relation to mean annual hydrogen ion (kg ha^{-1} yr^{-1}) deposition in precipitation (adapted from Henderson et al. 1981).

3.2 PLANT RESPONSE TO ACIDIC DEPOSITION

3.2.1 Leaf Response to Acidic Deposition (D. S. Shriner)

Any discussion of foliar effects of acidic deposition must be prefaced by a recognition that our knowledge of the potential effects are drawn from experimental observations with simulated rain solutions rarely typical of ambient events. As a result, in the absence of field observation of effects due to ambient precipitation events, it is important to recognize that these experimental observations are most useful for understanding mechanisms of effect, and less so for extrapolation to field-scale impacts.

Most of the terrestrial landscape being impacted by acidic deposition is covered by a minimum of one layer of vegetation. As a result, a large proportion of the incident precipitation ultimately affecting soils and surface water chemistry has previously contacted vegetation surfaces. The fact that vegetation surfaces are perhaps the most probable primary receptors of deposited pollutants raises two important issues regarding the interactions between water droplet and receptor surface:

1) effects of incident precipitation chemistry on the receptor surface structure and function; and

2) effects of the receptor surface on incident precipitation chemistry.

3.2.1.1 Leaf Structure and Functional Modifications--Based on experimental evidence with simulated rain, a wide range of plant species is believed to be sensitive to direct injury from some elevated level of wet acidic deposition (Evans et al. 1981b, Shriner 1981; see also Section 3.4). Other species have been noted to be tolerant of equally elevated levels (to pH 2.5 for up to 10 hours total exposure) without visible injury (Haines et al. 1980). These results suggest that generalizations about sensitivity to injury may be difficult, and some understanding of the mechanisms by which injury may occur is necessary. The sensitivity of an individual species of vegetation appears to be influenced by structural features of the vegetation, which 1) influences the foliage wettability; 2) makes the foliage more vulnerable to injury (e.g., through differential permeability of the cuticle); or 3) retains rainwater due to leaf size, shape, or attachment angle. In those instances where one or more of the above conditions renders a plant potentially sensitive to acidic deposition, effects may be manifested in alterations of leaf structure or function.

Injury to foliage by simulated acidic precipitation largely depends on the effective dose to which sensitive tissues are exposed. The effective dose, that concentration and amount of hydrogen ion, and time period responsible for necrosis of an epidermal cell, for example, are influenced by the contact time of an individual water droplet or film on the foliage surface (Evans et al. 1981b, Shriner 1981). Contact time,

in turn, can be regulated by the wettability of the leaf, or by leaf morphological features that prevent rapid runoff of water from the surface. Physical characteristics of the leaf surface (e.g., roughness, pubescence, waxiness) or the chemical composition of the cutin and epicuticular waxes determine the wettability of most leaves (Martin and Juniper 1970).

For injury to occur at the cellular level, the ions responsible must penetrate these protective physical and chemical barriers or enter through stomata (Evans et al. 1981b). Crafts (1961a) has postulated that cuticle penetration occurs through micropores. Evidence indicates that these micropores are most frequent in areas such as at the bases of trichomes and other specialized epidermal cells (Schnepf 1965). However, the occurrence of such micropores is not well documented for all plant cuticles (Martin and Juniper 1970). Hull (1974) demonstrated that basal portions of trichomes are more permeable than adjacent areas; cuticles of guard cells and subsidiary cells are preferred absorption sites (Dybing and Currier 1961, Sargent and Blackman 1962). In addition, Linskens (1950) and Leonard (1958) found that the cuticle near veins is apparently a preferential site for absorption of water-soluble materials.

Perhaps as important as the greater density of micropores associated with these specialized cells is Rentschler's (1973) evidence that, at least in certain species, epicuticular wax is less frequently present on certain of these specialized epidermal cells. Such an absence of wax, in combination with increased cuticular penetration at those sites, would tend to maximize the sensitivity of those sites. Evans et al. (1977a,b; 1978) have determined that approximately 95 percent of the foliar lesions occurring on those plant species observed by them occurred near the bases of such specialized epidermal cells as trichomes, stomatal guard and subsidiary cells, and along veins. Stomatal penetration by precipitation, on the other hand, is thought to be infrequent (Adam 1948; Gustafson 1956, 1957; Sargent and Blackman 1962) and is considered a relatively insignificant route of entry of leaf surface solutions (Evans et al. 1981b).

Solution pH has also been shown to influence the rate of cuticular penetration in studies with isolated cuticles (Orgell and Weintraub 1957, McFarlane and Berry 1974). The rate of penetration of acidic substances increased with a decrease in pH, while the rate of penetration of basic substances increased with an increase in pH (Evans et al. 1981b).

Preliminary work by Shriner (1974) suggested that, in addition to the physical abrasion of superficial wax structure by raindrops, leaves exposed to rainfall of pH 3.2 appeared to weather more rapidly than did leaves of pH 5.6 control treatment plants. However, it was impossible to determine from those experiments whether chemical processes at the wax surface were responsible for the differences or whether the acidic rain induced physiological changes that retarded regeneration of the

waxes and recovery from mechanical damage. The latter explanation may be the most tenable because the waxes would be expected to resist chemical reaction with dilute strong acids (Evans et al. 1981b), and because numerous reports of physiological imbalance resulting from acidic precipitation exposure exist (Shriner 1981). Hoffman et al. (1980) proposed a mechanism by which precipitation acidity can act as a chemical factor in weathering epicuticular waxes. They pointed out that the wax composition, as polymeric structures of condensed long-chain hydroxy carboxylic acids, may result in an "imperfect" wax matrix in which the uncondensed sites containing hydroxy functional groups are more readily weathered. Strong acid inputs to such a system would oxidize and release a wide range of carbon chain acids from the basic waxy matrix, conceivably yielding the type of change in weathering rate Shriner observed.

Rentschler (1973) and, more recently, Fowler et al. (1980) have shown relationships between the superficial wax layer of plants and plant response to gaseous air pollution. The work of Fowler et al. compared the rate of epicuticular wax degradation of Scots pine needles from "polluted" and unpolluted sites in the field. These "polluted" sites included exposure to both dry deposition of gaseous pollutants and wet deposition as acid rain, making it impossible to distinguish between relative effects of the two forms of deposition. Needles at the polluted site showed greater epicuticular wax structure degradation during the first eight months of needle expansion. Determing the quantity of wax per unit leaf area showed very small differences between polluted and clean air sites. Fowler et al. concluded that observed differences (by scanning electron microscopy) were "due more to changes in form than gross loss of wax." Since the fine structure of the wax layer is controlled largely by the chemical composition of the wax (Jeffree et al. 1975), the observed changes may also reflect stress-induced changes in wax synthesis. Fowler et al. estimated that increased water loss due to accelerated breakdown of cuticular resistance would only influence trees if water were a limiting factor. They concluded that "the extra water loss may reduce the period (or degree) of stomatal opening" and that the magnitude of the effect on dry matter productivity would not be greater than 5 percent at their polluted site. Because study sites used by Fowler et al. were exposed to gaseous sulfur dioxide as well as to acidic precipitation, their work does not allow identification of a single causative factor.

Histological studies of foliar injury caused by acidic precipitation have revealed evidence of modification of leaf structure associated with plant exposure to acidic precipitation (Evans and Curry 1979). Quercus palustris, Tradescantia sp., and Populus sp. exposed to simulated acidic precipitation experienced abnormal cell proliferation and cell enlargement. In Quercus (oak) and Populus (poplar) leaves, prolonged exposure to treatment at pH 2.5 produced hypertrophic and hyperplastic responses in mesophyll cells. Lesions developed, followed by enlargement and proliferation of adjacent cells, resulting in formation of a gall on adaxial leaf surfaces. In poplar test plants,

this response involved both palisade and spongy mesophyll parenchyma cells, while in oak test plants, only spongy mesophyll cells were affected (Evans and Curry 1979). Because other similar histological studies have not been reported, it is impossible to evaluate how frequent or widespread such structural modification may be. Because species that have been reported to show hyperplastic and hypertrophic response of leaf tissues were consistently injured less than species that did not show these responses, gall formation may be linked to characteristics common to species tolerant of acidic precipitation exposure.

Several studies have reported modification of various physiological functions of the leaf as a result of exposure to simulated acidic precipitation. Sheridan and Rosenstreter (1973), Ferenbaugh (1976), Hindawi et al. (1980), and Jaakhola et al. (1980) reported reduced chlorophyll content as a result of tissue exposure to acidic solutions. Ferenbaugh, however, observed that significant reduction in chlorophyll content did not occur at pH 2.0, and that chlorophyll content slightly increased at pH 3.0. Irving (1979) also reported higher chlorophyll content of leaves exposed to simulated precipitation at pH 3.1. Hindawi et al. observed a steady reduction in chlorophyll content in the range between pH 3.0 to 2.0, and found no change in the ratio of chlorophyll a:b.

Ferenbaugh (1976) determined photosynthesis and respiration rates of test bean plants exposed to simulated acidic precipitation. Respiration and photosynthesis were significantly increased at pH 2.0. Ferenbaugh concluded that because growth of the plants was significantly reduced, photophosphorylation was uncoupled by the treatments. Irving (1979) reported increased photosynthetic rates in some soybean treatments, attributing them to increased nutrition from sulfur and nitrogen components of the rain simulant, which overcame any negative effect of the pH 3.1 treatment. Jacobson et al. (1980) reported a shift in photosynthate allocation from vegetative to reproductive organs as a result of acidic rain treatments of pH 2.8 and 3.4, also suggesting that the primary effect was not on the photosynthetic process itself.

3.2.1.2 Foliar Leaching - Throughfall Chemistry--Rain, fog, dew, and other forms of wet deposition play important roles as sources of nutrients for vegetation and as mechanisms of removal from vegetation of inorganic nutrients and a variety of organic substances: carbohydrates, amino acids, and growth regulators (Kozel and Tukey 1968, Lee and Tukey 1972, Hemphill and Tukey 1973, Tukey 1975). Tukey (1970, 1975, 1980) and Tukey and Morgan (1963) have extensively reviewed the leaching of substances from plants as the result of water films on plant surfaces.

During periods between precipitation events, the vegetation canopy serves as a sink, or collection surface, upon which dry particulate matter, aerosols, and gaseous pollutants accumulate by gravitational sedimentation, impaction, and absorption. Throughfall can be defined as that portion of the gross, or incident, precipitation that reaches the

forest floor through openings in the forest canopy and by dripping off leaves, branches, and stems (Patterson 1975). Throughfall generally amounts to between 70 and 90 percent of gross rainfall, with the balance divided between stemflow and interception loss to the canopy.

Chemical enrichment of throughfall has been well documented for a broad variety of forest species (Tamm 1951, Madgwick and Ovington 1959, Nihlgard 1970, Patterson 1975, Lindberg and Harriss 1981). This enrichment has three potential sources: 1) reactions on the leaf surface in which cations on exchange sites of the cuticle are exchanged with hydrogen from rainfall; 2) movement of cations directly from the translocation stream within the leaf into the surface film of rainwater, dew, or fog by diffusion and mass flow through areas devoid of cuticle (Tukey 1980); and/or 3) washoff of atmospheric particulate matter that has been deposited on the plant surfaces (Patterson 1975, Parker et al. 1980, Lindberg and Harriss 1981).

The exchange of hydrogen ions in precipitation for cations on the cuticle exchange matrix can result in significant scavenging of hydrogen ions by a plant canopy. Eaton et al. (1973), for example, found the forest canopy to retain 90 percent of the incident hydrogen ions from pH 4.0 rain (growing season average), resulting in less acidic (~ pH 5.0) solutions reaching the forest floor. The removal of H^+ by exchange processes in the forest canopy does not eliminate the effects of H^+ deposition on the forest ecosystem, however. Cations leached from the foliage may eventually be leached from the ecosystem if the anion associated with H^+ inputs (SO_4^{2-} or NO_3^-) is mobile (see Figure 2-1, Chapter E-2). Plant response to this may be 1) accelerated uptake to compensate for foliar cation losses, or 2) reduced foliar cation concentrations, if H^+ inputs and foliar exchange are of significant magnitude and duration. In either event, the introduction of H^+ with a mobile anion will cause the net loss of cations from the ecosystem, whether the H^+ cation exchange occurs in the forest canopy or the soil. Further aspects of cation leaching are discussed in Chapter E-2 (soils).

An example of the second case has recently been hypothesized by Rehfuess et al. (1982) for Norway spruce in high elevation forests of eastern Bavaria. Trees experiencing symptoms of decline and dieback were paired with non-symptomatic trees in the same stands and site conditions. Large differences were noted in foliar content, particularly of older leaves, of Ca and Mg, with declining trees consistently showing lower levels of Ca and Mg content than healthy trees. The Mg contents were characterized by the authors as in "extreme deficiency," with calcium in "poor supply." The authors further speculated that since these nutrient deficiences occurred on soils varying considerably in content of both elements, that soil depletion was probably not the dominant contributing factor, but rather that the deficiency is mainly a consequence of enhanced leaching of Ca and Mg from the foliage as a result of acidic deposition of strong acids. The authors further speculated that Ca and Mg uptake from soil pools may be

inadequate to replace this foliar leaching. Such nutritional disorders have been reported to subsequently make foliage more susceptible to additional leaching (Tukey 1970).

Separating relative contributions of internal (leached) and external (washoff) fractions of throughfall enrichment is difficult and has been attempted infrequently. Parker et al. (1980) have reviewed those attempts to estimate the importance of dry sulfur deposition to throughfall enrichment by sulfate-sulfur (Table 3-1). For those studies that have attempted such an analysis, the estimated percentage contribution of dry deposition to throughfall enrichment ranged from 13 to 100 percent, or from 0.3 to 14.4 kg ha^{-1} yr^{-1}. Parker et al. concluded that for temperate hardwood forests in industrialized regions, 40 to 60 percent of annual net throughfall (throughfall enrichment) for sulfate is due to washoff of dry deposition, with 30 to 50 percent being typical for conifers of the same regions. For hardwoods and conifers in regions typified by low background levels of dry sulfur deposition, washoff may range from 0 to 20 percent of throughfall enrichment. Similar data have been developed for several trace elements (Lindberg and Harriss 1981).

Through the application of simulated rainfall in controlled experiments, precipitation acidity has been studied as a variable influencing the leaching rate of various cations and organic carbon from foliage (Wood and Bormann 1974, Fairfax and Lepp 1975, Abrahamsen et al. 1977). Foliar losses of potassium, magnesium, and calcium from bean and maple seedlings were found to increase as the acidity of simulated rain increased. Tissue injury occurred below pH 3.0, but significant increases in leaching rates occurred as high as pH 4.0 (Wood and Bormann 1974). Phaseolus vulgaris L. foliage exposed by Evans et al. (1981a) to citrate-phosphate buffer solutions with a range in acidity from pH 5.7 to pH 2.7 also demonstrated that greater acidity of these solutions preferentially leached greater amounts of calcium, nitrate, and sulfate, while less acidic solutions leached greater amounts of potassium and chloride. Abrahamsen and Dollard (1979) observed that Norway spruce (Picea abies (L.) Karst) lost greater quantities of nutrients under their most acidic treatments, but no related change in foliar cation content occurred, in contrast to the observations of Rehfeuss et al. (1982) discussed above. Wood and Bormann (1977) noted results similar to those of Abrahamsen and Dollard (1979) for eastern white pine (Pinus strobus L.).

3.2.2 Effects of Acidic Deposition on Lichens and Mosses (L. L. Sigal)

The objective of this section is to review the literature on the effects of acidic deposition on lichens and mosses and also to review the literature that describes the effects of realistic, low levels of gaseous sulfur dioxide (SO_2) on lower plants (Grennfelt et al. 1980). Several researchers (Skye 1968, Turk and Wirth 1975) have concluded that SO_2 toxicity and pH effects are not independent factors.

TABLE 3-1. REPORTED VALUES FOR SULFATE-SULFUR DEPOSITION RATES FOR THROUGHFALL AND INCIDENT PRECIPITATION IN WORLD FORESTS

Forest system	Reference	S deposition kg ha^{-1} yr^{-1}		Precipitation amount (cm)
		Incident	Throughfall	
Subalpine balsam fir, New Hampshire	Cronan 1978	24.4	46.4	203[d]
Hemlock, British Columbia	Feller 1977	11.0[a]	40.0	245[c]
Conifers, southern Norway	Haughbotn 1973	32.3[b]	111.2	77
Conifers, southern Norway	Haughbotn 1973	17.7	69.1	77
Conifers, southern Norway	Haughbotn 1973	10.0	21.1	77
Beech, central Germany	Heinrichs and Mayer 1977	24.1[d]	47.6	106
Spruce, central Germany	Heinrichs and Mayer 1977	24.1	80.0	106
Hemlock-spruce, southeastern Alaska	Johnson 1975	0	16.4	270
Tropical rain forest, Costa Rica	Johnson 1975	12.5	23.3	390
Douglas fir, Washington	Johnson 1975	4.0	5.2	165

TABLE 3-1. CONTINUED

Forest system	Reference	S deposition kg ha^{-1} yr^{-1}		Precipitation amount (cm)
		Incident	Throughfall	
Subalpine silver fir, Washington	Johnson 1975	16.8[f]	5.3	300
Hardwoods, Amazonian Venezuela	Jordan et al. 1980	44.5	16.7	391
Hardwoods, Amazonian Venezuela	Jordan et al. 1980	46.6	19.6	412
Hard beech, New Zealand	Miller 1963	8.4	10.4	135
Beech, Southern Sweden	Nihlgard 1970	7.9[d]	18.5	95
Spruce, Southern Sweden	Nihlgard 1970	7.9[d]	54.2	95
Oak, Southern France	Rapp 1973	16.4	22.6	NA
Loblolly pine, North Carolina	Wells et al. 1975	7.9[a]	9.9	NA
Chestnut oak, Tennessee	Lindberg et al. 1979	13.2[b,e]	32.0	143
Mixed oak, Tennessee	Kelly 1979	8.7[a]	15.0	154
Mixed oak, Tennessee	Kelly 1979	11.3[a,b]	14.0	75

TABLE 3-1. CONTINUED

[a]Scaled up from a subannual estimate.

[b]In vicinity of factory or power plant.

[c]Mean of extreme estimates.

[d]Includes stem flow.

[e]Several years data.

[f]Little throughfall.

Lichens and mosses are considered by some researchers (Nieboer et al. 1976) to be among the most pollution sensitive plants, and by others to be more sensitive and better indicators of chronic pollution than vascular plants (Hawksworth 1971, Nash 1976, Guderian 1977, Winner et al. 1978). In addition to their roles in the ecosystem, they are also valuable as biomonitors of air quality. However, it must be noted that lichens and mosses integrate the effects of all ambient pollutants, and in most cases, their use as bioindicators is only an index of general air pollution.

Lichens are sensitive to air pollutants such as sulfur dioxide, (Ferry et al. 1973), ozone and peroxyacetyl nirate (PAN) (Nash and Sigal 1979, Sigal and Taylor 1979), fluorine (Nash 1971, Roberts and Thompson 1980), and metals (Rao et al. 1977; lead, Lawrey and Hale 1981; nickel, Nieboer et al. 1972; mercury, Steinnes and Krog 1977; zinc, Nash 1975; and chromium, Schutte 1977). Scientists in many countries have demonstrated that it is possible to correlate the distribution of lichens around air pollution sources with mean levels of air pollutants. Laboratory and transplant studies have corroborated the data from field investigations. However, the importance of peak concentrations of pollutants relative to long-term average levels has not been established. Excellent summaries on the theory and application of lichens in pollution studies have been published by Ferry et al. (1973), Gilbert (1974), Hawksworth and Rose (1976), Le Blanc and Rao (1975), Richardson and Nieboer (1981), Skye (1968, 1979), and Saunders (1970). In addition, the air pollution literature is regularly indexed in the British journal "The Lichenologist" (1974-81).

Moss species are also sensitive to air pollution (Gilbert 1968, 1970; Nash 1970; Nash and Nash 1974; Stringer and Stringer 1974; Turk and Wirth 1975; Winner and Bewley 1978a,b). However, less attention has been given to mosses in air pollution research. Laboratory studies with mosses have shown that 1) photosynthesis decreases in relation to a decrease in pH of sulfuric acid solutions (Sheridan and Rosenstreter 1973), 2) sulfite and bisulfite solutions reduce photosynthesis (Inglis and Hill 1974, Ferguson and Lee 1979), and 3) growth of four species of Sphagnum moss was reduced when they were fumigated for several months with mean SO_2 concentration of 130 $\mu g\ m^{-3}$ (Ferguson et al. 1978). It has been suggested that sulfate at "feasible" atmospheric concentrations has no effects upon photosynthesis in mosses; however, the fall in pH that accompanies the oxidation of atmospheric SO_2 to SO_4 is capable of reducing photosynthesis (Ferguson and Lee 1979). The phytotoxic effect of SO_2 for both mosses and lichens is known to be greater at low pH (Gilbert 1968, Puckett et al. 1973, Inglis and Hill 1974, Hallgren and Huss 1975).

The generally accepted mechanisms of injury are disruption of cell and chloroplast membranes (Wellburn et al. 1972, Puckett et al. 1974, Malhotra 1976, Ferguson and Lee 1979), and destruction of chlorophyll (Rao and Le Blanc 1966, Nash 1973, Puckett et al. 1973). Susceptibility to SO_2 injury is greatest when lichens are in a moistened or saturated

condition (Rao and Le Blanc 1966; Nash 1973, 1976; Turk et al. 1974). In an air-dried state, lichens have been shown to be relatively insensitive to SO_2 (Showman 1972, Nash 1973, Turk et al. 1974, Marsh and Nash 1979).

The sensitivity of lichens to air pollutants is due to a number of factors: (1) they rapidly absorb moisture in different forms (e.g., rain, fog, dew) and most toxic substances dissolved in the water (Richardson and Nieboer 1981); (2) they are long-lived, and accumulated sulfur metabolites, metals, etc. are not eliminated seasonally (Nash 1976); (3) they lack a vascular system with which to eliminate pollutants through translocation (Nieboer et al. 1976); (4) they lack structures such as epidermis and stomata to exclude pollutants (Sundstrom and Hallgren 1973); (5) they probably have less buffering capacity than vascular plants (Nieboer et al. 1976); and (6) the relationship of the alga and the fungus is delicately balanced; air pollution probably disrupts that balance, resulting in disassociation and destruction of the plant (Neiboer et al. 1976).

The ecology of lichens can be drastically changed by air pollutants. As a result, ecosystems are affected because lichens are integral parts of many relationships and processes. As pioneer species in disturbed areas (Treub 1888), lichens initiate soil formation (Ascaso and Galvin 1976) and stabilize soil (Rychert and Skujins 1974, Drouet 1937). They fix an estimated 10 to 50 percent of the newly-fixed nitrogen in old growth forests in the United States (Denison 1973, Becker 1980, Rhoades 1981). They act as sinks for air pollutants and contribute to the cleansing of the atmosphere (A. C. Hill 1971).

Many invertebrates (mites, caterpillars, earwigs, snails, slugs, etc.) as well as vertebrates (caribou, reindeer, squirrels, woodrats, voles) feed partly or wholly on lichens (Llano 1948, Richardson 1975, Gerson and Seaward 1977, Richardson and Young 1977). Other animals have adaptive camouflage that resembles lichen-covered trees or rocks (Richardson and Young 1977). The interrelations among birds and lichens and insects are multifaceted. Birds use lichens for nest-building, camouflage, and feeding behavior (Kettlewell 1973, Ewald 1982), while many insects have co-evolved with lichens to escape predation from birds (Cott 1940).

Reports of injury to lichens at low levels of SO_2 are found in several recent studies. Showman (1975) found that Parmelia caperata and P. rudecta were absent in regions around a coal-fired power plant when the annual SO_2 average exceeded 50 $\mu g\ m^{-3}$. Will-Wolf (1980) found that Parmelia caperata and P. bolliana showed morphological alterations in areas where maximum SO_2 levels were 389 $\mu g\ m^{-3}$, and annual averages were 5 to 9 $\mu g\ m^{-3}$. Eversman (1978) found decreased respiration rates in Usnea hirta after field fumigations with SO_2 at about 47 $\mu g\ m^{-3}$ for 96 days, and plasmolysis of algal cells in both U. hirta and Parmelia chlorochroa after 31 days of SO_2 at the same concentration. Le Blanc and Rao (1975) concluded that long-range

average concentrations for SO_2 between 16 to 79 $\mu g\ m^{-3}$ (0.006 to 0.03 ppm) cause chronic injury to epiphytes.

In the Ohio River Valley, maximum annual averages of SO_2 ranged from about 50 to 80 $\mu g\ m^{-3}$ in 1977 and 1978. Maximum 1-hr averages ranged from 300 to 500 $\mu g\ m^{-3}$ (Mueller et al. 1980). At the same sites (Rockport and Duncan Falls), mean rainfall pH for August 1978 to March 1980 were 4.12 and 4.36, with ranges of 3.17 to 5.64 and 3.24 to 6.03, respectively [digital (9 track tape) or hard copy (printout) versions of these data are available upon request directly from Peter K. Mueller at EPRI]. Recent experimental evidence shows that photosynthesis was reduced by 40 percent in the lichen Cladina stellaris by field fumigations with fluctuating SO_2 concentrations of less than 655 $\mu g\ m^{-3}$ (0.25 ppm; Moser et al. 1980). Laboratory exposures of the same lichen species wetted by artifical precipitation having a pH = 4.0 and a sulfate concentration = 10.00 $mg\ \ell^{-1}$ reduced photosynthesis by 27 percent (Lechowicz 1981). From these and succeeding data, it appears that at least some of the mechanisms of injury for SO_2 and acid precipitation are similar and that existing, long-term low levels of the pollutants are influencing lichen distribution on a regional scale.

The effect of direct acidic deposition on lichens is a new area of research and therefore has produced few published results other than those of Lechowicz (1981). Evidence from previous laboratory studies of the effects of pH on lichens is indirect and based generally on aqueous solutions of sulfur compounds. Puckett et al. (1973, 1974) found that low pH enhanced aqueous sulfur dioxide toxicity in buffered solutions even when the exposure times were brief. D. J. Hill (1971) found that sulfite in buffered solutions was toxic at pH 4.0 and below but not toxic at pH 5.0 and above. Turk and Wirth (1975) found that damage to lichens exposed to sulfur dioxide and subsequently submersed in buffer solutions from pH 8.0 to pH 2.0 increased with increasing acidity. Baddeley et al. (1971) studied the effect of pH in buffered solutions on the respiration of several lichen species found in eastern North America. Exposure times were short, about 15 minutes, but respiration was clearly pH-dependent, and there were definite pH optima for each species, mostly acidic (pH 4.0). Repeated exposures might show different patterns of respiration.

Little is known about the effects of acidic deposition on nitrogen fixation by lichens. Denison et al. (1977) reported a trend toward decreased nitrogen fixation in the lichens Lobaria pulmonaria and L. oregana as a function of decreasing pH of the water in which the lichens were soaked. These results must be considered preliminary, and additional work in this area is needed because lichens can be important contributors of fixed nitrogen in forest ecosystems (Forman 1975, Pike 1978, Becker 1980, Rhoades 1981), in tundra and grasslands (Alexander 1974), and in deserts (Shields et al. 1957, Rychert and Skujins 1974).

Evidence from the few existing field studies of acid precipitation effects on lichens (Robitaille et al. 1977, Plummer 1980) is

inconclusive because separating pH effects from potential ambient SO_2 (or other gaseous pollutant) toxicity is impossible. Few of the studies that suggest a pH response in lichens (Brodo 1974) actually include the measurement of pH of the aqueous solutions in which the lichens are bathed. Several field studies suggest that acidification of lichen substrates may prevent establishment and development of lichen propagules (Barkman 1958, Skye 1968, Gilbert 1970, Grodzinska 1979). Other studies (Abrahamsen et al. 1979, Dahl et al. 1979) show that lichens alter the chemistry of "rainwater" flowing over granite surfaces partly covered with lichens. Pyatt (1970) notes that lichens are capable, to some extent, of exerting a modifying influence upon the environment. According to Gilbert, the pH and buffer capacity of the lichen thallus and substrate are important for the survival and regeneration of lichens in polluted areas because pH and buffer capacity control the distribution and proportions of toxic compounds in solution and the rates of breakdown of these compounds. Under conditions of acid precipitation and reduced buffer capacity, heavy metal absorption by lichens is increased (Rao et al. 1977).

3.2.3 Summary (D. S. Shriner and L. L. Sigal)

Leaf structure may play two roles in the sensitivity of foliar tissues to acidic precipitation: 1) leaf morphology may selectively enhance (broad-leaved species) or minimize (needle or laminar-leaved species) the surface retention of incident precipitation; and 2) specific cells of the epidermal surface, by virtue of a more permeable cuticle or the absence of waxes, may be initial sites of foliar injury. Once such a lesion occurs, further development of local lesions appears to be enhanced by water collected in the depression formed by the necrotic tissue.

Information on the effects of acidic deposition on the accelerated weathering of epicuticular wax of plants is very preliminary and at present must be considered no more than a "testable hypothesis." Should further research support the hypothesis, virtually all of the important functions of the wax layer could be subject to alteration due to acidic deposition.

Chlorophyll degradation may occur following prolonged exposure to acidic precipitation. Conclusive linkage to decreased photosynthetic rates is currently missing, but premature senescence resulting from chlorophyll degradation may reduce overall photosynthetic capacity of plants affected in this manner. Further study is needed before photosynthetic rate, chlorophyll content, and premature senescence can be causally linked to acidic deposition exposure. Because simulated acid precipitation experiments have been conducted at extreme ranges, more attention must be paid to pH values commonly observed in nature.

Acid deposition is frequently partially neutralized by cation exchange and other reactions on leaf surfaces. These reactions reduce the direct inputs of H^+ to soils, but they do not prevent cation losses from the ecosystem. If the anion associated with acidic

deposition is mobile, cation losses will occur whether H^+ is exchanged in the canopy or soils.

Information on which to assess the effects of acidic deposition on lichens is inadequate. Studies should investigate the direct effects of H^+ concentration and the other acidic deposition components (S, N) on lichens. A comparison of process-level physiological mechanisms of response to acidic deposition is necessary, followed by an analysis of the resulting effects, if any, on the overall growth, yield, or ecosystem function of lichens. In addition, the relevance of laboratory studies to field observations must be established. Given the sensitivity of lichens to related stress agents, they are probably sensitive to acidic deposition. In certain ecosystems (e.g., boreal forests) lichens are a major system component, and potential effects should be regarded as a serious concern for long-term ecosystem stability.

3.3 INTERACTIVE EFFECTS OF ACIDIC DEPOSITION WITH OTHER ENVIRONMENTAL FACTORS ON PLANTS

Several important, but often overlooked, indirect effects of acidic deposition are potential interactions with other pollutants, alterations of host-insect interactions, host-parasite interactions, and symbiotic associations (Figure 3-2). These relationships could involve a direct influence of acidic deposition on a host plant; a direct influence of acidic deposition on an insect, microbial pathogen, or microbial symbiont; or a direct influence of acidic deposition on the interactive process of plant and agent, i.e., infestation, disease, or symbiosis (Figure 3-2).

3.3.1 Interactions with Other Pollutants (J. M. Skelly and B. I. Chevone)

The available literature concerning interactive effects of acidic precipitation and gaseous air pollutants on terrestrial vegetatation consists of only three separate studies. Shriner (1978b) examined the intreaction of acidic precipitation and sulfur dioxide or ozone on red kidney bean (Phaseolus vulgaris) under greenhouse conditions. Treatments with simulated rain at pH 4.0 and multiple O_3 exposures resulted in a significant reduction in foliage dry weight. Simulated precipitation and sulfur dioxide in combination did not affect photosynthesis or biomass production. Troiano et al. (1981) exposed two cultivars of soybean to ambient photochemical oxidant and simulated rain at pH 4.0, 3.4, and 2.8 in a field chamber system. The interactive effects of oxidant and acidic precipitation were inconclusive, with seed germination greater in plants grown in the absence of oxidant at each acidity level. Irving and Miller (1981) also examined the response of field-grown soybeans to simulated acidic rain at pH 5.3 and 3.1 in combination with sulfur dioxide and ambient ozone concentrations. No interactive effects on soybean yield occurred from acid treatments with sulfur dioxide. Sulfur dioxide alone, however, resulted in substantial yield reductions.

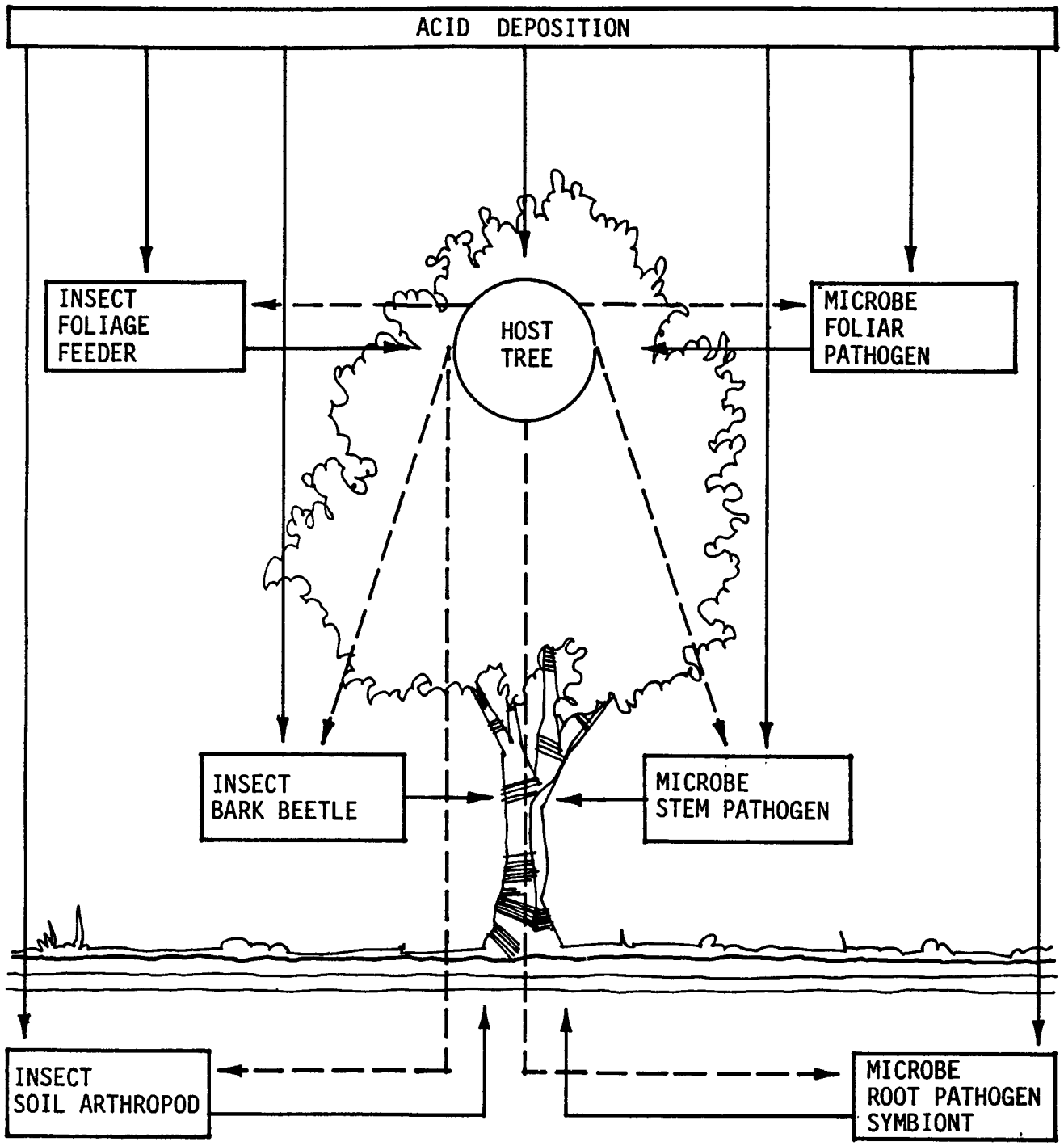

Figure 3-2. Acid deposition may influence insects, pathogens, and symbionts associated with forest trees by direct influence (solid arrows) or indirect influence via host alteration (dashed arrows). Direct influence on soil inhabiting insects and microbes is judged less likely than direct influence on aboveground organisms. Alterations of soil pH or chemistry by acid deposition may indirectly impact soil organisms.

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With information from only three studies, current assessment of the potential detrimental interactive effects of gaseous air pollutants and acidic rain on terrestrial plants can be considered only preliminary. No studies have been conducted with non-agricultural vegetation which, because of potential soil impacts, is considered more sensitive to the indirect effects of acidic precipitation.

Research efforts at present have addressed the indirect interaction of acidic precipitation and gaseous pollutant stress to plants. Plants have been exposed to pollutants individually so that any interactive effects are mediated through the plant response, whether directly or indirectly to each pollutant. With this exposure regime, each pollutant may predispose the plant to additional injury and elicit a more sensitive response to the second pollutant. It is advantageous, under these conditions, to use experimental systems that are most sensitive to both acidic inputs and gaseous pollutant stress. Due to crop management practices, agronomic systems are probably least sensitive to increased acidic input and alterations in soil physiochemical properties. Additional research in which both acidic precipitation and gaseous pollutants can exert their individual effects on the various components of an ecosystem is required.

Effects of acidic deposition on soil chemistry and nutrient recycling are unlikely to occur rapidly (Chapter E-2, Section 2.3). After more than a decade of research in Scandinavia, the observed changes in forest soil chemical properties that can be attributed to acidic precipitation still remain undetermined (Overrein et al. 1980). It is, therefore, unlikely that interactive effects of acidic deposition and gaseous pollutants on plants, which may be expressed through changes in soil properties, will become evident within a single growing season. Because only annual plants have been used in interactive studies, the effect of acidic rain in combination with other air pollutants stressing perennial plant species on a yearly basis for several years is unknown. Also, research efforts have not addressed the temporal relationship between precipitation events and the occurrence of other gaseous air pollutants in the ambient atmosphere.

No information exists on the interaction of a gaseous air pollutant with a wet leaf surface. Such direct interactions can occur only with the same frequency as precipitation events, but liquid phase reactions, especially with SO_2, can alter the chemical form of the pollutant species. Sulfur dioxide in water can exist as the hydrated sulfur dioxide molecule, the bisulfite ion, or the sulfite ion, depending upon the pH of the solution (Gravenhorst et al. 1978). At pH greater than 3.5, hydrated sulfur dioxide dissociates almost completely into hydrogen ions and bisulfate ions. Increased solubility of sulfur dioxide can occur if the bisulfite ion is oxidized irreversibly to the sulfate ion. This oxidation process can be catalyzed by metal cations, specifically iron (Fuzzi 1978) and manganese (Penkett et al. 1979). Particulate deposits on the leaf surface, containing either iron or manganese, may act as sources of these catalysts. Depending upon the rate of this oxidation and the mechanism(s) involved, increased dissolution of

gaseous sulfur dioxide will occur in leaf surface water, generating additional hydrogen ions. Whether such reactions do occur at the leaf surface, the extent to which they occur, and their importance in pollutant stress to plants are unknown.

3.3.2 Interactions with Phytophagus Insects (W. H. Smith)

The damaging influence of high population densities of certain insects can be very visible and cause widespread forest destruction; however, substantial evidence supports the hypothesis that forest insects, even those that cause massive destruction in the short run, may play essential and beneficial roles in forest ecosystems in a long-term context. These roles may involve regulating tree species competition, species composition and succession, primary production, and nutrient cycling (Huffaker 1974, Mattson and Addy 1975). As a result, assessing interrelationships between acidic deposition and phytophagous insects is important.

Air pollutants may directly affect insects by influencing growth rates, mutation rates, dispersal, fecundity, mate finding, host finding, and mortality. Indirect effects may occur through changes in host age structure, distribution, vigor, and acceptance. Few researchers have investigated the effects of acidic deposition on insects. Some studies relative to acidity effects on aquatic insects are available (e.g., Borstrum and Hendrey 1976). Terrestrial arthropods, on the other hand, have been the subject of very few studies. Hagvar et al. (1976) have concluded that acidic precipitation from western and central Europe increases the susceptibility of Scots pine forests to the pine bud moth (Exoteleia dodecella).

Various studies have presented data indicating that species composition or population densities of insect groups are altered in areas of high air pollution stress, for example, roadside (Przybylski 1979) or industrial (Sierpinski 1967, Novaskova 1969, Lebrun 1976) environments. Further specific information is available on the general influence of polluted atmospheres on population characteristics of forest insects (Templin 1962; Schnaider and Sierpinski 1967; Sierpinski 1970, 1971, 1972a,b; Boullard 1973; Wiackowski and Dochinger 1973; Hay 1975; Charles and Villemant 1977; Sierpinski and Chlodny 1977; Dahlsten and Rowney 1980). Johnson (1950, 1969) has reviewed much of the literature dealing with air pollutants and insect pests of conifers. One of the most comprehensive literature reviews available concerning forest insects and air contaminants has been presented by Villemant (1979). Recently, Alstad et al. (1982) provided an excellent overview of the effects of air pollutants on insect populations.

3.3.3 Interactions with Pathogens (W. H. Smith)

Abnormal physiology, or disease, in woody plants follows infection and subsequent development of an extremely large number and diverse group of microorganisms within or on the surface of tree parts. All stages of tree life cycles and all tree tissues and organs are subject,

under appropriate environmental conditions, to impact by a heterogeneous group of microbial pathogens including viroids, viruses, mycoplasmas, bacteria, fungi, and nematodes. As with insect interactions, microbes and the diseases they cause play important roles in succession, species composition, density, composition, and productivity. In the short term, the effects of microbial pathogens may conflict with forest management objectives and assume a considerable economic or managerial as well as ecologic significance (Smith 1970).

The interaction between air pollutants and microorganisms in general is highly variable and complex. Babich and Stotzky (1974) have provided a comprehensive overview of the relationships between air contaminants and microorganisms. A specific air pollutant, at a given dose, may be stimulatory, neutral, or inimical to the growth and development of a particular virus, bacterium, or fungus. In fungi, fruiting body formation, spore production, and spore germination may be stimulated or inhibited.

Microorganisms that normally develop in plant surface habitats may be especially subject to air pollutant influence. These microbes have received considerable research attention and have been the subject of review (Saunders 1971, 1973, 1975; Smith 1976). Numerous comprehensive reviews have summarized the interactions between air contaminants and plant diseases (Laurence 1981). Heagle (1973) summarized nearly 100 references and found that sulfur dioxide, ozone, or fluoride had been reported to increase the incidence of 21 diseases and decrease the occurrence of nine diseases in a variety of nonwoody and woody hosts. Treshow (1975) has provided a detailed review concerning the influence of sulfur dioxide, ozone, fluoride, and particulates on a variety of plant pathogens and the diseases they cause. Treshow lamented the fact that most of the data available deal with in vitro or laboratory accounts of microbe-air pollutant interactions, while only a few investigations have examined the influence of air pollutants on disease development under field conditions.

A review provided by Manning (1975) pointed out that most research attention has been directed to fungal pathogen-air pollutant interactions. Greater research perspective is needed concerning air pollution influence on viruses, bacteria, nematodes, and the diseases they cause. Macroscopic agents of disease, most importantly true- and dwarf-mistletoes, must also be examined relative to air pollution impact, especially in the western part of North America, where the latter are extremely important agents of coniferous disease.

Forest trees, because of their large size, extended lifetimes, and widespread geographic distribution are subject to multiple microbially-induced diseases frequently acting concurrently or sequentially. The reviews of Heagle (1973), Treshow (1975), and Manning (1975) considered a variety of pollutant-woody plant pathogen interactions but were not specifically concerned with forest tree disease. In their review of the impact of air pollutants on fungal pathogens of forest trees of Poland, Grzywacz and Wazny (1973) cited

literature indicating that air pollution stimulated the activities of at least 12 fungal tree pathogens while restricting the activities of at least 10 others.

Our understanding of the influence of acidic deposition on pathogens and the diseases they cause is meager. Shriner (1974, 1975, 1977) has provided us with some valuable perspectives in this important but understudied area. Falling precipitation and the precipitation wetting of vegetative surfaces (see Section 3.2.1), play an enormously important role in the life cycles of many plant pathogens. Recognizing this, Shriner (1974, 1975, 1977) has examined the effects of simulated rain acidified with sulfuric acid on several host-parasite systems under greenhouse and field conditions. The simulated precipitation he employed had a pH of 3.2 and 6.0, approximating the common range of ambient precipitation pH.

Applying simulated precipitation of pH 3.2 resulted in (1) an 86 percent restriction of telia production by Cronartium fusiforme (fungus) on willow oak, (2) a 66 percent inhibition of Meloidogyne hapla (root-knot nematode) on kidney bean, (3) a 29 percent decrease in percentage of leaf area of kidney bean affected by Uromyces phaseoli (fungus), and (4) both stimulated and inhibited development of halo blight of kidney bean caused by Pseudomonas phaseolicola (bacterium). In the latter case, the influence of acidic precipitation varied and depended on the particular stage of the disease cycle when the exposure to acidic precipitation occurred. Simulated sulfuric acid rain applied to plants prior to inoculation stimulated the halo blight disease by 42 percent. Suspension of inoculum in acidic precipitation decreased inoculum potential by 100 percent, while acidic precipitation applied to plants after infection occurred inhibited disease development by 22 percent.

Examining willow oak and bean leaves with a scanning electron microscope revealed distinct erosion of the leaf surface by rain of pH 3.2 (see Section 3.2). This may suggest that altered disease incidence may be due to some change in the structure or function of the cuticle (see Section 3.2.1.1). Shriner has also proposed that the low pH rain may have increased the physiological age of exposed leaves. Shriner (1978a) concluded his initial experiments by suggesting that he had not established threshold pH levels at which significant biological ramifications to pathogens occur from acidic precipitation. He did suggest, however, that artificial precipitation of extremely low pH probably alters infection and disease development of a variety of microbial pathogens.

In recent years, a very serious disease of hard pines caused by a twig and leaf pathogen called Gremmeniella abietina has increased in importance in the northeastern United States. The disease, termed Scleroderris canker, was first reported on red pine in New York in 1959. Currently, G. abietina is causing significant large tree mortality in Vermont and New York. Because it may be more than coincidence that this region is included within the highest acidic precipitation zone of North

America, Paul D. Manion, SUNY, Syracuse, initiated an acidic rain Scleroderris research project. The laboratory and field studies reported to date indicate the disease may be affected by precipitation pH, but there was no indication that abnormally high acidified rain increased disease incidence. In fact, the opposite may be true. That is, acidic rain may reduce the importance of the canker disease (Raynal et al. 1980, Bragg 1982, Manion and Bragg 1982).

Armillariella mellea is an extremely important forest tree root pathogen throughout the temperate zone. The fungus is geographically very wide-spread, has an extremely broad host range, and is especially significant in causing disease in trees under stress. Shields and Hobbs (1979) have indicated that soil pH is related to disease development caused by A. mellea. If acidic deposition influences soil pH (see Chapter E-2) or tree vigor, it may indirectly impact tree susceptibility to A. mellea infection. In the northeast, spruce decline in high elevation forests has been a recent concern. A. mellea is associated with spruce trees exhibiting dieback and decline symptoms in northern New England and may play an important role in the morbidity and mortality of this species. The habitats of soil pathogens such as A. mellea are buffered relative to plant-surface habitats, so for acidic deposition to influence these pathogens an alteration of soil pH or chemistry or host susceptibility would have to occur.

Fusiform rust caused by C. fusiforme is the most important disease of managed pines in the southeast. Bruck et al. (1981) applied simulated rain of various pH levels to loblolly pine at the time of inoculation with rust basidiospores. Significantly fewer galls formed on trees treated with simulated rain at pH 4.0 or less than formed on trees treated with rain at pH 5.6.

Various bacterial species are important components of tree leaf microfloras. Lacy et al. (1981) observed that populations of Erwinia herbicola and Pseudomonas syringae were reduced on soybean leaves when host plants were treated with water acidified to pH 3.4 relative to leaves exposed to distilled water (pH 5.7).

3.3.4 Influence on Vegetative Hosts That Would Alter Relationships with Insect or Microbial Associate (W. H. Smith)

As Section 3.2 discussed, exposure to acidic deposition may lead to acidification of plant surfaces, leaf cuticle erosion, and foliar lesions. Foliar lesions could release plant volatiles attractive or repulsive to insect pests or may serve as infection courts for microbial disease agents.

The influence of acidic deposition leached chemicals on insects infesting tree leaves or bark could prove attractive, repulsive, or provide chemical orientation. In the case of surface microbes, leached compounds may inhibit vegetative growth or spore germination (alkaloids, phenolic substances) or stimulate vegetative growth (as nutrients) or spore germination (as inducers or nutrients--sugars, amino acids,

vitamins). Leaching of toxic radioelements from plant surfaces could have a restrictive impact on plant surface biota (Myttenaere et al. 1980).

Plant growth and yield may be stimulated or inhibited by acidic deposition. If growth is either stimulated or suppressed, it is probable that differential influence on insects and pathogens would follow. In the case of some host-pathogen and host-insect relationships, a tree under stress is more vulnerable to infestation or infection. Bark beetles and root-infecting or canker forming fungi are generally more successful in less vigorous individuals. Trees exhibiting vigorous growth, on the other hand, may be predisposed to more serious impact from certain rust fungi and other disease agents.

3.3.5 Effects of Acidic Deposition on Pesticides (J. B. Weber)

Pesticides are used annually to manage pests in terrestrial and aquatic systems. The majority of these materials are organic chemicals that selectively control unwanted and injurious insects, pathogens, or weeds. They are applied directly to animals, vegetation, soils, and/or inland waters, but ultimately they end up in soils and/or waters. The behavior and fate of pesticides in the environment depend upon the following:

(1) method of application of the pesticide;

(2) chemical properties of the pesticide;

(3) edaphic properties of the system;

(4) dissipation routes of the pesticide; and

(5) climatic conditions.

No studies on effects of acidic deposition on pesticides were found in the literature; however, pH changes have been reported to affect factors 1 through 5 listed above.

Foliar absorption and injury from herbicides applied directly to vegetation have been reported to be greatly enhanced by lowering the pH for both phenoxyacetic acid (Crafts 1961b) and dinitrophenol (Crafts and Reiber 1945) type compounds. Acidic conditions promote formation of the un-ionized species that more readily penetrate and injure vegetative membranes than do ionized species. Thus, acidic deposition could conceivably result in enhanced injury to weeds and/or crops in certain instances. The most likely possibility of this occurring would be in herbicide applications to forests, pastures, minimum-tillage crop production systems, or aquatic systems where the foliage has had ample time to accumulate acidic deposition.

Chapter E-4 (Section 4.4) reports that acidic deposition causes significant lowering of the pH of inland waters in certain instances.

This would have a substantial effect on the direct biological activity and longevity of herbicides used in aquatic weed and algae control. One would expect a significant increase in the herbicidal activity of the phenoxyacetic acid compounds. Aquatic herbicides such as simazine would perform less satisfactorily under acidic conditions since many investigators (Armstrong et al. 1967, Jordan et al. 1972) have reported that chloro-s-triazines decompose at a much faster rate under acidic conditions. This would make it necessary to increase the rates of chloro-s-triazine herbicides and to make more frequent applications for satisfactory aquatic weed control in waters where the pH levels were below normal levels.

Organic pesticides are categorized into five major types depending on ionizing characteristics. Examples of the five types are:

(1) cationic (diquat, paraquat);

(2) basic (atrazine, simazine, prometryn);

(3) acidic (2,4-D, fenac, picloram)

(4) phosphates and arsenates (glyphosate, DSMA); and

(5) nonionic (alachlor, carbaryl, methomyl).

Changes in pH levels in waters or soil solutions affect the ionizing properties of basic and acidic properties to the greatest extent. At lowered pH levels acidic and basic pesticides tend to be more readily adsorbed by soil particulate matter, hence less biologically active and less mobile (Weber 1972, Weber and Weed 1974). Under such circumstances, higher rates of these pesticides would be required to provide satisfactory performance, and the longevity of the chemicals may be affected, depending on their modes of decomposition.

Pesticides degraded biologically would be affected by changes in microbial populations. Captan, dicamba, amitrole, vernolate, chloramben, crotoxyphos (Hamaker 1972), metribuzin (Ladlie et al 1976), 2,4-D and MCPA (Torstensson 1975), and prometryn (Best and Weber 1974) were reported to persist longer under acidic conditions than under neutral conditions. Conversely, diazinon and diazoxon (Hamaker 1972) were degraded more readily at lower pH levels.

Pesticides degraded chemically are directly affected by soil pH levels. Malathion and parathion (Edwards 1972) persisted much longer in acidic soils than in neutral soils, while atrazine (Best and Weber 1974) and simazine were degraded much more rapidly under acidic conditions than under neutral conditions.

3.3.6 Summary (W. H. Smith)

A review of the evidence on the interaction of acidic deposition with other pollutants, insect and microbial pests, does not allow

generalized statements concerning stimulation or restriction of biotic stress agents, or their activities, by acidic deposition. Certain studies report stimulation of pest activities associated with acidic deposition treatment, while other studies report restriction of pest activities following treatment. No studies report significant interactive effects between acidic deposition and other pollutants, although the potential for such effects is very real.

Future research must combine field and controlled environment studies. Mechanisms for acidic deposition impact on predisposition/protection of forest trees to/from disease caused by microbial pathogens, and infestation caused by phytophagous insects must be examined. Evidence available comes from laboratory and controlled environment studies, but no evidence on this topic from studies employing large trees under field conditions exists.

We cannot, however, rule out the possibility of indirect, subtle interaction of acidic deposition with other pollutants, phytophagous insects, and microbial pathogens.

No known studies demonstrate that acidic deposition on plant surfaces directly affects the biological activity of pesticides. However, ample evidence shows that pH of aqueous solutions of certain herbicides greatly affects herbicidal activity, and observed effects were greatest between pH levels of 6.0 and 3.0. These occurrences have been reported for herbicides applied to terrestial and aquatic weeds.

No studies show indirect effects of acidic deposition on pesticide inactivation, mobility, and decomposition in soils; however, ample evidence shows that soil pH greatly affects all of these processes. It is likely that if acidic deposition is found to affect soil and water pH, then pesticide behavior and fate will likewise be affected.

3.4 BIOMASS PRODUCTION

3.4.1 Forests (S. B. McLaughlin, D. J. Raynal, and A. H. Johnson)

Changing levels and patterns of emissions of atmospheric pollutants in recent decades have resulted in increased exposure of extensive forests in Europe and North America to both gaseous pollutants and acid precipitation. Reports of decreased growth and increased mortality of forest trees in areas receiving high rates of atmospheric pollutant deposition have stressed the need to quantify the rates of changes in forest productivity and identify the causes of such changes. The complex chemical nature of combined pollutant exposures and the fact that these pollutants may have both direct effects to vegetation and indirect (possibly beneficial) effects makes quantification of such effects particularly challenging. The complexity of forest growth and succession and the sensitivity of forest trees to natural environmental stresses add further to the challenge of quantifying effects of anthropogenic pollutants on forest productivity.

Such quantification requires that several critical tasks be addressed: (1) definition of the chemical nature of the present and past air quality within the regions of principal concern, (2) documentation of the basis for assuming that detectable effects may be occurring within those regions, and (3) identification of the types of effects that might be produced under present and likely future exposure regimes.

A critical need in evaluating stress effects on perennial forest systems is documenting the magnitude, rate, and point of inception of historical changes in air quality. Unfortunately, the maximum period of record for the present National Atmospheric Deposition Program (NADP) network is four years, while ozone monitoring data have not been collected by standardized methods in network fashion beyond 1975. The most recently published estimates of historical changes in isopleths of precipitation acidity (Likens and Butler 1981) suggest that initial intensification of acidity of northeastern precipitation may have begun in the 1950's. However, because of the limited data points and the uncertain chemical techniques used, the validity of these earliest data has been questioned (see Chapter A-8). Other sources of information currently being developed include emissions inventories coupled with regional air dispersion modeling, evaluation of historical stream and lake chemistry data, historical reconstruction of weathering rates of marble monuments, and analysis of changes in elemental composition of annually-formed lake sediments and tree rings. Collectively, these techniques offer possibilities for documenting the period of intensification of atmospheric deposition of anthropogenic pollutants. (Further discussion of such documentation can be found in Chapter A-8).

3.4.1.1 Possible Mechanisms of Response--A wide variety of potential direct and indirect responses of forest trees to acid deposition have been hypothesized based on fundamental responses of biological systems to acidity and other stresses (Tamm and Cowling 1976). Included among these are increased leaching of nutrients from foliage, accelerated weathering of leaf cuticular surfaces, increased permeability of leaf surfaces to toxic materials, water, and disease agents, altered reproductive processes, and altered root-rhizosphere relations. In addition to the direct effects of acidity from contact with foliage, roots, and rhizosphere organisms, a major area of interest is the indirect effects of increased acidity on soil nutrient availability to vegetation and the consequences of soil leaching losses to aquatic systems (SMA 1982). Many of the key processes to be considered in evaluating the effects of acidic deposition on forest systems are identified schematically in Figure 3-3. The diversity of these processes illustrates the complexity of potential interactions of acidic deposition with forest systems and the need for better understanding of system level integration of potential effects on multiple processes.

Forest responses must be examined both from the perspective of today's mature forests which have been produced over the last 50 to 100 years (a period of significant changes in atmospheric emissions) as well as with respect to the forests of the future, which by contrast are

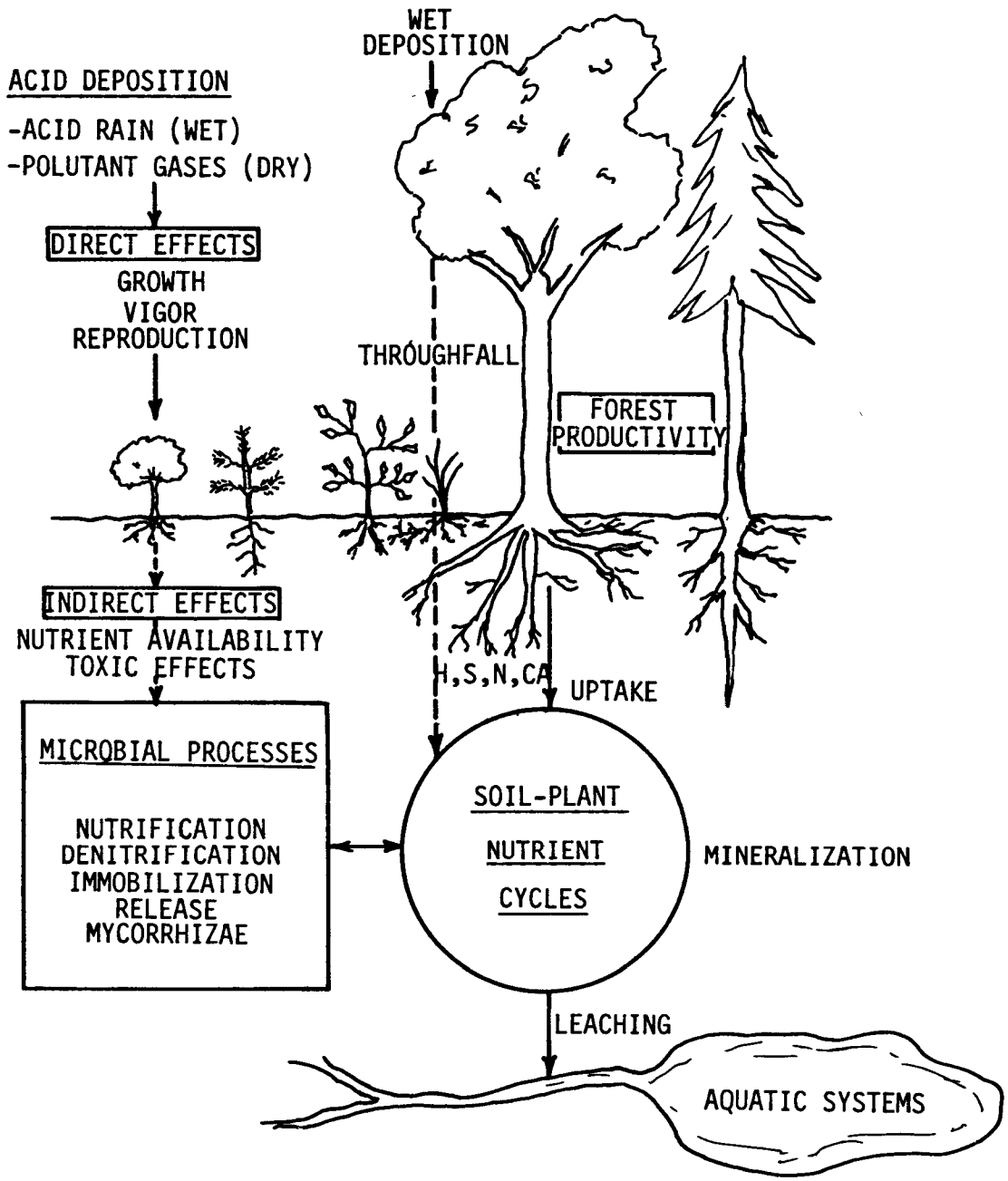

Figure 3-3. Key components and processes to be considered in evaluating effects of acidic deposition on forested ecosystems.

growing under atmospheric stresses that will likely span their entire life cycle. Thus, productivity of these forests may be more influenced by alteration of the potentially more sensitive life stages including reproduction, seedling establishment, and growth.

Seedling emergence, establishment, and early growth phases are considered to be potentially among the most susceptible stages affected (Abrahamsen et al. 1976, Likens 1976, Lee and Weber 1979, Raynal et al. 1980). Additionally, reproductive phases of growth may be the most sensitive to acidic deposition (Likens 1976, Cowling, 1978, Jacobson 1980. Various controlled field and laboratory studies in Scandinavia and in the United States have been conducted to quantify possible effects of simulated acid rain on seed germination, seedling establishment, and growth of trees in field plots.

3.4.1.2 Phenological Effects--Plants may respond to the deposition of acidic substances in a manner which depends on genetic characteristics of the species; sensitivity of individual developmental stages; timing, duration, frequency, and severity of deposition events; and nature of meteorological and microenvironmental conditions (Cowling 1978). Thus, a complete assessment of the influences of acidic deposition on plants must include consideration of phenology--changes in life cycle stages as affected by environment and season. Seed germination and seedling emergence and establishment are early growth phases potentially susceptible to acidic deposition (Abrahamsen et al. 1976; Lee and Weber 1979; Raynal et al. 1982a,b). As well, mature and reproductive phases of growth may be sensitive to acidic deposition (Likens 1976, Cowling 1978, Jacobson 1980, Evans 1982). However, differences in the sensitivity of vegetation to acidic deposition are not documented from natural field studies.

Plant growth, development, and reproduction may be affected by acidic deposition both positively and negatively. Response depends upon species sensitivity, plant life cycle phase, and the nature of exposure acidity. Considerable variation in plant species susceptibilty exists, and at the individual level the effect of acidification on different plant organs or tissues, including marketable crops, may vary widely. Controlled environment studies indicate that the deposition of acidic and acidifying substances from the atmosphere may have stimulatory, detrimental, or no apparent effects on plant growth, development, and reproduction. Both stimulatory and detrimental effects may simultaneously occur, making determination of both acute and chronic effects quite difficult. For example, tree seedling growth may be enhanced by deposition of nitrate and possible sulfate when soils are deficient in these while concomitantly foliar injury may occur due to hydrogen ion deposition. Because many biotic and abiotic factors interact to influence plant performance, plant dieback or reduction in growth or yield must be evaluated in terms of physiological stress, soil toxicity and nutrient deficiency problems, plant disease, and direct and indirect effects of acidic precipitation, if chronic effects of deposition of acidic substances are to be fully characterized.

3.4.1.2.1 Seed germination and seedling establishment. Laboratory studies indicate that a wide range of sensitivity of seed germination to acidic substrate conditions exists (Abrahamsen et al. 1976, Lee and Weber 1979, Raynal et al. 1982a). Studies focused on woody plants reveal that seed germination of some species, including yellow birch and red maple, is inhibited, but other species, such as sugar maple, are not affected when exposed to substrate acidity of pH 3.0 or less (Raynal et al. 1982a). In some coniferous species such as white pine and white spruce, substrate acidity of pH 3.0 may promote seed germination, but it produces no effect in other species such as eastern hemlock. Figure 3-4 illustrates the contrasting response of seed germination of three tree species to different substrate acidity levels.

Interaction of substrate solution reaction (pH) and osmotic potential may be significant, and the effect of acidity may vary due to differences in ionic characteristics of the germination medium (Chou and Young 1974, Abougendia and Redman 1979). Leaching of various substances from the seed or fruit coat by acidic solutions may also occur, subsequently causing neutralization. The necessity of continually adjusting the pH of in vitro solutions to maintain constant acidity levels in germination studies suggests that seed tissues may effectively buffer the germination medium, thus reducing potential detrimental effects of acidic deposition (Raynal et al. 1982a). Under natural field conditions, vegetation canopy, litter, organic matter, and mineral soils may further buffer emerging seedlings from highly acidic deposition (Raynal et al. 1982b, Mollitor and Raynal 1982). Thus, seeds are often protected from direct influence by acidic deposition and seed germination typically may be minimally affected, as indicated by much of the research to date.

Emergence and establishment of the seedling have been shown to be more sensitive to low substrate pH than is seed germination itself (Abrahamsen et al. 1976, Lee and Weber 1979, Raynal et al. 1982b). Certain species, such as sugar maple, show no detrimental effect of acidity on seed germination at pH 3.0 but may be inhibited at the establishment phase, as shown in studies of effects of simulated acidic precipitation on juvenile growth (Raynal et al. 1982a,b). Injury to the emerging seedling radicle and hypocotyl may be direct, due to hydrogen ion concentration, and/or indirect, resulting from increased susceptibility to microbial pathogens that tolerate acidic conditions and changing nutrient levels (Raynal et al. 1982b). Seedling growth studies in which young plants are exposed to simulated acidic precipitation have shown that juvenile plants may exhibit reduced or stimulated growth, depending on the species (Wood and Bormann 1974, Raynal et al. 1982b).

Possible changes in soil nutrient status associated with acidic deposition must be considered in evaluating plant growth response to acidification (see Section 2.3). Some workers (Benzian 1965, Abrahamsen et al. 1976, Abrahamsen 1980) have demonstrated that optimal height growth of coniferous seedlings (including species of pine, spruce, and fir) occurs in soils having a pH between 4.0 and 5.0. Whether hydrogen

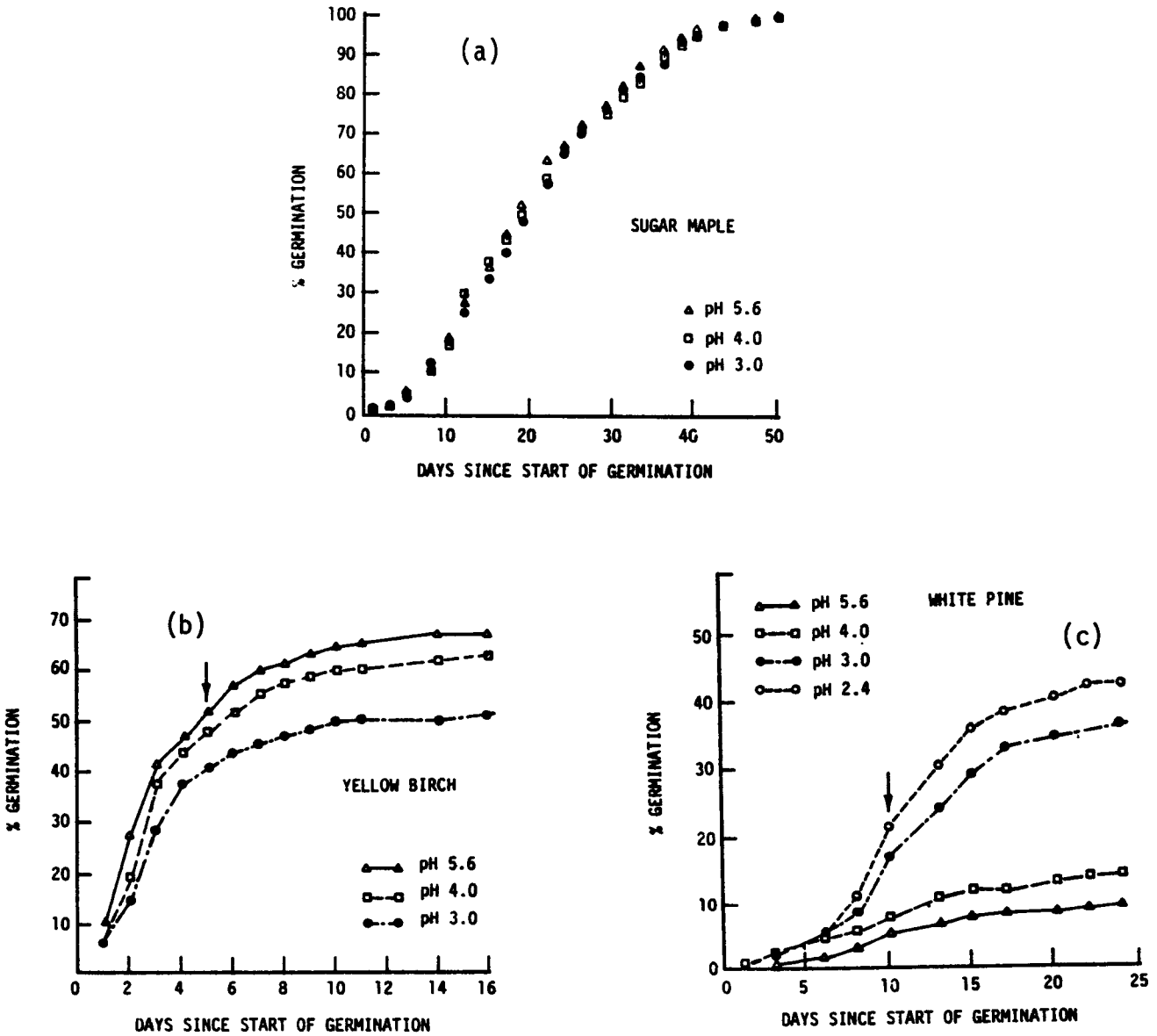

Figure 3-4. Mean cumulative percent germination of sugar maple, yellow birch, and white pine seeds subjected to different substrate acidity levels. Arrows indicate point at which differences in response become significant ($p < 0.05$) determined by Tukey's test for mean separation following analysis of variance. Data show contrasting responses of species to increasing acidiy: (a) no significant difference at pH 3.0, 4.0, and 5.6 for sugar maple, (b) decreased germination in yellow birch at pH 3.0 compared with that at pH 4.0 and 5.6 (no significant difference between pH 4.0 and 5.6), and (c) increased germination in white pine at pH 2.4 and 3.0 compared with that at pH 4.0 and 5.6 (no significant difference between 2.4 and 3.0 or 4.0 and 5.6). Adapted from Raynal et al. (1982a).

ion deposition directly influences seedling growth or whether it, in association with the deposition of other cations and anions, causes variation in soil nutrient characteristics affecting growth is not fully known (Abrahamsen 1980). When nutrients in soil are not limiting for plant growth, detrimental effects of deposition of acidifying substances are not likely to occur. However, at low fertility levels, simulated acidified canopy throughfall of pH 3.0 or less has been found to promote seedling growth in some species (Raynal et al. 1982b). Such a benefical response could result from deposition of nitrate or other nutrients. (See Chapter E-2 for detailed discussions of forest nutrient effects.)

Even where growth is stimulated by acidic deposition, however, foliar injury may simultaneously occur in some species (Raynal et al. 1980, 1982b). Thus, competitive promotive and inhibitory effects of acidic deposition may concomitantly affect seedling growth and development. It is, therefore, not surprising that studies of the effects of simulated acidic precipitation or forest canopy throughfall on plant growth have produced variable results, ranging from no apparent effects, stimulation of growth, and inhibition of growth (Wood and Bormann 1974, Matiziris and Nakos 1977, Raynal et al. 1980).

3.4.1.2.2 Mature and reproductive stages. Studies of interference of acidic deposition on flower or cone development in flowering plants and conifers have not been made. Should highly acidic precipitation events coincide with floral or gamete development, pollination, or fruit or seed set, effects on plant populations and regeneration processes could possibly be altered. Numerous studies reveal that various air pollutants, including sulfur dioxide and ozone, may cause reductions in cone size and weight (Smith 1981). Studies of air pollutant effects on pollen germination and pollen tube elongation suggest that pollen function may be altered because of acidification of floral tissues, including stigmas (Karnosky and Stairs 1974). Findings that red and white pine pollen germination and tube elongation were greater in a relatively unpolluted site compared with one of high pollution incidence provide circumstantial evidence that pollen gametogenesis and development may be altered by acidic deposition (Houston and Dochinger 1977). Evaluating acidic precipitation effects on plant reproduction demands that the coupling of effects of air pollution and acidification be understood.

Controlled-environment studies of effects of simulated acidic precipitation on agricultural crops indicate differential sensitivity of species and contrasting effects on different plant parts (Evans and Lewin 1981, Lee et al. 1981; see also Section 3.4.2). Research by Evans and Lewin (1981) indicates that yield of pinto beans may be reduced by simulated acid rain because of a decrease in the number of seeds per pod. In contrast, under similar exposure conditions, soybean yield showed an increase due to a larger dry mass per seed.

3.4.1.3 Growth of Seedlings and Trees in Irrigation Experiments--Abrahamsen (1982) has reviewed field experiments in Sweden and Norway designed to determine the effects of artificial acidification on growth

of forest trees and tree seedlings. In Swedish experiments (Tamm and Wiklander 1980), young (18-yr-old) Scots pine were irrigated below the canopy with dilute sulfuric acid (annual application, 50 to 150 kg ha^{-1} H_2SO_4 in one application per year) in both with and without prior addition of fertilizer. After 6 years of application a negative correlation between treatment acidity and basal area growth was found on the fertilized plots (< 10 percent decrease at highst acidity) whereas growth responded positively (approximately + 30 percent increase at highest acidity level) on the unfertilized plots. Increased nitrogen uptake was considered a probable cause of positive responses. Results of these studies were complicated by changes in nutrient availability in the soil and associated with the effects of high acidity on soil fungi, bacteria, and competing understory vegetation (Tamm and Wiklander 1980).

In Norwegian experiments (Abrahamsen et al. 1976, Tveite and Abrahamsen 1980) a variety of combinations of acidified groundwater treatment (pH values between 6.0 and 2.0 by H_2SO_4 addition), treatment volume (25 to 50 mm per month) application technique (below or above canopy), lime application 500 to 4500 kg CaO ha^{-1}), and tree species (lodgepole pine, Norway spruce, silver birch, and Scots pine) were used. The overall effects of these experiments were small where treatment effects were found after 4 to 7 years of treatment application (Tveite 1980a). In studies with Scots pine, positive growth effects were found at pH levels of 3.0, 2.5, and 2.0 after 4 years of treatment, followed by significant growth reduction by pH 2.0 in the 5th year. Norway spruce showed reduced diameter growth at all acid treatment levels on the year after 6 years of prior treatment. Height growth of silver birch was stimulated by rainfall acidity. Lime application had little or no effect on observed responses. Effects of acid irrigation on foliar nutrient levels were also generally small (Tveite 1980b).

In evaluating the results of the Scandinavian irrigation experiments Abrahamsen (1980) concluded that the data give "no substantial evidence of effects on tree growth at acidity levels presently found in precipitation." However, he cautions that acid effects produced particularly at highest acidity levels may be partly attributable to soil effects that were artifacts of the highly acid treatment levels and hence not representative of longer-term responses to be expected under actual field conditions.

Such results corroborate findings of researchers in the United States who have demonstrated differential effects of simulated acidic precipitation on plant growth (Wood and Bormann 1977; Raynal et al. 1980, 1982b). Conclusions regarding plant growth response from experiments where vegetation and soils have been subjected to accelerated acidic deposition rates or concentrated acidic inputs must be viewed with caution, however, for reasons discussed in Chapter E-2, Section 2.3.1.

3.4.1.4 Studies of Long-Term Growth of Forest Trees--The evidence for effects of regional-scale anthropogenic pollutants on productivity of forests comes from a limited number of studies in the United States and

Europe in which long-term growth trends determined from tree rings have been analyzed. In Scandinavia, where acid precipitation was first recognized and studied as an environmental problem, research on changing patterns of tree growth based on tree-ring chronologies have provided circumstantial evidence of growth declines that occurred at about the time acidity of rainfall is thought to have intensified. In Norway, research by Abrahamsen et al. (1976) and Strand (1980) showed in Norway spruce and Scots pine a decrease in growth (generally less than 2.3 percent per year) that became evident around 1950, primarily in the eastern third of the country. These responses could not be clearly associated with the geographical patterns of most acid rainfall, which occurred in the southern (pH average = 4.3) rather than the eastern (pH average = 4.5) part of the country. Some drawbacks of these studies, however, were that individual sites were not characterized with respect to soil chemical characteristics, and neither the influences of climate nor aging trends were removed from the data.

Preliminary analysis of differences in responses between sites of differing productivity class (high vs low) in southern Norway showed no differences in response to acidic precipitation (Abrahamsen et al. 1976). On the other hand, studies in Sweden by Jonsson (1975) and Jonsson and Sundberg (1972) involving Scots pine and Norway spruce showed similar temporal trends in growth reduction beginning around 1950, and these effects were most pronounced in areas of greatest expected susceptibility to acidic deposition. Site susceptibility was estimated based on the average pH of precipitation and pH and ion content of lakes and rivers in 1965 and 1970 and the distribution of soil types. Jonsson (1975) concluded from these studies that "acidification cannot be excluded as a possible cause of poorer growth development, but may be suspected to have had an unfavorable effect on growth within the more susceptible regions." Differences in growth reductions between susceptible and non-susceptible regions were estimated to be in the range of 0.3 to 0.6 percent per year.

Since this original study, a second study has been initiated covering an additional 9 years, 1965-1974, since the first survey was completed (Jonsson and Svensson 1983). These data confirmed the earlier downward trend beginning in 1950 but showed a period of increased productivity beginning in the mid- to late 1960's. For sites of relatively poor quality, growth of both pine and spruce in the 1970's had increased substantially since its minimum in the mid-60's but was still substantially less than that attained up to 1940. The overall trend was still downward over the interval 1910-1974. By contrast, growth of these species on good sites showed an upswing in the 1965-74 interval which resulted in a growth rate equal to or above that attained during the preceding 50 years. In explaining these trends and summarizing the results of their own and the Norwegian SNSF project the Swedes make the following statements (SMA 1982).

> "A conceivable explanation of these changes is that the mathematical model that was used has not compensated for or caught those effects in the ground that are the results of more

long-term cyclical changes in climate. These changes may, for example, affect the supply of nitrogen in the ground that is available to plants. It must also be noted that the Swedish forests have to take increased quantities of nitrogen that are deposited along with precipitation. This gives a fertilizing effect. There are at the present time no clear signs or evidence of either increased or reduced forest production resulting from the effects of acid precipitation on Scandinavian forestland and its fertility."

The final report on the Norwegian SNSF project makes the point that:

"decreases in forest growth due to acid deposits have not been demonstrated. The increased nitrogen supply often associated with acid precipitation may have a positive growth effect. This does not exclude, however, the possibility that adverse influences may be developing over time in the more susceptible forest ecosystems. The most serious consequence for terrestrial ecosystems of regional acidification at levels currently observed in Norway may be the increased rate of leaching of major elements and trace metals from forest soils and vegetation. This also has a bearing on the aquatic systems receiving these effluents. From an ecological point of view it is difficult to forecast the ultimate results of the atmospheric acidification and related air pollutants on terrestrial systems and to judge the rate and even the direction of changes. In the more susceptible areas it seems, however, to be a question of proportion and time required rather than whether any ecological effects appear or not."

In examining the Scandinavian work it is important to note that the character of their atmospheric emissions and the chemistry of their rainfall have changed dramatically in recent years, resulting in substantial increases in nitrogen inputs from the atmosphere. Emission of SO_2 in Sweden increased 85 percent (from 240 to 445 thousands of tons of S yr^{-1}) during the interval 1950 to 1970, but had decreased back to 240 tons yr^{-1} by 1978. Sulfate in precipitation showed a substantial (65 percent) increase (from 55 to 90 microequivalents per liter) during the interal 1955 to 1964, but then remained constant through 1974. By contrast, nitrate levels increased by 33 percent (15 to 20 meq ℓ^{-1}) from 1955 to 1964 and by 1974 had reached 35 meq ℓ^{-1}, a level 133 percent above that in 1955 (SMA 1982). Thus, while it will be difficult to interpret the Scandinavian tree-ring studies until both climatic and age-related trends are removed from the data, the most recent analysis suggests the possibility that relatively recent significant increases in atmospheric inputs of nitrogen (coupled with the trends in atmospheric chemistry) may be an important factor in most recent changes in growth patterns.

In the United States, Cogbill (1976) examined growth of beech, birch, and maple in the White Mountains of New Hampshire and red spruce

in the Smoky Mountains of Tennessee. From analysis of tree-ring chronologies, he concluded that no synchronized regional decrease in radial growth had occurred. The ring chronologies presented for all of the species he studied, however, showed evidence of a decreasing growth trend from around 1960 until 1970. More recent studies in New York by Raynal (1980) with red spruce and white pine and by Johnson et al. (1981) in the New Jersey pine barrens with pitch, shortleaf, and loblolly pine have shown patterns of decline among most of these species during the past 26 years.

In New Jersey, a strong statistical relationship between annual variation in stream pH and growth rates suggested that acidic precipitation may have been a growth-limiting factor for the past two decades (Johnson et al. 1981). Stream pH, in this poorly buffered soil system, was closely correlated with precipitation pH during a 36-month period of concurrent records. Of the trees examined, approximately one-third showed normal growth, one-third showed noticeable abnormal compression of annual increments during the past 20 to 25 years, and the remainder showed dramatic reduction in annual growth over this time interval. This effect was evident in trees of different species and at different sites and occurred regardless of age or whether trees were planted or native. An interesting response of both these trees and the four species examined by Puckett (1982) in southeastern New York was a change in the influence of climate on tree growth over the past 25 to 30 years. Increased sensitivity of trees in these studies to climatic variables suggests the possibility that changes in the physiological relationship of these trees to their growing environment may have occurred during recent decades.

Of the above studies, only that of the pine barrens by Johnson et al. (1981) examined the possible influences of gaseous pollutants on observed growth trends. In those studies, growth reponses were demonstrably unrelated to O_3 levels. Although uncertain, we might anticipate that gaseous air pollutants would also have played only a minor influence on growth trends observed in Scandinavia where the density of gaseous pollutant sources is rather low and concentrated in coastal areas (SMA 1982). In central Europe where Ulrich et al. (1980) have reported dieback and decline of Norway spruce and beech and in inland areas of the eastern United States, contributions of gaseous pollutants, primarily O_3 and SO_2, can be considered to have changed over the same time spans as has acid precipitation and thus should be considered in any study of long-term growth effects.

3.4.1.5 Dieback and Decline in High Elevation Forests--Within the United States, the forests presently receiving the highest levels of acidic deposition are those at high elevations in the northeast. Forests characterized by varying proportions of spruce, fir, and white birch occur at the high elevations of the Appalachian Mountains from eastern Canada to North Carolina. The northern boreal forests of New York, Vermont, and New Hampshire have received considerable attention with respect to the potential for acidic deposition impacts. Although the mountain summits are remote from large point sources of sulfur, they

receive extraordinarily high rates of H^+, sulfur, and heavy metal deposition (Lovett et al. 1982, Friedland et al. 1983). In addition, the vegetation is subjected to very acid cloud moisture for a considerable portion of the year (Johnson et al. 1983). Typically, cloud moisture pH is in the range 3.5 to 3.7, whereas ambient precipitation is about pH 4.1 to 4.3. Another cause for attention stems from the quantitative documentation of a red spruce decline in the Green Mountains of Vermont, the causes of which are obscure at present (Siccama et al. 1982).

The northern boreal forests are characterized by red spruce (Picea rubens), balsam fir (Abies balsamea) and white birch (Betula papyrifera var. cordifolia) in the canopy, mountain ash (Pyrus americana) and mountain maple (Acer spicatum) as important understory trees, and an herb layer dominated by ferns (Dryopteris sp.) and Oxalis montana (Siccama 1974). The lowermost elevation to which the boreal forests extend varies from 250 m above sea level in Maine and Nova Scotia to 750 m in New Hampshire and Vermont, 900 to 1000 m in the Adirondack and Catskill Mountains of New York, and about 1500 m in North Carolina (Oosting 1956, Siccama 1974). The presence of boreal vegetation is believed to be related to the incidence of cloud moisture, with the boreal vegetation occupying the often cloud-capped upper slopes, and hardwoods holding the lower elevation sites (Nichols 1918, Davis 1966, Vogelmann et al. 1968, Siccama 1974). In the Green Mountains of Vermont, the boreal forests are above cloud base for 800 to 2000 hours per year, depending on elevation (Johnson et al. 1983).

Although there is considerable interest in cloud moisture pH and there are several ongoing studies in the mountains of the Northeast (H. Vogelmann, University of Vermont; F. H. Bormann, T. G. Siccama, Yale School of Forestry; G. E. Likens, J. Eaton, Cornell University; V. Mohnen, J. Kadlecek, State University of New York, Albany; C. V. Cogbill, Center for Northern Studies), there are few published data. Data from especially designed cloud moisture collectors at Mt. Moosilauke, NH, indicate that growing season cloud moisture pH is generally in the mid-3 range (Lovett et al. 1982). The few reported cloud pH measurements obtained from airplane flights suggest that growing season cloud moisture pH is distinctly lower than moisture precipitated from the cloud, and that clouds are most acid near cloud base (Scott and Laulainen 1979). The current indication is that cloud moisture pH is approximately 0.5 pH units lower than ambient rain or snow pH, but considerably more data are needed to characterize the nature of cloud acidity. The implication is that boreal forest vegetation is exposed to moisture with pH of 3.0 to 4.0 frequently and for a total of 30 to 80 days per year.

In the mountainous areas of New England, precipitation increases with altitude. Lovett (1981, in Cronan 1983) estimates precipitation rates of 240 cm yr^{-1} in the balsam fir forests of New Hampshire. Low-elevation precipitation in New England ranges from about 100 to 150 cm yr^{-1}. Siccama (1974) determined that growing season throughfall increased by 2.9 cm per 100 m^{-2} in the Green Mountains of Vermont due

to increased rainfall and an increase in the cloud moisture intercepted by vegetation. Vogelmann et al. (1968) report that at 1087 m in the Green Mountains, open collectors fitted with screens to intercept cloud moisture collected 66.8 percent more water than control collectors without screens. Throughfall collectors placed under balsam fir at 1250 and 1300 m in the White Mountains collected 8 percent more water than precipitation collectors placed in the open at the same elevation, and 36 percent more water than precipitation collectors located at 520 and 640 m. Thus, high precipitation rates coupled with intercepted cloud moisture probably produce H^+ deposition rates far in excess of the regional rates reported by precipitation collection networks based on samples collected at lower elevation.

Cronan (1983) estimated H^+ input to the canopy at 77 to 100 meq m^{-2} for the 6 month period May through October, 1978 in the high elevation fir stands. The hardwood canopy at 520 and 640 m received 50 to 62 meq H^+ m^{-2} during this period. Based on Cronan's data, it appears that the boreal forest canopy is not effective at neutralizing atmospherically deposited H^+ as throughfall collectors indicated that the H^+ input to the forest floor under fir was 98 mg m^{-2} for the growing season. Probably the best estimate of H^+ deposition has been made by Lovett et al. (1982), who used field collection of cloud moisture samples and modeling of cloud droplet interception to estimate H^+ deposition in the subalpine zone of the White Mountains to be ~ 340 meq m^{-2} yr^{-1}.

As a result of the substantial input and the inferred low neutralization capacity of the canopy (Cronan 1983), the potential for accelerated leaching of bases is high, but to date, no quantitative data from high elevation forests indicate if the rate has actually increased over the past few decades. Changes in soil pH are not expected to be rapid, as the forest floor of the boreal zone soils is naturally extremely acid. Siccama (1974) reported soil pH in H_2O of 3.4 to 3.7 in the forest floor (O horizons) at Camels Hump, Vermont in the mid-1960's. Johnson et al. (1983) found that at the same sites, pH was slightly but not significantly higher in 1980.

Estimates of dry deposition have not been made for high-elevation forests, but as wind velocities increase with altitude (Siccama 1974) and as conifers have a high surface area and have foliage all year, dry deposition may add substantially to the quantity of atmospherically deposited H^+ processed.

A decline of red spruce (but not fir or white birch) has been quantitatively documented in the Green Mountains of Vermont (Siccama et al. 1982) and observed in New York and New Hampshire (Johnson et al. 1983). An overall reduction of approximately 50 percent in basal area and density was observed in the Green Mountains between 1965 and 1979. Trees in all size classes were affected. The primary cause is presently unknown, but it is not likely to be successional dynamics, climatic changes, insect damage, or primary pathogens (Hadfield 1968, Roman and Raynal 1980, Siccama et al. 1982). Studies of pathogens in declining

spruce indicate the presence of secondary fungal pathogens, with Armillaria mellea, Fomes pini, and Cytospora kunzii most prominant (Hadfield 1968). Hadfield (1968) speculated that the infected trees had been weakened by the drought of the early 1960's prior to invasion by the fungi. Using the framework of Manion (1981), the spruce decline has the characteristics of a complex biotic-abiotic disease related to environmental stress. Currently, there are no data which implicate acidic deposition as a contributing stress, nor are there data which rule out all of the possible pathways by which acidic deposition could affect forest trees.

At present, serious dieback of spruce (Picea abies) and fir (Abies alba) is under study in Germany. From long-term, intensive, ecosystem-level studies, Ulrich (Ulrich et al. 1980; Ulrich 1981a,b, 1982) suggested that acidic deposition has contributed to changes in H^+ generation and consumption which have caused soil acidification, mobilization of Al, mortality of fine roots, and ultimately, dieback and decline in spruce, fir, and beech (Fagus sylvatica). That contention is based on careful documentation of changes in soil solution chemistry, a nearly parallel decrease in fine root biomass and increase in soil solution Al concentrations during the growing season, and nutrient solution studies which indicated that the ratio of uncomplexed Al (i.e., Al^{3+}) to Ca found in the soil solution was sufficient to cause abnormal root growth and development. While those findings suggest the possibility of Al toxicity, they are not definitive. Bauch (1983) determined that the roots of declining spruce and fir were Ca deficient, but had the same levels of Al as healthy spruce and fir. Rehfuess (1981) has observed declining fir on calcareous soils which would seem to preclude Al toxicity or Ca deficiency in those cases. More recently, however, Rehfuess et al. (1982) noted Mg and possible Ca deficiencies by foliar analysis even in base-rich soils. They speculate that accelerated foliar leaching may be reponsible (see Section 3.2.1.2). Rehfuess points out that the parallel change in soil solution Al and fine root biomass noted by Ulrich was not synchronized in that marked decreases in fine root biomass preceded the increase in soil solution Al. Rehfuess cites several studies (Goettsche 1972, Deans 1979, Persson 1980) in support of his contention that late summer declines in fine root biomass are naturally controlled, and need not be related to Al levels. Ulrich's extrapolation of nutrient solution Al:Ca levels to the field situation are also questionable, since the soil matrix may alter the availability of those and other plant-essential or phytotoxic elements.

The hypothesis of Ulrich appears to have limited applicability to the North American spruce decline, where dieback and decline is most prominent in the high elevations where soils are Borofolists or Cryofolists which have ~ 80 percent organic matter by weight (Friedland et al. 1983), and Al toxicity would likely be masked by complexation with organic matter (Ulrich 1982). Data on spruce root chemistry from Camels Hump, VT, indicate that Ca:Al ratios increase with increasing elevation. As mortality increases with elevation, it is

not likely that imbalances of Al and Ca in root tissue are the major cause of spruce decline (Lord 1982, Johnson et al. 1983).

Whether the red spruce decline is related to acidic deposition has been the focus of considerable speculation. The deline is widespread, easily discerned, dramatic, and of unknown origin. It has occurred in an environment that receives very high annual input of H^+ from the atmosphere and where trees are frequently subject to intensely acid cloud moisture; hence, it is logical that research on acidic deposition effects in high-elevation forests has been initiated.

At present, there are few testable hypotheses regarding how acidic deposition could have contributed to spruce mortality. The Al toxicity proposed by Ulrich (1981a,b; 1982) is not supported by the data collected to date. The foliar leaching hypothesis of Rehfuess et al. (1982) remains untested as yet, however.

The spruce decline appears to be a stress-related disease, where the trees are probably predisposed to stress by the site conditions where some short-term stress, possibly the drought of the early 1960's triggered a loss of vigor, and where biotic stress imposed by fungal attack is sufficient to cause widespread mortality. Acidic deposition could act to intensify the predisposing stresses, exacerbate the effects of the triggering stress, or increase the susceptibility to fungal attack, and those possibilities warrant research in the future.

3.4.1.6 Summary--At present there is no proof that acidic deposition is currently limiting growth of forests in either Europe or the United States. From field studies of mature forests trees it is apparent that altered growth patterns of principally coniferous species examined to date have occurred in recent decades in many areas of the northeastern U.S. and in some areas of Europe with high atmospheric deposition levels. Recent increases in mortality of red spruce in the northeastern U.S. and Norway spruce and beech in Europe add further to the concern that forests are undergoing significant adverse change, however, no clear link has been established between these changes and anthropogenic pollutants, particularly acidic rainfall. This must be presently viewed from the perspective of two possible hypotheses: (1) recent changes are purely circumstantial and not in an way linked to acid precipitation, or (2) we have not yet adequately studied a very complex association in which multiple and interactive factors may be involved and responses may be subtle and chronic.

It is too early to conclude that acidic deposition has not nor will not affect forest productivity. Irrigation studies with seedlings and young trees provide no indication of immediate alarm yet are difficult to interpret because of potential artifacts of experimental protocols. Detecting responses of mature forest trees is made difficult by the complexities of competition, climate, and site factors, the potential interactions between acid precipitation, gaseous pollutants, and trace metals, and the lack of control or unattended sites with which acid precipitation impacted sites can be compared. Although the task

of assessing potential impacts of forest productivity will assuredly be difficult, the potential economic and ecological consequences of even subtle changes in forest growth over large regions dictates that it should be attempted.

To address these problems it will be necessary to evaluate the long-term dynamics of forest systems over a broad enough range of environmental conditions to document both whether systematic changes have occurred and the extent to which such changes are linked to variables such as levels of deposition of anthopogenic pollutants, soil fertility, moisture status, species composition, and stand stocking. A combination of approaches will be needed: dendroecological studies to document past growth patterns of trees in a broad range of conditions, permanent long-term growth plots to study changes in stand dynamics, and forest growth models to examine the potential long-term significance of changing growth rates to forest growth and compensation. The above approaches will be correlative in nature and should be used to focus on the range of conditions in which responses have occurred. However, they must also be coupled with mechanistic studies aimed at specific mechanisms of effect before acid precipitation effects on forest productivity are ever conclusively established or refuted.

3.4.2 Crops (P. M. Irving)

A considerable number of studies on the vegetative effects of acidic precipitation have been published in the last 5 years. However, because of limitations in research design, few of these studies can be used to estimate crop loss realistically. Among the large scale field studies which are most potentially useful for estimating yield effects, differences in methodologies make intercomparisons difficult and results appear to be inconsistent. The following is a discussion of the approach used in acid precipitation effects studies, an analysis of the design limitations of those studies, and a comparison of their methodologies and results.

3.4.2.1 Review and Analysis of Experimental Design--The most widely used method for making crop loss assessments in the past has been field surveys in which observers estimate vegetation injury from visible symptoms under ambient conditions and subjectively relate leaf damage to yield loss. Since visible injury to crops has never been reported as the result of ambient acid precipitation, experiments using simulated rain in field or controlled environment (i.e., greenhouse, growth chamber, laboratory) studies have been used to determine the threshold acidity levels that produce visible injury.

Three general approaches have been used to determine impacts on plants from acidic deposition: (1) Determination of a dose-response function for a specific species in a defined environment; (2) classification of relative sensitivity based on morphological, physiological, or genetic characteristics; (3) determination of mechanisms of action. Both field and controlled-environment methodologies with simulated rain have been used in these approaches.

Only dose-response studies provide quantitative data to estimate growth and yield effects.

3.4.2.1.1 Dose-response determination. Current methods for determining whether crop yield losses are occurring from acid rain exposure include dose-response studies to mathematically relate yield to pollutant dose. The term 'dose-response' suggests a univariate relationship; however, a number of potentially important variables comprise 'acid rain dose' (see next section). Complex, factorial designs and multivariate analyses may be necessary to describe the relationships adequately. Dose-response studies of pollutant effects on crops fall into two basic categories: (1) field studies and (2) controlled-environment studies. Each type of study has its advantages and limitations.

Field studies are often a more realistic means of estimating actual effects because the experimental plants can be grown under normal environmental conditions, especially if common agricultural practices are used. Because different environmental conditions related to geography (i.e., temperature, soil type, and water availability) may lead to different responses, field studies are useful in estimating regional impacts of pollutants when similar experiments are performed in various regions and then compared. Field research, however, demands considerable time and labor and is thus expensive. Adding to the expense is the need for either a high degree of replication so that the sometimes subtle treatment effects can be observed above the differences caused by environmental variability or a large number of treatment plots for response surface analyses. Reliable dose-response predictions cannot usually be made without at least 2 to 3 years of replicate studies conducted using normal agronomic practices.

A lack of comparable unpolluted (control) plots is also a problem for field studies in most regions. This has led to the use of such devices as open-top chambers for the elimination of gaseous pollutants from field plots and to the use of rain exclusion shelters. Experiments using these devices must be designed properly for valid comparisons to be made. For example, in a study by Kratky et al. (1974), plots of tomato plants were placed inside and outside plastic rain shelters in the Kona district of Hawaii during a volcanic eruption period. The plants growing outside the rainshelter received rain with a pH of 4.0 and produced no salable yield, while plants under the shelter averaged 5 kg per plant of salable fruit. However, an explanation other than acid rain should be considered for the Kratky study because of a possible shelter effect. Dry deposited materials from the volcanic eruption, possibly acidic, may have been dissolved by rainfall on leaf surfaces outside the shelter but remained in the non-reactive dry form inside the shelter. Thus rainfall, acidic or not, would have had an effect by acting as a wetting agent. The problem of separating the effects of dry deposition when it occurs in conjunction with wet deposition is one facing all field researchers.

Controlled-environment studies are useful indicators of potential effects and may suggest subtle changes not measureable in an

uncontrolled situation. Controlled studies also allow the investigator to reduce the dimensionality or number of variables in the experiment. These types of studies, for example, may be necessary to determine which characteristics of rain (i.e., intensity, droplet size, ionic composition) must be simulated in field studies. Their use is limited, however, because plants may be more sensitive to stress when grown under short photoperiod, low light intensity, medium temperature, and adequate soil moisture (Leung et al. 1978), conditions which frequently occur in a growth chamber or greenhouse as compared to the field. Since controlled-environment studies may overestimate acid rain stress because of greater plant sensitivity, they should be used with caution when assessing potential damage. For example, Lee and Neely (1981) found chamber-grown radish and mustard greens to be more sensitive to simulated acidic rain than were field-grown plants. Troiano et al. (1982) observed that greenhouse-grown plants developed foliar injury more readily from acid rain simulants than did field-grown plants. Since light intensity and wind speed affect cuticular development (Juniper and Bradley 1958), which in turn affects leaf wettability, greenhouse-grown plants may be affected more by acidic deposition than field plants because of decreased wax development (see Section 3.2.1.1). On the other hand, under some conditions plants may be more stressed in controlled environments (due to restricted root growth or lower photosynthetic rate) and thus less susceptible to treatment stress because of lower metabolic rates and thus lower pollutant uptake.

Soil factors, nutrition and cultural practices (i.e., application of fertilizer, pesticides and other chemicals, irrigation, planting schedules) may all affect the sensitivity of a plant to pollution and therefore should be recorded in experimental methods and, for greater accuracy, should reflect common agricultural conditions as closely as possible. To determine the interaction of these factors with pollutant effects, controlled environment studies are necessary.

Pollutants rarely occur alone, and since pollutant combinations have been found to cause more-than-additive or less-than-additive effects (Ashenden and Mansfield 1978, Jacobson et al. 1980), the concentrations of other pollutants should be monitored and reported in conjunction with acid precipitation studies. Exposures of various pollutant combinations in controlled studies are necessary to determine interactive effects.

3.4.2.1.2 Sensitivity classification. There may be considerable variability in sensitivity to pollutant stress between plant communities, species within communities, cultivars within species, and growth stages of cultivars (Heggestadt and Heck 1971; see also Section 3.4.1.2). Gaseous pollutants (i.e., ozone, sulfur dioxide) have been found to affect certain crop cultivars more than others, and limited information indicates that this is also true for cultivar response to acidic precipitation (see following section). Because it would be prohibitively expensive and time-consuming to perform dose-response studies on all crop cultivars, some experimental studies are aimed at identifying plant characteristics that can be used to indicate a plant's

relative sensitivity or resistance to acidic deposition. For example, leaf wettability, which is related to surface morphology, has been suggested as a parameter that may indicate sensitivity to acidic precipitation (Evans et al. 1977a).

It has been suggested that crop classes can be grouped according to their sensitivity to acid precipitation. Based on a study of 28 different crops, Lee et al. (1981) reported that inhibition of marketable yield was observed only in the dicotyledons that were studied, and within this group root crops, leaf crops, cole crops, tuber crops, legumes and fruit crops were ranked in decreasing order of sensitivity. But the data are contradicted by other studies. For example, Evans et al. (1982) in a study of two root crops found radishes to be resistant and garden beets to be sensitive to simulated acidic precipitation.

Plant response may also be related to stage of development when exposure occurs. The possibility that a particular life stage may be more susceptible to an acid precipitation event than other stages must be considered when researchers investigate and report acid precipitation effects.

3.4.2.1.3 Mechanisms. Studies having the objective of determining mechanisms of action of an air pollutant (mechanistic) can provide information to explain the basis of an observed plant growth response. In studies of this type, measurements are made to determine effects on basic processes such as photosynthesis, respiration, transpiration, and metabolism. Examples of such measurements include CO_2 uptake and emission, leaf diffusive resistance, metabolite pools, and enzyme activities. This information may then be interpreted and applied through the use of plant growth models to predict total plant response. Physiological measurements may also be used to support and explain plant yield response. For example, Irving and Miller (1980), using a $^{14}CO_2$ assimilation technique in the field, reported that SO_2 exposures reduced both photosynthesis and yield of soybeans but that acid rain treatments had apparently stimulated the photosynthetic rates with no effect on soybean yield. Usually physiological determinations alone are in adequate to estimate the economic damage of pollutants to crops.

3.4.2.1.4 Characteristics of precipitation simulant exposures. The effects of a pollutant on crop yield may be defined by correlating yield variations with variations in pollutant dose. Acidic precipitation, however, consists of a number of variables that may have an effect on crop yield. For example, the sulfate and nitrate concentrations, which are frequently correlated with the hydrogen ion concentration of the rain, may be more important in affecting plant response than the pH of the rain (Irving and Sowinski 1980). Lee and Neely (1980) found that simulated rain acidified with sulfuric acid resulted in a different effect on the growth of mustard green, onion, fescue, radish, lettuce, and orchard grass than simulated rain at the same pH, acidified with sulfuric and nitric acids (2:1 equivalent weight ratio; refer to Tables

3-2 and 3-3 in Section 3.4.2.2). Acid rain dose should therefore be described by concentrations of sulfate, nitrate, and other important ions (e.g., NH_4^+, Ca^{2+}, Mg^{2+}, etc.), as well as hydrogen ion (pH). For a complete analysis, it may be necessary to determine the effect of each individual ion as well as their combination so that all important ions are simulated at levels found in polluted and unpolluted rain.

Plant injury responses are a function of pollutant concentration and exposure time or quantity (i.e., acid rain dose = $[H^+ \times cm\ rain] + [SO_4^{2-} \times cm] + [NO_3^- \times cm]$. Response to a given dose of gaseous pollutant is frequently greater if deposited in a shorter exposure time. Response to acid rain, however, may be positively correlated with the amount of time the leaf is wet. When comparing experimental results, one must compare concentration and duration of exposure to understand the response in terms of dose and rate. In the case of acid rain, reporting the pH of applied precipitation is inadequate without total dose or deposition of important ions (i.e., kg ha^{-1} of SO_4^{2-}, NO_3^-, and H^+), rate or intensity (i.e., cm hr^{-1}), duration, and frequency. Physiological systems can be quite resilient due to activation of defense and repair systems during periods of stress. Therefore, time between stress events may be important for repair functions. It has been reported that the "recovery" period between gaseous pollutant exposures may affect the total plant response. Similarly, the number of "dry" days between precipitation events may influence the net response of a plant to acidic deposition. Because of differences in leaf wettability, plants may respond differently to a rain or mist; thus droplet size is yet another important characteristic (see Section 3.2.1.1).

3.4.2.1.5 Yield criteria. Because crop production is measured in terms of the yield of a marketable product, it is useful to express pollutant injury in terms of the economically valuable portion of the crop. However, this is not easily applied uniformly in experimental studies. Leaf injury estimates have been commonly used to assess pollution damage, but economic loss is not always closely related to leaf damage (Brandt and Heck 1968). Assessing loss based on visible injury may overestimate or underestimate the economic loss. For example, in a study of defoliation effects on yield, Jones et al. (1955) found no reduction in root yield or sugar content of sugar beets after removal of 50 percent of the leaves. Irving and Sowinski (1981) reported increased yield of greenhouse-grown soybeans that had also exhibited necrosis as a result of acid rain exposures. Increased yield was also reported by Lee et al. (1980) for alfalfa that exhibited foliar injury from acidic rain. Conversely, chlorosis or necrosis of leaves could result in considerable economic loss of a crop such as lettuce or mustard greens without causing measurable changes in leaf weight.

3.4.2.2 Experimental Results--To allow comparisons of acid precipitation effects research by investigators using various techniques, it is necessary (although perhaps not sufficient) to describe the experimental conditions, the dose, and the responses for each

investigation in comparable units. Accordingly, calculations were made, based on information in the literature or by personal communication, to describe each investigation in comparative terms. These changes in units were made only for comparison purposes. None of the experimental results described below have been changed from those of the orginal author. Given the experimental design limitations discussed in the previous section, conclusions based on the following research results must be made cautiously.

3.4.2.2.1 Field studies. The studies described in Table 3-2 were performed in the field, using accepted agricultural practices to the extent experimental design would permit. Because hydrogen, sulfate, and nitrate ions are those components of precipitation that are believed to most likely affect the growth and yield of crops, they were used in describing the precipitation dose. In all experiments, simulated rain was applied at regular intervals during the life cycle of the crop and, except for 'Beeson' and 'Williams' soybeans, was applied in addition to ambient precipitation. Thus, total deposition received by the crop is the sum of simulant plus ambient loadings.

Among the 14 crop cultivars (9 species) studied, only one exhibited a consistantly negative yield effect at all acidity levels used (garden beet), three were negatively affected by at least one of the acidity levels used in the study ('So. Giant Curled' mustard green, 'Pioneer 3992' field corn, and 'Amsoy' soybean), and six had higher yields from at least one acidity level ('Champion' and 'Cherry Belle' radish, 'Vernal' alfalfa, 'Alta' fescue, 'Beeson' soybean, and 'Williams' soybean). The most frequent response reported to result from simulated acidic rain was "no effect" ('Red Kidney' kidney bean, 'Davis' and 'Wells' soybean, 'Cherry Belle' radish, 'So. Giant Curled' mustard green, 'Improved Thick Leaf' spinach, and 'Vernal' alfalfa). Some experiments demonstrated both positive and negative response to acid rain, depending on the H^+ concentration. There is little evidence for a linear response function, however, since no effect frequently occurred at doses greater than those producing positive or negative response. Except for garden beet, this was true for each study that reported a negative response to at least one level of acidic deposition. For example, a 9 percent decrease in the yield of corn resulted from treatments with 42 times the ambient H^+ deposition (six times ambient H^+ concentration), but no effect occurred at 132 and 187 times (pH 4.0, 3.5, 3.0, respectively). In the garden beet study, the yield decrease from acid rain was not the result of lower beet root weights but because of fewer number of marketable roots per plot. Perhaps the acid rain treatments affected germination or seedling establishment. The ratio of sulfate:nitrate ions in the precipitation simulant also affected the response of some plants (i.e., alfalfa, fescue, mustard green; Table 3-2), independent of pH.

A comparison of studies on five different cultivars of soybeans by four different investigators appears to indicate that the 'Amsoy' cultivar may be more susceptible to acidic deposition than 'Beeson',

TABLE 3-2. FIELD RESEARCH ON CROP GROWTH AND YIELD AS AFFECTED BY ACID PRECIPITATION

Total deposition kg ha^{-1} (simulant + ambient)			Simulant concentration mg ℓ^{-1}				Rate cm hr^{-1}	Events #	Events hr events^{-1}	Droplet size µm	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$						
Alfalfa, 'Vernal', Medicago sativa L. (Lee and Neely 1980)												
0.017	2.13	2.26	0.0025	0.53	0.753	0.7	0.67	26	1.5	1200	5.6	Control
0.171	13.31	2.26	0.10	4.83	0.753	6.4	0.67	26	1.5	1200	4.0	9% greater yield than pH 5.6
0.833	38.89	2.26	0.316	14.67	0.753	19.5	0.67	26	1.5	1200	3.5	No effect on yield compared to pH 5.6
2.611	120.84	2.26	1.00	46.19	0.753	61.3	0.67	26	1.5	1200	3.0	No effect on yield compared to pH 5.6
0.011	0.75	0.30	0.016	1.07	0.434	2.5					4.8	Ambient
0.017	2.13	2.26	0.0025	0.53	0.753	0.7	0.67	26	1.5	1200	5.6	Control
0.271	9.07	7.89	0.10	3.20	2.92	1.1	0.67	26	1.5	1200	4.0	No effect on yield compared to pH 5.6
0.833	30.44	19.64	0.316	11.42	7.44	1.5	0.67	26	1.5	1200	3.5	No effect on yield compared to pH 5.6
2.611	89.15	60.85	1.00	34.00	23.29	1.5	0.67	26	1.5	1200	3.0	No effect on yield compared to pH 5.6
0.011	0.75	0.30	0.016	1.07	0.434	2.5					4.8	Ambient
(Garden) Beet, 'Perfected Detroit V-904', Beta vulgaris L. (Evans et al. 1982)												
0.077			0.002	1.26	3.04	0.4	35.0	19	0.001	353	5.7	10% greater shoot growth, 16% greater root yield than ambient
0.078			0.010	5.47	3.04	1.8	35.0	19	0.001	353	4.0	Lower number of marketable roots per plot than ambient or pH 5.7
0.082			0.079	37.07	3.04	12.2	35.0	19	0.001	353	3.1	Lower number of marketable roots per plot than ambient or pH 5.7
0.090			1.995	106.6	3.04	35.1	35.0	19	0.001	353	2.7	Lower number of marketable roots per plot than ambient or pH 5.7
0.077			0.087								4.1	Ambient
Corn, 'Pioneer 3992' Zea mays L. (Lee and Neely 1980)												
0.028	4.03	4.75	0.0025	0.53	0.753	0.7	0.67	58	1.5	1200	5.6	Control
0.594	19.51	17.33	0.10	3.20	2.92	1.1	0.67	58	1.5	1200	4.0	9% lower yield; no effect on growth compared to pH 5.6
1.847	67.20	43.54	0.316	11.42	7.44	1.5	0.67	58	1.5	1200	3.5	No effect on growth or yield compared to pH 5.6
5.814	198.16	135.47	1.00	34.00	23.29	1.5	0.67	58	1.5	1200	3.0	No effect on growth or yield compared to pH 5.6
0.014	0.96	0.39	0.016	1.07	0.434	2.5					4.8	Ambient
Fescue (Tall), 'Alta', Festuca elatior L. var. arundinacea Schreb. (Lee and Neely 1980)												
0.017	2.13	2.26	0.0025	0.53	0.753	0.7	0.67	26	1.5	1200	5.6	Control
0.271	13.31	2.26	0.10	4.83	0.753	6.4	0.67	26	1.5	1200	4.0	24% greater yield than pH 5.6
0.833	38.89	2.26	0.316	14.67	0.753	19.5	0.67	26	1.5	1200	3.5	19% greater yield than pH 5.6
2.611	120.84	2.26	1.00	46.19	0.753	61.3	0.67	26	1.5	1200	3.0	No effect on yield compared to pH 5.6
0.011	0.75	0.30	0.016	1.07	0.434	2.5					4.8	Ambient
0.017	2.13	2.26	0.0025	0.30	0.753	0.7	0.67	26	1.5	1200	5.6	Control
0.271	9.07	2.26	0.10	3.20	2.92	1.1	0.67	26	1.5	1200	4.0	No effect on yield compared to pH 5.6
0.833	30.44	2.26	0.316	11.42	7.44	1.5	0.67	26	1.5	1200	3.5	No effect on yield compared to pH 5.6
2.611	89.15	2.26	1.00	34.00	23.29	1.5	0.67	26	1.5	1200	3.0	No effect on yield compared to pH 5.6
0.011	0.75	0.30	0.016	1.07	0.434						4.8	Ambient
Kidney Bean, 'Red Kidney', Phaseolus vulgaris L. (Shriner and Johnston 1981)												
	13.02	5.57	0.001	0.02	0.12	0.2	3.0	27	0.17	900	6.0	Control
1.14	98.05	5.57	0.631	50.0	0.12	417	3.0	27	0.17	900	3.2	No effect on growth or yield compared to pH 6.0
	12.99	5.37		2.30	0.95	2.4						Ambient

[a]Effects are reported when statistical significance is $\leq$ 0.05 level.

TABLE 3-2. CONTINUED

Total deposition kg ha^{-1} (simulant + ambient)			Simulant concentration mg ℓ$^{-1}$				Rate cm hr^{-1}	Events #	Events hr events^{-1}	Droplet size µm	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	SO_4^{2-}:NO_3^-						
Mustard Green, 'So. Giant Curled', Brassica japonica Hort. (Lee and Neely 1980)												
0.033	2.78	1.95	0.0025	0.53	0.753	0.7	0.67	16	1.5	1200	5.6	Control
0.189	9.66	1.95	0.10	4.83	0.753	6.4	0.67	16	1.5	1200	4.0	No effect on growth or yield compared to pH 5.6
0.535	25.40	1.95	0.316	14.67	0.753	19.5	0.67	16	1.5	1200	3.5	No effect on growth or yield compared to pH 5.6
1.629	75.83	1.95	1.00	46.19	0.753	61.3	0.67	16	1.5	1200	3.0	No effect on growth or yield compared to pH 5.6
0.029	1.93	0.78	0.016	1.07	0.434	2.5					4.8	Ambient
0.033	2.78	1.95	0.0025	0.53	0.753	0.7	0.67	16	1.5	1200	5.6	Control
0.189	7.05	5.45	0.10	3.20	2.92	1.1	0.67	16	1.5	1200	4.0	31% lower yield; 29% lower root wt than pH 5.6
0.535	20.20	12.68	0.316	11.42	7.44	1.5	0.67	16	1.5	1200	3.5	No effect on yield or growth compared to pH 5.6
1.629	56.33	38.04	1.00	34.00	23.29	1.5	0.67	16	1.5	1200	3.0	33% lower yield; 24% lower root wt than pH 5.6
0.029	1.93	0.78	0.016	1.07	0.434	2.5					4.8	Ambient
Radish, 'Champion', Raphanus sativis L. (Troiano et al. 1982)												
0.106			0.0025	0.72	0.31	2.3	1.0	5	1	1900	5.6	No effect on yield but 5% higher shoot wt than ambient
0.130			0.06	2.9	1.4	2.1	1.0	5	1	1900	4.2	7% higher root wt (yield) than pH 5.6
0.231			0.32	11.7	5.8	2.0	1.0	5	1	1900	3.5	7% higher root wt (yield) than pH 5.6
0.733			1.585	55.6	27.6	2.0	1.0	5	1	1900	2.8	13% higher root wt (yield) than pH 5.6
0.105			0.17					9			3.8	Ambient
0.139			0.0025	0.72	0.31	2.3	1.0	6	1	1900	5.6	12% lower root wt (yield), 7% higher shoot wt than ambient
0.169			0.06	2.90	1.40	2.1	1.0	6	1	1900	4.2	3% higher root wt (yield) than pH 5.6
0.243			0.32	11.70	5.80	2.0	1.0	6	1	1900	3.5	11% higher root wt (yield) than pH 5.6
0.915			1.58	55.60	27.6	2.0	1.0	6	1	1900	2.8	17% higher root wt (yield) than pH 5.6
0.138			0.16					11	1		3.8	Ambient
Radish, 'Cherry Belle', Raphanus sativus L. (Lee and Neely 1980)												
			0.0025	0.53	0.753	0.7	0.67	12	1.5	1200	5.6	Control
			0.10	4.83	0.753	6.4	0.67	12	1.5	1200	4.0	No effect on growth or yield compared to pH 5.6
			0.316	14.67	0.753	19.5	0.67	12	1.5	1200	3.5	25% greater yield than pH 5.6
			1.00	46.17	0.753	61.3	0.67	12	1.5	1200	3.0	No effect on growth or yield compared to pH 5.6
			0.026	0.96	0.471	2.5					5.6	Ambient
			0.0025	0.53	0.753	0.7	0.67	12	1.5	1200	5.6	Control
			0.10	3.20	2.92	1.1	0.67	12	1.5	1200	4.0	No effect on growth or yield compared to pH 5.6
			0.316	11.42	7.44	1.5	0.67	12	1.5	1200	3.5	No effect on growth or yield compared to pH 5.6
			1.00	34.00	23.29	1.5	0.67	12	1.5	1200	3.0	No effect on growth or yield compared to pH 5.6
			0.026	0.96	0.471	2.5					5.6	Ambient
Radish, 'Cherry Belle', Raphanus sativus L. (Evans et al. 1982)												
0.018			0.002	1.26	3.04	0.4	35.0	9	0.001	353	5.7	No effect on growth or yield compared to pH 4.06 (ambient)
0.081			0.010	5.47	3.04	1.8	35.0	9	0.001	353	4.0	No effect on growth or yield compared to pH 5.7
0.090			0.079	37.07	3.04	12.2	35.0	9	0.001	353	3.1	No effect on growth or yield compared to pH 5.7
0.129			1.995	106.6	3.04	35.1	35.0	9	0.001	353	2.7	No effect on growth or yield compared to pH 5.7
0.081			0.087								4.1	Ambient

[a]Effects are reported when statistical significance is $\leq$ 0.05 level.

TABLE 3-2. CONTINUED

Total deposition kg ha^{-1} (simulant + ambient)			Simulant concentration mg ℓ$^{-1}$				Rate cm hr^{-1}	Events #	Events hr events^{-1}	Droplet size µm	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$						
Soybean, 'Amsoy', Glycine max (L.) Merr. (Evans et al. 1981c)												
			0.10	1.4	3.90	0.4	35.0	41	0.001	353	4.0	No effect on growth or yield compared to pH 4.1
			0.794	28.3	3.90	7.3	35.0	41	0.001	353	3.1	No effect on growth or yield compared to pH 4.1
			1.995	83.0	3.90	21.3	35.0	41	0.001	353	2.7	11.5% lower seed wt; lower seeds and pods/plant than 4.1
			10.0	265.0	3.90	67.9	35.0	41	0.001	353	2.3	No effect on yield; lower number pods/plant than 4.1
			0.79	2.64	1.62	1.6	2.7	29	4.7		4.1	Ambient-control
Soybean,[b] 'Beeson', Glycine max (L.) Merr. (Toriano et al. 1983)												
0.229	2.88	0.32	0.10	4.321	2.18	2.1	1.27	18	1	730	4.0	Control
0.916	10.21	1.16	0.40	15.28	7.84	1.9	1.27	18	1	730	3.4	No effect on yield; 8% lower seed size 18% greater seed/pods than pH 4.0
3.262	39.97	4.49	1.58	59.18	30.45	1.9	1.27	18	1	730	2.8	32% greater yields; 17% greater seed size than pH 4.0
0.218	10.51	1.40	0.10					13			4.0	Ambient
Soybean, 'Davis', Glycine max (L.) Merr. (Heagle et al. 1983)												
0.198	6.19	3.06	0.005	0.27	0.15	1.8	1.5	30	0.5	900	5.3	Control
0.496	7.25	4.06	0.10	1.55	0.46	3.4	1.5	30	0.5	900	4.0	No effect on growth of yield
1.976	93.19	13.19	0.63	28.10	3.39	7.9	1.5	30	0.5	900	3.2	No effect on growth of yield
4.965	256.31	32.75	1.58	80.30	9.65	8.3	1.5	30	0.5	900	2.8	No effect on growth of yield
			0.06	1.71	0.83	2.1		41			4.2	Ambient
0.216	11.13	6.68	0.004	0.20	0.15	1.3	1.7	25	0.5	900	5.4	Control
0.431	25.25	7.60	0.08	0.54	0.48	1.1	1.7	25	0.5	900	4.1	No effect on growth or yield
1.717	127.33	14.5	0.63	13.00	3.00	14.3	1.7	25	0.5	900	3.2	No effect on growth or yield
10.834	683.91	63.31	3.98	248.00	21.00	11.8	1.7	25	0.5	900	2.4	No effect on growth or yield
			0.08	3.90	2.31	1.7		29			4.1	Ambient
Soybean, 'Wells', Glycine max (L.) Merr. (Irving and Miller 1981)												
0.077	9.02	3.81	0.0025	4.80	2.48	1.9	2.0	11	0.33	1800	5.6	No effect on yield; 4% greater wt/seed than ambient
0.464	18.72	4.26	0.871	39.18	4.96	7.9	2.0	11	0.33	1800	3.06	No effect on yield; 4% greater wt/seed than 5.6
0.076	8.90	2.82	0.081	6.07	3.00	2.0		15			4.1	Ambient
Soybean,[b] 'Williams', Glycine max (L.) Merr. (Troiano et al. 1983)												
0.229	2.88	0.32	0.10	4.32	2.18	2.0	1.27	18	1	730	4.0	Control
0.916	10.21	1.16	0.40	15.28	7.84	1.9	1.27	18	1	730	3.4	No effect on yield; 17% lower seed size than 4.0
3.262	39.97	4.49	1.58	59.18	30.45	1.9	1.27	18	1	730	2.8	24% greater yield; 22% greater seed size than pH 4.0
0.218	10.51	1.40	0.10					13			4.0	Ambient
Spinach, 'Improved Thick Leaf', Spinacia oleracea L. (Lee and Neely 1980)												
0.033	2.72	1.91	0.0025	0.53	0.753	0.7	0.67	15	1.5	1200	5.6	Control
0.134	9.17	1.91	0.10	4.83	0.753	6.4	0.67	15	1.5	1200	4.0	No effect on growth or yield
0.503	23.93	1.91	0.316	14.67	0.753	19.5	0.67	15	1.5	1200	3.5	No effect on growth or yield
1.529	71.18	1.91	1.00	46.17	0.753	61.3	0.67	15	1.5	1200	3.0	No effect on growth or yield
0.029	1.93	0.78	0.016	1.07	0.434	2.5					4.8	Ambient
0.033	2.72	1.91	0.0025	0.53	0.753	0.7	0.67	15	1.5	1200	5.6	Control
0.134	6.76	5.16	0.10	3.20	2.92	1.1	0.67	15	1.5	1200	4.0	No effect on growth or yield
0.503	19.06	11.94	0.316	11.42	7.44	1.5	0.67	15	1.5	1200	3.5	No effect on growth or yield
1.529	52.93	35.71	1.00	34.00	23.29	1.5	0.67	15	1.5	1200	3.0	No effect on growth or yield
0.029	1.93	0.78	0.016	1.07	0.434	1.0					4.8	Ambient

[a]Effects are reported when statistical significance is ≤ 0.05 level.
[b]Field plots sheltered from ambient deposition.

'Davis', 'Williams' or 'Wells'; however, the experimental conditions such as soil type and characteristics of the rain simulant in the 'Amsoy' study were markedly different than the other studies and may be responsible for the observed effect. Figure 3-5 indicates the location and results of the four soybean field studies in relation to the principal production regions and soil types. The one cultivar that responded negatively to acid rain treatments ('Amsoy') was grown in an area with a sandy soil, unlike the other studies. The simulated rain used in this study was applied more frequently and also had high concentrations of heavy metals (i.e., 20 ppb Cd, 50 ppb Pb, 100 ppb F; Evans et al. 1977) that were not present in the rain simulants used by other investigators. The 'Beeson' and 'Williams' cultivars, which were studied in a location near the 'Amsoy' study, but with more structured soil, reponded positively to the acid rain treatments when ambient ozone was removed. The 'Davis' and 'Wells' cultivars were studied in major soybean-growing areas with highly buffered soils and had no response to acid rain treatments as much as ten times more acidic than ambient. This comparison suggests that the region may be an important component of the response because of differences in major soil types, cultivars grown, climatic conditions, and ozone concentrations. Perhaps of equal importance is the presence of toxic heavy metals which become more soluble with increases in acidity of simulated rain.

In the five separate studies of radish (two cultivars), a positive linear correlation between yield and acidity was observed in two studies (Troiano et al. 1982), a non-linear positive correlation was observed in another study (Lee and Neely 1980), and no effect was reported in two studies (Lee and Neely 1980, Evans et al. 1982). The differences in results could be due to factors such as cultivar differences, environmental variability, or differences in total deposition of H^+, SO_4^{2-}, NO_3^-, or SO_4^{2-} to NO_3^- ratios.

Experimental results from some of these studies also demonstrate that the response of unharvested biomass is not a reliable predictor of yield response. Effects on marketable yield will not necessarily be reflected in changes in shoot or root growth. For example, field corn (Table 3-2) exhibited lower grain yield at pH 4.0 but no effect on shoot growth. The results from these studies are inadequate to indicate and whether the average concentration or total deposition of H^+, SO_4^{2-}, NO_3^- is important in determining yield response.

3.4.2.2.2 Controlled environment studies. As with the field studies, experimental conditions, dose, and response in all controlled environment studies are expressed in comparable units, based on calculations from published and private communications (Table 3-3). To compare total deposition in Tables 3-2 and 3-3 multiply g m^{-2} (Table 3-3) by 10 to obtain kg ha^{-1} (Table 3-2). A comparison of effects on the same species grown in a controlled environment as opposed to in the field indicates a similar response in most species (alfalfa, spinach, mustard green, soybean) although radishes exhibited a negative effect in a controlled environment and a positive effect in the field. In

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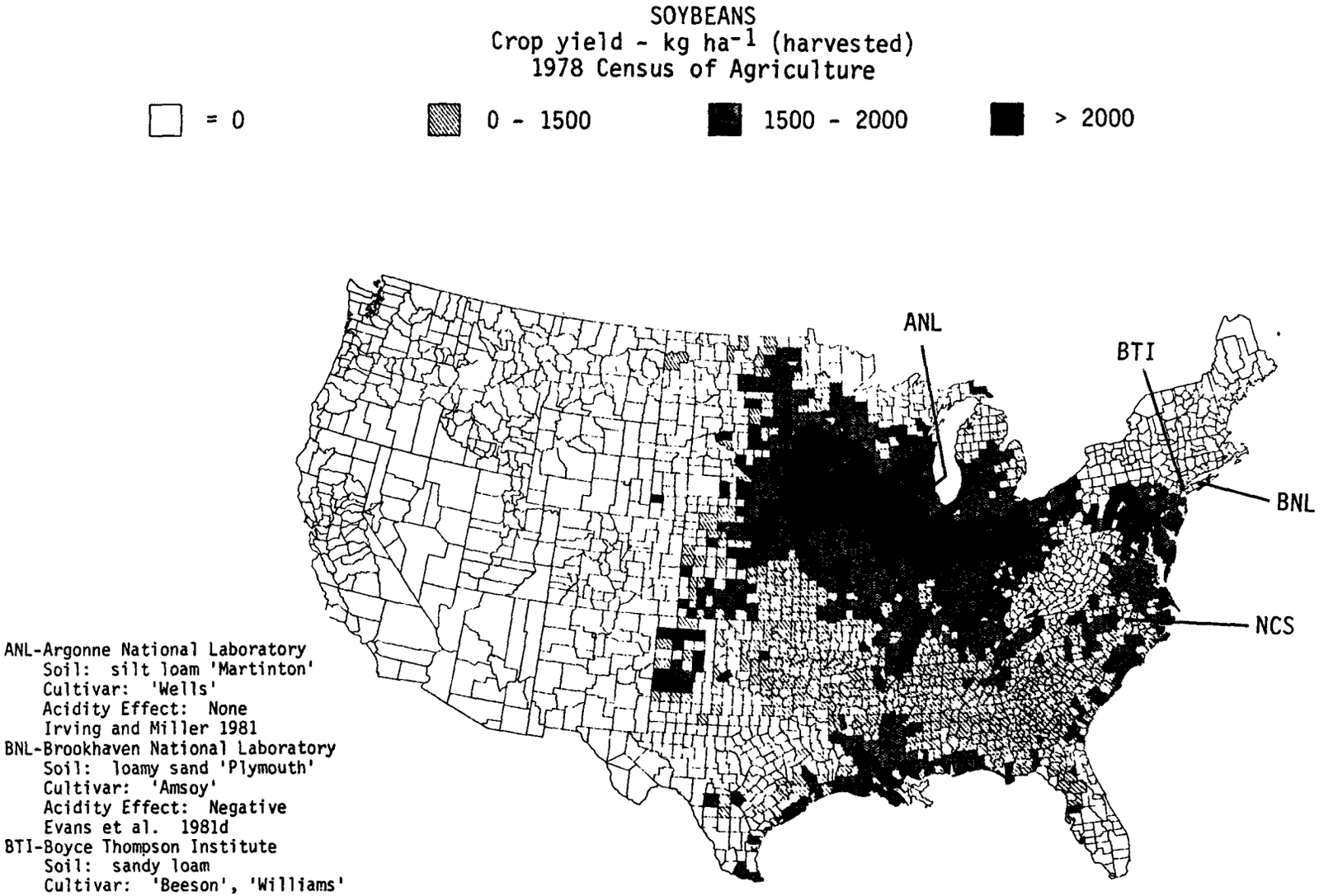

ANL-Argonne National Laboratory
Soil: silt loam 'Martinton'
Cultivar: 'Wells'
Acidity Effect: None
Irving and Miller 1981
BNL-Brookhaven National Laboratory
Soil: loamy sand 'Plymouth'
Cultivar: 'Amsoy'
Acidity Effect: Negative
Evans et al. 1981d
BTI-Boyce Thompson Institute
Soil: sandy loam
Cultivar: 'Beeson', 'Williams'
Acidity Effect: Positive
Troiano et al. 1983
NCS-North Carolina State University
Soil: sandy clay loam 'Appling'
Cultivar: 'Davis'
Acidity Effect: None
Heagle et al. 1983

Figure 3-5. Location of four soybean field studies, indicating production regions and soil types.

TABLE 3-3. CONTROLLED ENVIRONMENT STUDIES ON CROP GROWTH AND YIELD AS AFFECTED BY ACID PRECIPITATION

Total deposition g m^{-2} (Σ events)			Simulant concentration mg ℓ^{-1}				Rate cm hr^{-1}	Events #	Events hr $events^{-1}$	Droplet size μm	Fertilizer N-P-K	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$							
Alfalfa, 'Vernal', Modicago sativa L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.300	0.417	0.0025	0.53	0.74	0.7	0.67	56	1.5	1200	67-252-252[b]	5.6	Control
0.056	2.744	0.417	0.10	4.90	0.74	6.6	0.67	56	1.5	1200	67-252-252	4.0	No effect market yield, increased shoot wt
0.177	17.35	0.417	0.316	30.99	0.74	41.8	0.67	56	1.5	1200	67-252-252	3.5	31% greater market yield, increased shoot/root wt
0.56	54.92	0.417	1.00	98.07	0.74	132.5	0.67	56	1.5	1200	67-252-252	3.0	No effect growth or market yield
Barley, 'Steptoe', Hordeum vulgare L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.238	0.335	0.0025	0.53	0.74	0.7	0.67	45	1.5	1200	112-224-224[b]	5.6	Control
0.045	2.205	0.335	0.10	4.90	0.74	6.6	0.67	45	1.5	1200	112-224-224	4.0	No effect growth or market yield
0.142	13.945	0.335	0.316	30.99	0.74	41.8	0.67	45	1.5	1200	112-224-224	3.5	No effect growth or market yield
0.45	44.13	0.335	1.00	98.07	0.74	132.5	0.67	45	1.5	1200	112-224-224	3.0	No effect growth or market yield
Beet, 'Detroit Dark Red', Beta vulgaris L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.140	0.193	0.0025	0.53	0.74	0.7	0.67	26	1.5	1200	112-224-224[b]	5.6	Control
0.026	1.274	0.193	0.10	4.90	0.74	6.6	0.67	26	1.5	1200	112-224-224	4.0	No effect growth or market yield
0.082	8.057	0.193	0.316	30.99	0.74	41.8	0.67	26	1.5	1200	112-224-224	3.5	No effect growth or market yield
0.26	25.50	0.193	1.00	98.07	0.74	132.5	0.67	26	1.5	1200	112-224-224	3.0	43% decrease market yield; decrease root/shoot growth
Bibb lettuce, 'Limestone', Lactuca sativa L. (Cohen et al. 1981, Lee et al. 1981)													
0.0002	0.048	0.067	0.0025	0.53	0.74	0.7	0.67	9	1.5	1200	112-224-224[b]	5.6	Control
0.009	0.441	0.067	0.10	4.90	0.74	6.6	0.67	9	1.5	1200	112-224-224	4.0	No effect growth or market yield
0.028	2.789	0.067	0.316	30.99	0.74	41.8	0.67	9	1.5	1200	112-224-224	3.5	No effect growth or market yield
0.09	8.826	0.067	1.00	98.07	0.74	132.5	0.67	9	1.5	1200	112-224-224	3.0	No effect growth or yield; decrease root growth
Bluegrass, 'Newport', Poa pratensis L. (Cohen et al. 1981, Lee et al. 1981)													
0.002	0.382	0.472	0.0025	0.53	0.74	0.7	0.67	72	1.5	1200	224-448-448[b]	5.6	Control
0.072	3.528	0.472	0.10	4.90	0.74	6.6	0.67	72	1.5	1200	224-448-448	4.0	No effect market yield or growth
0.227	22.31	0.472	0.316	30.99	0.74	41.8	0.67	72	1.5	1200	224-448-448	3.5	No effect market yield or growth
0.720	70.61	0.472	1.00	98.07	0.74	132.5	0.67	72	1.5	1200	224-448-448	3.0	No effect market yield or growth
Broccoli, 'Italian Green Sprouting', Brassica oleracea L. var. Botrytis L. (Cohen et al. 1981, Lee et al. 1981)													
0.0006	0.117	0.164	0.0025	0.53	0.74	0.7	0.67	22	1.5	1200	168-224-224[b]	5.6	Control
0.022	1.078	0.164	0.10	4.90	0.74	6.6	0.67	22	1.5	1200	168-224-224	4.0	No effect market yield or growth
0.070	6.819	0.164	0.316	30.99	0.74	41.8	0.67	22	1.5	1200	168-224-224	3.5	No effect market yield or growth
0.22	21.58	0.164	1.00	98.07	0.74	132.5	0.67	22	1.5	1200	168-224-224	3.0	25% lower market yield

[a]Effects are reported when statistical significance is ≤ 0.05 level.
[b]Fertilizer as kg ha^{-1} of $N\text{-}P_2O_5\text{-}K_2O$.
[c]Fertilizer as percentage of $N\text{-}P_2O_5\text{-}K_2O$.

TABLE 3-3. CONTINUED

Total deposition g m^{-2} (Σ events)			Simulant concentration mg ℓ^{-1}			Rate cm hr^{-1}		Events #	hr events^{-1}	Droplet size μm	Fertilizer N-P-K	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$							
Bush bean, 'Blue Lake 274', Phaseolus vulgaris L. (Johnston et al. 1982)													
0.000004	0.001	0.001	0.0025	0.60	0.83	0.7	1.64	18	0.67	900	0-20-0[c]	5.6	Control
0.00017	0.008	0.001	0.10	5.33	0.70	7.6	1.64	18	0.67	900	0-20-0	4.0	No effect yield; older leaves aged more rapidly
0.000004	0.001	0.001	0.0025	0.60	0.83	.7	1.64	16	0.67	900	0-20-0[c]	5.6	Control
0.00017	0.007	0.001	0.10	5.33	0.70	7.6	1.64	16	0.67	900	0-20-0	4.0	No effect
0.00083	0.041	0.001	0.631	30.70	0.75	40.9	1.64	16	0.67	900	0-20-0	3.2	Higher trifoliate chlorophyll; lower shoot wt/pod number; no effect pod wt
Cabbage, 'Golden Acre', Brassica oleracea L. var. Capitata L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.270	0.379	0.0025	0.53	0.74	0.7	0.67	51	1.5	1200	224-224-224[b]	5.6	Control
0.051	2.499	0.379	0.10	4.90	0.74	6.6	0.67	51	1.5	1200	224-224-224	4.0	No effect growth or yield
0.067	15.80	0.379	0.316	30.99	0.74	41.8	0.67	51	1.5	1200	224-224-224	3.5	No effect growth or yield
0.51	50.02	0.379	1.00	98.07	0.74	132.5	0.67	51	1.5	1200	224-224-224	3.0	No effect growth or yield
Carrot, 'Danvers Half Long', Daucus carota L. var. Sativa DC (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.230	0.327	0.0025	0.53	0.74	0.7	0.67	44	1.5	1200	224-224-224[b]	5.6	Control
0.044	2.156	0.327	0.10	4.90	0.74	6.6	0.67	44	1.5	1200	224-224-224	4.0	27% lower market yield
0.139	13.636	0.327	0.316	30.99	0.74	41.8	0.67	44	1.5	1200	224-224-224	3.5	45% lower market yield; decrease shoot wt
0.44	43.15	0.327	1.00	98.07	0.74	132.5	0.67	44	1.5	1200	224-224-224	3.0	44% lower market yield; decrease shoot wt
Cauliflower, 'Early Snowball', Brassica oleracea L. var. Botrytis L. (Cohen et al. 1981, Lee et al. 1981)													
0.0006	0.122	0.171	0.0025	0.53	0.74	0.7	0.67	23	1.5	1200	224-224-224[b]	5.6	Control
0.023	1.127	0.171	0.10	4.90	0.74	6.6	0.67	23	1.5	1200	224-224-224	4.0	No effect growth or yield
0.073	7.128	0.171	0.316	30.99	0.74	41.8	0.67	23	1.5	1200	224-224-224	3.5	No effect growth or yield
0.23	22.56	0.171	1.00	98.07	0.74	132.5	0.67	23	1.5	1200	224-224-224	3.0	No effect growth or yield
Corn, 'Golden Midget', Zea mays L. (Cohen et al. 1981, Lee et al. 1981)													
0.0005	0.11	0.149	0.0025	0.53	0.74	0.7	0.67	20	1.5	1200	168-336-336[b]	5.6	Control
0.020	0.980	0.149	0.10	4.90	0.74	6.6	0.67	20	1.5	1200	168-336-336	4.0	No effect market yield or growth
0.063	6.198	0.149	0.316	30.99	0.74	41.8	0.67	20	1.5	1200	168-336-336	3.5	No effect market yield or growth
0.20	19.61	0.149	1.00	98.07	0.74	132.5	0.67	20	1.5	1200	168-336-336	3.0	13% greater market yield
Fescue, 'Alta', Festuca elatior L. var. arundinacea Schreb. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.31	0.439	0.0025	0.53	0.74	0.7	0.67	59	1.5	1200	168-336-336[b]	5.6	Control
0.059	2.891	0.439	0.10	4.90	0.74	6.6	0.67	59	1.5	1200	168-336-336	4.0	No effect market yield; decreased root growth
0.186	18.20	0.439	0.316	30.99	0.74	41.8	0.67	59	1.5	1200	168-336-336	3.5	No effect market yield or growth
0.59	57.86	0.439	1.00	98.07	0.74	132.5	0.67	59	1.5	1200	168-336-336	3.0	No effect market yield; decreased root growth

[a]Effects are reported when statistical significance is ≤ 0.05 level.
[b]Fertilizer as kg ha^{-1} of $N\text{-}P_2O_5\text{-}K_2O$.
[c]Fertilizer as percentage of $N\text{-}P_2O_5\text{-}K_2O$.

TABLE 3-3. CONTINUED

Total deposition g m^{-2} (Σ events)			Simulant concentration mg ℓ^{-1}				Rate cm hr^{-1}	Events #	Events hr $events^{-1}$	Droplet size μm	Fertilizer N-P-K	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$							
Green pea, 'Marvel', Pisum sativum L. (Cohen et al, 1981, Lee et al. 1981)													
0.001	0.150	0.208	0.0025	0.53	0.74	o.7	0.67	28	1.5	1200	67-224-224[b]	5.6	Control
0.028	1.372	0.208	0.10	4.90	0.74	6.6	0.67	28	1.5	1200	67-224-224	4.0	No effect growth or market yield
0.088	8.677	0.208	0.316	30.99	0.74	41.8	0.67	28	1.5	1200	67-224-224	3.5	No effect growth or market yield
0.28	27.46	0.208	1.00	98.07	0.74	132.5	0.67	28	1.5	1200	67-224-224	3.0	No effect growth or market yield
Green pepper, 'California Wonder', Capsicum annuum L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.20	0.283	0.0025	0.53	0.74	0.7	0.67	38	1.5	1200	224-448-448[b]	5.6	Control
0.038	1.86	0.283	0.10	4.90	0.74	6.6	0.67	38	1.5	1200	224-448-448	4.0	No effect market yield or growth
0.128	11.78	0.283	0.316	30.99	0.74	41.8	0.67	38	1.5	1200	224-448-448	3.5	20% greater market yield; increased shoot growth
0.380	37.27	0.283	1.00	98.07	0.74	132.5	0.67	38	1.5	1200	224-448-448	3.0	No effect market yield; decreased shoot growth
Kidney bean, 'Red Kidney', Phaseolus vulgaris L. (Shriner 1978a)													
0.0004	0.007	0.043	0.001	0.02	0.12	0.2/416	3.0	24	0.17	900		6.0	Control
0.029	2.274	0.043	*	0.02/50	0.12	0.2/416	3.0	24	0.17	900	6.0/3.2/6.0[d]		75% increased pod number; greater shoot and root wt
0.095	7.564	0.043	*	0.02/50	0.12	0.2/416	3.0	24	0.17	900	3.2/6.0/6.0		50% lower pod number; greater shoot wt
0.105	8.32	0.043	*	0.02/50	0.12	0.2/416	3.0	24	0.17	900	6.0/6.0/3.2		50% lower pod number; greater shoot wt
0.107	9.831	0.043	*	0.02/50	0.12	0.2/416	3.0	24	0.17	900	3.2/3.2/6.0		No effect pod number; lower shoot/root wt
0.134	10.59	0.043	*	0.02/50	0.12	0.2/416	3.0	24	0.17	900	6.0/3.2/3.2		75% greater pod number; greater root wt
0.200	15.88	0.043	*	0.02/50	0.12	0.2/416	3.0	24	0.17	900	3.2/6.0/3.2		No effect pod number; lower shoot/root wt
0.229	18.14	0.043	0.631	50	0.12	416.67	3.0	24	0.17	900		3.2	50% greater pod number; lower shoot wt; greater root wt
Lettuce, 'Oakland', Lactuca sativa L. (Jacobson et al. 1980)													
0.00096	0.02304	0.02976	0.002	0.48	0.62	0.77	0.80	3	2.0	900	Half-strength	5.7	Control
0.03024	0.13824	1.7856	0.63	2.88	37.20	0.08	0.80	3	2.0	900	Hoaglands	3.2	No effect growth or yield
0.03024	0.78384	0.95232	0.63	16.33	19.84	0.82	0.80	3	2.0	900		3.2	7% increase root wt; 24% increase apical leaf wt
0.03024	1.38336	0.11904	0.63	28.82	2.48	11.6	0.80	3	2.0	900		3.2	10% increase root wt; 29% increase apical leaf wt
Mustard green, 'So. Giant Curled,' Brassica japonica Hort. (Cohen et al. 1981, Lee et al. 1981)													
0.0004	0.074	0.104	0.0025	0.53	0.74	0.7	0.67	14	1.5	1200	112-224-224[b]	5.6	Control
0.014	0.687	0.104	0.10	4.90	0.74	6.6	0.67	14	1.5	1200	112-224-224	4.0	14% lower market yield
0.044	4.339	0.104	0.316	30.99	0.74	41.8	0.67	14	1.5	1200	112-224-224	3.5	No significant effect
0.14	13.73	0.104	1.00	98.07	0.74	132.5	0.67	14	1.5	1200	112-224-224	3.0	31% lower market yield

*0.001/0.631.
[a]Effects are reported when statistical significance is $\leq$ 0.05 level.
[b]Fertilizer as kg ha^{-1} of N-P_2O_5-K_2O.
[d]pH sequence is: 10 events prior to Halo blight infection/3 events during infection period/11 events post infection.

TABLE 3-3. CONTINUED

Total deposition g m^{-2} (Σ events)			Simulant concentration mg L^{-1}			Rate cm hr^{-1}	Events		Droplet size μm	Fertilizer N-P-K	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$	#	hr events^{-1}				
Oats, 'Cayuse', Avena sativa L. (Cohen et al. 1981, Lee et al. 1981)												
0.001	0.254	0.357	0.0025	0.53	0.74	0.7	0.67	48	1.5	1200	112-224-224[b]	5.6 Control
0.048	2.354	0.357	0.10	4.90	0.74	6.6	0.67	48	1.5	1200	112-224-224	4.0 No effect market yield or growth
0.152	14.87	0.357	0.316	30.99	0.74	41.8	0.67	48	1.5	1200	112-224-224	3.5 No effect market yield; increased root growth
0.48	47.07	0.357	1.00	98.07	0.74	132.5	0.67	48	1.5	1200	112-224-224	3.0 No effect market yield or growth
Onion, 'Sweet Spanish', Allium cepa L. (Cohen et al. 1981, Lee et al. 1981)												
0.002	0.34	0.484	0.0025	0.53	0.74	0.7	0.67	65	1.5	1200	336-336-336[b]	5.6 Control
0.065	3.185	0.484	0.10	4.90	0.74	6.6	0.67	65	1.5	1200	336-336-336	4.0 No effect market yield or growth
0.205	20.14	0.484	0.316	30.99	0.74	41.8	0.67	65	1.5	1200	336-336-336	3.5 No effect market yield or growth
0.65	63.75	0.484	1.00	98.07	0.74	132.5	0.67	65	1.5	1200	336-336-336	3.0 No effect market yield; increased shoot growth
Orchardgrass, 'Potomac', Dactylis glomerata L. (Cohen et al. 1981, Lee et al. 1981)												
0.001	0.19	0.260	0.0025	0.53	0.74	0.7	0.67	35	1.5	1200	112-224-224[b]	5.6 Control
0.035	1.715	0.260	0.10	4.90	0.74	6.6	0.67	35	1.5	1200	112-224-224	4.0 No effect market yield; decreased root growth
0.111	10.85	0.260	0.316	30.99	0.74	41.8	0.67	35	1.5	1200	112-224-224	3.5 No effect market yield or growth
0.35	34.32	0.260	1.00	98.07	0.74	132.5	0.67	35	1.5	1200	112-224-224	3.0 23% greater market yield; increased root growth
Pinto bean, 'Univ. Idaho 111', Phaseolus vulgaris L. (Evans and Lewin 1981)												
0.003	8.533	1.365	0.002	5.0	0.80	6.2	0.72	45	0.33	353	manure and	5.7 Control
1.355	64.033	1.365	0.794	37.52	0.80	46.9	0.72	45	0.33	353	limestone	3.1 No effect yield
2.149	102.16	1.365	1.259	59.86	0.80	74.8	0.72	45	0.33	353	added	2.9 28% lower seed yield
3.405	162.49	1.365	1.995	95.21	0.80	119.0	0.72	45	0.33	353		2.7 29% lower seed yield
5.396	258.16	1.365	3.162	151.27	0.80	189.1	0.72	45	0.33	353		2.5 39% lower seed yield
Potato, 'White Rose', Solanum tuberosum L. (Cohen et al. 1981, Lee et al. 1981)												
0.001	0.276	0.387	0.0025	0.53	0.74	0.7	0.67	52	1.5	1200	247-224-224[b]	5.6 Control
0.052	2.548	0.387	0.10	4.90	0.74	6.6	0.67	52	1.5	1200	224-224-224	4.0 No effect yield; increased shoot growth
0.164	16.11	0.387	0.316	30.99	0.74	41.8	0.67	52	1.5	1200	224-224-224	3.5 11% greater market yield; increased shoot growth
0.52	51.00	0.387	1.00	98.07	0.74	132.5	0.67	52	1.5	1200	224-224-224	3.0 8% lower market yield
Radish, 'Cherry Belle', Raphanus sativus L. (Cohen et al. 1981, Lee et al. 1981)												
0.0003	0.064	0.089	0.0025	0.53	0.74	0.7	0.67	12	1.5	1200	112-224-224[b]	5.6 Control
0.012	0.588	0.089	0.10	4.90	0.74	6.6	0.67	12	1.5	1200	112-224-224	4.0 No effect growth or market yield
0.033	3.719	0.089	0.316	30.99	0.74	41.8	0.67	12	1.5	1200	112-224-224	3.5 Lower market yield
0.12	11.77	0.089	1.00	98.07	0.74	132.5	0.67	12	1.5	1200	112-224-224	3.0 Lower market yield; decreased shoot growth
Red clover, 'Kenland', Trifolium pratense L. (Cohen et al. 1981, Lee et al. 1981)												
0.001	0.300	0.417	0.0025	0.53	0.74	0.7	0.67	56	1.5	1200	67-336-336[b]	5.6 Control
0.056	2.744	0.417	0.10	4.90	0.74	6.6	0.67	56	1.5	1200	67-336-336	4.0 No effect growth or market yield
0.177	17.35	0.417	0.316	30.99	0.74	41.8	0.67	56	1.5	1200	67-336-336	3.5 No effect growth or market yield
0.56	54.92	0.417	1.00	98.07	0.74	132.5	0.67	56	1.5	1200	67-336-336	3.0 No effect growth or market yield

[a]Effects are reported when statistical significance is ≤ 0.05 level.
[b]Fertilizer as kg ha^{-1} of $N\text{-}P_2O_5\text{-}K_2O$.

TABLE 3-3. CONTINUED

Total deposition g m^{-2} (Σ events)			Simulant concentration mg ℓ^{-1}			Rate cm hr^{-1}		Events #	Events hr $events^{-1}$	Droplet size μm	Fertilizer N-P-K	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	$SO_4^{2-}:NO_3^-$							
Ryegrass, "Linn', Lolium perenne L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.31	0.432	0.0025	0.53	0.74	0.7	0.67	58	1.5	1200	112-224-224[b]	5.6	Control
0.055	2.842	0.432	0.10	4.90	0.74	6.6	0.67	58	1.5	1200	112-224-224	4.0	No effect market yield; decreased root growth
0.183	17.97	0.432	0.316	30.99	0.74	41.8	0.67	58	1.5	1200	112-224-224	3.5	No effect market yield; decreased root growth
0.58	56.88	0.432	1.00	98.07	0.74	132.5	0.67	58	1.5	1200	112-224-224	3.0	No effect market yield; decreased root growth
Spinach, 'Improved Thick Leaf', Spinacia oleracea L. (Cohen et al. 1981, Lee et al. 1981)													
0.0004	0.074	0.104	0.0025	0.53	0.74	0.7	0.67	14	1.5	1200	112-224-224[b]	5.6	Control
0.014	0.687	0.104	0.10	4.90	0.74	6.6	0.67	14	1.5	1200	112-224-224	4.0	No effect growth or yield
0.044	4.339	0.104	0.316	30.99	0.74	41.8	0.67	14	1.5	1200	112-224-224	3.5	No effect growth or yield
0.14	13.73	0.104	1.00	98.07	0.74	132.5	0.67	14	1.5	1200	112-224-224	3.0	No effect growth or yield
Soybean, 'Amsoy 71', Glycine max (L.) Merr. (Evans et al. 1981d)													
0.004	9.755	1.561	0.002	5.0	0.80	6.2	0.72	78	0.17	353	manure and	5.7	Control
1.549	73.20	1.561	0.794	37.52	0.80	46.9	0.72	78	0.17	353	limestone	3.1	11% greater seed yield; decreased shoot growth
6.169	295.12	1.561	3.162	151.27	0.80	189.1	0.72	78	0.17	353	added	2.5	11% lower seed yield; decreased shoot growth
Soybean, 'Wells', Glycine max (L.) Merr. (Irving and Sowinski 1980)													
0.002	0.669	0.721	0.0025	0.96	1.03	1.0	21.2	10	0.33	2300	15-30-15[c]	5.6	1:1 SO_4:NO_3; control
0.002	0.980	0.490	0.0025	1.40	0.70	2.0	21.2	10	0.33	2300	15-30-15	5.6	2:1 SO_4:NO_3; control
0.002	1.113	0.371	0.0025	1.6	0.53	3.0	21.2	10	0.33	2300	15-30-15	5.6	3:1 SO_4:NO_3; control
0.105	3.738	3.731	0.15	5.34	5.33	1.0	21.2	10	0.33	2300	15-30-15	3.8	No effect growth or yield compared to 1:1 control
0.105	2.485	5.530	0.15	7.09	3.55	2.0	21.2	10	0.33	2300	15-30-15	3.8	No effect growth or yield compared to 2:1 control
0.105	5.600	3.619	0.15	8.00	5.17	1.5	21.2	10	0.33	2300	15-30-15	3.8	Lower root nodule wt compared to 3:1 control; no effect yield
0.700	20.55	18.55	1.0	29.36	26.50	1.0	21.2	10	0.33	2300	15-30-15[c]	3.0	No effect growth or yield compared to control
0.700	25.52	12.82	1.0	36.45	18.32	2.0	21.2	10	0.33	2300	15-30-15	3.0	No effect growth or yield compared to control
0.700	29.40	9.800	1.0	42.00	14.00	3.0	21.2	10	0.33	2300	15-30-15	3.0	25% greater yield than 1:1 control, 19% greater than 2:1 control
Strawberry, 'Quinalt', Fragaria chiloensis Duchesne var. ananassa (Cohen et al. 1981, Lee et al. 1981)													
0.002	0.42	0.595	0.0025	0.53	0.74	.7	0.67	80	1.5	1200	224-336-336[b]	5.6	Control
0.080	3.920	0.595	0.10	4.90	0.74	6.6	0.67	80	1.5	1200	224-336-336	4.0	51% greater market yield; increased shoot growth
0.253	24.79	0.595	0.316	30.99	0.74	41.8	0.67	80	1.5	1200	224-336-336	3.5	72% greater market yield; increased shoot/root growth
0.800	78.46	0.595	1.00	98.07	0.74	132.5	0.67	80	1.5	1200	224-336-336	3.0	72% greater market yield; increased shoot/root growth

[a]Effects are reported when statistical significance is ≤ 0.05 level.
[b]Fertilizer as kg ha^{-1} of N-P_2O_5-K_2O.

TABLE 3-3. CONTINUED

Total deposition g m^{-2} (Σ events)			Simulant concentration mg L^{-1}				Rate cm hr^{-1}	Events #	Events hr $events^{-1}$	Droplet size µm	Fertilizer N-P-K	pH	Effect[a]
H^+	SO_4^{2-}	NO_3^-	H^+	SO_4^{2-}	NO_3^-	SO_4^{2-}:NO_3^-							
Swiss chard, 'Lucullus', Beta vulgaris var. cicla L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.17	0.238	0.0025	0.53	0.74	0.7	0.67	32	1.5	1200	168-224-224[b]	5.6	Control
0.032	1.568	0.238	0.10	4.90	0.74	6.6	0.67	32	1.5	1200	168-224-224	4.0	No effect market yield or growth
0.101	9.92	0.238	0.316	30.99	0.74	41.8	0.67	32	1.5	1200	168-224-224	3.5	No effect market yield or growth
0.32	31.38	0.238	1.00	98.07	0.74	132.5	0.67	32	1.5	1200	168-224-224	3.0	No effect market yield or growth
Timothy, 'Climax', Phleum pratense L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.17	0.256	0.0025	0.53	0.74	0.7	0.67	33	1.5	1200	112-224-224[b]	5.6	Control
0.033	1.617	0.256	0.10	4.90	0.74	6.6	0.67	33	1.5	1200	112-224-224	4.0	No effect market yield or growth
0.104	10.23	0.256	0.316	30.99	0.74	41.8	0.67	33	1.5	1200	112-224-224	3.5	No effect market yield or growth
0.33	32.36	0.256	1.00	98.07	0.74	132.5	0.67	33	1.5	1200	112-224-224	3.0	24% greater market yield
Tobacco, 'Burley 21', Nicotiana tabacum L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.127	0.179	0.0025	0.53	0.74	0.7	0.67	24	1.5	1200		5.6	Control
0.024	1.176	0.179	0.10	4.90	0.74	6.6	0.67	24	1.5	1200		4.0	No effect growth or yield
0.076	7.438	0.179	0.316	30.99	0.74	41.8	0.67	24	1.5	1200		3.5	No effect growth or yield
0.24	23.537	0.179	1.00	98.07	0.74	132.5	0.67	24	1.5	1200		3.0	No effect growth or yield
Tomato, 'Patio', Lycopersicon esculentum Mill. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.27	0.379	0.0025	0.53	0.74	0.7	0.67	51	1.5	1200	224-448-448[b]	5.6	Control
0.051	2.50	0.379	0.10	4.90	0.74	6.6	0.67	51	1.5	1200	224-448-448	4.0	No effect market yield, increased shoot growth
0.161	15.80	0.379	0.316	30.99	0.74	41.8	0.67	51	1.5	1200	224-448-448	3.5	No effect market yield, increased shoot growth
0.510	50.02	0.379	1.00	98.07	0.74	132.5	0.67	51	1.5	1200	224-448-448	3.0	31% greater market yield, decreased root growth
Wheat, 'Fieldwin', Triticum aestivum L. (Cohen et al. 1981, Lee et al. 1981)													
0.001	0.244	0.342	0.0025	0.53	0.74	0.7	0.67	46	1.5	1200	112-224-224[b]	5.6	Control
0.046	2.254	0.342	0.10	4.90	0.74	6.6	0.67	46	1.5	1200	112-224-224	4.0	No effect market yield; decreased root growth
0.145	14.255	0.342	0.316	30.99	0.74	41.8	0.67	46	1.5	1200	112-224-224	3.5	No effect market yield; decreased root growth
0.46	45.11	0.342	1.00	98.07	0.74	132.5	0.67	46	1.5	1200	112-224-224	3.0	No effect market yield; decreased

[a]Effects are reported when statistical significance is $\leq$ 0.05 level.
[b]Fertilizer as kg ha^{-1} of N-P_2O_5-K_2O.

general, total deposition of H^+, SO_4^{2-}, and NO_3^- applied was greater in the controlled environment studies than in the field studies because of a higher deposition rate or greater number of exposures.

There were 34 crop varieties (28 species) studied in controlled-environment experiments; six exhibited a negative response from acid rain exposure (pinto bean, mustard green, broccoli, radish, beet and carrot), eight exhibited a positive response (alfalfa, tomato, green pepper, strawberry, corn, orchard grass, timothy, and 'Oakland lettuce'), 17 showed no effect (bush bean, 'Wells' soybean, spinach, 'Limestone' lettuce, cabbage, cauliflower, onion, fescue, bluegrass, ryegrass, swiss chard, oats, wheat, barley, tobacco, green pea, and red clover), and three species showed both positive and negative yield response depending on the H ion concentration (potato, 'Amsoy 71' soybean), or conditions of exposure (kidney bean).

3.4.2.3 Discussion--Interpreting and comparing results of experiments on the effects of acidic deposition on crop plants must include considering the exposure conditions, simulant characteristics, dose rate, and total dose of important ions (H^+, SO_4^{2-}, and NO_3^-). Unexplained inconsistencies among experimental results could be due to differences in experimental design or exposure conditions. For example, in all field studies except those of 'Champion' radish and 'Beeson' and 'Williams' soybeans, the ratio of sulfate to nitrate in the rain simulant differed among treatments and was usually much higher than the sulfate:nitrate ratio in ambient rain. Rain chemistry data from the National Atmospheric Deposition Program (NADP) indicate that weekly precipitation pH values can vary widely for a particular area (i.e., an range of pH 3.7 to 6.8 for New York) while the SO_4^{2-} to NO_3^- ration appears to be independent of pH (Figure 3-6). Because preliminary evidence indicates that plants are affected by the sulfate:nitrate ratio in rain (Irving and Sowinski 1980, Lee et al. 1980), the differences reported among treatments in these investigations may be the result of this ratio rather than the hydrogen ion deposition. All published experiments used treatments having the same chemistry from event to event although the chemistry of ambient rain can fluctuate greatly from one event to another (Figure 3-6). Some crops may be affected by peak concentrations of acidity while others may respond to the total deposition of ions. No experiments separating the peak versus total loading response have yet been reported, although Irving et al. (1981) found that rain with a chemistry that varied from event to event had a different effect on plant growth than did a constant rain chemistry with the same mean pH.

The majority of the 14 crop cultivars studied in the field and the 34 studied in controlled environments exhibited no effect on growth or yield as a result of exposure to simulated rain more acidic (usually up to 10 times more acidic) than ambient. The growth and yield of some crops, however, were negatively affected by acidic rain while others exhibited a positive response. The 9 percent reduction in the yield of field corn exposed to pH 4.0 rain (0.594 kg ha^{-1} depositon of H^+) is an alarming result; however, treatments with greater acidity levels

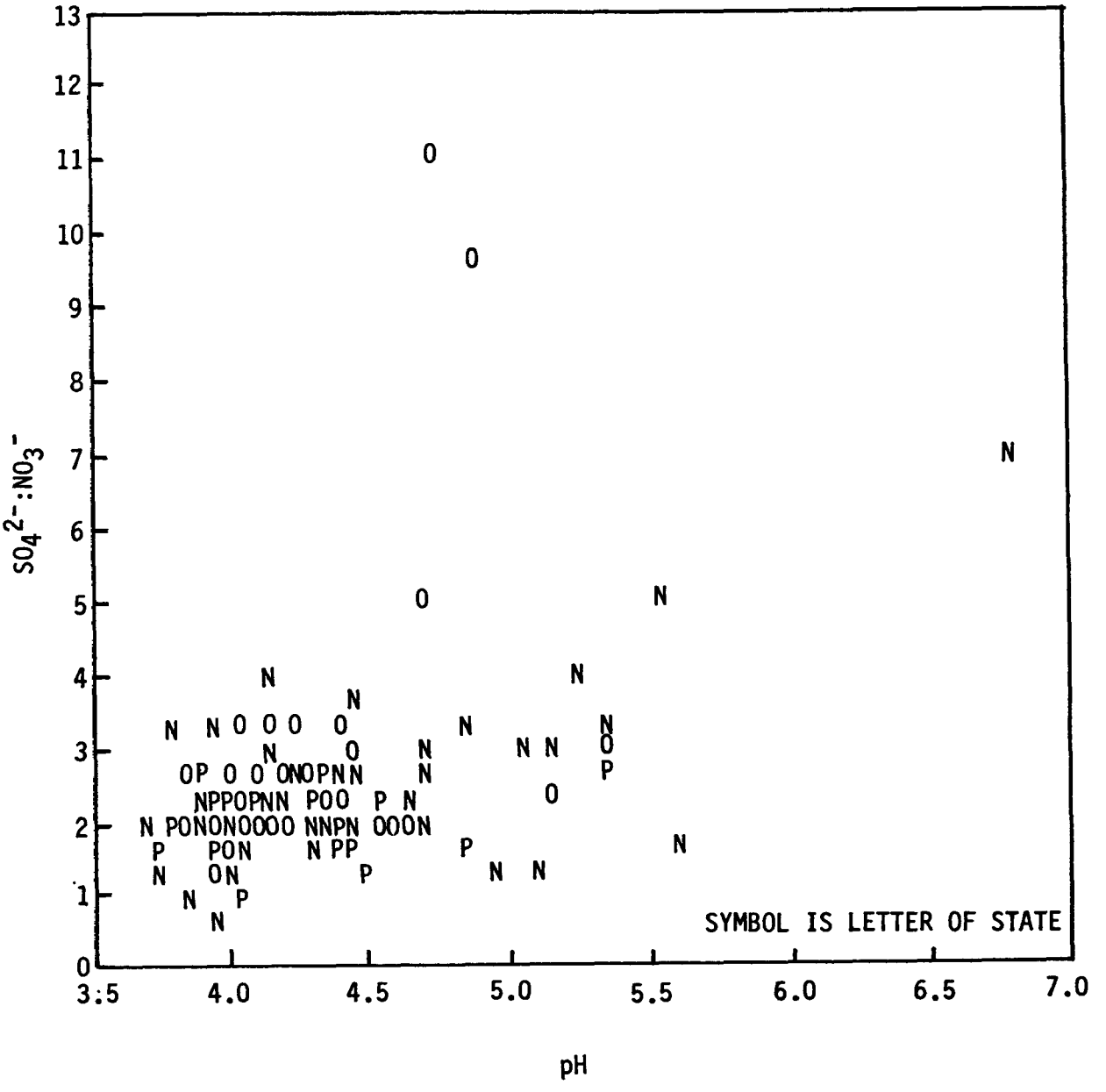

Figure 3-6. Ratio of SO_4^{2-} to NO_3^- versus pH of precipitation in New York (N), Pennsylvania (P), and Ohio (O) during the growing season. Data are from the NADP network, 1979.

produced no effect on the corn yield. The experiment was repeated the following year with similar (although not statistically significant) results and for a third year with no negative effects observed (J. J. Lee, pers. comm.). The reduction in the yield of one ("Amsoy") of the five cultivars of soybeans that have been studied suggests that genetic or soil factors or the presence of heavy metals in the rain simulant may control plant response to acidic rain. If these possibilities are substantiated, ramifications of the negative effects of acid rain observed in the above two studies could be considerable since soybeans and field corn are two of the most economically important agricultural crops in the United States. For reasons discussed in this review, however, these studies do not offer definitive proof that ambient acidic precipitation is damaging corn and soybean production.

The positive response of some crops to acidic rain suggests a fertilizer response to the sulfur and nitrogen components of the rain. The net response of a plant to acid rain appears to result from the interaction between the positive effects of sulfur and nitrogen nutrition and the negative effects of acidity. Input of nutrients to plant systems from rainfall has been documented since the mid-19th century (Way 1855). Calculations made in a number of regions in the United States estimate the seasonal atmospheric deposition of nutrient species, particularly sulfate and nitrate, to agricultural and natural systems and the implications of this deposition on plant nutrient status.

Estimates by Hoeft et al. (1972) of 30 kg S ha^{-1} per year and 20 kg N ha^{-1} per year deposited in precipitation in Wisconsin indicated the importance of atmospheric sources of these elements, although N requirements certainly could not be completely satisfied in this way. Jones et al. (1979) reported that atmospheric S is a major contribution to the agronomic and horticultural crop needs for S as a plant nutrient in South Carolina. Although the amount of S and N in a single rain event is small compared to a fertilizer application, it is known that foliar applications of plant nutrients may stimulate plant growth and yield (Garcia and Hanway 1976). The repeated exposure of plants to rain, especially during the critical reproductive stage, suggests that nutritional benefits from rain may be significant, even in comparison to a one-time fertilizer application.

Reports of most acid rain field studies contain little or no characterization of the soil conditions. Soil fertility may determine whether a plant responds positively or negatively to acidic precipitation. Long-term effects of acidic deposition on poorly managed, unamended agricultural soils may have negative effects on crop productivity through the leaching of soil nutrients or mobilization of toxic metals. This effect has more potential for becoming significant in those soils with low cation exchange capacity (low in clay and organic matter), low sulfate retention capacity, and high permeability (sands). Although such an effect may not become measurable for decades or more, it will be most important in forage crops that are not usually highly managed. Some speculation exists that agricultural management practices may be modified as a result of acidic deposition but

agricultural soil scientists generally accept that the influence of acidic deposition on the need for additional fertilizer and lime application is probably miniscule.

Another consideration that may be important in controlling the impact of ambient acid precipitation, is that crop cultivar recommendations are based on productivities obtained under ambient conditions of acidic deposition. Therefore, crops currently being grown may have been selected, indirectly, for their adaptations to rainfall acidity and the presence of other pollutants.

3.4.2.4 Summary--

1) Because of limitations in research design, differences in methodologies and inconsistent results, it is difficult to compare research results directly or arrive at an overall conclusion regarding crop response to acidic deposition without a thorough description and comparison of experimental methods.

2) Complex factorial research designs and multivariate analyses may be necessary to describe adequately the relationship between acid rain dose and plant response rather than the simple univariate approach (treatment pH vs yield) used in the past.

3) Given the above limitations to making generalizations about past research, analysis of experimental results from field and controlled environment experiments indicates that the majority of crop species exhibited no effect on growth or yield as a result of exposure to simulated acidic rain (acidity treatments had pH values of 4.2 or less). Growth and yield of a few crops in some studies, however, were negatively affected by acidic rain, while other crops exhibited a positive response.

4) Interpretation of available research results suggests that the net response of a crop to acidic deposition is the result of the interaction between the positive effects of sulfur and nitrogen fertilization, the negative effects of acidity, and the interaction between these factors and other environmental conditions such as soil type and presence of other pollutants. Available experimental results appear to indicate that the effects of acidic precipitation on crops are minimal and that when a response occurs it may be positive or negative. However, many crops and agricultural systems have not been adequately studied.

3.5 CONCLUSIONS

Chapter E-3 has examined vegetative response to acidic deposition, reviewing literature from studies that shed light on divers plant-pollutant relationships. Documented experiments concern widely varying situations, from controlled-environment studies to field

studies, and from intensively managed agricultural systems to natural plant communities. Controlled-environment studies are useful indicators of potential effects and may suggest subtle changes not easily measurable in an uncontrolled situation. Field studies, however, are a more realistic means of estimating actual effects because in these studies experimental plants are grown under normal agricultural conditions.

The following statements summarize Chapter E-3:

- Leaf structure may play two roles in the sensitivity of foliar tissues to acidic deposition: 1) leaf morphology may selectively enhance or minimize surface retention of incident precipitation, and 2) specific cells of the epidermal surface may be initial sites of foliar injury. Information on the effects of acidic deposition on the accelerated weathering of epicuticular wax of plant leaves is very preliminary. Chlorophyll degradation may occur following prolonged exposure to acidic precipitation (Section 3.2.1).

- Leaching mechanisms are major factors in nutrient cycling in terrestrial ecosystems and are critical to the redistribution of nutrients within these cycles. If the rate of leaching exceeds the rate of mineral nutrient uptake, plant growth and yield reductions are likely (Section 3.2.1.).

- Under laboratory conditions, gaseous pollutant combinations and integration have well defined effects. However, ozone is the single most important gas pollutant to plant life located at great distances from the industrial and urban origin of nitrogen oxides and hydrocarbon precursors. Direct effects due to ozone include foliar injury and growth and yield reductions in numerous agronomic and forest species (Section 3.3.1).

- A review of the evidence on the interaction of forest trees, insect and microbial pests, and acidic deposition does not allow generalized statements concerning stimulation or restriction of biotic stress agents, or their activities, by acidic deposition. Certain studies report stimulation of pest activities associated with acidic deposition treatment, while other studies report restriction of pest activities following treatment. Further research must combine field and controlled environment studies. Available evidence suggests that the threshold of ambient pH capable of influencing certain insect and microbial pests lies within the range of pH 3.0 to 4.0 (Sections 3.3.2, 3.3.3, and 3.3.4).

- Performance and longevity (persistence) of certain pesticides depend on the pH of the systems to which these pesticides are applied or in which they ultimately reside; thus, it is likely that acidic deposition will have significant but limited effects (Section 3.3.5).

- At present we have no direct evidence that acidic deposition currently limits forest growth in either North America or Europe, but we do have indications that tree growth reductions are occurring, principally in coniferous species that have been examined to date, that these reductions are rather widespread, and that they occur in regions where rainfall acidity is generally quite high, or pH is low (~ pH 4.3) for an annual average (Section 3.4.1).

- Controlled environment studies indicate that the deposition of acidic and acidifying substances may have stimulatory, detrimental, or no apparent effects on plant growth and development. Response depends upon species sensitivity, plant life cycle stage, and the nature of exposure to acidity. Some simulation studies have indicated that acidic deposition may result in simultaneous stimulation of growth and the occurrence of visible foliar injury (Section 3.4.1).

- The majority of crop species studies in field and controlled-environment experiments exhibited no effect on growth or yield as a result of exposure to simulated acidic precipitation (pH 3.0). In a few studies, though, growth and yield of certain crops were negatively affected by acidic deposition, while others exhibited positive responses (Section 3.4.2).

- A crop's net response to acidic deposition results from a combination of the positive effects of sulfur and nitrogen fertilization, the negative effects of acidity, and the interaction between these factors and other environmental conditions such as soil type and presence of other pollutants (Section 3.4.2).

- Available experimental results do not appear to indicate that the negative effects of acidic precipitation outweight the positive effects, however, many crops and agricultural systems have not been properly or adequately studied (Section 3.4.2).

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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-4. EFFECTS ON AQUATIC CHEMISTRY

4.1 INTRODUCTION (J. N. Galloway)

In the last decade, acidification of streams and lakes, with subsequent biological damage, has become a well reviewed effect of acidic deposition (NAS 1981, U.S./Canada 1981, NRCC 1981). However, confusion, ignorance, and debate still cloud our knowledge of past, current, and future trends in the acidification of aquatic systems, the key processes that control the acidification, and the degree of permanency of biological effects.

This chapter critically reviews how aquatic chemistry responds to acidic deposition. Initially, basic definitions and concepts regarding acidic deposition, terrestrial and aquatic systems, measurements of sensitivity using alkalinity, and the different time scales of acidification are presented. These definitions are followed by a detailed listing of the important characteristics of terrestrial and aquatic system subcomponents that ameliorate or enhance the effect of acidic deposition. The theoretical and practical sensitivity of aquatic systems to acidic deposition is discussed with locations of sensitive and affected sensitive systems documented. Aquatic systems considered include lakes, streams, and estuaries. The degree of acidification of these systems is examined in the light of existing models, and the models are critically reviewed. The role of S and N in the acidification process is addressed. The status of our knowledge on acidification of aquatic systems is presented in the context of asking what will happen if depositions of S and N compounds from the atmosphere increase or decrease. As a final section, the interaction of aquatic acidification with the metal and organic biogeochemical cycles is addressed and an assessment of knowledge is presented.

4.2 BASIC CONCEPTS REQUIRED TO UNDERSTAND THE EFFECTS OF ACIDIC DEPOSITION ON AQUATIC SYSTEMS

The following concepts concerning effects of acidic deposition on aquatic systems will serve as a foundation for critically assessing our current knowledge.

4.2.1 Receiving Systems (J. N. Galloway)

Receiving systems are terrestrial, wetland, and aquatic. Their component parts include:

a. Terrestrial Components

(1) forest, crop, or grass canopy

(2) litter layer

(3) organic soil layer

(4) inorganic soil layer

(5) bedrock

b. Wetland Components

(1) vegetation - mosses and other semi-submerged plants

(2) water - stream, pond, swamp

c. Aquatic Components

(1) stream

(2) lake

(3) sediment

These systems and their components are linked, so the effects of atmospheric deposition on one component can cause secondary effects in another component. The hydrologic pathway controls which components are affected by (or linked to) other components. For example, water (precipitation) first hits the tree canopy, then travels through successive layers of the terrestrial system before it enters wetlands adjacent to the terrestrial system and then finally the lake. Therefore, the effects of atmospheric deposition on any one component of the terrestrial-wetland-aquatic system depend not only on the composition of the atmospheric deposition but also on the effect of the atmospheric deposition on every system 'upstream' from the component of interest. For example, the effect of atmospheric deposition on aquatic systems depends on what is in the atmospheric deposition and its effect on all components of the terrestrial and wetland systems that it contacts prior to discharge into the aquatic system (Figure 4-1).

Therefore, when discussing effects on components of terrestrial, wetland, or aquatic systems we are incorrect to investigate only the component of interest. Rather, all components either directly or indirectly linked to the specified component should also be included in the study. This point will become especially pertinent in Section 4.3.2, when it is shown that decreases in sulfur deposition from the atmosphere may not result in decreases in lake acidification until the terrestrial system above the lake recovers. Instances where the terrestrial system is less important are (1) lake systems with a large lake/watershed area ratio and (2) lake and stream systems that receive runoff or snowmelt that has had little contact with the terrestrial systems.

The composition of aquatic systems is controlled by not only physical and chemical processes but also by biological processes. In discussing the concept of system sensitivity and determining the degree of acidification, we cannot ignore the biological component because,

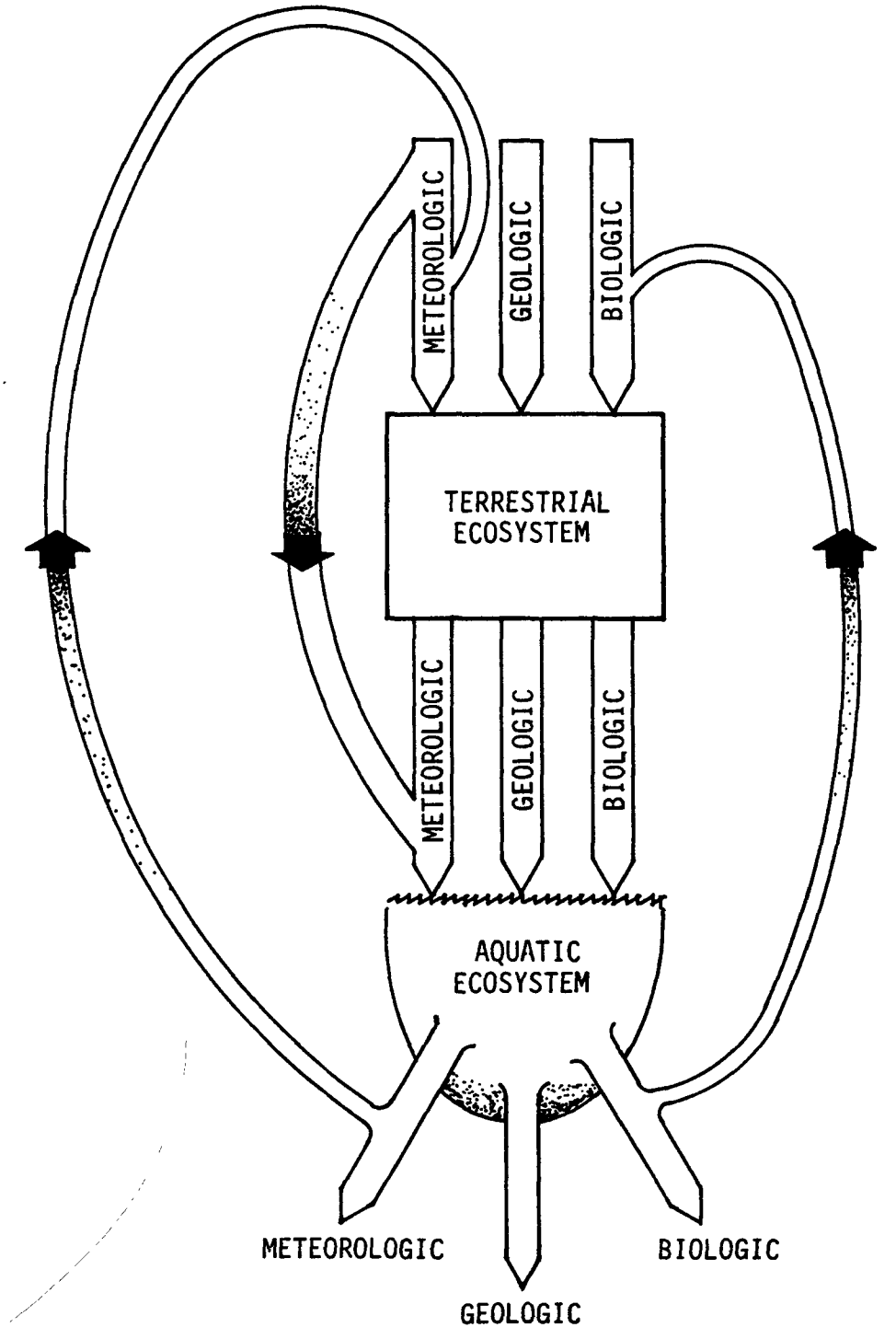

Figure 4-1. Diagrammatic model of the functional linkages between terrestrial and aquatic ecosystems. Vectors may be meteorologic, geologic, or biologic components moving nutrients or energy along the pathways shown. Adapted from Likens and Bormann (1974).

depending on location, type, and productivity, the biological component can make waters more sensitive, less sensitive, more acidified, or less acidified. Specific details on the importance of the biological systems in mediating the chemical response of an aquatic system to acidic deposition can be found in Section 4.3.2.6.

Additional details on the terrestrial systems are found in this section (following) and in Chapters E-2 and E-3 on soils and vegetation, respectively. The next chapter, Chapter E-5, discuss the effects of acidification of aquatic systems on biota.

4.2.2 pH, Conductivity, and Alkalinity (M. R. Church)

Three important analytical measures for evaluating acidification of ground or surface waters are pH, conductivity, and alkalinity. Definitions of these three quantities are briefly given here. A later section (4.3.3.2.1) examines problems concerning the comparability of historical and more recent pH, conductivity, and alkalinity data.

4.2.2.1 pH--In 1909 the Danish chemist S. P. L. Sørensen introduced the term pH when he used exponential arithmetic to express the concentration of hydrogen ions in aqueous solution. He formulated his definitive equation as

$$C_H = 10^{-P} \qquad [4\text{-}1]$$

where C_H was the hydrogen ion concentration and P was the hydrogen ion exponent, which Sørenson then wrote as P_H and which we now write as pH (Bates 1973). For a number of reasons, too detailed to explore here, pH as originally defined by Sørensen is not a measure of either hydrogen ion activity or concentration (Feldman 1956, Bates 1973). Fortunately, this fact, in and of itself, does not adversely affect measurements of surface water acidification. A practical (Feldman 1956) or operational (Bates 1973) pH scale has been defined:

$$pH_{(x)} = pH_{(s)} + \frac{(E_x - E_s)\,F}{RT \ln 10} \qquad [4\text{-}2]$$

where $pH_{(s)}$ is the assigned pH of a standard solution, E_s the emf produced in a pH cell by the solution, F the Faraday constant, R the universal gas constant, T the temperature in °K, and E_x the potential produced in the pH cell by an unknown solution X, which then by definition has a pH of $pH_{(x)}$.

4.2.2.2 Conductivity--Conductivity (or specific conductance) measures a solution's ability to conduct an electric current. This capacity is a function of the individual mobilities of the dissolved ions, the concentrations of the ions, and the temperature of the solution. As the "ohm" is the standard unit of resistance, the "mho" (ohm spelled backwards) is the standard unit of conductance. Conductivity is conductance per unit length of a substance of unit cross section and is

usually reported as μmho cm^{-1} or the equivalent μsiemens cm^{-1}. Distilled water may have a conductivity as low as 0.5 μmho cm^{-1}, and some naturally occurring surface waters in the United States may have conductivities as high as 1500 μmhos cm^{-1} (Golterman 1969, American Public Health Association 1976, Skougstad et al. 1979).

The rationale for measuring conductivity in relation to acidification of surface waters is threefold. First, low conductivity values in surface waters generally indicate a lack of buffering and thus susceptibility to acidification (Ontario Ministry of the Environment 1979). (In some cases, however, organic compounds may contribute to buffering but only very little to conductivity.) Second, low conductivity has been correlated with sparsity of fish populations in low pH lakes (Leivestad et al. 1976, Wright and Snekvik 1978). Third, increases in conductivity over time in surface water under some circumstances can be used to infer acidification of that water body (Nilssen 1980). Hydrogen ions have extremely high mobilities in solution and contribute greatly to conductivity. As a body of water becomes acidified over time, increases in hydrogen ion concentrations could lead to an appreciable increase in conductivity (e.g., from pH 5.0 to pH 4.5, an increase of approximately 7 μmho cm^{-1}, using a value of 0.313 μmho cm^{-1} per μeq ℓ^{-1} free H^+; see Wright and Snekvik 1978). In the absence of other data (e.g., pH, alkalinity, acidity) such a change with time could possibly be used to infer acidification, provided, of course, no other reasonable explanation was apparent.

4.2.2.3 Alkalinity--Alkalinity measures the ability of an aqueous solution to neutralize acid. For this reason it is also known as acid neutralizing capacity, or ANC. In most natural freshwaters, buffering is predominantly due to species of the carbonate system (Stumm and Morgan 1981). In the very dilute surface waters often studied in relation to acidification, total inorganic carbon concentrations are low; therefore, ANC due to the carbonate system is also low. It is not unusual to find in these systems that other species, such as naturally formed weak organic acids (when dissociated) and aluminum-hydroxy compounds leached from soils and sediments, contribute measurably to ANC so that an appropriate expression for this quantity is

$$ANC = (HCO_3^-) + 2\,(CO_3^{2-}) + (AlOH^{2+}) + 2\,(Al(OH)_2^+) + 4\,(Al(OH)_4^-) + (RCOO^-) + (OH^-) - (H^+) \quad [4\text{-}3]$$

where $(RCOO^-)$ represents dissociated organic acids (Bisogni and Driscoll 1979). In some waters organic acids may dominate both the pH and buffering of natural waters. North American areas with waters of this type include parts of the south and southeast, the upper midwest,

locations in the northeast (see General Introduction for map defining regions) and the Atlantic maritime provinces of Nova Scotia and Newfoundland--all regions noted for their highly colored brownwater lakes and streams. Naturally acidic brownwater lakes and streams are discussed further in Section 5.2.1. For discussion of buffering due to organic systems see Bisogni and Driscoll (1979), Wilson (1979), and Section 4.6.3.2.

The operational procedure for determining ANC is acidimetric titration with strong acid to an appropriate end point. Methods for performing such titrations and theoretical treatment of the pertinent equilibria have been detailed in many publications (e.g., Golterman 1969, American Public Health Association 1976, Loewenthal and Marais 1978, Skougstad et al. 1979, Stumm and Morgan 1981).

4.2.3 Acidification (J. N. Galloway)

Acidification is defined as the loss of alkalinity. Those aquatic systems for which acidic deposition may cause acidification or loss of alkalinity, to levels that result in biological change are termed sensitive. Loss of alkalinity can be either chronic or acute, identified as long-term acidification and short-term acidification, respectively. Short-term acidification refers to the development of strong acidity (i.e., alkalinity < 0) during acid episodes (e.g., spring snowmelt) lasting for periods of days or weeks. Because of the relatively short exposure periods, biological effects occur only at those very low alkalinity levels (< 0). Long-term acidification, on the other hand, refers to the gradual loss of alkalinity over periods of years or decades. As a result of chronic exposures, biological effects may occur at alkalinity < 100 $\mu eq\ \ell^{-1}$ (Chapter E-5, Section 5.10.4), and waters with alkalinity < 200 $\mu eq\ \ell^{-1}$ are generally considered sensitive as defined in Section 4.3.2.6.1.

4.3 SENSITIVITY OF AQUATIC SYSTEMS TO ACIDIC DEPOSITION (J. N. Galloway and P. J. Dillon)

The previous sections pertaining to aquatic systems have presented concepts and definitions required to assess our knowledge of how aquatic systems are affected by acidic deposition. This section and the ones following begin our assessment by identifying important components in deposition processes and receiving systems that will control the response of aquatic systems to acidic deposition. Later sections then examine what is known about this response.

4.3.1 Atmospheric Inputs

Five factors must be considered when we assess the role of atmospheric deposition in the acidification of aquatic and terrestrial ecosystems. These are the components (total vs wet vs dry) of the deposition that are measured, the chemical species in the deposition, the concentration of the substances in the deposition relative to their loading (input rate), the location of the deposition (considering a

geographic scale as well as considering the different components [e.g., leaf vs soil] of any system), and the temporal distribution of the loadings.

4.3.1.1 Components of Deposition--To assess the impact of acidic deposition we must know the total input (wet and dry). A major part of the current North American effort regarding deposition monitoring is devoted to "wet-only" measurement. These data are inadequate for assessing impact on aquatic and terrestrial ecosystems because they underestimate total deposition, not only near major point sources of SO_x, NO_x (Dillon et al. 1982) but also in remote areas (Galloway et al. 1982a). Relatively few attempts have been made to measure dry deposition separately (Lindberg et al. 1982). In a few cases (e.g., Dillon et al. 1982) "calibrated" lakes and watersheds have been used to infer dry or total deposition of acidic substances. In other cases, "bulk" deposition measurements (made with a continuously open collector) have been used. Although these collect an undefined portion of the dry deposition, this information is more useful for chemical budget calculations than "wet only" measurements unaccompanied by dry deposition measurements. See Chapter A-8 for further discussion of deposition monitoring.

In addition to H^+ deposition, it is also important to measure the contributions of SO_4^{2-} and NO_3^- and NH_4^+ (see Section 4.4.1 and Chapter A-8). In some systems, NO_3^- is significantly utilized (chemically or biologically), resulting in the internal production of ANC (Harvey et al. 1981, Dillon et al. 1982). In some cases, SO_4^{2-} is stored in terrestrial watersheds by the process of sulfate adsorption (N. M. Johnson 1979), a process that may also generate ANC if the SO_4^{2-} is reduced or if strong acid is simultaneously stored. SO_4^{2-} may also be reduced in lakes, resulting in production of ANC (Cook et al. 1981). This production of ANC is only important on a long-term basis if it is net production, i.e., a net reduction of NO_3 and SO_4 on an annual basis. In other systems SO_4^{2-} apparently acts as a conservative substance within the limits of error in the measurement of the dry deposition fluxes (Likens et al. 1977, Galloway et al. 1983c).

Once wet or dry deposited, SO_2 and SO_4^{2-} have the same pathways through the terrestrial and aquatic systems; therefore, the effect of S on aquatic systems is not dependent on chemical speciation or type of deposition.

Virtually all of the ammonium ion, NH_4^+, deposited from the atmosphere on terrestrial and aquatic systems is used chemically or biologically in those systems (Likens et al. 1977, NAS 1981) in many cases resulting in a decrease in ANC. NH_4^+ deposition is "significant" (25 percent to 50 percent) relative to H^+ deposition. For example, at Harp Lake, Ontario, about 25 percent of the net input of acid was from NH_4^+ deposition (Dillon et al. 1979). Therefore, measuring only free acid (H^+) is inadequate for assessing the impact of acidic deposition on systems.

The input rate of basic cations is also important because without it the net loss of base cations from the watershed cannot be calculated.

4.3.1.2 Loading vs Concentration--Because the ANC of some components of the systems receiving acidic deposition is not renewed (other than over geologic time), the total loading (or input rate) is the factor that determines how long those components will be able to assimilate acidic deposition. The ability of some other components to assimilate acidic deposition may depend on the concentration as well as the total loadings of the acids. The assimilation capacities of components that have a continually renewed ANC, (e.g., a lake's epilimnion that has ANC produced through primary production) or those where reaction rates are controlled by hydrologic factors (e.g., reaction between acidic deposition and silicate bedrock) are sensitive to the amount of water passing through components as well as the concentration of acid.

In general, current measurements of acidic deposition include both the concentration of important substances and the total loading rate of those substances with the exception of dry deposition as discussed in Section 4.3.1.1.

4.3.1.3 Location of the Deposition--Deposition of acidic substances is well measured in most areas where the geological terrain has low capability to neutralize acids and where the wet deposition is known to be relatively high (> 20 meq strong acid m^{-2} yr^{-1}; see Chapter A-8).

On a smaller scale, the relative magnitude of deposition on different components (leaf, soil, water surfaces, etc.) of specific ecosystems is more poorly understood. For example, the ability of the vegetation in a terrestrial system, particularly the forest canopy, to enhance deposition of acidic substances relative to other components of the system (e.g., bedrock or soil surfaces, water surfaces) has been demonstrated (Parker et al. 1980) but needs to be quantified in further studies.

Other factors, such as the relative deposition to the terrestrial component of a watershed vs directly on the surface water, are also important. These factors determine the relative importance of the pathways that the deposited substances follow, which in turn controls the overall assimilation capacity of the system.

4.3.1.4 Temporal Distribution of Deposition--To assess their impact on receiving systems, the input rates of acids or acidifying substances must be considered on a seasonal and a short-term (i.e., episodic) basis as well as on a long-term (annual) basis.

Seasonal inputs are particularly important in areas where snowpack formation and subsequent release of a major portion of the annual deposition during snowmelt to groundwaters and surface waters occur (Jeffries et al. 1979, Galloway et al. 1980b). In some cases (e.g., Central Ontario) during snowmelt the ground is frozen. As a result,

the release of ions occurs at a time when the terrestrial system cannot assimilate the ions as efficiently as it can at other times.

Short-term variations in deposition, on even an episodic basis, may be important in some instances. Flow paths may be altered on a short-term basis, resulting in shortened reaction times and less assimilation of the acidic deposition.

The seasonal variation in deposition has been frequently investigated; short-term variations are more poorly studied and need further quantification.

4.3.1.5 Importance of Atmospheric Inputs to Aquatic Systems--

4.3.1.5.1 Nitrogen (N), phosphorus (P) and carbon (C). Only recently have researchers appreciated the importance of precipitation inputs of various cations and anions, especially N and P to the nutrient balance of inland freshwaters (e.g., Gorham 1958, 1961; Vollenweider 1968, Schindler and Nighswander 1970, Likens 1974, Likens and Borman 1974). Concentrations of inorganic and organic N and P in rain and snow may be small, but the total input by storm, by season, or by year may be a significant source of these nutrients for aquatic organisms, particularly in nutrient-poor lakes (Likens et al. 1974). Direct inputs of nutrients in precipitation to lakes are particularly important in areas with granitic geologic substrates, especially if the ratio of lake surface area to terrestrial drainage area is large (Likens and Bormann 1974). In addition, the gaseous exchanges of nitrogenous compounds in many lakes may be important but are poorly understood (Likens 1974).

Based on relatively few data, some 50 percent of the P and 56 percent of the dissolved N for oligotrophic lakes may come from direct precipitation (Likens et al. 1974). With human influences in the watershed (urbanization, agriculture, etc.) runoff inputs to aquatic ecosystems increase and direct precipitation inputs become much less important to the total budget, even though the absolute amount provided by precipitation remains the same. Where terrestrial inputs of N and P dominate, lakes are usually much more biologically productive, if not eutrophic (Likens et al. 1974).

Preliminary data suggest that organic carbon inputs in precipitation may be ecologically significant for some aquatic ecosystems, particularly oligotrophic lakes. Mean concentrations averaged about 6 mg C ℓ^{-1} in precipitation and accounted for 28 percent of the total allochthonous inputs of organic carbon for a small oligotrophic lake in New Hampshire (Jordan and Likens 1974).

4.3.1.5.2 Sulfur. Two sources provide sulfur for surface waters: rock weathering and atmospheric deposition. In the absence of significant sulfur sources in bedrock, atmospheric deposition is the primary source (Cleaves et al. 1970). This is especially true in areas receiving acidic deposition, where atmospheric sulfate becomes the dominant anion in low alkalinity waters (Gjessing et al. 1976, Oden

1976a, Henriksen 1979, Wright et al. 1980, Galloway et al. 1983c). This dependence is illustrated by plotting the mean and range of excess SO_4^{2-} (over and above that supplied by sea salt cycling) export from watersheds across North America on a line that transects the region of large atmospheric deposition of SO_4^{2-} (Figure 4-2). The wet deposition of excess SO_4^{2-} at each location is shown in the same figure, with estimated total SO_4^{2-} deposition shown at four locations. There is a clear positive relationship between excess SO_4^{2-} deposition and SO_4^{2-} in the runoff. The influence of the increased SO_4^{2-} deposition on aquatic chemistry is large, for on an equivalent basis, the increase in the SO_4^{2-} has to be matched by an increase in a cation, either protolytic (proton donating) (e.g., H^+, Al^{n+}) or non-protolytic (e.g., Ca^{2+}, Mg^{2+}, etc.) (Galloway et al. 1983c). An increase in the former will result in loss of alkalinity (acidification) of the waterbody. An increase in the latter will result in a loss of cations from the terrestrial system. Both effects can potentially alter biological communities in the respective ecosystem (see Sections 4.4 and 4.6).

4.3.2 Characteristics of Receiving Systems Relative to Being Able to Assimilate Acidic Deposition

The anthropogenic acids transported via the atmosphere may be deposited directly into aquatic systems (lakes, streams, wetlands) or onto terrestrial systems that drain into the aquatic systems. Each of the components or subsystems of these systems may be capable of assimilating some or all of the acid deposition received. This section discusses the factors that determine the quantitative capability of the subsystems to assimilate acidic deposition.

4.3.2.1 Canopy--Throughfall and stemflow have elevated levels of most elements relative to incident rainfall (Miller and Miller 1980) and even, in at least one report, relative to snowfall (Fahey 1979). The changes in chemical content result from washdown of particles filtered from the atmosphere by the vegetation, and from leaching of the vegetation (the crown in the case of throughfall, the bark as well in the case of stemflow). The process of particle washdown is, of course, completely independent of any ability of the canopy to assimilate acidic deposition. On the other hand, leaching of cations from the canopy may represent a signficant assimilation capacity. However, the relative importance of each process is generally unknown. Although there are conflicting reports, some generalizations may be made.

Stemflow has a lower pH than does incident precipitation, either because of leaching of organic acids or washdown of acidic aerosols (Miller and Miller 1980).

Throughfall in deciduous forests has usually been found to have elevated pH and increased cation (Ca^{2+}, Mg^{2+}) concentration (Likens et al. 1977, Cole and Johnson 1977). The relative importance of washdown of filtered particles and of cation exchange with the leaf is unknown. Direct uptake of SO_2 (Fowler 1980) and ammonium (Miller and

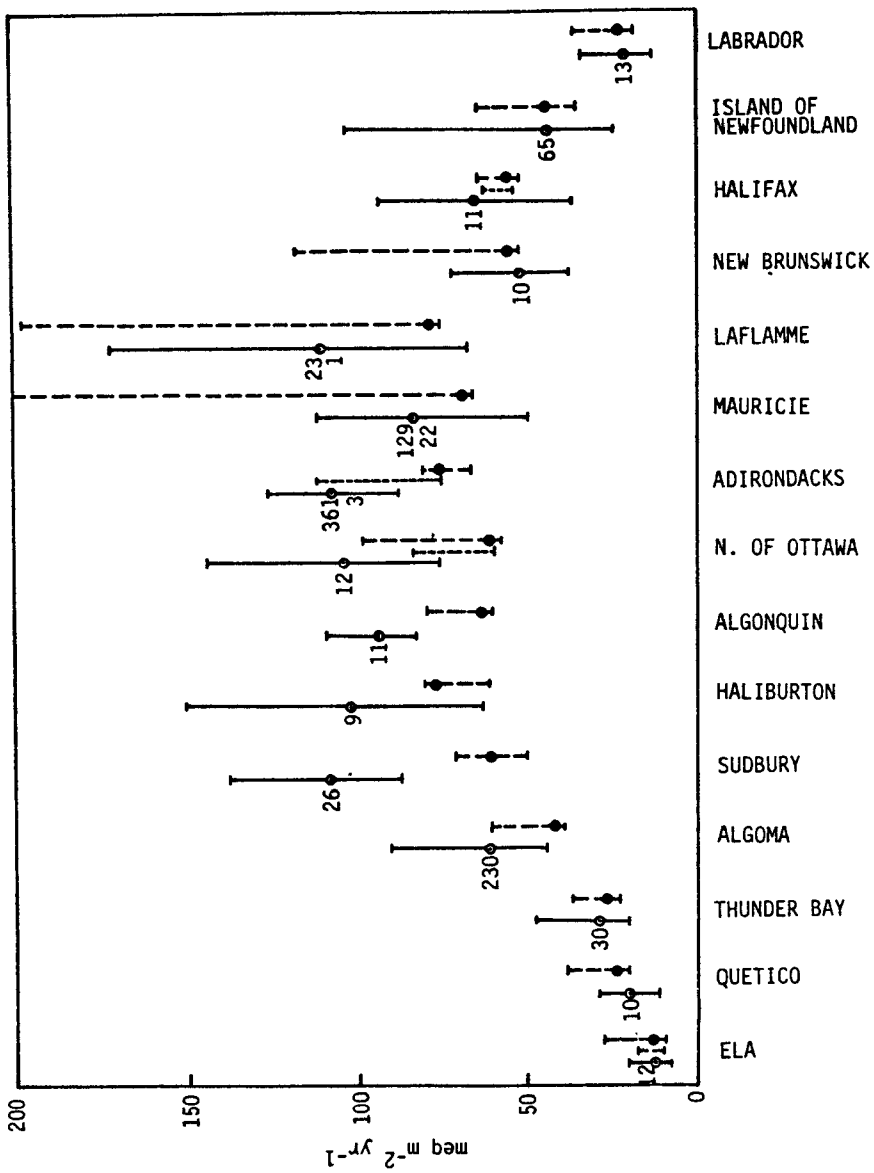

Figure 4-2. Mean and range of basin specific yield of excess sulfur (|—o—|)(U.S./Canada 1982) compared with atmospheric excess sulfur deposition (|—•—|) in precipitation for 1980 (Barrie and Sirois 1982). Also shown are the ranges of wet plus dry deposition of sulfur (|---|) calculated from the 1980 measurements of SO_x in the atmosphere at 4 Canadian Acid Precipitation Network Stations (Barrie 1982).

Miller 1980) also may contribute to the acidity of the throughfall. The throughfall pH of in coniferous forests has been reported to be decreased relative to pH of precipitation (Horntvedt and Joranger 1976), although cation content is increased.

However, the amount of throughfall or stemflow is less than incident precipitation (Ford and Deans 1978, Miller and Miller 1980). Therefore, an increase in concentration of substances in throughfall relative to precipitation does not necessarily indicate that the canopy has supplied materials as a result of either washdown or leaching. The loading of each substance beneath the canopy must be compared to that above the canopy before the occurrence of either process can be ascertained.

4.3.2.2 Soil--The surficial material accumulated on the bedrock of North America is extremely complex in both physical and chemical properties. This surficial material assimilates acidic deposition through dissolution, cation exchange, sulfate adsorption, and biological processes.

In general, surficial materials containing carbonate minerals have abundant exchangeable bases and can assimilate acidic deposition to an almost unlimited extent. Regions of North America with soils formed in situ on limestone, dolomite, or marble provide adequate neutralizing capacity under all loading conditions. Soils formed in situ on carbonate-cemented, carbonate-interbedded, or carbonate clastic sedimentary rocks may have reduced assimilation capacity under very high acidic deposition conditions, but effects of acidic deposition on streams and lakes are probably minimal. As a result of the transport of surficial material in the glaciated areas, it is possible to find carbonate-containing deposits on non-carbonate bedrock.

The ability of surficial materials that contain no carbonate minerals to assimilate acidic deposition results from cation exchange reactions, silicate-mineral dissolution reactions and, in some cases, Fe and Al oxide dissolution. The result of these reactions is an increase in the concentrations of major cations (particularly Ca^{2+}, Mg^{2+}, and possibly Na^{+} and K^{+}), and Al and Fe in the runoff water leaving the watersheds. This ability is affected by:

1) the chemical nature of the surficial material, in particular the cation exchange capacity (CEC) and the base saturation (BS),

2) the permeability of each layer of the soil,

3) the surface area (or grain size) of the soil particles, and

4) the amount (depth and/or mass) of soil in the watershed.

The most important of these factors are the CEC (the total amount of cations that can be exchanged for H^{+}; Table 4-1) and the BS (the proportion of the total exchangeable cations that consists of Ca^{2+},

TABLE 4-1. TYPICAL CATION EXCHANGE CAPACITIES OF SOIL COMPONENTS (FROM MCFEE ET AL. 1976)

SOIL COMPONENTS	CEC[a] (meq 100 g^{-1})
Organic matter (humus)	200
Silicate clays	
vermiculite	150
montmorillorite	100
kaolinite	10
illite	30
Hydrous oxide clays	4
Silts and sands	negligible

[a]Variation is commonly 40% of these mean values.

Mg^{2+}, Na^{+}, and K^{+}). The organic layer of the soil has a high CEC (McFee et al. 1976). Fresh organic litter has a substantial BS component, so it has the potential to assimilate acidic deposition if the BS is high, but potential is low if the BS is low.

The permeability of the soil layers is also important because it determines the contact time of the percolating water with the soil particles. Loosely-packed organic material in the upper layer is usually highly permeable and so may provide little assimilation capacity, especially in cases of high input of water. As the surface area of the soil particles in the organic layer increases, the permeability of the layer decreases, both factors increasing the H^{+} assimilation capacity of the soil, whether it is a result of surface cation exchange reactions or silicate or metal oxide dissolution reactions. However, the proportion of the soil consisting of very small particles (i.e., clays) may increase to the point where permeability of a specific layer is decreased very significantly. In some cases, impermeable layers may effectively eliminate the potential for assimilation of acidic deposition by deeper soil layers.

The depth of the surficial material in a watershed is, of course, also very important. Areas with extremely shallow (1 m) till often have only an organic layer and a well-weathered layer (horizon) that may have little assimilation capacity left (i.e., have low BS). Areas with deep tills (e.g., till plains, kames, moraines, eskers, spillways, outwash, and alluvial formations) will almost always have high capacity for assimilating acidic deposition because of their moderate to high BS at greater depth, combined with their large amounts of unweathered material. Further evaluation of soils as they affect aquatic systems is found in Chapter E-2.

Another soil process important in controlling the response of aquatic systems to acidic deposition is sulfate adsorption. Soils with large sulfate adsorption capacities will essentially act as sinks for the atmospheric sulfur, preventing it from reaching the aquatic system. Generally, soils in unglaciated regions have much greater sulfate adsorption capacities (see Chapter E-2, Section 2.2.8) and hence will be protected from extreme acidification of aquatic systems (relative to the northeastern United States) until the sulfate adsorption capacity is saturated. Estimates of the length of that period are decades to centuries (Galloway et al. 1983a).

4.3.2.3 Bedrock--The ability of bedrock to neutralize acidic deposition is controlled by:

1) chemical composition of the bedrock,

2) effective reaction surface area, and

3) retention time or contact time of water with the bedrock.

Carbonate minerals in the bedrock result in rapid assimilation of the strong acids by dissolution and in production of bicarbonate ion. Bedrock types containing no carbonate minerals may neutralize acidic deposition by the dissolution of silicate minerals, which is an extremely slow process relative to carbonate dissolution.

Massive, impermeable bedrock's effective surface area for chemical reaction is minimal. Acidic deposition contacts only the upper surface layer, so the slow dissolution process will modify water chemistry only marginally, regardless of which silicate material is involved. Bedrock exhibiting only jointing or fracturing will provide relatively greater surface area for reaction, but complete assimilation will only occur at considerable depth, probably affecting the chemistry of the groundwater pool but having little effect on stream and lake chemistry. The maximum extent of surface reactions will be attained by silicate bedrock having a porous nature, e.g., weakly cemented sandstone.

Slower movement of acidic waters through silicate bedrock will result in greater assimilation. Massive igneous beds will shed water with only a short contact time, while more permeable sandstone beds will increase contact time.

Table 4-2 summarizes the assimilation capacity of various bedrock types. Surficial geology, including glacial deposits, soils, and unconsolidated material, has a greater influence on a system's ability to assimilate acidic depositon. Bedrock influence on surface water chemistry is mainly indirect through derived unconsolidated material.

4.3.2.4 Hydrology--

4.3.2.4.1 Flow paths. The extent of reaction of the strong acid components of deposition with each component of the substrate (i.e., bedrock, soil) depends in most cases on the time of contact with that substrate, thus the flow path of water is important in determining the total assimilating capacity of the terrestrial system. Time of contact is important because only surface reactions (adsorption, ion exchange) occur rapidly for aluminosilicate minerals; slow diffusion processes control subsequent reaction rates. Reaction rates with carbonate (bedrock, or in soil) are rapid; therefore, these areas are not sensitive to acidic deposition. Because the groundwater pool often has a slow turnover rate (i.e., contact time is long), assimilation of H^+ is expected.

The contact time of runoff waters in the organic and inorganic layers of the soil profile depends on many factors: topography (e.g., basin slope, soil thickness), meteorology (e.g., precipitation rate, season), etc. These factors affect the degree of soil saturation, which in turn determines contact time.

In areas with snowpacks, contact time is reduced during snowmelt because of the quick saturation of the soils by the first stages of melting. In areas where the soil freezes, contact time is even further

TABLE 4-2. BUFFERING CAPACITY OF VARIOUS BEDROCK TYPES (ADAPTED FROM HENDREY ET AL. 1980b)

Buffering capacity	Bedrock type
Low to none	Granite/Syenite or metamorphic equivalent
	Granitic gneisses
	Quartz sandstones or metamorphic equivalent
Medium to Low	Sandstones, shales, conglomerates or their metamorphic equivalents (no free carbonate phases)
	High-grade metamorphic felsic to intermediate volcanic rocks
	Intermediate igneous rocks
	Calc-silicate gneisses with no free carbonate phases
Medium to high	Slightly calcareous rocks
	Low-grade intermediate to mafic volcanic rocks
	Ultramafic rocks
	Glassy volcanic rocks
'Infinite'	Highly fossiliferous sediments or metamorphic equivalents
	Limestones or dolostones

reduced. In both cases, the impact of snowmelt on runoff (and therefore on stream and lake) chemistry is great (Jeffries et al. 1979, Johannessen et al. 1980, Overrein et al. 1980). In central Ontario, the upper 1.0 to 1.5 m of the soil is usually frozen each winter (Jeffries 1981, pers. comm.) so spring runoff may flow over the soil layer or through only the top few cm. In other areas (e.g., Adirondacks, White Mountains in New Hampshire), surface soil layers freeze only when little snowpack develops during winter.

4.3.2.4.2 Residence times. It is often assumed that headwater lakes are more sensitive to acidic deposition than are other lakes (Gjessing et al. 1976, Minns 1981). This assumption may arise, in part, because headwater lakes

a) often have longer hydrologic residence times than lakes downstream, simply because their total catchment area-lake area ratio is smaller (hydrologic residence time is a function of lake volume rather than lake area so lake morphometry must also be considered);

b) often are at higher elevations (on a regional basis) and therefore have few or no soil deposits in their watersheds; and

c) often have poorly developed soils in their watersheds.

Lakes with smaller catchment area-lake area ratios will usually receive a greater proportion of their total input of water via deposition directly on the lake surface. The acids in the deposition on the lake surface have not been assimilated by any other system. On the other hand, even in systems with small watersheds, assimilations of hydrogen ion in the terrestrial systems can be $\geq$ 50 percent on an annual basis (Galloway et al. 1980a, Wright and Johannessen 1980, Jefferies et al. 1981). Therefore, as the catchment area-lake area ratio increases, the ability of the overall watershed (terrestrial catchment + lake) to assimilate the acidic deposition falling on it increases.

A long hydrologic residence time is favorable (i.e., makes a lake less sensitive) if a major portion of the ANC that enters the lake results from internal processes. If water renewal rate is slow, the ANC provided by processes such as primary production will build up from year-to-year rather than be lost from the lake via outflow.

In summary, the relative importance of the ANC supplied by internal processes in a lake vs the acid assimilation capability of the terrestrial watershed will determine, for a particular lake, whether a long hydrologic residence time is beneficial or detrimental.

4.3.2.5 Wetlands--Very little is known about the role of wetlands in assimilating acidic deposition. In addition to neutralization by alkalinity present in the aqueous component of the wetland, other processes may contribute to assimilation, including 1) reduction reactions and 2) ion exchange reactions.

Reduction reactions (e.g., NO_3^- reduction, SO_4^{2-} reduction, Fe^{3+} reduction) occur in the aqueous portion of the wetland under anaerobic conditions, e.g., under ice-cover during the winter. They may also occur in the sediments, which are typically high in organic content and are anaerobic at all times. The ANC produced by these reduction reactions may, however, be temporary (Section 4.3.2.6.2) if the reactions are reversed when the water is oxic, or if the water is removed (e.g., by evaporation) exposing the sediments to the atmosphere. Some of the ANC produced is permanent if, for example, sulfide produced from SO_4^{2-} reduction is stored as FeS. In other cases, oxygen demand in the wetland may be high enough at all times because the high organic content and relatively shallow water depth keep the aqueous component anoxic. The reduction processes may, in these cases, produce permanent ANC.

Cation exchange reactions with the sediments or detrital material in the wetland may result in significant assimilation of strong acid if the BS is appreciable. However, this is probably seldom the case. In fact, some wetlands, particularly Sphagnum bogs, have been shown to produce mineral acidity (Clymo 1963) by means of cation exchange reactions.

4.3.2.6 Aquatic--The ability of an aquatic system to assimilate acidic deposition must be considered with respect to time frame, i.e., the ability of the system to prevent long-term acidification vs short-term acidification. This, in turn, depends on the system's ability to assimilate acidic deposition at all times so that no fluctuations in pH or alkalinity result in mineral acidity at any time, even during major hydrologic events such as snowmelt or stormflow.

4.3.2.6.1 Alkalinity. A threshold alkalinity, below which an aquatic system would have the potential for becoming acidic to a point where biological effects might occur, can be estimated. The following material provides support for a quantitative estimate of such a threshold. It should be clearly recognized that the presentation emphasizes the long-term (years/decades) concept of lake and stream acidification. Also, the computed threshold ignores any acid assimilation of acidic deposition by the watershed, the importance of which is noted in the preceding sections. As a result, the estimate to follow represents an upper threshold limit for systems receiving present levels of acidic deposition. Using this threshold to estimate the number of systems sensitive to the long-term inputs of acidic deposition would likely result in an overestimate. However, this same threshold would underestimate the number of aquatic systems that are susceptible to short-term (days/weeks) acidification.

The instantaneous ability, i.e., excluding watershed influences, of lake or stream water to assimilate acidic deposition is quantitatively measured as the ANC or alkalinity of the water (Stumm and Morgan 1970). HCO_3^- is an adequate measure of ANC in most lakes because other contributing species (e.g., ammonia--NH_3, borate--$B(OH)_4^-$) are of minor importance.

Alkalinity frequently has been used to assess the sensitivity of lakes to acidic deposition, and subjective criteria have been established to "classify" lakes; e.g., lakes in Ontario were classified as having extreme sensitivity if 0 to 40 μeq alkalinity ℓ^{-1} was measured, moderate sensitivity if 40 to 200 μeq alkalinity ℓ^{-1} was measured, etc. (Anon 1981). The boundary between "sensitive" and "insensitive" that is commonly used is 200 μeq ℓ^{-1} of alkalinity before the onset of acidification (Hendrey et al. 1980b). Altshuller and MacBean (1980) classified lakes as "susceptible" if alkalinity was measured as < 200 μeq ℓ^{-1}. Calcite saturation index (CSI)--a measure of the degree of saturation of water with respect to $CaCO_3$ (calcite) that integrates alkalinity, pH, and Ca concentration--has also been used (Kramer 1979, unpub. manuscript; Harvey et al. 1981). In another case (Minns 1981), simple assessment of lake sensitivity has been based on ionic strength (conductivity), with the unstated assumption that ionic strength must be a good correlate of alkalinity.

To understand why an alkalinity of < 200 μeq ℓ^{-1} was selected as indicative of sensitivity, it is first necessary to explore the relationship between pH and alkalinity in oligotrophic systems. A typical relationship between alkalinity and pH for oligotrophic systems is obtained by plotting pH versus alkalinity for 928 streams and lakes in New York State (Figure 4-3, individual points not shown). This graphical relationship between pH and alkalinity will be used in two ways. First, it will illustrate dependence of pH changes on the magnitude of the initial alkalinity. Secondly, it will be used to relate alkalinity changes to pH changes and subsequent biological effects. This linkage is needed because the literature on the chemical effects of acidic deposition on aquatic ecosystems uses alkalinity as the critical variable and not pH. However, those researchers investigating biological changes due to acidic deposition relate the biological changes to changes in pH and not alkalinity. Therefore, to be able to relate changes in alkalinity of aquatic systems due to acidic deposition to changes in biological systems due to changes in pH, we use Figure 4-3.

The logic behind alkalinities < 200 μeq ℓ^{-1} as an upper long-term sensitivity limit is as follows:

- On a regional basis, the maximum increase of SO_4, due to acidic deposition, in aquatic systems is ~ 100 μeq ℓ^{-1} (Harvey et al. 1981, NRCC 1981). Therefore, the maximum alkalinity decrease that could have occurred over time is ~ 100 μeq ℓ^{-1} (see explanation, Section 4.4.3).

- Biological effects due to acidification become apparent as alkalinities decline to about 65 to 35 μeq ℓ^{-1} and pH's between 6.5 and 6.0 (Figure 4-3; Chapter E-5, Table 5-16).

- Given the above two points, if systems with alkalinities < 200 μeq ℓ^{-1} are acidified to the maximum amount (Δ alkalinity = 100 μeq ℓ^{-1}), then resulting

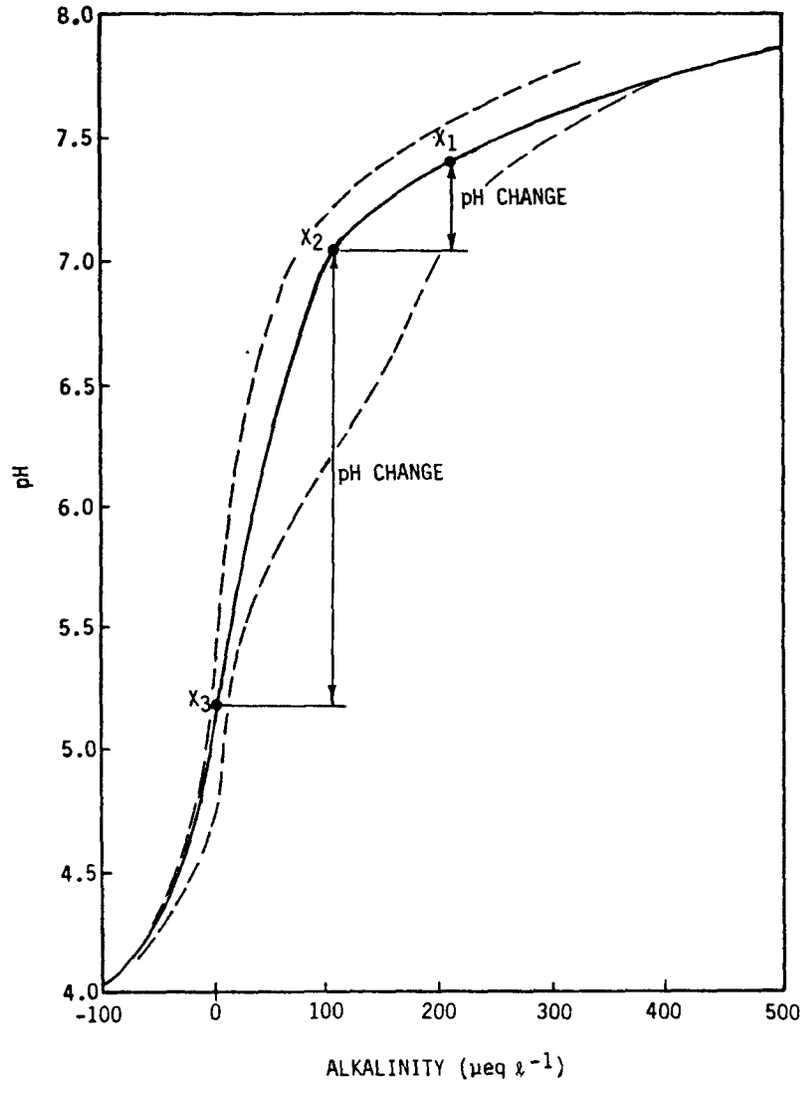

Figure 4-3. The change in pH for a given change alkalinity at two alkalinity levels and an example of pH-alkalinity relationship for aquatic systems. The alkalinity data were obtained by a single or multiple endpoint titrations using a pH meter. The solid S-shaped line represents the median values. The dashed lines form a 68% band (analogous to one standard deviation). Each line is a smoothed (cubic spline) moving average of five points of the appropriate percentiles (2, 16, 50, 84, 98) computed from the data at each 0.1 pH point. Adapted from Hendrey (1982).

alkalinities will be < 100 $\mu eq\ \ell^{-1}$, which is near the threshold for biological effects on a long-term basis. In addition, there is a short-term consideration. If an aquatic system that was originally at 200 $\mu eq\ \ell^{-1}$ is acidified to 100 $\mu eq\ \ell^{-1}$, there may be no biological effects on a long-term basis, but there could be some on the short-term basis. During spring snowmelt, alkalinity reductions of > 100 $\mu eq\ \ell^{-1}$, lasting several weeks, have been reported (Galloway et al. 1980b, Galloway and Dillon 1982).

This is graphically illustrated in Figure 4-3, where 200 $\mu eq\ \ell^{-1}$ is represented by X_1. If acid precipitation is added to the system, the alkalinity could decrease to ~ 100 $\mu eq\ \ell^{-1}$ (X_2). This assumes that acidification is immediate and that the only chemical effect of the added acid is the loss of HCO_3^-. Thus, it represents an upper limit (see Section 4.4.3.1.1.1). Note that this acidification has only resulted in a small pH change (~ pH 7.4 to 7.1). However, future inputs of acidic deposition on a long-term basis (years/decades) or any short-term acidification (days/weeks) will probably result in large pH decreases, with subsequent biological effects, because the system is now poorly buffered.

Systems of alkalinities ~ 200 $\mu eq\ \ell^{-1}$ that are exposed to high current levels of acidic deposition (annual average pH $\leq$ 5.0) are only minimally sensitive. [Natural pH of precipitation in eastern North America is most certainly greater than pH 5.0 due to the absence of large sources of sulfur and nitrogen oxides (Galloway and Whelpdale 1980).] However, systems with < 100 $\mu eq\ \ell^{-1}$ of alkalinity that are exposed to the same acidic deposition are very sensitive. For example, point X_2 represents a system that started with 100 $\mu eq\ \ell^{-1}$. Point X_3 represents the same system after it is exposed to current levels of acidic deposition. The subsequent large decrease in pH and alkalinity will influence a large variety of biological responses.

In summary, the boundary between sensitive and nonsensitive aquatic systems is chosen to be 200 $\mu eq\ \ell^{-1}$ after consideration of (1) current levels of acidic deposition (annual average pH $\leq$ 5.0), (2) the relationship between pH and alkalinity in oligotrophic systems, and (3) the pH and alkalinity values at which changes in them will result in biological effects. The choice of 200 $\mu eq\ \ell^{-1}$ of alkalinity identifies all aquatic systems possibly sensitive to long-term acidification as a result of current levels of acidic deposition but underestimates those systems sensitive to short-term acidification.

Although parameters such as alkalinity and calcium saturation index (CSI) probably provide reasonable estimates of the instantaneous ability of the lake water to neutralize acidic deposition, they have two drawbacks: the interpretation of degree of sensitivity is subjective, and the methodology relies on only a static measure. The renewal rate of ANC is undoubtedly more important and ultimately governs a lake's

sensitivity. Renewal rate of ANC in a lake depends on the rate of ANC supply from the lake's watershed which, in turn, depends on many factors (see preceding sections); the importance of direct atmospheric deposition on the lake surface (since this will have alkalinity < 0) relative to the total water budget; and the internal renewal rate of alkalinity. As long as the total input of alkalinity, including external and internal sources, remains positive, the lake will not become acidic (i.e., will not have mineral acidity) because alkalinity is a conservative parameter. However, short-term acidification (e.g., at snowmelt) may occur in lakes that will never experience long-term acidification.

4.3.2.6.2 Internal production/consumption of ANC. The internal production of alkalinity is usually overlooked in considerations of lake sensitivity, but it may be very important, especially in lakes with low alkalinity. In the epilimnion, the major pathway for the production of alkalinity is primary production (Brewer and Goldman 1976, Goldman and Brewer 1980). The generation of alkalinity depends upon the use of NO_3^- as a nitrogen source by algae:

$$106\ CO_2 + 16\ NO_3^- + HPO_4^{2-} + 122\ H_2O + 18\ H^+ \rightarrow$$

$$C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2. \qquad [4\text{-}4]$$

Although it is well known that NH_4^+ is preferred over NO_3^- (Lui and Rolls 1972, McCarthy et al. 1977), mass balances of the two species in most north-temperate lakes are such that NO_3^- use surpasses NH_4^+ use (Harvey et al. 1981; Dillon, unpub. studies). Any NH_4^+ use results in a decrease in alkalinity in the lakewater (D. W. Schindler, unpub. studies). However, a net gain of ANC can result from NO_3^- uptake during primary production since the inorganic NO_3^- is converted to organic nitrogen and stored permanently in the lake's sediments.

The uptake of NO_3^- (corrected for uptake of NH_4^+) is often in the range of 10 to 20 $\mu eq\ \ell^{-1}$ over the summer in oligotrophic north-temperate lakes (Dillon 1981). The net uptake calculated on a whole-year basis, on the other hand, may be closer to 5 $\mu eq\ \ell^{-1}$. Even this lesser amount may be significant; e.g., in a lake with mean depth of 10 m, this represents a production of 50 meq alkalinity $m^{-2}\ yr^{-1}$, an amount comparable to the deposition of strong acids in many parts of eastern North America.

Therefore, an increase in nutrient levels may increase the alkalinity generation if NO_3^- is used as the N-source, on a net basis, and the organic N is lost permanently to the sediments. Fertilization with NH_4^+, on the other hand, may result in lake acidification (D. W. Schindler 1981, pers. comm.). Nutrient status is therefore very important in determining the sensitivity of a lake to acidic deposition.

In most lakes (i.e., those with vernal circulation), the alkalinity of the whole lake is uniform at the initiation of stratification. If no internal production or use of alkalinity occurred in the hypolimnion, it would serve as a "reserve" pool for the lake, because the external inputs of strong acids (atmospheric deposition, runoff) enter the epilimnion. However, internal processes within the hypolimnion may also deplete or produce alkalinity (Schindler et al. 1980, Cook 1981, Harvey et al. 1981, Kelly et al. 1981, unpub. manuscript).

Acidification of lakes by acidic deposition results in increased transparency (Dillon et al. 1978, Schindler et al. 1980, Harvey et al. 1981, Schindler and Turner 1982, Yan 1983). Therefore, hypolimnetic primary production (by phytoplankton or periphyton), and associated production of ANC, may be elevated relative to non-acidic lakes of equivalent nutrient and morphometric status.

Under oxic conditions, respiration of organic matter (produced principally in the epilimnion and metalimnion) results in a decrease in alkalinity or depletion of ANC:

$$C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2 \rightarrow 106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4. \quad [4\text{-}5]$$

This reaction may occur in the hypolimnetic water or at the sediment water interface. As mentioned earlier, some of the organic matter produced in the lake is permanently stored in the sediments (i.e., respiration < production).

Under anoxic conditions, several microbial processes that occur in the hypolimnion (or in the surficial sediments) and that require organic material produce alkalinity:

$\underline{SO_4^{2-}}$ reduction

$$C_{106}H_{263}O_{110}N_{16}P_1 + 53\ SO_4^{2-} + 106\ H^+ \rightarrow 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 106\ H_2O + 53\ H_2S \quad [4\text{-}6]$$

$\underline{NO_3^-}$ reduction

$$5\ C_6H_{12}O_6 + 24\ NO_3^- + 24\ H^+ \rightarrow 30\ CO_2 + 12\ N_2 + 42\ H_2O \quad [4\text{-}7]$$

$\underline{Mn^{4+}}$ reduction

$$C_{106}H_{263}O_{110}N_{16}P_1 + 236\ MnO_2 + 472\ H^+ \rightarrow 236\ Mn^{2+} + 106\ CO_2 + 8N_2 + H_3PO_4 + 366\ H_2O \quad [4\text{-}8]$$

Fe^{3+} reduction

$$C_{106}H_{263}O_{110}N_{16}P_1 + 424\ FeOOH + 848\ H^+ \rightarrow$$
$$424\ Fe^{2+} + 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 742\ H_2O. \qquad [4\text{-}9]$$

However, the alkalinity produced by some of these processes may be temporary. Fe^{2+} and Mn^{2+} (and NH_4^+) production is probably largely temporary, with the reverse reaction occurring as soon as oxic conditions again prevail at overturn. NO_3^- reduction occurs in hypolimnia or in lake sediments, but the N_2 evolution makes the reaction irreversible; therefore, this represents a source of permanent alkalinity. SO_4^{2-} reduction results in permanent alkalinity if the S^{2-} formed is irreversibly lost to the sediments. Any S^{2-} (HS^-, H_2S) left in the water column at fall circulation is re-oxidized to SO_4^{2-}, with concurrent loss of alkalinity.

Therefore, the critical factor with respect to the ability of a lake's hypolimnion to assimilate acidic deposition is its oxygen regime. At the Experimental Lakes Area, Schindler et al. (1980), Kelly et al. (1981), and Cook (1981) studied fertilized and unfertilized lakes that had anoxic hypolimnia and consequent summer alkalinity production. Increased SO_4^{2-} input resulted in increased alkalinity generation. In Muskoka and Haliburton counties (Dillon et al., unpub. results) and in the Sudbury area (Yan and Miller 1982), most study lakes did not have large anoxic zones in their hypolimnia and SO_4^{2-} loss was not observed. Fertilized lakes (Yan and Lafrance 1982) were an exception, however.

4.3.2.6.3 Aquatic sediments. The potential for lake sediments to assimilate acidic deposition is not quantitatively understood. The same microbial processes that occur in hypolimnia occur in lake sediments, but the contribution of alkalinity to the overlying waters is controlled by slow diffusion processes.

That sediments also supply ANC by chemical pathways can be inferred from neutralization experiments near Sudbury, Ontario (Dillon and Smith 1981). The acidified lakes studied had reduced pH (of ~ 4.0 to 4.5) in the upper 5 cm of the sediments, with pH of 6.0 to 7.0 at greater depth. Following neutralization of three study lakes (with $CaCO_3$ plus $Ca(OH)_2$), the pH of the upper sediments increased to the same levels as the deep sediments. Sediment consumption of the added ANC varied from 33 to 60 percent of the total added to the lake. The sediments were therefore able to supply 0.9 to 3.0 eq m^{-2} of BNC. Over the subsequent five years, one of the three neutralized lakes was reacidified. The pH of the upper 5 cm of sediment decreased to levels comparable to those measured prior to neutralization of the lake.

The same processes that occur in soils may occur in lake sediments. Hongve (1978) has suggested that cation exchange in lake sediments may result in acidification of lakewater by Ca^{2+} exchange for H^+. He suggested, however, that the reverse process will occur with increased

lake acidity. These results were demonstrated in laboratory experiments only.

4.3.3 Location of Sensitive Systems (J. N. Galloway)

Identification of aquatic systems sensitive to acidic deposition ideally should take into account all factors outlined in Section 4.3.2. Unfortunately, for most of these parameters, regional data are not available nor do we have a clear understanding of how parameters interact. The alkalinity of a surface water does reflect a combination of many relevant factors. Aquatic systems with alkalinity < 200 $\mu eq\ \ell^{-1}$ have been defined in Section 4.3.2.6.1 as sensitive to acidification by acidic deposition. These systems can be located by direct analyses of alkalinity over large areas or by use of geological and soil maps to identify areas that will have aquatic systems with low alkalinities. The advantage of the first method is that the alkalinity is determined by an actual measurement. The disadvantage is that thousands of measurements have to be made of lower order streams and headwater lakes to determine the sensitivity on a regional basis and that in the absence of measurements no mechanism to estimate the alkalinity exists. The advantage of the second method is that broad regional determinations can be made, but the major disadvantage is that no fine detail is available. Therefore, the proper way to address this issue is to use the regional data on bedrock and soil characteristics to determine general areas of sensitivity and then to follow up with alkalinity surveys in the regions designated as sensitive.

The state of our knowledge is illustrated with four figures. Using bedrock geology as a criterion, Galloway and Cowling (1978) made a rough approximation of sensitive areas in North America (Figure 4-4). Their identification was improved by the addition of soils and surficial geology information to determine sensitive systems for eastern Canada (NRCC 1981; Figure 4-5). For the soils of the eastern United States, McFee (1980) used CEC and percent BS to indicate the areas where soils would be expected to be sensitive to acidic deposition (Figure 4-6). Significant portions of the soils within the areas designated "sensitive" or "slightly sensitive" would provide low buffering capacity and therefore would have little ability to neutralize acidic inputs as they passed through the soil.

As a check on the use of soil characteristics and bedrock geology as predictors of low alkalinity waters, Hendrey et al. (1980b) using Norton's (1980) methods, compared surface water alkalinities waters with sensitivity predicted on the basis of geology on a county by county (U.S.) basis; they found clear correlations. Haines et al. (1983b) surveyed New England lakes and compared alkalinities with predictions (by Norton) of sensitivity on a drainage basin basis; high correlations existed.

As mentioned earlier, instead of using maps of soil characteristics and bedrock geology to predict areas of low alkalinity, actual values of alkalinity may be measured and displayed on a map. Omernik and Powers (1982) used such an approach, as is shown in Figure 4-7.

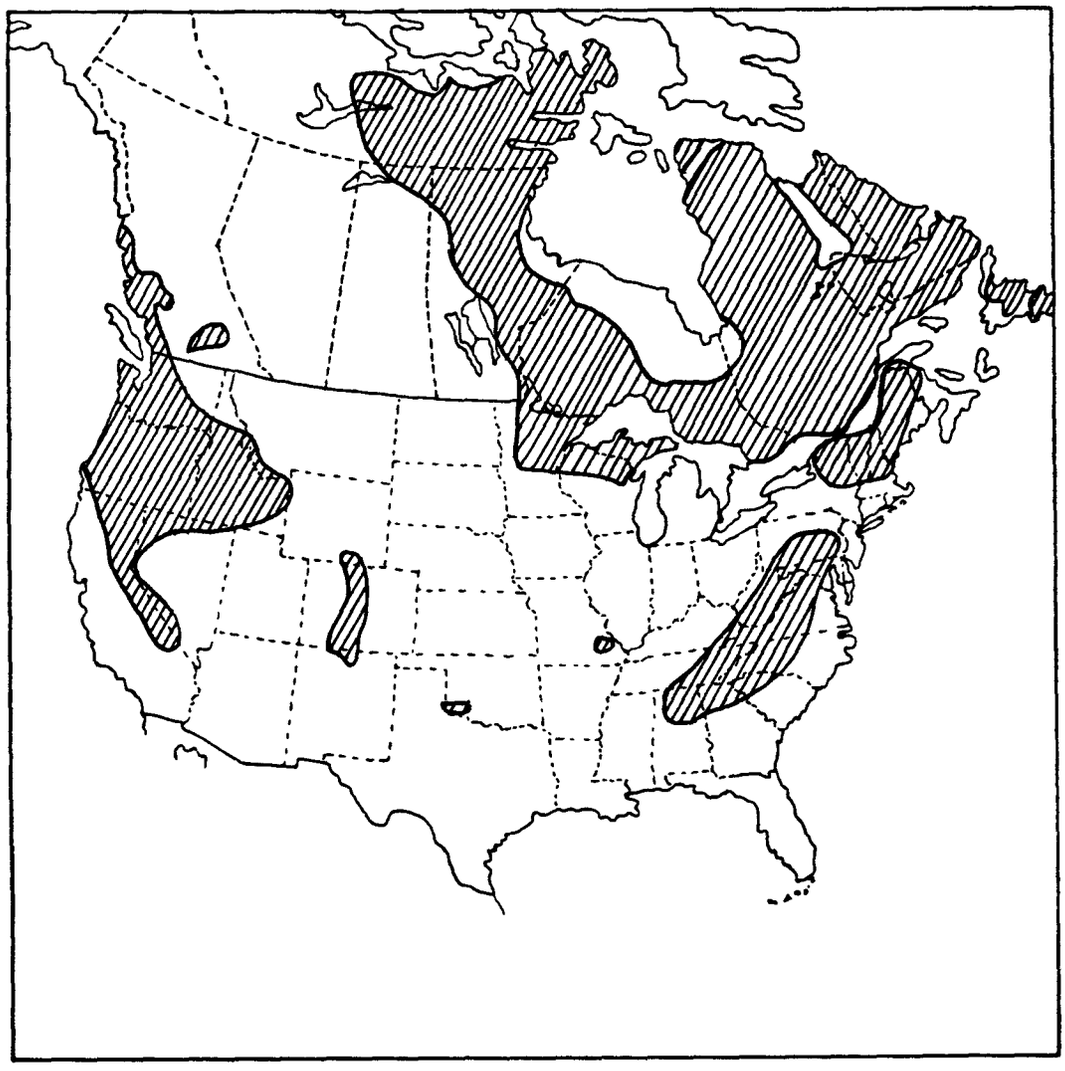

Figure 4-4. Regions in North America containing lakes that are potentially sensitive, based on bedrock geology, to acidification by acid precipitation. Adapted from Galloway and Cowling (1978).

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HIGH SENSITIVITY
Granite, granite gneiss, orthoquartzite, syenite

INTERMEDIATE-HIGH SENSITIVITY
Volcanic rocks, shales, greywacke sandstones, ultramafic rocks, gabbro, mudstone, and metamorphic equivalents

INTERMEDIATE-LOW SENSITIVITY
Calcareous clastic rocks, carbonate rocks interbedded or interspersed with non-calcareous sedimentary, igneous and metamorphic rocks

LOW SENSITIVITY
Limestone, dolomite and metamorphic equivalents

Figure 4-5. Map of areas containing aquatic systems in eastern Canada that are potentially sensitive , based on bedrock geology and surficial soils, to acidic deposition. Adapted from NRCC (1981).

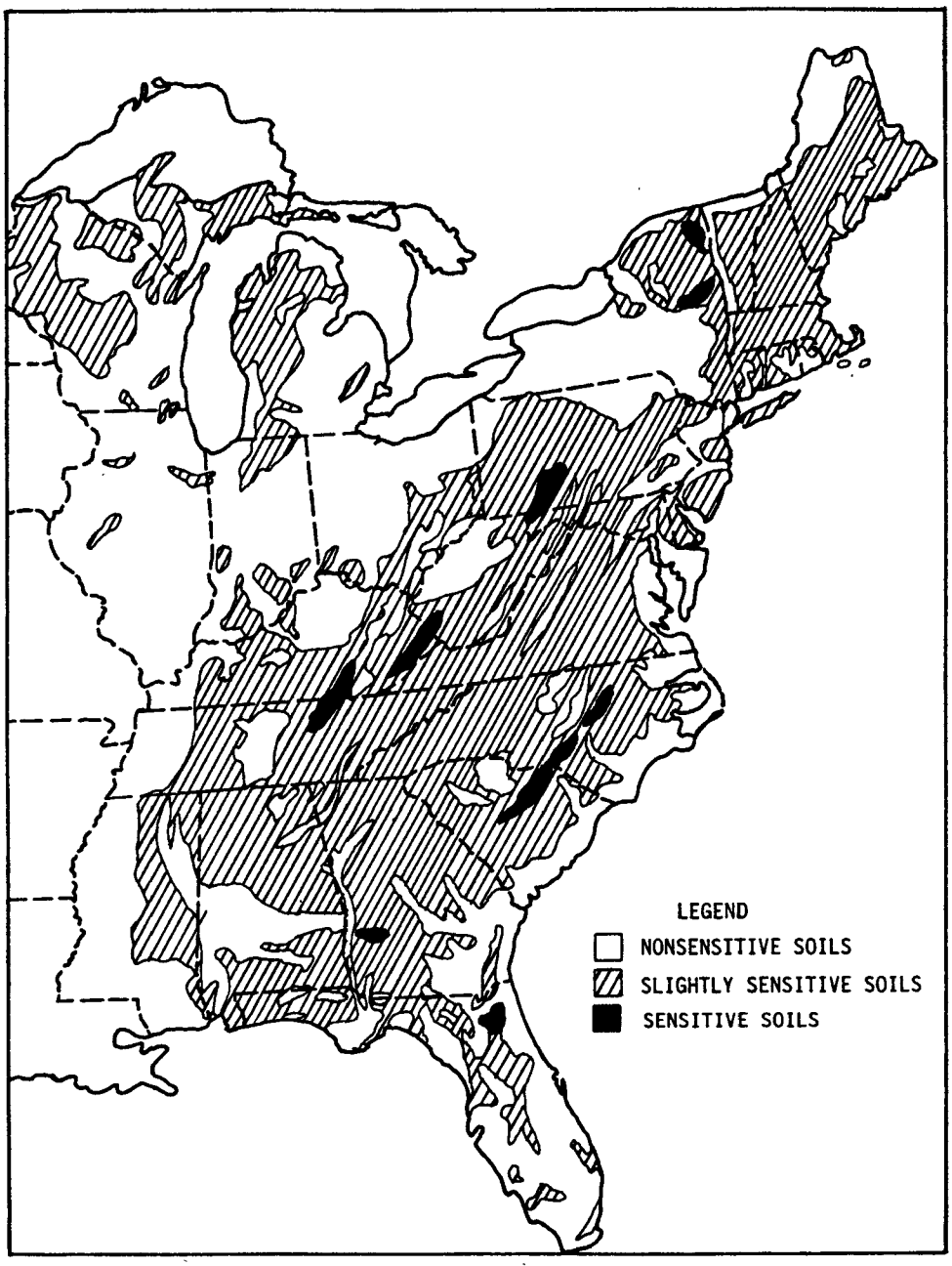

Figure 4-6. Regions with significant soil areas that are potentially sensitive to acidic deposition. Adapted from McFee (1980). See also discussion of soil sensitivity in Chapter E-2, Section 2.3.5.

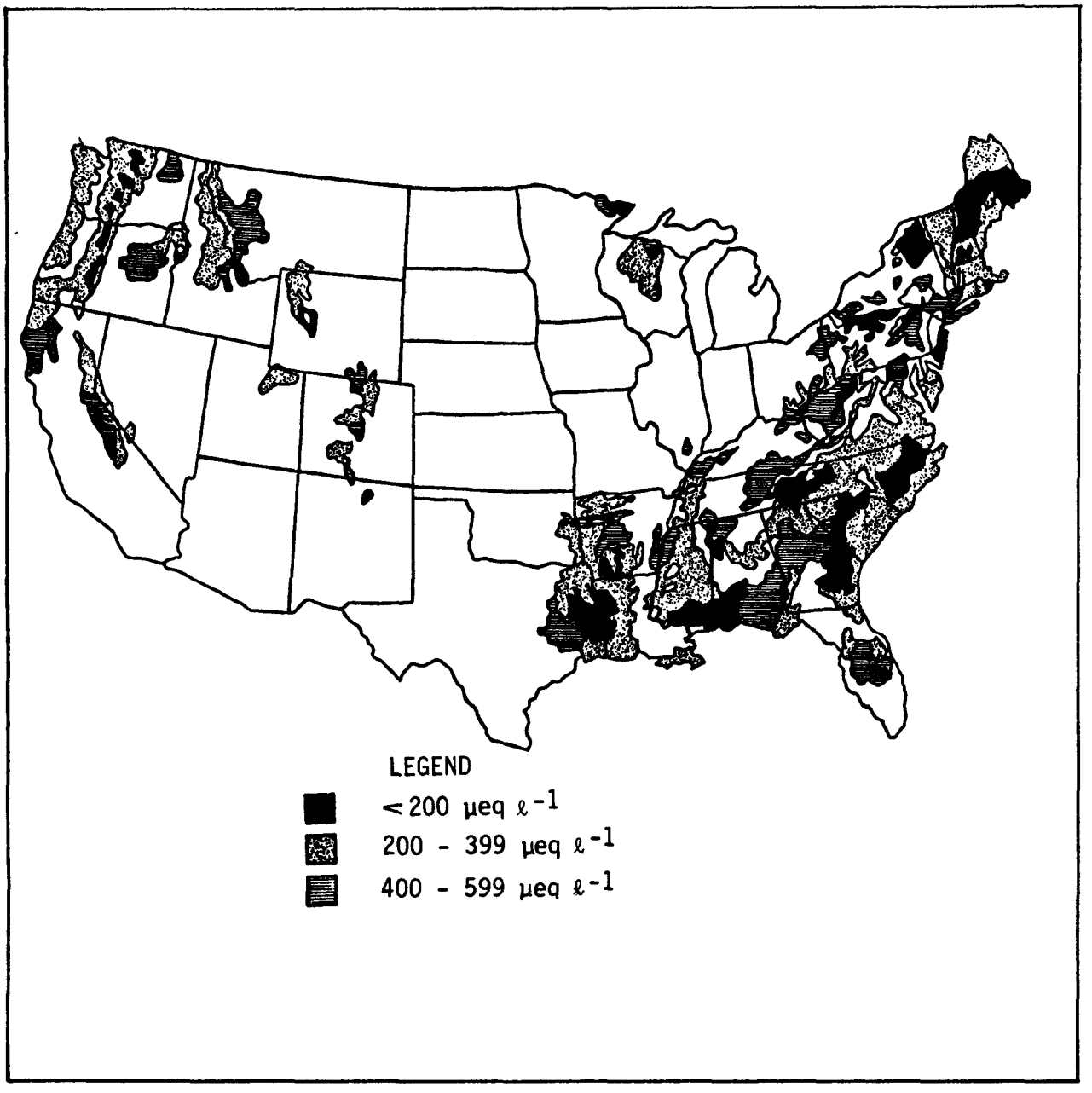

Figure 4-7. Total alkalinity of surface waters. Adapted from Omernik and Powers (1982).

The map is a useful presentation of regions where waters of low alkalinity might be found. In essence, the map was created using a predictive technique. Specifically, existing data on surface water alkalinity were compiled and then correlated with geology, soils, climatic, physiographic, and human factors. These correlations were used to predict mean annual alkalinities for regions without data. There are problems with this predictive technique, that while not terminal, need to be realized. First, if the compiled data are not themselves representative of a region (e.g., if they are weighted towards small or large watersheds instead of a representative mixture) the resulting correlations and predictions will also be biased. Second, it is difficult to estimate the errors involved in the prediction. Third, and as the authors note, a certain degree of averaging was required to create a map on the scale of the United States. Therefore, the ranges cited are for the mean annual alkalinities of most surface waters in a given region. In areas where substantial heterogeneities in soil, geology, elevation, etc. occur there may be large variations from the mean. Unfortunately, sensitive areas generally occur in regions with large variations in elevation and soil thicknesses.

Some of these problems can be resolved by field testing the predictions of the method. However, these field tests will be site specific. A good test in one area would not necessarily mean that all regions would be as well behaved.

We know large regions in North America contain aquatic systems with low alkalinity that are presumably sensitive to acidic deposition. These regions are found throughout much of eastern Canada; New England; the Allegheny, Smoky, and Rocky Mountains; and the Northwestern and North Central United States (Galloway and Cowling 1978, NAS 1981, NRCC 1981) and parts of the south and east coasts of the United States (Omernik and Powers 1982). However, a large amount of more detailed survey work is required to determine the levels of alkalinity and the degree of sensitivity of individual aquatic systems.

4.3.4 Summary--Sensitivity

The sensitivity of aquatic systems to acidic deposition depends on the composition of the deposition, the total rate of the loading (wet plus dry deposition), the temporal distribution, and the characteristics of the receiving system.

Atmospheric deposition is a major source of chemicals to aquatic systems. The chemicals supplied by atmospheric deposition in important quantities include P, Ca, Mg, S, N, Pb, Zn, H, Cl, Na, and Cd. Of these, the concentrations of Pb, Zn, Cu, Cd, S, NO_x, and H, in atmospheric deposition in eastern North America are apparently directly controlled by anthropogenic activities (Chapters A-2 and A-3; see also Sections 4.3.1.5 and 4.6.1.1). The effects of S on aquatic systems are independent of type of deposition (wet or dry) or chemical speciation (e.g., SO_2, SO_4). It is the total deposition of the total element that controls the effect in aquatic systems.

The effects of acidic deposition on aquatic systems depend upon the characteristics of the receiving systems. Three such characteristics determine the ability of the receiving systems to assimilate acidic deposition. The characteristics are size, composition, and hydrological residence time. The smaller the receiving system, the less likely it will be able to assimilate the acidic deposition. The greater the watershed to surface water ratio, in general, the greater the ability to assimilate acids. The ability of systems to assimilate the acidic deposition also depends upon the composition and characteristics of the soil in exchange. Small systems with calcareous rock, for example, are much better able to assimilate the acidic deposition than small systems with granite bedrock and low CEC, percent BS, and sulfate adsorption capacity. The hydrologic residence time is also important. For, generally, the longer the acidic deposition stays in contact with the system the more it is assimilated. The longer the hydrologic time in the terrestrial system, the less the effect of the acidic deposition on the aquatic system. The aquatic systems that tend to be the most sensitive to acidic deposition are located in the areas 'downstream of' terrestrial systems that are small, have slowly weathering soil and bedrock, have short hydrologic residence times, and are unable to assimilate the acidic deposition that falls into them.

After consideration of the maximum loss of alkalinity that could be caused by acidic deposition and the alkalinity range where biological effects begin, sensitive aquatic systems are defined as those alkalinities < 200 $\mu eq\ \ell^{-1}$ (see Section 4.3.2.6.1). Such systems are located through much of eastern Canada, New England, the Allegheny, Smoky and Rocky Mountains, the Northwestern and North Central United States and parts of the south and east coasts of the United States.

4.4 MAGNITUDE OF CHEMICAL EFFECTS OF ACIDIC DEPOSITION ON AQUATIC ECOSYTEMS

The previous sections have laid a foundation of important definitions, concepts and characteristics of deposition and receiving systems. The following sections discuss what is known about the degree of acidification of sensitive systems, and the methods used to determine the degree and rate of acidification.

4.4.1 Relative Importance of HNO_3 vs H_2SO_4 (J. N. Galloway)

H_2SO_4 is the more important in acidification of aquatic systems for two reasons. First, in most areas impacted by acidic deposition, atmospheric H_2SO_4 loading exceeds the HNO_3 loading. The second reason that increases the importance of H_2SO_4 relative to HNO_3 has to do with the terrestrial system associated with the aquatic system. Specifically, for aquatic systems dependencies are controlled by the ability of the terrestrial system to retain SO_4^{2-} and NO_3^-. In the case of SO_4^{2-}, because its concentration varies little seasonally or year-to-year in a given volume of surface water (e.g., stream or lake epilimnion), the spatial variability is the most important. This variability is controlled by the SO_4^{2-} adsorption

capacity (SAC) of the soils in the terrestrial system. In the northeastern United States and eastern Canada, the SAC of the soils is low; thus the SO_4^{2-} concentrations in the surface waters are higher than those in the mid-Atlantic region of the United States, which has soils with a higher SAC (Chapter E-2, Section 2.3.3.2; sulfate adsorption in soils).

In the case of NO_3^-, regional variability is overwhelmed by seasonal variability. During most of the year, the hydrologic residence time in the soil is sufficient to allow for rapid uptake of NO_3^- (Likens et al. 1977). Of the NO_3^- released from the terrestrial system to the aquatic system, most comes during periods of high flow (spring snowmelt, large intense rainstorms). During these types of events the rate of nitrogen transport through the system is faster than the rate of uptake within the terrestrial system. In addition to constraints of the hydrologic residence times on NO_3^- transport through soil systems, a temperature dependency also exists. During warm periods (e.g., summer), when biological acitivity is the highest, NO_3^- is efficiently retained by the terrestrial systems. However, during colder periods (e.g., winter) there is often a maximum of NO_3^- concentrations (Likens et al. 1977).

Therefore, the two periods that allow a larger flux of N from the soil system to the lakes with subsequent increased NO_3^- concentrations are winter base flow and spring snowmelt. This is illustrated by a 37-month record of the NO_3- concentration in the outlet of Woods Lake, a small oligotrophic lake in the Adirondack Mountains, NY, (Figure 4-8) and by two of the inflows to Harp Lake in Southern Ontario (Figure 4-9). The NO_3 values are highest in the winter and during spring snowmelt (usually in March and April). Therefore, during most of the year, because H_2SO_4 deposition is greater than HNO_3 deposition in most areas and because there is greater retention of HNO_3 by the terrestrial system, H_2SO_4 is more important than HNO_3 in causing acidification of aquatic systems.

Due to the increased importance of HNO_3 (relative to H_2SO_4) in acidification of the spring snowmelt and the effects of the large pH and alkalinity decreases (Table 4-3) on sensitive life forms and life stages, it is necessary to explore further the relative roles of HNO_3 and H_2SO_4 during spring acidification. Galloway et al. (1980b) studied the role of NO_3 as a source of acidity for Woods and Panther Lakes, acidified during the 1979 snowmelt. They found that in the two lakes alkalinity decreased during snowmelt because of dilution of base cations (C_B) and an increase in HNO_3 in the lake epilimnion (Figure 4-10). Although SO_4 concentrations changed only slightly in Woods and Panther Lakes during snowmelt, SO_4^{2-} still contributed to the acidification in an indirect manner, namely, by causing long-term alkalinity reductions (as opposed to episodic). Thus, the episodic reduction of alkalinity due to NO_3 is added to the long-term reduction in alkalinity due to SO_4 (see Sections 4.4.2 and 4.4.3). Galloway et al. (1980b) concluded that the primary cause of the increased NO_3 concentration was release from the snowpack. An

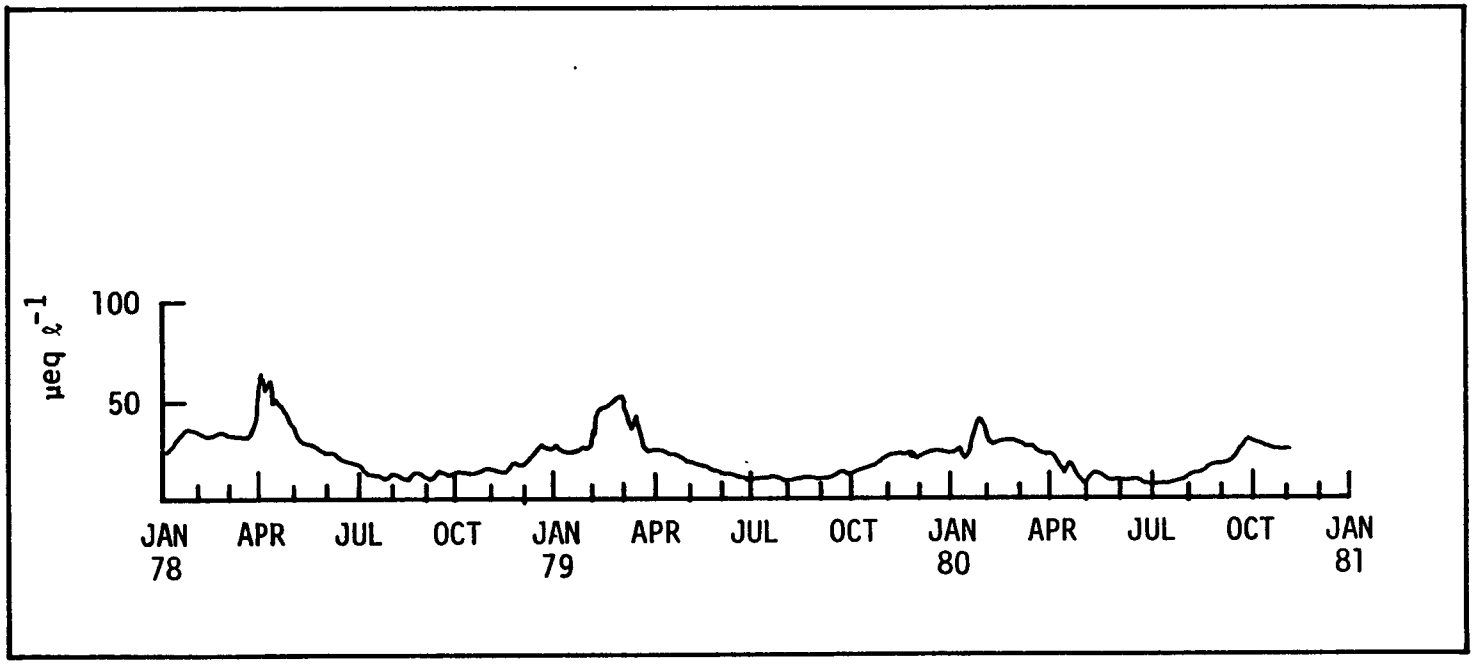

Figure 4-8. The concentration of NO_3 in the outlet of Woods Lake, Adirondack Mountains, NY. Adapted from Galloway and Dillon (1982).

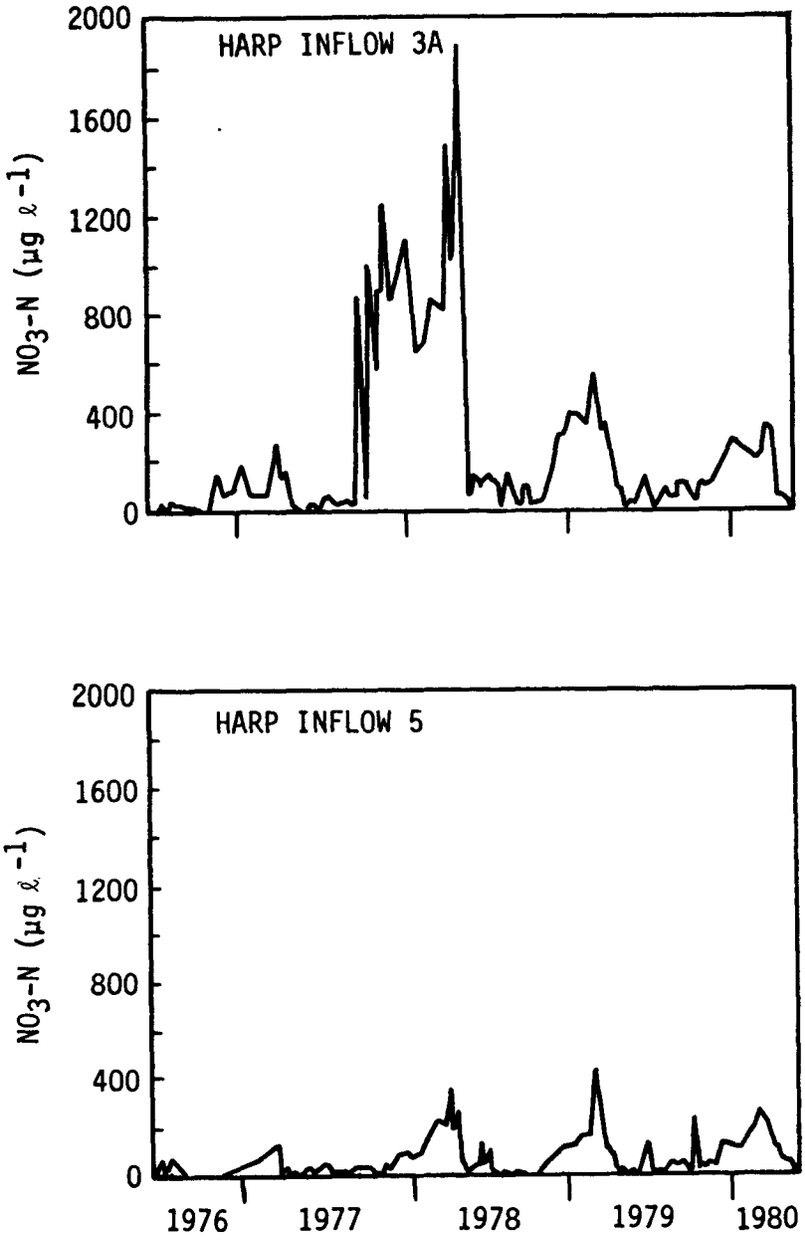

Figure 4-9. Nitrate concentration in inflow 3A and inflow 5 to Harp Lake, Ontario, for a 4-year period (June 1976 - May 1980). Adapted from Galloway and Dillon (1982).

TABLE 4-3. MAGNITUDE OF pH AND ALKALINITY DECREASES OF LAKES AND STREAMS DURING SPRING SNOWMELT (GALLOWAY ET AL. 1980a; 1980b; JEFFRIES ET AL. 1979)

	Prior to Melt		During Melt		Δ	
	pH	Alk $\mu eq\ \ell^{-1}$	pH	Alk $\mu eq\ \ell^{-1}$	pH	Alk $\mu eq\ \ell^{-1}$
Adirondack Mountains, New York, USA						
Panther Lake, 1979	6.6	162	4.8	-18	1.8	180
Woods Lake, 1979	4.8	-38.5	4.5	-42.2	0.3	4.0
Sagamore Lake, 1979	6.1	28.8	4.9	-16.7	1.2	45.5
Southern Ontario, Canada						
Harp Lake #4, 1978	6.6	108	5.4	8	1.2	100
Dickie Lake #10, 1978	4.8	-16	4.5	-32	0.3	16
Paint Lake #1, 1978	5.5	61	5.0	8	0.5	53

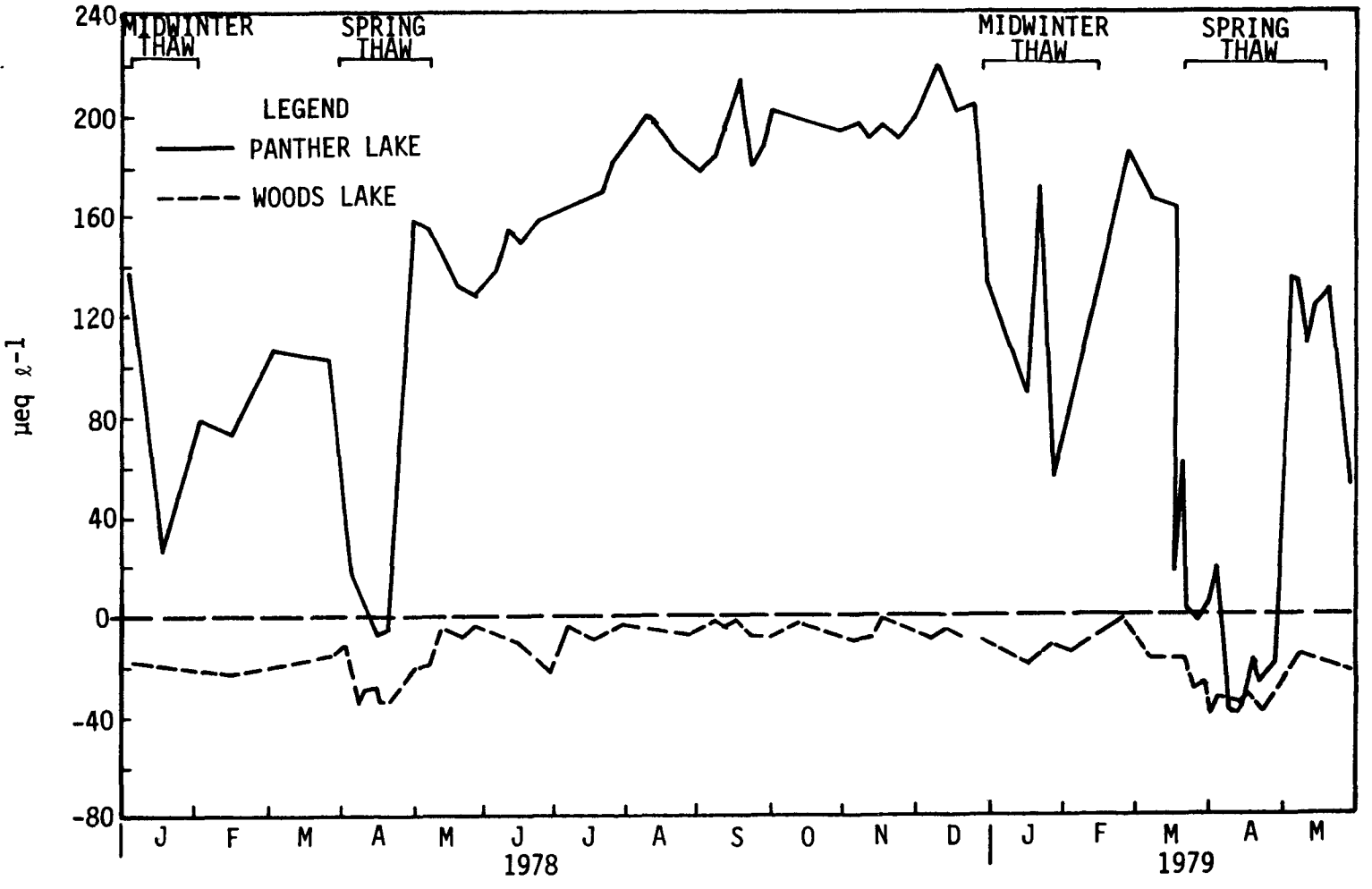

Figure 4-10. Temporal trends in alkalinity at outlets of Woods and Panther Lakes. Adapted from Galloway et al. (1980a).

analysis of two additional snowmelt periods (1978, 1980) supports this conclusion (Galloway et al. 1983b).

The chemical changes that accompany the decreases in pH and alkalinity, however, are not consistent from study area to study area. For example, Jeffries and Snyder (1981) found that SO_4^{2-} levels increase in several streams in the Muskoka-Haliburton area of Ontario at peak flow during snowmelt. On the other hand, Johannessen et al. (1980) reported decreasing SO_4^{2-} during snowmelt in streams in Norway. Three of six streams studied by Jeffries and Snyder (1981) exhibited declining NO_3^- concentrations associated with peak H^+ concentrations, a finding opposite to that of Galloway et al. (1980b) in the Adirondacks.

In summary, during most of the terrestrial biological productivity, SO_4^{2-} is the most important anion causing acidification. However, in winter and in areas with snowpacks, in the spring NO_3 can become more important both in an absolute sense and relative to SO_4^{2-}. The effects of H_2SO_4 and HNO_3, on acidification of aquatic ecosystems are:

- H_2SO_4 causes long-term (decades) alkalinity reductions on a regional basis.
- HNO_3 cause episodic short term (weeks) alkalinity reductions that are in addition to the long-term reductions caused by H_2SO_4.

4.4.2 Short-Term Acidification (J. N. Galloway)

Acidification of lakes and streams during major hydrologic events has been demonstrated in Norway (Gjessing et al. 1976, Henriksen and Wright 1977, Johannessen et al. 1980), Sweden (Oden and Ahl 1970, Hultberg 1977), Finland (Haapala et al. 1975), Ontario (Scheider et al. 1979, Jeffries et al. 1979, Jeffries and Synder 1981) and the northeastern United States (Johannessen et al. 1980, Galloway et al. 1980b, 1983c). The hydrologic event leading to acidification has usually been snowmelt; however, periods of heavy rain have resulted in decreases in alkalinity and pH in at least one case (Scheider et al. 1979).

Episodic events have resulted in decreases in pH of greater than or equal to one pH unit in several reported cases (Table 4-3). For example, the change in pH of Harp Lake Inflow #4 during the snowmelt of 1978 was 1.2 pH units (Jeffries et al. 1979) while the alkalinity decrease was 100 $\mu eq\ \ell^{-1}$. During the 1979 spring snowmelt, the pH and alkalinity decreases in Panther Lake epilimnion were 1.8 pH units and 180 $\mu eq\ \ell^{-1}$, respectively (Galloway et al. 1980a,b). Streams in Ontario, Canada and New York, USA with lower pre-melt pH's and alkalinities had correspondingly smaller decreases (Table 4-3).

Based on the studies cited above and on other available data sets (Leivestad and Muniz 1976, Schofield 1980) it is reasonable to expect

that the pH levels during spring snowmelt may approach pH 4.3 to 4.9. This is the same pH range observed for chronic, long-term acidification (Section 4.4.3; Pfeiffer and Festa 1980, Haines et al. 1983b). The difference is that in episodic acidification, aquatic systems with pH's as high as 7.0 can be acidified to pH < 5.0. While in long-term acidification, aquatic systems with pH's of > 6.5 are, on the average, too well buffered to be acidified to pH < 5.0.

To predict the importance of episodic events in 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. To construct a model to make these predictions, one must know the following:

a) the amount of the chemical of interest and of water stored (mass/area in the watershed, the hydrological pathway that the snowmelt follows (Section 4.3.2.4), and the biogeochemical interactions that occur en route (e.g., ion exchange, biological uptake),

c) the volume of the lake that interacts with the runoff (determined partly by temperature patterns),

d) the chemical composition and amount of the snowmelt relative to the composition and amount of the baseflow.

e) the relative importance of natural vs anthropogenic induced changes in runoff composition during snowmelt.

Factors a, d, and e have been measured in a few studies (e.g., Johannessen et al. 1980, Galloway et al. 1982a). Factors b and c have rarely been investigated. Before a predictive model is available, long-term (i.e., multi-year) measurements of all of these factors are required in a variety of different geographical locations.

4.4.3 Long-Term Acidification (J. N. Galloway)

Affected sensitive aquatic systems must have three characteristics. First, they must have waters with alkalinities < 200 $\mu eq\ \ell^{-1}$ (Figures 4-4 to 4-7). Second, they must receive acidic deposition (pH $\leq$ 4.5; Figure 4-11). Third, they must be shown to have been acidified by acidic deposition. Overlaying Figures 4-4 and 4-7 (sensitivity to acidic deposition) on Figure 4-11 (occurrence of acidic deposition) suggests regions that potentially may have been impacted. Documentation that aquatic systems have been acidified (lost alkalinity) by acidic deposition has been provided by three techniques: (1) analysis of temporal trends in alkalinity and pH, (2) paleolimnological analysis, and (3) investigation of the importance and source of SO_4 in aquatic systems.

Studies that have used the first technique, historical pH/alkalinity data, to identify waters acidified by acidic deposition are reviewed in

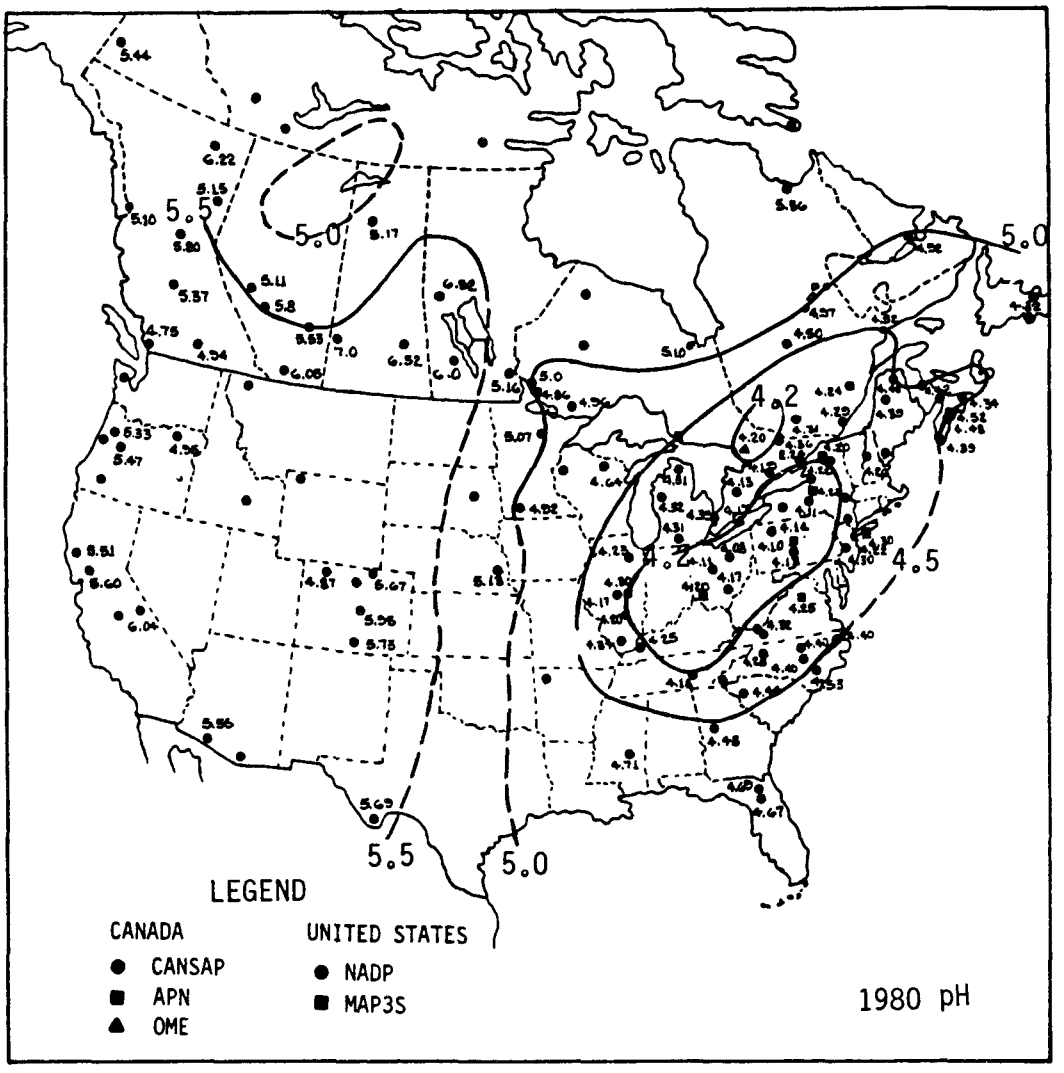

Figure 4-11. pH from weighted average hydrogen concentration for 1980 for wet deposition samples (reproduced from Barrie et al. 1982)

Section 4.4.3.1. In some of the studies, problems exist with the comparison of old data to recent data. The errors associated with the comparison may preclude an absolute statement that each of the aquatic systems has been acidified. However, the fact that many studies point to decreased alkalinity is strong circumstantial evidence for acifidication by acidic deposition.

Supporting this circumstantial evidence is the analysis of diatoms in lake sediment cores. While such analysis has been used successfully in Scandinavia the technique is still being developed for use in the United States (Section 4.4.3.2).

A technique for implicitly circumnavigating the problems of incomplete or imprecise trend data has been proposed by Galloway et al. (1983c). The approach is based on considerations of solution electrical neutrality ($\Sigma c_i = \Sigma a_i$ where c_i is the normality of the ith cation and a_i is the normality of the ith anion). It is most applicable to clear water lakes and streams (no organic ions) with no source of sulfur in the bedrock of the drainage basins. Marine aerosol content corrections should also be performed.

The basis for the technique is that the concentration of SO_4^{2-} in clear water lakes and streams has increased due to atmospheric deposition. With the increase in SO_4^{2-} has to come an increase in a positive ion, H^+, Ca^{2+}, Mg^{2+}, etc. If H^+ increases, the aquatic system is acidified (i.e., alkalinity decreases). If the concentration of Ca or another non-protolytic cation increases, only, then no loss of alkalinity occurs. For example, Figure 4-12 shows the two extremes with chemical changes that can occur to an aquatic system when the SO_4 concentration increased by a factor of five. In one extreme, the increase in the SO_4 anion is balanced by an increase in the non-protolytic base cations (Alternative I, Figure 4-12). In the second extreme, the increase in SO_4 is balanced by an increase in H^+, which causes a reduction of alkalinity (Alternative II, Figure 4-12). Since these are extremes, the real world lies somewhere in between and depends on the characteristics of the soil and the hydrologic pathway. In sensitive systems (bedrock and soil with low ANC and short hydrologic path lengths), Alternative 2 appears to be a closer approximation to the process that has occurred. As support of this Henriksen (1982), in an analysis of long-term time series for the concentrations of Ca and Mg over gradients of acidic deposition, concludes the increases in SO_4 in lakes are balanced by increases in H^+ ($\geq$ 60 percent) and increases in base cations ($<$ 40 percent). Therefore, in aquatic systems with a predominant atmospheric source of SO_4^{2-} and with alkalinities less than 200 eq $^{-1}$, the increases in SO_4^{2-} will cause decreases in alkalinity, i.e., acidification, although the magnitude/significance of the decrease is dependent on watershed characteristics.

The beginning of this section stated that affected sensitive systems had three characteristics--they were sensitive, receiving acidic deposition, and had been shown to be acidified. Using the information on temporal trends in Section 4.4.3.1.2 and studies on the role of

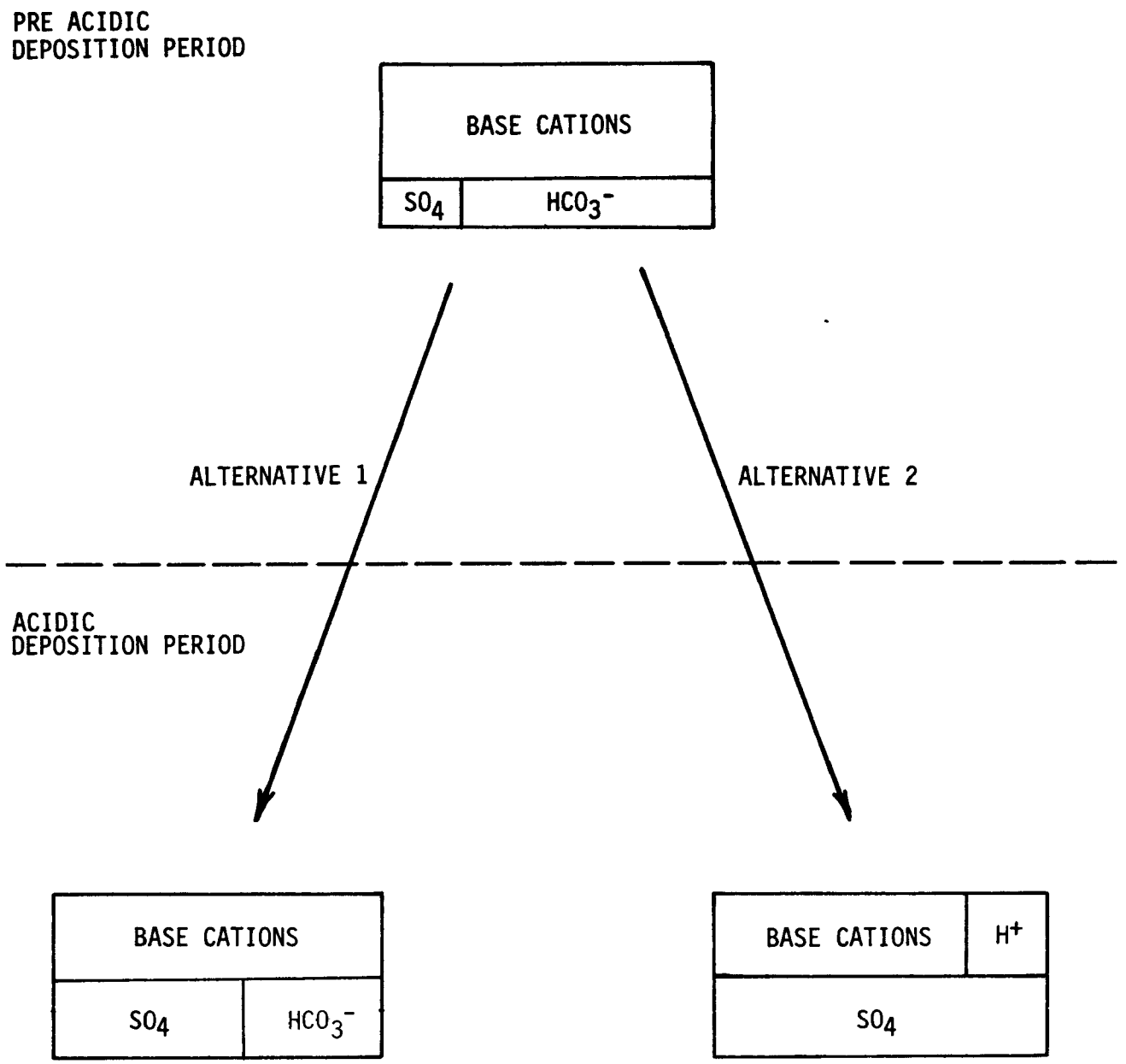

Figure 4-12. Two extremes for the response of aquatic systems to a 5-fold increase in SO_4. The length of the boxes relates to $\mu eq\ \ell^{-1}$.

Figure 4-13. The response of aquatic systems to atmospheric deposition of acidic and acidifying substances from local or regional (long-range) sources. The numbers refer to the following references, which conclude that acidic deposition has caused acidification of aquatic systems.

1. Gordon and Gorham (1960), Beamish et al. (1975), Dillon et al. (1978)

2. Bobee et al. (1982)

3. Watt et al. (1979, 1983, Wiltshire and Machell (1981)

4. Davis et al. (1978), Norton et al. (1981b)

5. Schofield (1976c), Pfeiffer and Festa (1980), Galloway and Dillon (1982), Galloway et al. (1983c)

6. Shaffer and Galloway (1983)

7. Gordon and Gorham (1963)

8. A. H. Johnson (1979)

9. Burns et al. (1981), Johnson et al. (1981)

The letters refer to the following references where possible acidification of aquatic systems has been studied but not found.

A. McCarley (1983)

B. Schindler and Ruszczynski (1983)

C. Logan et al. (1982)

D. Zeman (1973), Feller and Kimmins (1979)

E. Melak et al. (1983)

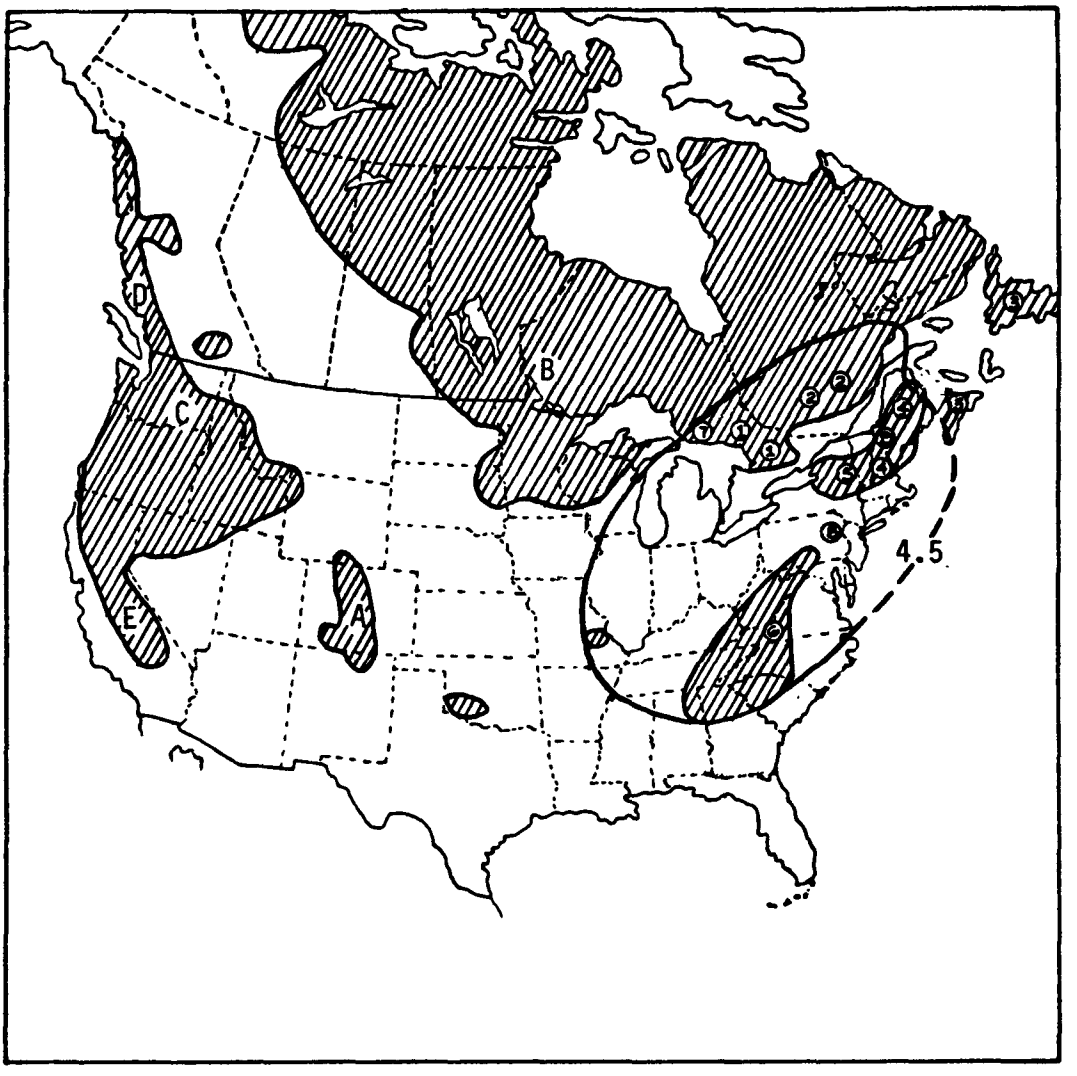

Figure 4-13.

atmospheric sulfur in aquatic systems, Figure 4-13 indicates (by numbers) the areas that have been shown to be acidified. All numbers fall in sensitive areas receiving acidic deposition. In addition to the studies showing where acidification has occurred, the letters on Figure 4-13 represent studies where the atmospheric sulfur has been shown not to have acidified the aquatic system because of its low concentration.

The maximum degree of acidification of freshwaters by acidic deposition depends on the total increase in acid anions (primarily SO_4^{2-}, Section 4.4.1). For each $\mu eq\ \ell^{-1}$ increase in SO_4^{2-}, the maximum loss of alkalinity is 1 $\mu eq\ \ell^{-1}$ (Section 4.4.1). Studies of SO_4 in aquatic systems across depositional gradients (Figure 4-2), and sulfur budget studies for watersheds and lakes (Galloway et al. 1983c, Dillon 1981) and determination of excess SO_4^{2-} in aquatic systems (Likens et al. 1977, Harvey et al. 1981, NRCC 1981) indicate that the maximum increase in SO_4, and therefore maximum loss of alkalinity in aquatic systems as a result of acidic deposition, is 100 $\mu eq\ \ell^{-1}$. The actual loss will certainly be less and will depend on the availa- bility of base cations in terrestrial systems receiving acidic deposi- tion. This maximum alkalinity decrease is merely a boundary condition that can be compared to measured or estimated degrees of acidification.

4.4.3.1 Analysis of Trends based on Historic Measurements of Surface Water Quality (M. R. Church)--

4.4.3.1.1 Methological problems with the evaluation of historical trends. In assessing the effects of acidic precipitation on the chemistry of surface waters, investigators have searched laboratory records and the literature for historical data with which to compare present day measurements. The three water chemistry variables most widely cited in this regard are pH, conductivity, and alkalinity (Section 4.2.2). A discussion of how methodology for their determination has changed with time and the comparability of historical and current data are presented here.

4.4.3.1.1.1 pH

4.4.3.1.1.1.1 pH-early methodology--Many of the early measurements of surface water pH in areas of North America and Scandinavia were made colorimetrically with acid-base indicators. Materials for visual colorimetry are inexpensive and readily portable and, thus, highly amenable to use in rugged, remote field locations, often the site of "acidification" problems and studies. An excellent discussion of acid-base colorimetric indicators is presented by Bates (1973), who recommends the works of Kolthoff (1937) and Clark (1928) for even more exhaustive accounts, descriptions, and discussions of colorimetric indicator use.

Acid-base indicators are weak acids or bases that change color with the loss or gain of a proton (or protons). Such behavior may be represented by the simplified equilibrium formulation

$$HIn\ (Color\ A) \rightleftarrows In^{-}\ (color\ B) + H^{+}\ . \qquad [4\text{-}10]$$

Indicators are used to measure the pH of an unknown aqueous solution as follows. When the optical characteristics or "color tone" of an unknown (with indicator added) match the color tone of a standard reference solution (to which indicator has also been added), then the two solutions are assumed to have the same pH. Sometimes the color tone of the unknown solution plus indicator is matched with calibrated colored discs, each indicating a different pH. The band of pH over which the color change of an indicator is detectable (by a colorimeter or by the human eye) is called the transformation range. For visual color comparisons using two-color indicators, transformation range is generally on the order of two pH units (Golterman 1969, Bates 1973). As Haines et al. (1983a) noted the best results are achieved near the mid-point of the transformation range of each indicator.

The key assumption in indicator use is that identical color tone of an unknown and a standard solution of the same temperature to which indicator has been added implies identical pH, under some circumstances, however, as Bates (1973) explains, this is not true.

One reason this assumption may be false can be explained with the aid of the equation

$$pa_H = pK_{HIn} + \log \frac{\alpha}{1-\alpha} + \log \frac{\gamma_{In}}{\gamma_{HIn}} \qquad [4\text{-}11]$$

where pa_H is defined by Equation 4-2, pK_{HIn} is the thermodynamic dissociation constant of the acid form of the indicator, is the fraction of the indicator in the form In, and γ_{In} and γ_{HIn} are the activity coefficients of the dissociated and undissociated forms of the indicator, respectively. Color matching (by eye or instrument) indicates only that the term $\log \alpha/1-\alpha$ is the same for the unknown and the standard solutions. However, if the activity coefficient ratio (the last term in Equation 4-11) of the indicator is not the same in both the standard and the unknown solutions, the pH of the solutions will not be the same when the colors are identical. This is called the "salt error" and can be estimated by comparing the "true" or electrometric (hydrogen electrode) pH of a series of solutions having different ionic strengths with their respective values of pH as implied by use of the indicator (Bates 1973). Salt effects can be minimized by adjusting the ionic strengths of the buffer solution or the unknown solution so they are nearly equal. Such adjustments, however, may cause changes in the reference or unknown pH, introducing further uncertainties.

Another potential source of error is that the addition of an indicator to a solution may actually change the pH of that solution. This is most likely in poorly buffered waters, such as those readily susceptible to acidification. To overcome this problem the pH of the indicator solution can be adjusted so it is close enough to the pH of the unknown solution that no pH change occurs when the two are mixed. This

can be accomplished by a trial and error technique using portions of the sample to be determined plus a variety of indicators.

Bates (1973) indicates that when the above cautions are observed and correction or adjustment is made for salt effects, an accuracy and a precision of 0.05 to 0.1 pH unit can be expected "in properly standardized routine measurements of buffered solutions." It is likely that colorimetric determinations of pH made in the field, often under adverse conditions and often on poorly buffered solutions, probably seldom approach such accuracy or precision (Boyd 1977, 1980; Haines et al. 1983a). Indeed, many details (including exact methodology) of historical pH measurements made with indicators are often "lost in antiquity," lending further uncertainty to their reliability. Fortunately, many of the investigators of acidification trends in surface water pH values appreciate these considerations (e.g., Wright 1977, Overrein et al. 1980).

4.4.3.1.1.1.2 pH-current methodology--Today, most pH measurements are made electrometrically (potentiometrically) both in the laboratory and, with the advent of more reliable portable pH meters, in remote field locations as well.

The "practical" or "operational" pH was defined in Equation 4-2 (see Section 4.2.2.1). To define standard potentials and set the pH scale, cells of the following type are used:

$$Pt;\ H_2(g),\ Soln.\ X \mid KCl(satd.) \mid \text{reference electrode.} \qquad [4\text{-}12]$$

The reference electrode is usually either a calomel or silver-silver chloride electrode (Bates 1973, Durst 1975), which is a primary cell. For most day-to-day laboratory measurements and all field measurements researchers use secondary cells in which the hydrogen gas electrode is replaced by a glass electrode. The proper use of commonly available commercial pH assemblies (cell plus meter circuitry) has been discussed in many books, journal articles, and laboratory manuals (e.g., Feldman 1956, Golterman 1969, Bates 1973, Durst 1975, American Public Health Association 1976, Westcott 1978, Skougstad et al. 1979).

An important potential source of error in electrometric pH measurements of surface waters is the residual liquid-junction potential. Liquid-junction potentials arise at the point of contact of the reference electrode and the solution being tested. Liquid-junction potentials are a function of, among other things, the ionic strength of the solution being tested. Therefore, the liquid-junction potential formed in a high ionic strength medium (e.g., buffer) is different from that formed in a low ionic strength medium (e.g., dilute acidification-prone surface water). The difference between these liquid-junction potentials is the "residual liquid-junction potential" (Bates 1973). Such a potential can introduce errors on the order of 0.04 pH unit when ignored in measurements of dilute precipitation samples (Galloway et al. 1979). This type of error can be minimized by equalizing the ionic strength of the test and reference solutions. Three ways to do this are to 1) add inert salts

(e.g., KCl) to the dilute test solution (this may introduce impurities, thus altering the pH), 2) dilute the standard solution (which alters its pH--a correction must be applied), or 3) use dilute strong acid standards (these are not normally reliable pH standards--they must be frequently calibrated by titration) (Bates 1973, Galloway et al. 1979).

Another potential source of error in electrometric pH measurements of dilute solutions is the streaming potential. Errors arise when measurements are made on dilute solutions while they are flowing or being agitated. Errors of this sort as large as 0.5 pH unit have been reported for precipitation samples (Galloway et al. 1979). To eliminate such error, measurements should be made only on quiescent solutions.

Under rigorous conditions in a properly equipped laboratory, routine electrometric pH measurements can probably approach, at best, an accuracy and a precision of $\pm$ 0.02 pH unit. Most field measurements of the pH of dilute surface waters probably have an accuracy and precision of no better than $\pm$ 0.05 unit.

4.4.3.1.1.1.3 pH-comparability of early and current measurement methods--Inasmuch as both colorimetric and electrometric measurements (using secondary cells) are based on operational or practical pH (designated by the primary pH cell and scale), the methods are directly comparable. Attention has been, and should continue to be, placed on the limits of reliability of the measurement methods as discussed above.

4.4.3.1.1.1.4 pH-general problems--Independent of the methodology employed, several factors can influence pH measurements of surface waters and the use of such measurements to estimate the degree of acidification over time. Principal among these factors is the variation in the pH of surface waters over relatively short time intervals. The most dramatic and important "short-term" changes in surface water pH values are those seasonal changes associated with spring snowmelt and ice-out periods, during which pH may drop sharply due to release of acid held in ice and snow (Wright 1977, Overrein et al. 1980, Galloway et al. 1980b, Hendrey et al. 1980a). Surface water pH values during the rest of the year may be considerably higher than those during snowmelt. Obviously, time of year must be taken into account when we compare past and present pH measurements in an effort to assess acidification.

Less important but potentially meaningful effects are pH changes associated with the uptake and release of CO_2 and/or HCO_3^- by aquatic plants. Most lakes studied in conjunction with acidification problems are usually oligotrophic, and these changes are probably small. Yet another factor to consider (especially in streams) is the occurrence of local sources of groundwater high in CO_2. One method sometimes used to account for variable CO_2 concentrations is to report the pH value after a sample has been thoroughly agitated to equalize its CO_2 partial pressure with that in the laboratory. It must be noted, however, that the CO_2 concentration in a laboratory can vary considerably from day to day and is nearly always well above that commonly considered to be the global mean (Church 1980). A number of methods may be employed to

overcome this problem and to insure comparability between laboratories and within a laboratory on a day to day basis. These methods include equilibrating solutions with outside air or determining the partial pressure of CO_2 in solutions or in the laboratory atmosphere. Better yet would be to equilbrate all samples by bubbling with bottled air of a known and standardized CO_2 content.

4.4.3.1.1.2 Conductivity

4.4.3.1.1.2.1 Conductivity methodology--The apparatus for measuring conductivity consists of a cell of two electrodes (often platinum) and a Wheatstone bridge. The latter is used to balance the resistance of standard or unknown solutions in which the cell is immersed. Solutions of KCl are used to standardize the instrument by calculation of the cell constant. Important corrections due to temperature variation are also required. Conductivity is routinely reported as $\mu mho\ cm^{-1}$ at 25.0 C. Detailed instructions for the measurement of the conductivity of surface water samples can be found in standard laboratory manuals (e.g., Golterman 1969, American Public Health Association 1976, Skougstad et al. 1979). The precision of conductivity measurements of surface water samples seems inversely related to the sample conductivity, with relative standard deviations being as great as 10 percent at levels of conductivity as low as those often reported in studies of acidification of surface waters (American Public Health Association 1976, Skougstad et al. 1979). Inasmuch as this figure pertains to measurements made under laboratory conditions it is to be expected that measurements made with portable battery-powered conductivity meters in the field would be less precise.

4.4.3.1.1.2.2 Comparability of early and current measurement methods--Routine measurements of conductivity are always made with the type of apparatus described above, so historical and recent data should be roughly comparable, if the instrumentation has been properly calibrated and used. Data published in the literature concerning otherwise comparable lakes lying in acidic and unaffected areas show that acidified lakes tend to have higher conductivities (Wright and Gjessing 1976, Dillon et al. 1979), most likely reflecting the higher hydrogen (and to a much lesser extent sulfate and nitrate) ion concentrations found in those lakes. Continuous monitoring of some surface waters in southern Norway has shown increases in conductivity over a period of decades coinciding with decreases in pH and increases in transparency of lakes (Nilssen 1980), all changes associated with effects of acidic deposition.

It must be noted here that many factors, not just inputs of acids, may cause increases in the concentrations of dissolved salts, and thus conductivity, in surface waters. In fact, increases in conductivity certainly may be associated with both increases and decreases in pH and alkalinity. For this reason observed increases in conductivity should not be used by themselves to infer that acidification has occurred.

4.4.3.1.1.2.3 General problems--Conductivity can be expected to vary seasonally (e.g., it may be much higher during snowmelt than at

other times). Therefore, comparison of historical and recent measurements to assess acidification should take into account time of year when the measurements were made. Temporary changes in conductivity of surface waters may also occur during rainfall events. In short, any factor that alters ionic concentrations will alter conductivity.

4.4.3.1.1.3 Alkalinity. Procedures routinely used to determine ANC of surface waters have changed significantly over the years, so estimating acidification as the decrease in ANC with time may be extremely difficult (Dillon et al. 1978, Ontario Ministry of the Environment 1979, Zimmerman and Harvey 1979, Jeffries and Zimmerman 1980, National Research Council of Canada 1981).

4.4.3.1.1.3.1 Early methodology--Historically, acidimetric titrations have usually been performed to an endpoint of pH 4.5 determined electrometrically or to an end point determined by a colorimetric indicator (usually methyl orange) or mixed indicators (e.g., bromcresol green-methyl orange). ANC measured in this way has been termed total fixed endpoint alkalinity or TFE (Dillon et al. 1978, Ontario Ministry of the Environment 1979, Jeffries and Zimmerman 1980). These procedures can lead to two types of problems.

First, the assumption that the endpoint of pH 4.5 is close to the equivalence point for titration of the predominating inorganic carbon species is true only for samples with relatively high total inorganic carbon content (i.e., ~ 2.5 mM total inorganic carbon; Golterman 1969) and ANC. For samples with relatively low total inorganic carbon and ANC (like those usually considered in studies of surface water acidification) the titration endpoint should be at a higher pH (e.g., near pH 5.0 for total inorganic carbon of ~ 0.2 mM) to approximate the equivalence point (Golterman 1969, American Public Health Association 1976, Dillon et al. 1978, Ontario Ministry of the Environment 1979, Zimmerman and Harvey 1979, Jeffries 1980, National Research Council of Canada 1981). Methods currently in routine use account for this fact.

Second, unless detailed notes have been kept of titrations to some endpoint determined with a colorimetric indicator, it may be impossible to determine exactly what the pH was at the finish of the titration. For example, the indicator methyl orange has a pKa of 3.5. The transition range for this indicator is usually given as pH 4.5 to 3.1 (e.g., Bell 1967, Golterman 1969), over which range the color changes from yellow to orange to pink to red. Careful analysts prepare standard solutions of known pH to which indicator is added so they can tell by comparison to the sample being titrated precisely when the titration has reached the pH that they have a priori selected as the endpoint. Unfortunately, many early titration data are accompanied by notations only to the effect that such-and such an indicator was used. In such cases it may be impossible to determine the endpoint pH of the titration.

4.4.3.1.1.3.2 Current methodology--Determining ANC of surface water samples is now commonly done by acidimetric titration to the (HCO_3^- - H^+) equivalence point (inflection point) of the titration curve.

This point can be readily determined by using differential electrometric titration methods or Gran's (1952) procedure (see Stumm and Morgan 1981). ANC determined in this fashion is termed total inflection point alkalinity or TIP (Dillon et al. 1978, Ontario Ministry of the Environment 1979, Jeffries 1980).

As discussed previously in Section 4.2.2.3 (and later in Section 4.6.3.2) organic compounds may contribute significantly to ANC in waters low in total inorganic carbon and of low pH. This contribution becomes important in the pH range below that of the (HCO_3^- - H^+) equivalence point (see Bisogni and Driscoll 1979, Wilson 1979). Because of this fact it is likely that most TFE alkalinity titrations fail to measure any possible contribution of organics to the buffering of natural waters. Gran's procedure in which the solution is titrated to quite low pH values and total ANC determined by linear back extrapolation is able to account for such buffering, should it exist.

4.4.3.1.1.3.3 Comparability of early and current measurement methods--As stated by the Ontario Ministry of the Environment (1979)

> "Almost all past water quality surveys conducted on Precambrian Shield waters have employed a TFE method [note added: i.e., to ~ pH 4.5] and hence, unrealistically high estimates of acid buffering capabilities will be drawn from the data. This fact is true no matter whether an extremely sensitive potentiometric TFE procedure was used or an insensitive field titration (indicator, eye dropper titrant addition, etc.) method was employed. The most appropriate use of the TFE alkalinity data obtained from past surveys is (a) to define water systems which are not acid susceptible, (b) to suggest where further sampling is warranted, and (c) in the case of high quality potentiometric data, to infer relative levels of susceptibility for lakes in the 0-20 mg ℓ^{-1} ($CaCO_3$) (0-400 μeq ℓ^{-1}) alkalinity range. The data base on "absolute" or correct water alkalinity values is very small; there is a great need for improving this situation as quickly as possible."

Discussions of the differences between TFE and TIP have been presented by Zimmerman and Harvey (1979), Jeffries (1980), and the National Research Council of Canada (1981). As pointed out in some detail by the National Research Council of Canada (1981), a rigorous correction may be made from TFE to TIP in the situation where (1) TFE has been precisely determined to a known endpoint pH and (2) the total inorganic carbon concentration of the sample is known (or can be closely estimated). Unfortunately, in most cases TFE has historically been determined using colorimetric titration procedures, and total inorganic carbon concentrations are not known. Conversion of such values to accurate TIP alkalinities has proven to be nearly impossible (Jeffries 1980). Obviously, such difficulties exist in comparing past and present data regardless of whether the data come from Canada, Scandinavia, or the United States.

As always, when one compares samples taken years apart care must be taken so that short-term variability in ANC (e.g., due to snowmelt,

rainstorms, uptake of HCO_3^- by aquatic plants) will not distort evaluations of long-term trends.

4.4.3.1.1.4 Summary of measurement techniques. Each of the three types of measurements (i.e., pH, conductivity, alkalinity) discussed here has something to recommend its continued use in the study of surface water 'acidification'. Conductivity seems to be the least informative of the measurements, but it is likely that historical measures of this variable are the most accurate and consistent (with current data) of the measures discussed. Although in comparison to current pH data historical measures of pH are somewhat unreliable, a relative wealth of pH measurements exists in comparison to early data for conductivity and alkalinity. As discussed above, early measurements of alkalinity are often of little use due to procedural problems. In addition, they are relatively scarce. Knowledge of the alkalinity of surface waters and changes in alkalinity with time, however, are important considerations in the study of 'acidification'.

It is clear that in relation to historical data no overall best analytical measurement of surface water chemistry exists for evaluating acidification of lakes and streams. The authors recommend that pH, alkalinity, and conductivity should continue to be routinely measured in surface water acidification studies, taking into careful consideration the detailed sampling and analytical techniques outlined in the articles and manuals referenced above.

4.4.3.1.2 Analysis of trends.

4.4.3.1.2.1 Introduction. Numerous studies of temporal trends in the pH, alkalinity, or conductivity of selected North American surface waters have appeared in the peer reviewed scientific literature or in readily available technical reports. The following is a brief review of the material presented in these reports and articles.

In considering each of these studies the critical reader should bear in mind all of the potential problems of bias (in both sampling and chemical analysis) that may or may not have been taken into account, reported, and discussed by the principal investigators. As an example of the kinds of problems that may exist with regard to unbiased sampling, Figures 4-10 and 4-14 serve to illustrate the kinds of seasonal variations that may occur in alkalinity and pH at the outlets of Adirondack lakes. Not shown in these figures are the kinds of shorter term variations that may occur over a day due to biological activity or the longer term variations that may result from extended periods of either drought or higher than usual precipitation. Given the kinds and ranges of variation that occur it is clear that significant potential often exists for sampling bias and resulting misinterpretation of observed temporal "differences" in pH or alkalinity. This potential is, of course, greatest when data from two discrete points in time are compared rather than a more complete time series of data.

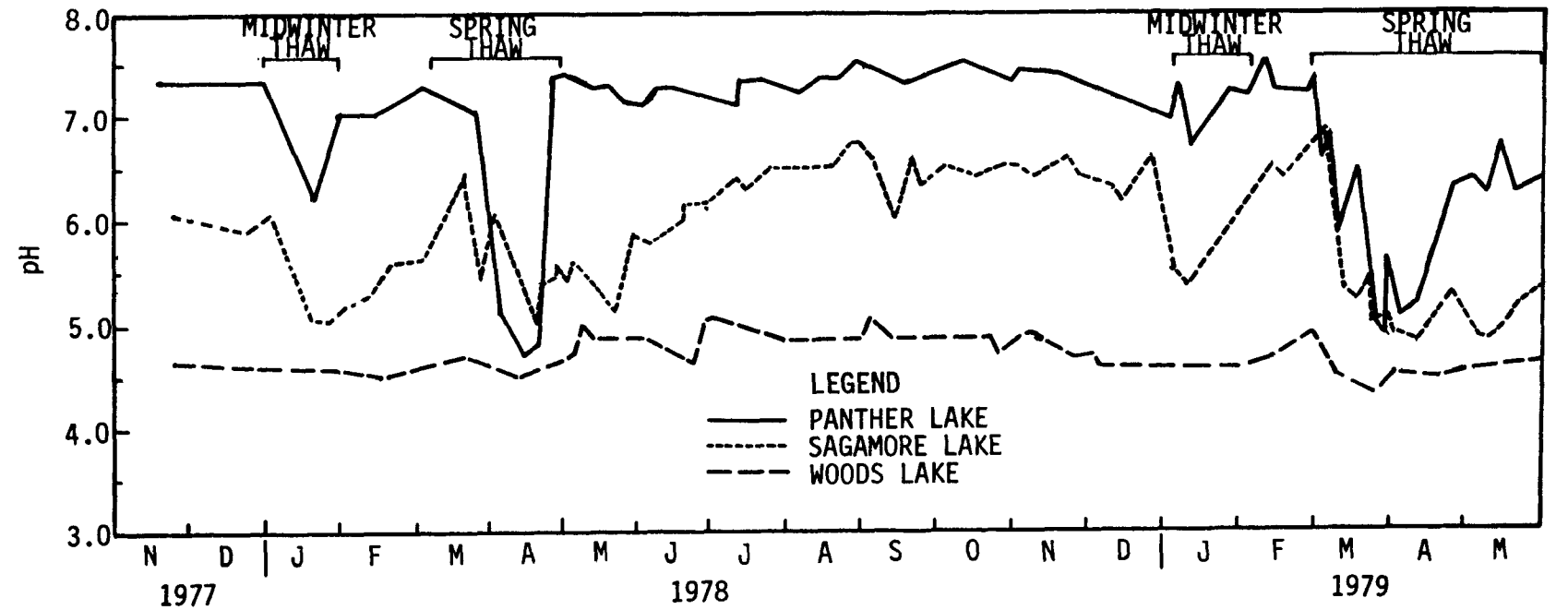

Figure 4-14. Temporal trends in pH at outlets of Woods, Panther, and Sagamore Lakes. Adapted from Galloway et al. (1980b).

Each of the following reviews presents the pertinent information given by the authors in their original manuscripts. The authors may possess considerably more information concerning their research than they were able to present in their original publications. The location and evaluation of such unreported information is clearly outside of the scope of this review. Only that information presented in the original technical report or journal article is reviewed here. In some cases the information presented by the original authors does not demonstrate "beyond a shadow of a doubt" that their sampling was completely unbiased. But this does not mean then that their sampling was necessarily biased, and it is not the duty or intent of this reviewer to focus unduly on such omissions or to speculate irresponsibly on their importance. Major critical discussions are presented here only on important points of reasonable debate for which sufficient information was presented by the authors.

4.4.3.1.2.2 Canadian studies

South-Central Ontario (Beamish and Harvey 1972).

Beamish and Harvey (1972) were the first investigators to present evidence of decreases in lake pH in North America attributable to acidic precipitation. They studied chemistry changes and loss of fish populations in lakes of the La Cloche Mountains, an area that has quartzite geology and that receives acidic precipitation. The acidity of the precipitation is directly attributable to smelters at Sudbury, Ontario, 65 km to the northeast. During the period of their study (1969-1971) Beamish and Harvey found the pH of rainwater ranged from 3.6 to 5.5 and the pH of melted snow ranged from 2.9 to 3.8.

The authors began their study with Lumsden Lake, a small oligotrophic lake in a watershed devoid of either human habitation or industry. The study was then expanded to include a total of 150 lakes in the region. For some of these other lakes earlier (pre 1968) data were available from studies performed by the Ontario Department of Lands and Forests.

In all of the studies, samples were taken between April and November (most often in August and September). Beamish and Harvey (1972) measured pH in the field with a Sargent-Welch Model PBL portable pH meter standardized at pH 7.0 and 4.0 before and after each series of readings. Prior to 1970 they repeated their pH measurements on shore with a Fisher Model 310 expanded scale pH meter. All measurements were made promptly in the field to avoid the kind of pH changes they observed with time (probably due to CO_2 degassing). In studies prior to 1968 the Ontario Department of Lands and Forests measured pH with a Hellige comparator (Beamish and Harvey 1972). No other details of sampling or analytical procedures were given.

Beamish and Harvey (1972) found "little vertical stratification" in pH in Lumsden Lake and nearby George Lake and only "some seasonal variation." Their principal finding with regard to lake chemistry was

that for lakes in and to the east of the La Cloche Mountains pH had decreased with time (Table 4-4). For 11 lakes sampled prior to 1961 H^+ concentration had increased 10- to 100-fold by 1971. The average change in the mean annual pH for all 22 lakes was minus 0.16 unit. The authors found that 26 lakes in a region just north of the La Cloche Mountains were less acidic and had apparently experienced lesser decreases in pH (Table 4-5). They attributed these facts, at least partially, to the presence of outcrops of carbonate-bearing rocks in that area. The authors concluded that "the increases in acidity appear to result from acid fallout in rain and snow. The largest single source of this acid was considered to be the sulfur dioxide emitted by the metal smelters of Sudbury, Ont." (Beamish and Harvey 1972).

South-Central Ontario (Beamish et al. 1975).

Beamish et al. (1975) reported on the relationship between various fish populations and water chemistry in George Lake, Ontario, for the period 1967-1973. In that report they cited evidence for a trend of pH decrease in the lake.

Over the period 1968 to 1973 they measured pH electrometrically in the field or in the laboratory within 12 hours of sampling. From a regression of 28 such measurements plus one measurement "using a dye indicator method" in 1961 they arrived at a linear decline in lake pH of 0.13 unit per year, on the average. The correlation coefficient for this regression was 0.85. Discarding the 1961 data point, they arrived at a linear mean annual decline of 0.13 with a correlation coefficient of 0.65 (Beamish et al. 1975). In their report they provided no other details of their sampling methods or analytical procedures.

South-Central Ontario (Dillon et al. 1978).

As part of a study on the effects of acidic precipitation on lakes in south-central Ontario, Dillon et al. (1978) collected alkalinity data for four lakes for which some historical data existed. These lakes were Walker Lake, Clear Lake, Harp Lake, and Jerry Lake. Precipitation in the region has a mean pH between 3.95 and 4.38.

The authors sampled Clear Lake three times in the period June-August 1977 and found TIP alkalinities ranging from 2 to 25 ($\mu eq\ \ell^{-1}$). This was a decrease from a TIP alkalinity of 33 ($\mu eq\ \ell^{-1}$) reported for the year 1967 by Schindler and Nighswander (1970).

Dillon et al. (1978) reported TFE alkalinities (measured potentiometrically to pH 4.5) of 153 ($\mu eq\ \ell^{-1}$) for the epilimnion and 130 ($\mu eq\ \ell^{-1}$) during a non-stratified period for Walker Lake in 1976. These were decreases from TFE values of approximately 180 ($\mu eq\ \ell^{-1}$) during 1974 (from unpublished data of the Ontario Ministry of the Environment) and approximately 400 ($\mu eq\ \ell^{-1}$) during 1971 (several samples on a single date; Michalski 1971).

The authors did not find any noticeable differences between the TFE alkalinities of Harp Lake (137 to 152 $\mu eq\ \ell^{-1}$) or Jerry Lake (137

TABLE 4-4. EARLIEST AND 1971 pH MEASUREMENTS ON LAKES IN AND TO THE EAST OF THE LA CLOCHE MOUNTAINS (BEAMISH AND HARVEY 1972)

Lake	Township	Date	pH	Avg annual change in pH units
Broker[a]	Attlee	Sept/61[b]	6.8	-0.21
		Aug/71	4.7	
Carlyle	Carlyle	May/68[b]	5.5	-0.13
		Aug/71	5.1	
David	Stalin and Goschen	Aug/61[b]	5.2	-0.09
		Aug/71	4.3	
Freeland	Killarney	June/69	5.2	-0.20
		Sept/71	4.8	
George	Killarney	Sept/61[b]	6.5	-0.18
		Sept/71	4.7	
Grey[a]	Sale	Sept/59[b]	5.6	-0.13
		Sept/71	4.1	
Johnnie	Goschen and Carlyle	Aug/61[b]	6.8	-0.20
		Aug/71	4.8	
Kakakise	Killarney	June/68[b]	6.0	-0.10
		Aug/71	5.7	
Killarney	Killarney	Aug/69	4.5	-0.05
		Sept/71	4.4	
L & F 24	Carlyle	Sept/67[b]	6.0	-0.25
		Aug/71	5.0	
Lumsden	Killarney	Sept/61[b]	6.8	-0.24
		Aug/71	4.4	
Lumsden II	Killarney	June/69	4.6	-0.30
		Oct/71	4.0	
Lumsden III	Killarney	June 69	4.6	-0.30
		Oct/71	4.0	
Mahzenazing[a]	Carlyle and Humboldt	Sept/61[b]	6.8	-0.15
		Aug/71	5.3	
Nellie	Roosevelt	Sept/69	4.5	-0.05
		Aug/71	4.4	
Norway	Killarney	Sept/69[b]	4.5	0.00
		Aug/71	4.5	
O.S.A	Killarney	/61[b]	5.6	-0.12
		Sept/71	4.3	
Spoon[a]	Kilpatrick and Humboldt	Sept/61[b]	6.8	-0.12
		Aug/71	5.5	
Sunfish[a]	Humboldt	Sept/61[b]	6.8	-0.24
		Apr/71	4.4	
Threenarrows	Killarney, Roosevelt, and Stalin	Nov/69[b]	5.2	0.00
		Aug/71	5.2	

TABLE 4-4. CONTINUED

Lake	Township	Date	pH	Avg annual change in pH units
Tyson[a]	Sale and Humboldt	Aug/55[b]	7.4	-0.16
Unnamed Lake[a] (46°01'30"NS1°24'W)	Killarney	June/69 Oct/71	5.7 5.2	-0.25
Mean of 22 lakes				-0.16

[a]Located east of the La Cloche Mountains.

[b]pH determined by the Ontario Department of Lands and Forests.

TABLE 4-5. EARLIEST AND 1971 pH MEASUREMENTS ON LAKES NORTH OF THE LA CLOCHE MOUNTAINS (BEAMISH AND HARVEY 1972)

Lake	Township	Date	pH	Avg annual change in pH units
Anderson	Merritt	Aug/60[a]	7.4	-0.09
		Oct/71	6.4	
Annie	Bevin and Sale	/61[a]	5.6	-0.09
		Aug/71	4.7	
Bear	Roosevelt and Dieppe	Aug/68[a]	6.5	-0.07
		Aug/71	6.3	
Brazil	Foster	Aug/67[a]	7.5	-0.20
		Aug/71	6.7	
Deerhound	Curtin	Sept/68[a]	7.0	-0.10
		Aug/71	6.7	
Elizabeth	Foster	Sept/68[a]	6.5	+0.33
		Sept/71	7.5	
Frank	Goschen	/60[a]	6.9	-0.03
		Oct/71	5.6	
Fox	Gosch	July/60[a]	6.1	-0.07
		Sept/71	5.3	
Griffin	Merrit	Aug/60[a]	7.8	-0.10
		Oct/71	6.7	
Hannah	Foster, Truman, Curtin and Roosevelt	Aug/68[a]	7.0	-0.10
		Aug/71	6.7	
Hanwood	Roosevelt	Aug/67[a]	7.0	-0.25
		Oct/71	6.0	
Lang	Curtin	Aug/68[a]	6.5	+0.10
		Oct/71	6.8	
Leech	Roosevelt	Aug/67[a]	6.5	-0.13
		Oct/71	6.0	
Little Bear	Roosevelt	Aug/68[a]	6.5	-0.27
		Oct/71	5.7	
Little Hannah	Truman	Aug/68[a]	7.5	-0.33
		Aug/71	6.5	
Little Panache	Louise and Dieppe	July/68	8.5	-0.35
		May/70	7.8	
Long	Eden, Waters, and Broder	Nov/69[a]	6.5	+0.15
		Sept/71	6.8	
Loon	Merritt and Foster	Sept/68[a]	6.5	0.00
		Oct/71	6.5	
Plunge	Roosevelt	Aug/68[a]	6.6	-0.20
		Oct/71	6.0	
St. Leonard	Foster	Sept/68[a]	6.8	-0.03
		Aug/71	6.7	

TABLE 4-5. CONTINUED

Lake	Township	Date	pH	Avg annual change in pH units
Simon	Graham	Aug/60[a]	6.1	+0.03
		Sept/71	6.4	
Spring	Merritt	Aug/66[a]	7.0	-0.16
		Oct/71	6.2	
Stratton	Foster	Sept/68[a]	7.0	-0.10
		Aug/71	6.7	
Walker	Truman and Roosevelt	Aug/68[a]	6.5	-0.07
		Aug/71	6.3	
Whitefish	Whitefish Indian Reserve	Aug/60[a]	6.3	+0.01
		Oct/71	6.4	
White Oak	Tilton and Halifax	Nov/69[a]	4.2	-0.05
		Oct/71	4.1	
Mean of 26 lakes				-0.08

[a]pH determined by the Ontario Department of Lands and Forests.

to 168 $\mu eq\ \ell^{-1}$) in 1978 and earlier values reported by Nicholls (1976).

Dillon et al. (1978) discussed in detail their analytical methodology but did not give any details of their sampling procedures or any information on possible short-term variations in alkalinity.

Halifax, Nova Scotia (Watt et al. 1979).

Gorham (1957) reported on the chemistry of 23 lakes near Halifax, Nova Scotia, sampled in December 1955. Twenty-one years and two weeks later, Watt et al. (1979) attempted to sample these same lakes to look for water chemistry changes that may be associated with sulfur emissions from industrial sources near Halifax. They found one lake to be filled, one to be inaccessible, and five to have significant local disturbances--leaving 16 lakes to be compared to the 23 studied by Gorham.

Watt et al. (1979) took considerable care to sample in the manner Gorham (1957) used. They measured pH with a Fisher Accumet Model 230 pH meter before and after sample CO_2 equilibration with the laboratory atmosphere and stated that "since both studies used glass-electrode pH meters, the combined error for the pH differences should be less than $\pm$ 0.07" (Watt et al. 1979). They also measured specific conductivity, alkalinity and acidity, even though the last two variables were not determined by Gorham (1957).

Watt et al. (1979) performed variance analysis on the samples from the 16 lakes and found that pH differences associated with geology had not changed since the study by Gorham (1957) but that pH values of the lakes did differ significantly from those found in 1955. They found current pH values from 3.89 to 6.17 (before air equilibration). In 1955, pH values in these lakes ranged from 3.95 to 6.70 (before air equilibration) (Gorham 1957). Watt et al. (1979) plotted 1977 pH values vs 1955 pH values (Figure 4-15) and found that all points were below the 1:1 line, that the pH drop was significant to the $P < 0.001$ level, and that the slope was significantly less than one ($P < 0.001$). They also found that conductivity in the lakes increased significantly ($P < 0.001$) over the 21-year period. The authors reported that recent pH data from other Nova Scotia lakes and from lakes in New Brunswick and on Prince Edward Island, when compared with data reported by Hayes and Anthony (1958), tend to confirm a trend towards lake acidification in these areas.

Watt et al. (1979) did not measure precipitation pH but did note that mean sulfur emissions from the Halifax metropolitan area were approximately double in 1977 the amount they were in 1955. The authors concluded that it was "clearly unnecessary to look beyond local sources (i.e., to long-range atmospheric transport) for an explanation of the acidic condition of lakes in the Halifax area" (Watt et al. 1979).

Nova Scotia and Newfoundland (Thompson et al. 1980).

Thompson et al. (1980) reported temporal trends in the pH of Nova Scotia and Newfoundland rivers. In their report they discussed data

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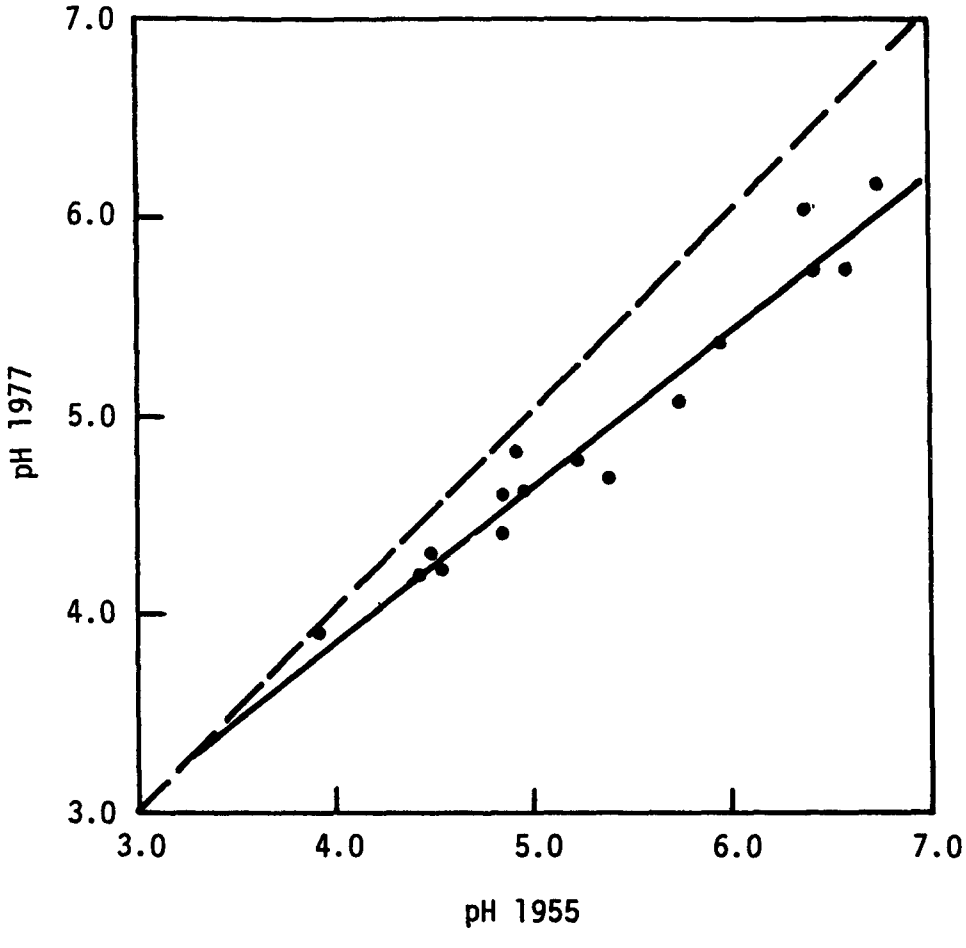

Figure 4-15. Relationship between pH values for 16 lakes (near Halifax, Nova Scotia) in 1977 and 1955. Dashed line is line of no change; all values are below this line and drop in pH is significant to $p < 0.001$ level. Slope of least-squares equation (solid line) is significantly less than that of dashed line ($p < 0.001$) indicating greater pH declines in in higher pH lakes. Adapted from Watt et al. (1979).

given by Thomas (1960) for the years 1954-56 and more recent data reported by the Water Quality Branch of Environment Canada. The more recent data are stored in the data archive NAQUADAT.

Three Nova Scotia rivers were studied--the Tusket River, the Medway River, and the St. Mary's River. Samples were taken approximately monthly in 1955 (Thomas 1960) and in the years 1965-74. Samples were kept tightly stoppered in the dark, and "the pH's used for comparison were measured in the laboratory, at room temperature" (Thompson et al. 1980). Thompson et al. (1980) compared the discharges on days of sampling to mean annual discharges and concluded that "although sampling in various years was commonly biased toward either high or low flow, there was no consistent relationship between mean pH and such bias . . . the calculated pH's are reasonable, representative and comparable." No other information was provided on sampling or analysis. The value of discharge weighted mean pH of the rivers decreased from roughly 5.2 to 4.4 (Tusket River), 5.7 to 4.9 (Medway River), and 6.2 to 5.5 (St. Mary's River).

The three Newfoundland rivers studied were the Isle Aux Morts River, the Garnish River, and the Rocky River. Sampling and analysis were as for the Nova Scotia rivers. Although plots of discharge weighted mean annual pH of these rivers over the period 1971-78 appear quite variable, the authors believe that these data together with the data for the Nova Scotia rivers indicate a general steady decrease in pH until 1973 and a steady increase afterwards. The increase is apparently attributed to decreased acid loading to the Atlantic Provinces since 1973 "presumably because of changed weather patterns" (Thompson et al. 1980). The authors presented no appropriate statistical evidence in support of any of the "apparent" trends.

4.4.3.1.2.3 United States studies.

New England (Maine) (Davis et al. 1978).

Davis et al. (1978) studied 1936 pH readings taken from 1368 Maine lakes during the period 1937-74 in an effort to see if they could find pH decreases associated with the acidic precipitation of that area ($4.4 < pH < 5.0$ since at least 1956; Cogbill 1976; Likens 1976). Samples and data were from a variety of sources (Davis et al. 1978) but apparently most samples were taken over the deepest portion of each lake, near mid-day, during the summer. Wallace-Tiernan colorimetry was used to measure pH "until the 1960's"; then pH was measured with portable meters. "The two methods were found to agree within 0.1 pH units (sic)" (Davis et al. 1978).

The authors noted initially that the mean pH of 196 samples from 1937-42 was 6.81 and that the mean for 289 samples from 1969-74 was 6.09--a 5.2-fold acidity increase. They also noted that most of the change seemed to occur in the early 1950's and that overall the change might have been greater if it had not been for some cultural euthrophication beginning in the 1950's. The authors realized that these preliminary results might have been affected by regional edaphic differences

in lake types and also by differences in precipitation acidity across the state. Amounts and seasonal patterns of precipitation also may have played a part (Davis et al. 1978). In an attempt to minimize such potential regional distortions, they analyzed the data by using three procedures based on H^+ concentration changes in individual lakes.

They found 258 lakes had pH readings separated by at least a year. There was a mean of 2.9 readings per lake and a mean of 12.7 years between successive readings (pairs) for a total of 376 pairs during the period 1937-74.

Procedure I of Davis et al. (1978) was as follows. They used data pairs to calculate slopes (H^+ concentration vs time) for individual lakes and then mean slopes from 1937-74. The mean slopes were added to obtain a total H^+ concentration change for the entire period. Given a starting pH of 6.89 (mean of 123 values 1937-42), the final (1974) pH would be 5.79, an increase on acidity of 12.6 times. Using a t-test, the authors also found that the mean annual increase in H^+ concentration based on the mean slopes for each year was significantly different from zero change with $p < 0.0001$. The authors noted, however, that this procedure more strongly weights data pairs with long time separations, thus possibly invalidating the use of a t-test.

The second procedure Davis et al. (1978) used was to average the 376 single slope values. This gave a mean of 1.15×10^{-7} M yr^{-1} H^+ concentration change. By t-test, this mean is significantly different from zero at $p < 0.1$, but not at $p < 0.05$. If a disproportionately greater decrease in pH occurred in the 1950's (as the authors hypothesized), this procedure would give greater weighting to the more frequent data pairs beginning about that time and would thus overestimate total change (Davis et al. 1978).

Procedure III the authors used was to weight each data pair (H^+ concentration) slope linearly in inverse proportion to the time interval between each reading. These weighted slopes were then averaged for each year that they applied. Using an initial pH of 6.89 in 1937, the authors noted that pH decreased by 1950 to only 6.83. By 1961, however, the pH had decreased to 5.91, so 73 percent of the increase in acidity occurred in this latter time period. The authors believed that this 73 percent increase in acidity was actually an underestimate for this time period.

Davis et al. (1978) also discussed some alkalinity data they had for 44 of the 258 lakes cited above. These data were from the period 1939-71, a total of 96 values and 52 pairs. No information was given on the analytical method(s) used to determine alkalinity. Applying their Procedure I to those data, they obtained a decrease of about 6.34 ppm (as $CaCO_3$; from 11.82 to 5.48 ppm, typically; corresponding to a decrease of 127 $\mu eq\ \ell^{-1}$ from 236 to 109 $\mu eq\ \ell^{-1}$) over the period. This was much less than expected from pH changes from the same period and from observed relationships between pH and alkalinity. The authors noted that "the discrepancy may be due in large part to the inadequate sampling and great variance of the alkalinity data, including the fact that 67 percent of the pairs had their initial member in 1960 or later" (Davis et al. 1978).

The authors concluded from their study that between the years 1937-74 H^+ concentration in Maine lakes increased about 10^{-6} M and pH decreased from about 6.85 to 5.95. Further, nearly three-quarters of this change occurred in the 1950's. "This is the first demonstration of a pH decrease due to acidic precipitation on a large region of lowland lakes in the United States" (Davis et al. 1978).

New England (Maine, New Hampshire, Vermont) (Norton et al. 1981a).

Norton et al. (1981a) measured pH in 94 New England lakes (82 in Maine, 8 in New Hampshire, 4 in Vermont) for which historical pH existed from the period 1939-46. The lakes sampled were small, oligotrophic-mesotrophic, and located in forested areas on non-calcareous bedrock. The recent sampling (1978-80) was done during July-October but not on the same monthly dates as the historic sampling. These samples were collected at 1 m depths, and the lakes were stratified at the time of sampling.

The pH values of the recent samples were measured in the field with (1) a portable pH meter with combination electrode, and (2) a Hellige color comparitor. Except for three spurious cases of low pH lakes, the authors found that "reasonable agreement exists for these two methods, especially at higher pH's" (Norton et al. 1981a).

The authors presented their results in plots of (1) old colorimetric pH vs recent colorimetric pH, and (2) recent colorimetric pH vs recent electrometric pH (Figures 4-16 and 4-17). They concluded that their study "confirms the results of Davis et al. (1978) regarding an overall decrease in the pH of Maine lakes" (Norton et al. 1981a).

New England (New Hampshire) (Hendrey et al. 1980b, Burns et al. 1981).

During 1936-39 the New Hampshire Department of Fish and Game conducted a biological survey of waters in the White Mountains of that state. Their survey included measurement of pH of headwater streams and measurement of alkalinity and pH for small lakes. In 1979 Burns et al. (1981) resampled 38 of these waters and made determinations of alkalinity and pH (note: the data for this study were also presented and discussed by Hendrey et al. 1980b). Since at least 1955-56 this area has been receiving precipitation with a weighted annual pH less than 4.5 (Cogbill and Likens 1974).

The sampling rationale and analytical methodology used by Burns et al. (1981) were exactly the same as used in their study of North Carolina streams. A detailed discussion of these methods is presented in that section of this review.

Burns et al. (1981) found that 90 percent of the 38 samples showed a decrease in pH between the late 1930's and 1979 (mean pH 6.66 in 1936-39 and mean pH 6.06 in 1979). Mean H^+ concentration was 0.22 ($\mu eq\ \ell^{-1}$) in 1936-39 and 0.87 ($\mu eq\ \ell^{-1}$) in the 1979 samples. A t-test showed this increase to be significant at the $p < 0.02$. "However,

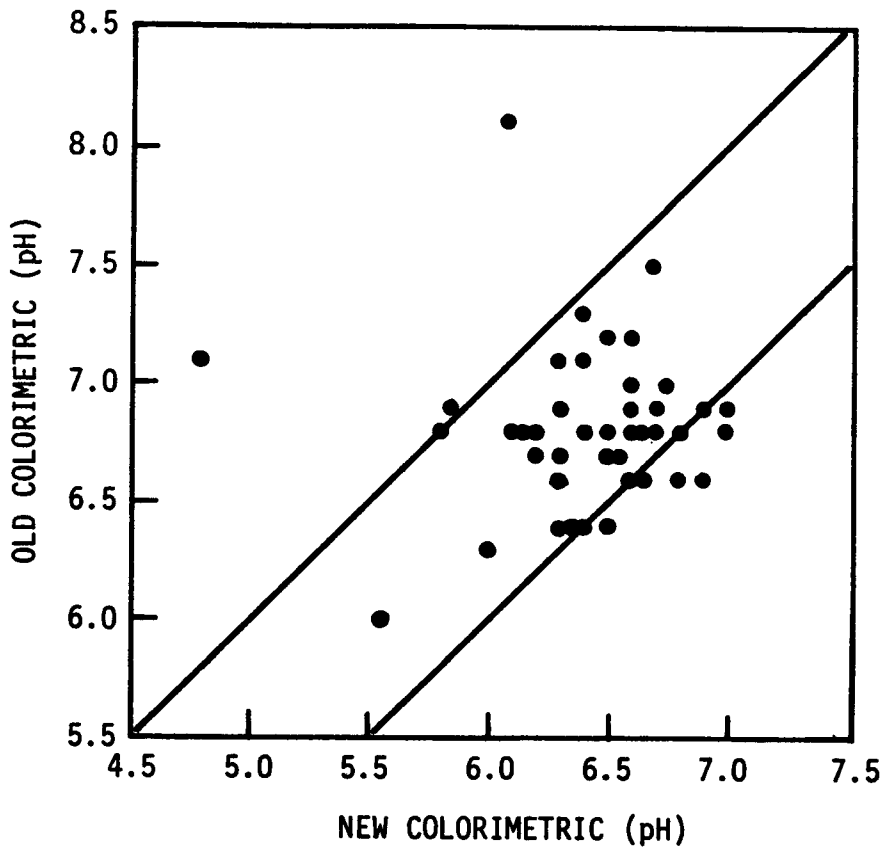

Figure 4-16. Old lake water pH (colorimetric) vs recent lake water pH (colorimetric). Adapted from Norton et al. (1981a).

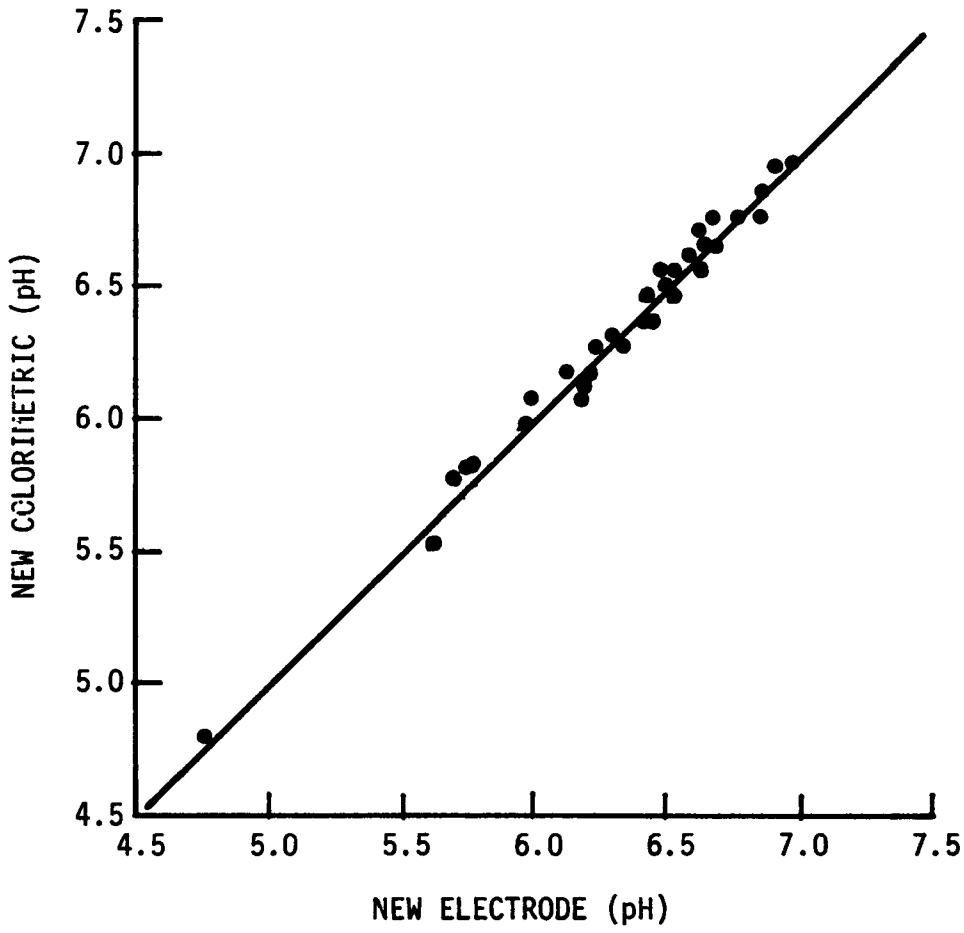

Figure 4-17. Recent lake surface water electrode pH vs recent colorimetric pH.

when the errors associated with comparing the colorimetric data to the electrometric data are considered, the difference in pH between the 1960's (sic--the authors meant 1930's, Burns pers. comm.) and 1979 may not be significant" (Burns et al. 1981). The authors had historical alkalinity values for only five lakes in New Hampshire. Alkalinity decreased at all five sites (mean decrease 103 percent of original), but the authors noted that there were not enough samples to make a valid statistical comparison. (See also the review of the North Carolina study by the same authors for a critical discussion of comparison of their alkalinity values with historical measurements.)

New York (Schofield 1976a).

Schofield (1976a) reported on a 1975 survey of water chemistry and fish status of 217 Adirondack lakes located at elevations greater than 610 m. For 40 of these lakes, pH data exist from the period 1929-37. Frequency distribution plots (Figure 4-18) of lake pH for the two data sets illustrate the apparent pH decrease with time (Schofield 1976a). During the period September 5, 1974-April 9, 1975 the weighted mean pH of precipitation on this area on a storm-by-storm basis was 4.23 (range 3.94 to 4.83) (Schofield 1976b). Schofield (1976a) did not present any information on sampling or analytical methodology for pH for the data sets, stating only that they were "comparable data."

New York (Pfeiffer and Festa 1980).

In the summer of 1979 the New York Bureau of Fisheries Lake Acidification Studies Unit sampled 396 ponded Adirondack waters. For 138 of these waters historical pH data from the period 1930-34 existed. As part of their report on the acidity status of Adirondack lakes, Pfeiffer and Festa (1980) compared the pH values of these lakes in 1979 to the values of the period 1930-34.

The 1979 sampling was done via helicopter and samples were taken at a depth of 1 m. No information was given on the sampling during the period 1930-34. For the samples taken in 1979, pH was determined in the laboratory, using both a pH meter and a Hellige colorimetric comparitor. These determinations were made on the samples after each sample had been equilibrated with the laboratory atmosphere. The only information given on the pH determinations of the 1930-34 samples was that the measurements were made using a Hellige comparitor.

Pfeiffer and Festa (1980) reported that their colorimetric and electrometric measurements on the samples taken in 1979 disagreed markedly and that the Hellige comparitor consistently overestimated pH throughout the range of sample values and especially drastically at the lower values. Schofield (1981) compared Hellige comparitor measurements to pH meter measurements for similar samples, concluding that agreement between the two methods was much better than found by Pfeiffer and Festa (1980) and that the discrepancies found by these authors were due "to errors in pH meter measurements."

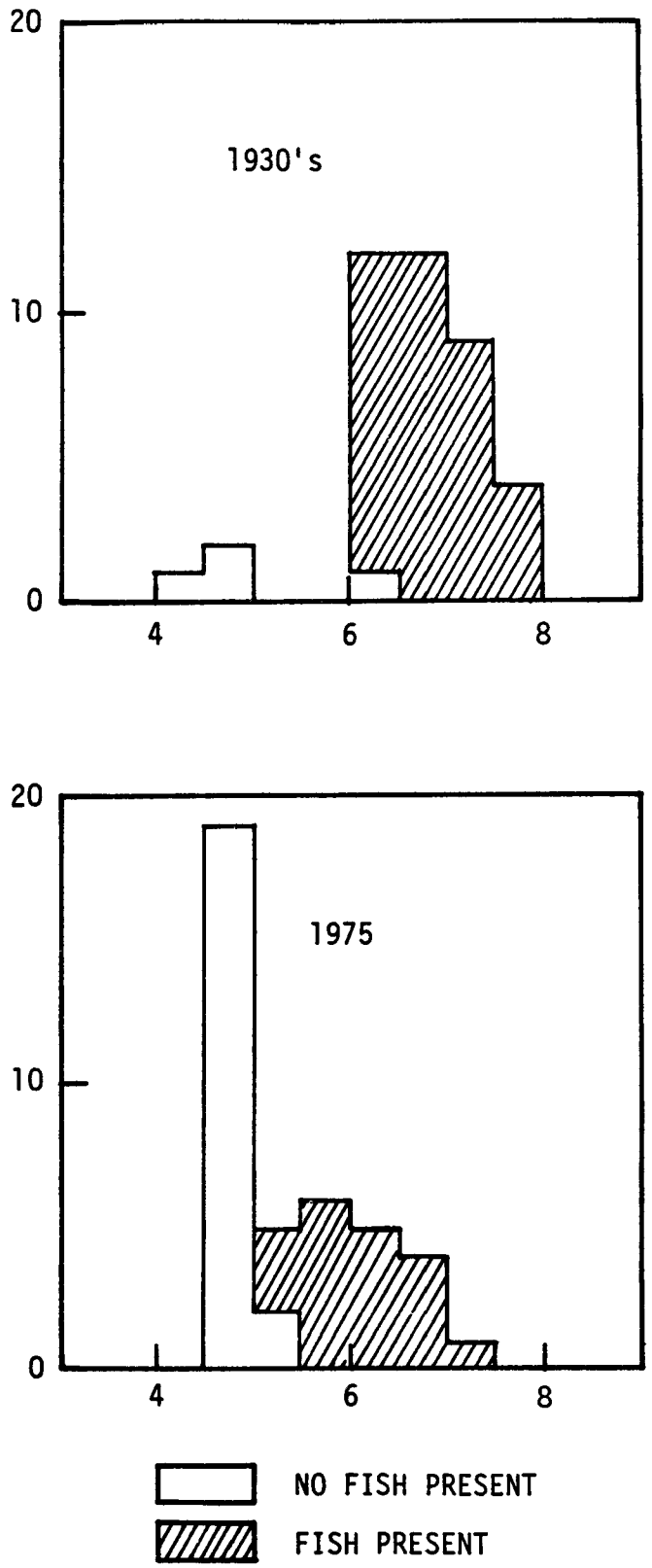

Figure 4-18. Frequency distribution of pH fish population status in 40 Adirondack lakes greater than 610 m elevation, surveyed during the period 1929-37 and again in 1975. Adapted from Schofield (1976a).

To minimize any potential bias in the comparison of pH measurements over time, Pfeiffer and Festa (1980) used only colorimetric measurements in their data analysis. They presented their results graphically (Figure 4-19). They concluded that "historic readings obtained in the 1930's were generally higher than comparable current determinations for the same group of waters. This reflects a general deterioration of water quality during the 40-year time frame between samplings" (Pfeiffer and Festa 1980). The authors did not explain the apparent differences between the pH distribution of the lakes on which they reported and the pH distribution of the lakes described by Schofield (1976a). Like Schofield (1976a), however, they attributed the observed deterioration of water quality to the acidic precipitation in the region.

New Jersey (A. H. Johnson 1979).

Searching for evidence of temporal trends, A. H. Johnson (1979) examined 17 years of pH data for two small headwater streams (McDonalds Branch and Oyster Creek) in the New Jersey Pine Barrens. Precipitation in the area had a mean pH of 4.4 in 1970, 4.25 for seven months in 1971, and 3.9 from May 1978 to April 1979. Nearly all of the data for the study came from two sources: U.S. Geological Survey sampling and analyses from 1963-78 and a University of Pennsylvania trace metal study in 1978-79. The USGS samples were collected randomly with a frequency of 2 to 12 per year. This sampling was not biased seasonally for McDonalds Branch but was slightly biased consistently throughout the study towards a greater representation of Spring samples for Oyster Creek. The University of Pennsylvania samples were collected weekly in McDonalds Branch only from 1978 through 1979. Johnson presented little information on sample pH analyses except that "all pH values were measured with a glass electrode."

Johnson (1979) had varying levels of confidence in the pH data. Those data he considered most reliable were from samples on which cations balanced anions within 15 percent and calculated conductance balanced measured conductance within 15 percent. He performed regressions of stream pH vs time for different groups of data (Table 4-6 and Figure 4-20) and found for most groups that a significant decrease existed. Johnson noted no evidence that oxidation of geological sulfides, changes in land use, or changes in the amount of precipitation were responsible for the long-term trends. He concluded "it appears that the decrease in stream pH is a real phenomenon and not attributable to differences or bias in sampling or measurement. The data collected to date are consistent with the postulation of an atmospheric source for the increased H^+."

Pennsylvania (Arnold et al. 1980).

In an effort to assess temporal changes in pH and alkalinity of Pennsylvania surface waters, Arnold et al. (1980) examined five existing water quality data bases. Nearly all of the data examined were from streams. Arnold et al. found 314 instances where data were taken at least one year apart at the same location or "sufficiently close

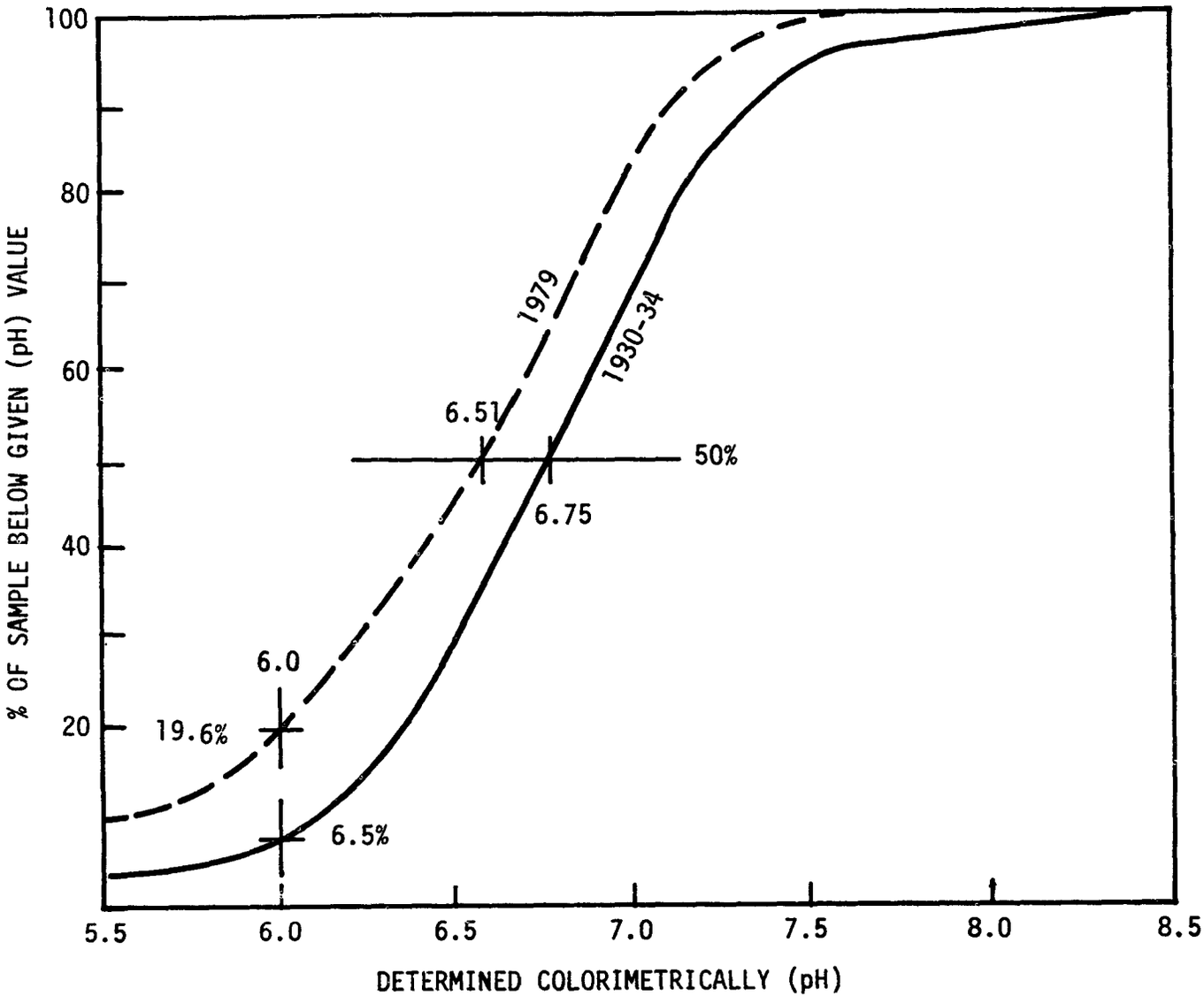

Figure 4-19. Cumulative comparison of historic and recent pH values for a set of 138 Adirondack lakes. Adapted from Pfeiffer and Festa (1980).

TABLE 4-6. REGRESSIONS OF STREAM pH ON TIME: N IS THE NUMBER OF SAMPLES, r IS THE CORRELATION COEFFICIENT, AND P IS THE LEVEL OF SIGNIFICANCE; a_0 AND a_1 ARE COEFFICIENTS IN THE REGRESSION $pH = a_0 + a_1x$, WHERE x IS THE NUMBER OF MONTHS AFTER JUNE 1963 (A. H. JOHNSON 1979)

Data source	N	a_0	a_1	r	P	Δ μeq H^+ per liter (1963-1978)
	McDonalds Branch, New Jersey Pine Barrens					
USGS data, 1963-78	90	4.42	-0.0022	-0.22	0.05	+57
USGS data + UP data[a]	100	4.49	-0.0030	-0.32	0.01	+80
USGS data, anion equivalents balance cation equivalents; measured and calculated specific conductances are equal	36	4.35	-0.0012	-0.29	ns[b]	+29
	Oyster Creek, New Jersey Pine Barrens					
All USGS data	78	5.10	-0.0047	-0.56	0.01	+48
USGS data, anion equivalents balance cation equivalents; measured and calculated specific conductances are equal	26	4.89	-0.0027	-0.53	0.01	+26

[a]Includes all data collected by the U.S. Geological Survey (USGS) from 1958 to 1978 and the monthly average pH of University of Pennsylvania (UP) samples.

[b]Not significant.

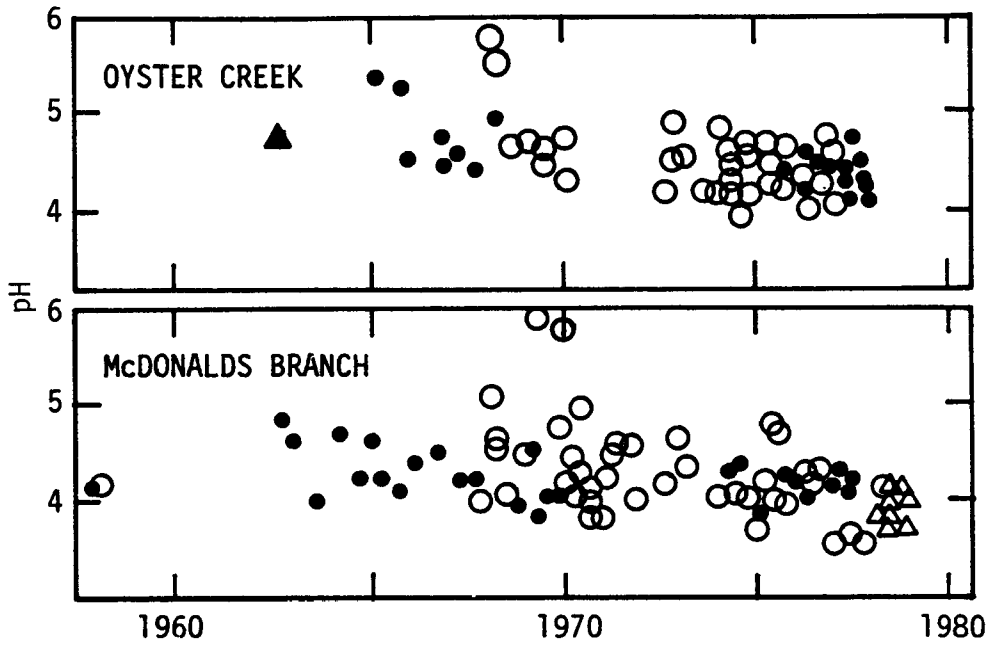

Figure 4-20. Stream pH 1979. Closed circles represent samples in which anion and cation equivalents balanced and calculated and measured specific conductances were equal. Open circles are samples for which the chemical analyses were incomplete or for which discrepancies in anion and cation and conductivity balances could not be attributed to errors in pH. The closed triangle represents the average pH determined in a branch of Oyster Creek in a 1963 study. Open triangles are monthly means of pH data collected weekly from May 1978 to January 1979 during a University of Pennsylvania trace metal study.

(generally within one mile with no major tributaries or influences between)." Of these 314 cases, 107 (34 percent) showed decreases in pH, alkalinity, or both. The mean pH of the "earliest" of these 107 cases of decrease was 7.31 (range 5.8 to 8.8), whereas the mean pH of the "most recent" was 6.94 (range 4.9 to 8.3). The mean change in pH was a decrease of 0.37 unit, and the range of change was -1.3 to +0.2 units. For alkalinity, the mean of the "earliest" samples was 834 ($\mu eq\ \ell^{-1}$) (range 100 to 4000 $\mu eq\ \ell^{-1}$), and the mean of the "most recent" was 532 ($\mu eq\ \ell^{-1}$) (range 40 to 3720 $\mu eq\ \ell^{-1}$). The mean net change was a decrease of 302 ($\mu eq\ \ell^{-1}$) and the range was (-2100 to +360 $\mu eq\ \ell^{-1}$). The average time span between the "earliest" and "most recent" samples was 8 1/2 years; the range was 1 to 27 years. Arnold et al. (1980) concluded that "although the data upon which this report is based are not sufficiently strong to define statistically valid relationships, it seems clear that there is a definite overall trend toward increasing acidity in many Pennsylvania streams ...."

Although the authors presented and discussed the means and ranges of pH and alkalinity decreases for those cases where decreases were found (34 percent of the total), they did not present or discuss the overall changes for the 314 total cases examined. If 34 percent of the total cases decreased, then 66 percent must have remained the same or increased. This, plus the fact that five separate data bases were used, that very little information was presented concerning sampling, and that no information was presented about analytical procedures gives rise to some serious questions concerning this study. Also of concern is the fact that decreases over a period as short as one year are considered part of a "definite overall trend" (Arnold et al. 1980). Yet another consideration in studies such as this has been noted by Schofield (1981); "it is obvious that detection of significant, long-term pH changes in acidifying systems, still in a bicarbonate buffered state, cannot be made reliably because normal metabolism induced changes in CO_2 levels would likely obscure any pH change resulting from decreased alkalinity. Thus interpretations of long-term pH changes in the range of 6-7 must be viewed with caution." Given the possible variability (not to mention potential bias) in data taken from a variety of sources (perhaps arrived at by a variety of procedures), the mean decreases in pH and alkalinity of only those cases that did decrease in the study seem not so profound. They may, indeed, only represent inherent scatter in such a data set. To cite these as evidence of a "definite overall trend" (Arnold et al. 1980) seems premature.

North Carolina (Hendrey et al. 1980b, Burns et al. 1981).

In the period 1961-64 the North Carolina Division of Inland Fisheries measured the pH and alkalinity of a number of North Carolina headwater mountain streams. Burns et al. (1981) resampled 38 of these streams in 1979, attempting to discern any changes in stream chemistry that might have occurred in association with the acidic precipitation that falls in the area (weighted annual pH 4.7 to 5.2 in 1955-56 and < 4.5 in 1979). The data discussed by Burns et al. (1981) were also presented and discussed by Hendrey et al. (1980b).

Burns et al. (1981) used detailed maps to resample at exactly the locations of the original samples. The authors considered the possible sampling bias inherent in representing by a single sample the chemistry of a stream "where pH could fluctuate daily as well as seasonally. It was assumed that daily and seasonal fluctuations were random and normally distributed if the new samples were taken during the day and at the same time of year as the previous ones."

Significant differences existed in the analytical methods used for the early and recent data sets. For the 1961-64 samples, pH was measured with a Hellige colorimetric kit and alkalinity was determined by titration to a colorimetric (methyl-orange) endpoint. For the 1979 samples, pH was determined electrometrically and alkalinity by Gran's plots. The authors compared pH measurements by Hellige kit to those with their pH meter and found that they "agreed to within $\pm$ 0.15 of a pH unit" (Burns et al. 1981). To correct for the possible overtitration of alkalinity (past the true equivalence point to some arbitrary endpoint) and thus the overestimation of alkalinity for the 1961-64 samples, the authors subtracted 32 ($\mu eq\ \ell^{-1}$) from each of the historical values. Unfortunately, this may not have been a valid procedure. Crude calculations using the mean pH and alkalinity of the 38 early samples indicate that the equivalence point for the alkalinity titrations is near pH 5.0. A correction of 32 ($\mu eq\ \ell^{-1}$) assumes that the actual titration endpoint was at pH 4.5. No records exist to indicate that this was the case (Burns, personal communication). All that is known is that a methyl-orange technique was used. The pKa of methyl-orange is 3.5 and its transition range (yellow-orange-pink-red) is roughly pH 4.5 to 3.1 (Bell 1967, Golterman 1969). Not only is it impossible to know what color (and thus pH) the original analyst used as an endpoint, it may be that a color transition is not even observable at the pH 4.5 point assumed by the authors. If, for example, the titration endpoint for the early samples was actually pH 4.0, a correction of 100 ($\mu eq\ \ell^{-1}$) would be required. This level of uncertainty in the correction between techniques is quite large compared to the mean differences in alkalinity found by the authors--146 ($\mu eq\ \ell^{-1}$) in 1961-64 compared to 80 ($\mu eq\ \ell^{-1}$) by Gran's titration in 1979. This would seem to cast doubt upon the authors' findings that "the decrease in alkalinity between the 1960's and 1979 was statistically significant at the 0.02 probability level using a t-test" (Burns et al. 1981). The authors did not find a significant temporal trend in pH (mean 6.77 in 1961-64 and mean 6.51 in 1979).

Florida (Crisman et al. 1980).

Crisman et al. (1980) reported pH changes in 13 poorly buffered oligotrophic lakes (known as the Trail Ridge lakes) in northern Florida. They monitored the lakes quarterly (1978-79) and found a mean annual pH of 4.98. The mean annual precipitation pH at the time of the study was 4.58. "Comparison of the present data with that collected over the past 20 years indicates that the mean pH of the Trail Ridge lakes has declined an average of 0.5 pH units (sic) since 1960" (Crisman et al. 1980). The

authors neither presented further information on their sampling or analytical methods for pH, nor did they present any historical data or their sources for such data.

California (McColl 1981).

The San Francisco Bay area of California receives part of its water supply from two Sierra Nevada reservoirs--Pardee and Hetch Hetchy. These reservoirs are located in an area underlain principally by Mesozoic granite and are subject to acidic deposition resulting from NO_x and SO_2 pollution generated in the Bay area (McColl 1980, 1981). Measurements of pH have been made weekly in untreated reservoir outlet waters for the two reservoirs since 1954. Alkalinity has been measured weekly (by titration to a pH 4.5 endpoint) in Pardee outlet water since 1944. McColl (1981) reported on results of analyses of these data up to the year 1979.

McColl (1981) performed linear regressions of both the pH data (as annual average H^+ concentration) and the alkalinity data vs. time. The results of the regression analyses are shown in Figures 4-21 and 4-22. The increases in (H^+) and decreases in alkalinity are clear. Further analyses by McColl showed that (1) mean annual (H^+) of the two reservoirs was correlated ($r = 0.51$, $p < 0.02$), (2) that rates of increase of (H^+) did not vary significantly on a seasonal basis, and (3) yearly precipitation did explain a small percentage of the variance in mean annual (H^+) of the release water but that time was by far the most important factor.

McColl (1981) considered the possible influence of logging and mining within the reservoir watersheds on the observed trends in (H^+) and alkalinity, concluding that these activities could not account for the trends. He similarly considered and dismissed as unimportant the possible effects of atmospheric increases in CO_2.

McColl (1981) concluded from his analyses "It is clear that the (H^+) of waters in both reservoirs has increased since at least 1954, if not 1944. On the basis of indirect evidence and correlative data discussed ... I conclude that the most likely cause is the increased acidity of atmospheric depositions, especially those resulting from emissions of nitrous oxides by automobiles."

4.4.3.1.3 Summary--trends in historic data. Numerous studies have examined temporal changes in surface water chemistry in areas that have "sensitive" terrain and that receive precipitation more acidic than pH 4.7. A consistent (and sometimes major) drawback of these studies is a lack of clear documentation of the "historic" data used. Often it is unproven that these crucial data are unbiased, either by sampling or by the analytical procedures used. Many authors recognize this problem; Davis et al. (1978) stated of their work, "the unconventional and imperfect means which we used to reconstruct the pH history of Maine lakes were made necessary by the deficiencies of the only data set

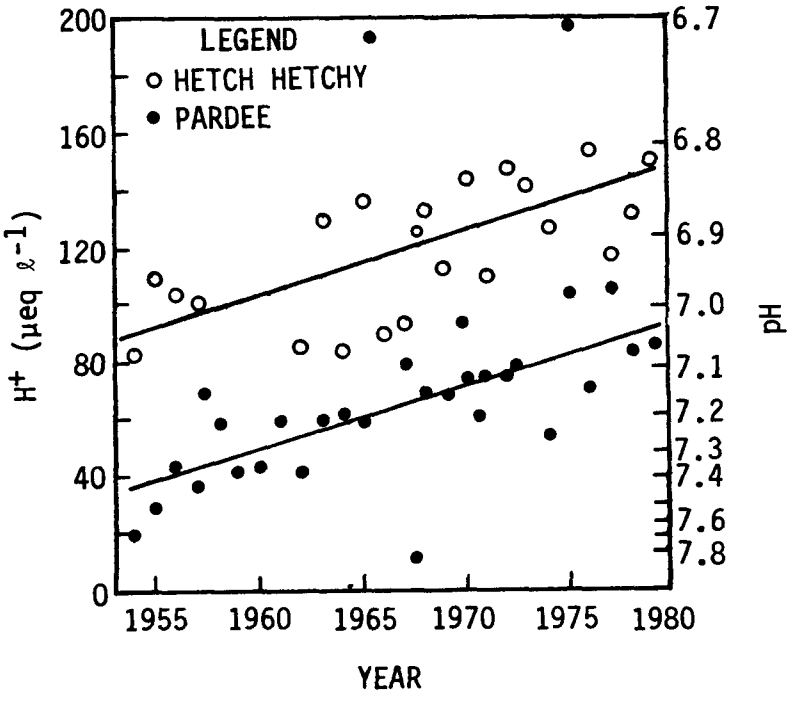

Figure 4-21. Increasing acidity at Pardee and Hetch Hetchy, shown by hydrogen ion activity vs year, for the period 1954-79.

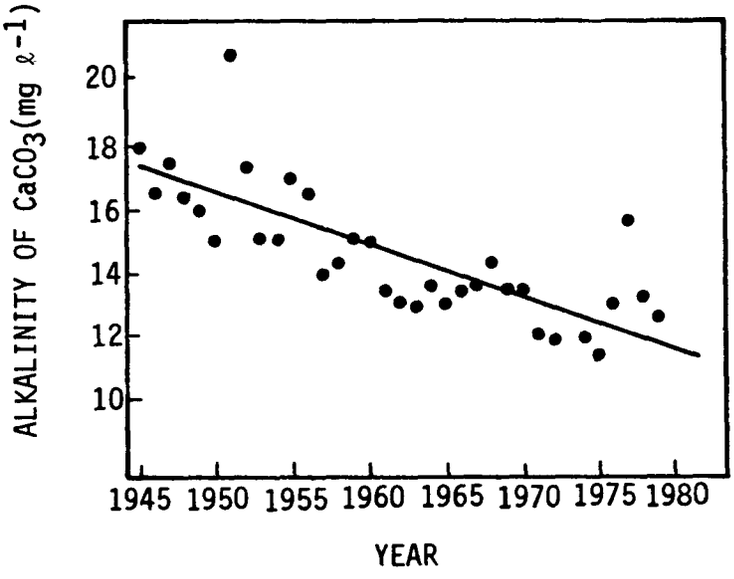

Figure 4-22. Decreasing alkalinity at Pardee, shown by alkalinity as $CaCO_3$ vs year, for the period 1944-79.

available." However, in every case reviewed here, the scientists who performed these studies concluded that pH and/or alkalinity decreased in at least some of the waters studied.

Surely in regions where acidic substances are deposited there exist lakes and rivers (in otherwise undisturbed watersheds) that have not experienced recent decreases in pH or alkalinity. Such an occurrence, however, is not a valid argument against the phenomenon of surface water acidification. The body of evidence in toto from the studies reviewed above indicates that in some regions of acidic deposition, otherwise undisturbed lakes and streams are being acidified. Particularly noteworthy by its absence is any body of data indicating consistent decreases in alkalinity or pH of surface waters in otherwise unaffected regions (see Section 4.4.3.3) not receiving acidic deposition.

This reviewer is unaware of any natural process that would cause decreases in pH and/or alkalinity at the rates indicated by the studies (of apparently otherwise unaffected regions) reviewed here. Until appropriate evidence is presented in support of some such natural process or until some other reasonable explanation of the data presented above is put forth, the only logical conclusion is that acidic deposition in these regions is causing acidification of some surface waters. Furthermore, it is only reasonable to assume that in regions of similar sensitivity that receive similar levels of acidic deposition other surface waters are being acidified.

4.4.3.2 Assessment of Trends Based on Paleolimnological Technique (R. B. Davis and D. S. Anderson)--

To assess the impact of acidic precipitation and associated pollutants on lake ecosystems, scientists have begun to analyze the record contained in the lake sediment (Norton and Hess 1980, Davis et al. 1980). The sediment contains a diversity of physical, chemical, and biological evidence which starts thousands of years ago deep in the sediments and proceeds upward toward the sediment surface to cover the period of the industrial revolution and recent technological activities. By applying paleolimnological techniques including the dating of the sediment (Birks and Birks 1980), researchers can reconstruct chronological sequences of pollution inputs to lakes (e.g., lead) and responses of the lake biota (e.g., plankton). Among the specific studies being carried out is the identification and enumeration of the many kinds of diatom remains (their siliceous shells) preserved in the sediments. Diatoms are sensitive indicators of water pH; the various species differ in that each is more or less restricted to a different pH range. By careful study of these pH relationships for present-day diatom assemblages, it is possible to calibrate the sedimentary diatom record so that the past pH of lake waters can be inferred. Thus, a dated record of lake acidification can be constructed by studying sediments cores.

The paleolimnological approach is useful for assessing the impact of acidic precipitation, because for the vast majority of acidification-susceptible lakes no record of past, direct pH measurement exists. Where such direct data exist, they (1) postdate 1920, (2) are usually only for

one year or a short series of consecutive years, (3) are ordinarily only for mid-summer when pH's are highest, and (4) are usually made by colorimetric pH indicators (pre 1965) which themselves may alter the pH of poorly buffered waters. Paleolimnological pH reconstruction provides a nearly continuous record based on a single technique, from the present to the past (including pre-1920). It solves the difficult problem of the direct sampling of short-term variation in pH by integrating daily, seasonal, and annual variation in single sediment samples encompassing an entire year or small number of years' deposits.

4.4.3.2.1 Calibration and accuracy of paleolimnological reconstruction of pH history. Davis et al. (1983) have been calibrating the sedimentary diatom record of pH by deriving "transfer functions" (Webb and Clark 1977) from the study of subfossil diatoms in surface-sediments (uppermost 0.5 or 1.0 cm) from the deepest part of 31 lakes in northern New England and 36 lakes in Norway. Davis et al. have developed regression equations relating these subfossil diatom assemblages to pH of the surface waters in the lakes. The regression coefficients are used as transfer functions to infer down-core pH. These regressions have standard errors (s_e) ranging from + 0.23 to + 0.54 pH units. The errors for the New England data are greater than those for Norway, partly because the pH readings in New England are limited to mid-summer. Regressions on Nygaard's (1956) alpha index, based on Hustedt (1937-39) pH preference categories, provide less precise pH inferences, especially for lakes pH < 6.2. This probably is a result of the semi-quantitative nature of Hustedt's categories, the uncertainty in assigning individual taxa to categories and possibly additional uncertainties. Several factors responsible for variance in the surface-sediment data sets would have remained more or less constant at any given lake during the past two or three centuries. For example, elevation and lake morphometry would have been constant, and concentrations of certain elements in the water (e.g., K and Cl) are likely to have changed little. Thus, any relative changes in pH inferred down-core at individual lakes are probably more accurate and precise than the regression statistics for the surface-sediment data would suggest.

4.4.3.2.2 Lake acidification determined by paleolimnological reconstruction. Quantifying this paleolimnological approach and applying it to lakes affected by acidic precipitation are quite recent techniques. The methods are time-consuming, and pH reconstructions have been completed for only a small number of lakes. In southern Norway, reconstructions for seven acidic (pH < 5.7) lakes indicate that acidification started between 1850 and 1930 (different dates at different lakes) and that the total decrease in pH by 1980 was 0.06 to 0.83 units (depending on lake; average decrease 0.40 units) (Davis et al. 1983). Before this acidification, these lakes were "naturally" all quite acidic (pH 5.0 to 6.0) and were highly susceptible to further acidification. In southern Sweden, Almer et al. (1974) estimated a pH decrease from "about 6.0 to 4.5" for Stora Skarsjon occurring between 1943 and 1973. Also in southern Sweden, Renberg and Hellberg (1982) report for Gardsjon a pH decrease from 6.1 to 4.5 starting in the 1950's; in Harvatten a decrease from 5.9 to 4.1 (no dates); and in Lysevatten from 6.2 to 5.3 (no starting date) until liming occurred in 1974.

The results for the northeastern United States are, so far, less clear. Reconstructions for 6 acidic lakes in northern New England (Davis et al. 1983) indicate that acidification started between 1900 and 1970 (different dates at different lakes) and that the total decrease in pH by 1980 was 0.20 to 0.35 units (depending on lake; average decrease 0.26 units). However, in at least three cases the pH decrease may have resulted in part from a recovery from an earlier, mild eutrophication (and elevated pH) associated with lumbering or other disturbance. Del Prete and Schofield (1981) report a pH decrease of 0.6 units for another Adirondack lake, but this is based on only one sample (0 to 1 cm vs all deeper samples), and the deeper sediment is not dated. In two other Adirondack lakes, the diatom record indicated no pH change.

To clarify these relationships, Davis et al. are continuing paleolimnological studies of pH change in acidification-susceptible lakes in the northeastern United States. An impediment to this research in the United States is the scarcity of recently well-monitored (for pH) acidification-susceptible lakes. This hampers efforts to develop more precise transfer functions for inferring past pH.

4.4.3.3 Alternate Explanations for Acidification-Land Use Changes (S. A. Norton)--

Land use changes may directly affect the pH (and related chemistry) of surface waters in a number of ways, including variations in the groundwater table; accelerated mechanical weathering or land scarification; decomposition of organic matter; long-term changes in vegetation; and chemical amendments. Details of each are presented below.

4.4.3.3.1 Variations in the groundwater table. The water table in mineral or organic soils generally marks a transition from aerobic to anaerobic conditions. This transition is particularly sharp in saturated, organic-rich soils. With a lowering of the groundwater table due to drought, lowered lake levels, or drained terrestrial systems (e.g., bogs), previously anaerobic and reduced material is exposed to oxygen. The following types of reactions may occur:

$$FeS_2 + O_2 + H_2O \rightarrow Fe(OH)_3 \text{ or } FeO(OH) \text{ or } Fe_2O_3 + 2H^+ + SO_4^{2-}$$

$$Mn^{2+}X + O_2 + H_2O \rightarrow MnO_2 + H_2X$$

$$\text{Organic matter} + \text{Decay} \rightarrow NO_3^- + H^+ + CO_2$$

The associated H^+ production is commonly accompanied by accelerated loss of cations from the ecosystem (Likens et al. 1966, Damman 1978).

4.4.3.3.2 Accelerated mechanical weathering or land scarification. These processes may result from logging, fires, slope failure, and other disturbances of the land surface. The exposure of relatively unweathered material to chemical weathering results in accelerated leaching of cations from watersheds. If uptake of nitrogen from decaying organic material occurs, the pH of surface waters may rise along with cation concentrations. This results in eutrophication trends in downstream

waters (Pierce et al. 1972). Readjustment of the system may take decades, with concurrent long-term changes in surface water chemistry, including pH.

4.4.3.3.3 Decomposition of organic matter. Long-term trends in the net production of biomass result in near steady-state chemistry for aquatic ecosystems but, depending on the direction of the trend (aggrading or degrading), the water quality parameters have different values (Nilsson et al. 1982). The net loss of organic matter generally results in accelerated production of nitric acid, CO_2, and increases in cations--all other conditions being kept the same. However, a change in stored biomass is generally accompanied by other changes such as changes in canopy interception of aerosols, changes in evapotranspiration, or changes in surface water temperatures, so the individual effects are difficult to sort out.

4.4.3.3.4 Long-term changes in vegetation. Long-term changes in vegetation bring about various physical and chemical changes in the soils and watershed which result in long-term changes in surface water chemistry. For example, Harriman and Morrison (1980) have demonstrated that spruce reforestation in Scotland resulted in acidification of streams and increased export of cations. It is not clear whether this is due to indigenous tree-related processes as compared to the pre-existing peaty soil vegetation or is due to changes in aerosol capture of acidic components or to changes in hydrology.

Certain vegetation types (e.g., conifers) produce abundant humic material which can produce acidity. Thus, the appearance of these vegetation types in a succession could yield long-term declines in pH as well as dissolved organic material concentrations. The appearance of Sphagnum sp. because of changes in the moisture regime could also result in acidification of surface waters due to the highly effective cation exchange capacity of Sphagnum with associated release of H^+. Malmer (1974) reviewed the Swedish literature relating to reversion of farmland to forests and finds that the chemical changes (increased organic content, lower pH, lower exchangeable metals) are the same as those that have also been attributed to acidic precipitation.

4.4.3.3.5 Chemical amendments. Adding some fertilizers (such as ammonium phosphate) to agricultural soils has an acidifying effect on soils, and this could be transmitted to surface waters (along with elevated levels of phosphate). This potential acidification is generally recognized and the affected soils are amended with a base, $CaCO_3$, with subsequent elevation of pH. In regions where agriculture is on the wane and reforestation is underway, the implicit cessation of $CaCO_3$ application might result in a decline in the pH of surface waters, erroneously suggesting natural acidification.

4.4.3.3.6 Summary--effects of land use changes or acidification. Drabløs et al. (1980) examined historical land-use changes in southern Norway and their relationship to regional lake acidification and decreasing fish populations. They found no relationship. Thus, although

changing land use may locally alter the pH regime of lakes and streams, it appears clear that regional lake acidification and episodic pH depression occur in response to increased atmospheric deposition of strong acid, primarily H_2SO_4.

4.4.4 Summary--Magnitude of Chemical Effects of Acidic Deposition (J. N. Galloway)

The aquatic systems that are most likely to be influenced by atmospheric deposition are those with alkalinity of less than 200 $\mu eq\ \ell^{-1}$. Large areas of Canada and the United States contain such systems. For example, approximately 80 percent of New England, by virtue of the geology, has surface waters with less than 200 $\mu eq\ \ell^{-1}$. Eastern Canada provinces range from 90 percent (Quebec) to 20 percent (New Brunswick).

Of the aquatic systems that are potentially susceptible to acidification (Figures 4-4 to 4-7), only ones located in eastern North America and small regions of western North America are receiving acidic deposition ($pH \leq 5.0$; Figure 4-11; see also Chapter A-8, Section 8.4).

Acidification of aquatic systems receiving acidic deposition has been noted in several instances (Figure 4-13).

Acidification of aquatic systems and acidic deposition is supported by the following lines of evidence:

- Due to acidic deposition, SO_4 concentrations have increased in aquatic systems in most of eastern North America. The increase in SO_4 has to have been matched by an increase in C_B or H^+. Since aquatic systems with original low alkalinities are characterized by watersheds with low C_B/H^+ ratios in the soil, a large portion of the increase in SO_4 will have to be matched by an increase in H^+, i.e., decreased alkalinity.

- Although there are problems with comparing old and new data, overall, the analysis of temporal records shows decreases in alkalinity and pH in aquatic systems of eastern North America receiving acidic deposition.

- The limited application of paleolimnologic indicators shows acidification of aquatic systems.

- Acidified aquatic systems are only found in areas receiving acidic deposition ($pH \leq 5.0$). In areas not receiving acidic deposition ($pH \geq 5.0$), acidification of sensitive aquatic systems is not found.

- No other possibilities exist to explain the regional scale of acidification that has occurred. For example, changing land use is at times advanced as one explanation. However, in areas with identical changes in land use, it is only those areas receiving acidic deposition that are acidified.

H_2SO_4 is the primary cause of the long-term acidification of aquatic systems on a regional basis. The maximum decrease in alkalinity that can occur due to acidic deposition depends on the maximum long term increase in SO_4^{2-}. In the northeastern United States and southeatern Canada this is about 100 $\mu eq\ \ell^{-1}$. The actual decrease in alkalinity depends on how much of the increased SO_4^{2-} is balanced by increases in base cations. One estimate (Henriksen 1982) is that for a 100 $\mu eq\ \ell^{-1}$ increase in SO_4^{2-} and NO_3^- there will be an approximately 60 $\mu eq\ \ell^{-1}$ decrease in alkalinity. The pH change associated with an alkalinity decrease of 60 $\mu eq\ \ell^{-1}$ can range a few tenths of a pH unit to 2 pH units. Those systems with the lowest initial alkalinities will show the greatest loss of alkalinity due to acidic deposition because of the scarcity of exchangeable cations in the terrestrial system.

The time scales of long-term acidification are on the order of years to decades in areas with low SO_4 adsorption capacities (Northeast and North Central United States) and decades to centuries in areas with high SO_4 adsorption capacities (Southeast United States). If acidity of deposition decreases, it is reasonable to believe the time scales of recovery will be of similar magnitude (Galloway et al. 1983a).

In addition to long-term acidification (years and decades) by H_2SO_4, short-term acidification (days to weeks) occurs as a result of the combined action of H_2SO_4 and HNO_3 in areas that develop acidic snowpacks or receive a large amount of rain over a short period of time. Losses of alkalinity of 200 $\mu eq\ \ell^{-1}$ and reduction of pH from 7.0 to 4.9 have been reported due to the action of both SO_4^{2-} and NO_3^-.

4.5 PREDICTIVE MODELING OF THE EFFECTS OF ACIDIC DEPOSITION ON SURFACE WATERS (M. R. Church)

The predictive modeling of the effects of acidic precipitation on the chemistry of natural waters is an extremely complicated task requiring a great amount of data, knowledge, insight, and skill. Two avenues exist for approaching the problem--empirical modeling and mechanistic modeling. Each approach has its advantages and disadvantages.

Empirical models, in general, have two principal advantages. First, they integrate the processes between inputs and outputs, thus eliminating the need for precise knowledge of the behavior of controlling mechanisms. Second, they are usually very simple computationally. Empirical models do have certain drawbacks, however. One drawback is that long periods of data may be required to verify that an observed relationship between inputs and outputs represents a steady state. Other drawbacks include the problems of verifying the validity of applying a relationship observed in one geographic area to another area and extrapolating from one observed loading rate (or regime) to another. Finally, because they are almost always based on assumptions of steady state, empirical models possess no time component; they cannot predict the time required to reach a new output level.

Mechanistic models, of course, have a different set of pros and cons. The principal attraction of mechanistic modeling is that if accurate mathematical representations of all (or the most important) of the physical/chemical/biological processes involved can be devised and properly related to one another, then a variety of extrapolations may be made with confidence. Such extrapolations include the application of the model (with appropriate calibration) to a variety of geographic areas; the use of the model to estimate rates of change (e.g., of the alkalinity or pH of a lake); and the prediction of responses to almost any loading scenario.

Along with this potential for widespread application, however, go certain problems. The first, and perhaps the most obvious, is that the knowledge may not exist to allow formulation of accurate representations of all (or even the most important) physical/chemical/biological processes of interest. Second, mechanistic models (especially of lake-watershed eco-systems) require extensive calibration for the region to which they will be applied. Such calibration can be very time consuming and expensive. Third, to be used predictively, mechanistic models that operate with a relatively short time-step (say, less than one week) require a correspondingly fine-scale source of predicted input. This requires a separate method (or model) to generate inputs of precipitation form, amount, and quality as stochastic variations around annual (or even seasonal) means. This task, by itself, is somewhat involved and time consuming. The last drawback to the mechanistic approach is that as the representations of controlling processes become more detailed and intertwined, the time and effort required to perform the calculations increases substantially, even to the point where significant amounts of computer time may be needed to perform long-term simulations.

A variety of models exist or are currently being developed to deal with the problem of predicting the effects of various levels of acidic deposition on the chemistry of surface waters (e.g., Almer et al. 1978; Henriksen 1980, 1982; Christophersen and Wright 1981; Thompson 1982; Chen et al. 1982; Christophersen et al. 1982; Schnoor et al. 1982). The models range from simple empirical approaches to very computationally complex formulations. A comprehensive review of all of these efforts is beyond the scope of this chapter. Instead, a fairly complete yet brief review is presented of those three empirical models that are, so far, the best known and most referenced of existing approaches.

4.5.1 Almer/Dickson Relationship

Almer et al. (1978) plotted lake pH vs lake sulfur loading (gm S m^{-2} yr^{-1} "concentration of 'excess' sulfur multiplied by yearly runoff") for Swedish lakes. They found "titration curve"-type patterns for data from sets of lakes occurring in areas of similar bedrock. They plotted two curves (Figure 4-23): One for waters "with extremely sensitive surroundings" and one for waters with "slightly less sensitive surroundings" (Almer et al. 1978). The authors did not define any

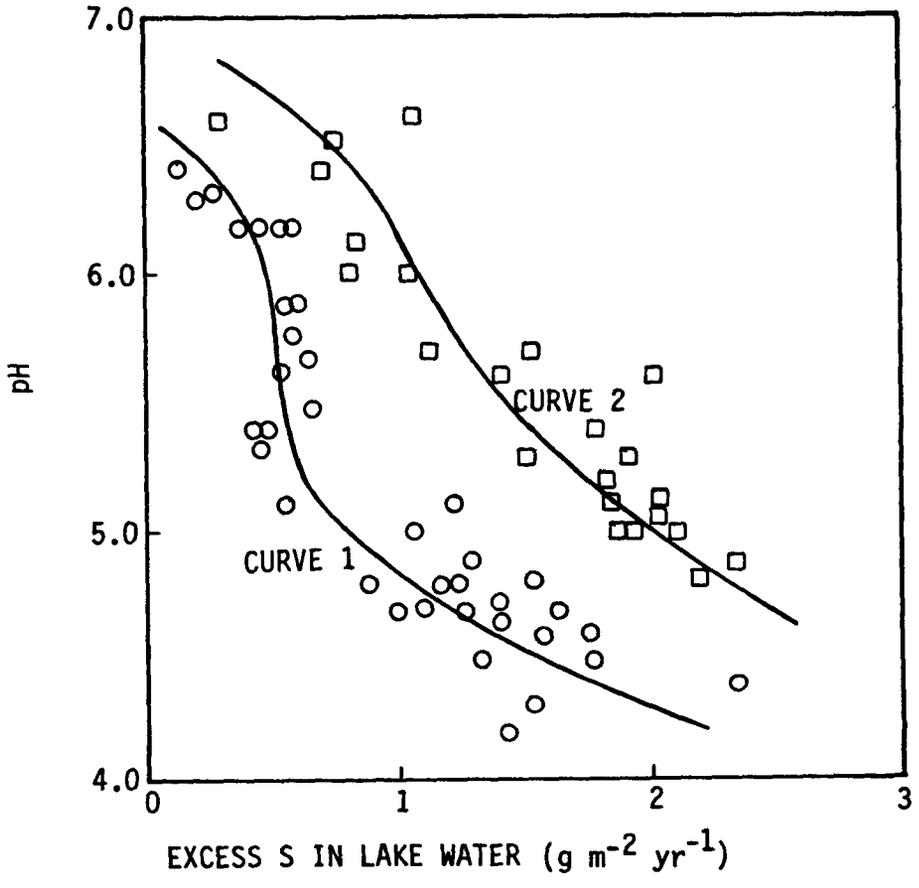

Figure 4-23. The pH values and sulfur loads in lake waters with extremely sensitive surroundings (curve 1) and with slightly less sensitive surroundings (curve 2). Load = concentration of "excess" sulfur multiplied by the yearly runoff. Adapted from Almer et al. (1978).

objective method for classifying lakes with regard to their surroundings and responses to sulfur loadings (e.g., "extremely sensitive" or "slightly less sensitive"). This limits their approach as a general tool for predicting the pH of lakes as a function of sulfur loadings.

At first glance, using such a treatment of data might seem to be a way to help determine the levels of sulfate deposition (to watersheds) that may have adversely affected lake water quality (pH). Closer examination of the approach, however, demonstrates that care must be taken in making such an application. For example, the quantity "excess S in lake water" must be carefully distinguished from the quantity "total excess S deposited". Unfortunately, confusion about this question and the original designation of the abscissa of Figure 4-23 has led to several mislabelings of reproductions of the original figure (e.g., Glass 1980, Loucks et al. 1981, U.S./Canada 1981). If Figures 4-24 and 4-25 (adapted from Almer et al. 1978) can be compared (note that they represent data roughly four years apart), they show that the relationship is quite variable for the regions of Sweden for which the "Almer/Dickson Relationship" was derived. Not only is more excess sulfur deposited than shows up in lake water (indicating some sulfate retention), but also the isopleths of the two plots are not parallel, indicating that this retention is different in different regions.

As this example illustrates, the crux of the problem in applying the "Almer/Dickson Relationship" is the translation of the abscissa of Figure 4-23 from a representation of "excess S in lake water" to some more primary or causative factor (e.g., areal rate of total excess sulfur deposition, areal rate of wet excess sulfur deposition, concentration of sulfate in precipitation, pH of precipitation, etc.). Such a translation requires quantitative knowledge of the relationships among such things as concentrations in lake waters, concentrations in precipitation, ratios of wet to dry deposition, amounts of precipitation, amounts of runoff, etc. In turn, the statistical estimation of these types of relationships for any region requires large amounts of data for that specific region.

Beyond the problems described above, other pertinent factors involved in the use of the "Almer/Dickson Relationship" must be considered. It is important to note that several assumptions are inherent in the approach.

First, Almer et al. (1978) assumed that within each of the two sets of lakes represented by the curves of Figure 4-23, initial (e.g., prior to deposition of strong acids) steady-state values of alkalinity were all the same. Second, they assumed that the current pH values and the current excess sulfur concentrations they observed in lake water were both at steady state. No evidence was offered in support of either of these assumptions. Finally, there is the problem of hysteresis. No data exist to indicate that as a result of decreases in SO_4^{2-} loading rates, previously acidified lakes would "return" along the curves of Figure 4-23 to higher steady-state pH values. Conditions extant have not permitted such observations to be made, and there is perhaps no clear scientific consensus on this problem.

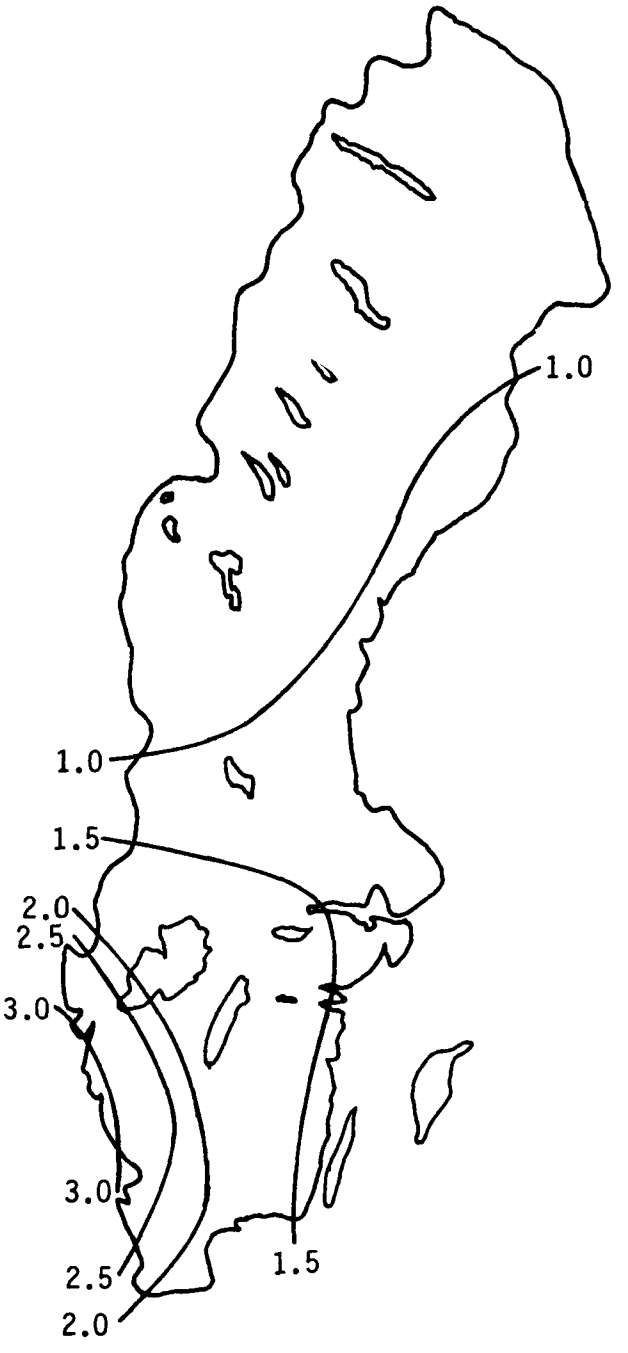

Figure 4-24. Atmospheric load of "excess" sulfur from precipitation and dry deposition, 1971-72 (g S m^{-2} yr^{-1}). Dry deposition calculated from a deposition velocity of 0.8 cm s^{-1}. Adapted from Almer et al. (1978).

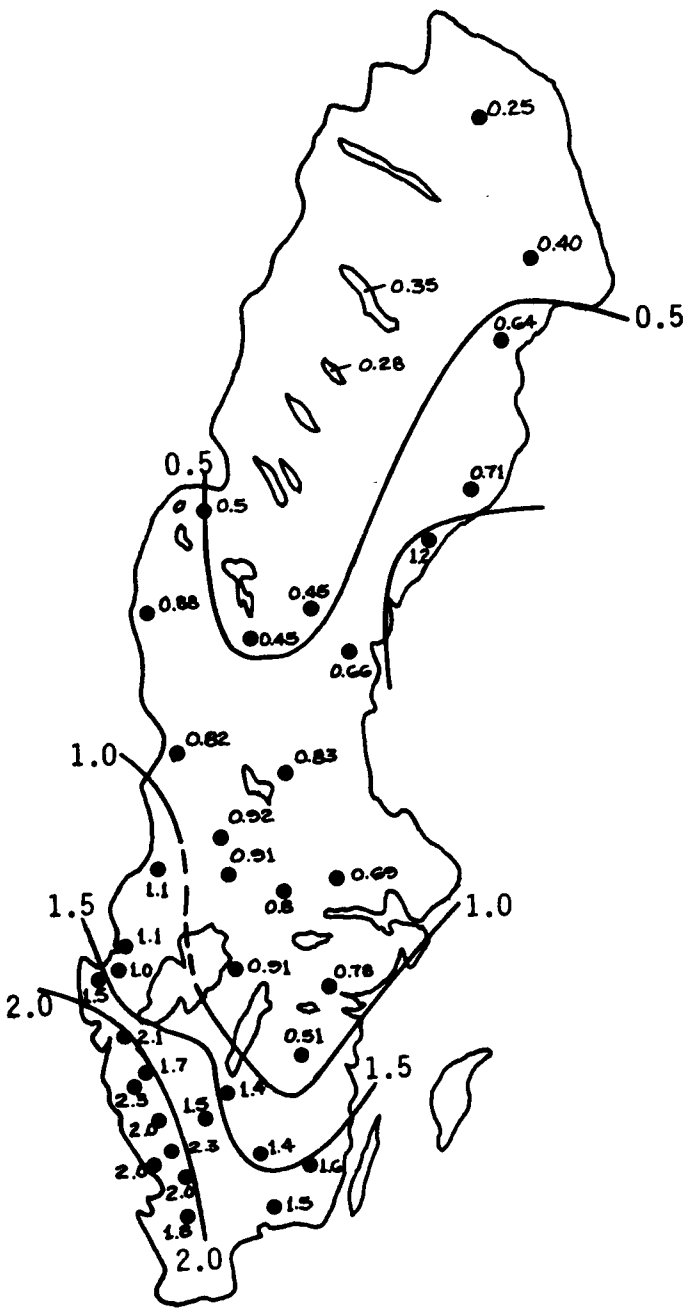

Figure 4-25. "Excess" sulfur in lake water per year (g S m^{-2} yr^{-1}). (Concentration of "excess sulfur multiplied by the yearly runoff.) Adapted from Almer et al. (1978).

As a minimum condition, before the Almer/Dickson Relationship can be applied to the problem of predicting the effects of changes in acidic deposition on the chemistry of surface waters in any geographic region, reliable quantitative relationships between primary factors (e.g., wet sulfate deposition) and sulfate concentrations in surface waters must be developed. Further, all assumptions inherent in the approach require testing and validation.

4.5.2 Henriksen's Predictor Nomograph

The contributions of Henriksen (1979, 1980, 1982) to the empirical study of the effects of atmospheric and edaphic factors on the chemistry of oligotrophic lakes in Scandinavia are well known. Among his contributions is the "predictor nomograph"--an empirical relationship intended to be used as a tool in predicting effects of varying levels of acidic deposition on the pH of lakes.

Using data from 719 lakes in southern Norway (Wright and Snekvik 1978), Henriksen (1980) compared the concentration of excess (above sea salt contributions) calcium plus excess magnesium with excess sulfate concentrations in the pH ranges 4.6 to 4.8 and 5.2 to 5.4 (see Figure 4-26) and found "highly significant" linear correlations. Axes of excess calcium concentration (parallel to the axis of excess calcium plus magnesium) and excess sulfate in precipitation and pH of precipitation (both parallel to the axis of excess sulfate in lake water) complete the predictor nomograph. These final axes were developed from local empirical relationships. Henriksen (1980) used an independent data set from a survey of 155 Norwegian lakes to test his nomograph and found that it correctly predicted pH groupings approximately 85 percent of the time. Henriksen (1982) concluded that the relationships depicted by the predictor nomograph corroborated his hypothesis that for the lakes he studied (clear headwater oligotrophic lakes on granitic or siliceous bedrock) "acidified waters are the result of a large scale acid base titration." He further concluded that the nomograph was capable of predicting the effects that a change in precipitation pH might have on the pH status of lakes of the type he studied in the region he studied.

As with all predictive constructs, or models, a number of key assumptions (all clearly recognized and noted by Henriksen 1980, 1982) are involved in the use of the predictor nomograph.

One assumption or condition for using the model is that it not be used for lake waters with significant concentrations of organic acids. This is because (1) these acids may affect lake pH independent of precipitation acidity and (2) analyses for calcium and magnesium include these ions bound to organics; thus ionic concentrations of excess Ca^{+2} plus excess Mg^{+2} may be overestimated.

A second factor in the use of the nomograph involves the possible increased leaching of base cations from soils by acidic precipitation. In his original work, Henriksen (1980) assumed no increased leaching of base cations but noted the possible importance such an event would hold

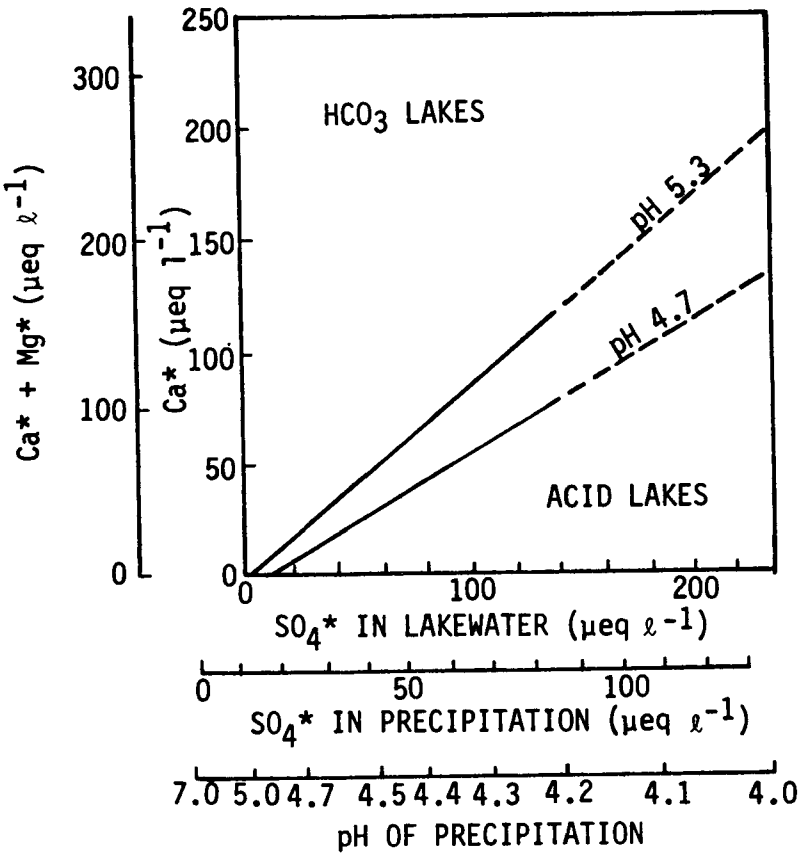

Figure 4-26. A nomograph to predict the pH of lakes given the sum of non-marine calcium and magnesium concentrations or non-marine calcium concentration only and the non-marine sulfate concentrations in lake water or either the weighted-average non-marine sulfate or the weighted-average hydrogen ion concentration in precipitation. Adapted from Henriksen (1980). * denotes seasalt corrected values.

for use of the nomograph. He has subsequently studied this question in more detail, using data from lakes in North American and Scandinavia (Henriksen 1982).

He examined data from lakes in areas of similar geology over a gradient of deposition acidity, and he also compared time trend data of calcium and magnesium in certain waters. Unfortunately, he found no clear cut answer to the question. In some cases, there was evidence of increase in base cation concentrations (up to 0.63 for Lake Rishagerodvatten, Sweden). In other cases, there was none. In an effort to overcome these difficulties and conflicting data, Henriksen (1982) used his best judgment to designate a maximum value of "base cation increase factor" of 0.4 $\mu eq\ (Ca^* + Mg^*)/\mu eq\ SO_4^*$. That is, for every $\mu eq\ \ell^{-1}$ increase in excess sulfate (SO_4^*) concentration in a lake, a maximal increase in excess calcium plus magnesium ($Ca^* + Mg^*$) concentration would be 0.4 $\mu eq\ \ell^{-1}$. It must be noted that in at least one case, Henriksen (1982) found a greater increase factor than this--0.63 for Lake Rishagerodvatten, Sweden. Care should be exercised in the application of this "base cation increase factor" for predictive purposes. It may vary significantly from region to region (or watershed to watershed within a region) as a function of soil chemical properties (e.g. sulfate adsorption capacity, cation exchange capacity, base saturation), soil depth, and the path of precipitation through the soil. In fact, it seems reasonable to assume that for some regions initially experiencing acidic deposition, the "increase factor" may be as high as 1.0. Certainly more quantitative research is needed on this question.

Another condition noteworthy in the use of the predictor nomograph is the premise that all data used in its construction and verification represent steady state conditions. Due to the large number of lakes and deposition events and periods sampled, the data requirements to verify this condition for the nomograph are astronomical and virtually impossible to satisfy. As an article of faith it must be assumed that the data employed do represent steady state conditions. For many of the lake data (especially at the "edges" or extremes of conditions) this probably is not a bad assumption. Lake data representing transitory conditions are, perhaps, more suspect.

A final question to consider in regard to the predictor nomograph is its application to geographic regions other than (but similar to) the one for/from which it was developed. This is always a key question with such empirical models. Even if the general approach is accepted as sound, common sense dictates that the empirical relationships found in southern Norway and Sweden may not pertain to even seemingly analogous conditions elsewhere. (Certainly this is true of the axes relating precipitation chemistry to excess sulfate concentrations in lakes. Most acidic precipitation in North America contains relatively more nitric acid than does acidic precipitation in Scandinavia.) The inconsistencies encountered by Bobee et al. (1982) and Haines et al. (1983b) in attempting to apply the nomograph to lakes in Quebec and New England, respectively, should be noted in this regard. It may very well be that

the predictor nomograph will have to be modified to accommodate local relationships for whatever region for which application is attempted.

4.5.3 Thompson Cation Denudation Rate Model (CDR)

As seen in the previous discussions of the Almer/Dickson relationship and the Henriksen predictor nomograph, the quantification of the interrelationships of sulfate loading, base cation concentrations, and surface water pH seem to hold promise for understanding and predicting surface water chemistry in some situations. These interrelationships have been explored also by Thompson (1982), who has related surface water pH to excess sulfate loading and the rate of cation loss from watersheds (the Cation Denudation Rate or CDR). As with the prior models, her approach is restricted to relatively unbuffered surface waters with low concentrations of organic acids in areas with acid-resistant bedrock, till, and soils.

Thompson's model derives from charge balance and holds that a plot of excess sulfate concentration vs the sum of base cation concentrations yields a series of lines representing constant bicarbonate concentration. If CO_2 partial pressure is constant, then each line also represents constant pH. If CDR (concentration x discharge ÷ watershed area) is plotted against atmospheric excess sulfate loading rate (equivalent to acid loading) and if runoff is specified at 1 m yr^{-1}, then an equivalent representation applicable to lakes or streams is generated (Thompson and Hutton 1981, Thompson 1982) (see Figure 4-27).

A number of important assumptions apply to this approach. First, all non-sea salt sulfate must come from atmospheric loading alone. Second, all sulfate deposited in a watershed must flow through the watershed *without being retained (on a net basis)*. Third, all sulfate must be accompanied by protons as it enters and leaves the watershed. The difficulties with each of these assumptions and the everyday application of such a model have been thoroughly described in the preceding discussions of the Almer/Dickson Relationship and the Henriksen predictor nomograph. Another difficulty or necessary assumption relates to both the constancy and quantification of P_{CO2} in any set of waters to which the model may be applied. Significant variations in CO_2 partial pressures in surface waters are well known.

Yet another point worth considering is the fact that Thompson (1982) tested this approach in some highly colored lakes and rivers of Nova Scotia (Figure 4-28). Although she noted that the pH values of these rivers "have been thought to be dominated by naturally-occurring organic acids", Thompson (1982) feels that "their low pHs can be explained quite well on the basis of simple inorganic chemistry." A way to resolve this question is through Gran titrations for weak and strong acids. Apparently, such a study has not been conducted. The CDR model has yet to be thoroughly verified with any other data sets.

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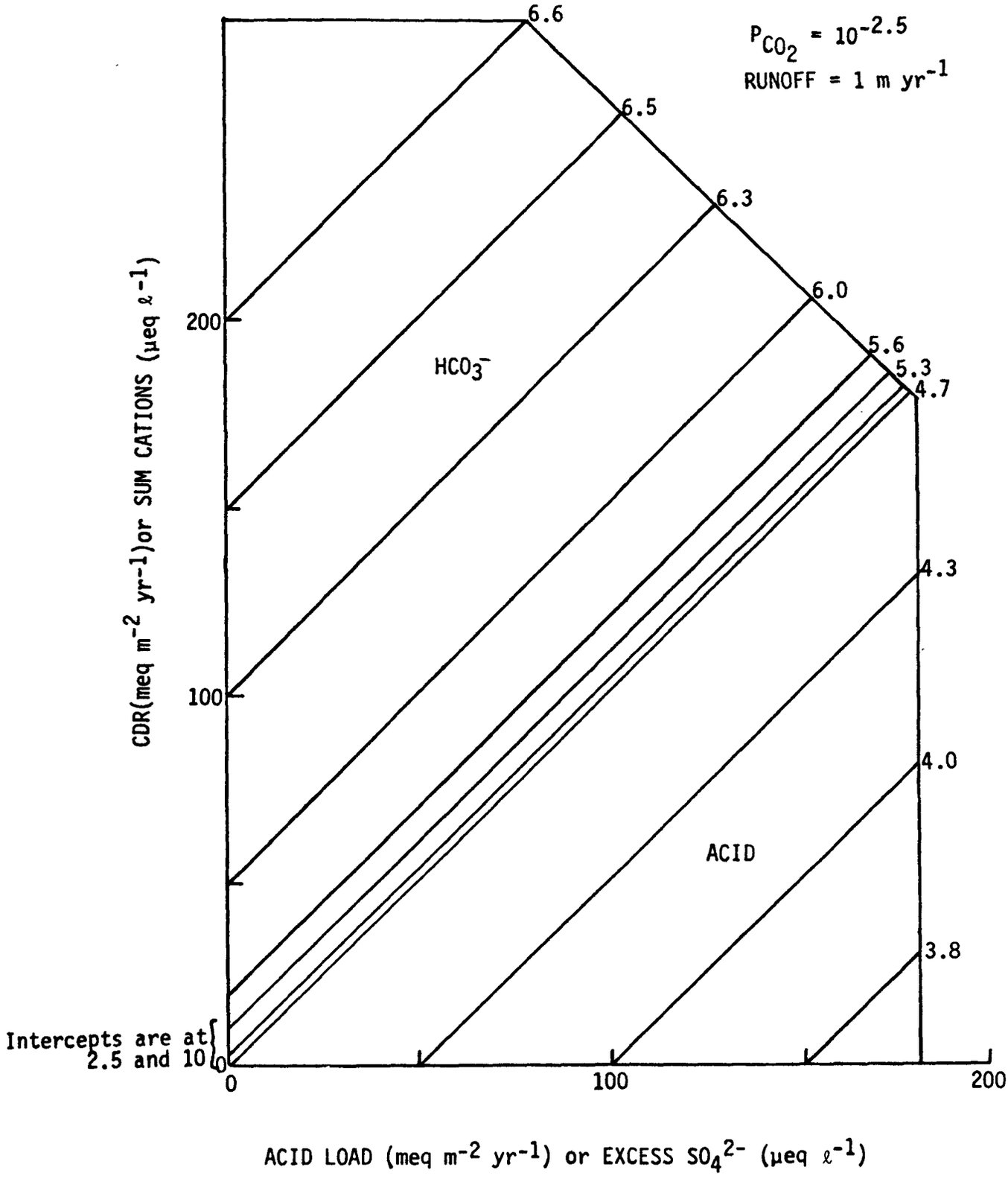

Figure 4-27. A plot of the model that relates pH and sum of cations to excess SO_4 - in concentration units, or pH and CDR to rate of excess SO_4 - loading in rate units.

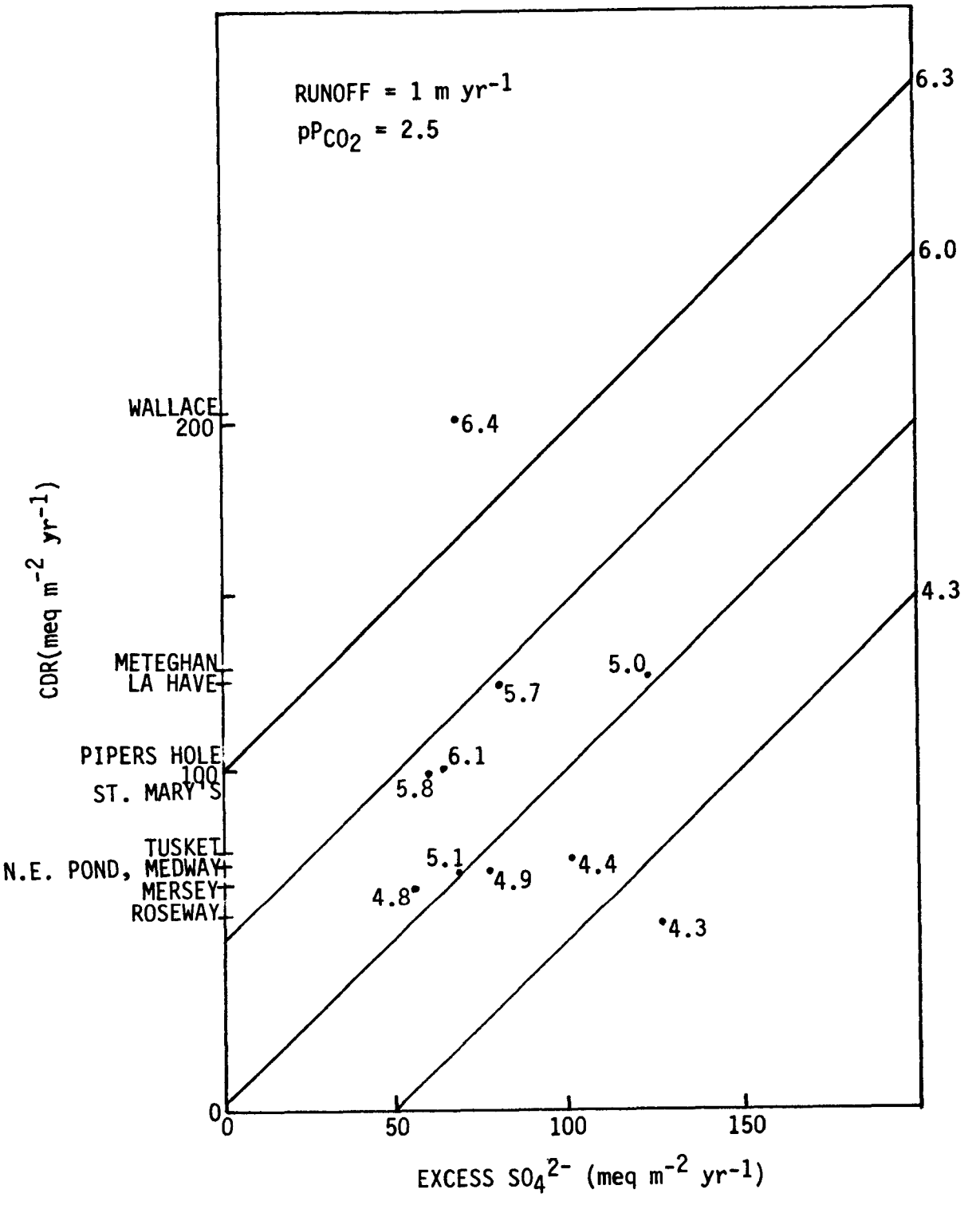

Figure 4-28. CDR plot for rivers with mean runoff near 1 m yr^{-1}, 1973 excess SO_4 - loads, and mean or median river pH.

4.5.4 Summary of Predictive Modeling

As is evident in the preceding discussions, there is still much to learn about a number of key factors that influence the ways in which lakes/watersheds respond to acidic deposition, and thus the ways in which these responses may be modeled and predicted, even on the most basic levels. Factors that appear to be of primary importance but about which our knowledge is still inadequate include: 1) the ability of soils to retain sulfur inputs from atmospheric deposition; 2) the effects of acidic inputs on cation exchange and leaching from soils; 3) the mobilization of aluminum compounds from soils due to acidic deposition; 4) the effects of acidic inputs on mineral weathering; 5) the presence or absence of hysteresis in those processes and their effects as a function of increasing or decreasing inputs of acids (Galloway et al. 1983a).

In short, predictive modeling of the acidification of surface waters is still in an infant stage. Some interesting ideas have been put forth and some progress is being made but there is still a very long way to go before any model will be able to be used with quantitative confidence. Certainly none of the three models discussed briefly here have been verified adequately for "off-the-shelf" application in North American waters. Such an application without a clear recognition and statement of all the assumptions and limitations contained in these approaches would violate virtually every rule concerning the prudent use of predictive models (Reckhow and Chapra 1981, Bloch 1982).

4.6 INDIRECT CHEMICAL CHANGES ASSOCIATED WITH ACIDIFICATION OF SURFACE WATERS

Acidic deposition is composed of NH_4^+, SO_4^{2-}, NO_3^-, H^+, and basic cations. The previous sections have discussed the chemical effects acidic precipitation has in aquatic systems by direct altering the concentrations of these same chemicals. There are additional indirect effects on other chemicals. Specifically, the addition of acidic deposition to terrestrial and aquatic systems can disrupt the natural biogeochemical cycles of some metal and organic compounds to such a degree that biological effects occur. The following three sections discuss these chemical effects and assess the state of our knowledge. The first section (4.6.1) focuses on metals in general; the second (Section 4.6.2) specifically on aluminum. Elevated levels of aluminum in acidified surface waters have been demonstrated to be toxic to aquatic biota (Chapter E-5, Section 5.6) and thus are of particular concern. Potential interactions between acidic deposition and organic carbon cycles are discussed in Section 4.6.3.

4.6.1 Metals (S. A. Norton)

The impact of acidic precipitation or, more broadly, atmospheric deposition on metal mobility in aquatic ecosystems may be divided into four areas:

1) Increased loading of metals from atmospheric deposition to terrestrial and aquatic ecosystems.

2) Direct effects of atmospheric deposition on metal release rates from or to aquatic ecosystems.

3) Secondary effects of atmospheric deposition on metal release rates from or to aquatic ecosystems--both positive and negative.

4) Changes in aqueous speciation of metals and consequent biological effects.

4.6.1.1 Increased Loading of Metals From Atmospheric Deposition--In many instances enhanced loadings of metals are associated with elevated levels of NH_4^+, SO_4^{2-}, NO_3^-, and H^+ in acidic deposition. Although this excessive of metals is apparently related to industrial activities, historic measurements of metals in atmospheric deposition are not sufficient for establishment of temporal trends. Indirect evidence for increasing atmospheric deposition of metals is as follows:

a) Contemporary variations in atmospheric deposition of metals (e.g., Pb and Zn) are closely related to the geographic distribution of fossil fuel consumption, smelting, and transportation (which uses the internal combustion engine) (Lazrus et al. 1970). Where these sources are absent, metal deposition rates are lower (Galloway et al. 1982b). Thus, as fossil fuel consumption and other processes expand, injection of metals into the atmosphere increases and atmospheric deposition increases.

b) Ombrotrophic peat bogs, those having no source of water other than precipitation, receive all their nutrients and non-essential metals from atmospheric deposition. Some elements are relatively immobile (e.g., Pb) and, after deposition, do not chemically migrate as the peat accumulates. Increased concentrations of lead in recent peat in eastern Massachusetts (up to 1.2 x over background) suggest increases in atmospheric deposition of at least 3.5 x over the past few decades (Hemond 1980). Absolute chronology in accumulating peat generally can only be estimated; thus absolute increases cannot be rigorously established. Other elements (e.g., Zn and Cu) are increased in concentration in modern peat as compared to "old" peat, but chemical mobility at the low pH of peat interstitial waters, variable redox conditions, and biological recycling do not permit the precise calculation of absolute increases of atmospheric deposition of these metals.

c) 'Continuously' accumulating snow is believed to record or reflect changes in the chemistry of atmospheric deposition of metals. However, fractional melting, ablation, erosion and deposition of snow, and other factors obscure absolute

deposition rates. Nonetheless, it is clear that the deposition of Pb and Zn (fossil fuel-related elements) has greatly accelerated over the last 100 to 150 years in areas as remote as Greenland (Herron et al. 1976, 1977). The relative increases depend on background (pre-pollution) values and the emission (and subsequent deposition) rates for specific metals.

d) Galloway and Likens (1979) showed higher concentrations of Pb, Au, Ag, Zn, Cd, Cr, Cu, Sb, and V in modern sediments relative to older sediments of relatively undisturbed lakes. Norton et al. (1981a) and Johnston et al. (1981) demonstrated that concentrations of Pb, Zn, Cu, Cd, and V are higher in modern sediments than in older sediments and established that the ubiquitous (in northern New England) and essentially synchronous (ca. 1860-80) increases correlate with the initial rapid increase in the consumption of fossil fuel in this country. Because these lakes are relatively undisturbed, these changes are interpreted to be caused by increases in the rate of atmospheric deposition of these metals, starting prior to 1860.

e) Hanson et al. (1982) have shown that Pb concentrations in the organic soil horizons of high elevation spruce/fir forests of New England, New Brunswick, and Quebec are related to the pH of precipitation. Low pH is associated with high Pb (Lazrus et. al. 1970). Groet (1976) demonstrated spatial variation in the northeastern United States of concentrations of heavy metals in bryophytes, mosses, and liverworts (known concentrators of atmospherically-deposited metals). Highest concentrations are related to regional industrialization.

f) The litter, fermentation, and humic layers of organic soils of fir forests represent successively longer time period and progressively more decayed material. The concentration of lead, which is chemically immobile (probably because of adsorption), is highest in the fermentation layer (but nearly the same as in the litter layer), suggesting increased deposition of Pb (Reiners et al. 1975, Hanson et al. 1982). Although Pb can be removed mechanically by erosion andvertical displacement, rates of deposition can be derived if the age of litter is known and mechanical erosion is nil. Siccama et al. (1980) studied white pine forest soils in central Massachusetts collected at two times (separated by 16 years) and found a higher rate of Pb accumulation in recent litter. Many workers have demonstrated spatial and temporal trends for other elements (e.g., Zn) which parallel those for Pb, but quantitatively assessing increased deposition rates cannot be done because of the nonconservative nature of the other elements.

4.6.1.2 Mobilization of Metals by Acidic Deposition--The stoichiometry of chemical weathering reactions and cation exchange and experimental evidence (e.g., Cronan 1980), suggests that increasingly acidic precipitation should increase the release of cations (any positively charged aqueous species) from soils and aquatic sediments. Empirical evidence from the United States for accelerated release of cations due to acidic deposition over a long time period, however, is rare. Oden (1976a) cited evidence for long-term increasing Ca concentrations in Swedish rivers, but long-term land use changes on the scale of 10 to 100 years (including vegetation succession) (Nilsson et al. 1982) may cause similar results (Section 4.4.3.3).

Paleolimnological evidence from sediment cores (Hanson et al. 1982) indicates that detritus deposited in lakes has been, in undisturbed watersheds, progressively more depleted in recent time with respect to easily mobilized elements, e.g., Zn, Mn, Ca, and Mg. These decreases in concentration start as early as about 1880 and are interpreted to result from increased leaching of these elements from the terrestrial ecosystem. Similar changes are not seen in areas that have only recently received acidic deposition (e.g., Swedish Lappland, Norton, unpub. data). Deposition rate and concentration data for sediments from undisturbed lakes in New England indicate continuously increasing values for Pb for all lakes for about 100 years. The values for Zn increase continuously to the present for lakes with a pH > 6.0 and decrease in younger sediments for lakes with pH < 5.5, suggesting recent acidification of those lakes with decreasing Zn (as well as Ca, Mn, and possibly Mg).

Field and laboratory soil lysimeter studies by Cronan and Schofield (1979) and Cronan (1980) indicate that modern soil solutions have chemistry (e.g., Al concentrations) that is inconsistent with the historical soil horizon development. This is interpreted to be due to more acidic influx to the soil from acidic precipitation, causing Al leaching where before Al was accumulating.

Episodic decreases in the pH of surface waters (linked quantitatively to meteorological events) are commonly accompanied by increases in dissolved Al (Schofield and Trojnar 1980) and other elements, suggesting the direction of changes to be expected in the mobilization of metals from soils, bedrock, and sediments as precipitation becomes more acidic (Norton 1981).

Data sets for metal concentrations of lake waters versus pH suggest that, because of solubility relationships, mobility of certain metals (Al, Zn, Mn, Fe, Cd, Cu) should be relatively greatly increased with increasingly acidic precipitation (Norton et al. 1981b, Schofield, 1976b, Wright and Henriksen 1978). Other metals (K, Na, Ca, Mg), the concentration of which is in the $\geq$ 0.1 ppm range, will also be affected but to a lesser degree relative to initial concentrations.

Accelerated cation release (from aquatic sediments) has also been demonstrated during experimental acidification of surface waters. In the field, Hall and Likens (1980) observed increased release of Al, Ca, Mg,

K, Mn, Fe, and Cd due to artificial acidification of streams. In isolated columns in lakes and in whole lake acidification experiments, Schindler et al. (1980) observed increased leaching of Fe, Mn,and Zn from the sediments. Andersson et al. (1978), Hongve (1978), Davis et al. (1982), and Norton (1981) demonstrated in laboratory sediment/water core microcosms that accelerated leaching of metals from sediment occurs during acidification.

4.6.1.3 Secondary Effects of Metal Mobilization--Secondary effects of acidic deposition may lead to increased or decreased metal mobility. For example, the release of Hg from sediments and soils and production of methyl mercury is promoted by more acidic waters (Wood 1980).

Secondary effects may be operative but have not been demonstrated. For example, increases of Pb (as Pb^{2+}) and SO_4^{2-} may result in immobilization of both Pb^{2+} and SO_4^{2-} as the insoluble salt, $PbSO_4$. Similarly Nriagu (1973) has suggested that excess Pb^{2+} may immobilize PO_4^{2-}. This could cause a reduction in available phosphate for aquatic ecosystems. Al sulfate minerals (Nordstrom 1982) are now suggested as being a control on Al and/or SO_4^{2-}. Increased Al^{3+} in acidified soil waters could also immobilze phosphate. Alternatively, desorption from or solution of FeOOH from "B" soil horizons in well drained soils could liberate adsorbed phosphate. These potentially important mechanisms have not been thoroughly investigated in the context of acidic precipitation. Very probably $PO4^{3-}$ availability will be strongly affected by increased concentrations of Fe^{3+} and Al^{3+} in soil and and surface waters.

4.6.1.4 Effects of Acidification on Aqueous Metal Speciation--The chemical form of dissolved metals is important in determining the total mobility of a metal and the biological effects related to acidification of aquatic ecosystems. In general, most metals are complexed less at lower pH values because few HCO_3^-, CO_3^{2-}, OH^- and other weak acid ligands are present. Limits for concentrations of metals for toxicity to organisms (Gough et al. 1979) are generally based on experiments where the water chemistry is not well characterized so such limits are probably excessively high. Some toxicity limits have been defined for "soft" and "hard" water (e.g., Howarth and Sprague 1978). The upper limits for toxicity for hard water are generally much higher than for soft water, reflecting the probable importance of speciation.

4.6.1.5 Indirect Effects on Metals in Surface Waters--The rate of deposition of several metals from the atmosphere is increased due to anthropogenic activities. The metals include Pb, Au, Ag, Zn, Cd, Cr, Cu, Sb, and V. Primary and secondary effects of acidic deposition on metal mobility include increased solubility of Al, Zn, Mn, Fe, Cd, Cu, K, Na, Ca, and Mg. These metals are mobilized by acidic deposition both from the terrestrial system and from lake sediments.

As aquatic systems acidify, speciation of metals changes. The direction of changes is generally to a more biologically active species.

4.6.2 Aluminum Chemistry in Dilute Acidic Waters (C. T. Driscoll)

4.6.2.1 Occurrence, Distribution, and Sources of Aluminum--Aluminum is the third most abundant element within the earth's crust (Garrels et al. 1975). It occurs primarily in aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks and as clay minerals in well-weathered soils. In high elevation, northern temperate regions, the soils encountered are generally podzols (Buckman and Brady 1961). The podzolization process involves mobilizing aluminum from upper to lower soil horizons by organic acids leached from foliage as well as from decomposition in the forest floor (Bloomfield 1957; Coulson et al. 1960a,b; Johnson and Siccama 1979). Aluminum largely precipitates in lower soil horizons (Ugolini et al. 1977). Ugolini et al. (1977) have observed that during podzolization little aluminum mobilizes from the adjacent watershed to surface waters. Stumm and Morgan (1970) report a median aluminum value of 10 μg Al ℓ^{-1} for terrestrial waters, while Bowen (1966) gives an average concentration of 240 g Al $^{-1}$ for freshwaters including bogs. It is noteworthy that values of aluminum reported for circumneutral waters are generally greater than levels predicted by mineral equilibria (Jones et al. 1974). Because of the tendency for aluminum-hydroxy cations to polymerize through double OH bridging when values of solution pH exceed about 4.5 (Smith and Hem 1972), a considerable fraction of the "dissolved" aluminum reported in many analyses of natural water having near-neutral or slightly acidic pH may consist of suspended microcrystals of aluminum hydroxide. Hem and Robertson (1967) have shown that crystals having a diameter near 0.1 m were relatively stable chemically. Filtration of samples through 0.4 m porosity membranes, a common practice in clarifying natural water prior to analysis, may fail to remove such material (Kennedy et al. 1974). However, the concentrations of dissolved aluminum are generally low in most circumneutral natural waters due to the relatively low solubility of natural aluminum minerals.

Superimposed on the natural podzolization process is the introduction of mineral acids from acidic deposition to the soil environment. It has been hypothesized that these acids remobilize aluminum soluble previously precipitated within the soil during podzolization or held on soil exchange sites (Cronan and Schofield 1979). Elevated levels of aluminum have been reported in acidic waters within regions susceptible to acidic deposition (Table 4-7).

Many investigators have observed an exponential increase in aluminum concentration with decreasing solution pH (Hutchinson et al. 1978, Dickson 1978a, Wright and Snekvik 1978, Schofield and Trojnar 1980, Vangenechten and Vanderborght 1980, Hultberg and Johansson 1981, Driscoll et al. 1983). This phenomenon is characteristic of the theoretical and experimental solubility of aluminum minerals. Researchers have hypothesized several mechanisms for the solid phase controlling aluminum concentrations in dilute water systems, including poorly crystallized 1:1 clays (Hem et al. 1973) kaolinite (Norton 1976), aluminum trihydroxide (May et al. 1979, Johnson et al. 1981, Driscoll et al. 1983), basic aluminum sulfate (Eriksson 1981) and exchange on soil organic matter

TABLE 4-7. ALUMINUM CONCENTRATION IN DILUTE ACIDIC WATERS

Location	Description	pH Range	Al Range $\mu g\ Al\ \ell^{-1}$	Reference
Lakes				
Sweden	Swedish West Coast, 1976	4.0 - 7.4	10 - 670	Dickson 1978a
Norway	Regional Survey, 1974-77	4.2 - 7.8	0 - 740	Wright et al. 1977
Scotland	Southwestern Scotland, 1979	4.4 - 6.4	25 - 310	Wright et al. 1977
Belgium	Moorland pools Northern Belgium, 1975 - 1979	3.5 - 8.5	300 - 8000	Vangenechten and Vanderborght 1980
USA	Adirondacks, 1977-1978	3.9 - 7.2	4 - 850	Driscoll 1980
Canada	Ontario various locations, 1980	4.1 - 6.5	6 - 856	Kramer 1981
Canada	Sudbury, Ontario	4.3 - 7.0	150 - 1150	Scheider et al. 1975
Streams				
USA	Adirondacks, 1977-1978	4.0 - 7.6	92 - 1170	Driscoll 1980
USA	Adirondacks, 1977	4.4 - 6.5	100 - 1000	Schofield and Trojnar 1980

TABLE 4-7. CONTINUED

Location	Description		pH Range	Al Range μg Al ℓ$^{-1}$	Reference
Streams (cont.)					
USA	Hubbard Brook	stream order 1	4.73	710	Johnson et al. 1981
		2	4.94	320	
		3	5.09	210	
		2	5.19	200	
		3	5.54	150	
		3	5.46	190	
		4	5.51	180	
		4	5.58	160	
		5	5.68	150	
		average	4.90	230	
Groundwaters					
Sweden	West Coast, 1977-1978		3.8 - 5.7	100 - 2600	Hultberg and Johansson 1981
USA	Hubbard Brook seepwater, 1979		4.6 - 6.5	0 - 700	Mulder 1980

(Bloom et al. 1979). Johnson et al. (1981) and Driscoll et al. (1983) compare and discuss solution characteristics of New Hampshire and Adirondack waters, respectively, with the theoretical solubility of a variety of aluminum minerals. Eriksson (1981) observed that calculated values of aquo aluminum in soil solutions from Sweden were similar to values predicted from mineral solubility reported by van Breemen (1973) for Al (OH) SO_4, at a given pH. This lead Eriksson (1981) to suggest that atmospheric deposition of sulfate has acidified and transformed aluminum oxides to basic aluminum sulfate in Swedish soils. Unfortunately, Eriksson (1981) failed to consider fluoride, sulfate, and organic complexation reactions when computing aquo aluminum levels. Therefore, as suggested by Nordstrom (1982), it is doubtful that aluminum sulfate minerals (e.g., jurbanite, alunite, basaluminite) control aquo aluminum levels in waters acidified by acidic deposition. In actuality it is extremely difficult to identify a specific solution controlling phase. Analysis of soils and sediments by x-ray diffraction has failed to confirm the presence of hypothesized solution controlling minerals of aluminum (Driscoll et al. 1983).

4.6.2.2 Aluminum Speciation--Dissolved monomeric aluminum occurs as aquo aluminum, as well as hydroxide, fluoride, sulfate, and organic complexes (Robertson and Hem 1969, Lind and Hem 1975). Past investigations of aluminum in dilute natural waters have often ignored non-hydroxide complexes of aluminum (Cronan and Schofield 1979, N. M. Johnson 1979, Eriksson 1981). Driscoll and coworkers (Driscoll et al. 1980, Driscoll 1980, Driscoll et al. 1983) have fractionated Adirondack waters into inorganic monomeric aluminum, organic monomeric aluminum, and acid soluble aluminum. They observed that inorganic monomeric aluminum levels increased exponentially with decreasing solution pH. Organic monomeric aluminum levels were strongly correlated with total organic carbon (TOC) concentration but not pH. Acid soluble aluminum levels were relatively constant and not sensitive to changes in either pH or TOC. Driscoll et al. (1983) reported that organic complexes were the predominant form of monomeric aluminum in Adirondack waters, on the average accounting for 44 percent of monomeric aluminum. Aluminum fluoride complexes were the second major form of aluminum and the predominant form of inorganic monomeric aluminum, accounting for an average of 29 percent of the monomeric aluminum. Aquo aluminum and soluble aluminum hydroxide complexes were less significant than aluminum fluoride complexes. Aluminum sulfate complexes were small in magnitude.

4.6.2.3 Aluminum as a pH Buffer--Dilute water systems are characteristically low in dissolved inorganic carbon (DIC) due to limited contact with soil. Because dilute waters are inherently low in DIC, they are limited with respect to inorganic carbon buffering capacity. Consequently, non-inorganic carbon acid/base reactions, such as hydrolysis of aluminum and protonation/deprotonation of natural organic carbon, may be important in the pH buffering of dilute waters.

Several researchers have investigated organic carbon, weak acid/base systems in dilute waters. Dickson (1978a) observed that elevated levels of aluminum increased the BNC of Swedish lakes. Waters were strongly

buffered by aluminum in the pH range 4.5 to 5.5 The BNC of aluminum was particularly evident when acidified lakes were treated with base (limed). Aluminum BNC was comparable in magnitude to hydrogen ion and inorganic carbon BNC; therefore, the presence of aluminum substantially increased base dose requirements and the cost associated with the restoration of acidified lakes.

Johannessen (1980) investigated non-hydrogen/inorganic carbon buffering in Norwegian waters. While reiterating the importance of aluminum as a buffer in dilute acidified waters, she also evaluated the role of natural organic acids. Natural organic matter reduced the degree to which aluminum hydrolyzed in the pH range 5.0 to 5.5, presumably due to complexation reactions, and therefore decreased the buffering of aluminum. Natural organic matter also participated in proton donor/acceptor reactions; the extent to which total organic carbon (TOC) would dissociate/associate protons was 7.5 μeq mg organic carbon^{-1}. Johannessen (1980) concluded that organic carbon was the most important weak acid/base system in acidic Norwegian waters because of the high organic carbon concentration relative to aluminum.

Glover and Webb (1979) evaluated the acid/base chemistry of surface waters in the Tovdal region of southern Norway. The BNC of hydrogen ion was small compared to the BNC of weak acid systems. These investigators suggested that of the total weak acid BNC, 40 to 60 μeq ℓ^{-1} could be attributed to dissolved aluminum and silicon, while 20 to 50 μeq ℓ^{-1} could be attributed to natural organic acids. Solution titrations were characterized as having a major proton dissociation constant (Ka) of 10^{-6} to 5 x 10^{-7}, in addition to some less well defined ionization at higher pH values.

In a comparable study, Henriksen and Seip (1980) evaluated the strong and weak acid content of surface waters in southern Norway and southwestern Scotland. In addition to a titrametric analysis, the aluminum, dissolved silica, and TOC content of water samples were determined. Weak acid concentrations, determined by a Gran (1952) calculation, were evaluated by multiple regression analysis. Most of the variance in the weak acid concentration could be explained by the aluminum and TOC content of the waters. Thus, it was concluded that the weak acid content of acidified lakes in southern Norway and Scotland was largely a mixture of aluminum and natural organic acids.

Driscoll and Bisogni (1983) quantatively evaluated weak acid/base systems buffering dilute acidic waters in the Adirondack region of New York State. Natural organic acids were fit to a monoprotic proton dissociation constant model (pKa = 4.41), and the total, organic carbon proton dissociation/association sites were observed to be empirically correlated to TOC concentration. Aquo-aluminum levels, calculated from field observations, appeared to fit an aluminum trihydroxide solubility model.

Calculated buffering capacity (β) is plotted against pH in Figure 4-29 for a hypothetical system that has some properties in common with

Adirondack waters (Driscoll and Bisogni 1983). Buffering capacity is defined as the quantity of strong acid or base (mols ℓ^{-1}) which would be required to change the pH of a liter of solution by one unit. Conditions specified for the construction of Figure 4-29 are indicated in the figure title. Aluminum species may dominate the buffer system at low pH if these conditions are fulfilled, suggesting that the lower limit of pH observed in acidic waters with elevated aluminum levels may be controlled by the dissolution of aluminum. At higher pH values the buffer system is dominated by inorganic carbon and would be even more strongly dominated if carbonate solids were present.

It is noteworthy that aluminum polymeric cations and particulate species, that may occur in acidic solutions, provide some solution buffering (both ANC and BNC). However, these large units may be slow to equilibrate with the added titrant. Therefore, ANC and BNC determinations have limitations in acidic waters due to heterogeneity phase problems.

4.6.2.4 Temporal and Spatial Variations in Aqueous Levels of Aluminum--Pronounced temporal and spatial variations in levels of aqueous aluminum have been reported for acidic waters. Schofield and Trojnar (1980) observed that high aluminum levels occurred during low pH events in streams, particularly during snowmelt. Driscoll et al. (1980) also observed this phenomenon but attributed aluminum increases to inorganic forms of aluminum. During low flow conditions, neutral pH values were approached in streams (pH 5.5 to 7.0) and inorganic monomeric aluminum levels were low. During summer months, levels of TOC in streams increased and organically complexed aluminum levels increased. As mentioned previously, levels of organic monomeric aluminum were strongly correlated with surface water TOC (Driscoll et al. 1983).

Johnson et al. (1981) studied temporal and spatial variations in aluminum chemistry of a first-through-third order stream system in New Hampshire. Observations of temporal variations in aluminum were similar to those reported for the Adirondacks (Driscoll et al. 1980, Schofield and Trojnar 1980). Johnson et al. (1981) reported decreases in hydrogen ion and aluminum levels with increasing stream order. They suggested a two-step process for the neutralization of acidic deposition. Mineral acidity entering the ecosystem from atmospheric deposition was converted to a mixture of hydrogen ion and aluminum BNC (acidity) in headwater streams and was subsequently neutralized through the dissolution of basic cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) containing minerals within the soil environment.

Johnson et al. (1981) observed a shift in aluminum speciation with increasing stream order. Aquo aluminum and aluminum hydroxide complexes decreased substantially with increasing stream order. Alumino-fluoride complexes remained constant throughout the experimental reach. Alumino-organic forms increased in concentration with decreasing elevation.

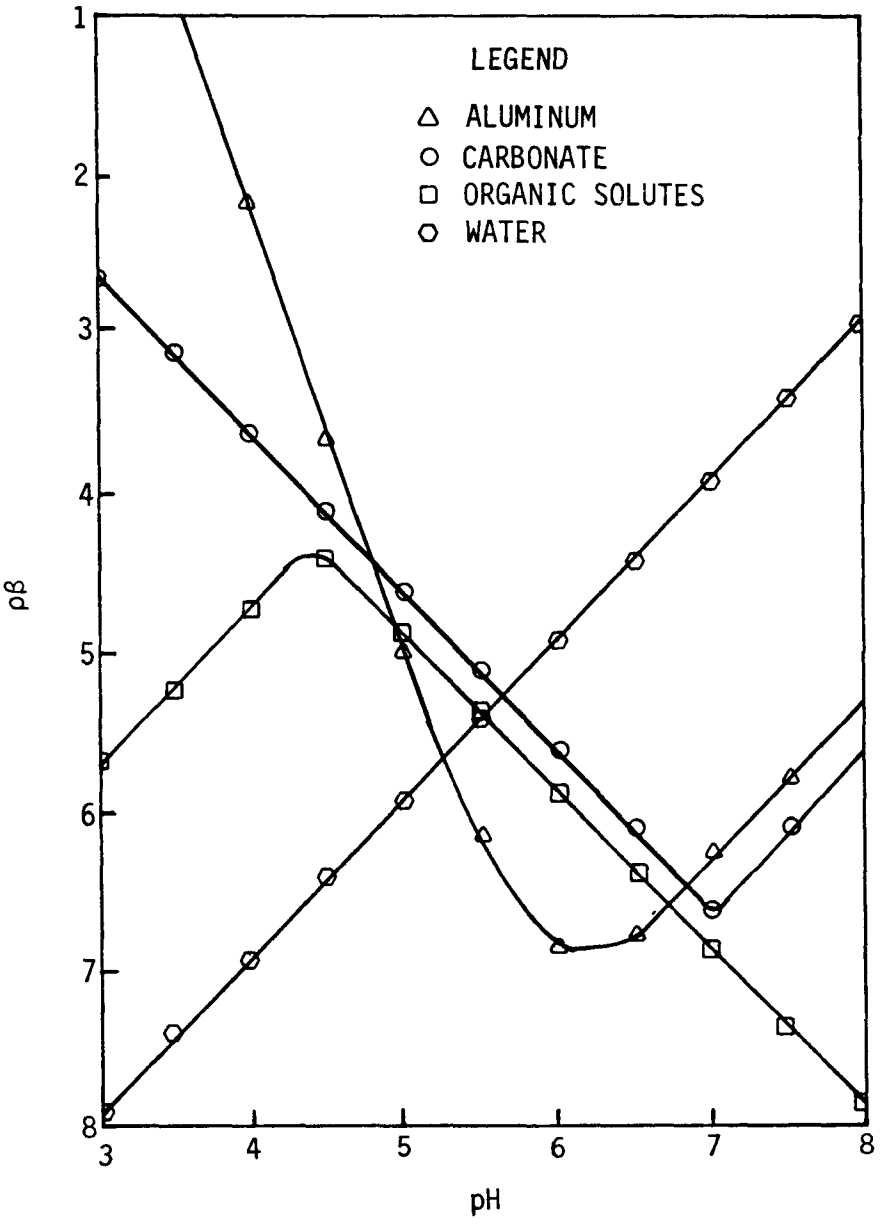

Figure 4-29. Buffer capacity diagram for dilute Adirondack water systems (Driscoll and Bisogni 1983). Equilibrium with aluminum trihydroxide (pKso = 8.49), organic solutes (CTorg = 2×10^{-5}, pKorg =4.4) and atmospheric carbon dioxide ($Pco_2 = 10^{-3.5}$ atm) were assumed.

Driscoll (1980) has evaluated temporal and spatial variations in aluminum levels in acidic lakes. During summer stratification, monomeric aluminum levels were low in the upper waters and increased in concentration with depth. Low aluminum levels reported in the upper waters during the summer coincided with elevated pH and ANC values. The increased pH and ANC values were attributed to algal assimilation of nitrate (Brewer and Goldman 1976). During ice cover, pH (and ANC) values were low and aluminum levels high directly under the ice. The pH values increased and aluminum values decreased with depth. The clinograde distribution of pH and aluminum observed during ice cover periods has been attributed to reduction processes in sediments (e.g., denitrification). These processes generate ANC, which diffuses into the lower waters. During fall and spring turnover, aluminum is evenly distributed throughout the water column of acidic lakes. Aluminum levels were particularly high during the spring season because of inputs of low pH, high aluminum stream water associated with spring snowmelt.

Few studies have considered temporal and spatial variations in aluminum chemistry of groundwaters. Hultberg and Johansson (1981) have observed acidification events in groundwater chemistry in Sweden. They hypothesized that much of the atmospheric input of sulfur was retained within the terrestrial ecosystem as reduced sulfur forms. During extremely dry conditions, the water table was lowered and pools of reduced sulfur within the soil become oxidized by molecular oxygen entering the zone. Very low values (< 4.0) and very high aluminum levels (> 40 mg Al ℓ^{-1}) have been reported in groundwater by Hultberg and coworkers (Hultberg and Wenblad 1980, Hultberg and Johansson 1981) when a prolonged dry period was followed by a rainfall event. It is difficult to conclusively attribute groundwater to atmospheric deposition of sulfate. A possible source of the acidity in the groundwater studied by Hultberg and Johansson (1981) was the oxidation of reduced iron minerals, likely to have been present naturally in the upper part of the zone of saturation. This oxidation would have occurred when the water table declined due to dry weather and molecular oxygen entered the zone. The hydrogen ion produced by iron oxidation with molecular oxygen would not be significantly mobilized in the groundwater until the water table increased again to a more normal level.

4.6.2.5 The Role of Aluminum in Altering Element Cycling Within Acidic Waters--In acidic water systems conditions of supersaturation with respect to aluminum trihydroxide have been reported (Driscoll et al. 1983). During conditions of supersaturation, aluminum will hydrolyze, forming particulate aluminum oxyhydroxide. The acid-soluble aluminum fraction mentioned earlier would include the microcrystalline hydroxide particles and their polymeric hydroxycation precursors. Smith and Hem (1972) observed that during the polymerization process, aluminum hydroxide units displayed metastable ionic solute behavior until they contained from 100 to 400 aluminum atoms. When particles developed to that size their behavior was characteristic of a suspended colloid. Microcrystalline particles have a very large specific surface area and may adsorb or co-precipitate organic and inorganic solutes. The cycling

of orthophosphate (Huang 1975, Dickson 1978a), trace metals (Hohl and Stumm 1976) and dissolved organic carbon (Dickson 1978a, Davis and Gloor 1981, Driscoll et al. 1983, Hall et al. 1982) within acidic surface waters may be altered by adsorption on aluminum oxyhydroxides. However, few studies have addressed this specific hypothesis.

Huang (1975) studied the adsorption of orthophosphate on Al_2O_3. He observed an adsorption maximum at pH 4.5. While Huang (1975) studied the adsorption of high levels of orthophosphate (10^{-4} to 10^{-3} M), much higher than would be observed in natural dilute water systems, his observations of phosphate aluminum interactions may be generally applicable.

Dickson (1978a) observed that when acidic lake water, elevated in aluminum, was supplemented with orthophosphate (50 and 100 μg P ℓ^{-1}), dissolved phosphorus was removed from solution. The removal of phosphorus was most pronounced at pH 5.5. Dickson (1978a, 1980) suggested that aqueous aluminum may substantially alter phosphorous cycling within acidic surface waters through adsorption or precipitation reactions. This hypothesis is noteworthy because phosphorus is often the nutrient limiting algal growth in dilute surface waters (Schindler 1977). Any decrease in aqueous phosphorus induced by adsorption on aluminum oxyhydroxides may result in a decrease in algal growth and an accompanied decrease in algal generated ANC (see Section 4.7.2). Any decrease in ANC inputs would result in an aquatic ecosystem more susceptible to further acidification.

Aluminum forms strong complexes with natural organic matter (Lind and Hem 1975). Complexation substantially alters the character of natural organic acids. Driscoll et al. (1983) observed that DOC was removed from the water column of an acidic lake after $CaCO_3$ addition. They hypothesized that DOC sorbed to the particulate aluminum that had formed within the water column shortly after base addition. Driscoll (1980) observed decreases in water column TOC during conditions of super saturation with respect to $Al(OH)_3$ in an acidic lake. He hypothesized that natural organic carbon was scavenged from solution by particulate aluminum formed in the water column. Davis (1982) has studied the adsorption of natural dissolved organic matter at the γ - Al_2O_3/ water interface. He observed that natural organic matter adsorbs by complex formation between the surface hydroxyls of alumina and acidic functional groups of organic matter. Davis (1982) indicated that DOC adsorption was maximum at pH 5. Davis and Gloor (1981) reported that DOC associated with molecular weight fractions greater than 1000 formed strong complexes with the alumina surface, but low molecular weight fractions were weakly adsorbed. Davis (1982) suggests that under conditions typical for natural waters almost complete surface coverage by adsorbed organic matter can be anticiapted for alumina. Organic coatings may be important with respect to subsequent adsorption of trace metals and anions.

Hall et al. (1982) observed a decrease in DOC levels of a third order stream in New Hampshire after aluminum chloride ($AlCl_3$) addition.

In addition, a reduction in surface tension occurred at the air-stream interface and was attributed to a decrease in the solubility of DOC due to interactions with aluminum.

DOC loss to acidic waters is significant in several respects. DOC represents a weak base that serves as a component of solution ANC (Johannessen 1980, Driscoll and Bisogni 1983). DOC also serves as an aluminum complexing ligand. Complexation of aluminum by organic ligands mitigates aluminum toxicity to fish (Baker and Schofield 1980). Therefore, any loss of DOC may translate to an environment less hospitable to fish.

4.6.3 Organics (C. S. Cronan)

4.6.3.1 Atmospheric Loading of Strong Acids and Associated Organic Micropollutants--This first subsection deals with the association (but not necessarily interaction) between anthropogenic strong acids and organic micropollutants introduced to aquatic systems via long-range transport and wet/dry deposition processes. Methods for isolating and characterizing organic micropollutants in natural samples have been described by Gether et al. (1976) and Heit et al. (1980). These methods were used by Lunde et al. (1976) to identify a wide range of organic pollutants in rain and snow samples from Norway, including alkanes, polycyclic aromatic hydrocarbons, phthalic acid esters, fatty acid ethyl esters, and many other chemicals of industrial origin. Concentrations ranged from one to several hundred ng ℓ^{-1}, with PCB concentrations registering five times higher than freshwater or seawater.

In a related study, Alfheim et al. (1978) examined the access of certain non-polar organic pollutants to lakes and rivers in Norway. Results indicated that PCB concentrations in water samples from a lake in southern Norway were considerably lower than in melted snow from the same area. Two explanations were offered to account for these observations: (1) the PCB's in the water column may have been associated with particulate matter, preventing them from being detected in the dissolved phase, and (2) terrestrial humic substances may have complexed the PCB's and related pollutants, thereby reducing their leaching into lakes and rivers.

The studies by Heit et al. (1981) focused on the historical patterns of organic pollutant deposition to remote Adirondack lakes. Using lake sediment cores and advanced analytical techniques, they found the following results. First, all of the nonalkylated 3- to 7-ring parental PAH's, with the exception of perylene, decreased in concentration with sediment depth. Surface concentrations of many of these compounds approached or exceeded levels reported for sediments from urban and industrialized areas, while baseline levels lower in the core were similar to those reported for pristine areas such as in northern Ontario. Overall, the data indicated that all of the parental PAH compounds except perylene entered these Adirondack lakes primarily through anthropogenic rather than natural processes.

These investigations by Alfheim et al. (1978, 1980) and Heit et al. (1981) have shown that a broad range of organic micro-pollutants may originate in industrial centers and be carried downwind to remote ecosystems by long-range atmospheric transport. Thus, similar patterns and processes may contribute to the atmospheric transport and deposition of both anthropogenic strong acids and organic micro-pollutants.

4.6.3.2 Organic Buffering Systems--Organic and/or aluminum weak acid buffer systems may dominate the acid-base chemistry of surface waters in watersheds characterized by the following kinds of features: granitic bedrock, thin or impermeable surficial deposits, steeper slopes, high water tables, or extremely permeable siliceous surficial deposits. In such soft water ecosystems, organic and aluminum weak acids may provide the only buffering protection against further acidification by anthropogenic strong acids. Likewise, natural humic materials may themselves have sufficiently low pka constants that they contribute to the free acidity of surface waters. Organic weak anions may be particularly significant in providing ANC below pH 5.0, with the greatest buffer intensity for the organics exhibited in the range of pH 4.5 (Figure 4-29) (Driscoll 1980).

The organic species responsible for contributing to the buffer capacity of these soft water lakes include a range of hydrophilic and hydrophobic, low and high molecular weight compounds. These organic solutes may range from simple carboxylic acids like malic acid to complex polyphenolic compounds like the model fulvic acid described by Schnitzer (1980). On the average, these organic acids in natural waters might be expected to contribute 5 to 10 μeq of anionic charge per mg carbon (Driscoll 1980; Cronan, unpub. data), and perhaps 5 to 20 μeq per mg organic carbon in total acidity (Schnitzer 1978, Henriksen and Seip 1980). Historically, organic acid buffer systems were probably relatively common in soft water aquatic systems. However, the relative importance of aluminum buffering Section 4.6.2.3) may have increased recently in those soft water lakes that have experienced modern acidification from atmospheric deposition (Henriksen and Seip 1980).

4.6.3.3 Organo-Metalic Interactions--Acidification of surface waters may affect metal-organic associations and trace metal speciation. Stability constants for metal-fulvic acid (FA) complexes have been shown to decrease with decreasing pH. For example, the conditional stability constant for Pb^{2+}-FA at pH 5.0 is 4.1, whereas it is 2.6 at pH 3.0; likewise, the Zn^{2+}-FA stability constant at pH 5.0 is 3.7, but is 2.4 at pH 3.0 (Schnitzer 1980). Because of this effect of pH on metal-organic complexation, one might expect lake acidification to result in decreased concentrations of organically-complexed metals and correspondingly higher concentrations of free inorganic trace metals. Simultaneously, the decreases in pH could lead to increased protonation of organic acid functional groups, thereby increasing the hydrophobic character of the organic acids. This process could affect the adsorption of humic materials on mineral surfaces and could also affect interactions between humic/fulvic monomers. The net result of this could be to

increase clay interlayer adsorption of fulvic acids (with associated clay degradation) and to increase the polymerization and settling of aquatic humic materials (Schnitzer 1980).

Along similar lines, there may be very important biological consequences resulting from acidification of natural waters containing metal-organic complexes. Driscoll et al. (1980) and others have already shown that free inorganic species concentrations of trace metals like aluminum are significantly more toxic than are the organically-complexed forms. Thus, where atmospheric deposition leads to a shift from organically complexed to free inorganic species of trace metals, there may be attendant impacts on aquatic biota.

4.6.3.4 Photochemistry--Another interaction that has been described is the effect of decreasing pH on the coloration or light absorption of aquatic humic materials. For instance, Schindler (1980) and Schindler and Turner (1982) found that lake coloration and extinction coefficients decreased with decreasing pH, even though no measurable change in the DOC occurred. This change in lake transparency resulted in an increase in primary productivity in the experimental lake. In addition, the acid-induced increases in transparency accelerated the rates of hypolimnion heating and thermocline deepening; at the same time, there was no significant effect on the lake's total heat budget. In terms of processes, the data were interpreted to indicate that acidification caused a qualitative change in the structure of aquatic humus and its ability to absorb light. Almer et al. (1978) also found evidence of changes in lake transparency associated with lake acidification in Sweden; however, they observed lower concentrations of DOC in transparent acidified lakes. According to their data, this scavenging of organic carbon from the lake water column may have been largly due to the formation of insoluble organic-aluminum coloids and the subsequent sedimentation of these particulates to the lake bottom.

4.6.3.5 Carbon-Phosphorus-Aluminum Interactions--The potential impact of acidic deposition upon aluminum leaching and phosphorus availability has been discussed in Section 4.6.2.5 and described by Dickson (1980) and Cronan and Schofield (1979). As Dickson (1980) has shown experimentally, increased concentrations of inorganic aluminum in freshwaters may cause increased precipitation of aluminum phosphates from the water column, resulting in decreased biological availability of phosphorus. However, where humic materials are present, the organic ligands will tend to bind the aluminum preferentially, leaving the phosphorus uncomplexed. Therefore, one would assume that where one finds increased concentrations of aquatic humic materials these will tend to decrease the toxic potential of aluminum leached from soils and will tend to preserve the availability of phosphorus in aluminum-rich waters.

4.6.3.6 Effects of Acidification on Organic Decomposition in Aquatic Systems--Lake and stream acidification associated with atmospheric deposition may also cause reductions in the rate of organic matter turnover and may ultimately lead to decreased nutrient cycling and

availability (Chapter E-5, Section 5-8). Traaen (1980) found that organic matter decomposition was retarded at pH 4.0 to 4.5 compared to control streams and suggested that this effect could be important for lakes dependent upon allochthonous inputs of carbon. Friberg et al. (1980) observed that leaf litter decay was much slower in an acid stream (pH 4.3 to 5.9) than in a paired stream at pH 6.5 to 7.3. This was interpreted to indicate that stream acidification caused biotic disturbances among the aquatic decomposer populations. Finally, Francis and Hendrey (1980) compared the decomposition rates for leaf litter in three nearby lakes at pH 5.0, 6.0, and 7.0. Results indicated that decomposition of beech leaves was inhibited considerably and bacterial populations were approximately an order of magnitude lower in the most acidic lake. These studies suggest a need to investigate what holistic import reduced organic matter turnover in acidified aquatic systems will have.

4.7 MITIGATIVE STRATEGIES FOR IMPROVEMENT OF SURFACE WATER QUALITY (C. T. Driscoll and G. C. Schafran)

4.7.1 Base Additions

The most effective means of regulating acidification would be to control hydrogen ion inputs. For atmospheric inputs this involves many political, social, economic, and energy related considerations. An alternative strategy is to symptomatically treat acidified waters by chemical addition. Various substances have been proposed for use as neutralizing agents (Grahn and Hultberg 1975); however, only lime [CaO, $Ca(OH)_2$ and limestone ($CaCO_3$)] have been used to any extent. Two base addition strategies have been practiced: direct lake addition and watershed/stream addition. While direct lake addition is the less expensive approach, the relative effectiveness of the two strategies has not been evaluated. In addition, the positive and negative consequences of these strategies have not been fully evaluated.

A variety of methods for the treatment of acidic waters associated with mine drainage have been researched and developed (Hodge 1953, Pearson and McConnell 1975a,b). Because mine drainage is often extremely acidic and contains elevated levels of hydrolyzing metals, it is extremely difficult to extrapolate base addition concepts and technology developed for mine drainage to dilute acidic waters. Therefore, this critical assessment will address only base addition to dilute water systems. Fraser et al. (1982) and Fraser and Britt (1982) compiled a detailed review of base addition technology and effects which should be referred to for information beyond the scope of this document.

4.7.1.1 Types of Basic Materials--Several types of basic materials have been used or proposed for neutralizing acidified surface waters. These materials include calcium oxide, calcium hydroxide, calcium carbonate, sodium carbonate, olivine, fly ash, and industrial slags (Grahn and Hultberg 1975). There are many considerations in selecting a base material to be used in neutralization. Scheider et al. (1975) have summarized these considerations.

1) It must be readily available in large quantities.

2) It should be relatively inexpensive.

3) It must be safe to handle and store using conventional safety precautions.

4) It should have a high neutralization potential; i.e., a small quantity of chemical should be capable of neutralizing a large quantity of water.

5) Adding a known quantity of chemical must produce a predictable change in pH. This is critical if pH sensitive organisms are already living in the lake.

6) It must be amenable to a relatively simple application technique such that a large quantity of chemical could be applied in a short period of time with a minimum of labor and equipment.

7) It must provide for a natural deficiency in the aqueous acid neutralizing capacity; i.e., it should be a normal component of the pH buffer system.

8) It should not initiate any significant ion exchange process in the lake sediment which could impair the quality of the lake water.

9) It must not add any extraneous contaminants to the lake water.

Calcium oxide (quicklime, CaO) and calcium hydroxide (hydrated lime, $Ca(OH)_2$) have been used to neutralize acidified surface waters. These materials are relatively inexpensive and effective. Lime is generally used in a powdered form and is very soluble when added to water. Because lime is a soluble strong base, it readily increases the pH of dilute solutions. If the solution is in contact with atmospheric carbon dioxide after strong base addition, the pH will slowly decrease. This is because atmospheric carbon dioxide will dissolve into solution, neutralize the hydroxide, and eventually form a bicarbonate solution.

$$Ca^{2+} + 2OH^- \xrightarrow{CO_2 \text{ introduction}} Ca^{2+} + 2OH^- + 2CO_2 = Ca^{2+} + 2HCO_3^-$$

Acidified waters generally have a low aqueous buffering capacity. As a result, large increases in pH will occur upon addition of typical quantities of strong base (200 to 400 $\mu eq\ \ell^{-1}\ yr^{-1}$). Lake water pH values which were below 5.0 prior to neutralization may increase to above 10.0 immediately after strong base addition. This may result in pH shock to organisms. These problems are accentuated within certain

microenvironments, particularly if mixing is incomplete. As a result, dosage control must be carefully monitored.

Calcium oxide is an extremely corrosive material that generates considerable heat when contacting water, which makes handling and storage very difficult. Calcium hydroxide is less hazardous and does not generate heat upon contact with water.

Calcium carbonate, commonly referred to as limestone, is a slightly soluble base. Dissolution of limestone is slow, and a maximum pH of 8.3 is realized when an aqueous system is in equilibrium with $CaCO_3$ and atmospheric CO_2 (Stumm and Morgan 1970). The dissolution kinetics of limestone are a function of solution characteristics, impurities in the stone, and the surface area of the stone (Pearson and McDonnell 1975a). Limestone commonly contains a significant amount of magnesium (often called dolomitic limestone). The greater the magnesium component in the limestone the slower the dissolution rate. For acidified surface water applications, enhanced dissolution rates of slightly soluble bases are generally desirable. Therefore, it is best to use a high purity stone (e.g., low magnesium content). Limestone can be obtained in a variety of sizes. Powdered limestone (agricultural limestone, 0 to 1 mm) is often used in water neutralization efforts. Dissolution is enhanced because of the large surface area associated with the small particles. Larger stone (0.5 to 2 cm) may be used for limestone barriers in streams (Section 4.7.1.3.2) or limestone contactors in springs.

An important consideration with regard to limestone dissolution is solution characteristics. Dissolution rates are greatest in solutions of low pH, low dissolved inorganic carbon, and low calcium. This condition is characteristic of dilute acidified waters. Another important consideration is the presence of hydrolyzing metals (Al, Fe, Mn) and dissolved organic carbon. Upon increases in pH, these components may deposit on the surface of the stone, inhibiting dissolution and therefore decreasing the effectiveness of the base. Pearson and McDonnell (1975a) observed that the dissolution rate of $CaCO_3$ decreased by up to 80 percent when $CaCO_3$ was coated with iron and aluminum.

Calcium carbonate is generally favored for use as a base because inorganic carbon is directly supplied upon dissolution and dissolution rates are relatively slow. Aquatic organisms are less prone to pH shock with $CaCO_3$ treatment than with strong base addition.

Sodium carbonate (Na_2CO_3, soda ash) is a soluble base which has been used as a neutralizing agent (Lindmark 1981). Sodium carbonate is readily soluble and directly applies dissolved inorganic carbon to solution. Therefore, it is an effective base because there are minimal losses due to incomplete dissolution while fluctuations in pH are less extreme. Sodium carbonate is generally an expensive base and therefore might not be used in lieu of calcium base sources ($Ca(OH)_2$, $CaCO_3$) (see Section 4.7.1.2.2).

Olivine $(Mg, Fe)_2 SiO_4$, is a natural silicate mineral that has been used in neutralization efforts (Hultberg and Andersson 1981). Olivine is a continous reaction series in which magnesium and ferrous iron can freely substitute for each other. Upon dissolution of $Fe_2 SiO_4$, iron will oxidize and precipitate as $Fe(OH)_3$ and thereby contribute to the acidification of water. Therefore, the effectiveness of olivine as a neutralizing agent increases with increasing magnesium content. Olivine is a slightly soluble mineral; therefore, dissolution characteristics and application difficulties associated with biological, chemical fouling will be in some ways similar to those associated with $CaCO_3$.

Fly ash is a material of diverse chemical composition. Western coals have been found to produce fly ash that is characteristically basic (enriched in calcium) while combustion of eastern coals generally results in an acidic fly ash (enriched in iron) (Edzwald and DePinto 1978). Basic fly ash has been shown to be effective in the neutralization of acidified waters. Neutralization by fly ash is accomplished by the release of hydroxyl ion rather than inorganic carbon to solution.

Fly ash is a waste byproduct so finding a way to use it is desirable. Waste deposits of basic fly ash are primarily located in the midwestern United States while most of the acidic waters are located in the northeast. Costs of transporting fly ash would probably be prohibitive and certainly less economical than using alternative neutralizing agents located in the northeast. Another problem associated with fly ash is trace metal contamination. Edzwald and Depinto (1978) have indicated that release of trace metals to solution from fly ash is comparable to that released from sediments upon acidification to pH 4.0.

It has been proposed that industrial slags could be used in the neutralization of acidic waters (Grahn and Hultberg 1975). One type of slag formation is the use of calcium carbonate to produce metals from ores. Basic slags formed in this and other processes vary considerably with respect to physical and chemical properties (Grahn and Hultberg 1975). Basic slags are largely composed of calcium (CaO) and silicon (SiO_2) oxides. While basic slags may contain similar calcium (CaO) levels, dissolution rates and therefore neutralization characteristics can vary considerably. The dissolution rate of CaO within a slag is a function of the manner in which CaO is bound to SiO_2 (Grahn and Hultberg 1975). Slags that increase solution pH to the 6.0 to 8.0 range and have long term neutralizing properties are the most desirable for lake and stream management applications. The determination of slag dissolution characteristics may be accomplished through laboratory testing. The trace metal content of slags may be high; therefore, potential for metal leaching exists.

Costs associated with fly ash or basic slags, should they be found acceptable for use, would be largely attributed to transportation and

handling, as these materials are waste products. Resistance to the use of these materials may be encountered if a substance the public perceives as "waste" is recommended for application to pristine waters.

4.7.1.2 Direct Water Addition of Base--Direct water addition of base is the most common management strategy for acidified lakes. It has been practiced in Sweden, Norway, Canada, and in the United States. The sources and sinks of hydroxide within an acidified lake environment are not quantitatively known; therefore there is no rational means of computing base dose requirements. Likewise, there is no accepted method for applying base to acidified lakes.

4.7.1.2.1 Computing base dose requirements. Addition of base to acidified waters should not be done arbitrarily. For cost effective use, a rational method for base dose determinations should be used; however, to date none have been developed. Hydroxyl ion sinks are gaseous, aqueous, and solid in nature. These sinks include atmospheric carbon dioxide, aqueous hydrogen ion, aluminum, inorganic carbon, and organic carbon, as well as exchange with lake sediments.

It is desirable to impart sufficient inorganic carbon ANC to a water so that future inputs of acid may be neutralized without a drastic decrease in pH. Consumption of base by base neutralizing components must be realized before residual ANC can be imparted to water. A description of the aqueous base neutralizing capacity (BNC aq) can be described by thermodynamic expressions:

$$BNC\ aq = 2[H_2CO_3] + [HCO_3^-] + 3[Al^{+3}] + 2[Al(OH)^{+2}]$$
$$+ [Al(OH)2^+] + 3[Al\text{-}F] + 3[Al\text{-}SO_4] + [RCOOH] + [H^+]$$
$$- [Al(OH)_4^-] - [OH^-]$$

where Al-F is the sum of all aqueous aluminum-fluoride complexes (mols ℓ^{-1}),

$Al\text{-}SO_4$ is the sum of all aluminum - sulfate complexes (mols ℓ^{-1}), and

RCOOH is the dissolved organic carbon base neutralizing capacity (mols ℓ^{-1}).

Driscoll et al. (1983) found that aquo-aluminum levels in Adirondack waters appear to follow an aluminum trihydroxide solubility model. The speciation of aluminum can be calculated with aluminum, fluoride, sulfate, and pH determinations as well as pertinent thermodynamic equilibrium constants. Dissolved organic carbon can exert some base neutralizing capacity in dilute waters. From observations of Adirondack waters, Driscoll and Bisogni (1983) developed an empirical formulation relating aquatic humus (dissolved organic carbon, DOC) to the mols of proton-dissociable organic acid/base:

$$C_T = 2.62 \times 10^{-6} (DOC) + 7.63 \times 10^{-6}$$

where DOC is the dissolved organic carbon concentration (mg C ℓ^{-1}) and

C_T is the total, organic carbon proton dissociation/ association sites (mols ℓ^{-1}).

A monoprotic proton dissociation constant (pKa=4.4) was also developed for Adirondack surface waters. From these relationships the contribution of BNC from aquatic humus may be quantified:

$$[RCOOH] = \frac{C_T \times [H^+]}{K_a + [H^+]}.$$

Other metals (Cu, Mn, Zn, Ni, Fe) are not included in the BNC equation due to the low concentrations usually found in natural waters. Collectively, BNC realized from these metals is not substantial compared to other aqueous components. However, these metals may exert substantial BNC when concentrations are high. High concentrations would most likely be found in acidified waters located near large industrial areas, where atmospheric deposition of metals is high. This condition has been observed in the Sudbury region of Ontario, Canada, where levels of copper and nickel have been observed at concentrations greater than 1.0 mg ℓ^{-1} (Scheider et al. 1975, Yan and Dillon 1981).

If equilibrium with atmospheric carbon dioxide is assumed, an upper limit of the aqueous BNC may be estimated. Driscoll and Bisogni (1983) have made such an analysis to neutralize a "typical" Adirondack lake (Table 4-8) to pH 6.5 (Table 4-9). It is apparent that a substantial portion of the aqueous BNC is associated with the hydrolysis of aluminum, and this should not be overlooked when one computes base dose requirements for acidified waters.

In determining BNC of an aquatic system, one must consider the lake sediment as well as the overlying water. One of the consequences of lake acidification is the accumulation of organic sediments. These sediments have considerable exchange capacity and contribute significantly to the overall BNC of the aquatic system. During the acidification process, BNC associated with sediment exchange sites buffers the overlying water. Upon neutralization, the sediment exchanges back into the water column, consuming added base. Neutralization of the water occurs quickly after base addition, whereas the exchange with the sediment may be slow.

Base additions ($CaCO_3$ and/or $Ca(OH)_2$) of 477, 196 and 477 μeq ℓ^{-1} were applied to Middle, Lohi, and Hannah Lakes, respectively, in the Sudbury region of Ontario, Canada (Dillon and Scheider 1983). Of

TABLE 4-8. COMPONENTS OF BASE NEUTRALIZING CAPACITY IN TYPICAL ADIRONDACK LAKE WATER (ADAPTED FROM DRISCOLL AND BISOGNI 1983)

Parameter	Value
pH	4.95
Inorganic Monomeric Aluminum	0.2 mg Al ℓ^{-1}
Aluminum Fluoride forms	0.105 mg Al ℓ^{-1}
Aluminum Sulfate forms	0.005 mg Al ℓ^{-1}
Free Aluminum	0.04 mg Al ℓ^{-1}
$Al(OH)^{2+}$	0.03 mg Al ℓ^{-1}
$Al(OH)_2^{+}$	0.02 mg Al ℓ^{-1}
TOC	5.0 mg C ℓ^{-1}

TABLE 4-9. AMOUNT OF BASE REQUIRED TO NEUTRALIZE BASE NEUTRALIZING CAPACITY OF TYPICAL ADIRONDACK LAKE WATER TO pH 6.5 (ADAPTED FROM DRISCOLL AND BISCOGNI 1983)

Acid component	Base required (eq ℓ^{-1})
Hydrogen Ion	1.1 x (10^{-5})
Carbonate	1.3 x (10^{-5})
Aluminum	2.0 x (10^{-5})
Organic Carbon	0.4 x (10^{-5})

these applications 161, 86 and 148 $\mu eq\ \ell^{-1}$ (or 34, 44 and 31 percent, respectively, of the base applied) were consumed by reactions with lake sediments. Therefore, sediment reaction would appear to be a major component of overall-lake base demand.

Determining sediment base demand of a lake is difficult; no accepted methods are available. Scheider et al. (1975) determined the base demand of sediments from Sudbury lakes by titrating sediments with $Ca(OH)_2$ to a pH of 8.0 and arbitrarily assuming a reactive layer of 5 cm in the lakes. Intralake variations in sediment base demand up to a factor of 10 were noted.

Through studies of base application to improve fish production in southeastern U.S. lakes, Boyd (1982) has developed a table in which sediment pH and texture are used to calculate base dose requirements.

Menz and Driscoll (1983) used experimental data obtained from Sudbury, Ontario and Adirondack, NY, liming experiments to develop a sediment base-demand model. The base-demand of sediments (meq m^{-2}) as a function of the increase in ANC (due to base addition) of the water column was fit to a Langmuir-type model:

$$SD = \frac{SD_{max} + ANC_a}{K + ANC_a}$$

where: SD is the sediment demand of base (meq m^{-2}),

SD_{max} is the maximum demand of base (meq m^{-2}),

ANC_a is the increase in water column ANC after base addition ($\mu eq\ \ell^{-1}$), and

K is the sediment demand constant ($\mu eq\ \ell^{-1}$).

This sediment demand model was coupled to aqueous thermodynamic calculations (see above) to determine the overall base demand of a lake. Base dose calculations using the simle model proposed by Menz and Driscoll (1983) depend on the volume of water to be treated, the sediment surface area, the solution water quality, the length of time over which the lake is to be treated, and the ANC the lake is to be increased to after treatment.

Another element of uncertainty in base dose calculations is base dissolution efficiency. For soluble bases (e.g., $Ca(OH)_2$, Na_2CO_3) a dissolution efficiency of 100 percent may be a reasonable assumption. However, the dissolution efficiency of sparingly soluble bases (e.g., $CaCO_3$, olivine) will depend on the method of application, the size and the impurity content of the base, and the extent of base-particle coating (e.g., Al, Fe, organic matter) that impeded dissolution. Driscoll et al. (1982) observed an accumulation of $CaCO_3$ coated with

organic detritus and metals within the sediments of a limed lake. Conversely, Dillon and Scheider (1983) observed complete dissolution of $CaCO_3$ after application to Sudbury lakes.

To develop a rational means for determining base dose requirements, further research is needed to enhance our quantitative understanding of components that exert a base demand in acidic lakes and of base application efficiency.

Base dose application rates have been reported in the literature. In southern Sweden, direct water addition doses needed for neutralization have been noted: 200 to 400 $\mu eq\ \ell^{-1}$ annually (Bengtsson et al. 1980), which corresponds to 1000 to 1500 $\mu eq\ ha^{-1}$ of watershed yr^{-1}. Blake (1981) has reported dose requirements of 7340 $\mu eq\ CaCO_3$ ha of lake surface $area^{-1}$ for initial treatment of Adirondack lakes. The period of time over which these levels are effective was not reported.

4.7.1.2.2 Methods of base application. Managing acidified waters by adding chemicals is a relatively new concept that has been practiced to only a very limited degree. Chemical addition strategies have generally evolved through trial and error, and there is no single, accepted method for applying chemicals to surface waters. The following are some of the reported methods of chemical application.

It has been suggested that waters amenable to neutralization should be ranked so lakes used for fishing and recreation are treated first (Blake 1981). These waters are generally accessible lakes, which are less costly to treat than remote waters. To determine the benefit derived from neutralization, a cost-benefit ratio can be used. This cost-benefit ratio (Blake 1981) might compare the cost of neutralization to the value derived by anglers. Lakes with a low cost-benefit ratio might be considered for lake neutralization programs. Lakes having long retention times should be favored over those with shorter retention times (< 1 yr). Because lakes with short retention times experience a relatively fast "washout" of base-induced ANC, these systems are susceptible to reacidification and the effective period of neutralization is short.

Once lakes to be neutralized are selected, application procedures must be planned. The method of application and the location of base addition should be optimized for the maximum dissolution of base, worker safety, and minimum cost.

Several ideas for the optimum placement of $CaCO_3$ have been presented in the literature. Sverdrup and coworkers (Bjerle et al. 1982, Sverdrup 1982, Sverdrup and Bjerle 1982) have developed a model to describe $CaCO_3$ dissolution after application in acidic lakes. The major parameters influencing $CaCO_3$ dissolution are particle settling depth and solution characteristics. Sverdrup (1982) indicates that particles larger than 60 μm in diameter dissolve to only a limited extent in dilute acidic systems and therefore are of little use in lake

liming. Calcium carbonate resting on (or within) lake sediments has very slow dissolution rates. This may be attributed to burial, limited turbulence, or coating of $CaCO_3$ particles by hydrous metal oxides or organic matter. Therefore, dissolution during water column sedimentation should be maximized for the most efficient application of base. Sverdrup's (1982) calculations suggest that $CaCO_3$ should be applied in the deepest portion of a lake.

Driscoll et al. (1982), however, indicate that turbulence will enhance dissolution. They suggest $CaCO_3$ should be placed in the littoral zone where turbulence will enhance the dissolution rate. Within the littoral zone, areas that are sandy and not laden with organic detritus provide the best location for $CaCO_3$ placement. If $CaCO_3$ is placed in organic sediments, particles may become buried or coated with metal and/or organic matter. If applied to the littoral region, $CaCO_3$ should be dispersed so only a thin layer accumulates on sediments. This will ensure that a large surface area of base directly contacts the water and increases dissolution efficiency. Driscoll et al. (1982) observed that when $CaCO_3$ was applied in a thick (> 0.5 cm) layer coating by organic detritus and metals curtailed dissolution; when deposits were spread thin (< 0.5 cm) the $CaCO_3$ dissolved before becoming coated.

The application of base materials has been accomplished in several ways. Transport and application vehicles include trucks, boats, helicopters, and airplanes. The accessibility of the water to be neutralized largely determines the method selected. Two prevalent methods of application are by boat or helicopter.

Application by boat is usually limited to readily accessible lakes and ponds. For an efficient operation, base transported by truck must by easily transferred to a boat. This necessitates unloading the truck close to the water. Lime ($Ca(OH)_2$) transported in bags is a commonly used base in boat application. These bags are loaded onto the boat and then emptied as the boat moves slowly through the water. Calcium carbonate may also be applied in this manner. Scheider et al. (1975) mixed lake water and base on board a boat, water was pumped into a hopper where base was poured from a bag and mixed, with the resulting slurry discharged into the backwash of the boat. Using one 5 m boat and a five-man crew, approximately 7.3×10^3 kg was applied in an average working day.

Large amounts of powdered $CaCO_3$ have been applied to an Adirondack lake by using a pontoon barge ($\sim 3 \times 10^3$ kg capacity). (Driscoll et al. 1982). The base was transported to the application site and washed off the barge with water supplied by a gasoline-powered fire pump. In this manner a three-man crew can apply 30×10^3 kg of $CaCO_3$ in an average working day.

Helicopters have been used to transport large quantities of base to remote areas. Blake (1981) has discussed different methods of helicopter application. Transporting bagged lime by helicoper into

lakes in the winter was not a viable application method due to the considerable labor required, extremely low temperatures, and swirling snow that made flying difficult. Another attempted procedure involved mixing water and lime in a fire-fighting water bucket and spreading the slurry on the lake surface. This technique proved inadequate because mixing equipment and a large crew were needed. In addition, transporting large quantities of water was required. The most practical method was direct lime application with a "bucket" ($\sim 1 \times 10^3$ kg capacity) suspended from a helicopter. Upon flying over a lake the pilot opened a trap door, thereby dropping the lime to the lake. The most efficient variation of this operation involved two buckets, with one in use while the other was being filled.

In Norway, agricultural limestone ($CaCO_3$) has been applied on a frozen lake (Hinckley and Wisniewski 1981). After limestone was applied by a manure spreader in a 2 meter wide strip along the shoreline, a snow blower blew the limestone and snow mixture into a 10-meter strip. Upon ice melt the base mixed with the lake water, resulting in neutralization.

Sodium carbnoate (soda ash) is not generally used as a neutralizing material. However, Lindmark (1981) has hypothesized that the sodium from soda ash will exchange with cations on sediment exchange sites. Treated sediments containing sodium may exchange with inputs of base neutralizing capacity (e.g. H^+, Al) and serve to buffer the lake against reacidification. Lindmark (1981) suggests that calcium binds irreversibly with sediment exchange sites; therefore, calcium treatments will not introduce the sediment buffering that sodium treatments may provide. Lindmark (1981) argues that the effectiveness of soda ash offsets its higher chemical cost (Table 4-10) and is therefore economically competitive with more conventional basic materials (e.g., $Ca(OH)_2$, $CaCO_3$). Lindmark's hypothesis is controversial because monovalent cations do not compete effectively with polyvalent cations for sites on an exchanger in dilute solutions.

To neutralize with soda ash a 10 percent solution of sodium carbonate has been applied to sediments of an acidified lake (Lindmark 1981). The sodium carbonate was mixed on land and pumped to a moveable raft, and a land-based compressor that supplied air to the raft. From the raft, air and the sodium carbonate solution were piped to a chemical rake (10 m wide) that moved along the lake bottom. Bubbles of compressed air were released 15 cm below the sediment surface, helping to break up the sediment. Sodium carbonate was injected directly within the sediments. In this manner, good contact with the base was assured. Unfortunately, data are not currently available to evaluate the cost-effectiveness of sodium carbonate treatment. Since soda ash is a relatively expensive base, more research is needed before this technology can be evaluated as a potential lake management tool.

Neutralizing acidified waters through base addition is a relatively new strategy that has not yet been extensively practiced. Application methods must be chosen that will be compatible with the

TABLE 4-10. CHEMICAL COST COMPARISON OF NEUTRALIZATION AGENTS[a]

Chemical	Form supplied	Equivalent weight (g eq^{-1})	Cost[a]	
			Mass basis (dollars x 10^{-3} kg^{-1})	Equivalence basis (dollars eq^{-1})
$CaCO_3$	bags (325 mesh)	50	20.90	1.04×10^{-3}
$Ca(OH)_2$	bulk	37	35.75	1.32×10^{-3}
$Ca(OH)_2$	bags	37	46.75	1.73×10^{-3}
CaO	bulk	28	34.38	9.62×10^{-4}
Na_2CO_3	bulk	53	101.20	5.36×10^{-3}
$(Mg,Fe)_2SiO_4$[b]	bulk (100 mesh)	86	22.00	1.89×10^{-3}
H_3PO_4	agricultural grade (70% solution)	5.75[c]	6.49	3.73×10^{-5}

[a]Chemical costs as reported in Chemical Marketing Reporter, August 31, 1981.

[b]This analysis assumes the above stoichiometry, however this may vary from source to source.

[c]Equivalent weight is computed based on the assumption that NO_3^- is the nitrogen source, which is assimilated and never reoxidized within the aquatic system (see Section 4.7.2.1).

constraints inherent with each site. If base addition becomes a more widespread procedure to mitigate acidification, new techniques for application will be developed, along with the refinement of existing methods.

4.7.1.3 Watershed Addition of Base--Watershed addition of base, including stream treatment, is a relatively new strategy that has been evaluated to only a limited degree. Research addressing watershed addition of base has been conducted largely by Swedish scientists (Bengtsson et al. 1980, Hultberg and Andersson 1981). This discussion will essentially reflect upon the Swedish experience, in addition to addressing pertinent biogeochemical concepts.

4.7.1.3.1 The concept of watershed application of base. The concept of base addition to watersheds was developed to overcome the potential introduction of BNC (H^+, Al) to a neutralized lake by ground-water and streams (Section 4.4.1.4). Watershed/stream base treatment theoretically should enhance the neutralization of ground and stream waters and result in a more complete and compatible neutralization.

There is considerable experience to draw upon with respect to neutralization of soils, since applying lime (agricultural grade $CaCO_3$) is a common agricultural practice. However, forest ecosystems are considerably different than agricultural ecosystems, and it is difficult to extrapolate from one to the other.

The acid/base chemistry of soil systems is extremely complex, with reactions such as cation exchange, mineral dissolution, and biological uptake all influencing soil solution acidity. In forest soils derived from silicate bedrock, the bulk of the cation exchange capacity may be attributed to natural organic matter and to a lesser extent clay minerals (e.g., kaolinite, vermiculite, illite). The exchangeable cations are largely basic cations (Ca, Mg, Na, K) and/or acidic cations (Al, H). At near neutral pH values, the exchangeable cation pool is largely comprised of basic cations. As soil pH decreases, the exchangeable acidity (Al, H) is thought to increase. Another reaction of interest is biological uptake of cations. Forest biomass requires cationic nutrients (e.g., Ca, Mg, K) for growth. An aggrading forest will assimilate basic cations and tend to deplete soil pools.

Cation exchange and biological uptake reactions are significant considerations with regard to watershed liming. Forest soils are generally nutrient poor and elevated in exchangeable acidity. Upon addition of base [$Ca(OH)_2$, $CaCO_3$] to a forest soil, a considerable shift in ionic equilibria would ensue. The introduction of elevated levels of calcium would result in a Ca^{2+} - H^+ exchange on soil exchange sites. The release of protons would neutralize the associated hydroxide or carbonate introduced in the liming process. Biological uptake of calcium may result from calcium addition; this would generate protons as well and neutralize the associated basic anion.

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Terrestrial acid/base reactions are much more complicated and more poorly understood than aquatic acid/base reactions. It is difficult to evaluate, much less quantify, perturbations in acid/base chemistry that result from watershed liming. As a result, assessing the efficiency of a watershed liming program is difficult.

Stream neutralization techniques have also been attempted. Stream neutralization is of interest because streams are valuable aquatic resources and maintaining stream water quality is of concern. An important consideration is the fact that acidic streams may flow into acidic lakes and influence lake biogeochemistry. When an acidified lake is limed, it will still experience the introdution of BNC (Al, H) from stream inputs. Aquatic organisms (particularly fish) that use the stream for feeding or reproduction may be adversely affected by the extensive aluminum hydrolysis resulting from the introduction of acidic stream water to a neutralized lake. Stream (and watershed) liming could help minimize this water quality problem.

4.7.1.3.2 Experience in watershed liming. Experiments with watershed liming are limited to those conducted in Sweden (Bengtsson et al. 1980). Agricultural lime (powdered $CaCO_3$, 0 to 0.5 mm) has been transported to the watershed in large trucks and applied as a slurry with a sprayer truck. In this manner one man is able to apply 40×10^3 kg of $CaCO_3$ per day (Hinckley and Wisniewski 1981). The $CaCO_3$ dose required to achieve adequate neutralization of water systems is generally two orders of magnitude greater than that of direct water addition (Bengtsson et al. 1980). This is undoubtedly due to the many base consuming processes that occur within forest soil systems. Application rates are generally in the range of 5000 to 7000 kg $CaCO_3$ ha^{-1} yr^{-1}. Powdered olivine (0 to 1 mm), a magnesium iron silicate, has also been used as a base in watershed application experiments (Hultberg and Andersson 1981).

Water quality information resulting from watershed application experiments has not been published; however, authors indicate that watershed liming efforts have been successful (Bengtsson et al. 1980, Hultberg and Andersson 1981). Hultberg and Andersson reported that some damage to the terrestrial environment may be associated with liming. Sphagnum moss was severely damaged as a result of $CaCO_3$ addition. Damage to lichens, spruce needles, and other types of moss was also observed. Similar damage occurred with olivine application experiments; however, the extent of damage was considerably less than that from $CaCO_3$ addition.

There are problems associated with stream neutralization practices. It is reasonable to say that no cost effective method of achieving stream neutralization has been developed. Problems center around the drastic temporal changes in water flow and water quality that occur in headwater streams. During spring and autumn, water flow and solution BNC are high. During summer, water flow and BNC are low. A successful neutralization scheme must adequately account for the tremendous temporal fluctuation in base dose requirements of acidic streams.

Four approaches have been attempted to achieve stream neutralization. The simplest approach is $CaCO_3$ addition to the streambed (Hultberg and Andersson 1981). This has been attempted with both coarse (5 to 15 mm) and fine (0 to 0.5 mm) $CaCO_3$. Coarse $CaCO_3$ will tend to stay in the stream bed, but neutralization is generally inadequate because of the rather low surface area of the stone. Fine $CaCO_3$ will more readily dissolve (due to a greater surface area) but is more influenced by stream turbulence. Powdered $CaCO_3$ tends to be transported to pools, where it settles within organic detritus, or it can be washed into a lake. In these sites $CaCO_3$ is ineffective in supplying BNC to streams.

Another approach to achieve stream neutralization is the limestone barrier. Driscoll et al. (1982) constructed a limestone barrier of perforated 55-gallon drums filled with $CaCO_3$ (5 to 15 mm), in an attempt to neutralize an acidic stream. The barrels were placed across the width of the stream, 2-barrels high with loose limestone filling spaces between the barrels. Screens were placed upstream to filter out debris that might clog the pores of the barrier. Stream neutralization was accomplished for approximately one week, largely due to fine material associated with the larger stone. The coating of the stone by hydrolyzed aluminum, iron, and organic detritus quickly curtailed further neutralization. The coating diminished calcium carbonate dissolution and rendered the barrier ineffective as a means of achieving neutralization.

Diversion wells have been used to treat acidic streams in Sweden (Swedish Ministry of Agriculture Environment Committee 1982). Diversion wells consist of a cylinder embedded within a stream bank or channel and filled with $CaCO_3$. A pipe diverts stream water, by gravity, to the cylinder. Water is introduced through the bottom of the cylinder and flows upward through the $CaCO_3$ bed. Water neutralized by passage through the cylinder bed overflows back into the stream, increasing the ANC. The upflow velocity results in particle abrasion, which aids to restrict particle coating. A series of diversion wells may be placed in a stream such that the inflow pipes will be located at various levels of stream stage. Thus during high-flow conditoins several diversion wells would be operating and treating a large volume of flow. As stream flow decreases, the stream depth would decrease; therefore the number of operating wells and volume of water treated would decrease.

A fourth type of stream neutralization, automated base addition systems, is the most effective means of supplying ANC to acidic streams. However, they are extremely expensive in terms of both capital and operating costs. Swedish scientists have used river silos (cylindrical storage bins) to accomplish stream neutralization (Hinckley and Wisniewski 1981). These silos hold 30×10^3 kg of base and can meter up to 1300 kg day^{-1} of base into a stream. Each silo costs approximately $20,000 (1981 dollars). The rate at which base is metered from the silo to the stream is activated by pH or flow sensing devices. An automated system, like the river silos, would seem to be the best

means of applying an adequate base dose to varying water flow and quality conditions.

In addition to cost, however, there are several problems associated with automated stream treatment systems. The silos may be used only in easily accessible streams, and the automated operation is not entirely reliable and will malfunction occasionally. Also, stream base addition requirements are considerable during high flow conditions; silos must be constantly refilled during spring and autumn (Hinckley and Wisniewski 1981). These problems are not severe in themselves, but they imply that stream neutralization efforts may be interrupted periodically. Interruption of base addition will most likely occur during high flow, low pH conditions (spring, autumn, and winter) when water quality conditions are most critical. Periodic discontinuities in base addition have severe implications for aquatic organisms. The response of water quality and aquatic organisms to acute fluctuations in ANC, from equipment malfunctions, needs to be evaluated before automated base addition systems are implemented as part of a stream management program.

4.7.1.4 Water Quality Response to Base Treatment--Lake water neutralization by base addition may be accomplished by direct base addition or by watershed/stream input neutralization. Few studies of the water quality response in groundwater or streams as a result of neutralization are reported in the literature. Likewise, an evaluation of lake neutralization by watershed/stream input neutralization has not been made. As a result, this discussion of the water quality response to base treatment reflects only the results reported from direct base addition studies.

- Transparency increases immediately following base addition especially in colored waters (Yan and Dillon 1981, Hultberg and Andersson 1981). This appears to be due to the removal of dissolved organic matter by co-precipitation with metals (Yan and Dillon 1981). The long term consequence, however, has been the reduced transparency in neutralized lakes. Decreases in epilimnion thickness and decreased hypolimnetic temperatures have been associated with these transparency changes (Yan and Dillon 1981). Upon reacidification, transparency has increased.

- A natural consequence of base addition is the resulting increase in pH. Response of pH is dependent on the neutralizing agent used. When soluble base such as $Ca(OH)_2$ is applied, pH increases sharply and a maximum pH is realized shortly after addition. This increase in pH is followed by a decline in pH due to atmospheric carbon dioxide influx. When equilibrium with CO_2 is approached, stabilization of pH results. If acidic inputs are significant through either streamflow, groundwater infiltration, or sediment cation exchange, a gradual but steady decrease in pH will occur.

When a slightly soluble base (e.g., $CaCO_3$) is added to an aquatic system, the pH increase is less dramatic. With calcium carbonate addition the rate of pH increase depends on particle size and degree of water contact. Increases in stone surface area exposed to solution enhance dissolution rates, resulting in a more rapid pH increase. Acid neutralizing capacity also increases after base addition (Bengtsson et al. 1980). ANC increases are initially considerable but may decrease significantly with slight decreases in pH.

- Increases in dissolved inorganic carbon result from neutralization. Increases in pH from less than 5.0 to greater than 6.5 cause dissolved inorganic carbon equilibria to shift from a H_2CO_3 (CO_2[aq] + H_2CO_3) dominated system to a bicarbonate dominated system. If the environment is open to atmospheric carbon dioxide, increases in dissolved inorganic carbon will result. When a noncarbonate base (e.g., $Ca(OH)_2$) is added, the increase in inorganic carbon is due entirely to atmospheric CO_2, whereas when a carbonate base (e.g., $CaCO_3$) is added, inorganic carbon increases are due to the base itself as well as atmospheric CO_2.

- Trace metals concentrations generally decrease after base additions to acidified waters. Metals found in elevated concentrations in acidified waters include Al, Mn, and Zn. Of these trace metals aluminum is probably of the most concern, with concentrations of 0.2 to 1.0 mg Al ℓ^{-1} commonly observed (Driscoll 1980). As solution pH increases, due to base addition, aluminum hydrolyzes and precipitates. It has been observed that aluminum in hydrolyzed forms is toxic to fish (Driscoll et al. 1980). In Swedish liming experiments, fish kills were experienced shortly after base application (Dickson 1978b). Fish stocking should be attempted only after hydrolyzed aluminum has settled from the water column.

Addition of base generally results in decreased concentrations of other trace metals in addition to aluminum (Scheider et al. 1975, Yan et al. 1977, Driscoll et al. 1982). Sediment trap analyses support water column data, showing a rapid accumulation of metals in traps following an increase in pH. Decreases in trace metal levels from the water column may be explained by hydrolysis and precipitation, or adsorption on hydrous aluminum oxides formed by base addition. Adsorption on metal precipitates is also considered to be a mechanism by which dissolved organic carbon and phytoplankton are removed from the lentic environment.

Sulfate response to neutralization appears to be minimal. Comparing lakes that had been neutralized to control lakes showed no significant variation in temporal changes in sulfate (Scheider et al. 1975).

Basic cation chemistry, excluding the cation associated with base addition, appears to be unaltered by neutralization. Levels of calcium

are observed to increase, as expected, due to dissolution of calcium-based chemical neutralizing agents. The temporal increase in calcium concentration will depend on the dissolution rate of base. Calcium levels increase quickly with soluble bases ($Ca(OH)_2$) and more slowly with slightly soluble bases ($CaCO_3$). Once the initial dissolution has occurred, calcium levels peak in concentration and then decline due to export from the lake or exchange with sediments.

A major problem associated with lake neutralization is the potential for reacidification. Reacidification results in the resolubilization of trace metals (Al, Mn, and Zn) which are presumably introduced from the lake sediments (Driscoll et al. 1982). Reacidification does not result in an immediate reintroduction of dissolved organic carbon (DOC). It appears that DOC must be reintroduced to the water column from terrestrial inputs (e.g., stream and groundwater inflows) and therefore takes considerable time to appear. The loss of DOC implies that there are few available organic ligands to complex trace metals, particularly aluminum, that enter the water column during reacidification. This translates to a decrease in water quality, particularly with respect to potential for aluminum toxicity to fish.

Another consideration is input of stream water (and groundwater) to neutralized lakes. The introduction of acidic water to a neutralized lake results in a localized metal hydrolysis region at the stream (and groundwater)--lake interface. This may have implications with respect to aluminum toxicity to fish, particularly those fish that associate with stream systems for reproduction and feeding. If aluminum is hydrolyzing in this environment it may be unsuitable for habitation by fish. Any program to stock fish in a neutralized lake must consider problems associated with acidic stream/groundwater quality entering the lake environment.

4.7.1.5 Cost Analysis, Conclusions and Assessment of Base Addition--

4.7.1.5.1 Cost analysis. It is extremely difficult to make a cost comparison of different acidified lake management strategies. It is relatively easy to tabulate capital, chemical, labor, and operating costs, but any economic evaluation must be based on the effectiveness of the treatment. Little is known of the effectiveness and efficiency of various treatment strategies. As a result, any economic evaluation of management strategies for acidified waters should be viewed with caution.

Costs of chemicals that have been proposed for use in neutralization efforts are listed in Table 4-10, which shows the considerable range in chemical costs. This tabulation is somewhat misleading because it does not incorporate application efficiency into the analysis. Soluble bases ($Ca(OH)_2$, CaO, Na_2CO_3) are undoubtedly the most efficient means to add base, while slightly soluble bases ($CaCO_3$, $MgFeSiO_4$) and phosphorus (Section 4.7.2.2) are potentially less

efficient. Very little is known about the relative efficiency of neutralization strategies, and without such an understanding chemical cost comparisons are difficult.

Costs involved in neutralization efforts will vary greatly with lake location and accessibility. Blake (1981) determined costs for six accessible ponds treated (by boat) in 1977-78 and four remote ponds treated (by helicopter) in 1978-79, totaling 79 ha and 39 ha, respectively. Neutralization cost for accessible ponds was \$131 ha^{-1} while cost for the remote ponds was \$341 ha^{-1}. These were experimental efforts, so costs may be substantially reduced if base addition is implemented on a routine basis. Costs for liming remote ponds by helicopter on a routine basis were estimated to average \$247 ha^{-1}. This was based on the following costs: helicopter - \$250 hr^{-1}, lime - \$44 x 10^{-3} kg^{-1} delivered onsite, travel expenses - \$100 day-1, the ability to apply 4.5 x 10^3 kg of lime hr^{-1}, and the use of an eight-man ground crew at \$35 day^{-1} $person^{-1}$ (Blake 1981). Neutralization of a series of lakes has been shown to be the most efficient operation. Four ponds treated in 1977 by a three-man crew cost approximately \$74 ha^{-1} (Blake 1981).

Costs associated with application by boat are not detailed in the method described by Scheider et al. (1975). However, a comparative cost analysis may be determined. A five-man crew using a 5-meter boat was able to apply 7.3 x 10^3 kg day^{-1} of hydrated lime. Since the major costs of base addition are associated with labor and the cost of base, a reasonable comparative estimate can be formulated.

Using chemical, labor, and transportation cost data obtained by the above and other investigators, Menz and Driscoll (1983) estimated the costs of neutralizing acidic Adirondack lakes through a program of base addition. In this analysis lakes were subdivided as accessible (those lakes with access by road so they can be treated by boat) and inaccessible (those lakes with no road access and requiring helicopter treatment). Costs to treat accessible lakes for a 5-year treatment period were approximately \$50.75 per surface hectare. Chemical transportation cost to the site represented the major component of cost for the treatment of accessible lakes. The cost to treat inaccessible lakes for a 5-year treatment period was approximately \$500 per surface hectare. Most of this cost was associated with the cost of applying the chemical. It is noteworthy that costs vary, from lake to lake, with the desired target pH (and ANC), and with the treatment period. Overall results were derived from water quality data from 777 of the 2,877 Adirondack lakes sampled to date (Pfeiffer and Festa 1980). The estimated annual cost for a 5-year base addition program for the lakes in this sample would be in the range of 2 to 4 million dollars, depending on the specific target pH of the water.

Presently, the support for most lake neutralization programs comes directly from government agencies. Sweden has been the most active, with over 300 individual projects involving 1000 lakes and waterways

(Bengtsson et al. 1980). As concern for the problem increases, private groups (i.e., sportsman clubs, lake associations) may become actively involved in neutralization programs. However, limited resources will probably prevent the neutralization and management of all acidified lakes.

4.7.1.5.2 Summary - base additions. Base addition is currently the most viable strategy available for managing acidified lakes. Methods used to compute base application requirements are crude due to our lack of understanding of the efficiency of treatment techniques and sediment interactions. A benefit associated with base addition is the alteration of the chemical environment (e.g., increases in pH and calcium, decreases in trace metal levels). Such a chemical alteration might result in an environment more hospitable to desirable aquatic biota (e.g., decreases in Sphagnum, increases in fish populations). However, in addition to the benefits associated with base addition, there are costs. These costs include financial as well as environmental costs. Environmental costs 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. These and other environmental costs have not been fully evaluated prior to base addition of acidified lakes.

Base addition has become a popular strategy to mitigate water quality problems associated with acidification. However, before base addition is implemented as a regional, acidified lake management alternative it should be more thoroughly evaluated.

4.7.2 Surface Water Fertilization

Soft water lakes are generally thought to be phosphorus growth limited (N/P > 12). As a result, fertilization by phosphorus addition might serve as a means of restoring acidified lakes. However, this hypothesis has been researched and evaluated only to a limited degree. This analysis is a summary of the limited studies on nutrient addition to acidified waters, as well as an extrapolation of some concepts pertinent to natural waters. Further research is needed to effectively evaluate lake response and consequences associated with nutrient addition.

4.7.2.1 The Fertilization Concept--The concept of phosphorus addition as a strategy for the management of acidified lakes is twofold:

1. To supply ANC through biological uptake of nitrate; and

2. To increase aquatic biomass and species diversity.

The idea of supplying ANC through biological uptake of nutrients, is summarized by the following stoichiometric expression (Stumm and Morgan 1970).

$$106\ CO_2 + 16\ NO_3^- + H_2PO_4^- + 122\ H_2O + 17\ H^+ \text{ (+ Trace Elements, Energy)}$$

photosynthesis↑ ↓ respiration

$$C_{106}\ H_{262}\ O_{110}\ N_{16}\ P \text{ (algal protoplasm)} + 138\ O_2$$

This is a generalized relationship and may vary significantly from ecosystem to ecosystem, as well as temporally within a given aquatic system. Regardless of the inadequacies of the stoichiometric expression, it provides a framework through which microbially mediated changes in solution acid/base chemistry might be understood.

The stoichiometric expression suggests that uptake of nutrients by algae will result in the consumption of protons or the generation of ANC within the aquatic environment. This essentially results from the assimilation of nitrate as a nitrogen source. For the organism to maintain an electroneutrality balance, the uptake of nitrate must be countered by an equivalent cation uptake (or anion release). In the above expression this is realized through hydrogen ion uptake.

This expression is somewhat simplistic, for in actuality a number of additional factors should be considered.

1) Although nitrate nitrogen is generally the predominant nitrogen source in aerobic waters, uptake of ammonium or organic nitrogen could occur. Under these circumstances the stoichiometry would significantly change. In fact, assimilation of ammonium as a nitrogen source would result in consumption of ANC (Brewer and Goldman 1976).

2) Plants require certain cations as nutrients (e.g., Ca^{2+}, Mg^{2+}, Fe). The uptake of cations by algal protoplasm would diminish the quantity of ANC generated through photosynthesis.

3) Although carbon fixation through photosynthesis results in generation of ANC, respiration will result in consumption of ANC. This process may partially account for why acidic lakes have a higher ANC in summer months than in winter months. Therefore, only net removal of reduced nitrogen associated with algal material through lake outflow or permanent burial in sediments will result in a net production of microbially mediated ANC.

The concept of acid neutralizing changes generated by phytoplankton growth has been studied by Brewer and Goldman (1976). Such processes may be important in dilute water acid/base chemistry. According to the above stoichiometric expression, 4.8×10^{-3} μeq of ANC would be generated per microgram of net algal biomass produced, or 5.5×10^{-1} μeq of ANC would be generated per μg of net phosphorus fixed by algal uptake.

The second reason for nutrient addition is to replenish the biomass of acidified lakes. Hendrey et al. (1976) have suggested that phytoplankton biomass is reduced by lake acidification. Dillon et al. (1979) suggest that phytoplankton biomass is better correlated with total phosphorus levels than with pH. However, acidification may alter phosphorus cycling (Section 4.7.2.2). Nutrient addition may help replenish phosphorus lost (possibly) by acidification and increase the productivity and species composition of these lakes.

4.7.2.2 Phosphorus Cycling in Acidified Water--Phosphorus cycling is reasonably well understood in circumneutral lakes (Hutchinson 1975). Generally phosphorus will enter a lake through direct atmospheric precipitation, groundwater, or stream flow. It may be exported from the lake by groundwater or stream flow. Within the lake, phosphorus may be assimilated by phytoplankton or macrophytes. Once in the form of particulate phosphorus, it may be consumed by organisms, released to the water by oxidation reactions, or lost to the sediments. Within the sediments, phosphorus may be released by decomposition processes. This released phosphorus may bind with aluminum, calcium, or iron or diffuse vertically back into the water column.

In acidified waters aluminum might alter phosphorus cycling through precipitation or adsorption reactions. Aluminum can directly precipitate with orthophosphate to form $AlPO_4$ (varacite). A more plausible mechanism by which aqueous phosphorus levels might be regulated is adsorption on hydrous aluminum oxides (Huang 1975). The adsorption is pH dependent with a maximum near pH 4.5. It is likely that increases in pH of acidic water result in the formation of hydrous aluminum oxides. These oxides would serve as an adsorbent that could effectively scavenge phosphorus from the water column.

Upon nutrient addition to an acidic lake, competition between algae and aluminum for a given phosphorus molecule will ensue. It is difficult to state how phytoplankton uptake of phosphorus is altered by the presence of aqueous aluminum. This competition is undoubtedly complicated and altered by environmental conditions such as pH, general water chemistry, light, and temperature.

Although changes in water quality may result on a short term basis, most of the added phosphorus will be lost to the sediments (Schindler et al. 1973, Scheider et al. 1976). The degree to which sedimented phosphorus diffuses back to the water column is virtually unknown for acidic lakes. However, because these systems are generally aerobic, have reduced decomposition rates, and undoubtedly contain significant levels of amorphous iron and aluminum oxides that potentially bind phosphorus, it is doubtful that significant vertical diffusion of phosphorus occurs. If fixed nitrate associated with algal uptake of phosphorus is lost from the system, applying phosphorus has been efficient from the standpoint that ANC was produced in the water column. However, if fixed nitrate reaches the sediment, is oxidized, and diffuses to the water column while the associated phosphorus remains in the sediment, phosphorus application would be inefficient (no net

generation of ANC to the water column resulting). Schindler et al. (1973) have indicated that nitrogen sedimentation and removal are less efficient than phosphorous sedimentation and removal.

4.7.2.3 Fertilization Experience and Water Quality Response to Fertilization--As mentioned previously there has been limited experience with fertilization of acidic lakes. Most of the work has been accomplished by Canadian scientists (Scheider et al. 1975, 1976; Scheider and Dillon 1976; Dillon et al. 1977, 1979). Generally a desirable water column phosphorus level is chosen for a particular lake, and a model such as that of Dillon and Rigler (1974) is used to calculate the required phosphorus dose. Usually H_3PO_4 is applied because of its low cost, ease of handling, and solubility (Table 4-10). Application is usually made in the late spring or early summer; periodic additions may be made throughout the summer to enhance assimilation efficiency.

Nutrient addition has generally been used to increase the standing crop of food chain components within a lake. To accomplish this, phosphorus addition has generally been practiced after liming. Phosphorus consuming reactions are minimized by precipitating aluminum with base and allowing aluminum to settle out of the water column prior to any phosphorus addition.

Few data have been reported on ANC changes as a result of phosphorus addition. However, Dillon and Scheider (1983) observed decreases in inorganic nitrogen (largely nitrate) and increases in total organic nitrogen folowing nominal orthophosphate additions of 10 to 15 $\mu g\ P\ \ell^{-1}$ to neutralized lakes (Hannah and Middle) in the Sudbury region of Ontario, Canada. They calculated the theoretical increase in ANC resulting from observed changes in nitrogen chemistry for fertilized lakes (Hannah and Middle) in comparison to a neutralized lake that received no phorphorus addition (Lohi Lake). The ANC generated from nitrogen transformations for the fertilized lakes was 2 to 8 $\mu eq\ \ell^{-1}$ greater than the control lake. In addition, the ANC generated from nitrogen transformations declined dramatically after phosphorus additions were terminated.

Observed changes in aquatic biota have been more significant. Small additions of total phosphorus resulted in significant increases in phytoplankton biomass of neutralized Canadian lakes (Dillon et al. 1979). No single observation in phytoplankton species composition has been reported. Shifts to communities dominated by Chrysophytes (Langford 1948), by blue greens (Smith 1969), and by different groups in different years of fertilization (Schindler et al. 1973) have been reported. Shifts in green or bluegreen algae dominance can generally be attributed to the nitrogen to phosphorus ratio within the lake (Schindler 1977).

Dillon et al. (1979) observed changes in phytoplankton resulting from small levels of phosphorus added to a limed lake (Middle Lake, Ontario). In the first year after addition blue-green algae biomass increased significantly. The second year after fertilization, green

algae were generally dominant. Fertilization of a second lake (Hannah Lake, Ontario) resulted in an increase in biomass but no change in the structure of the phytoplankton community. Although increases in phytoplankton biomass were evident, no conclusions with regard to changes in zooplankton population could be made from this study.

In enclosure experiments within a limed lake, Scheider et al. (1975) observed that fertilization with phosphorus and wastewater effluent resulted in an increase in the standing stock of bacteria, phytoplankton, and zooplankton. Hultberg and Andersson (1981) investigated nutrient addition as a means of supplementing liming efforts in Sweden. They reported few results except for a shift in lake phytoplankton from Peridineans to primarily chlorophyceans, which they attributed in part to fertilization.

Little work has been done with water chemistry response to phosphorus addition. Dickson (1978b) has observed the precipitation of phosphorus added to acidic lake water; precipitation was most dramatic at pH 5.5. The presence of DOC inhibited the precipitation of phosphorus by aluminum. Scheider et al. (1975) observed decreases in phosphorus added to enclosure experiments. They attributed this to precipitation of the phosphorus by metals.

4.7.2.4 Summary-Surface Water Fertilization--It is difficult to critically assess phosphorus addition as a management strategy to improve the water quality of acidic lakes because the general process has not been effectively evaluated. While the chemical costs associated with phosphorus addition are low (Table 4-10) applications may not be efficient, particularly in view of potential interactions with aluminum (Schindler et al. 1973, Scheider et al. 1976). In the few studies conducted, the benefits accrued to the ecosystem have not been evaluated.

4.8 CONCLUSIONS

Acidification of lakes and streams, with resultant biological damage, has been widely acknowledged in the last decade (NAS 1981, NRCC 1981, U.S./Canada 1982). Assessing causal relationships remains difficult, however, because effects of acidic deposition on any one component of the terrestrial-wetland-aquatic systems depend on not only the composition of the atmospheric deposition but also on the effect of the atmospheric deposition on every system upstream from the component of interest. Composition of aquatic systems results, moreover, from biological processes in addition to chemical and physical processes; thus, assessing results of acidification on all three processes is required. Our knowledge of past, current, and future acidification trends, of critical processes that control acidification, and of the degree of permanency of biological effects remains incomplete and subject to debate.

of aquatic chemistry and acidic deposition, the chapter listed those characteristics of terrestrial and aquatic systems that ameliorate or enhance the effect of acidic deposition. It then discussed aquatic systems' theoretical and practical sensitivity to acidic deposition and identified locations of sensitive and affected systems. The chapter also considered the interaction of aquatic acidification with the metal and organic biochemical cycles and then concluded by discussing alternative methods for improving water quality where acidification has occurred.

The following statements summarize the content of this chapter.

- Each of several components of aquatic or terrestrial systems may assimilate some or all acidic deposition falling in a watershed. These components are vegetative canopy, soils, bedrock, hydrology, wetlands, or an aquatic system itself (Section 4.2.1).

- Soils assimilate acidic deposition through dissolution, cation exchange, and biologic processes. Generally, soils containing carbonate materials have abundant exchangeable bases and can assimilate acidic deposition to an almost unlimited extent. Soils that contain no carbonate materials can assimilate acidic deposition because of cation exchange reactions, silicate-mineral dissolution reactions, and in some cases Fe and Al oxide dissolution. Assimilation ability is affected by soil chemical nature (especially CEC and BS), the permeability at each layer, the surface area of the soil particles, and the amount of soil in the watershed (Section 4.3.2).

- Hydrology, specifically flow paths and residence times, can determine the extent of reactions between strong acid components of deposition and each component the water contacts. Flow paths and residence times are controlled by many factors, including topography and meteorology (Section 4.3.2.4).

- 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 the body of water, nutrient status is very important in determining the sensitivity of a lake to acidification (Section 4.3.2.6).

- Aquatic systems sensitive to acidification by acidic deposition are commonly waters with pH and alkalinities towards the lower end of the spectrum. The boundary between sensitive and insensitive that is used is 200 $\mu eq\ \ell^{-1}$ of alkalinity

(Section 4.3.2.6.1). This concentration is chosen because in North America acidic precipitation has resulted in about 100 $\mu eq\ \ell^{-1}$ of potential acidification of surface water (Harvey et al. 1981, Church and Galloway 1983), and because biological effects due to acidification begin when aquatic systems reach alkalinities of ~ 100 $\mu eq\ \ell^{-1}$.

- Regions in North America contain aquatic systems sensitive to acidification. These regions are found throughout much of eastern Canada; New England; the Allegheny, Smokey, and Rocky Mountains; and the Northwest and North Central United States (Galloway and Cowling 1978, NAS 1981, NRCC 1981). However, a large amount of more detailed survey work is required to determine the levels of alkalinity and degree of sensitivity (Section 4.4.3).

- Studies uniformly point to acidification of some surface waters in eastern Canada and the northeastern United States (Section 4.4.3.1.2).

- Although changing land use may locally alter the pH regime of lakes and streams, it appears that regional lake acidification and episodic pH depression occur in response to increased atmospheric deposition of strong acid, primarily H_2SO_4 (Section 4.4.3.3).

- Addition of acidic deposition to terrestrial and aquatic systems can disrupt the natural biogeochemical cycles of some metal and organic compounds to such a degree that they can cause biological effects (Section 4.6). The chemical form of dissolved metals is important in determining the total mobility of a metal and the biological effects related to acidification of aquatic ecosystems. Acidification increases the concentration of many metals in surface waters and changes speciation toward more biologically active forms.

- Waters may be treated with base substances to neutralize the effects of acidic deposition. Only lime and limestone have been used to any extent in either direct lake additions or watershed/stream additions. Several other materials have been proposed, but tests for effectiveness and operability must be conducted. Organic carbon addition and surface water fertilization have also been proposed but also must be tested (Section 4.7).

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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-5. EFFECTS ON AQUATIC BIOLOGY

5.1 INTRODUCTION (J. J. Magnuson)

The loss of fish populations from seemingly pristine oligotrophic waters was the first and most obvious indication that atmospheric deposition was affecting aquatic ecosystems (Dannevig 1959, Beamish and Harvey 1972, Cowling 1980). Changes in water chemistry, particularly increases in acidity, were found to be associated with these local fish extinctions. Later studies have included the effects of acidification on other aquatic organisms, such as those associated with bottom substrates (the benthos), tiny plants and animals floating freely in the water column (the plankton), and rooted aquatic plants (macrophytes). The resultant literature is large, widely scattered, and varies considerably in its scientific merit. The purpose of this chapter is to review and evaluate this literature critically, and to summarize the effects of acidification on aquatic organisms.

The chapter begins with a section on naturally acidic waters, including a discussion of what organisms occur in such habitats and how their distributions relate to distributions in habitats recently acidified by man's activities. Subsequent sections critically evaluate the literature regarding the response of benthic organisms, macrophytes and wetland plants, plankton, fishes and other aquatic biota to acidification. These are followed by a discussion of ecosystem-level responses to acidification and a section on mitigative options. The final section summarizes the known effects of acidification on aquatic biota and indicates potential effects that need to be addressed.

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.

Evidence linking changes in aquatic communities to acidification can be divided into three types. The first type consists of field observations, which are 1) descriptions of conditions before and after

acidification is suspected to have occurred or 2) contemporary comparisons of water bodies thought to exhibit different degrees of acidification. Problems exist with this type of correlation approach. For example, before and after studies may be difficult to interpret if methodologies have changed in the interim, or if other factors such as land-use practices have also changed. In comparative studies, pH is frequently correlated with other limnological parameters (e.g., lake size, nutrient concentrations), making it difficult to attribute inter-lake biotic differences solely to differences in pH. Despite these problems, field observations provide the earliest indications of changes in biotic communities and provide a basis for forming hypotheses that can be further evaluated when consistent trends are observed in repeated studies.

The second type of evidence consists of field experiments, which range from modifying the conditions of enclosures in a lake (Muller 1980) to intentionally acidifying an entire lake or stream (Schindler et al. 1980b; Hall et al. 1980). These studies generally minimize the problem of confounding factors, which plague field observation studies, and have contributed much to our understanding of how organisms are affected by the acidification process. However, experimental manipulations that focus on one variable may miss effects which are due to the interaction of several variables. For example, acidifying an entire lake may not reveal a major reason for fish kills in waters acidified by acidic precipitation, namely aluminum released when the surrounding watershed is also acidified. A great difference also exists between the time scale of experimental acidifications (which typically occur over a period of months or a few years) and of regional acidification (which occurs over many years).

The third type of evidence consists of laboratory experiments, whereby the effect of a particular stress (low pH, aluminum) is evaluated after all other variables are carefully controlled. These experiments typically consist of bioassays involving one species and one or a small number of stresses. Most of our understanding of the physiological effects of low pH on aquatic organisms is due to such studies. As with field experiments, these studies are time consuming, expensive and have yielded data on only a few species. Predicting community-level changes from laboratory bioassays on a few species is difficult. A species may experience reduced growth or reproduction in the laboratory at a low pH, but may prosper in an acidified lake at the same pH if its competitors suffer even greater reductions in growth and reproduction.

It is obvious that all three types of evidence provide certain kinds of information yet have certain drawbacks. The strongest conclusions regarding the effects of acidification on aquatic organisms will be reached when all three types of evidence yield consistent results. Examples of such cases are given in the conclusions section (Section 5.10.1).

The significance of changes in species abundances or community composition lies in how these changes affect important ecosystem processes. These processes include primary production (the production of new plant tissue through photosynthesis), nutrient recycling (re-use of nutrients released through decomposition of organic material), and trophic interactions (transfer of energy from plants to herbivores to carnivores). A schematic presentation of these processes and how they may be affected by acidification is given in Section 5.8 (Figure 5-17). While direct toxic effects of acidification on organisms have been relatively easy to document, assessing effects on ecosystem processes has proven more difficult. We know, for example, that certain species of algae become dominant under acidic conditions, yet how this affects the food supply to higher trophic levels, or how total primary productivity is affected has not been well studied. The growth of algal mats in acidified lakes has been observed, yet how this seal over the bottom sediments will affect nutrient cycling has not been measured. Most effort to date has involved describing responses of various taxa to the acidification process. Future work will need to consider how these changes affect ecosystem processes.

5.2 BIOTA OF NATURALLY ACIDIC WATERS (J. J. Magnuson and F. J. Rahel)

Naturally acidic lakes and streams occur throughout the world and have been known in the United States since at least the 1860's (Hutchinson 1957, Patrick et al. 1981). These naturally acidic waters provide insight into the pH range normally tolerated by aquatic organisms. Such information is useful in assessing how recent pH declines attributed to cultural acidification might affect aquatic life. This chapter's purpose is to summarize the literature on naturally acidic waters and to examine the influence of low pH on plants and animals found in such habitats. North American waters are emphasized, but reference to other geographic areas is made when cosmopolitan taxa are involved. Methods for distinguishing between naturally acidic and culturally acidified waters are discussed in Chapter E-4, Section 4.4.3.

5.2.1 Types of Naturally Acidic Waters

Naturally occurring acidic waters fall into three groups. In the first group are inorganic acidotrophic waters associated with geothermal areas or lignite burns, where pH values between 2.0 and 3.0 are not uncommon (Waring 1965, Brock 1978, Hutchinson et al. 1978). Among the most extreme values recorded are pH 0.9 for Mount Ruapehu Crater Lake, New Zealand (Bayly and Williams 1973), pH 1.7 from Kata-numa, a volcanic lake in Japan (Hutchinson 1957), and pH's below 2.0 for several springs in Wyoming (Brock 1978). The high acidity is due to sulfuric acid, which arises from the oxidation of sulfides such as hydrogen sulfide (H_2S) and pyrite (FeS_2). In addition to being extremely acidic, these waters frequently contain elevated metal concentrations and are often heated. Assessing the biological effects of low pH under these conditions is difficult, but such sites have provided insight into the lower pH limit for various taxa (Brock 1973, 1978). This type of naturally acidic aquatic habitat occurs in North America mainly in the

west, and has been most extensively studied in the Yellowstone Park region of Wyoming (Van Everdingen 1970, Brock 1978).

The second group of naturally acidic waters consists of brownwater lakes and streams associated with peatlands, cypress swamps, or rainforests, depending on latitude (Janzen 1974, Moore and Bellamy 1974). Their acidity is derived from organic acids leached from decayed plant material and from hydrogen ions released by plants such as Sphagnum mosses in exchange for nutrient ions (Clymo 1967). These waters commonly have pH's in the range of 3.5 to 5.0 and owe their dark color to large amounts of dissolved organic matter. As with acidic geothermal waters, brownwaters have other qualities besides low pH that may limit aquatic life. For example, they are characterized by low concentrations of many of the inorganic ions necessary for plant growth and osmotic balance in animals (Clymo 1967). There is some evidence that the dissolved humic compounds may be toxic to amphibians, even at neutral pH (Gosner and Black 1957, Saber and Dunson 1978). Low oxygen and high carbon dioxide concentrations are also present in some brownwater habitats (Welch 1952, Kramer et al. 1978). Finally, the low primary productivity of brownwaters may mean that even physiologically tolerant species may be excluded due to food unavailability (Janzen 1974, Bricker and Gannon 1976). Brownwater habitats in North America are associated with either northern peatlands (Jewell and Brown 1929, Cole 1979, Johnson 1981) or with southeastern swamplands (Beck et al. 1974, Forman 1979, Kirk 1979).

The third type of naturally acidic habitat consists of ultra-oligotrophic waters. They are especially common where glaciation has 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. They often have pH's in the 5.5 to 6.5 range, and most of the acidity appears due to carbonic acid (H_2CO_3). These lakes tend to be small and have low concentrations of dissolved ions (Chapter E-4, Section 4.3.2). In North America, this type of naturally acidic lake occurs in large areas of eastern Canada and the northeastern United States, as well as in sections of western United States and northern Florida (Shannon and Brezonik 1972, Galloway and Cowling 1978). Many of the lakes which have been, or will be, affected by acidic precipitation belong in this category (see Chapter E-4, Section 4.3.2).

5.2.2 Biota of Inorganic Acidotrophic Waters

In North America, the most extensively studied inorganic acidotrophic waters are those of the Yellowstone Park region in Wyoming. Certain species of eucaryotic algae, fungi, and bacteria have demonstrated remarkable adaptation to this acidic environment and often form extensive mats (Brock 1978). For example, the alga Cynanidium caldarium was found at pH 0.05, while the bacterium Sulfolobus acidocaldarius thrived in a thermal spring at pH 0.9 and 60 C. Lower pH limits for other taxa in this environment are summarized by Brock (1978)

and include a pH near 0.0 for fungi, pH 3.0 for Sphagnum mosses, and pH 2.5 to 3.0 for vascular plants such as sedges (Carex and Eleocharis spp.) and ericacid shrubs (blueberries, cranberries). Although generally considered eurytropic, blue-green algae are conspicuously absent from these acidic environments. Brock (1973, 1978) has assembled data showing that these algae are intolerant of pH's below 4.0. The inability to survive under acidic conditions may be due to their lack of membrane-bound chloroplasts that, in eucaryotic algae, prevent the acid-labile chlorophyll from being decomposed at low pH.

In ponds exposed to sulfur fumigations from burning bituminous shales, the euglenoid Euglena mutablis was present at pH 1.8 (Hutchinson et al. 1978, Havas and Hutchinson 1982). The red chironomid, Chironomus riparius, and the rotifer, Brachionus urceolaris, were abundant at pH 2.8, but no copepods or cladocerans were present.

Among the few insects reported from acidic thermal waters is the ephydrid fly Ephydra thermophila (Brock 1978). This fly breeds in streams at pH 2.0 and is the basis of a food chain involving several invertebrate predators. Extensive surveys of invertebrates in the acidic geothermal waters of North America have not been done, but it seems reasonable that other invertebrate taxa might tolerate such low pH. For example, in streams polluted by acidic mine wastes, species of rotifers, midges, alderflies and dytisscids have been found at pH's near 3.0 (Roback 1974, Harp and Campbell 1967, Parsons 1968).

Vertebrates such as amphibians and fish appear unable to survive in inorganic acidotrophic habitats, but again no extensive surveys have been undertaken. Surprisingly, waterfowl do not avoid these lakes, and Canadian geese have been reported to nest on Turbid Lake in Yellowstone Park (pH ~ 3.0) (Brock 1978).

Another group of inorganic acidotrophic lakes that have been well studied are the volcanic lakes of Japan (Ueno 1958). Some of the organisms present in these lakes belong to cosmopolitan genera and hence provide insight into the lowest pH which may be tolerated by North American genera. Aquatic mosses (e.g., Rhynchostegium aplozia) dominate the plant community, although reeds (Phragmites) occur along the margins of most lakes, even at pH's below 3.0. Diatoms (Pinnularia) and rotifers (Rotaria) have been observed at pH 2.7. A small caldera lake filled with water at pH 3.0 but fertile enough to support moderate phytoplankton production contained several genera of Crustacea (Simocephalus, Chydorus, Macrocyclops) and a rotifer (Brachionus). The teleost Tribolodon hakonensis from Lake Osoresan-ko (pH 3.5) occurs at the lowest pH reported for any fish species (Mashiko et al. 1973).

While the work done on inorganic acidotrophic waters has revealed some outstanding examples of extreme pH tolerance, in general, these waters have very low species diversity and monocultures of tolerant species are common.

5.2.3 Biota in Acidic Brownwater Habitats

Brownwater habitats do not experience the extremes of temperature, pH, and metal concentrations common to inorganic acidotrophic waters; consequently they contain a greater diversity of organisms. They are, however, characterized by low ion concentrations, reduced light penetration and, frequently, low dissolved oxygen concentrations. These variables interact with the acidic pH (3.5 to 5.0) to determine species richness and biological production.

Among the genera of macrophytes reported from acidic brownwater lakes are Alternanthera, Ceratophyllum, Isoetes, Juncus, Limnobium, Nuphar, Potamogeton and Utricularia (Jewell and Brown 1924, Griffiths 1973, Stoneburner and Smock 1980). Many brownwater lakes, however, are characterized by the absence of macrophytes, which is generally attributed to the stained water and the lack of a firm substrate on the lake bottom (Welch 1952, McLachlan and McLachlan 1975, Marshall 1979). The shoreline plant community has been well described for northern bogs and includes sedges (Carex), ericacid shrubs (Vaccinium chamaedaphe) and mosses (Sphagnum) (Gates 1942, Heinselman 1970, Vitt and Slack 1975). The characteristic tree along the shore of southeastern brownwater lakes is the cypress (Taxodium) (King et al. 1981).

Phytoplankton have classically been described as present at low densities (Birge and Juday 1927, Welch 1952, Stoneburner and Smock 1980). Recent work has emphasized the predominance of small-bodied algae (the nannoplankton) in these waters (Bricker and Gannon 1976). Although species from most phytoplankton phyla have been reported, certain genera of desmids (Xanthidium, Euastrum, Hyalotheca) and diatoms (Asterionella, Eunotia, Actinella, Anomoeoneis, Pinnularia, Melosira) are especially characteristic (Woelkerling and Gough 1976, Marshall 1979, Patrick et al. 1979, Stoneburner and Smock 1980). As with the phytoplankton, the zooplankton in acidic dystrophic lakes are frequently dominated by small-bodied forms, particularly rotifers (Brachionus, Keratella, Monostyla, Polyarthra) and copepods (Diaptomus, Cyclops) (Welch 1952, Smith 1957, Bricker and Gannon 1976, Marshall 1979). Relatively few cladocerans have adapted to this environment although species from the following genera have been reported: Alona, Bosmina, Chydorus, Daphnia, Diaphanosoma, Eubosmina, Leptodora, and Pleuroxus (Marshall 1979, Von Ende 1979, Stoneburner and Smock 1980). In lakes where fish are absent or where darkly stained water and low hypolimnetic oxygen offer some protection from fish predation, dipteran larvae of the genus Chaoborus are an important part of the zooplankton community (Von Ende 1979).

A peculiar phenomenon in many acidic brownwater lakes is the large standing crop of zooplankton relative to phytoplankton. This paradox has lead to suggestions that bacteria and suspended organic matter (tripton) may be important food sources for zooplankton in these lakes (Bayly 1964, Bricker and Gannon 1976, Stoneburner and Smock 1980).

The benthic community in acidic dystrophic lakes is typically impoverished. This is particularly true of small bogs where a deep layer of decaying peat obliterates any sand or gravel substrate and prevents macrophyte growth. Such lakes have dipteran larvae (Chaoboridae and Chironomidae), dragonflies and damselflies (Odonata), and alderflies (Sialidae) as their main benthic invertebrates (Welch 1952, McLachlan and McLachlan 1975). Even habitats with more diverse substrates still have few benthic species although caddisflies (Trichoptera), whirligig beetles (Gyrinidae), and cranefly larvae (Tipulidae) are sometimes present (Smith 1961, Patrick et al. 1979). Jewell and Brown (1929) described an interesting invertebrate community living in pools in the sphagnum mat of a Michigan bog at pH 3.5 to 4.0. Air-breathing forms like beetles (Dytisicidae, Haliplidae, Helodidae, Hydrophilidae) and mosquito larvae (Culex) predominated in these low-oxygen pools, although several dragonfly species (Odonata) and the cladoceran, Acantholebris curvirostri, were also present.

Notably absent from acidic bog waters are mayflies (Ephemeroptera); crustaceans such as amphipods, ostrocods and crayfish; molluscs (snails, clams); sponges; and annelids (oligochaetes, leeches) (Pennak 1953, Wetzel 1975). The absence of organisms that have a calcified exoskeleton is not unexpected in brownwater habitats due to the low pH and the extremely low concentration of calcium. An exception to this generalization is the occurrence of the fingernail clam (Pisidium) in bog lakes at pH's below 5.0 (Griffiths 1973).

Summaries of fish species distribution in relation to pH exist for both northern and southern brownwater habitats (Frey 1951, Hastings 1979, Rahel and Magnuson 1983). Slow growth and low species diversity characterize the fish assemblages in these waters (Smith 1957, Garton and Ball 1969). In northern midwestern lakes where ice cover occurs, winter anoxia interacts with pH to determine the structure of fish assemblages (Rahel 1982). Lakes with adequate winter oxygen concentrations are dominated by yellow perch (Perca flavescens), sunfish (family Centrarchidae), and bullheads (Ictalurus spp.), even down to pH 4.5. If winter oxygen concentrations are low enough to exclude predators, minnows (family Cyprinidae) dominate the fish fauna, but only if the pH is above 5.2 to 5.4. Lakes that are both very acidic (pH below 5.2) and experience winter anoxia contain only yellow perch and the central mudminnow (Umbra limi). Other species that can survive in acidic northern brownwaters but are probably excluded because suitable habitat or spawning areas are missing are the northern pike (Esox lucius), and brook trout (Salvelinus fontinalis) (Jewell and Brown 1924, Smith 1961, Dunson and Martin 1973).

Southeastern brownwater lakes and streams (pH 4.0 to 5.0) have a more diverse fish fauna than do similar northern waters (Wiener and Giesy 1979, Frey 1951, Laerm et. al 1980). Among the more common taxa are various species of sunfish, pickerel (family Esocidae), catfish (family Ictaluridae), and killifish (family Cyprinidontidae), along with the American eel (Anguilla rostrata), lake chubsucker (Erimyzon

sucetta), eastern mudminnow (Umbra pygmaea), pirate perch (Aphredoderus sayanus), and the yellow perch.

With the exception of the golden shiner (Notemigonus crysoleucas), ironcolor shiner (Notropis chalybaeus), and the swamp darter (Etheostoma fusiforme), minnows and darters are conspicuously absent from acidic brownwaters, even though they may be abundant in nearby neutral waters (Frey 1951, Laerm et al. 1980, Rahel and Magnuson 1983). Predation from bass and pike may exclude these small-bodied fishes from many habitats, but even when predators are absent, minnows and darters are rarely found below pH 5.2. Other acid sensitive species are the smallmouth bass (Micropterus dolomieui), and walleye (Stizostedion vitreum).

5.2.4 Biota in Ultra-Oligotrophic Waters

The third category of naturally acidic waters consists of ultra-oligotrophic lakes and streams. Hydrogen ion concentrations fluctuate in these waters as a function of photosynthetic activity and carbon dioxide concentrations, with pH typically varying between 5.5 and 7.0. Low nutrient concentrations result in low biological productivity at all trophic levels. Most aquatic taxa are able to tolerate the hydrogen ion concentration of these lakes and thus other physical/chemical factors (e.g., thermal conditions) or biotic interactions (predation and competition) are important in determining species composition.

A great diversity of taxa has been reported from ultra-oligotrophic lakes, but certain groups are characteristic of this lake type. In the phytoplankton, for example, crysophytes and diatoms (Chrysophyta) along with desmids and other green algae (Chlorophyta) are diagnostic of oligotrophic conditions (Hutchinson 1967). Numerous other algae are usually present at low densities (Schindler and Holmgren 1971, Baker and Magnuson 1976).

Copepods appear to dominate the zooplankton community, but numerous other taxa have been recorded in surveys of oligotrophic waters (Patalas 1971, Torke 1979). Factors like lake depth and size, thermal regimes, phytoplankton abundance, and fish predation appear to be more important than pH in determining zooplankton community structure in these lakes (Anderson 1974, Green and Vascotto 1978).

Benthic communities are diverse, although certain genera of midge larvae (Tanytarsus, Chaoborus) along with fingernail clams (Pisidium), the amphipod Pontoporeia, and the mysid Mysis relicta have classically been associated with oligotrophy (Hamilton 1971, Brinkhurst 1974, Wetzel 1975). In acidic streams (pH less than 5.7), mayflies (Ephemeroptera), molluscs, some caddisfly genera (Hydropsyche), and the amphipod (Gammarus) are rare, even though they are abundant in downstream sections having a higher pH (Sutcliffe and Carrick 1973). These taxa are also missing from streams affected by acidic mine drainage (Roback 1974). Shell-forming molluscs and crustaceans may be excluded from oligotrophic waters because of low calcium concentrations, even though the pH is circumneutral. Crayfish, for example, were absent from softwater Wisconsin lakes having calcium concentrations below 2 mg ℓ^{-1} regardless of lake pH (Capelli 1975).

Aquatic macrophytes typical of oligotrophic waters have been summarized by Hutchinson (1967) and Seddon (1972). Among the representative genera are Bidens, Elatine, Eriocaulon, Isoetes, Juncus, Lobelia, and Sparganium. Most of these have a distinct physical form, consisting of stiff leaves placed in a close rosette or on short, unbranched stems as opposed to the long-stemmed, branched leaf typical of hardwater macrophytes (Fasset 1930). Species occurring in oligotrophic waters are probably not restricted to the low nutrient conditions present there but are likely excluded from more fertile waters by competition from other macrophyte species (Hutchinson 1967).

Identifying fish assemblages typical of oligotrophic waters is complicated by human activities that affect community composition, such as stocking, over-exploitation, and eutrophication (Regier and Applegate 1972). Many high-elevation Palearctic lakes were probably barren of fish following deglaciation, although the very long and poorly documented history of fish introductions by humans makes it impossible to know what percent were fishless (Nilsson 1972, Donald et al. 1980). These coldwater lakes today are dominated by salmonids (trout and salmon) and coregonids (whitefish and ciscoes). Oligotrophic lakes with slightly warmer thermal regimes (because they are shallower or are located at lower altitudes or farther south than the salmonid lakes) are dominated by percids (yellow perch) and certain centrarchids (typically the smallmouth bass, Micropterus dolomieui) and rock bass (Ambloplites rupestris) (Adams and Olver 1977, Rahel and Magnuson 1983).

As with the other faunal groups, the low productivity and biotic interactions (predation/competition) of these lakes probably have a bigger influence on the species composition than pH per se. For example, many small-bodied fish species (e.g., minnows and darters) are commonly absent from oligotrophic lakes even though they can tolerate the pH's typical of these waters (Rahel and Magnuson 1983). Competition, or more likely predation by larger species, may exclude these fish from biologically unproductive lakes where there are few macrophytes to provide refuges. Another example involves yellow perch and whitefish (Coregonus spp.) which only successfully coexist in large, cold lakes where the pelagic whitefish can avoid competition from the more littoral-based yellow perch (Svardson 1976).

5.2.5 Summary

Naturally acidic waters provide insight into the lowest pH tolerated by various groups of aquatic organisms (Table 5.1). While life has been found in the most acidic environments sampled, the general observation is that species diversity declines as pH decreases. The most tolerant organisms are from the lower trophic levels, with some bacteria and algae able to flourish at pH's below 1.0. Invertebrates are rarely found below pH 3.0, and fish are generally limited to pH's above 4.0. Some organisms (especially certain genera of bacteria) are true acidophiles, unable to grow and reproduce at neutral pH (Brock 1978). However, most organisms occurring in acidic environments survive

TABLE 5-1. LOWER pH LIMITS FOR DIFFERENT GROUPS OF ORGANISMS IN NATURALLY ACIDIC WATERS

Group	Approx. Lower pH limit	Examples of Species Occurring at Lower pH Limit	Reference
Bacteria	0.8	Thiobacillus thiooxidans, Sulfolobus acidocaldarius	Brock 1978
	2-3	Bacillus, Streptomyces	Brock 1978
Plants			
Fungi	0	Acontium velatum	Brock 1978
Eucaryotic algae	0	Cyanidium caldarium	Brock 1978
	1-2	Euglena mutabilis, Chlamydomonas acidophila, Chlorella	Brock 1978
Blue-green algae	4.0	Mastigocladus, Synechococcus	Brock 1978
Vascular plants	2.5-3	Eleocharis, Carex, Ericacean plants, Phragmites	Brock 1978 Hargreaves et al. 1975 Ueno 1958
Mosses	3.0	Sphagnum	Brock 1978
Animals			
Protozoa	2.0	Amoebae, Heliozoans	Brock 1978
Rotifers	3.0	Brachionus, Lecane, Bdelloid	Hutchinson et al. 1978
	3.5	Collotheca, Ptygura	Edmondson 1944
Cladocera	3.0	Simocephalus, Chydorus	Ueno 1958
Copepods	3.0	Macrocyclops	Ueno 1958
	3.6	Cyclops	Hutchinson et al. 1978
Insects	2.0	Ephydra thermophila	Brock 1978
	3.0	Chironomus riparius	Hutchinson et al. 1978
	5.8	Mayflies	Sutcliffe and Carrick 1973
Amphipods	5.8	Gammarus	Sutcliffe and Carrick 1973
Clams	4.5	Pisidium	Griffiths 1973
	6.0	Most other species	Pennak 1978
Snails	5.8	Amnicola	Pennak 1978
	6.2	Most other species	Pennak 1978
Fish	3.5	Tribolodon hakonensis	Mashiko et al. 1973
	4.0	Umbra limi	Rahel and Magnuson 1983
	4.5	Sunfishes (Centrarchidae)	Rahel and Magnuson 1983

quite well at neutral pH but are excluded from such environments by competitively superior species.

Species distributions in natural pH gradients provide a means of assessing the long-term effects of low pH exposure, integrated over all life history stages and all physiological functions. Such information is seldom obtained in laboratory bioassays, which are generally short-term, focused on one or two physiological responses, and ignore the potential for genetic adaptation to acid stress. Species' acid sensitivity inferred from distributions in naturally acidic waters may be useful in selecting species to monitor in waters undergoing cultural acidification. For example, acid tolerance rankings of fish species, based on distributions among naturally acidic Wisconsin lakes (Figure 5-1), were correlated with acid tolerance rankings from culturally acidified Canadian lakes (Figure 5-2). This allowed predictions of which fish species should be monitored in Wisconsin lakes susceptible to acidification (Rahel and Magnuson 1983).

Studies of species distributions relative to pH are subject to misinterpretation if other correlated factors are not adequately considered. Among the factors that can interact to influence species distributions are pH, metal concentrations and temperature in geothermal waters; pH, oxygen concentrations, and substrate composition in dystrophic waters; and pH, low nutrient concentrations, and predation in ultra-oligotrophic waters. The problem of separating out the effects of confounded factors is illustrated by work on the distribution of rotifers in Wisconsin lakes. Alkaline waters (above pH 7.0) contained relatively few species of rotifers but large numbers of individuals. In contrast, acidic waters (below pH 7.0) contained large numbers of species but few individuals (Pennak 1978). Hence, rotifer species diversity increased with decreasing pH. However, this was probably because competitive interactions were influenced by factors correlated with pH, not because most species of rotifers could not tolerate neutral pH. In another example, Weiner and Hanneman (1982) failed to find a relationship between reduced fish growth and low pH in a set of naturally acidic Wisconsin lakes, even though growth reductions at low pH are consistently observed in laboratory bioassays (Section 5.6.4.1.3). They attributed the lack of correlation between fish growth and pH to the overriding effects of population density.

Experimental manipulations offer potential for separating the effects of these confounding factors from the effects of pH. A good example is the alkalinization of an acidic brownwater lake (Smith 1957). When the pH was raised by adding lime, several stocked fish species reproduced successfully for the first time. However, as the pH returned to its former level, reproduction stopped, indicating that hydrogen ion concentration was the limiting factor.

In some cases, naturally acidic environments are free of the confounding stresses associated with culturally acidified environments. This is especially true of metal toxicants, which are common in waters affected by acidic mine drainage or acidic precipitation (Parsons 1977,

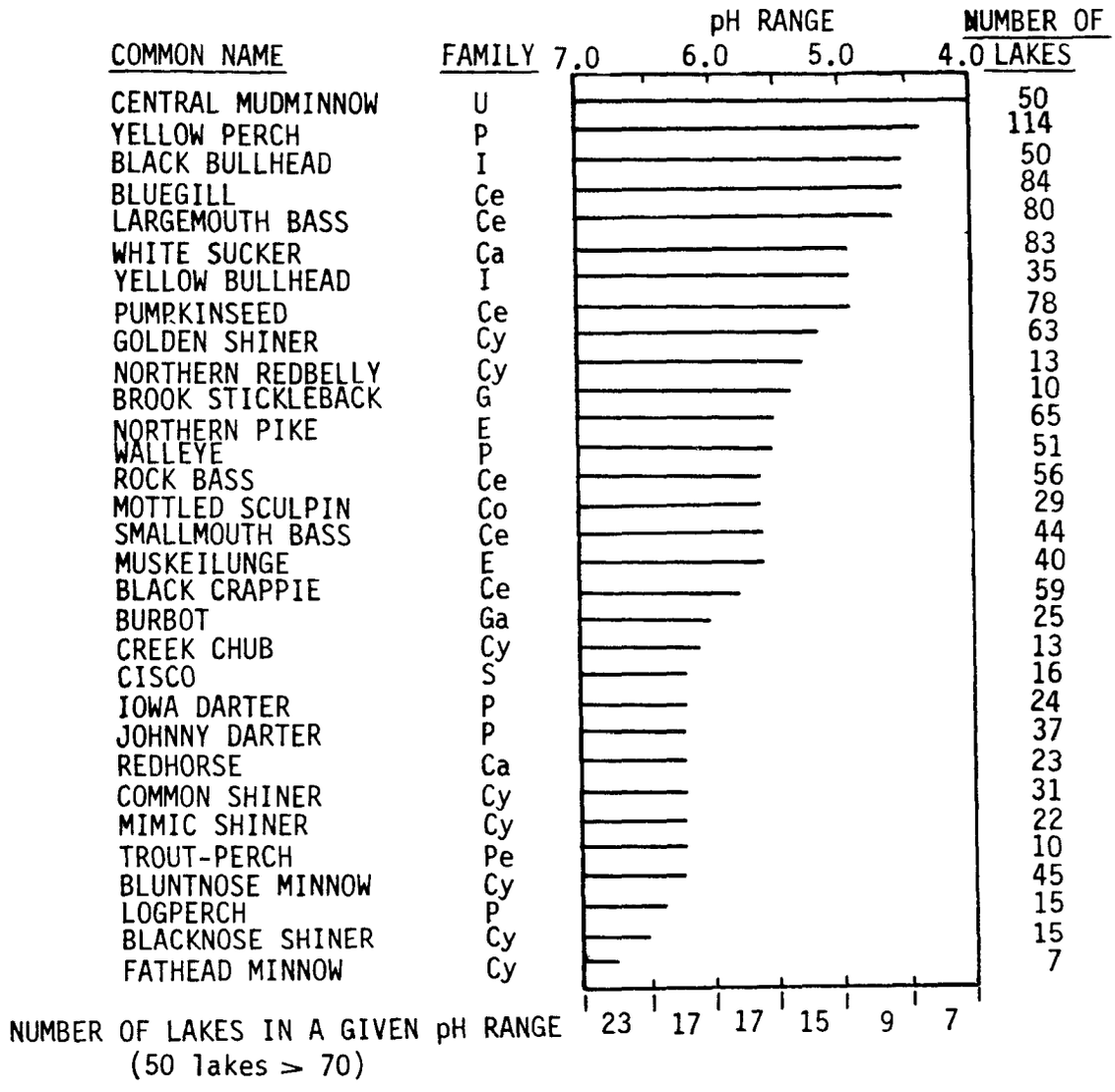
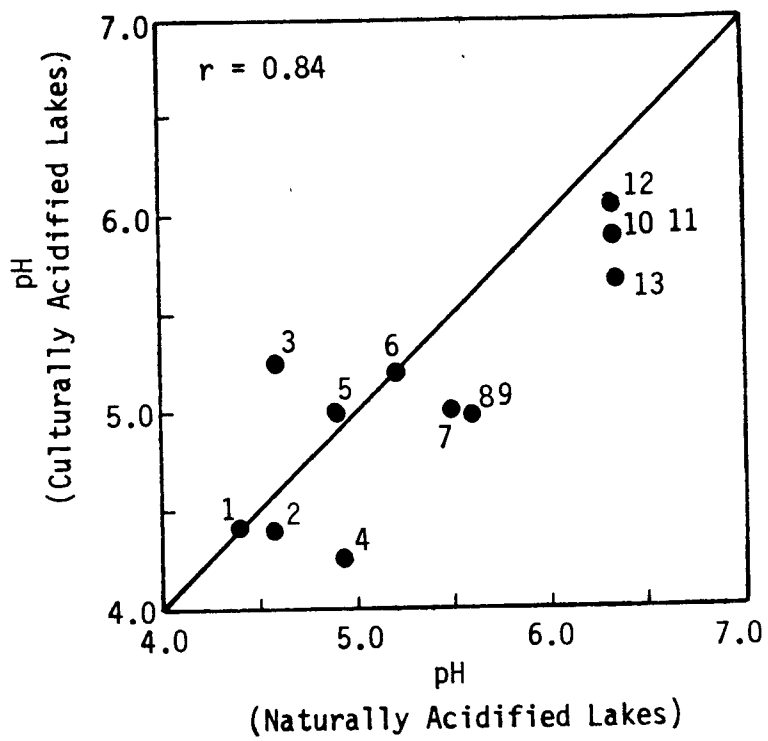


Figure 5-1. The distribution of 31 fish species in relation to pH for 138 northern Wisconsin lakes. Family names are abbreviated as follows: Catostomidae (Ca), Centrarchidae (Ce), Cyprinidae (Cy), Esocidae (E), Gadidae (Ga), Gasterosteidae (G), Ictaluridae (I), Percidae (P), Percopsidae (Pe), Salmonidae (S), Umbridae (U). Adapted from Rahel and Magnuson (1983).



1. YELLOW PERCH
2. BLUEGILL
3. LARGEMOUTH BASS
4. PUMPKINSEED
5. WHITE SUCKER
6. GOLDEN SHINER
7. NORTHERN PIKE
8. ROCK BASS
9. SMALLMOUTH BASS
10. IOWA DARTER
11. JOHNNY DARTER
12. BLUNTNOSE MINNOW
13. COMMON SHINER

Figure 5-2. Lowest pH of which fish species appeared unaffected in culturally acidified lakes (Harvey 1980) compared to the lowest pH at which they occurred in naturally acidic lakes. Diagonal line separates species occurring at lower pH in naturally acidic lakes (upper) from those that occur at a lower pH in culturally acidified lakes (lower). Adapted from Rahel and Magnuson (1983).

Cronan and Schofield 1979) but rare in acidic brownwater and ultra-oligotrophic lakes. As a result of organic complexation, comparison of fish species distributions relative to pH in these different water types has helped to identify aluminum toxicity, not pH, as the major reason for spring fish kills in lakes affected by acidic precipitation (Muniz and Leivestad 1980a).

Data on the biota of naturally acidic environments will continue to be instructive in studies of culturally acidified waters and should be especially useful in evaluating the long-term effects of chronic acid stress.

This section is summarized as follows:

1. Naturally acidic lakes fall into three major groups:

   - inorganic acidotrophic waters (pH commonly less than 4.0)
   - dystrophic waters (pH commonly 3.5 to 5.0)
   - ultra-oligotrophic waters (pH commonly 5.5 to 7.0)

2. In naturally acidic waters, hydrogen ion concentration can be strongly implicated as limiting the occurrence of:

   - invertebrates with calcified exoskeletons below pH 5.5 (mayflies, Gammarus, snails, clams)
   - blue-green algae below pH 4.0
   - some species of minnows (Cyprinidae) and darters (Percindae) below pH 6.0
   - several species of sunfish (Centrarchidae) below pH 4.5

These pH limits for survival and reproduction are similar to those observed in culturally acidified waters.

3. Lower safe pH limits inferred from a species distribution among naturally acidic waters may not always be valid for culturally acidified waters. For example, these limits may be:

   - too low if other stresses (e.g., aluminum) are present in culturally acidified lakes, or
   - too high if species are absent from naturally acidic lakes because of factors other than low pH: e.g., high temperature or metals in inorganic acidotrophic waters; low sodium, and calcium concentrations or unsuitable habitat in dystrophic waters.

5.3 BENTHIC ORGANISMS (R. Singer)

5.3.1 Importance of the Benthic Community

The term benthos refers to the community of organisms which live in and on bottom sediments of lakes and streams. The following groups are important components of the benthos: microbes, periphyton, macroinvertebrates, Crustacea, Insecta, Mollusca, and Annelida (Table 5-3). These organisms interact with biological and chemical components of the water column by processing detritus, recycling inorganic nutrients, mixing sediments, and serving as a principal food source for fish, waterfowl, and riparian mammals. Most of the energy and nutrients in lakes and streams ultimately passes through the benthos, so any alteration of this community is likely to affect plankton, fish, and water chemistry. Studies of the effects of acidic precipitation on this community have begun only recently (Singer 1981a), and not all benthic components have received equal treatment.

Microbes rapidly colonize the surfaces of leaf litter and other organic debris. Many benthic macroinvertebrates then process the debris, further facilitating its decomposition by microorganisms. Macroinvertebrate "shredders" rip and chew leaves, vastly increasing surface area, and partially digest material as it passes through their guts. Without these invertebrates, organic detritus decomposes very slowly (Brinkhurst 1974).

After the macroinvertebrates have broken up the detritus, fungi, bacteria, and protozoans complete the digestion and release inorganic nutrients into the water. The pH of the water in part controls the solubility equilibria of these inorganic constitutents and largely determines whether they will be available for recycling by plants. In addition, the rate of decay depends on the metabolic efficiency of this microbial community, which is also pH dependent (Laake 1976, Gahnstrom et al. 1980).

Macroinvertebrates aerate sediments by their burrowing movements. The top few centimeters of sediments generally demonstrate large gradients of pH, Eh (oxidation-reduction potential--the concentration of free electrons), dissolved O_2, and other constituents (Hutchinson 1957). Losses or alterations of plant and animal communities have profound effects on the chemistry of this top layer of sediments (Mortimer's "oxidized microzone" 1941, 1942), yet little work has centered on this habitat in acidified lakes. Mitchell et al. (1981b) found that the presence of burrowing mayflies (Hexagenia) affected sulfur dynamics in sediment cores taken from acidic lakes. Sediment/water column biological and chemical interactions are difficult to study because events occur across strong chemical gradients over short distances (Mitchell et al. 1981b). These gradients are easily perturbed by experimental procedures, including in situ measurements. Despite these procedural difficulties, it is important to determine the influence of pH-related alterations of the sediment community on the chemistry and biota of the water column.

Benthic animals are at the base of most food chains that lead to game fish. It has been suggested that eliminating the amphipod Gammarus lacustris (Section 5.3.2.4) and most molluscs (Section 5.4.2.6) might reduce trout production by 10 to 30 percent (Økland and Økland 1980); however this prediction has not been verified. Rosseland et al. (1980) reported that trout in acidified waters shifted their diet from acid-sensitive invertebrates like mayflies and bivalves to acid-tolerant forms such as corixid bugs and beetles. Although decline of fish populations due to alteration of the benthic community has not been studied, stress on fish populations as a result of nutrient changes should be considered. Fish fry, which are more dependent on smaller invertebrate prey than are adults, might be more sensitive to changes in the benthic community. These effects have not been considered experimentally, however.

Finally, changes in the benthic plant community (Section 5.5) affect macroinvertebrate distribution. The littoral habitat is an important area for benthos, and alterations in plant community structures are likely to affect all other trophic levels. These interactions remain to be investigated, but Eriksson et al. (1980b) have suggested that many of the observed changes in water chemistry and plankton communities are due to biological alterations, not direct chemical toxicology. They reported an increase in clarity, alteration of planktonic communities, and even a drop in pH (by 0.5 units) when fish were eliminated from a neutral lake by poisoning. The results extend and verify similar work reported by Stenson et al. (1978).

Sources of energy to benthos include primary production by higher plants (macrophytes) and attached algae (periphyton), and energy derived from detritus raining from the water column above (autochthonous inputs) and from detritus washed into the basin (allochthonous inputs). Lakes (lentic systems) receive most of their energy from autochthonous sources, whereas streams (lotic systems) derive their energy from primarily outside, allochthonous sources (e.g., Wetzel 1975). Consequently, shredding and scraping benthic insects and crustaceans are relatively more important in streams than lakes, while detritus-consuming worms and midges are more abundant in lakes.

5.3.2 Effects of Acidification on Components of the Benthos

The diversity of benthic organisms is often confusing to non-specialists. It must be emphasized that the loss of fish populations is one of the last biological effects of acidification, and alterations in the benthic community integrate annual loadings at levels of stress which are not observable in fish populations. The ultra-oligotrophic lakes characteristic of sensitive areas harbor ecosystems which are unique. These ecosystems may be damaged at levels of acidification (pH < 6.5) that may not affect fish at all. The concept of an endangered ecosystem is as viable as the more generally accepted view of the endangered species.

Using historical collections and known water quality requirements of organisms allows specialists to generalize about past water chemistry parameters. Moreover, the low mobility and long life cycles of many benthic organisms allow one to make conclusions about the extremes of water quality fluctuations in past years.

5.3.2.1 Microbial Community--Studies of the effects of acidification on benthic protozoans have not been conducted. Other members of this community include bacteria and fungi. It was reported that acidification of lakes causes bacterial decomposers to be replaced by fungi (Hendrey et al. 1976, Hendrey and Barvenik 1978) and proposed (Grahn 1976, 1977; Hultberg and Grahn 1976) that the shift to fungi accounts for the observed (Leivestad et al. 1976) accumulation of detritus in acidic lakes. Liming of lakes to increase the pH brings a rapid restoration of normal microbial activity (Scheider et al. 1975, 1976; Gahnstrom et al. 1980).

Traaen (1976, 1977) showed that leaf packs in lakes were processed much more slowly at lower pH (5.0) than at higher pH (6.0) values, but he also cautioned (1977) that many other factors besides acidity can affect leaf processing. Burton (1982) has confirmed the impact of low pH on processing of organic matter. Friberg et al. (1980) reported an increased accumulation of detritus and a reduction in numbers of scrapping insects in an acidic (pH 4.3 to 5.9) as compared to a neutral (pH 6.5 to 7.3) stream. Hall et al. (1980) and Hall and Likens (1980a,b) artificially acidified a stream in Hubbard Brook, NH, and showed that scrapers were largely lost. In addition, they reported that insects that feed by collecting debris were inhibited.

Hall et al. (1980) observed a growth of basidiomycete fungus on birch leaves in an artificially acidified portion of a stream; such fungal growth was lacking in the non-acidified control section. Hultberg and Grahn (1976) and Grahn et al. (1974) described an accumulation of a "fungal mat" on the bottom of many acidified Scandanavian lakes. It is now understood that this coarse particulate material is a mixture of detritus, some fungi, and mostly algae (Stokes 1981) (Section 5.3.2.2). The original description of this layer of material as a "fungal mat" (Hendrey et al. 1976) was erroneous (Hendrey and Verticci 1980) due to the senescent, colorless state of the common blue-green algal (Phormidium spp.) component of the mat.

Some controversy exists regarding the effects on microbial metabolism brought about by acidification (Baath et al. 1979). The accumulation of detritus in acidic lakes suggests a reduction in decomposition by bacteria (Leivestad et al. 1976). The reduction of oxygen utilization by acidified cores (Hendrey et al. 1976) supports this view. Furthermore, liming increased oxygen consumption of previously acidic cores (Gahnstrom et al. 1980). At pH levels below 5.0, oxygen consumption, ammonia oxidation, peptone decomposition, and total bacterial numbers all declined (Bick and Drews 1973). In contrast, Schindler (1980) reported no change in decomposition rates in an artificially acidified lake, and Traaen (1978) observed no clear

changes in the planktonic bacterial populations from seven lakes of pH < 5.0 as compared to seven lakes of pH > 5.0. Traaen argued that acidic inputs should affect the plankton populations prior to affecting benthic algae. His results showed that the distribution of bacterial populations was more strongly influenced by organic inputs and temporal and spatial (depth) patchiness than by pH. Gahnstrom et al. (1980) reported that inhibition of oxygen uptake by sediments increased in acidic lakes as compared to reference lakes only in the littoral sediments. They argued that the inhibition of microbial activity in the littoral zone might be due to the inflow of acidic runoff, which is restricted to the epilimnion during snowmelt and autumn rains (Hendrey et al. 1980a). All these studies demonstrate that decomposition of organic material is inhibited below pH 5.0 but not necessarily by a reduction in standing crop of bacteria. The resulting accumulation of organic matter undoubtedly affects water chemistry, fish habitats, nutrient cycling, and primary productivity.

Microbial effects on other trophic systems probably involve alterations of sulfur, nitrogen, and phosphorus dynamics. Methylation of mercury (Tomlinson 1978, Jernelov 1980) and other heavy metals may have profound effects on higher trophic levels (Galloway and Likens 1979; refer also to Chapter E-6). The release of aluminum from sediments below pH 5.0 (Driscoll 1980) is another potentially serious impact that has not been adequately studied.

5.3.2.2 Periphyton--The periphytic community of algae lives attached to macrophytes and directly on sediments and makes important contributions to primary production and nutrient cycling, particularly in lotic (stream) systems. Changes in the species composition of this community reflect changes in the chemistry of both the water column and the sediments. These algae are an important food source for the grazing macroinvertebrates which are a principal source of food for fish. Algal seasonal growth and decomposition store and periodically release nutrients and other ions.

5.3.2.2.1 Field surveys. Acidic lakes develop periphytic communities dominated by species known to prefer acidic water, and dramatic decreases in species diversity below pH 5.5 have been observed (Almer et al. 1974; see Section 5.2). One of the most striking aspects of many acidified lakes is the presence of a thick mat of algae which overlies the substrate. This mat overgrows all the rooted plants and, to a large degree, physically and chemically isolates the lake bottom from the overlying water. The mat varies in shape, texture, and species composition from lake to lake, seemingly irrespective of water chemistry parameters. Three types of mats were described by Stokes (1981):

1) Cyanophycean mats, dominated by the blue-green algae Oscillatoria sp., Lyngbya sp., and Pseudoanabaena sp. in Sweden at pH 4.3 to 4.7 (Lazarek 1980) and Phormidium sp. in New York at pH 4.8 to 5.1 (Hendrey and Vertucci 1980). These mats are dark blue-green with occasional flecks of orange-colored carotene-rich material. They are thick,

felt-like, and encrusting. Stokes reported cyanophycean mats at depths of 2 to 3 m, but they have been observed as deep as 5 m in an acidic (< pH 4.9) Adirondack lake (Singer et al. 1983).

2) Chlorophycean mats, dominated by green algae like Mougeotia sp. and Pleurodiscus sp. at pH 3.9 to 5.0 in Canadian lakes (Stokes 1981). These mats are coarser than cyanophycean mats. They tend to be loosely packed, green to reddish purple, and may extend to 4 m deep. Unlike cyanophycean mats, chlorophycean mats are not compacted and do not retain their structural integrity when lifted. A chlorophycean mat developed after the experimental acidification of a whole lake was completed (Schindler and Turner 1982).

3) Chlorophycean epiphytic or periphytic algae dominated by green algae such as Spirogyra sp., Zygnema sp., Pleurodiscus sp., and Mougeotia sp., Oedogonium, and Bulbochaete. This community appears as bright grass-green clouds hanging from macrophytes and resting lightly on the bottom. They appear around pH 5.0 and have been reported in Canada (Stokes 1981), the Adirondacks (Hendrey and Vertucci 1980), and Sweden (Lazarek 1982). They also appeared in artificially acidified channels (Hendrey 1976), artificially acidified cylinders (Muller 1980, Yan and Stokes 1978), and in an artificially acidified lake at pH 5.6 (Schindler 1980).

I have observed all three types of mat communities in a survey of five Adirondack lakes below pH 4.9. These lakes were all about the same size (~ 30 ha), low in nutrients, located near each other, and similar in morphometry. Why one community dominates one lake but is not found in another is unknown. Part of the explanation may be that the three types of mats may represent stages in a pattern of seasonal succession. Lazarek (1982) has reported seasonal succession among epiphytes from one acidic (pH 4.3 to 4.7) Swedish lake. As these mats are the most conspicuously visible characteristics of acidified lakes, their significance and effects on other physical and chemical components deserve more attention.

5.3.2.2.2 Temporal trends. The shells of diatoms (Bacillariophyceae) are made of SiO_2 and are very resistant to weathering. Deposition of planktonic and benthic diatoms to sediments produces a record of the past populations in the lake once the cores are dated by radioactive decay (Norton and Hess 1980). The pH tolerance of many diatoms has been tabulated elsewhere (e.g., Lowe 1974). Thus the ancestral pH may be inferred from the stratigraphic record. This technique is subject to variances caused by macroinvertebrate mixing, local changes in pH sensitivity of species, and the numerous other factors besides pH that determine the distribution of species (Norton et al. 1981). Nonetheless, inferred pH generates a value that reflects the real water

column value to within < 1.0 pH unit, which often lies within the range of normal seasonal pH variation. The method's accuracy is even better for comparing groups of lakes with similar current pH values along a temporal gradient of past pH levels by regression analysis (Norton et al. 1981). The inferred pH values calculated from diatom stratigraphy related very well to the values estimated from using the shells of cladoceran remains (Norton et al. 1981).

Berge (1976) compared the diatom assemblages in sediments from seven Norwegian sites with the communities from the same sites as reported in 1949 and found no quantitative change in the diatoms in the 26-year period. However, he noted a marked shift towards species that required or preferred low pH. In an even longer period (ca. 1920-1978) Almer et al. (1974) reported a reduction in diatoms from cores taken from Scandinavian lakes which have become more acidic. Dam et al. (1980) reported a more obvious shift towards acid-tolerant diatoms in sediments from acidic Dutch lakes.

Three hundred years of diatom deposition in sediments was used to calculate pH values in two Norwegian lakes (Davis and Berge 1980). The pH tolerance of diatoms was determined from present-day distributions, and the pH in the past was inferred from the species composition in the dated sediment layers. One lake has remained constant at ~ pH 5.0 while the other went from pH 5.1 to 4.4 since 1918 (Davis et al. 1983).

More recently (Davis et al. 1983), results of sediment core analyses from nine Norwegian lakes and six New England lakes were compared. The range of pH tolerance of the diatoms was determined by studying current distributions in 36 Norwegian and 31 New England lakes. The three Norwegian Lakes which are currently acidic (pH < 5.0) have decreased in pH by 0.6 to 0.8 units since 1890-1927. The lakes currently above pH 5.0 have decreased 0 to 0.3 pH units since 1850. All six of the New England lakes decreased 0.2 to 0.4 units and some of these changes might be due to land use changes (reforestation) which are in the historical record. Another anomaly was the record of heavy metal pollutants in the sediments several decades prior to the changes in the diatom communities. This was ascribed to the buffering of the watershed, which released metals while retaining protons for many years, thus keeping the lake pH stable, or alternatively, to the former high emissions of neutralizing particulates like fly ash.

An interesting change in the diatom community structure is also apparent from an analysis of the data (Berge 1976, Dam et al. 1980, Davis and Berge 1980, Norton et al. 1981, Davis et al. 1983). The species of diatoms which indicate acidic (pH < 5.0) conditions are primarily benthic, whereas those from circum-neutral (pH 6.0 to 7.2) are planktonic. This implies that the diatom community shifts to benthic production in acidic lakes. Diatoms are common but not dominant members of the algal mats of present-day acidic lakes (Stokes 1981).

Del Prete and Schofield (1981) used sediment cores to study the succession of diatom species in three Adirondack lakes. They observed

an increase in dominance by acid-tolerant species in the most acid-impacted lakes. A trend towards species tolerant of low nutrient waters was also reported. Tabellaria fenestrata and Cyclotella stelligera increased in numbers most directly with increasing acidity, although some of the results were equivocal.

Coesel et al. (1978) have compared the desmid populations from a group of lakes in the Netherlands with community compositions reported in studies done in 1916-25, 1950-55, and with their own survey in 1977. Many of the species from the rich flora in the earliest survey were lost due to cultural eutrophication. In the most recent survey, those ponds that were not impacted by nutrient additions were affected by acidic deposition, as reflected by the paucity of desmid species. These ponds appeared to have undergone oligotrophication. The eutrophic ponds remained well-buffered and unchanged. Thus, the effects on community composition brought on by cultural eutrophication can be separated from the changes caused by acidification.

These studies of temporal trends demonstrate that many acidic lakes have become acidic in historic times, but they do not prove that this acidification is universally a consequence of atmospheric deposition. Deforestation, followed by eutrophication and reforestation, can cause the pH of a lake to rise and then fall. Even so, some lakes have fallen about 0.5 units in locally unperturbed watersheds in historic times.

5.3.2.2.3 Experimental studies. Muller (1980) studied the succession of periphyton in artificially acidified chambers held in situ in Lake 223, Experimental Lakes Area, in northwestern Ontario (Schindler et al. 1980b). At the control pH of 6.25, a succession occurred in the chambers from dominance by diatoms in the spring to dominance by green algae (Chlorophyta) in mid-July. In enclosures at pH < 6.0, Chlorophyta dominated the periphyton throughout the sampling period. Blue-green algae (Cyanophyta) were reduced and almost eliminated under the most acidic conditions. Muller observed no trend with respect to changes in biomass but noted a sharp decrease in species diversity (as measured by Hill's index) in the acidified (pH 4.0) chambers. Changes in primary production (^{14}C) showed no trend with pH. The dominance of the periphyton by Chlorophyta in the acidified samples was due almost entirely to the growth of Mougeotia sp., which by June represented 96 percent of the biomass and cell numbers at pH 4.0. This taxon was responsible for less than 4 percent of the biomass and cell numbers in the natural lake water. Interestingly, during May, the blue-green alga, Anabaena sp., rose from 3.4 percent of the biomass in the lake water (pH 6.2) to 4.3 percent at pH 4.0, but this species was almost absent by June. In spite of its low biomass this alga accounted for 25 percent and 41 percent of the total cell numbers in these two samples. Muller's (1980) work demonstrates the need to consider natural seasonal patterns of succession when we superimpose the effects of acidification on aquatic ecosystems. The only other report of seasonal changes in periphyton (Lazarek 1982) dealt with algae living attached to Lobelia dortmanna and verified the succession from diatoms to green algae (Mougeotia spp.) during the growing season.

Higher standing crops but lower rates of C-fixation per unit chlorophyll occurred in periphyton growing in artificial stream channels at reduced pH (Hendrey 1976). The total rate of ^{14}C-uptake was similar over a wide range of $[H^+]$. Increased standing crop was attributed to a combination of three mechanisms: 1) enhanced growth by acid-tolerant taxa, 2) reduction in grazing by the reduced macroinvertebrate population, and 3) inhibition of microbial decomposition (Hendrey 1976).

In an artificially acidified section of a softwater stream in New Hampshire, Hall et al. (1980) reported an increase in periphyton numbers and substrate chlorophyll a concentration. They did not perform a taxonomic analysis of the periphyton community.

Periphyton communities respond to acidification by alterations in species composition, increases in the standing crop, decreases in the amount of growth per unit of biomass, and formation of atypical mats which cover the substrate. These changes produce dramatic, visually obvious changes in lakes and streams at pH < 5.0.

5.3.2.3 Microinvertebrates--The responses of several minor groups of invertebrates to acidification have been studied. The Nematoda and Gastrotricha are both common but poorly studied inhabitants of interstitial water in sediments (meiofauna). They feed on detritus and other organic material lying between the grains of sand in sediments. The ubiquitous meiobenthic gastrotrich, Lepidodermella squammata, was almost totally eliminated under laboratory conditions below pH 6.4 (Faucon and Hummon 1976). Unfortunately, the pH gradient was achieved by mixing unpolluted creek water with water from a stream receiving acidic strip mine drainage, so it is not easy to generalize to streams receiving acidic deposition. Hummon and Hummon (1979) added $CaCO_3$ to the acidic mine drainage and showed that at the same pH, water with more carbonate (CO_3^{2-}) ameliorated the deleterious effects of acid stress. The extreme sensitivity of these animals to some component of the acidic water, possibly low CO_3^{2-} or high concentrations of metal ions, bears further investigation. Roundworms (Nematoda) normally have a ubiquitous distribution (Ferris et al. 1976). However, in an extensive survey of Norwegian lakes, sub-littoral sediments of acidic lakes had a scarcity of roundworms when compared to shallow sediments from the same lakes (Raddum 1976). No other mention is made of the Nematoda in the literature pertaining to the acidification of aquatic systems.

Freshwater sponges (Porifera) are epifaunal and directly exposed to changes in water chemistry alterations. However, their response to acidic deposition has not been studied. Jewell (1939) studied the distribution of Spongillidae from 63 lakes, bogs and rivers in Wisconsin with various levels of hardness and pH. She found that most of the species did have limited ranges of Ca^{2+} concentrations in which they flourished. Six common species were exposed to chemically modified water, and growth was observed. The lowest pH in this experiment was 5.9, but there were indications that the most important parameter was

the availability of $Ca(HCO_3)_2$. As filter feeders, sponges are important reprocessers of suspended organic matter and are particularly useful indicators of water quality because of the large volume of water which passes through their tissues.

Aquatic mites (Acarina) are not generally collected in surveys of benthic fauna, but Raddum (1976) noted that mites occurred in great abundance in the shallow water of an acid-impacted lake. At a depth of 0.5 m, mites were third in abundance after nematodes and midges (Chironomidae). At depths > 2 m almost no mites were observed. The shallow mites probably receive their nutrition from the shore or the water surface, rather than the lake substrate. In contrast, Wiederholm and Eriksson (1977) observed mites in deep water (> 10 m) in an acidic lake in Sweden, and Collins et al. (1981) reported no differences between the distribution of mites in acidic and control lakes. Clearly, much work needs to be performed on the distribution of this group to obtain a more complete understanding of how acidic precipitation affects their distribution.

5.3.2.4 Crustacea--Benthic crustaceans include familiar large forms like crayfish (Decapoda), sow bugs (Isopoda), and scuds (Amphipoda), but also smaller forms such as benthic copepods, mysids, cladocerans, and other branchiopods (e.g., Lepidurus). All these forms, whether large or small, contribute to the ecosystem dynamics by feeding on detritus or on smaller detritivores and thus converting the organic material into a form palatable to fish and other carnivores.

The distribution and characteristics of habitats containing the isopod Asellus aquaticus (aquatic sow bug) and the amphipod Gammarus lacustris (scud) were summarized by K. Økland (1979a, 1980a). Both of these species are important as food for fishes and as detritus processors. A. aquaticus populations were reduced below pH 5.2 and absent below pH of 4.8. While G. lacustris was able to out-compete A. aquaticus at pH 7.0, Asellus out-competed Gammarus at sites stressed by either acidic inputs or organic enrichment. A. aquaticus was widely distributed in acid-stressed lakes at pH 5.0 (K. Økland 1980b) but G. lacustris was inhibited below pH 6.0 (K. Økland 1980c) probably due to the low calcium concentration in the acidic water.

In the laboratory, Gammarus pulex demonstrated no avoidance of pH 6.4 to 9.6 (Costa 1967). However, within 12 to 15 minutes after the pH was lowered to 6.2 in one part of the tank, the amphipods began to stay near the alkaline side. Immature Gammarus performed this avoidance behavior faster than did adults.

Sutcliffe and Carrick (1973) verified that in England G. pulex is not normally found below pH 6.0, but they pointed out that it was found in France at pH 4.5 to 6.0. They suggested that the avoidance response (Costa 1967) might explain its limitation to near-neutral water, instead of direct mortality due to low pH. Laboratory studies (Borgstrom and Hendrey 1976) suggest, however, that direct mortality is important at pH $\leq$ 5.0. G. lacustris achieved 96 hr TL_{50} at pH 7.26 in Montana, but

populations from Utah withstood pH 5.7 in similar laboratory bioassays in hard (135 mg ℓ^{-1} $CaCO_3$ in Montana, 200 mg ℓ^{-1} $CaCO_3$ in Utah) water (Gaufin 1973). A different species, G. fossarum, from Germany, showed no mortality at pH 6.0, and had a 96 hr TL_{50} of ~ 4.7. At pH 5.0, 30 percent of the laboratory population survived for 10 days (Matthias 1982). K. Økland (1980a) ascribed these differences to the variable sensitivity of different populations.

Steigen and Raddum (1981) noted that A. aquaticus responded to acidification by leaving the water, so they confined some of the animals in wire-enclosed tubes. The confined individuals resorted to cannibalism, but the increased energetic demands Steigen and Raddum measured caused by the H^+ stress resulted in losses of total caloric value in the confined animals. The unconfined specimens left the water but returned to feed, sometimes cannibalistically, and the survivors gained in caloric content. This behavioral response may be the mechanism by which Asellus can tolerate more acidity than can Gammarus.

The opossum shrimp, Mysis relicta, is a bottom-dwelling crustacean characteristic of deep water. It enters the water column at night to feed on plankton and, in turn, provides food for fish (Pennak 1978). When Experimental Lake 223 was artificially acidified from pH 6.6 to 5.3, Mysis populations were eliminated at ~ pH 5.9 (Schindler and Turner 1982).

Eggs of the tadpole shrimp, Lepidurus arcticus (Eubranchiopoda, Notostraca) took longer to hatch and the larvae matured more slowly than normal at pH < 5.5 than at pH values > 5.5 (Borgstrom and Hendrey 1976). At pH < 4.5, larvae of L. arcticus died in two days and eggs never hatched. A survey from Sweden (Borgstrom et al. 1976) reported that L. arcticus was not found below pH 6.1.

Laboratory bioassays of the crustaceans Daphnia middendorffiana, Diaptomus arcticus, Lepidurus arcticus and Branchinecta paludosa have provided additional evidence (Havas and Hutchinson 1982) of the sensitivity of crustaceans to acid stress. Animals collected from an alkaline (pH 8.2) pond were exposed to naturally acidic water (pH 2.8) from a nearby pond which received aerial deposition from the Smoking Hills of the Canadian North West Territories. The acidic water was amended with NaOH to provide a range of pH treatments. A critical pH was 4.5, at which mortality drastically increased for all of the individuals. Mortality did not occur in control water lacking heavy metal contamination (Al, Ni, Zn). These authors suggested that their critical pH of 4.5 was lower than that reported in other studies because the water in the Smoking Hills area is higher in total conductivity (1.3 mho cm^{-1} than that of other acidic clear water systems (Havas and Hutchinson 1982).

An increased abundance of benthic cladocerans has been reported (Collins et al. 1981) from two of three acidic lakes studied in Ontario.

Crayfish are very important components of the benthos as detrital processors and as food for larger game fish. Species of crayfish show some variation in sensitivity to pH. Malley (1980) indicated that Orconectes virilis, in softwater of ~22 μmhos cm^{-1} conductivity and Ca^{2+} of 2.8 mg ℓ^{-1}, was stressed by pH < 5.5. However, Cambarus sp. was reported (Warner 1971) in a stream receiving acidic mine drainage at pH 4.6, Ca^{2+} of 12 mg ℓ^{-1}, and conductivity of 96 μmhos cm^{-1}. Cambarus bartoni was found in three acidic lakes (pH 4.6 to 4.9, ~3 mg ℓ^{-1} Ca^{2+}) and Orconectes propinquis was collected in one of three acidic lakes (Collins et al. 1981). I have seen Orconectes spp. in two lakes of pH 4.8 and 5.0 in the Adirondacks.

This apparent discrepancy in pH tolerances of various crayfish may not be entirely due to interspecific or inter-population differences. The crayfish Orconectes virilis has difficulty recalcifying its exoskeleton after molting at pH < 5.5. Uptake of $^{45}Ca^{2+}$ by crayfish stopped at pH 4.0 and was inhibited at pH 5.7 (Malley 1980). Infestation of this species by the parasitic protozoan Thelohonia sp and reduction in recruitment of young at pH 5.7 was also reported (Schindler and Turner 1982). Hence the tolerance of Cambarus to pH 4.6 from an acidic mine drainage stream may be due to the higher Ca^{2+} concentration in the stream compared to habitats affected by acidic deposition. The ameliorative effect of cations is suggested by the inability of the crayfish Astacus pallipes to transport $^{22}Na^{+}$ below pH 5.5 (Shaw 1960). Stress is a function of both low pH levels and low calcium levels, and the responses to these stresses undoubtedly vary between life cycle stages and species.

5.3.2.5 Insecta--The importance of insects in lakes and streams is discussed in Section 5.2. These animals are important ecologically but also, because their tolerance to various stresses is well known, they are important as water quality indicators.

Studies of benthic insects exposed to acid stress include surveys, mostly from Europe and Canada, and some experimental manipulations. Survey work involves presence-absence data from which tolerances have been assumed. The general conclusion drawn from surveys of lakes and streams (Sutcliffe and Carrick 1973; Conroy et al. 1976; Wright et al. 1975, 1976; Hendrey and Wright 1976; Leivestad et al. 1976; Wiederholm and Eriksson 1977; Raddum 1979; Friberg et al. 1980; Overrein et al. 1980) is that species richness, diversity, and biomass are reduced with increasing acidity. Because predation by fish is eliminated in some water and food should be abundant due to the accumulation of detritus (Grahn et al. 1974), one might suppose that insect biomass would increase. However, acidity imposes stresses that are as severe as predation (Henrikson et al. 1980b), and the lack of bacterial decomposition of detritus (Traaen 1976, 1977) may render the detritus unpalatable to insects (Hendrey 1976, Hendrey et al. 1976).

5.3.2.5.1 Sensitivity of different groups. The sensitivity of benthic insects to pH stress varies considerably among taxa and among different

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life cycle stages (Gaufin 1973, Raddum and Steigen 1981). Responses are physiological and behavioral.

Mayflies seem to be particularly sensitive to acidic conditions. Female mayfly adults (Baetis) did not lay eggs on otherwise suitable substrates in water pH < 6.0, although three different species were found within 200 to 300 m in neutral brooks with similar substrates (Sutcliffe and Carrick 1973). The adult presumably can detect high levels of acidity by dipping her abdomen into the water as she flies. Besides Baetis, the common mayflies Ephemerella ignita, and Heptagenia lateralis were absent only from the acidic region of the River Duddon, England (Sutcliffe and Carrick 1973). A Swedish survey (Nilssen 1980) also found mayflies to be sensitive to pH stress. A plot of the number of mayfly species vs pH of 35 lakes and 25 rivers indicated that the number of species decreased logarithmically with decreasing pH. Species were lost in two groups; one group did not appear below pH 6.5, and another decline in species numbers occurred below pH 4.5 (Borgstrom et al. 1976, Leivestad et al. 1976). In another survey (Fiance 1978) the distributional pattern of the mayfly, Ephemerella funeralis, was studied in the Hubbard Brook, NH, watershed during a 2-year period. Nymphs were absent from waters of pH < 5.5. The 2-year life cycle of this mayfly makes it particularly sensitive to irregular episodic stresses, because a single drop in pH may eliminate the insects for several years. In an experimentally acidified section of a New Hampshire stream (pH 4.0), mayfly (Epeorus) emergence was inhibited and drift of nymphs increased (Hall et al. 1980; Hall and Likens 1980a,b; Pratt and Hall 1981). These responses suggest that mayflies exhibit both behavioral and physiological responses to acidity.

Laboratory bioassays verified that mayflies were the most acid-sensitive order of insects (Bell and Nebeker 1969, Bell 1971, Harriman and Morrison 1980; Table 5-2). Exposing caged transplanted insects to acidified river water showed that mayflies could not survive and would try to leave in the drift (Raddum 1979).

In contrast, dragonflies and damselflies (Odonata) (Table 5-2) are much more resistant to low pH (Bell and Nebeker 1969, Bell 1971, Borgstrom et al. 1976). The dragonfly nymph Libellula pulchella tolerated pH 1.0 for several hours (Stickney 1922). Dragonfly nymphs (Anisoptera; Odonata) may be able to endure episodic acidic stress by closing their anus, through which they respire, but this behavior has not been investigated. Dragonflies burrow into sand and mud, turning over material and changing the structure of the habitat. They are also major predators on oligochaete worms, midges (Chironomidae), and small insects; they are even known to feed on tadpoles and small fish (Needham and Lloyd 1916).

Tolerance to acidification within the Plecoptera (stoneflies) is variable according to surveys (Sutcliffe and Carrick 1973, Leivestad et al. 1976), field manipulations (Raddum 1979; Hall and Likens 1980a,b) and laboratory studies (Bell and Nebeker 1969, Bell 1971). Stoneflies and mayflies are preferred trout food in streams, as evidenced by the

TABLE 5-2. RESULTS OF LABORATORY STUDIES ON pH TOLERANCE OF SELECTED INSECT NYMPHS. TL_{50} IS THE pH WHICH IS LETHAL TO 50% OF THE ORGANISMS. RESULTS OF DIFFERENT STUDIES ARE REPORTED HERE AS THE NEGATIVE LOGARITHM OF THE AVERAGE HYDROGEN ION CONCENTRATIONS

Organisms	pH 96 hr TL_{50}	pH Long-term TL_{50}	pH 50% successful emergence	References[a]
Ephemeroptera				
Baetis sp.	4.5			M
Cinygmula par	6.11			G
Ephemerella doddsi	4.10			G
Ephemerella grandis	3.6	5.8(48)		G
Ephemerella subvaria	4.65	5.38(30)	5.9	B, BN
Heptagenia sp.	6.17			G
Hexagenia limbata	5.66	5.5(33)[b]		G
Leptophlebia sp.	5.20			G
Rhithrogena robusta	4.60			G
Stenonema rubrum	3.32			B
Odonata				
Boyeria vinosa	3.25	4.42(30)	5.2	B, BN
Ophiogomphus ripinsulensis	3.50	4.30(30)	5.2	B, BN
Plecoptera				
Acroneuria lycorias	3.32	3.85(30)	5.0	B,BN
Acroneuria pacifica	3.8	5.8(90)		G
Arcynopteryx parallela	4.37			G
Isogenus aestivalis	5.08			G
Isogenus frontalis	3.68	4.50(30)	6.6	B, BN
Isoperla fulva	4.5			G
Nemoura cinerea	2.6			M
Pteronarcella badia	3.92	4.52(90)		G
Pteronarcys californica	4.44	4.95(90)		G
Pteronarcys dorsata	4.25	5.00(30)	5.8	B, BN
Taeniopteryx maura	3.25	3.71(30)	4.0	B, BN
Trichoptera				
Hydropsyche betteni	3.15	3.38(30)	4.7	B, BN
Hydropsyche sp.	3.28			G
Arctopsyche grandis	3.4			G
Limnephilus ornatus	2.82			G
Brachycentrus americanus	1.50	2.45(30)	4.0	B, BN
Brachycentrus occidentalis		4.3(90)		G
Cheumatopsyche sp.		4.52(90)		G

TABLE 5-2. CONTINUED

Organisms	pH 96 hr TL_{50}	pH Long-term TL_{50}	pH 50% successful emergence	References[a]
Diptera				
Atherix variegata				G
Holorusia sp.	2.8			G
Simulium vittatum	3.63	4.2(68)		G

[a]References: B = Bell 1971, BN = Bell and Nebeker 1969, G = Gaufin 1973, M = Matthias 1982.

[b]Seventy of 90 survived.

attempts of fishermen to mimic these body forms with their flies (Schweibert 1974). Plecoptera are ecologically very important components of streams, where smaller forms cling to rocks, feeding on the drift of detritus, and algae and larger forms seek smaller invertebrates as prey. Critical sensitivity of this group begins between pH 4.5 to 5.5, and their distribution generally follows that of mayflies, except for some tolerant forms like Taeniopteryx, Nemoura, Nemurella, and Protonemura (Raddum 1979).

Caddisflies (Trichoptera) include burrowers, sprawlers, filter feeders, predators, detritivores, and forms found specifically in running or standing water. They occupy many niches and are difficult to lump into generalizations. Most of the larvae live in cases made from local materials. Caddisflies have been found near pH 4.5 in field surveys (Sutcliffe and Carrick 1973, Leivestad et al. 1976, Raddum 1976) but not at pH 4.0 (Raddum 1979; Hall and Likens 1980a,b). Raddum (1979) observed that the running water caddisflies Rhyacophila nubila, Hydropsyche sp., Polycentropus flavomaculus, and Plectorenemia conspersa all survived pH 4.0 in the laboratory, but only P. conspersa did well in situ at pH 4.8. Raddum explained the loss of Rhyacophila and Hydropsyche in the field by alterations in their food supply. P. flavomaculatus became cannibalistic at pH 4.0, which may explain its absence in the stream but its survival when isolated during laboratory experiments. The problem of cannibalism points out the difficulties in relating laboratory studies to field observations. Another caddisfly, Limnephilus pallens, was collected from an alkaline (pH 8.2) pond and subjected to more acidic water both in the laboratory and in situ (Havas and Hutchinson 1982). The larvae survived in pH 3.5 water, and actually did better in metal contaminated sulfate-fumigated water. This acidic water was near the alkaline pond from which the caddisflies were collected, but no larvae lived in the acid pond. Possible explanations for the absence of the caddisflies from water in which they could survive were: 1) absence of suitable food, 2) sensitivity to the acidity during emergence, 3) absence of suitable case building material in the acidic pond.

Most other insects are largely unaffected or slightly favored in acidic lakes and streams. The alderfly, Sialis (Megaloptera), increased its emergence rates in an artificially acidified stream (Hall and Likens 1980a,b). It was found commonly in shallow water in an acidic (pH 3.9 to 4.6) Swedish lake (Wiederholm and Eriksson 1977) and in a highly variable (pH 6.2 to 4.2) Norwegian lake (Hagen and Langeland 1973).

Several true flies (Diptera) increase in relative abundance at low pH (Hagen and Langeland 1973, Wiederholm and Eriksson 1977, Raddum 1979, Collins et al. 1981, Raddum and Saether 1981). The most successful dipterans are the midges (Chironomidae), the predacious phantom midge (Chaoborus, Chaoboridae) and in streams, the black fly (Simulidae). Black fly adults are notorious as biting pests when they emerge in the spring. Often, the principal insects in acidic lakes are the midges (Chironomidae) Chironomus riparius (Havas and Hutchinson 1982) Procladius sp., Limnochironomous sp., Sergentia coracina,

Stichtochironomus sp. and phantom midges (Chaoborus) (Leivestad et al. 1976, Raddum and Saether 1981). These insects comprised 56 and 41 percent of the benthos of a Swedish acidic lake (pH 3.9 to 4.6) (Wiederholm and Eriksson 1977). Chironomids appear to be preadapted for acidification, because the same species are found in clearwater acidic lakes as in humic acid lakes (Raddum and Saether 1981). Uutala (1981) reported that the chironomid fauna of two acidic Adirondack lakes were reduced in biomass as compared to fauna in nearby control lakes. The different life cycle stages have variable responses to pH stress, but the molting period is the most sensitive (Bell 1970).

The dominance of the benthos of acidic lakes by midge larvae is not surprising, as these insects are abundant in almost all lakes, but the observed shift in dominant species does suggest that benthic community structure is altered. Direct toxicity is probably not the explanation for the absence of certain species. For example, some Orthocladius consobrinus tolerate pH 2.8 in the laboratory, but this species was not found in acidic pools (pH 2.8) in the Smoking Hills, even though it was found in nearby alkaline (pH 8.2) pools (Havas and Hutchinson 1982).

Other insects abundant in acidic waters are the true bugs (Hemiptera) like water striders (Gerridae), backswimmers (Notonectidae), and water boatmen (Corixidae), and beetles (Coleoptera) of the families Dytiscidae and Gyrinidae (Raddum 1976, Raddum et al. 1979, Nilssen 1980). These insects prey on other insects and small crustaceans, both benthic and planktonic. They are metabolically very active and receive most of their O_2 from the atmosphere, thus reducing the amount of soft body tissue exposed directly to the water, in contrast to gilled insects and crustaceans.

5.3.2.5.2 Sensitivity of insects from different microhabitats. Important generalizations are better made by analyzing the data after grouping the taxa by functional guilds and microhabitats rather than by phylogenetic associations (Merritt and Cummins 1978). Collins et al. (1981) compared three acidic softwater lakes (4.6 to 4.9) with 11 neutral softwater lakes in central Ontario and reported no significant decreases in populations of animals living in sediments (infauna). Observations of epifauna by scuba divers concurred with the general observation that acidic lakes have depauperitic mollusc and insect populations.

It is hardly surprising that infaunal communities, which are protected by the buffering capacity of the substrate, are less affected than epifaunal communities. Still, few studies have organized data in such a manner as to verify that epifaunal insects are indeed the targets of acid stress. Also, a perusal of the data presented above suggests that it is epifaunal forms with filamentous gills that are most sensitive to low pH. Air-breathing beetles and bugs survive low pH stress well as do infaunal forms with filamentous gills, such as the burrowing mayfly, Hexagenia. Metabolic and physical actions of Hexagenia nymphs increased the Eh, NH_3, inorganic S, SO_4, and decreased the pH as compared to control microcosms lacking nymphs or

with dead nymphs (Mitchell et al. 1981b). Thus, not only does the chemistry affect the biota, but conversely the biota alters the chemistry.

5.3.2.5.3 Acid sensitivity of insects based on food sources. Total invertebrate biomass in an acidic (pH 4.3 to 5.9) stream was ~ 2.6 times less than that of a neutral stream (pH 6.5 to 7.3) 6 km away in southern Sweden (Friberg et al. 1980). Organizing species lists into guilds based on eating methods shows that in the acidic water, shredders increased in relative abundance at the expense of scrapers. These data differ from those reported by Hall and Likens (1980a,b) from an artificially acidified stream in New Hampshire, where shredders and predators were not affected. The tolerance of predators, mostly predacious diving beetles (Dytiscidae), water striders (Gerridae) and water boatmen (Corixidae) has been noted in numerous corroborated surveys (Leivestad et al. 1976, Raddum et al. 1979). Shifts in the activities of these different functional guilds affect detritus processing and may be either a cause or a result of the inhibition of microbial detritus processing (Section 5.3.2.1).

5.3.2.5.4 Mechanisms of effects and trophic interactions. It is likely that other factors besides H^+ concentration stress organisms in acidified waters. (Overrein et al. 1980). Malley's (1980) work (see Section 5.4.2.4) suggests that reduced calcium deposition may limit insects as well as crustaceans. Havas (1981) suggested that Na^+ transport may be affected. Effects of increased Al concentrations on invertebrates have not been studied as intensively as they have with fish (Baker and Schofield 1980). Other metals, such as Hg (Tomlinson 1978) may also be important. Nutrient depletion, inefficient microbial digestion, substrate alteration, dissolved oxygen stress, and changes in other populations (e.g., fish predation) all may act on insect populations. The water boatman, Glaenocorisa propinqua propinqua a predator on zooplankton and other small invertebrates, is tolerant of acidity and is common in acidic lakes. The addition of perch to one-half of a lake divided by a net vastly reduced numbers of Glaenocorisa on the side with fish. The only change in water chemistry was a decrease in total phosphorus from 3-8 to 2-6 $\mu g\ \ell^{-1}$ when fish were added (Henrikson and Oscarson 1978). Different taxa respond in various ways. Some may make behavioral adaptations; others, like the water boatmen (Corixidae) can alter rates of Na^+ pumping (Vangenechten et al. 1979, Vangenechten and Vanderborght 1980).

For reasons which are not clear, a shift towards larger species within a higher taxon occurs (Raddum 1980). This may be due to reduced predation pressure on larger insects in the absence of fish or because larger species have less surface/volume and can cope better with chemical and osmotic stress. Increased abundance of insect predators may be due to the opening of this niche as a result of fish loss (Henriksen et al. 1980b) or due to the larger size of these predators. Community alterations, and even modifications of water column chemistry, have been traced to fish removal (Stenson et al. 1978) independent of pH changes. Thus, it is dangerously simplistic to ascribe changes in

community composition to merely the physical-chemical alterations of acidification without also considering the varied biological interactions.

Alterations in insect populations are likely to affect fish populations (Økland and Økland 1980). Rosseland et al. (1980) reported that corixids composed 15 percent of the gut content, by volume, of trout from neutral waters but 44 percent in a declining population from an acidic (pH < 5.5) stream. However, no causal relationship between shifts in diet and population decline can be made at this time.

5.3.2.6 Mollusca--Molluscs provide food for vertebrates (fish, ducks, muskrats, etc.). Clams are filter feeders and are important bio-indicators of water quality conditions. Snails scrape the substrate and the surfaces of aquatic plants, controlling the periphyton in waters in which they live. The impact of acidity on molluscan populations is dramatic. The calcareous shell of these animals is highly soluble at pH < 7.0 and acidic conditions require that the animals precipitate fresh $CaCO_3$ faster than it can dissolve.

The only thorough survey of clams and snails in acid-impacted waters was done in Norway (J. Økland 1969a,b, 1976, 1979a,b, 1980; K. Økland 1971, 1979b,c, 1980b; Økland and Økland 1978, 1980; Økland and Kuiper 1980). About 1500 localities, mostly lakes in Norway, were surveyed between 1953 and 1973. Fingernail clams (Sphaeriidae) and snails (Gastropoda) were sampled. Sphaeriidae live in sediments (infaunal) and no surveys of the more epifaunal unionid mussels have been conducted. Norway has 17 species of Pisidium and three of Sphaerium. None of these clams normally occurred below pH 5.0. The six most common sphaeriids were eliminated below pH 6.0. These common species were found in lakes with low alkalinities but with pH values ~6.0. Thus, their absence from these poorly buffered lakes serves as an indication of acidification, not just low $CaCO_3$ stress (Økland and Kuiper 1980).

Freshwater snails (Gastropoda) were reported to be stressed much like the clams from the Norwegian survey. Of the 27 species of snails reported in Norway, only five were found below pH 6.0 (J. Økland 1980). Snails could tolerate higher H^+ concentrations if the total hardness were higher, indicating that pH may stress snails by reducing the $CaCO_3$ availability (J. Økland 1979b). These authors (Økland and Økland 1980) estimated that the crustacean Gammarus lacustris and the molluscs accounted for 45 percent of the caloric input of trout, and they predicted that trout production could be reduced by 10 to 30 percent below pH 6.0 due to the loss of food resources. This prediction has not been supported by the fish surveys (Section 5.6.2).

Some additional distributional data, which corroborate the Øklands' conclusions cited above, have been reported from Sweden (Wiederholm and Eriksson 1977), Norway (Hagen and Langeland 1973, Nilssen 1980) and from a river in England (Sutcliffe and Carrick 1973).

These later authors emphasized the absence of the freshwater limpet snail Ancylus fluviatilis as an indicator of pH levels which frequently fall below 5.7. They also concluded that pH served to limit the distribution of molluscs by reducing the availability of $CaCO_3$, as measured by water hardness.

The physiological response of molluscs to pH stress was studied by Singer (1981b). In Anodonta grandis (Unionidae) from six lakes ir New York and Ontario with various levels of pH and hardness, marked differences in shell morphometry and ultrastructure were observed. The clams from alkaline lakes (pH > 7.2) had thick shells with fine layers of organic conchiolin interspersed. The clams from softwater neutral lakes had thinner shells, with relatively thick prismatic layers. Clams from a slightly acidic lake (pH 6.6) had thin shells with heavy plates of organic material substituting for the normal $CaCO_3$ matrix. Using unionid shells from museum collections as indicators of pre-acidification water quality was suggested.

5.3.2.7 Annelida--Aquatic worms have been used extensively as indicators of organic (Goodnight 1973, Brinkhurst 1974) and inorganic (Hart and Fuller 1974) pollution. With an increase in organic detritus and a decrease in O_2 concentrations, the benthic community is typically dominated by Tubifex spp. and Limnodrilus hoffmeisteri (Brinkhurst 1965, Howmiller 1977). Considering their tolerance of other stresses and the abundance of detritus, it is surprising that oligochaetes are reduced in biomass in acidic lakes. Raddum (1976, 1980) found few oligochaetes in water deeper than 20 m in 18 acidic lakes (pH < 5.5) and normal fauna in 16 other more neutral Norwegian oligotrophic lakes. The acidic lakes, however, had more oligochaetes than the non-acidic lake at a depth of 0.5 m. The difference in numbers at greater depths was more pronounced in the spring and autumn. Neutral lakes had three to four times the total number of oligochaetes per square meter. Raddum (1980) attributed the reduction in numbers of oligochaetes in acidic lakes to pollutants associated with acidic deposition (e.g., heavy metals and aluminum). These worms, however, are routinely collected in vast numbers directly below sewage and industrial effluents with far greater concentrations of pollutants (Hart and Fuller 1974, Chapman et al. 1980). An alternative explanation for their reduction in numbers might be the unpalatability of their detrital food due to the slower decomposition rates in acidic lakes (Traaen 1977). Oligochaetes are not normally abundant in nutrient-poor waters, and their low numbers in acidic lakes may be as much a function of the low nutrient level characteristic of acidic lakes as of pH.

One study that mentioned the distribution of leeches (Hirudinea) in acidic lakes (Nilssen 1980) reported that these worms disappeared below pH 5.5. Leeches characteristic of eutrophic waters (Hirudo medicinalis, Glossiphonia heteroclita) were absent from even mildly acidic lakes. Raddum (1980) reported that Hirudinea were restricted to waters above pH 5.5, largely because of the loss of prey below this pH, even though many leeches are detritivores and scavengers, not obligate carnivores (Pennak 1978). These anecdotal observations should be viewed with caution

because leeches are not always common in neutral oligotrophic lakes, and I saw an unidentified leech on the bottom of acidic Woods Lake (Herkimer Co., NY) while diving in 6 m of water.

5.3.2.8 Summary of Effects of Acidification on Benthos--Table 5-3 summarizes some of the expected consequences of acidifying a lake or stream to pH 4.5. The following generalizations may also be made, based on the best available current evidence.

1. Bacterial decomposition of litter in bags in situ and debris in vitro is reduced significantly ($p < .001$), as measured by respiratory rates and weight loss, between pH 6.0 and 4.0. Planktonic bacterial standing crops do not change significantly, although metabolic rates are depressed. Insects and crustaceans responsible for shredding and processing detritus are almost completely eliminated between pH 6.0 and 4.0.

2. In most acidified lakes below pH 5.0, a mat of algae covers most of the substrate from ~1 to 5 m to the limit of light penetration. These mats are of 3 types: a) an encrusting, felt-like, black to blue-green mat composed of blue-green algae (Cyanophyta) 0.5 to 2 cm thick; b) coarse, loosely compacted dark green mats composed of green algae (Chlorophyta) 1 to 4 cm thick; c) cloud-like layers of green filamentous algae (Chlorophyta) which rest on the bottom in depths as thick as 1.5 m. All three types of mats include debris, diatoms, fungi and bacteria. These mats are often the most visible aspect of acidified lakes. They may have profound effects on fish spawning habitats, nutrient cycling, and sediment chemistry, but their origin, differentiation into types, and chemical interactions have not been studied. They have been extensively noted in field surveys and have developed in artificially acidified chambers and stream channels below pH 5.0.

3. Many invertebrates are very sensitive to pH. Amphipods, which are an important fish food in rivers and some lakes, cannot tolerate pH < 6.0, based on field observations, laboratory bioassays, and field enclosure experiments. Snail populations are stressed below pH 6.0 and absent from the field below pH 5.2. Large mussels cannot survive below pH 6.6, but fingernail clams can survive in sediments with overlying water with pH values as low as 4.8. The crustacean water louse (Isopoda) and many species of stoneflies (Plecoptera), mayflies (Ephemeroptera), and caddisflies (Trichoptera) die at pH < 5.0, as determined by field observations and laboratory bioassays. Insects are often limited by mechanisms not related to direct toxicity. Some dragonflies and many predacious beetles (Coleoptera), and true bugs (Hemiptera) occur commonly in acidified (pH < 5.0) lakes. They fill the niche normally occupied by planktivorous fish and represent a major alteration of food chains. Most of these active predaceous insects receive their air supply from the surface.

TABLE 5-3. SUMMARY OF EFFECTS OF pH 4.5 WATER ON BENTHOS

Taxon	Common name	Microhabitats	Sensitivity to acid (pH 4.5) stress	References
Bacteria		All substrates.	Growth rate or O_2 uptake inhibited.	Bick and Drews 1973, Baath et al. 1979, Gahnstrom et al. 1980
Periphyton	Algae Blue-greens (Cyanophyta) Greens (Chlorophyta) Diatoms (Bacillariophyceae) Dinoflagellates (Pyrrophyta)	On plants (epiphytic) On rocks (epiplithic) On mud (epipelic) On "encrusting mat".	Increasing standing crop in lakes and streams.	Hendrey 1976, Hall et al. 1980, Yan and Stokes 1978, Hendrey and Vertucci 1980, Muller 1980
			Development of distinct types of periphyton communities.	Singer et al. In press, Stokes 1981
Crustacea Decapoda	Crayfish	Burrowers deposit feeders and grazers lakes and streams.	Sensitivity variable and highly species specific. Effects vary depending on other cation concentrations.	Malley 1980, Collins et al. 1981, Shaw 1960
Isopoda	Aquatic sowbug	Deposit feeder in lakes and streams, under rocks and in littoral vegetation.	Asellus aquaticus tolerant to ~ pH 5.0.	K. Økland 1978a, 1980b.
Amphipoda	Scud	Detritivore in lakes and slow-flowing areas of streams. Found among plant stems.	Not generally found below pH 6.0. Sensitive differences between species have been described.	K. Økland 1980a,b,c; Sutcliffe and Carrick 1973;

TABLE 5-3. CONTINUED

Taxon	Common name	Microhabitats	Sensitivity to acid (pH 4.5) stress	References
Eubranchiopoda	Tadpole shrimp	Small, often temporary, ponds or backwaters of streams; often only abundant seasonally.	Not found in Sweden pH 6.1. Growth reduction and hatching failure below pH 5.0.	Borgstrom et al. 1976, Borgtrom and Hendrey 1976
Insecta				
Ephemeroptera	Mayflies	Include burrowing and surface dwelling forms. Found in lakes and streams. Predators, detritivores, herbivores.	Sensitivity varies between groups but generally not tolerant	Sutcliffe and Carrick 1973, Nilssen 1980, Pratt and Hall 1981, Leivestad et al. 1976, Borgstrom et al. 1976, Raddum 1976
Odonata	Dragonflies (Anisoptera) Damselflies (Zygoptera)	Predators in mud, littoral debris, and rock substrates in lakes and streams.	Tolerant to prolonged severe acid stress.	Stickney 1922, Borgstrom et al. 1976, Bell and Nebeker 1969, Bell 1971
Plecoptera	Stoneflies	Predators, detritivores and herbivores in flowing streams.	Most genera are sensitive but some are tolerant (see text).	Sutcliffe and Carrick 1973; Leivestad et al. 1976; Hall and Likens 1980a,b; Raddum 1979
Trichoptera	Caddisflies	All benthic habitats.	Some genera are very tolerant, but others are sensitive (see text)	Sutcliffe and Carrick 1973; Leivestad et al. 1976; Hall and Likens 1980a,b; Raddum 1976, 1979

TABLE 5-3. CONTINUED

Taxon	Common name	Microhabitats	Sensitivity to acid (pH 4.5) stress	References
Diptera	True flies Midges (Chironomidae)	Major detritivores in lakes and enriched streams, living in mud or on substrates in tubes.	Most reports show increase in numbers, but some report decreases.	Raddum and Saether 1981, Uutala 1981
	Phantom ghost midge (Chaobotidae)	Predator on substrates and in water column of lakes	Tolerant of acid stress.	Wiederholm and Eriksson 1977, Leivestad et al. 1976
	Black flies (Simulidae)	Predatory in streams on rock substrates	Tolerant of acid stress	Leivestad et al. 1976
Hemiptera	True bugs Water striders (Gerridae) Backswimmer (Notonectidae) Water boatman (Corixidae)	Predators on water surface, in water column, and over substrates.	Tolerant of acid stress.	Raddum 1976, Raddum et al. 1979, Nilssen 1980
Coleoptera	Beetles Predacious diving beetle (Dytiscidae) Whirligig beetle (Gyrinidae)	Predators on water surface, in water column, and over substrates.	Tolerant of acid stress.	Raddum 1976, Raddum et al. 1979, Nilssen 1980
Mollusca Pelecypoda	Clams	Filter feeders in substrates, detritivores in lakes and streams.	All mollusca are highly sensitive to pH stress. The most tolerant are fingernail clams which are rarely found as low as pH 5.0.	J. Økland 1976, 1979b, 1980; K. Økland 1971, 1979b,c, 1980b; Økland and Økland 1978, 1980; Økland and Kuiper 1980; Singer 1981b

TABLE 5-3. CONTINUED

Taxon	Common name	Microhabitats	Sensitivity to acid (pH 4.5) stress	References
Annelida				
Oligochaeta	Aquatic earthworms	Detritivores in lakes and streams with soft substrates.	Standing crops low in acidic waters	Raddum 1976, 1980
Hirudinea	Leeches	Predators, detritivores.	Anecdotal observations report no leeches below pH 5.5.	Nilssen 1980, Raddum 1980

4. Forms which live on the substrate (snails, stoneflies, mussels, etc.) are more sensitive to pH drops than those which live in the substrate (e.g., fingernail clams, midge larvae burrowing mayflies). In those groups that have been studied in the laboratory (crayfish, backswimmers, molluscs), high calcium concentrations (> 2 mg ℓ^{-1} can ameliorate the effects of low pH.

Fish shift their food to available prey, but the nutritional effects of switching from a diet of largely amphipods, mayflies, and stoneflies to one of water boatmen, beetles, and water striders are not known. Effects on different age classes of fish are likely to vary. Changes in the rates of detrital processing and decomposition rates affect primary productivity and hence the whole ecosystem.

5.4 MACROPHYTES AND WETLAND PLANTS (J. H. Peverly)

5.4.1 Introduction

The softwater, low alkalinity, oligotrophic lakes in temperate regions susceptible to acidic deposition support a flora characterized by the isoetid or rosette plants. This contrasts with hard waters which support vittate species, having elongated stems with leaf nodes. Plants commonly observed in softwater lakes are listed in Table 5-4.

In general, emergent plants in these lakes grow only in a narrow band along the shore. The submerged, three-inch high isoetids extend from shore to the 3 to 4 m depth and coexist with some lilies and bladderwort. Beyond 4 m, Nitella spp., bladderwort, and mosses dominate.

Life in the water depends on the presence and growth of aquatic plants as well as other inputs from the basin (Section 5.3.1). Macrophytes stabilize the sediments; clear, cool and oxygenate the water; and provide colonization sites for insects, small plants and animals, and bacteria. These in turn are a major food source for the larger aquatic animals, such as fishes, amphibians, aquatic mammals, and waterfowl. Thus, aquatic plants fill an important role in the entire aquatic ecosystem.

Macrophyte growth in softwater lakes can be a major part of total lake production and is largely attributable to growth by isoetids (Hutchinson 1975, Hendrey et al. 1980b). Because isoetids are perennial and evergreen, they can continue to photosynthesize and produce oxygen under winter ice cover, and provide a stable, constant source of grazing material. Standing crop varies from < 5 to 500 g dry wt m^{-2} in August, but annual productivity is only about 50 percent of standing crops (Moeller 1978, Sand-Jensen and Sondergaard 1979).

Plant productivity in softwater lakes is not high because the carbon dioxide (CO_2) level in the water is low (.02 mM CO_2 at pH 5.0) and major nutrient minerals such as P, K, N, and Ca are in limited supply (Hutchinson 1975). However, these aquatic macrophytes have

TABLE 5-4. PLANTS COMMONLY OBSERVED IN SOFTWATER (LOW ALKALINITY) OLIGOTROPHIC LAKES

Species	Common Name	Type	Response to Acidification
Pontederia cordata L.	Pickerel weed	Emergent	Unknown
Juncus sp.	Rush	Emergent	Stimulated growth (Hultberg and Grahn 1976)
Sparganium spp.	Burreed	Emergent	Unknown
Brasenia schreberi Gmel.	Water shield	Floating leaves, rooted	Unknown
Nuphar advena Ait.	Yellow lily	Floating leaves, rooted	Unknown
Nymphaea odorata Ait.	White lily	Floating leaves, rooted	Unknown
Isoetes spp.	Quillwort	Submerged, rooted (iosetids)	Overgrown (Hultberg and Grahn 1976)
Lobelia dortmanna L.	--	Submerged, rooted (iosetids)	Overgrown (Hultberg and Grahn 1976) Oxygen evolution falls (Laake 1976)
Eriocaulon septangulare With	Pipewort	Submerged, rooted (iosetids)	Unknown
Myriophyllum tenellum Bigel	--	Submerged, rooted (iosetids)	Unknown
Potamogeton spp.	Pond weeds	Submerged, rooted	Decreased growth (Roberts et al. 1982)

TABLE 5-4. (CONTINUED)

Species	Common Name	Type	Response to Acidification
Eleocharis spp.	Spike rush	Submerged, rooted	Unknown
Utricularia spp.	Bladderwort	Submerged, unrooted	Unknown
Sphagnum sp.	Moss	Submerged, attached	Stimulated growth (Grahn 1977)
Drepanocladus spp.	Moss	Submerged, attached	Unknown
Fontinalis spp.	Moss	Submerged, attached	Unknown
Nitella spp.	Stonewort	Submerged, attached	Unknown

several means of overcoming such difficulties and producing enough tissue to support an aquatic animal community. First, aquatic macrophytes recapture up to 50 percent of their own respiratory CO_2 and store it in an internal gas chamber system for reuse in photosynthesis (Sondergaard 1979). Secondly, the isoetids are able to exist and grow in oligotrophic water, where other aquatic macrophytes cannot, by more efficient use of nutrients in the sediments. This is accomplished by the root systems, which are efficient sites for absorption of carbon, nitrogen, phosphorus, and potassium. The relative root-to-shoot ratio is large in these plants (0.5 to 0.6, Sondergaard and Sand-Jensen 1979), indicative of the greater role of roots in nutrient absorption. In addition, water in the sediments where the roots grow often has a carbon level of 1 to 5 mM (Wium-Andersen and Andersen 1972), 50 to 100 times that in the overlying water column. Vittate plants, which depend more on leaf absorption for carbon supply, cannot grow in these low carbon waters.

The accumulation of nutients in plant tissues, acquired through the roots from the sediments, recirculates sediment nutrients back into the overlying water, where they can be used by other organisms. For instance, in a 200 g dry wt m^{-2} crop of Eriocaulon septangulare, there would be about 50 g carbon, 2 g nitrogen, 0.1 g phosphorus, and 1.5 g potassium. About 0.24 g carbon, 0.2 g nitrogen, 0.01 g phosphorus, and 0.4 g potassium (Moeller 1975) would be dissolved in water 1 m deep over this meter square area. Clearly, nutrient release from such plant beds could increase the concentration of available nutrients in the water column.

Lilies and emergent plants can also obtain carbon by absorption of CO_2 from the atmosphere and translocation to carbon reserves in rhizomes under the water surface. Mosses and algae are not as involved in processes that transfer nutrients from sediments or air into the water column.

In addition to major nutrients, rooted aquatic macrophytes (including isoetids) are exposed to elevated levels of metals in the sediments (e.g. iron, manganese, copper, zinc, aluminum). These elements can also be absorbed by roots and transported to the shoots, where they are able to enter biological cycles slowly as the plants senesce and decay. However, concentration differences between sediment and water column levels of metals available for absorption are not always as great as for the major nutrients. This is especially the case where rooted plant activity is high, as oxygen release at the root surfaces (Wium-Andersen and Andersen 1972) raises the redox potential. This tends to precipitate iron and manganese compounds (Tessenow and Baynes 1978) and remove phosphorus from solution. Metals not affected by redox potential, like aluminum, would remain in solution in the rhizosphere, and still be available for uptake by the roots. Indeed, the aluminum contents of plant tissues (0.4 to 22 g kg^{-1}) from both neutral and acidified lakes (Al 0.03 to 0.2 mg ℓ^{-1}) in the Adirondacks and Ontario were elevated above Hutchinson's (1975) mean value of 0.36 g Kg^{-1} (Best and Peverly 1981, Miller et al. 1982).

Lilies interact much more with sediments than with water and generally tend to accumulate less of the above metals. The mosses and algae interact almost exclusivey with the water column and accumulate metals (Ca, K, Fe, Al) under certain water conditions. Aquatic macrophytes can recycle Fe, Mn, Cu, Zn, and Al metals from sediments, but they can also restrict exchange of Fe and Mn between water and sediment by oxidizing the top 15 to 20 cm of sediments (Tessenow and Baynes 1978).

Mosses and algae that grow close to the bottom not only absorb metals metabolically, but also physically adsorb them onto tissue surfaces. Sphagnum spp. are known to have especially high adsorption capacities for metals, including calcium, iron, aluminum, and potassium (Clymo 1963, Hendrey and Vertucci 1980). Metals adsorbed in this fashion are effectively removed from biological cycles for long periods, as the elements remain bound to dead tissues, which often persist for years. Mats of Sphagnum spp. and algae have formed on the bottom of some softwater lakes. Hultberg and Grahn (1976) suggested that mats of this nature decrease productivity by restricting exchange of nutrients between sediments and water.

The tissues produced by growing plants eventually die, releasing nutrient elements and metals back to the water by a variety of decay processes. Carbon dioxide is produced by plankton and microorganisms from this dead plant material, along with dissolved phosphorus, potassium, ammonia and calcium. The metals are released, often in a form complexed with organic acids that keeps them in solution, thus readily available for uptake.

5.4.2 Effects of Acidification on Aquatic Macrophytes

Direct effects of acidification on aquatic macrophytes have not been well-documented. However, in two reports of laboratory results, oxygen evolution was reduced up to 75 percent by a pH decrease from 7.0 to 4.0 in both softwater (Laake 1976) and hardwater plants (Roberts et al. 1982). In the field, nutrient ions and metals (such as calcium, magnesium, sodium, potassium, manganese, and iron) may be leached out of the tissues, especially during the episodic pH drops associated with snow melt. This could have a negative effect on plants in the spring when new growth is quite susceptible to nutrient imbalances.

Most effects of acidification on aquatic plant distribution and growth are indirect. Specifically, these would include decreased carbon supply for photosynthesis, nutrient depletion, increased metal concentrations, and decreased rates of nutrient recycling (Grahn et al. 1974, Andersson et al. 1978b, Schindler et al. 1980a). The dominance of isoetid species in soft water lakes of pH 5.5 to 6.5 is a response in part to low carbon and major nutrient availability in the water column. As acidic deposition causes the pH to decline, these factors become even more limiting. For instance, Lobelia dortmanna rooted in sediment cores showed a 75 percent reduction in oxygen production at pH 4.0 compared to the control (pH 4.3 to 5.5), and the period of flowering was delayed 10

days at the low pH (Laake 1976). As a result, species more tolerant of low nutrient supplies and higher metal concentrations may become dominant.

Measurements over 15 years in one acidified Swedish lake with a pH drop of 0.8 units between 1967 and 1973 showed that isoetid species were replaced by Sphagnum sp. and blue-green filamentous algae, which grew over the bottom in that time span, smothering the low-growing isoetids (Grahn 1977). This is viewed as detrimental to overall lake quality because Sphagnum beds are not a good habitat for most aquatic animals. In addition, Sphagnum tends to perpetuate the conditions that exclude other species by exchanging metabolically produced hydrogen ions for nutrients and metals in the water via adsorption processes. Thus, acidification and oligotrophication continue. As the Sphagnum grows, it forms a mat of increasing area. The dead stems decay slowly and continue to hold adsorbed elements. As a result of this mat barrier and because Sphagnum has no roots to exploit the sediment, interchange of dissolved nutrients between overlying water and sediments is minimized following Sphagnum invasion. With the exception of dense Sphagnum beds observed in Lake Colden (pH 4.9) in the Adirondack Mountains of New York State (Hendrey and Vertucci 1980), large expanding beds have not been observed in acidified waters of the northeast United States or Canada (Best and Peverly 1981, Wile 1981).

The effect of acidification on nutrient availability is unclear. Generally, slower breakdown of organic matter (including Sphagnum tissues) in acidic waters (see Section 5.8.2.1) would tend to decrease the amount of major nutrients available for plant growth. In addition, softwater lakes are inherently low in nutrients. In the Adirondacks, plant tissue concentrations of the major nutrients indicated that phosphorus was limiting in both acidic and nonacidic lakes (Best and Peverly 1981).

Other possible indirect effects of acidity on macrophytes are those associated with increased metal (aluminum, cadmium, iron, manganese, copper, lead, zinc) concentrations in water and sediments. Tissue analysis of isoetid plants from both acidified and nonacidified lakes in the Adirondacks and Ontario have shown elevated levels of aluminum, copper, iron, and lead in roots and shoots from acidic waters (Best and Peverly 1981, Miller et al. 1982). Concentrations of manganese, cadmium, and zinc were lower in plants from acidic waters, corresponding to one report of lower measured metal levels in sediment of an acidified lake (Troutman and Peters 1982).

Toxic tissue levels of metals discussed above are not presently known. Effects of increased metal accumulation on isoetid productivity are not clear, but these metals have been shown to be toxic to aquatic plants. Concentrations of Al, Zn, and Cu in sediments measured by Stanley (1974) produced 50 percent reduction in Myriophyllum spicatum root weight. However, these concentrations were greater than those reported to occur in acidified lake sediments, at least for Adirondack lakes (Best and Peverly 1981).

If metal concentrations increase in tissues, but do not inhibit growth, there is a potential for increased cycling of metals. However, Sphagnum spp. growth may be a positive factor, removing metals from the water by adsorption (Clymo 1963) and by barrier formation between the sediments and water.

Acidification of brown waters that contain organic acids causes clearing of the water column by organic precipitation with metals, especially aluminum (Almer et al. 1978). The result is increased light penetration to greater depths, with plant growth perhaps increased over a larger area. This could lead to a larger food base for aquatic animals and could be a positive factor if the increased growth is not represented solely by Sphagnum spp. and blue-green algae.

5.4.3 Summary

- There is currently no trend towards dominance of macrophyte communities by Sphagnum sp. in 50 oligotrophic, softwater lakes surveyed in North America. In fact, dominant species are the same in both acidified (pH less than 5.6) and non-acidified (pH 5.6 to 7.5) lakes.

- With continued acidification, shifts to Sphagnum spp.-dominated macrophyte communities have been documented in six Swedish lakes acidified for at least 15 years. This does not seem to be a general property of acidified lakes.

- Standing crops of macrophytes vary widely (5 to 500 g dry wt m^{-2}) in softwater, oligotrophic lakes, and acidification produces no definite trend in standing crop changes. Based on one report, annual productivity is equal to one-half the summer standing crop in a nonacidified lake. Oxygen production was reduced 75 percent at pH 4.0 versus pH 4.3 to 5.5 in one flow-through experiment.

- The only known effect of acidification on macrophytes in the field is that ofincreased metal content in the tissues, especially Al. In acidified lakes, mean aluminum concentration in plant tissue (dry wt basis) is 3.0 to 5.0 g kg^{-1} (about ten times higher than normal) while mean manganese concentration is 0.02 to 4.0 g kg^{-1} (about one-fifth of normal). In general, concentrations of iron, lead and copper are higher, while cadimium and zinc are lower in the tissues of plants from acidified lakes.

5.5 PLANKTON (J. P. Baker)

5.5.1 Introduction

The term plankton refers to organisms that live suspended within the water column, are generally small to microscopic in size, have limited or no powers of locomotion, and are more or less subject to

distribution by water movements (Wetzel 1975). The plankton community consists of animals (zooplankton), plants (phytoplankton), and microbes. Effects of acidification on zooplankton and phytoplankton will be considered within this section; effects of acidification on the microbial community were included in Section 5.3. Discussions focus on plankton communities within the open-water zone. Interactions with populations in littoral and benthic regions are important, but poorly understood with regard to potential effects of acidification.

Zooplankton and phytoplankton communites are usually quite complex, composed of a large number of species, and subject to significant spatial and temporal variations. These variations in occurrence and importance of species of phytoplankton and zooplankton make it difficult to obtain a representative sampling of the plankton community. Attempts at relating differences in plankton communities between lakes or within a given lake to acidity or other environmental parameters are hindered by this natural diversity and variability.

Six phyla of algae typically contribute to phytoplankton communities of freshwater ecosystems: Cyanophyta (blue-green algae), Chlorophyta (green algae), Pyrrophyta (primarily dinoflagellates), Chrysophyta (yellow-green algae; includes the chrysomonads and diatoms), Euglenophyta (euglenoids), and Cryptophyta (primarily cryptomonads). Photosynthesis by phytoplankton plays a significant role in the metabolism of lakes (Schindler et al. 1971, Jordan and Likens 1975, Wetzel 1975), and in determining the quantity of secondary or tertiary (e.g., fish) production within a lake (Smith and Swingle 1939, Hall et al. 1970, Makarewicz and Likens 1979).

The animal components of freshwater plankton communities also constitute a diverse collection of organisms from many phyla. The most important taxonomic groups are protists (Phylum Protozoa), rotifers (Phylum Aschelminthes, Class Rotifera, or as a separate Phylum Rotifera), insects (Phylum Arthropoda, Class Insecta), and two subgroups of the class Crustacea (Phylum Arthropoda), the Subclass Copepoda and the Order Cladocera (Subclass Branchiopoda) (Edmondson 1959). A large number of trophic levels are also represented--herbivores, omnivores, and carnivores. Thus, both the structure (variety in types of organisms represented) and function (energetic interactions among individual organisms) of the plankton community are complex.

Data on acidification and effects on plankton communities are limited almost entirely to field observations and correlations. Experiments designed to elucidate causal mechanisms for observed changes are, for the most part, lacking, at both the physiological and ecological level. The large number of interacting factors potentially involved in the reaction of plankton to acidification makes a critical analysis of currently available data very difficult. In some cases, results appear contradictory. With an increased understanding of causal mechanisms, many of these apparent contradictions should be resolved.

5.5.2 Effects of Acidification on Phytoplankton

5.5.2.1 Changes in Species Composition--In extensive surveys of acidic lakes in Norway, Sweden, eastern Canada, and the United States, altered species composition and reduced species richness (number of species) in the phytoplankton community were consistently correlated with low pH levels. Results from 18 field studies that support this conclusion are summarized in Table 5-5. Decreases in species richness appear most rapidly in the pH interval 5.0 to 6.0 (Almer et al. 1974, 1978; Leivestad et al. 1976; Kwiatkowski and Roff 1976). For example, in a survey of lakes in the west coast region of Sweden, lakes with pH values of 6.0 to 8.0 generally contained 30 to 80 species of phytoplankton per 100 ml sample. Lakes with pH levels below 5.0 had only about a dozen species. In some very acidic lakes (pH 4.0), only three species were collected (Almer et al 1978).

In general, species are lost from all classes of algae as pH declines. However, proportionally larger losses occur within some groups than in others. As a result, the dominant algae in acidic lakes are often different from those characteristic of circumneutral lakes.

In six out of nine investigations (Table 5-5), dinoflagellates (Phylum Pyrrophyta), and often the same species of dinoflagellates, were reported to dominate in acidic lakes. Almer et al. (1974, 1978) reported that the dominant species in acidic waters sampled in the west coast region of Sweden were Peridinium inconspicuum and Gymnodinium cf. uberrimum (both dinoflagellates). Stokes (1980) and Yan (1979) noted that, in lakes in the Sudbury Region of Ontario with pH values below 5.0, up to 50 percent of the biomass consisted of dinoflagellates, especially Peridinium limbatum and Peridinium inconspicuum. In Carlyle Lake (pH 4.8 to 5.1) near Sudbury, acidification experiments within limnocorrals resulted in the proliferation of Peridinium limbatum (a 75 percent increase in biomass). At pH 4.0 this single species accounted for 60 percent of the total phytoplankton biomass (Yan and Stokes 1978). Hendrey (1980) investigated 3 lakes in the Adirondack Region of New York State. In the most acidic lake (pH 4.9), Peridinium inconspicuum comprised a significant fraction of the biomass in the ice-free season. Species of chrysophyceans (Phylum Chrysophyta) were also important. The dominance of dinoflagellates in many acidic waters has not been adequately explained (National Research Council Canada 1981).

Dinoflagellates are not always reported as the dominant algal group in acidic environments. In a survey of Florida lakes, Crisman et al. (1980) reported that in the most acidic lakes (pH 4.5 to 5.0) green algae (Phylum Chlorophyta) accounted for about 60 percent of the total phytoplankton abundance. However, the genus Peridinium was also reported as a dominant taxon in these lakes. In Wavy Lake (pH 4.3 to 4.8) near Sudbury, Ontario, Conroy et al. (1976) noted that chrysophyceans (Phylum Chrysophyta) of the genus Dinobryon dominated. Together chrysophyceans and green algae constituted an average of 90 percent of the standing crop. In two non-acidic lakes sampled, these algae accounted for only 21 and 23 percent of the standing crop. On the

TABLE 5-5. SUMMARY OF OBSERVATIONS RELATING SPECIES DIVERSITY AND SPECIES COMPOSITION OF THE PHYTOPLANKTON COMMUNITY TO ACIDITY

Location (reference)	Reductions in species diversity	Dominant species in acid water	Species missing in acid water	General comments
1. Swedish West Coast (Almer et al. 1974 and 1978)	Numbers of species per 100 ml sample: pH 6-8: 30 to 80 species pH < 5: about 12 pH < 4: 3	In most acid waters: dinoflagellates (Pyrrophyta) - Peridinium inconspicuum Gymnodinium cf. uberrimum In a few lakes with pH about 4: green algae (Chlorophyta) - Ankistrodesmus convolutus Oocystis submarina Oocystis lacustris Other common species: chrysophyceans (Chrysophyta) - Dinobryon crenulatum Dinobryon sertularia green algae (Chlorophyta) Chlamydomonas sp.	The classes Chlorophyceae (Chlorophyta) and Chrysophyceae (Chrysophyta) had greatly reduced numbers of species Absence of diatoms (class Bacillariophyceae, Phylum Chrysophyta) and bluegreen algae (Cyanophyta) at pH <5: Chroococcus limneticus Merismopedia tenuissima Species common in oligotrophic lakes, but absent at pH <6: bluegreen algae (Cyanophyta) - Gomphosphaeria lacustris green algae (Chlorophyta) - Scenedesmus serratus chrysophyceans (Chrysophyta) - Dinobryon divergens Dinobryon bavaricum Dinobryon borgei Dinobryon sucecicum Kephyrion spirale Stichogloea doederleinii diatoms (Chrysophyta) - Rhizosolenia longiseta Cyclotella bodanica cryptophytes (Cryptophyta) - Rhodomonas minuta dinoflagellates (Pyrrophyta) - Ceratium hirundinella	One stop survey of 115 lakes in August 1972 and 60 lakes in Greatest change in species composition occurred in the pH interval 5 to 6
2. Swedish West Coast (Hultberg and Andersson 1982)	Following liming, number of species generally increased	Dominant species in acid, oligotrophic lakes: dinoflagellates (Pyrrophyta) - Peridinium inconspicuum Gymnodinium sp. Following liming, the importance of genus Peridinium declined Prevalent (30 to 40% of the biomass) in humic lake: bluegreen algae (Cyanophyta) - Merismopedia sp. green algae (Chlorophyta) - Oocystis sp.	Diatoms insignificant in all acid lakes Following liming, the importance of species of green algae (Chlorophyta) and chrysophyceans (Chrysophyta), and, in some cases, diatoms (Chrysophyta) increased	pre- and post-liming studies; long-term monitoring of four lakes

TABLE 5-5. CONTINUED

Location (reference)	Reductions in species diversity	Dominant species in acid water	Species missing in acid water	General comments
3. Southern Norway (Hendrey and Wright 1976, Leivestad et al. 1976)	Number of species identified per lake: pH > 4.5: 10 to 25 species pH 4 to 4.5: < 10		Decrease in importance of species of green algae (Class Chlorophyceae, Phylum Chlorophyta) No consistent trend relating pH to numbers of species of diatoms (Chrysophyta) or bluegreen algae (Cyanophyta)	One-stop survey of 55 lakes in October 1974
4. Southern Norway (Raddum et al. 1980)	The number of algal species collected at any one time was generally lower in clear water acid lakes			Periodic sampling of 13 lakes throughout an entire growing season
5. Canadian Shield-Sudbury Ontario (Stokes 1980)	Indices of both diversity and species richness declined with decreasing pH level	At pH < 5, up to 50% of the biomass consisted of dinoflagellates (Pyrrophyta) especially- Peridinium ~~limbatum~~ Peridinium inconspicuum However, this was not the case in a naturally acidic dystrophic lake	In oligotrophic lakes with pH < 5, importance of species of green algae (Chlorophyta) and chrysophyceans (Chrysophyta) ~~decreased~~	9 lakes (pH 3.9 to 7.0) sampled at monthly intervals for 2 summer seasons Acidic lakes near Sudbury, Ontario have high concentrations of metals that may influence phytoplankton
6. Sudbury Region of Ontario (Yan 1979)	Number of taxa observed in acidic lakes was less than in non-acidic lakes	Biomass in acid lakes dominated by a dinoflagellate (Pyrrophyta) Peridinium inconspicuum Proportion of the biomass contributed by dinoflagellates was correlated with hydrogen ion activity, but not with phosphorus concentration Most common genera in acid lakes: dinoflagellates (Pyrrophyta) - Peridinium cryptophytes (Cryptophyta) - Cryptomonas chrysophyceans (Chrysophyta) - Dinobryon green algae (Chlorophyta) - Chlamydomonas Oocystis	Non-acidic oligotrophic lakes typically dominated by chrysophyceans (Chrysophyta) and diatoms (Chrysophyta), but in acidic lakes sampled a dinoglagellate (Pyrrophyta) dominated	Comparison of 4 acidic lakes with 10 non-acidic lakes. Intensive sampling. Samples collected at a weekly or bi-weekly frequency at 2 m depth intervals at the deepest spot in each lake for one or two summer seasons The change in community structure apparently occurs over a pH range of 4.7 to 5.6

TABLE 5-5. CONTINUED

Location (reference)	Reductions in species diversity	Dominant species in acid water	Species missing in acid water	General comments
7. Sudbury Region of Ontario (Dillon et al 1979)			Following liming, dominance shifted from dinoflagellates (Pyrrophyta) and cryptophytes (Cryptophyta) to the chrysophyceans (Chrysophyta) more typically observed in circumneutral waters	Three of the acidic lakes sampled by Yan (1979) were limed 1973-1975; pH levels were raised from <4.7 to above 6
8. Sudbury Region of Ontario (Conroy et al. 1976)	In the two acidic lakes, a few genera usually dominated the biomass, resulting in a low diversity index. In the non-acidic lakes, the biomass was more evenly distributed throughout a large number of genera	In acidic Wavy Lake, the dominant genus was a chrysophycean (Chrysophyta) Dinobryon. Most of the species identified in Wavy Lake belonged to the green algae (Chlorophyta) and chrysophyceans (Chrysophyta). Together these two groups represented on the average 90% of the standing crop. In the 2 non-acidic lakes, these 2 groups accounted for only 21% and 23% of the standing crop In acidic Florence Lake, a considerable biomass of the bluegreen algae (Cyanophyta) Merismopedia sp. developed in August	Few or no diatoms (Chrysophyta) present in acidic waters while they dominated in non-acidic Millerd Lake and were significant in non-acidic Flack Lake Acidic Wavy Lake had few blue-green algae (Cyanophyta) In acidic Florence Lake, however, a considerable bloom of the bluegreen algae Merismopedia sp. developed in August Both of the non-acidic lakes also had substantial populations of bluegreen algae, although of different species	
9. LaCloche Mountain Region of Ontario (Kwiatkowski and Roff 1976)	Strong relationship between diversity of phytoplankton and pH level, with the diversity index dropping off sharply below pH 5.6 All of the major groups of phytoplankton decreased markedly in their numbers of species with increasing acid conditions. Comparing the highest pH lake sampled (pH about 6.7) with the most acid lake (pH about 4.4), the numbers of species of green algae (Chlorophyta) were reduced from 26 to 5; Chrysophyta (from 22 to 5; bluegreen algae (Cyanophyta) from 22 to 10. Numbers of species of diatoms	The important species in each lake shifted according to pH level. In the more neutral lakes, the green algae (Chlorophyta) comprised between 40 and 50% of the total algal flora, with bluegreen algae (Cyanophyta) accounting for only 30%. In acidic lakes, however, bluegreen algae constituted about 60%, and green algae only about 25% of the algal flora. Species common in acidic waters: Bluegreen algae (Cyanophyta) - Aphanocapsa sp. Chroococcus Prescottii Oscillatoria sp. Rhabdoderma lineare Green algae (Chlorophyta) - Carteria sp. Chlamydomonas sp. Chlorella ellipsoidea Closterium sp.	Aphanocapsa sp. Chroococcus dispersus Chroococcus limneticus Oscillatoria sp. Ankistrodesmus sp. Carteria sp. Chlamydomonas sp. Oocystis sp. Scenedesmus sp.	6 lakes sampled weekly for 2 months in 1972 and 1973 (lake pH range of 4.4 to 6.7) Lakes with similar pH values had similar species composition as evaluated by the coefficient of community and percentage similarity of community. Thus, community structure in these lakes reflected the pH gradient

TABLE 5-5. CONTINUED

Location (reference)	Reductions in species diversity	Dominant species in acid water	Species missing in acid water	General comments
9. Cont.	(Chrysophyta) collected in samples were also greatly reduced in the two most acidic lakes relative to the other lakes sampled	Cryptomonads (Cryptophyta) - (considered by the authors as in the Phylum Pyrrophyta) Cryptomonas erosa Cryptomonas ovata Dinoflagellates (Pyrrophyta) species of the genera Peridinium and Glenodinium, although present in some lakes, never reached significant proportions in either acidic or non-acidic lakes	Many of the species of diatoms (Chrysophyta) common to the more neutral lakes were absent from acidic lakes	
10. LaCloche Mountain Region of Ontario (Yan and Stokes 1978)		Phytoplankton community dominated by Peridinium limbatum (a dinoglagellate, Phylum Pyrrophyta), and Cryptomonas ovata (a cryptomonad, Phylum Cryptophyta, but considered by the authors in the Phylum Pyrrophyta) These 2 groups formed between 50-90% of the biomass in all collections		Intensively sampled one acid lake, Carlyle Lake (pH about 5.0), also studied by Kwiatkowksi and Roff, 1976. Samples collected at weekly intervals late June to late July, 1974
11. Ontario, North of Lake Huron (Johnson et al. 1970)	Species diversity lower in 2 acid contaminated lakes than in the circumneutral lake		Many species of the Class Chrysophyceae (Chrysophyta), the class Myzophyceae (Cyanophyta; bluegreen algae), and diatoms (Class Bacillariophyceae, Phylum Chrysophyta) developed in the circumneutral lake that were absent or occurred in only small numbers in the 2 acidic lakes	Three lakes - one circumneutral and two acidic lakes, acidified as a result of contamination by acid leachate from processing of local uranium ores Associated with low pH levels were high levels of calcium, sulfate, and nitrate, and, to a lesser extent, elevated heavy metals concentrations

TABLE 5-5. CONTINUED

Location (reference)	Reductions in species diversity	Dominant species in acid water	Species missing in acid water	General comments
12. Adirondack Region of New York State (Hendrey 1980, Hendrey et al. 1980b)	Total number of species identified in each lake decreased with increasing acidity: circumneutral lake - 64 intermediate - 38 acidic - 27	Species of the Class Chrysophyceae (Chrysophyta) dominated the biomass of the most acidic lake, although dinoflagellates (Pyrrophyta), especially Peridinium inconspicuum, comprised a significant fraction of the biomass in the ice-free season	Numbers of species of green algae (Chlorophyta) and blue-green algae (Cyanophyta) decreased most markedly Dinobryon spp. (Chrysophyta) are the typical dominant phytoplankters during the summer in Adirondack lakes	Intensive sampling of three lakes - one acidic (pH about 4.9), one intermediate (pH about 5.5), and one circumneutral (pH about 7.0)
13. Adirondack Region of New York State (Charles 1982)			All lakes with pH > about 5.8 had euplanktonic diatoms (class Bacillariophyceae, Phylum Chrysophyta) present in their surface sediments. Lakes with a lower pH had none.	Survey of sediment diatom assemblages and lake water characteristics for 39 lakes
14. Florida (Crisman et al. 1980)	Mean number of taxa in acidic lakes was 10.8 vs. 16.5 for non-acidic lakes	In most acidic lakes (pH 4.5 to 5.0), green algae (Chlorophyta) accounted for 60% of the total phytoplankton abundance; blue-green algae (Cyanophyta) only 25%. Opposite pattern in circumneutral lakes. Highly acidic lakes were dominated by: Green algae (Chlorophyta) - Scenedesmus, Ankistrodesmus, Staurastrum and several species of small coccoid green algae Dinoflagellates (Pyrrophyta) - Peridinium	In lakes of pH 6.5 to 7.0, bluegreen algae (Cyanophyta) made up 63% of total phytoplankton abundance, while green algae (Chlorophyta) were responsible for only 31%. Opposite pattern in acidic lakes	Survey of 13 poorly buffered lakes in northern Florida with pH levels below 5.6, and 7 comparable lakes in southern Florida but with pH levels above 5.6
15. Missouri (Lind and Campbell 1970)	Reduced species diversity in acid lake			Study of a very acid lake (pH 3.2 to 4.1) affected by strip mining)

TABLE 5-5. CONTINUED

Location (reference)	Reductions in species diversity	Dominant species in acid water	Species missing in acid water	General comments
16. England (Hargreaves et al. 1975)	Number of algal species present per water was negatively correlated with total acidity			Study of 15 waters with pH levels of 3.0 or less; most affected by strip mining activities
17. Smoking Hills Region, Northwest Terr., Canada (Hutchinson et al. 1978)	In these very acidic ponds, phytoplankton populations were depleted	Even at these extremely low pH levels, some species of algae still commonly occurred: Euglenoids (Euglenophyta) - Euglena mutablis Diatom (Chrysophyta) - Nitzshia sp. Dinoflagellate (Pyrrophyta) - Gymnodinium ordinatum		Ponds affected by spontaneous burning of bituminous shale deposits. pH values as low as 1.8
18. New Zealand (Brock and Brock 1970)			Lower pH limit below which bluegreen algae (Cyanophyta) were unable to grow is about 4.8 to 5.0. However, at lower temperatures (<56 C) then in the study waters, bluegreen algae may be able to tolerate more acid pH values	Analysis of algal populations along the pH gradient as acidic (pH about 3.8) thermal waters and alkaline (pH 8.2 to 8.7) hot springs flow into a lake, Waimangu Cauldron

other hand, during the experimental acidification of Lake 223, Ontario, from pH 6.7 to 7.0 in 1976 to pH 5.4 in 1980, the importance of chrysophyceans gradually decreased, with a corresponding increase in green algae (Phylum Chlorophyta) (Schindler and Turner 1982). Blooms of Chlorella, a green alga, within the hypolimnion (associated with increased water clarity) for the most part accounted for the increase in importance of green algae.

A dominance of blue-green algae in acidic waters has also been reported. Conroy et al. (1976) observed a bloom of blue-green algae (Merismopedia sp.) in acidic Florence Lake (pH 4.4 to 4.9) in Ontario. Hultberg and Andersson (1982) noted that blue-greens (again Merismopedia sp.) were prevalent in humic acid lakes in Sweden. Stokes (1980) noted that the typical dominance of dinoflagellates in acidic waters near Sudbury, Ontario did not apply to naturally acidic, dystrophic lakes. Thus, various circumstances, such as the presence of high concentrations of humic organic materials in the water, may be conducive to developing populations of blue-green algae under acidic conditions.

Another approach to assessing the effect of acidification on phytoplankton is to determine which taxa common in circumneutral lakes are missing or reduced in waters at low pH levels. Again, it is difficult to generalize. Of 11 papers dealing with this question (Table 5-5), in seven papers, diatoms (Class Bacillariophyceae, Phylum Chrysophyta) were reported to be reduced in importance in acidic waters; green algae (Phylum Chlorophyta) in six papers, blue-green algae (Phylum Cyanophyta) in five papers, and chrysophyceans (Class Chrysophyceae, Phylum Chrysophyta) in four papers. In many cases, shifts in acidity were also associated with a shift in major species within a given group of algae.

The observation that different species of algae are characteristic of waters with different pH levels has also been used to predict an approximate lake pH level based upon the composition of the algal flora within the lake. Because the siliceous cell walls of diatoms (both planktonic and benthic) are well preserved in lake sediments, this group of algae has most frequently been used in these analyses. Use of this technique for estimation of historic changes in pH is discussed in greater detail in Section 5.3.2.2.2.

5.5.2.2 Changes in Phytoplankton Biomass and Productivity--Available data on acidification and primary productivity in acidic lakes yield no clear correlation between pH level and algal biomass or productivity. Relative to primary productivity and/or phytoplankton biomass in circumneutral lakes, levels in acidic lakes in some cases are reduced, in others unchanged or even increased (Table 5-6).

Field correlations must be interpreted with care. For example, lakes low in nutrients may be particularly sensitive to acidification. At the same time, low nutrient levels limit primary productivity. As a result, any correlation between lake pH level and phytoplankton biomass or productivity may reflect only their common association with nutrient

TABLE 5-6. THE RELATIONSHIP BETWEEN LAKE ACIDITY AND PHYTOPLANKTON BIOMASS AND/OR PRODUCTIVITY--OBSERVED RESPONSE TO LOW pH

Significant Decrease	Significant Increase	No Change
In six lakes near Sudbury, Ontario, concentrations of chlorophyll *a* were positively correlated ($p < 0.01$) with pH; primary productivity (on a volumetric basis) was lowest in the most acidic lake (Kwiatkowski and Roff 1976).	In 58 lakes along the west coast of Sweden, the largest biomass of phytoplankton occurred in the most acidic lakes (pH 4.5), and the lowest biomass at intermediate pH levels (pH 5.1 to 5.6) (Almer et al. 1978).	The National Research Council of Canada (1981) collated measurements of algal biomass and productivity for oligotrophic lakes in the Canadian Shield Region of Ontario. Neither biomass nor production were significantly correlated with pH. Algal biomass was significantly ($p < 0.01$) correlated with total phosphorus concentration.
In three Adirondack lakes, the most acidic lake (pH 4.7 to 5.1) had the lowest level of chlorophyll *a*; the least acidic lake had the highest level of primary productivity (on an areal basis) (Hendrey 1980).	In acidification experiments within limnocorrals in Carlyle Lake (pH 4.8 to 5.1), near Sudbury, Ontario, after 28 days the biomass of phytoplankton was highest at the lowest pH tested (pH 4.0), and lowest at pH 6.0 and 6.5 (Yan and Stokes 1978).	In the fall of 1973, the pH of one Ontario lake, Middle Lake (pH about 4.4) was raised to around 7.0 by additions of base. Total phosphorus levels did not increase, nor did phytoplankton biomass (Yan 1979). Experimental increases in phosphorus levels in acidic lakes (with or without neutralization) have, however, induced significant increases in phytoplankton biomass (Dillon et al. 1978, Hendrey et al. 1980b).
In a survey of Florida lakes, mean chlorophyll *a* concentrations were significantly lower in acidic lakes (1.88 mg m^{-3}) than in non-acidic lakes (7.53 mg m^{-3}) (Crisman et al. 1980).	During experimental acidification of Lake 223 (Experimental Lakes Area in western Ontario), the pH decreased gradually from pH 6.7 to 7.0 in 1976 to pH 5.4 in 1980. Over that time period, chlorophyll and algal biomass increased significantly, associated with hypolimnetic algal blooms of *Chlorella*, and apparently in response to increased water clarity (Schindler and Turner 1982).	Within eight plastic enclosures in Eunice Lake, an oligotrophic lake with pH 6.5 in British Columbia, acid addition (minimum pH 5.5) resulted in no significant change in chlorophyll content. Additions of acid plus nutrients (minimum pH 5.0) increased algal biomass (Marmorek 1983).
		In three Swedish lakes sampled from 13 to 15 May 1975, rates of phytoplankton production per volume of water were somewhat lower in the most acidic lake (pH 4.6). However, because of greater water transparency in this acidic lake, measurable primary productivity was maintained to a greater depth. Levels of primary productivity on an areal basis, per square meter of lake surface, were similar in all three lakes (Almer et al. 1978).
		In 13 lakes in southern Norway, chlorophyll *a* content was not significantly correlated with lake pH (Raddum et al. 1980).

status and not a cause-and-effect relationship between pH and phytoplankton response.

Three investigators have reported lower levels of phytoplankton biomass and/or productivity in acidic lakes than in circumneutral lakes, based on measurements from six lakes near Sudbury, Ontario (Kwiatkowski and Roff 1976), three lakes in the Adirondacks, New York (Hendrey 1980), and a survey of Florida lakes (Crisman et al. 1980). None of these studies included a simultaneous analysis of nutrient availability. In addition, careful examination of data on primary productivity collected by Kwiatkowski and Roff (1976) indicates that, with the exception of two lakes, no clear relationship exists between productivity and lake pH. The productivity reported for the most acidic lake (pH 4.0 to 4.6, about 3 mg C m^{-3} hr^{-1}) is well within the range normally observed in non-acidic lakes in the region (0.3 to 6.9 mg m^{-3} hr^{-1}) (National Research Council Canada 1981). Values Kwiatkowski and Roff measured in the five remaining lakes were well above the norm. Thus, no conclusive data are available to support the hypothesis that acidification results in decreased algal biomass and productivity.

In contrast, three field surveys and four field experiments suggest that acidification causes no change, or perhaps even an increase, in phytoplankton biomass (Table 5-6). Surveys in Ontario (compiled in National Research Council Canada 1981) and Norway (Raddum et al. 1980) found no correlation between lake pH and algal biomass; in Sweden (Almer et al. 1978), the largest biomass occurred in the most acidic lakes. Acidification experiments within limnocorrols yielded no change (Marmorek 1983) or an increase (Yan and Stokes 1978) in algal biomass. Experimental acidification of an entire lake (Lake 223 in the Experimental Lakes Area, Ontario) also was associated with a significant increase in phytoplankton biomass (Schindler and Turner 1982).

Increased accumulations of phytoplankton in acidic waters may reflect either an associated increase in the rate of production or a decrease in the rate of loss (e.g., decreased predation). No studies report an increase in phytoplankton productivity with acidification or in acidic lakes, although data are not abundant. Two field surveys suggest no relationship between lake pH and primary productivity (Table 5-6). Predator-prey interactions within the plankton community are complex. Detailed studies related to effects of acidification on phytoplankton mortality are not available. Potential changes, based on ecological theory, are discussed in Section 5.5.4.

In a number of laboratory studies, primary productivity in algal cultures has been shown to be a function of pH level (e.g., Hopkins and Wann 1926, Bold 1942, Sorokin 1962, Brock 1973, Loefer 1973, Moss 1973, Cassin 1974). For each species, growth responses to pH form an inverted U-curve, with an optimum pH level for maximum growth, and significantly lower growth rates at lower and higher pH levels. The optimum pH for growth varies significantly between species. Moss (1973) found a lower limit for growth of most algal species at pH levels above 4.5 to 5.1. However, three of 33 species tested grew well at pH levels below 4.0.

Sixteen of 33 species were capable of significant growth below pH 5.0. No distinct differences were found between groups or types of algae with regard to minimum pH tolerated (Moss 1973). Blue-green algae in general (Phylum Cyanophyta), however, may be less tolerant of pH levels below 5.0 (Bold 1942, Brock 1973, Moss 1973).

The presence of an alga at a low pH level does not necessarily imply a preference for acidic conditions or that photosynthesis and growth are optimal (Hendrey et al. 1980b). The proliferation of Peridinium species at pH levels 4.0 to 5.0 does not mean that these organisms do best at pH levels 4.0 to 5.0, only that its competitors do less well.

The growth of algae in acidic waters indicates a physiological ability to tolerate low pH levels, and conditions associated with low pH, e.g., a shift in the form and availability of aqueous inorganic carbon and other necessary plant nutrients, and increased concentrations of some metals, especially aluminum (Chapter E-4, Section 4.6). Research has not yet clearly defined physiological responses of algae to acidic conditions, or why some species can tolerate higher acidity than others.

5.5.3 Effects of Acidification on Zooplankton

Results from 14 field surveys of zooplankton communites are summarized in Table 5-7. In each study, acidic lakes had fewer zooplankton species (e.g., Figure 5-3). In Norway, clearwater lakes with pH levels below 5.0 contained 7.1 species on the average as compared to 16.1 species in less acid lakes (pH > 5.5) (Overrein et al. 1980). Sprules (1975a,b) found nine to 16 species of crustacean zooplankton in lakes with pH levels above 5.0 in the LaCloche Mountain Region of Ontario, but only one to seven species in acidic lakes, pH < 5.0. In the northeastern United States, lakes with pH below 5.0 contained three to four species of planktonic crustaceans; lakes with pH above 5.5 contained six to 10 species (Confer et al. 1983). The greatest change in species number and types of dominant species occurred between pH 5.0 to 5.3 (Sprules 1975a, Roff and Kwiatkowski 1977).

Likewise, experimental acidification of Lake 223, Ontario, from pH 6.7 to 7.0 in 1976 to pH 5.4 in 1980, resulted in a decline in the number of zooplankton species present in the lake. A decrease in the mean epilimnetic pH from 6.1 to 5.8 was associated with the disappearance of one species; decrease to pH 5.6 led to the loss of two more species (Malley et al. 1982).

For the most part, species dominant in acidic lakes are also important components of zooplankton communities in non-acidic lakes in the same region. There is no invasion of new species.

Certain species of planktonic rotifers of the genera Keratella, Kellicottia, and Polyarthra tolerate acidic conditions and can be found in the pH range 4.4 to 7.9. In Scandinavia, species common in acidic

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TABLE 5-7. SUMMARY OF OBSERVATIONS RELATING SPECIES COMPOSITION, SPECIES DIVERSITY, AND BIOMASS OF THE ZOOPLANKTON COMMUNITY TO ACIDITY

Location (Reference)	General Observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
1. Southern Sweden (Almer et al. 1974 and 1978)	Number of species lower acid lakes In acid lakes, often just a few species occur but the number of individuals can be rather great In highly acidic lakes (pH <5) Polyarthra remata Bosmina coregoni, and Diaptomus gracilis often dominate	Polyarthra remata, Polyarthra vulgaris, Keratella cochlearis, and Kellicottia longispina common at most pH levels, 4.4 to 7.9 Polyarthra remata dominant in several lakes with pH < 5.5 Conochilus unicornis present in many lakes but less prevalent in acid waters Many of the other rotifers appear to have preferences above 5.5	Bosmina coregoni common and occurred at all pH levels All Daphnia species were sensitive to low pH levels. Only a few individuals found at pH < 6 Diaphanosoma brachyurum, Holopedium gibberum, and Leptodora kindti common but mainly at pH > 4.9 Bythotrephes longimanus found more frequently in lakes with pH < 5.4. At higher pH levels, fish predation may keep the population at low levels Common in non-acidic lakes: Diaphanosoma Holopedium Daphnia cristata Bosmina	Diaptomus gracilis and Cyclops spp. common at all pH levels Heterocope appendiculata occurred mostly at pH>5.5		One-stop survey of 84 lakes in August 1971 Samples collected with 75 μ mesh net
2. Southern Sweden (Hultberg and Anderson 1982)	In acidic lakes, zooplankton community dominated by a few species	Dominants in acid lakes: Polyarthra spp. Keratella cochlearis Kellicottia longispina Common after liming: Polyarthra spp. Keratella cochlearis Asplanchna priodonta Conochilus mincornis	Dominant in acid lakes: Bosmina coregoni Common after liming: Bosmina coregoni Diaphanosoma sp. Daphnia cristata Limnosida frontosa Holopedium gibberum Ceriodaphnia quadrangula	Dominants in acid lakes: Eudiaptomus gracilis Cyclops spp. Common after liming: Eudiaptomus gracilis		Pre- and post-liming studies. Effects of liming on zooplankton are difficult to evaluate due to simultaneous rotenone treatments

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
3. Southern Norway (Hendrey and Wright 1976)	Total number of species collected decreased with decreasing pH		Daphnia galeata absent at pH < 6.9 Eubosmina longispina common at all pH levels, 4.1 to 7.7 Holopedium gibberum occurred frequently at pH levels 4.2 to 7.2 Daphnia longispina appeared in samples pH 4.6 to 6.8	Eudiaptomus gracilis common over wide range of pH, 4.1 to 6.6 most frequently dominant at low pH levels; rarely dominant at pH>5.5 Heterocope saliens occurred pH 4.1 to 6.6 Ancanthodiaptomus denticornis and Mixodiaptomus laciniatus did not occur at pH < 5 Cyclops scutifer appeared at pH 4.6 to 7.7		One-stop survey of 57 lakes during fall 1974 Samples collected with single verticle haul of a 75 μ mesh net
4. Norway (Raddum et al. 1980; Raddum, 1978; Hobaek and Raddum 1980)	Number of species lower in acid lakes. In southern Norway, clearwater lakes with pH < 5 held on the average 7.1 species; equally acid humic lakes, 11.7 species; less acid (pH > 5.5) clearwater lakes, 16.1 species on average All major groups contributed to the lowered number of species, but cladocerans apparently most affected	Species occurring with equal frequency in acid and non-acid clearwater lakes: Kellicottia longispina Keratella serrulata Species more frequent in non-acidic lakes: Conochilus spp. Asplanchna sp. Keratella cochlearis Keratella hiemalis Species more frequent in acidic lakes: Polyarthra spp.	Species occuring with equal frequency in acid (pH < 5) and non-acid (pH > 5.5) clearwater lakes: Bosmina (Eubosmina) longispina Species more frequent in non-acid lakes: Holopedium gibberum Diaphanosoma brachyurum Ceriodaphnia quadrangula Daphnia longispina Daphnia galeata Bythotrephes longimanus Polyphemus pediculus Leptodora kindti	Species occurring with equal frequency in acid and non-acid lakes: Eudiaptomus gracilis Heterocope saliens Species more frequent in non-acid lakes: Cyclops scutifer Cyclops abyssorum Mesocyclops leuckarti	Chaeborus flavicans absent in clearwater acid lakes	Survey of 27 lakes; sampled (3 vertical net hauls, with 90 μ mesh net, per visit) from June to September 1977 - 1979

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
4. cont.	Some species tolerate acid conditions in the presence of humus, but are absent from acid clearwater lakes The species number of filter-feeders reduced in clear-water acid lakes. Changes for rapturial species not as obvious					
5. Southern Norway (Nilssen 1980)			Lower abundance of Daphnia longispina and Daphnia longiremus at pH<5.5 Bosmina longispina a dominant species at all pH levels, 4.5 to 7.0 Leptodora kindti absent at pH levels 5.0 to 5.5 In sediment cores from lake with pH 4.2 to 5.0, Daphnia longispina present below 3 to 4 cm, but absent in surface sediments and in the lake	Eudiaptomus gracilis a dominant species at all pH levels, 4.5 to 7.0 Cyclops scutifer common at all pH levels, 4.5 to 7.0 Heterocope saliens increased in abundance in more acid lakes (pH < 5.0)	Chaoborus flavicans absent at pH levels < 4.5 to 5.0 In sediment cores from lake with pH 4.2 to 5.0, Chaoborus flavicans remnants common below 3 to 4 cm, but absent in surface sediments and in lakes	Samples collected with 90 μ mesh net June - October 1973 and 1974 at fourth night intervals

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
6. LaCloche Mountain Region of Ontario (Roff and Kwiatkowski, 1977)	Signifacant reduction in number of species and numbers of individuals at lower pH levels (pH 4.4 to 4.8) Diversity index declined sharply below pH 5.3 Mean size of crustacean zooplankters identical in acid vs. non-acid lakes	Standing crop of rotifers reduced at pH levels 4.4 to 4.8 In all lakes with pH>5.8, rotifers represented by a variety of species with no one species being dominant In highly acidic waters (pH about 4.4), Keratella turocephala dominated. As the pH increased, Keratella cochlearis, Kellicottia bostonienis, and Kellicottia longispina increased in occurrence Polyarthra euryptera and Polyarthra dolichoptera rare at pH 4.7 to 5.0; absent pH<4.4 In highly acidic waters (pH about 4.4), Keratella taurocephala dominated. As the pH increased, Keratella cochlearis, Kellicottia bostoniensis, and Kellicottia longispina increased in occurrence. Polyarthra euryptera and Polyarthra dolichoptera rare at pH 4.7 to 5.0; absent pH < 4.4	Standing crop of cladocerans reduced at pH levels below 5; maximum at pH 5 to 6 Leptodora kindti found only at pH>5.0 Daphnia galeata mendotae Daphnia retrocurva, and Diaphanosoma leuchtenbergianum found in all lakes but rare at pH 4.4 to 4.8 Bosmina longirostris, Eubosmia tubicen, and Holopedium gibberum common in all lakes	Standing crops of cyclopoid copepods but not calanoid copepods reduced at pH levels 4.4 to 4.8 Diaptomus minutus occured abundantly in all lakes at all pH levels, 4.4 to 6.0 Diaptomus oregonensis and Epischura lacustris only encountered in lakes with pH>5.6 Cyclops bicuspidatus thomasi and Mesocyclops edax found in all lakes, pH 4.4 to 6.8		Six lakes with pH levels 4.0 to 7.1 samples at weekly intervals June and August 1972 and May and July 1973 Vertical haul with 60 μ mesh net; and Schindler-Patalas trap at various depths.

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
7. LaCloche Mountain Region of Ontario (Sprules 1975a, 1975b)	Above pH 5.0, communities with 9-16 species, 3-4 dominants in lakes with pH < 5.0, 1 to 7 species with only 1 or 2 dominants Discontinuity in species distribution at pH 5.0 to 5.2. 64% of all species identified occurred never or rarely at pH < 5.0. In some lakes, only *Diaptomus minutus* remains. Above pH 5.0, pH had little effect on tolerant species and only a slight effect on the total number of species In regression analyses, pH alone accounted for 53% of the variance in number of species		Tolerant species distributed independent of pH: *Bosmina* *Diaphanosoma leuchtenbergianum* *Holopedium gibberum* Never occur pH < 5.0: *Leptodora kindti* *Daphnia galcata mendotae* *Daphnia retrocurva* *Daphnia ambiqua* *Daphnia longiremis* Occur primarily in lakes with pH < 6.0: *Polypemus pediculus* *Daphnia catawba* *Daphnia pulicaria*	Tolerant species distributed independent of pH: *Mesocyclops edax* *Cyclops bicuspidatus thomasi* *Diaptomus minutus* Never occur pH < 5.0: *Tropocyclops prasinus mexicanus* *Epischura lacustris* *Diaptomus oregonesis* *Diaptomus minutus* dominant in most lakes pH < 5.0; in some cases the only species present		One-time sampling of 47 lakes from July to early September 1972 - 1973. Vertical hauls with either 75 μ or 110 μ mesh net pH ranged from 3.8 to 7.0

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
8. Sudbury Region of Ontario (Yan and Strus 1980)	Numbers of species reduced in acid lakes (pH 4.1 to 4.4) with an average of only 3.7 species per sample vs 10.6 in non-acid lakes Total community biomass lower in acid lakes than in nonacid lakes. Decreased biomass resulted from both a decrease in numbers (except in one lake) and the small size of the community dominants (primarily Bosmina longirostris) in acid lakes The greatest reductions were observed in the lake with the highest metal concentrations Contamination with copper and nickel appeared to have some effect on the zooplankton community over and above effects of low pH		Major species in non-acid lakes: Bosmina longirostris Holopedium gibberum Diaphanosoma leuchtenbergianum Daphnia galeata mendotae In acid waters, Bosmina longirostris accounted for an average of 79% of the total crustacean biomass vs 3% in non-acid lakes In acidic Clearwater Lake zooplankton community characterized by the importance of Bosmina longirostris, and the absence of Daphnia sp. and the other common cladocerans Holopedium gibberum and Diaphanosoma leuchtenbergianum	Major species in non-acid lakes: Cyclops bicuspidatus thomasi Tropocyclops prasinus mexicanus Diaptomus minutus Copepods contributed an average of 65% of the total biomass and 85% of the total individuals in non-acid lakes Diaptomum minutus formed between 44 and 73% of all crustacean zooplankton, and dominant in all non-acid lakes In acidic Clearwater Lake, zooplankton community characterized by the absence of Tropocyclops prasinus mexicanus and Mesocyclops edax and by the scarcity of Cyclops bicuspidatus thomasi and Diaptomus minutus		Sampled 4 acidic lakes (pH 4.1 to 4.4) and one less acidic lake (pH 5.7) in the vicinity of Sudbury plus 6 non-acidic lakes (pH 5.7 to 6.6) in Muskoka-Halib urton Regior of Ontario Acidic lakes also have high levels of copper and nickel which may adversely effect zoo-plankton Samples collected summers 1973-1977 as vertical hauls with 80 μ mesh tow net and at 2- to 3-m intervals with a plastic trap

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
9. Sudbury Region of Ontario (Yan et al. 1982)	In the non-acid lake, collections included 7 species on the average vs 3.7 from the acid lake	Rotifers generally form only about 1% of total zooplankton biomass in non-acidic oligotrophic lakes in the Sudbury area	Cladocerans unimportant in non-acid lake, forming <5% of the average biomass In the acid lake, Bosmina longirostris comprised 40% of the crustacean zooplankton biomass	Diaptomus minutus major contributor to total zooplankton biomass in the non-acid lake. Cyclops scutifer, Mesocyclops edax, and Tropocyclops prasinus mexicanus also important In the acid lake, Diaptomus minutus comprised 32% of the crustacean zooplankton biomass. Chydorus sphaericus and Cyclops vernalis also common	2 individuals of Chaoborus flavicans collected in non-acid lake. In the acidic lake, Chaoborus flavicans, Chaoborus albatus, and Chaoborus americanus occurred	Pre- and post-fertilization study of one acidic (pH about 4.6) and one non-acidic (pH about 6.0) lake only pre-fertilization data included here Samples collected in plexiglass trap at 1-, 4-, and 7-m; 76 μ mesh net
10. Georgian Bay Region of Ontario (Carter 1971)	Standing crop generally greater in very acid (pH 4.7 to 5.2) than in slighly acid or alkaline ponds About 14 species present in non-acid waters were absent from the very acid lakes		Species occurring in all ponds independent of pH: Bosmina longirostris Ceriodaphnia quadrangula Diaphanosoma leuchtenbergianum Species occurring only in less acid and alkaline ponds: Leptodora kindta Daphnia ambiqua Daphnia retrocurva Ceriodaphnia lacustris Bosmina coregoni coregoni Holopedium gibberum	Species occuring in all ponds independent of pH: Diaptomus reighardi Cyclops vernalis Cyclops bicuspidatus thomasi Mesocyclops edax Species occuring only in less acid and alkaline ponds: Epischura lacustris Diaptomus minutus Diaptomus oregonensis Tropocyclops prasinus mexicanus		32 ponds sampled to 10 times over a 3-year period. Samples collected with a Clarke-Bumpus or transparent zooplankton trap The acidity in these waters is attributed mainly to large amounts of organic (humic) acids

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
10. cont.			Bosmina longirostris was the most consistently abundant crustacean in all ponds. Its greatest numbers were usually found in the very acid ponds.			
11. Smoking Hills area in Northwest Terr., Canada (Hutchinson et al. 1978)		The only zooplankton present in these very acid waters (pH 2.8 to 3.6) were rotifers Branchionus urceolaris the dominant form				
12. Adirondack Region of New York State and White Mountain region of New Hampshire (Confer et al. 1983)	Number of zooplankton species and zooplankton biomass sharply related to pH ($p < 0.01$). For each unit decrease on pH lakes contained on the average 2.4 fewer species and 22.6 mg dry wt m^{2-} less zooplankton biomass		Identified pH range for distribution of species: Bosmuna longircotris, 5.2-6.7 Bosmina corrgoni, 4.5-7.2 Daphnia catawba, 5.2-6.7 Daphnia ambigua, 4.5-6.6 Holopedium gibberum, 4.5-7.2 Diaphanosomean leuchtenbergianum, 4.7-6.6 Polyphemus pedicutus, 4.7-7.2 Leptodora kindtii 6.3-6.4	Diaptomus minutus dominated at pH < 5. Identified pH range for distibutors of species: Diaptomus minutus, 4.5-7.2 Cyclops scutifer, 5.4-7.2 Mesocyclops edax, 4.5-6.7 Tropocyclops prasimus, 5.3-7.2 Epischura lacustris, 5.3-7.2	Chaoborus sp. occurred throughout the pH range 4.5 to 6.7	Two stop survey (July and August 1979) of 20 lakes (10 in NY; 10 in NH) Samples collected with Van Dorn sampler at 3-5 depths per lake All headwater lakes; pH ranged from 4.5 to 7.2

TABLE 5-7. CONTINUED

Location (reference)	General observations	Changes in species composition and abundance of: Rotifers	Cladocerans	Copepods	Others	Comments
13. Great Britain (Lowndes 1952)			Identified pH range for distribution of species: Diaphanosoma brachyurum, 4.3-9.8 Daphnia pulex, 5.8-9.2 Daphnia longispina, 7.0-9.2 Ceriodaphnia reticulata, 6.2-9.2 Ceriodaphnia quadrangula, 4.2-9.2 Bosmina longirostris, 6.9-9.2 Polyphemus pediculus, 4.6-9.2 Bythotrephes longimanus, 6.7-7.2 Leptodora kindti, 6.7-8.4	Identified pH range for distribution of species: Diaptomus gracilis, 4.7-9.2 Cyclops abyssorum, 6.2-7.3 Cyclops vernalis, 4.4-9.2 Cyclops bicuspidatus, 4.1-9.2		
14. Great Britain (Fryer 1980)	Number of species lower in low pH waters in pH range 3 to 7.		Fond in waters with pH < 5.0: Diaphanosoma brachyurum Ceriodaphnia quadrangula Bosmina coregoni Polyphemus pediculus	Found in waters with pH < 5.0: Cyclops abyssorum Tropocyclops prasinus		One-time sampling of 70 water bodies Acidity attributable primarily to high levels of organic (humic) acids

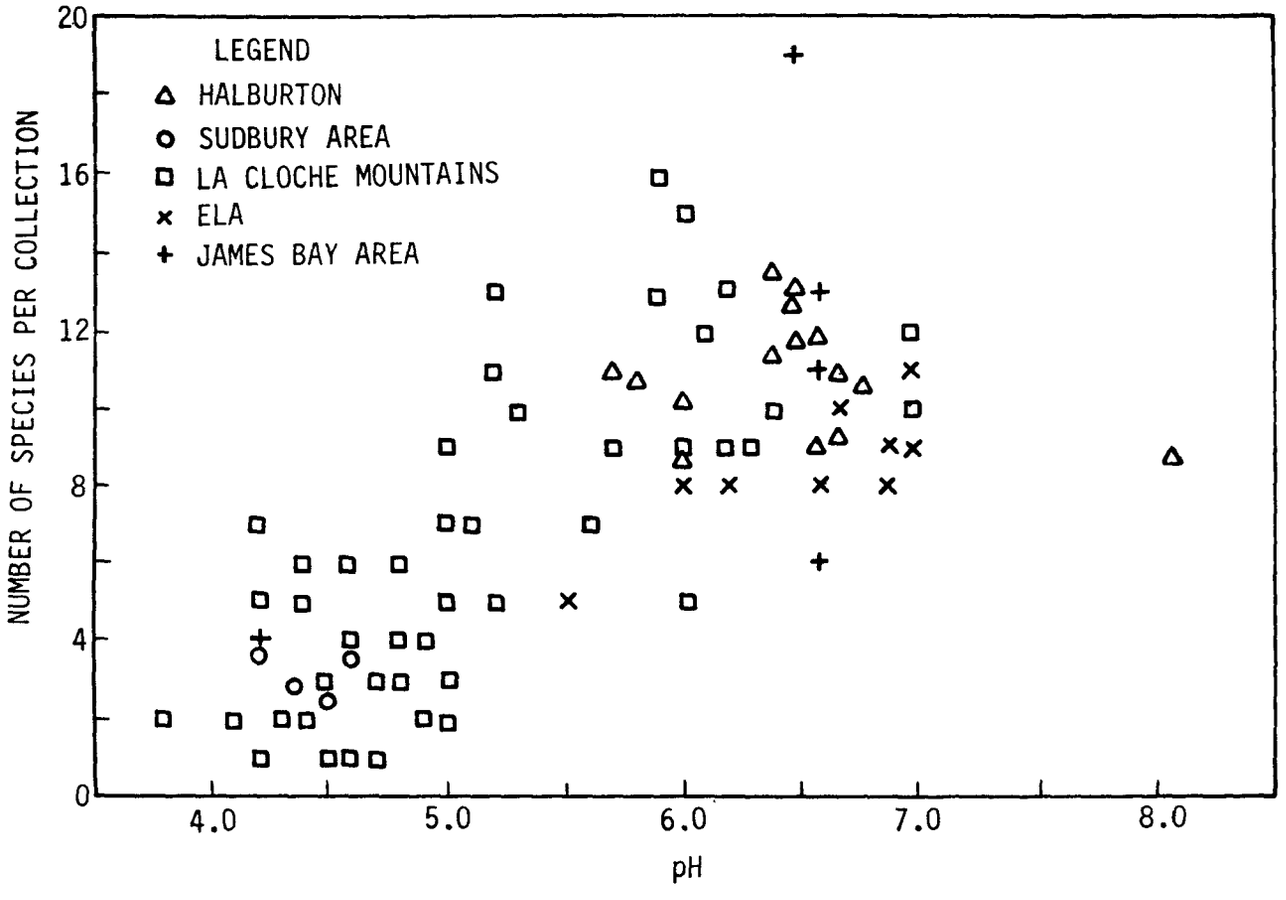

Figure 5-3. Relationship between the average number of species of planktonic crustaceans identified in each collection and pH of various lakes located on the Canadian Shield, Ontario. Adapted from NRCC (1981).

lakes were Keratella cochlearis, Keratella serrulata, Kellicottia longispina, Polyarthra remata, and Polyarthra vulgaris. Species reduced in abundance with acidification included Asplanchna priodonta, Conochilus unicornis, Conochilus mincornis, and Keratella hiemalis (Almer et al. 1974, 1978; Raddum 1978; Hultberg and Andersson 1982). In Ontario, species of Keratella and Kellicottia were also important in acidic lakes (Keratella taurocephala, Keratella cochlearis, Kellicottia bostoniensis, Kellicottia longispinia) (Roff and Kwiatkowski 1977). Experimental acidification of Lake 223, to pH 5.4, resulted in increased numbers of Polyarthra vulgaris, Polyarthra remata, Keratella taurocephala, and Kellicottia longispina (Malley et al. 1982).

Among crustacean zooplankters, several species of cladocerans appear sensitive to acidity. In particular, field surveys (Table 5-7) indicate that many species of the genus Daphnia are absent or uncommon below pH 5.5 to 7.0 (Lowndes 1952, Carter 1971, Almer et al. 1974, Sprules 1975a, Hendrey and Wright 1976, Hobaek and Raddum 1980, Yan and Strus 1980, Nilssen 1980). In addition, in laboratory experiments with Daphnia magna and Daphnia pulex, reductions in survival and reproduction, and physiological imbalances occurred at pH levels below 5.0 to 6.0 (Davis and Ozburn 1969, Potts and Fryer 1979).

Counterbalancing the scarcity of daphnids in acidic lakes is an increase in the abundance of species of the cladoceran genus Bosmina. In Scandinavia, Bosmina coregoni and Bosmina longispina were common at all pH levels greater than 4.1 to 4.5 (Almer et al. 1974, Hendrey and Wright 1976, Raddum 1978, Hultberg and Andersson 1982). In Ontario, Bosmina longirostris accounted for a large fraction of the zooplankton biomass in acidic lakes (pH < 5) (Carter 1971, Roff and Kwiatkowski 1977, Yan and Strus 1980, Yan et al. 1982). Other cladocerans common in temperate, oligotrophic lakes (e.g., Diaphanosoma brachyurum, Diaphanosoma leuchtenbergianum, Leptodora kindti, Holopedium gibberum, Polyphemus pediculus, Ceriodaphnia quadrangula, and Bythotrephes longimanus) often are less abundant in waters with pH levels below 4.7 to 5.0 (Table 5-7). Acidification of Lake 223 down to pH 5.4, however, resulted in no consistent trends in the numbers of Bosmina longirostris, Daphnia galeata mendotae, and Diaphanosoma brachyurum, and a possible increase in the numbers of Holopedium gibberum (Malley et al. 1982).

Copepods prevalent in acidic waters (pH 4.1 to 5.0) are Diaptomus gracilis in Scandinavia and Diaptomus minutus in North America (Table 5-7). In addition, frequently reported as common in acidic waters are Heterocope saliens in Scandinavia, and Cyclops vernalis, Cyclops bicuspidatus thomasi, and Mesocyclops edax in North America. Species noted as being more frequent in non-acidic lakes include Epischura lacustris, Diaptomus oregonensis, Tropocyclops prasinus mexicanus, Heterocope appendiculata, Ancanthodiaptomus denticornis, and Mixodiaptomus laciniatus. Similarly, experimental acidification of Lake 223 to pH 5.4 resulted in no consistent change in populations of Diaptomus minutus, Cyclops bicuspitatus thomasi, and Mesocyclops edax, but a decline in numbers of Tropocyclops prasinus mexicanus, and

extinction of Epischura lacustris below pH 5.8 and Diaptomus sicilis below pH 6.1 (Malley et al. 1982).

Experimental acidification of Lake 223, Ontario also resulted in the extinction of the opposum shrimp, Mysis relicta, an important planktonic predator, below about pH 5.6 (Malley et al. 1982).

Of the insects, midge larvae Chaoborus spp. are important zooplankters in many lakes. Little is known about effects of acidification on Chaoborus, although it appears to persist in some acidic environments down to pH 4.2 to 4.5 (Scheider et al. 1975, Yan et al. 1982, Confer et al. 1983, Marmorek 1983). On the other hand, Hobaek and Raddum (1980) observed that Chaoborus flavicans was absent in clear-water acid lakes (pH < 5.0). Nilssen (1980) reported the extinction of Chaoborus in an acidic lake (pH 4.2 to 5.0), where carapace remnants in bottom sediments verified its presence in earlier years.

No data on impacts of acidification on the productivity of the zooplankton community are available. Studies on changes in community biomass are also limited. Thus, the functional response of the zooplankton community to increasing levels of acidity is still largely unknown.

Three surveys of abundance of zooplankton in acidic lakes have been conducted, involving lakes near Sudbury, Ontario contaminated with both acid and metals (Yan and Strus 1980), lakes in the LaCloche Mountain Region of Ontario (Roff and Kwiatkowski 1977), and headwater lakes in the Adirondacks, New York, and White Mountain Region of New Hampshire (Confer et al. 1983). In each case, the biomass and/or numbers of zooplankton in acidic lakes were reduced relative to that in circumneutral lakes in the same region. Confer et al. (1983) reported an average decrease of 22.6 mg dry wt m^{-2} per unit drop in pH. Roff and Kwiatkowksi (1977) concluded that standing crops of rotifers, cladocerans, and cyclopoid copepods (but not calanoid copepods) were reduced at pH levels below 5.0. The mean size of crustacean zooplankters was, however, identical in acidic vs. non-acidic waters. Yan and Strus (1980) found total community biomass to be markedly lower (by almost 80 percent, on the average) in acidic lakes (pH 4.1 to 4.4) than in non-acidic lakes (pH > 5.7). Decreased biomass resulted from both a decrease in numbers of individuals (except in one acidic lake) and the small size of the dominant species (primarily Bosmina longirostris).

In contrast, experimental acidification of Lake 223, Ontario, and limno-corrals within Lake Eunice, British Columbia, resulted in no change, or even a slight increase, in zooplankton standing crops (Malley et al. 1982, Marmorek 1983). The lowest pH level attained in both these cases, however, was pH 5.4.

Although more data are necessary, particularly for regions outside Ontario, the tentative conclusion is that acidification to pH < 5.0

results in not only fewer species but also decreased biomass of zooplankton.

5.5.4 Explanations and Significance

5.5.4.1 Changes in Species Composition--The most discrete and identifiable changes that occur in plankton communities with acidification are a decline in the number of species and a shift in species composition. It is possible to speculate on why these changes occur and what they may mean to the system.

The species that predominate in an environment are those best adapted to survive and reproduce in that environment. Acidification changes the environment; thus, it is not surprising that the composition of the plankton community also changes.

Adaptation to acidic conditions, however, involves more than just an ability to tolerate low pH levels. Numerous other chemical, physical, and biological changes associated with acidification require organisms to make adjustments. Chemical changes associated with low pH include elevated concentrations of metals and alterations in the form and availability of plant nutrients, particularly inorganic carbon and phosphorus (Chapter E-4, Section 4.6.3.5). With increased acidity, lake transparency typically increases (Chapter E-4, Section 4.6.3.4), potentially altering physical mixing and thermal regimes. Finally, as the increased acidity directly and indirectly affects other organisms in the water, predator-prey and competitive interactions will shift. All these factors influence which (and how many) species will be important within an ecosystem. Unfortunately, at this time we do not know enough about tolerances and preferences of species for pH levels, concentrations of metals, etc. to elucidate which factors result in observed changes in species composition.

One factor that has received some attention is the possible importance of predator-prey interactions. Acidification results in a decline in abundance of fish (Section 5.6), important zooplankton predators. Changes in plankton communities in response to changes in fish populations have been clearly demonstrated in numerous studies (e.g., Brooks and Dodson 1965, Hall et al. 1970, Nilssen and Pejler 1973, Zaret and Kerfoot 1975, Andersson et al. 1978a, Lynch 1979, McCauley and Briand 1979, Henrikson et al. 1980a, b, and Lynch and Shapiro 1981). In general, in the absence of planktivorous fish, the zooplankton community is typically dominated by large-bodied species. Fish prey preferentially on larger, more-visible zooplankton (O'Brien 1979). With the elimination of fish, increased populations of relatively large-bodied carnivorous and omnivorous zooplankton (e.g., *Chaoborus* spp., *Leptodora kindti*, and, *Epischura lacustris* and *Mysis relicta*) consume smaller zooplankton species and reduce standing crops of small-bodied zooplankton to low levels (Dodson 1974). Often, as a result of increased zooplankton grazing on phytoplankton, inedible algal species constitute a greater proportion of the total phytoplankton biomass.

In acidic waters, however, the species of zooplankton that frequently dominate are relatively small. Bosmina coregoni, Bosmina longispina, and Bosmina longirostris are all small (maximum length about 0.5 to 0.7 mm) compared to other species of cladocerans common in non-acidic, temperate, oligotrophic lakes, e.g., Daphina longispina (2.2 mm), Daphnia galeata mendotae (2.3 mm), Daphnia ambigua (1.7 mm), Holopedium gibberum (1.2 mm), Diaphanosoma brachyurum (1.1 mm), and Ceriodaphnia quadrangula (0.9 mm) (Nilssen and Pejler 1973, Makarewicz and Likens 1979, Lynch 1980). Diaptomus minutus, a common copepod in acidic lakes in North America, has a maximum length of about 1.0 mm as compared to 1.2 mm for Cyclops scutifer and Mesocyclops edax (Makarewicz and Likens 1979).

Lynch (1979), in an experimental investigation of predator-prey relationships in a Minnesota pond, concluded that zooplankton community structure was controlled not only by the abundance of vertebrate predators, but also by the abundance of invertebrate predators and the relative competitive abilities of herbivorous zooplankters. Small-bodied zooplankton are presumably less susceptible to vertebrate predators but also more susceptible to invertebrate predators. Small-bodied zooplankton (including Bosmina longirostris) dominated in vertebrate-free environments when invertebrate predators (e.g., Chaoborus) were rare and the competitive dominant was of intermediate or small size. Janicki and DeCosta (1979) suggested that Bosmina longirostris dominates in acidic Cheat Lake (impacted by acid mine drainage) because of its high reproductive potential and the intolerance of its major predator, Mesocyclops edax, to acidic conditions. Populations of a number of crustacean planktonic predators including Epischura lacustris, Leptodora kindti, and Mysis relicta do seem to be reduced in acidic lakes, (Nilssen 1980, Schindler and Turner 1982; Table 5-7). Data on abundance of Chaoborus are scarce and somewhat contradictory (Section 5.5.3). The characteristic abundance of small-bodied zooplankton in acidic lakes may, however, be related to a reduced abundance of invertebrate predators. Data are insufficient for a detailed analysis of this hypothesis.

The elimination of fish and the reduced importance of predaceous zooplankton in acidic lakes are probably direct consequences of acidification. Changes in these populations occur while their food supplies are still abundant (National Research Council Canada 1981, Malley et al. 1982). The persistance of small-bodied herbivores is indicative of their tolerance of low pH and elevated metal concentrations. The dominance of small-bodied herbivores may, however, be the result of a complex interaction between declining fish populations, reduced invertebrate predation, increased water clarity, and the relative survival, growth, and reproductive capabilities of zooplankton species in acidic environments.

In addition to changes in zooplankton communities, associated with acidic conditions are marked shifts in the species composition of the phytoplankton community (Section 5.5.2), an important food source for zooplankton. Some algae are more edible than others (Porter 1977). A

high proportion of the phytoplankton in many acidic lakes are dinoflagellates, a relatively large phytoplankter that may be less readily consumed and digested by many herbivorous zooplankters. Yan and Strus (1980) found that the average diameter of the alga Peridinium inconspicuum, the dominant phytoplankter in acidic Clearwater Lake, was 14 μm. Yet, the maximum size of a particle likely to be ingested by Bosmina longirostris, the dominant zooplankter, was 10 to 14 μm, with 85 percent of the particles ingested usually less than 5 μm in diameter. The dominant phytoplankter, comprising almost one-half of the phytoplankton biomass in Clearwater Lake, may therefore be relatively unavailable as an energy source to the dominant zooplankter in the lake.

It is possible that the dominance of dinoflagellates in acidic waters reflects primarily the change in zooplankton community structure. The abundance of relatively small-bodied, herbivorous zooplankton may result in selective removal of edible algal taxa, and the subsequent dominance of the phytoplankton by larger, inedible forms. Yan and Strus (1980), however, discount this hypothesis. Based on observations in acidic Clearwater Lake, Ontario, Yan and Strus (1980) calculated that the filtering rate for zooplankton in this acidic lake was 5 to 18 times lower than estimated rates for non-acidic oligothrophic lakes in the same region. Assuming these calculations are correct, herbivore grazing should exert little control over phytoplankton community structure.

Alternatively the shift in the phytoplankton community may reflect relative tolerance to low pH and elevated metal levels. If the tolerant species of algae are also less edible, then transfer of energy from phytoplankton to herbivorous zooplankton may be reduced. This may occur even though the total biomass and productivity of these primary producers are comparable to those in circumneutral waters. Repercussions at higher trophic levels (e.g., fish) are possible, but the current level of understanding suggests that changes in phytoplankton community structure are relatively insignificant for the ecosystem as a whole compared to other documented ecological changes associated with acidification.

5.5.4.2 Changes in Productivity--Available data on acidification and primary productivity in acidic lakes yield no clear correlation between pH level and algal biomass or productivity. Primary productivity and/or phytoplankton biomass in a few cases were lower in acidic lakes relative to circumneutral waters; in other cases equal or even greater (Section 5.5.2.2, Table 5-6).

Changes in phytoplankton community biomass and productivity with increased acidity may reflect a balance between positive and negative factors. Differences in the importance of these factors between systems may account for inconsistencies in the response of different aquatic systems to acidic deposition.

The biomass of phytoplankton at any given time is a function of its rate of production vs. its rate of loss. In some acidic systems phytoplankton biomass accumulates (Almer et al. 1978, Yan and Stokes

1978), suggesting either an increase in primary productivity per unit biomass or a decrease in the loss function. No studies have indicated increased productivity per unit biomass with increased acidity (Section 5.5.2.2). Thus, most authors (Hendrey 1976, Hall et al. 1980) have concluded that any accumulation of algal biomass in acidic waters results from a decreased rate of loss or depletion, i.e., decreased grazing or decreased decomposition. Lower zooplankton biomass or shifts in zooplankton community structure (Section 5.5.3) may decrease grazing pressure on phytoplankton. Such a conclusion, however, is purely speculative.

As common as increased standing crops of phytoplankton are observations of decreased biomass associated with acidic conditions. Conclusions that phytoplankton biomass decreased with increasing acidity imply that either rates of production have decreased or rates of loss have increased, or that both have occurred. Although good evidence for lower primary productivity in acidic waters is lacking, there is a theoretical basis suggesting that a number of changes associated with acidification and acidic deposition could reduce productivity. Factors that could decrease primary productivity with declining pH levels include: (1) a shift in pH level below that optimal for algal growth; (2) an increase in metal concentrations above those optimal for growth; (3) decreased nutrient availability; and (4) a shift in species composition within the phytoplankton community to species with lower photosynthetic efficiencies.

Three primary mechanisms have been proposed whereby nutrient availability may be reduced in acidic environments: inhibition of nutrient recycling, decreased availability of inorganic carbon, and/or decreased availability of phosphorus. Grahn et al. (1974) suggested that a decreased rate of decomposition and the accumulation of coarse detritus, benthic algae, and macrophytes (especially Sphagnum) on the bottom of acidic lakes decreased recycling of nutrients and prevented exchange of nutrients and other ions between sediments and the overlying water (Sections 5.3 and 5.4). A reduction in these processes could significantly reduce quantities of nutrients available to primary producers (e.g., Kortmann 1980) and induce what Grahn et al. (1974) termed oligotrophication of the lake system. No data are available however to confirm this hypothesis.

Besides this decrease in nutrient cycling resulting from a biological perturbation, increased acidity may also decrease nutrient availability via chemical interactions. Potential effects on inorganic carbon and phosphorus have received the most attention.

At lower pH levels, the total quantity of inorganic carbon available for algal uptake is reduced and a greater proportion of it occurs as aqueous CO_2 rather than as bicarbonates or carbonates. The National Research Council Canada (1981) calculated that for a typical soft-water lake at pH 4.2 in equilibrium with the atmosphere, the quantity of inorganic carbon consumed by phytoplankton per day amounted to about 14 percent of the total dissolved inorganic carbon available in

the lake. Thus, it is possible that during periods of peak photosynthesis, phytoplankton may take up inorganic carbon from the water at a rate faster than it can be replaced by diffusion from the atmosphere. Phytoplankton productivity at these times may be carbon limited. The significance of these occasional limitations during periods of peak photosynthesis to annual levels of production has not been evaluated.

In oligotrophic lakes, phosphorus availability often limits primary production (Wetzel 1975, Schindler 1975). Chemical interactions between aluminum and phosphorus (Chapter E-4, Section 4.6.3.5) in acidic waters or within watersheds receiving acidic depositions, may decrease phosphorus availability with decreasing pH level and, as a result, decrease primary productivity. Despite considerable research on the chemical nature of aluminum-phosphorus interactions, no field studies regarding acidification of surface waters have been completed to confirm or reject this hypothesis.

Shifts in species composition within the phytoplankon community with increased acidity were discussed in preceding sections. It is possible that species of algae predominating in acidic waters have inherently lower levels of photosynthetic efficiency than do species dominant in similar but non-acidic waters. In this case, a reduced level of primary productivity may be an indirect effect of the shift in species composition. Following removal of the fish population from an oligotrophic, circumneutral lake in Sweden, not only did the species composition and diversity of the phytoplankton community change, but limnetic primary production was reduced (Henrikson et al. 1980a,b). It was hypothesized that, with the removal of fish, increased grazing pressure by zooplankton selected for relatively inedible forms of algae, and the inedible forms were less productive and less efficient users of available nutrients, in part because of their larger size. None of these hypotheses has been tested. Andersson et al. (1978a) also found decreased primary productivity in the absence of fish, and Redfield (1980) varied zooplankton grazing intensity and determined that concentrated grazing decreased algal productivity.

Despite these apparently good reasons for why acidification should decrease primary productivity, the available evidence suggestss that there is no consistent decrease. In part, this may reflect counterbalancing factors working to increase productivity with acidification, e.g., increased lake transparency or, to a lesser extent, increased nutrient availability resulting from plant nutrients associated with acidic deposition.

A notable feature of many acidic lakes is their remarkable clarity. Water chemistry changes with acidification that may contribute to increased water clarity are discussed in Chapter E-4, Section 4.6.3.4. As the absorption and scattering of light in the water decreases with acidification: (1) a greater amount of light may be available for photosynthesis; (2) light may penetrate to greater depths increasing the size of the euphotic zone; and (3) adequate light for photosynthesis may

extend down into the thermocline and hypolimnion where nutrient levels are generally higher (Johnson et al. 1970). Thus, photosynthesis per unit area of lake surface may increase.

Associated with acidic deposition are relatively large inputs of sulfate and nitrate (Chapter E-4, Section 4.4.1). Both are nutrients required for plant growth. Productivity in most oligotrophic lakes, however, is phosphorus-limited. Thus, nutrients associated with acidic deposition probably stimulate primary productivity very little. In the few lakes that are nitrogen-limited, the response may be more significant, but no studies are available to confirm this.

It is obvious that transformations in the structure and function of the plankton community with increased acidity are the result of a complex series of reactions. There is no simple explanation for why observed differences or changes occur, nor is there any reason to expect responses to be identical in different aquatic systems. Photosynthesis by phytoplankton plays a significant role in driving and controlling the metabolism of lakes (Section 5.5.1.2). Any decrease in productivity could have repercussions at all trophic levels, including reduced fish production. The limited evidence available (Section 5.6), however, indicates that direct effects of acidification on fish appear more important than indirect food chain effects. Thus, although acidification affects the quality and may, to a lesser extent, affect the quantity of plankton production, the significance of these changes to the aquatic ecosystem as a whole has yet to be established.

5.5.5 Summary

- Acidification results in a marked shift in the structure of the plankton community. For both phytoplankton and zoolankton, the total number of species represented decreases with increasing acidity. For zooplankton, the greatest change in species composition occurs in the pH range 5.0 to 5.3; for phytoplankton, in the pH interval 5.0 to 6.0.

- Zooplankton communities in acidic lakes are simplifications of communities typical of circumneutral lakes in the region. Species dominant in acidic lakes are also important components of zooplankton communities in non-acidic lakes. In Scandinavia, acidic lakes (pH < 5.0) are characterized by the prevalence of *Diaptomus gracilis*, and *Bosmina coregoni* or *Bosmina longispina*. In North America the typical dominant association in acidic waters is *Diaptomus minutus* and/or *Bosmina longirostris*.

- Generalizations about changes in community structure for phytoplankton populations with acidification are more difficult to make. In many acidic waters (but certainly not all), dinoflagellates (Phylum Pyrrophyta) predominate. Dinoflagellate species *Peridinium inconspicuum* and *Peridinium limbatum* in particular are reported as dominants, often

constituting large proportions of the total biomass. Dinoflagellates also occur in circumneutral lakes. Their abundance in acidic lakes is often counterbalanced by the absence of most planktonic species of diatoms and some common species of green algae, blue-green algae, and chrysophyceans.

- Despite the altered structure of the plankton community, productivity may remain unaffected. Relative to levels of primary (phytoplankton) productivity in circumneutral lakes, primary productivity in acidic lakes in some cases islower, in others equal. A cause-and-effect relationship between primary productivity and acidification has not yet been established. In two field experiments, increased acidity resulted in increased phytoplankton biomass. In one field experiment, acidification had no effect on phytoplankton biomass.

- Data on zooplankton productivity in acidic lakes are non-existent. In three lake surveys, zooplankton biomass was lower in acidic lakes than in circumneutral lakes in the same region. In contrast, in two field acidification experiments, zooplankton standing crop was unchanged, or even slightly increased.

- Shifts in the structure and function of the plankton community with acidification may represent both direct and indirect reactions to the decrease in pH level. Associated with the increased acidity are modifications in a large number of other chemical, biological, and physical aspects of the environment whose changes may affect the plankton community. Because of the complexities of these interactions, little is known about what controls potential changes in phytoplankton and zooplankton communities, why responses differ in different lakes, and the significance of these changes to other trophic levels. Loss of fish populations seems to occur independently of effects of acidification on lower trophic levels. However, phytoplankton and zooplankton do play significant roles in nutrient and energy cycling.

5.6 FISHES (J. P. Baker)

5.6.1 Introduction

The clearest evidence for impacts of acidification on aquatic biota is the documentation of adverse effects on fish populations. The literature is extensive and varied. Available data on effects of acidification on fish are of at least seven types:

1) historic records of declining fish populations in lakes and rivers, coupled with historic records of increasing acidity;

2) historic records of declining fish populations in lakes and rivers currently acidic but with no historic records on levels of acidity;

3) regional lake survey data and correlations of present-day fish status with present-day acidity levels in lakes and rivers;

4) data on success/failure of fish stocking efforts related to acidity of the surface water;

5) experimental acidification of aquatic ecosystems and observations of biological responses;

6) results of in situ exposures of fish to acidic waters; and

7) laboratory bioassay data on survival, growth, behavior and physiological responses of fish to low pH, elevated aluminum concentrations, and other water quality conditions associated with acidification.

Each of these data sets is reviewed: numbers (1) through (4) in Section 5.6.2, Field Observations; numbers (5) and (6) in Section 5.6.3, Field Experiments; and number (7) in Section 5.6.4, Laboratory Experiments. Combined, they provide strong evidence that acidification of surface waters has adverse effects on fish, in some cases resulting in the gradual extinction of fish populations from acidified lakes and rivers.

Loss of fish populations from acidified surface waters is not, however, a simple process and cannot be accurately summarized as "X" pH results in the disappearance of "Y" species of fish. At the very least, biological and chemical variation within and between aquatic ecosystems must be taken into account. For example, tolerance of fish to acidic conditions varies markedly, not only between different species but also between different strains or populations of the same species and among individuals within the same population. In addition, the water chemistry within an acidified aquatic system typically undergoes substantial temporal and spatial fluctuations. The survival of a population of fish may be more closely keyed to the timing and duration of acid episodes in relation to the presence of particularly sensitive life history stages, or to the availability of "refuge areas" during acid episodes, or to the availability of spawning areas with suitable water quality, than to any expression of the annual average water quality. Because of these complexities, summary of effects of acidification on fish in one or a few simple concluding tables can be misleading. In addition, our understanding of functional relationships between acidification and fish responses is still incomplete.

5.6.2 Field Observations

By themselves, field observations often fail to establish cause-and-effect responses definitively. Most extensive field observations are simply correlations between acidity of surface waters

and absence of various fish species. Unfortunately, only in a few instances are historic records available that provide concurrent documentation of the decline of the fish population and the gradual increase in water acidity. Clear demonstration that the absence of fish resulted from high acidity requires supporting evidence from experiments conducted in the field or laboratory. A review of observed fish population changes apparently related to acidification does, however, serve to establish the nature and extent of the potential impact of acidification on fish.

5.6.2.1 Loss of Populations

5.6.2.1.1 United States

5.6.2.1.1.1 Adirondack Region of New York State. The Adirondack region of New York State is the largest sensitive (low alkalinity) lake district in the eastern United States where extensive acidification has been reported (Chapter E-4, Section 4.4.3.1.2.3). The region encompasses approximately 2877 individual lakes and ponds (114,000 surface ha) (Pfeiffer and Festa 1980), and an estimated 9350 km (6700 ha) of significant fishing streams (Colquhoun et al. 1981). Twenty-two fish species are native to the region, including brook trout (Salvelinus fontinalis), lake trout (Salvelinus namaycush), brown bullhead (Ictalurus nebulosus), white sucker (Catostomus commersoni), creek chub (Semotilus atromaculatus), lake chub (Couesious plurebeus), and canmar shiner (Notropis cornutus) (Greeley and Bishop 1932). In addition, a variety of other species (e.g., smallmouth bass, Micropterus dolomieui; yellow perch, Perca flavescens) have been introduced into Adirondack waters, especially into the larger, more accessible lakes. Brook trout are frequently the only game fish species resident in the many small headwater ponds that are located at high elevations and are particularly susceptible to acidification (Pfeiffer and Festa 1980). Although native to the Adirondacks, in some waters brook trout populations were introduced and must be maintained by stocking due to a lack of suitable spawning area.

Information relevant to effects of acidification on Adirondack fish populations evolves primarily from three sources: (1) a comprehensive survey of water quality and fish populations in many Adirondack surface waters conducted by the New York State Conservation Department in the 1920's and 1930's (Greeley and Bishop 1932), followed by sporadic sampling of lakes and rivers up until the 1970's (data maintained on file by the State); (2) in 1975, a complete survey of all lakes (214) located above an elevation of 610 m (Schofield 1976b); and (3) from 1978 to the present, accelerated sampling by the New York State Department of Environmental Conservation (DEC) of low alkalinity lakes or lakes that contain particularly valuable fisheries resources (Pfeiffer and Festa 1980). In addition, a preliminary survey of fish populations and water quality for 42 Adirondack streams was completed by the DEC in 1980 (Colquhoun et al. 1981). None of these efforts has involved intensive studies of individual aquatic systems.

Evaluations of Adirondack data to date are limited to correlations of present-day fish status with present-day pH levels and, for a limited number of lakes, a comparison of current data with historic data on pH and fish population status. Each of the studies concluded that the geographic distribution of fish is strongly correlated with pH level, and that the disappearance of fish populations appears to have been associated with declines in pH. Indices of fish populations in Adirondack streams were statistically ($p < 0.05$) correlated with pH measurements (taken in the spring 1980) (Colquhoun et al. 1981). Schofield (1976b, 1981, 1982) noted fewer fish species in lakes with pH levels below 5.0 (Figure 5-4). Schofield and Trojnar (1980) also observed that poor stocking success for brook trout stocked into 53 Adirondack lakes was significantly ($p < 0.01$) correlated with low pH and elevated aluminum levels.

In many of the acid waters surveyed in the 1970's, no fish species were found. In high elevation lakes, about 50 percent of the lakes had pH less than 5.0 and 82 percent of these acidic lakes were devoid of fish. Thus, of the total lakes surveyed, 48 percent had no fish. High elevation lakes, however, constitute a particularly sensitive subset of Adirondack lakes, and these percentages do not apply to the entire Adirondack region. Unfortunately, neither a complete survey nor a random subsampling of all Adirondack lakes and streams has yet been attempted.

All lakes now devoid of fish need not, however, have lost their fish populations as a result of acidification or acidic deposition. A portion of these lakes never sustained fish populations. In addition, if earlier fish populations have disappeared, it must be demonstrated that acidification was the cause.

For 40 of the 214 high elevation lakes, historic records are available from the 1930's (Chapter E-4, Figure 4-18) (Schofield 1976b). In 1975, 19 of these 40 lakes had pH levels below 5.0, and also had no fish. An additional two lakes with pH 5.0 to 5.5 also had no fish. Thus, 52 percent had no fish. In the 1930's, only three lakes had pH levels below 5.0 and, again, none of these had fish at that time. One additional lake with a pH 6.0 to 6.5 also had no fish. Thus, in the 1930's, only 10 percent of the 40 lakes had no fish. This implies that 17 lakes (or 42 percent) have lost their fish populations over the 40-year period. If this holds true for high elevation lakes in general, then 39 percent (83 lakes) of the high elevation Adirondack lakes may have actually lost fish populations. However, this assumes that the subset of 40 lakes represents an unbiased subsample of the 214 high elevation Adirondack lakes.

For Adirondack lakes in general, the DEC reports that about 180 lakes (6 percent of the total), representing some 2900 ha (3 percent of the total), have lost their fish populations (Pfeiffer and Festa 1980, Schofield 1981). The basis for this estimation has not, however, been clearly delineated. Presumably, there are 180 lakes for which recent (1970's) fish sampling efforts have yielded no fish and for which

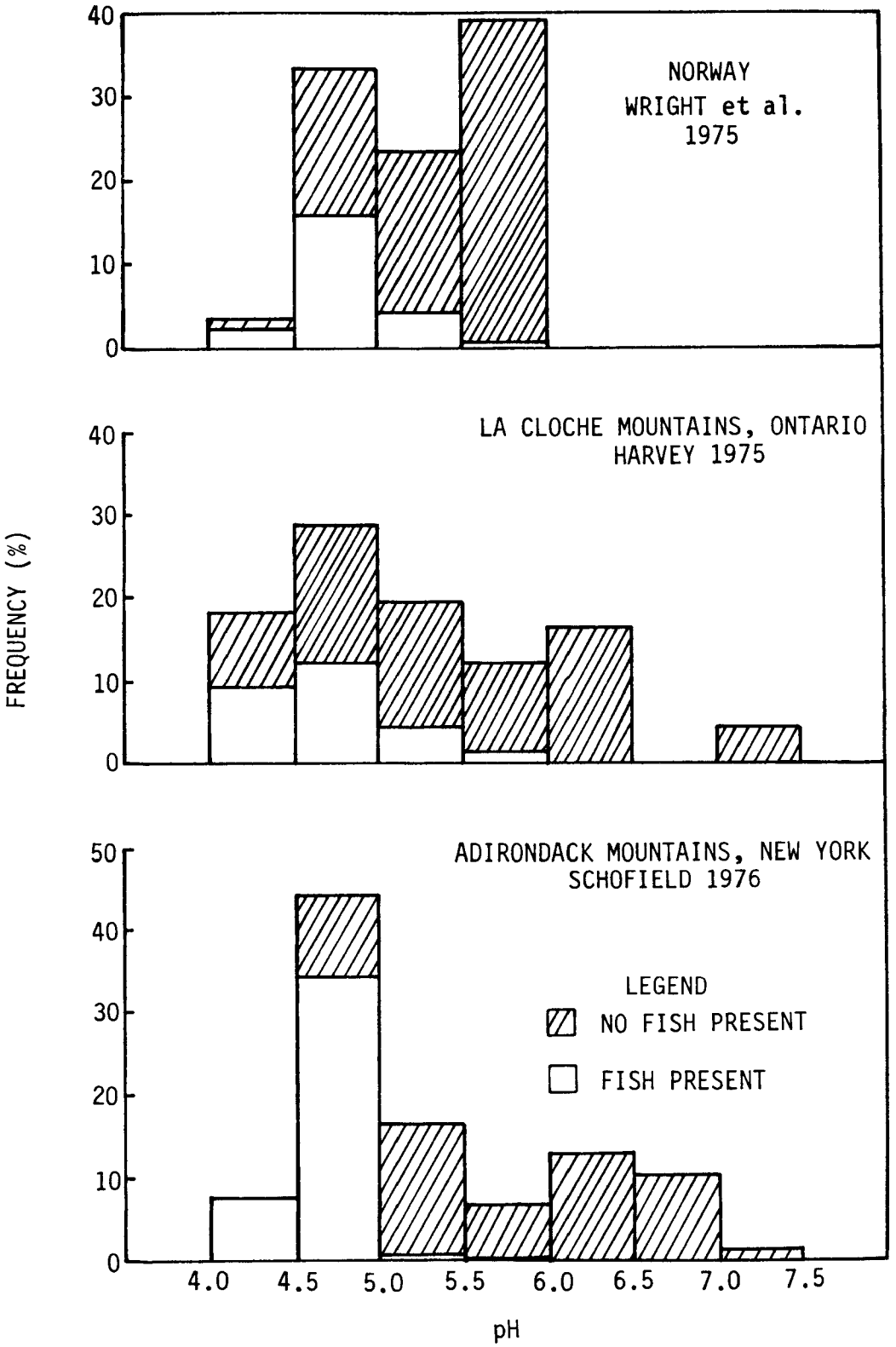

Figure 5-4. Distribution of fish in relation to lake pH.

historic records of fish surveys (1930's to 1960's) are available that indicate the presence of fish in earlier years. All are listed as former brook trout ponds (Pfeiffer and Festa 1980). Because the names of these lakes have not been published and the data are available only in DEC files, this important conclusion cannot be critiqued or validated.

It is also necessary to demonstrate that the loss of fish from Adirondack lakes has occurred as a result of acidic deposition and/or acidification of surface waters.

Retzsch et al. (1982) argued that "although precipitation acidity cannot be excluded as a possible cause, it represents only one of a number of factors that may alter fish populations in the Adirondacks." They consider that loss of fish populations in the Adirondacks may also be a result of (1) natural acidification with the development of naturally acidic wetlands adjacent to lakes (see Chapter E-4, Section 4.4.3.3.); (2) declines in the number of fish stocked into Adirondack lakes and changes in management practices; (3) introductions of non-native fish species; (4) increased recreational use and fishing pressure; and (5) construction of dams (manmade or beaver) and manipulations of lake levels and stream flow.

All of these reasons sound feasible, yet the DEC argues in return that loss of fish has occurred in the absence of alternative explanations other than acidification of surface waters (N.Y. DEC 1982). For example, inadvertent introductions of non-native fish species occur primarily in accessible low elevation waters that are generally not, at present, impacted critically by acidification. Nongame fish species, not subject to stocking, management, or fishing pressure, have also been reduced or eliminated. In addition, numerous waters located in the immediate proximity of high-use public campgrounds in the Adirondacks have maintained excellent trout populations throughout the years despite heavy fishing pressure (N.Y. DEC 1982). Dean et al. (1979) evaluated the impact of black fly larvacide on 42 Adirondack stream fish populations and found no significant differences in occurrence and density of fish in treated versus untreated streams. By default, acidification has been implicated as a factor causing the loss of fish in a number of lakes and streams.

A detailed analysis of the raw data set has not, however, been published that examines, for individual lakes, evidence for loss of fish populations and potential explanations for these losses, including acidification. Still, the data set in total is sufficient to conclude that loss of fish in the Adirondacks, at least for some surface waters, was associated with acidification. The number of fish populations adversely impacted, and the significance of these losses relative to the total resource available in the Adirondacks is, however, inadequately quantified at the present time.

5.6.2.1.1.2 Other regions of the eastern United States. Schofield (1982) summarized available data relating water acidity and fish

population status for areas in the eastern United States with waters potentially acidified by acidic deposition (Chapter E-4, Section 4.4.3.1.2.3). Very few of these studies, with the exception of studies in the Adirondack region, included comprehensive inventories of fish populations or historic changes in fish population status with time. Davis et al. (1978) noted that in Maine lakes biological effects have not yet been detected. Haines (1981a) discussed the potential for adverse effects of acidification on Atlantic salmon (Salmo salar) rivers of the eastern United States. Although the rivers were defined as "vulnerable," no discernable effect on salmon returns was reported. Crisman et al. (1980) sampled gamefish populations in the two most acidic lakes (pH 4.7 and 4.9) in the Trail Ridge area of northern Florida. Populations of largemouth bass (Micropterus salmoides) and bluegull sunfish (Lepomis macrochirus) exhibited no clear evidence of stress directly related to low pH values or elevated aluminum concentrations. In Pennsylvaniva, some fish species have disappeared from a few headwater stream systems (Arnold et al. 1980), but no consistent trends in the data set conclusively demonstrated acidification impacts (Schofield 1982). Section 5.2 reviews the distribution of fish in naturally acidic waters of the United States.

In regions of the United States, other than the Adirondack Mountain area of New York State, no adverse effects of acidic deposition and/or acidification on fish have been definitely identified. Discussions generally refer only to "potential impact."

5.6.2.1.2 Canada

5.6.2.1.2.1 LaCloche Mountain Region of Ontario. Information collected on fish populations in the LaCloche Mountain region of Ontario provides some of the best evidence of adverse effects of acidification on fish. The principal source of acid entering the LaCloche area is sulfur dioxide emitted from the Sudbury smelters located about 65 km northeast (Beamish 1976). Large acidic inputs have resulted in relatively rapid acidification of many of the region's lakes--acidification rapid enough that fish population declines, and in some cases extinctions, have occurred over the course of the 15 years that the lakes have been monitored by researchers from the University of Toronto (H. Harvey, R. Beamish, and other associates).

Metal concentrations measured in acidic waters in the LaCloche area ranged from 2 to 5 μg Cu ℓ^{-1}, 8 to 12 μg Ni ℓ^{-1}, 24 to 36 μg Zn ℓ^{-1}, and 1 to 4 μg Pb ℓ^{-1} (Beamish 1976). Because of atmospheric transport of metals from the relatively nearby Sudbury smelters, these values may be slightly greater than levels typical of acidic waters in other regions discussed in Section 5.6.2.

The LaCloche Mountains cover 1300 km^2 along the north shore of Lake Huron. Contained within this area are 212 lakes, approximately 150 of which have been surveyed for chemical characteristics; 68 for fish populations. Fish populations in several of the lakes have been studied in detail since the late 1960's and early 1970's (Beamish and Harvey

1972, Beamish 1974a,b; Beamish et al. 1975, Harvey 1975). Major sport fishes common in these lakes include lake trout, smallmouth bass, and walleye (Stizostedion vitreum). Other fish occuring very frequently are yellow perch, pumpkinseed sunfish (Lepomis gibbosus), rock bass (Ambloplites rupestris), brown bullhead, lake herring (Coregorus artedii), and white sucker. LaCloche Mountain lakes in general have waters with low ionic content and are quite clear, indicative of low organic acid content (Harvey 1975). Of 150 lakes surveyed in 1971, 22 percent had pH levels below 4.5 and 25 percent were in the pH range of 4.5 to 5.5 (Beamish and Harvey 1972).

Harvey (1975) noted that the number of species of fish in 68 LaCloche Mountain lakes was significantly ($p < 0.005$) correlated with lake pH (Figure 5-4). In addition, however, number of species of fish per lake was also significantly correlated with lake area and other physical features. Because small lakes tend to have low pH values, the effects of these two independent variables on fish may be confounded. A covariate analysis based on data presented in Harvey (1975) indicated, however, that the correlation with lake pH was still significant ($p < 0.005$) even after adjustment for differences in lake area. Of the 31 lakes with pH < 5.0, 14 had no fish. Fourteen lakes had pH values of 6.0 or greater, and all of these had at least one species of fish present with usually seven or more species occurring.

For the 68 LaCloche Mountain lakes surveyed during 1972-73, 38 lakes are known or are suspected to have had reductions in fish species composition (Harvey 1975). Based on historic fisheries information, some 54 fish populations are known to have been lost, including lake trout populations from 17 lakes, smallmouth bass from 12 lakes, largemouth bass from four lakes, wallyeye from four lakes, and yellow perch and rock bass from two lakes each. Assuming that lakes with current pH < 6.0 originally contained the same number of species as lakes with an equal surface area and pH > 6.0, an estimated 388 fish populations have been lost from the 50 lakes surveyed with pH < 6.0 (Harvey and Lee 1982).

The gradual disappearance of fish populations with time and with increased acidity has been described in detail for Lumsden Lake, George Lake, and O.S.A. Lake (Table 5-8; Beamish and Harvey 1972, Beamish 1974b, Beamish et al. 1975). Lake pH levels measured in 1961 by Hellige color comparator were 6.8, 6.5, and 5.5 in Lumsden, George, and O.S.A lakes, respectively. In 1971-73, pH levels measured in the three lakes with a portable pH meter were 4.4, 4.8 to 5.3, and 4.4 to 4.9, respectively. In the 1950's, eight species of fish were reported in Lumsden Lake. Over the period 1961-71, a drastic decline in the abundance of both game and non game fish occurred. In George Lake, during the interval 1961-73, lake trout, walleye, burbot, and smallmouth bass disappeared from the lake, and from 1967 to 1972 the white sucker population decreased in number by 75 percent and in biomass by 90 percent. For O.S.A. Lake in 1961, local residents reported good catches of lake trout and smallmouth bass. In 1972, intensive fish sampling

TABLE 5-8. LOSS OF FISH SPECIES FROM LUMSDEN LAKE AND GEORGE LAKE, ONTARIO (FROM BEAMISH AND HARVEY 1972, BEAMISH ET AL. 1975, HARVEY AND LEE 1982)

Date	Species information
Lumsden Lake	
1950's	Eight species present
1960	Last report of yellow perch Last report of burbot
1960-65	Sport fishery fails
1967	Last capture of lake trout Last capture of slimy sculpin
1968	White sucker suddenly rare
1969	Last capture of trout-perch Last capture of lake herring
1969	Last capture of white sucker
1970	Last capture of lake chub
George Lake	
1961	Last spawning of walleye
1965	Last capture of smallmouth bass
1966	Last spawning of lake trout Last capture of trout-perch
1970	Last capture of burbot Most white suckers fail to spawn
1971	Last capture of walleye Brown bullhead fail to spawn
1972	Northern pike, pumpkinseed sunfish, rockbass, brown bullhead, and white sucker fail to spawn Last capture of lake white fish
1973	Lake trout rare

TABLE 5-8. CONTINUED

Date	Species information
George Lake (continued)	
1974	Northern pike and pumpkinseed sunfish rare
1978	Few age classes of white suckers remain
1979	Brook trout and muskellunge rare White sucker, brown bullhead, rock bass, lake herring, and yellow perch present

yielded only four yellow perch, two rock bass, and eight lake herring. By 1980, no fish remained (Harvey and Lee 1980).

Harvey (1979) summarized the apparent tolerance of fish in the LaCloche Mountain region to pH, based on the occurrence of species in lake surveys and their disappearance with acidification (Figure 5-5). Beamish (1976) concluded that increased acidity was the principal factor resulting in the loss of fish populations.

5.6.2.1.2.2 Other areas of Ontario. Harvey (1980) estimated that approximately 200 lakes in Ontario have lost their fish populations. For the most part, however, these lakes are in the vicinity of Sudbury, Ontario. Studies that suggest fish loss in response to acidification for other areas of Ontario are very limited. Although the Muskoka-Haliburton region of Ontario receives large inputs of acidic deposition, and decreases in alkalinity have been suggested for some lakes (Chapter E-4, Section 4.4.3.1.2.2), no adverse effects on fish populations have been documented; pH values apparently have not decreased to levels harmful to fish.

5.6.2.1.2.3 Nova Scotia. In Novia Scotia, rivers with pH < 5.4 occur only in areas underlain by granitic and metamorphic rock; all flow in a southerly direction to the Atlantic Coast (Watt et al. 1983). Thirty-seven rivers within this region have historic records indicating that they sustained anadromous runs of Atlantic salmon. For 27 of these rivers (Table 5-9), almost complete angling catch records are available from annual reports of Federal Fishery Offices for the period 1936 to 1980. Of these 27, five rivers have undergone major alterations since 1936 that potentially could have impacted salmon stocks. For the 22 remaining rivers, 12 presently have pH > 5. Statistical analysis of angling catch from 1936 to 1980 indicated that only one of these 12 rivers had experienced a significant ($p < 0.01$) decline in salmon catch since 1936, one river a significant ($p < 0.05$) increase, and 10 no significant trend in angling catch with time. In contrast, of the 10 rivers with current pH < 5.0, nine have had significant ($p < 0.02$) declines in success since 1936, and one, no significant trend.

Salmon angling records for rivers with pH < 5.0 vs pH > 5.0 are compared in Figure 5-6. From 1936 through the early 1950's, angling catch in the two groups of rivers were similar. After the 1950's, angling catch in rivers with pH < 5.0 declined, while salmon catch in rivers with pH > 5.0 continued to show no significant trend with time.

Year-to-year variations in salmon catch are considerable, reflecting the many factors affecting angling success and reporting accuracy. Between the two groups of rivers (pH < 5.0 and pH > 5.0), however, occurrence of high and low success years, generally correspond. Both groups of rivers are well distributed along the 500 km Atlantic coastline of Nova Scotia. Tag return data suggest that salmon stocks in this area all share a common marine migratory pattern. Biological and physical factors leading to greater or lesser angler success (e.g., sea survival, river discharge rates, or juvenile year-class survival)

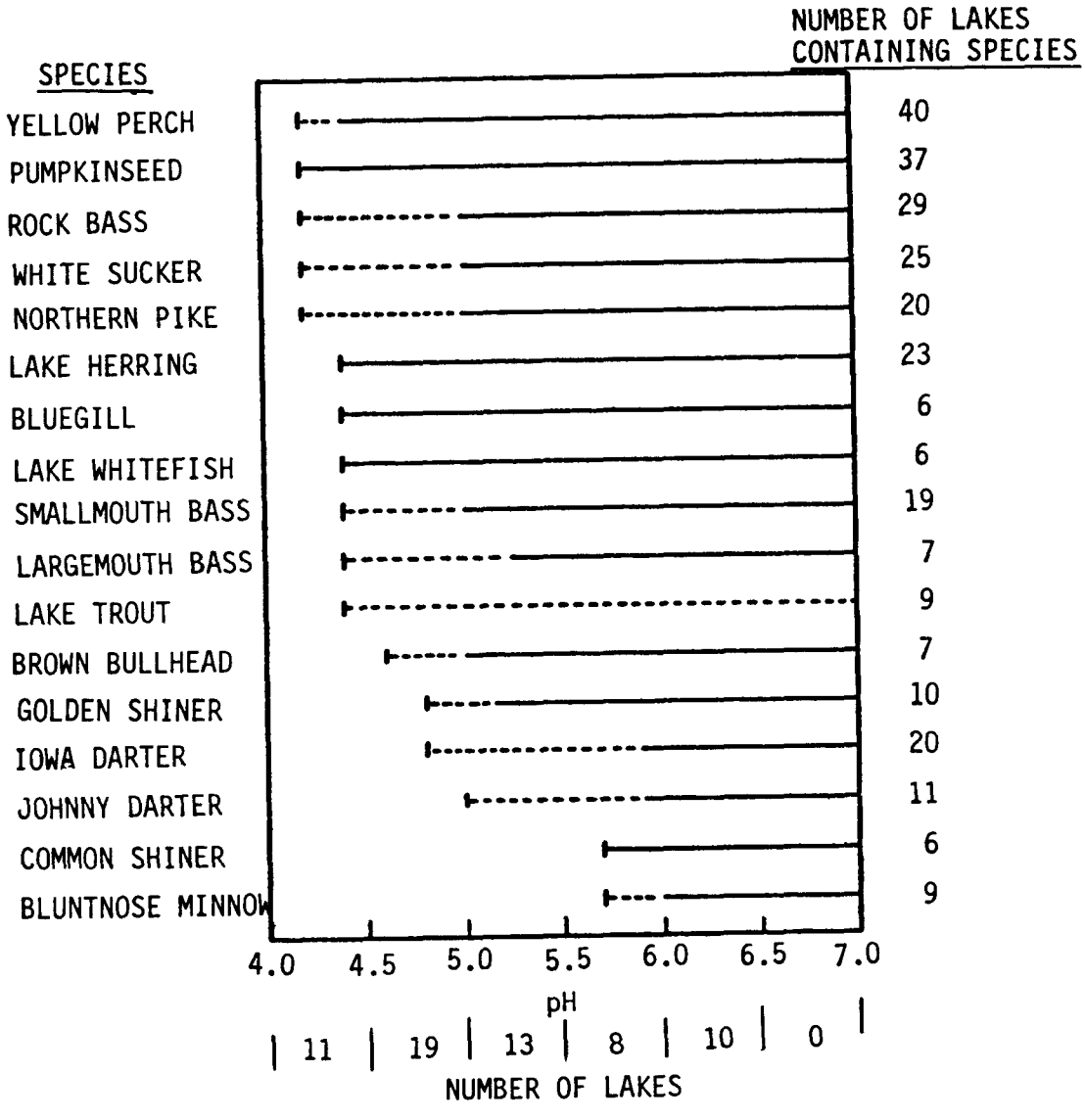

Figure 5-5. Frequency of occurrence of fish species in six or more La Cloche Mountain lakes in relation to pH. Vertical bar, lowest pH recorded; dashed line, stressed populations, e.g., missing year classes; solid line, populations which appear unaffected (Harvey 1979).

TABLE 5-9. MAJOR RIVERS IN NOVA SCOTIA ON THE ATLANTIC COAST, pH LEVELS AND STATUS OF ATLANTIC SALMON STOCKS

River	Mean[a] pH 1980-81	Range[b] pH 1979-80	Recorded Presence (+) or Absence (-) of Salmon[c] <1960	1980-82	Regression of Angling Catch on Year[d]
Musquodoboit[e]	6.7	6.6-6.9	+		-
St. Mary's	6.1	6.1-6.8	+	+	NS
LeHave*		6.0-6.1			D
Ecum Secum	5.7		+		NS
Petit	5.6		+		NS
Ship Harbour	5.6	5.6-5.9	+		NS
Gold	5.5	5.6-6.0	+	+	+
Salmon (Digby)		5.1-5.7			D
East Ship Harbour		5.3-5.4			D
West Ship Harbour		5.0-5.4			D
Moser	5.4	5.5-6.2	+		NS
Quoddy	5.4		+		NS
Kirby	5.4		+		NS
Medway[e]	5.4	5.2-5.8	+	+	NS
Salmon (Port Dufferin)	5.3		+		NS
Gaspereau	5.2		+		NS
Mersey[e]		4.9-5.4			D
Middle	5.0		+	+	-
Liscomb	5.0	5.0-5.3	+		NS
Ingram	5.0	5.0-5.5	+	+	-
Tangier	4.9		+	-	-
East	4.8	4.9-5.1	+	+	-
Tusket	4.8	4.5-4.8	+		-
Issacs Harbour	4.8		+		-
Nine Mile	4.8		+		-
Salmon (Lawrencetown)	4.7		+	-	-
Clyde	4.6	4.6-4.6	+	-	-
Barrington		4.5-4.7	+	-	
Jordan		4.4-4.6	+	-	
Sable		4.3-4.6	+	-	
Broad		4.3-4.5	+	-	
Roseway[e]		4.3-4.5	+	-	
Larry's[f]					

TABLE 5-9. CONTINUED

[a]Watt et al. 1983, Rivers with 1980-81 mean pH recorded have angling data available over the past 45 years and are represented in Figure 5-11.

[b]Farmer et al. 1981; pH range from three pH measurements per river--April or May 1979, September or November 1979, and February or March 1980.

[c]Watt et al. 1983; <1960 Presence/Absence based on catch records; 1980-82 based on electrofishing for juvenile salmon and/or catch data.

[d]Watt et al. 1983; 27 rivers with angling records 1936 to 1980--no significant trend (NS), significant increase in catch with time (+) decrease in catch with time (-), major disturbance in watershed (D).

[e]Historical pH records available.

[f]pH level reported as < 4.7 in Watt et al. 1983.

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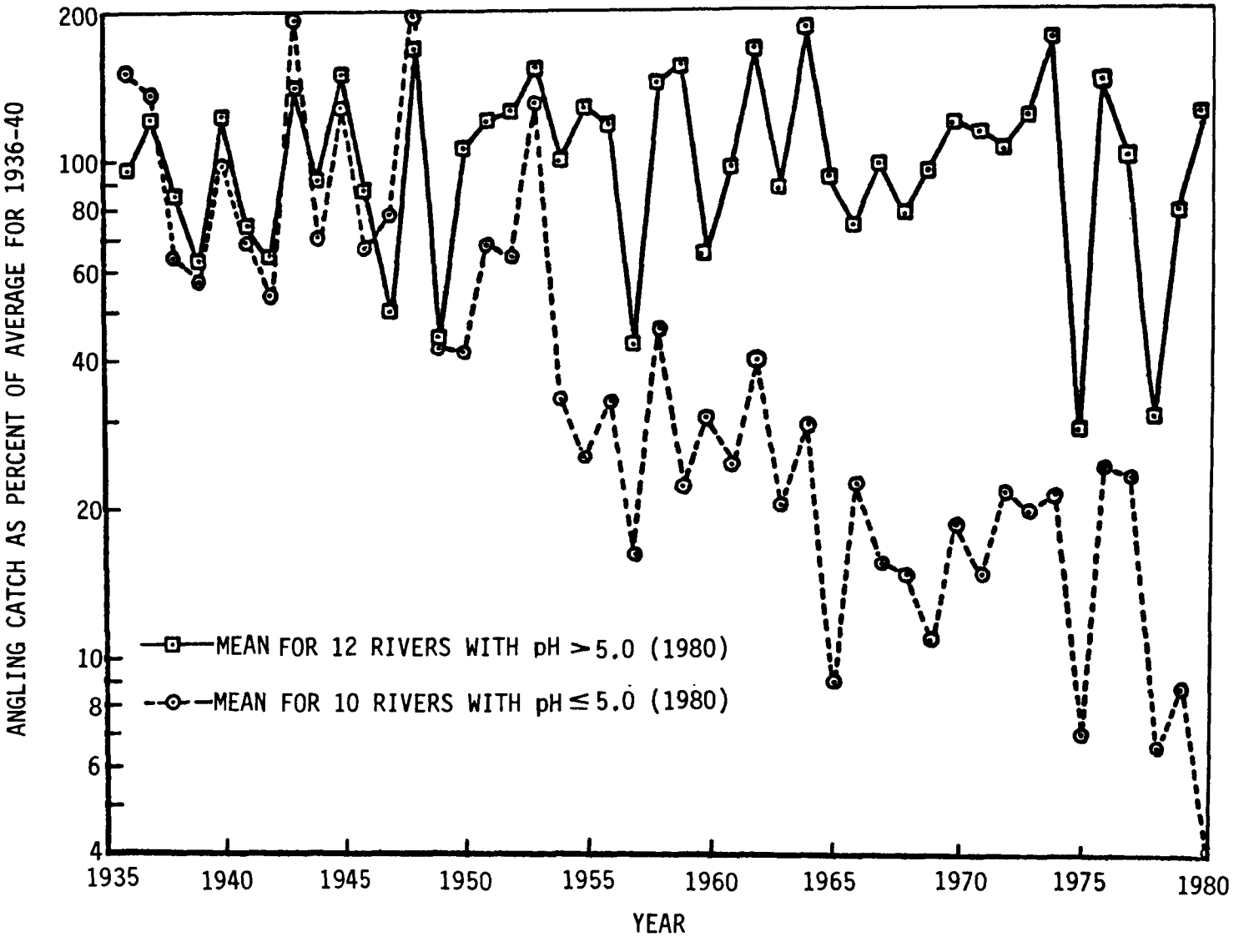

Figure 5-6. Average angling success for Atlantic salmon in 22 Nova Scotia rivers since 1936. Data were collected from reports of federal fishery offices and normalized by expressing each river's angling catch as a percentage of the average catch in that river during the first 5 years of record (1936-40) (Watt et al. 1983).

probably act uniformly over the entire area (Watt et al. 1983). Decreases in salmon catch over time are, on the other hand, clearly correlated with present-day pH values 5.0 and below.

Watt et al. (1983), concluded that at present in Nova Scotia, seven former salmon rivers with mean annual pH < 4.7 no longer support salmon runs (Table 5-9). An electrofishing survey in the summer of 1980 failed to find any signs of Atlantic salmon reproduction in any of these seven rivers. Farmer et al. (1980), however, observed that for the most part these rivers are all also naturally somewhat acidic (highly colored waters, indicating the presence of organic acids), and historically had relatively low fish production. Peat deposits and bogs are common to much of this area. Inputs from these materials probably contribute to the low pH levels and have some impact on salmon production. Historical records of pH for a few rivers within this area (Chapter E-4, Section 4.4.3.1.2.2) do, however, indicate that acidity has increased in recent years. Acidic conditions and acidification, therefore, probably contribute to the loss of Atlantic salmon populations in Nova Scotia.

The estimated lost (rivers with pH < 4.7) or threatened (rivers with pH 4.7 to 5.0) Atlantic salmon production potential represents 30 percent of the Nova Scotia resource, but only 2 percent of the total Canadian potential. Atlantic salmon rivers salmon in New Brunswick, Prince Edward Island, and other areas of Novia Scotia generally have pH levels above 5.4, and are not under any immediate acid threat (Watt 1981).

5.6.2.1.3 Scandinavia and Great Britian

5.6.2.1.3.1 Norway. Extensive information on acidification and loss of fish populations in Norwegian waters has been collected under the auspices of the joint research project SNSF--"Acid Precipitation-Effects on Forest and Fish," 1972-1980. Documentation of the effects of acidification on fish is derived principally from (1) yearly records of catch of Atlantic salmon in 75 Norwegian rivers from 1876 to the present; (2) a survey of water chemistry and fish population status in 700 small lakes in southern Norway in 1974-75; (3) collation of information on fish population status (current and historic) for some 5000 lakes in southern Norway, validated with testfishing in 93 lakes during 1976-79; and (4) detailed analyses of historic changes in fish population status related to land use changes with time in selected watersheds. Together these data provide strong evidence that acidification has had profound impacts on fish.

Statistical data for the yearly salmon catch from major salmon rivers in Norway have been recorded since 1876 (Figure 5-7) (Jensen and Snekvik 1972, Leivestad et al. 1976, Muniz 1981). While catch in all rivers declined slightly from 1900 until the 1940's, in 68 northern rivers the decline was followed by a marked increase, and catch in the 1970's equalled or exceeded that around 1900. In contrast, in seven southern rivers, annual catch dropped sharply over the years 1910-17, has declined steadily since then, and is now near zero. This decrease

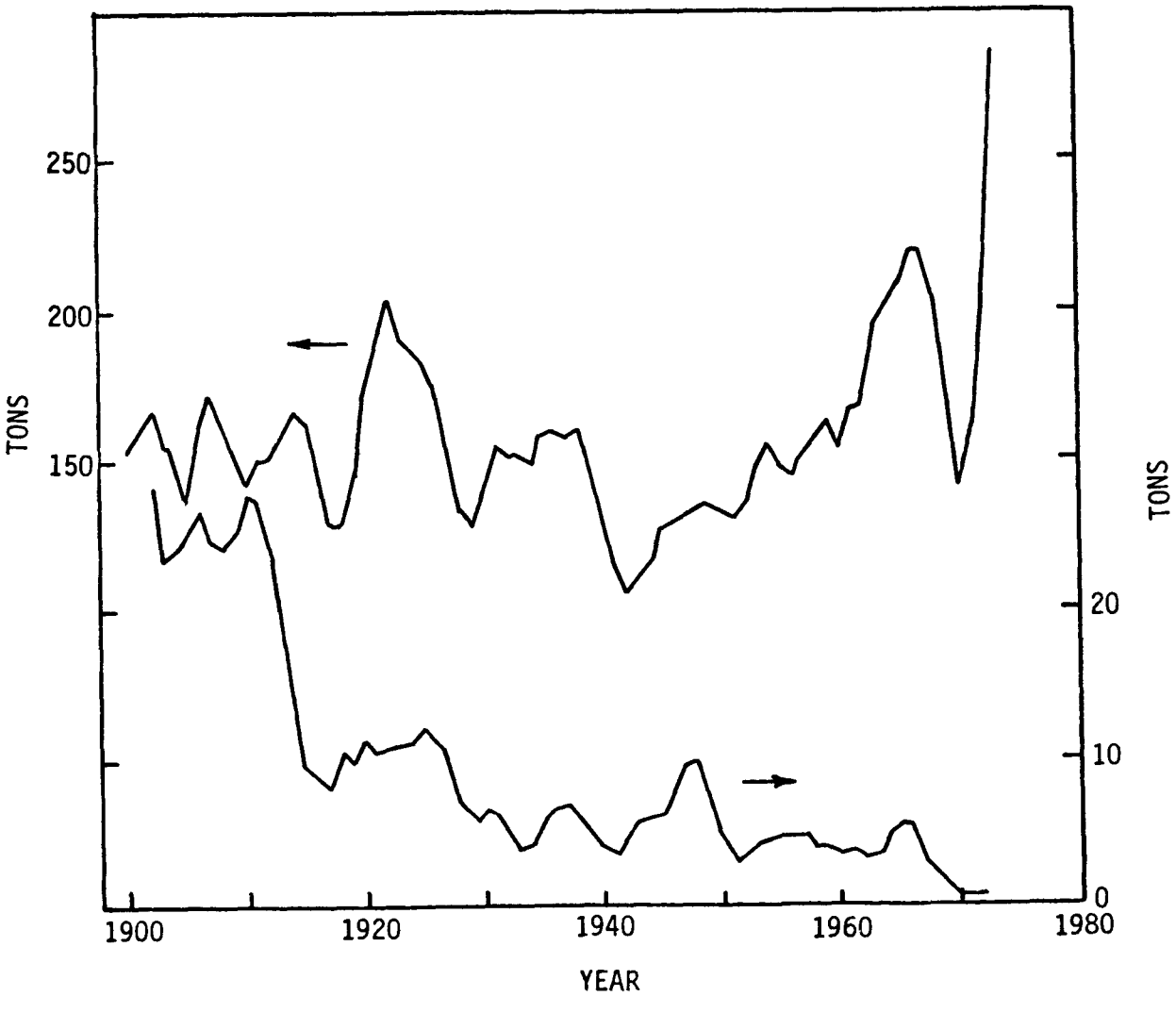

Figure 5-7. Yearly yield for Atlantic Salmon fisheries in seven rivers from the southermost part of Norway (bottom curve) compared with 68 rivers from the rest of the country (top curve). (Leivestad et al. 1976).

is reflected in all seven rivers and cannot be explained by known changes in exploitation practices. Massive fish kills of Atlantic salmon (Section 5.6.2.4) were reported in these rivers as early as 1911. Efforts over the last 50 years to restock with hatchery-reared fry and fingerlings have been unsuccessful. In the seven southern rivers, pH levels averaged 5.12 in 1975, as compared to an average pH of 6.57 for 20 of the 68 northern rivers. Leivestad et al. (1976) reported that acidity in southern rivers has been steadily increasing from 1966 to 1976 hydrogen ion concentration increased by 99 percent.

In 1974-75, the SNSF project completed a synoptic (nonrandom) survey of water chemistry and fish population status in 700 small to medium-sized lakes in Sørlandet (the four southernmost counties of Norway) (Wright and Snekvik 1978). Based on interviews with local residents, fish populations in lakes were classified as barren, sparse population, good population, and overpopulated. The principal species of fish was brown trout (Salmo trutta). Other important species were perch (Perca fluviatilis), char (Salvelinus alpinus), pike (Esox lucius), rainbow trout (Salmo gairdneri), and brook trout. About 40 percent of the 700 lakes were reported as barren of fish, and an additional 40 percent had sparse populations. Fish status was clearly related to water chemistry; most low pH, low conductivity lakes were either barren or had only sparse populations. Above pH 5.5, few lakes were barren. A stepwise multiple regression of fish status against chemical variables pH, NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and HCO_3^- indicated that pH and Ca^{2+} were the two most important chemical variables ($r = 0.53$).

The original data base on fish populations in Sørlandet collected by Jensen and Snekvik (1972) and Wright and Snekvik (1978) has gradually been extended to the whole country. By 1980, data on fish in more than 5000 lakes in the southern half of Norway had been collected by interviewing fisheries authorities, local landowners, local fishermen's associations, and other local experts (Sevaldrud et al. 1980, Overrein et al. 1980, Muniz and Leivestad 1980a). Interview data ware validated for 93 lakes by comparison with results from a standardized testfishing program. Interview data provided an accurate assessment of actual fish stocks for over 90 percent of the lakes (Rosseland et al. 1980).

At present, fish population damage has apparently occurred in an area of 33,000 km^2 in southern Norway. Twenty-two percent of the lakes at low elevations below 200 m have lost their brown trout populations; 68 percent of the trout populations in high altitude lakes above 800 m are now extinct. In 13,000 km^2 of this area, fish populations in all lakes are extinct, or near extinction. Water chemistry data are available for a subset of these 5000 lakes, and again fish population status is clearly correlated with pH (Figure 5-8).

Besides information on the current status of fish populations in these 5000 lakes, the SNSF project has also compiled available historic information on changes in fish populations with time. For almost 3000 lakes in Sørlandet, the population status of brown trout has been

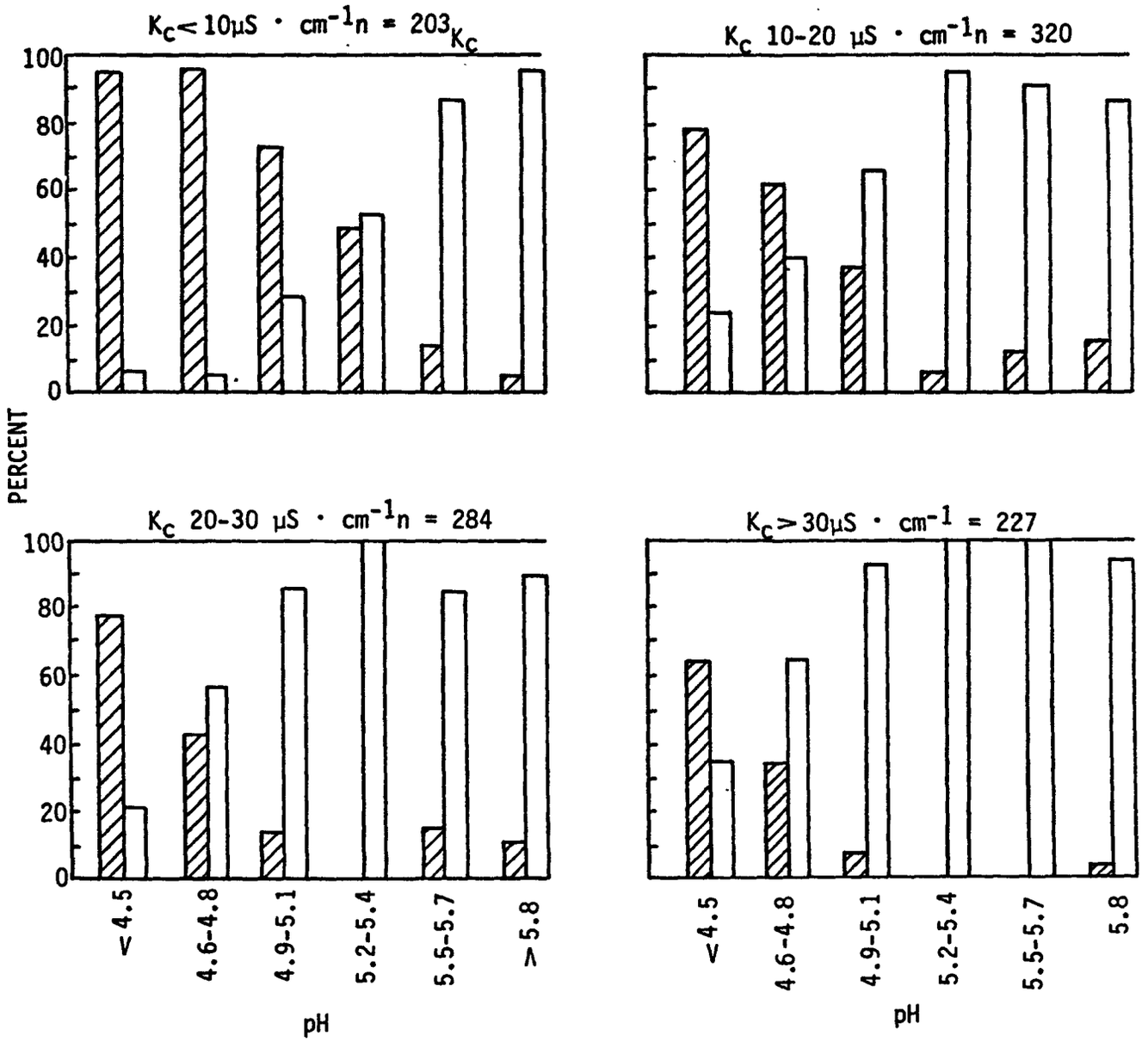

Figure 5-8. Status of brown trout populations from the affected areas in the four southernmost counties (Rogaland, Vest-Agder, Aust-Agder, and Telemark) in Norway grouped according to lake pH and conductivity. The data are given as percentage of lakes with or without trout within each class of pH and conductivity (Muniz and Leivestad 1980a).

recorded by local fishermen since about 1940. The time trend for loss of populations is diagrammed in Figure 5-9. The rate of disappearance of brown trout from lakes in Sørlandet has been particularly rapid since 1960. Today, more than 50 percent of the original populations have been lost, and approximately 60 percent of the remaining are in rapid decline (Sevaldrud et al. 1980). Attempts at restocking acidified lakes containing reduced populations have largely failed (Overrein et al. 1980).

A relationship between water acidity and fish population status or even water acidification and concurrent loss of fish populations does not necessarily implicate acidic deposition as the primary cause for adverse effects on fish. Evidence for the association between acidic deposition and acidification of surface waters is considered in Chapter E-4. However, several studies have been completed in Norway that examine alternate explanations for acidification, e.g., changes in land use, specifically as they relate to historic changes in fish populations (Drabløs and Sevaldrud 1980, Drabløs et al. 1980). In each of three study areas, no correlation between shifts in land use and human activities and changes in fish status was found. Areas that have experienced changes in land use (e.g., abandonment of pasture farms or discontinuance of lichen harvests) do not have any higher proportion of lakes with declines in fish population than do areas without such land use changes. In contrast, fish population declines are correlated with inputs of acidic deposition.

5.6.2.1.3.2 Sweden. Sweden has about 90,000 lakes, many of which have low alkalinity and are potentially sensitive to acidic deposition. Extensive surveys of acidification and fish population status, have not, however, been completed. In southern Sweden, 100 lakes with pH 4.3 to 7.5 were sampled in the 1970's (Almer et al. 1978). Apparently as a result of acidification (i.e., disappearance of fish was associated with current low pH levels in lakes), 43 percent of the minnow (Phoxinus phoxinus) populations, 32 percent of the roach (Rutilus rutilus), 19 percent of the artic char, and 14 percent of the brown trout populations had been lost. In a study of six lakes in southern Sweden, Grahn et al. (1974) cited historic pH data suggesting a pH decline of 1.4 to 1.7 units since the 1930's-40's and the simultaneous elimination of minnows, roach, pike and brown trout from two or more of these six lakes. Disappearances of populations of roach in lakes in southwestern Sweden were recorded as early as the 1920's and 1930's (although not definitely correlated with acidification) (Dickson 1975). In eastern Sweden, loss of roach from Lake Arsjon near Stockholm occurred in association with a decrease in pH readings: pH 5.1 to 5.3 in 1974 as compared to pH 6.0 measured colometrically in the 1940's (Milbrink and Johansson 1975).

5.6.2.1.3.3 Scotland. Investigations in Scotland (Harriman and Morrison 1980, 1982) indicated that intensive afforestation can result in acidification of streams and subsequent reduction and loss of fish populations. The role of acidic deposition in this acidification process has not yet been clearly established. In a study of 12 streams draining forested and nonforested catchments, an electrofishing survey

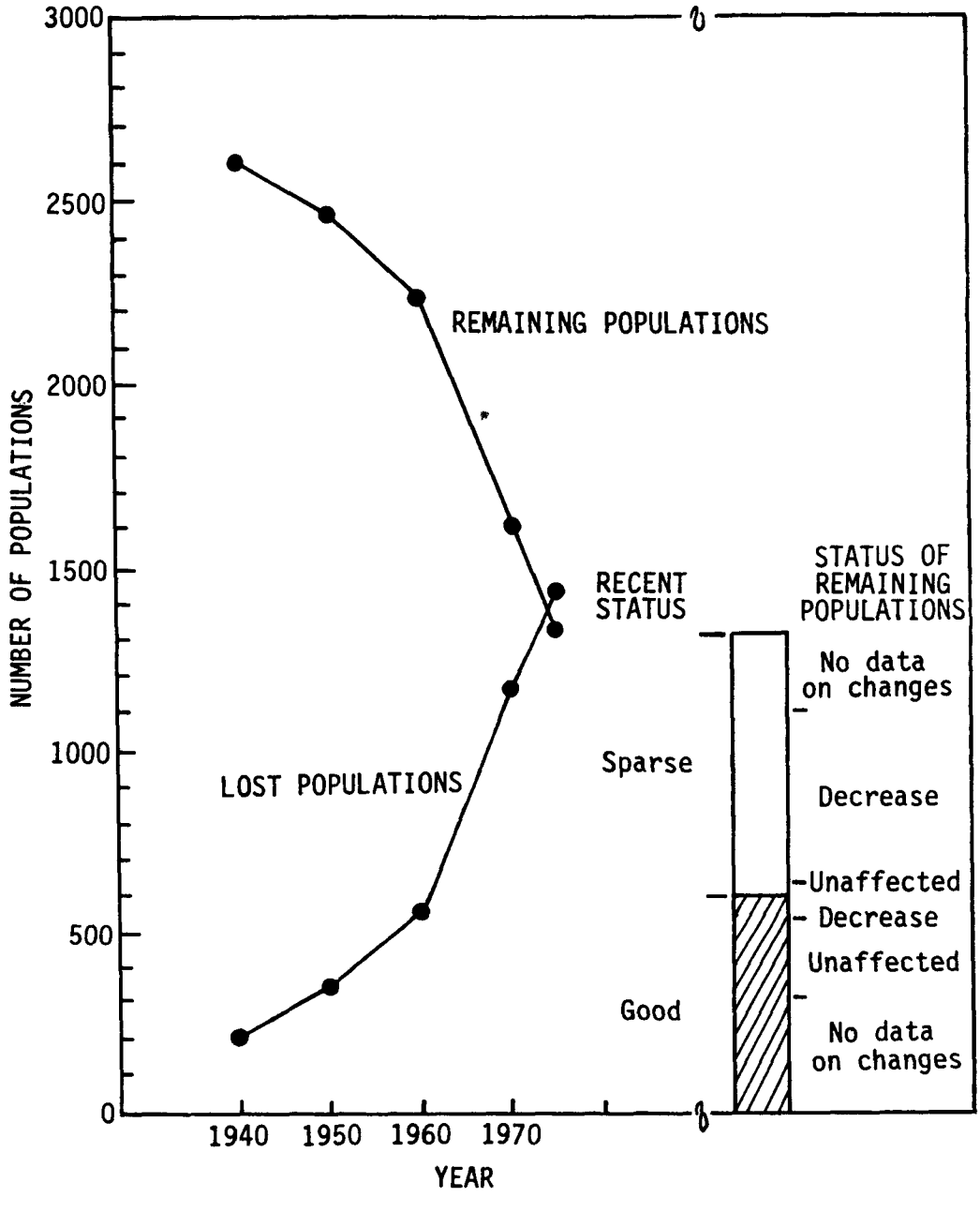

Figure 5-9. Time trend for population losses of brown trout in the affected areas in the four southernmost counties (Rogaland, Vest-Agder, Aust-Agder, and Telemark) in Norwy (Sevedrud et al. 1980).

failed to yield any trout in most streams draining forested catchments (mean pH 4.34), while moorland streams (mean pH 5.40) invaribly had resident trout populations.

5.6.2.2 Population Structure--The well-being of a population can be judged in part by examination of its age composition (National Research Council Canada 1981). Theoretically, age one fish should be more numerous than age two fish; age two fish more numerous than age three fish; age three fish more numerous than age four fish, etc. Two factors commonly alter this theoretical distribution: year selectivity and large natural variations in year class strength. Almost all procedures for sampling fish populations are size selective. Often, small, young fish are poorly sampled. In addition, relative numbers of fish in each age group may fluctuate greatly from year to year as a consequence of natural environmental and biological factors (e.g., year-to-year temperature variations, competition between age groups). The frequent absence of one or several age groups within a population may, however, be indicative of a population under stress or undergoing change. Studies of fish populations in acidic waters frequently reveal reduced or missing agre groups.

Deviations from the expected age class distribution in acidic lakes result in some cases from the absence of young fish; in others from the absence of older fish. A population with only fairly large, fairly old individuals, suggests that recruitment and/or reproduction have failed. A population with only young fish may imply the occurrence of a mortality factor acting only on fish after a certain age (e.g., after sexual maturity). Both types of distributions have been observed in acidic waters, although the absence of young fish occurs much more frequently. Decreased recruitment of young fish has been cited as a primary factor leading to the gradual extinction of fish populations in acidic waters (Schofield 1976a, Overrein et al. 1980, Haines 1981b).

Studies of lakes in the LaCloche Mountain region of Ontario by Beamish, Harvey, and others provide detailed observations of the structure of fish populations in acidic and acidifying lakes. White suckers were last reported in Lumsden Lake in 1969 (Table 5-8) at a pH of 5.0 to 5.2 (Beamish and Harvey 1972) (Section 5.6.2.1.2.1). Intensive sampling in 1967 yielded no young-of-the-year and very few age one fish, suggesting poor recruitment of white suckers in both 1967 and 1966. In contrast, in George Lake examination of the age distribution of white suckers in 1972 indicated no obviously missing year classes and thus no major reproductive failures prior to 1972 (pH 4.8 to 5.3) (Beamish et al. 1975). Although reduced in number, white suckers were still present in George Lake in 1979 (Harvey and Lee 1980). In 1972, O.S.A. Lake had a pH of about 4.5. Intensive sampling yielded only a small number of very old fish--eight lake herring aged 6 to 8 years, four yellow perch aged 8 years, and two rock bass aged 13 years (Beamish 1974b). By 1980, no fish remained in O.S.A. Lake (Section 5.6.2.1.2.1).

In addition to these intensive studies of individual lakes in the LaCloche Mountain region, Ryan and Harvey (1977, 1980) surveyed (through rotenone applications) the age distribution of populations of yellow perch and rock bass in 32 and 20 LaCloche Mountain lakes, respectively. For both species, lakes with lower pH levels had a higher frequency of populations missing the age 0 group (young-of-the-year). The most acidic lake yielding young-of-the-year yellow perch was characterized by a pH of 4.4, for rock bass by a pH of 4.8.

Absence of young age groups in fish populations from acidic and acidifying lakes has also been documented for a few lakes in the Adirondack region and in Scandinavia. In South Lake in the Adirondacks, white suckers netted in 1957-68 (pH 5.3 in 1968) ranged in length from 15 to 51 cm, suggesting a wide range of age classes. By 1973-75 (pH 4.9 in 1975), however, recruitment of young fish appears to have ceased. White suckers collected ranged from 30 to 49 cm in length. Five suckers captured in 1975 were aged 6 to 8 years (Schofield 1976a, Baker 1981). In Lake Skarsjon in Sweden, prior to lake liming (pH 4.5-5.5) only very large, old perch remained in the lake (Figure 5-10). One year after liming (pH ~ 6.0), reproduction was reestablished and two size classes of perch were present, both very large, old fish and a new group of small, one-year-old perch (Muniz and Leivestad 1980a).

Recruitment failure may result either from acid-induced mortality of fish eggs and/or larvae or because of a reduction in numbers of eggs spawned. Beamish and Harvey (1972) attributed the lack of reproduction in fish populations in LaCloche Mountain Lakes to a failure of adult fish to spawn. In Lumsden Lake in 1967, no spawning activity was observed in the lake or in the inlet or outlet streams during the normal spawning period. Mature female white suckers were found to be resorbing their eggs in June. In George Lake, in 1972 and 1973 about 65 to 75 percent of the population of female white suckers failed to release their ova to be fertilized. In 1973, most brown bullheads, rock bass, pumpkinseed sunfish, and northern pike had also not spawned when examined after their normal spawning period (Beamish et al. 1975). Biochemical analyses of fish from George Lake indicated that females exhibited abnormally low levels of serum calcium during the period of ovarian maturation. Lockhart and Lutz (1977) hypothesized that a disruption in normal calcium metabolism, induced by low pH, affected female reproductive physiology. In these lakes, therefore, failure of female fish to spawn was an important contributing factor to reproductive failures.

This response, failure of female fish to spawn, has not, however, been reported elsewhere. From a survey of 88 lakes in Norway, Rosseland et al. (1980) noted that female fish remaining in acidic lakes had normal gonads, and indications of unshed or residual eggs were rare. Studies conducted in Scandinavia and the United States (Schofield 1976a, Muniz and Leivestad 1980a) suggest that increased mortality of eggs and larvae in acidic waters is the primary cause of recruitment failures.

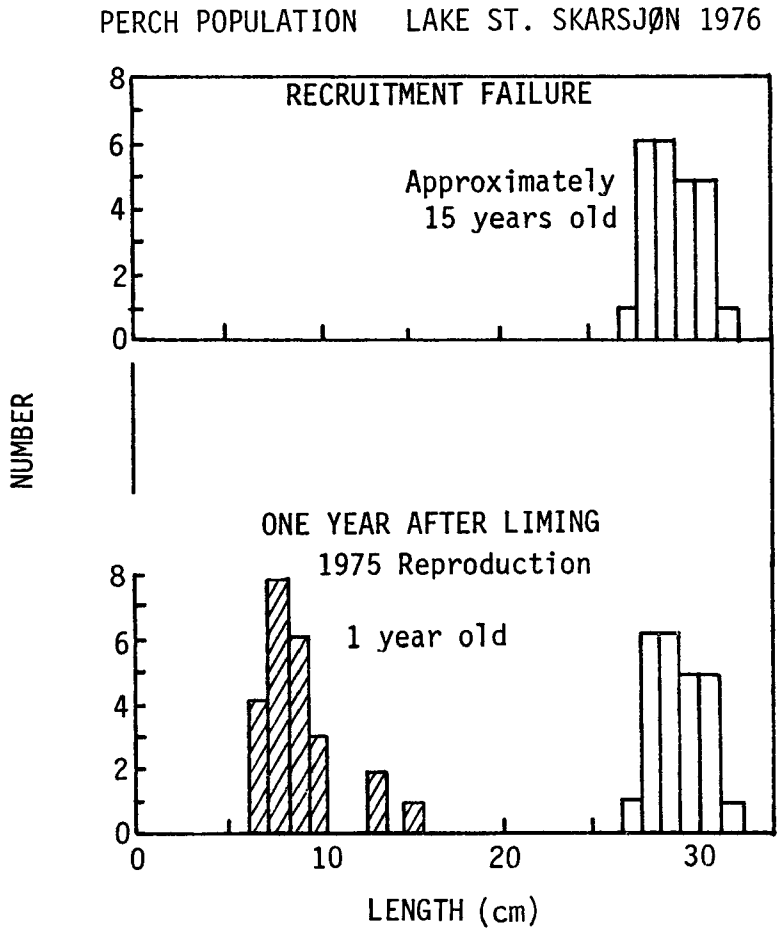

Figure 5-10. Liming of Lake St. Skarsjon, Sweden, in 1975 reestablised reproduction of perch population (Muniz and Leivestad 1980a).

In Norway, total mortality of naturally spawned trout eggs was observed in an acidic stream a few weeks after spawning (Leivestad et al. 1976).

In addition to the lack of young fish in a population, associated with recruitment failure as described above, in some cases loss of older fish has been observed in acidic waters. Three lakes in the Tovdal River, Norway, were test fished from 1976 to 1979 (Figure 5-11) (Rosseland et al. 1980). Before 1975, brown trout populations in these lakes were stunted and grew to 8 to 10 years of age. In 1975, the Tovdal River had a severe fish kill. Since 1976, no post-spawning brown trout (age 5 and up) have been found, and the population is dominated by young fish. Test fishing in autumn indicated the presence of maturing recruit-spawners. By each subsequent year, however, this age group had disappeared while their offspring survived. Researchers speculated that stress associated with spawning activities, coupled with acid-induced stress, resulted in significant post-spawning mortality (Muniz and Leivestad 1980a).

Harvey (1980) proposed that loss of older fish with acidification was also occurring in George Lake (LaCloche Mountain region) (colorimetric pH 6.5 in 1960; pH 5.4 in 1979). In 1967, white suckers up to 14 years of age occurred in the lake. By 1972, few fish were older than 6 years. Sampling in 1979 revealed a population with 90 percent of the white suckers aged 2 and 3 years.

It is unlikely that loss of older fish in either of these cases resulted from over-fishing.

5.6.2.3 Growth--Observations on fish growth in acidic waters and changes in growth rate over time with acidification suggest that indirect effects of acidification, via changes in food availability, are generally insignificant for adult fish. In very few cases have reduced growth rates been reported. For the most part, fish in acidic and/or acidified waters grow at the same rate or faster than fish in circumneutral waters in the same region.

Decreases in fish growth rate associated with acidification have been documented only for acidic lakes in the LaCloche Mountain region, Ontario. In 1975, Beamish et al. (1975) reported that growth rates for white suckers in acidic George Lake (pH 4.8 to 5.3, 1972-73) had declined over the period 1967 to 1973, and this was apparently associated with lake acidification. In more recent surveys, however, this trend appears to have reversed. Fish collected in 1978 and 1979 were larger (at a given age) than fish in 1972, and similar in size to fish collected in 1967 to 1968 (Harvey and Lee 1980). Therefore, even in this instance, consistent decreases in growth over time with increased water acidity have not occurred.

On the other hand, several studies suggest increased fish growth in acidic waters and/or with acidification. For two acidic lakes in the Adirondacks sampled in the 1950's and 1970's, numbers of brook trout caught decreased over the 20-year period, and significant increases in

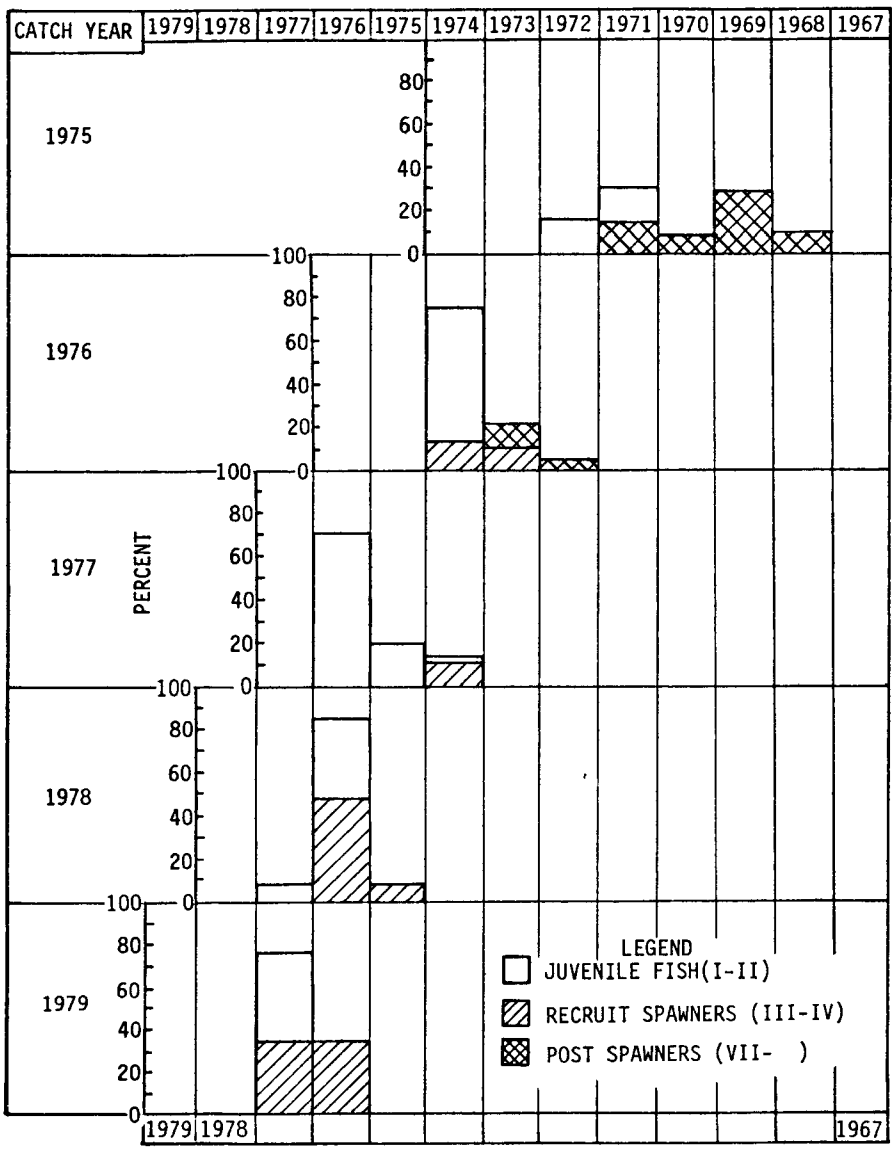

Figure 5-11. Age distribution of brown trout in Lake Tveitvatn, Tovdal, Norway (Rosseland et al. 1980)

fish growth were observed (Schofield 1981). Roach in acidic lakes (pH 4.6 to 5.5) in Sweden grew at substantially faster rates than roach in circumneutral lakes (pH 6.3 to 6.8) (Almer et al. 1974, 1978). Growth of rock bass in 25 LaCloche Mountain lakes was also significantly ($p < 0.05$) faster in lakes with greater acidity, even after adjustment for effects of lake depth on fish growth (Ryan and Harvey 1977, 1981). Jensen and Snekvik (1972) described a common pattern of change in lakes in Sørlandet, Norway over the last 50 years. Densities of fish in lakes declined, presumably associated with acidification and the onset of increased recruitment failure. Simultaneously, fishing quality increased, with a greater number of large trout available. Eventually, however, with continued recruitment failures, in many lakes populations disappeared entirely.

Rosseland et al. (1980), on the other hand, in a survey of 88 lakes in southern Norway, found no obvious tendency for increase in growth in sparse populations in acidic lakes, despite the fact that fish from acidic lakes had higher proportions of full stomachs and were in better condition (i.e., weighed more for a given length). Ryan and Harvey (1980, 1981) observed that yellow perch in 39 LaCloche Mountain lakes grew more quickly in more acidic waters up to age 3 years, but thereafter grew more slowly. In addition, yellow perch collected from George Lake in 1973 and 1974 (pH 4.6) at age 1 to 4 years were significantly larger than perch of the same age collected in 1966 (pH 5.8); this trend was reversed for age groups 5 years and older. Up to age 4, yellow perch feed primarily on plankton and benthic invertebrates. Large perch feed preferentially on small fish.

Fish growth reponse to acidification may be a complex function of two factors: acid-induced metabolic stress and food availability. Reduced growth in acidic waters as a result of physiological stress has been noted frequently in laboratory experiments (Section 5.6.4.1.3). Presumably, similar responses occur in acidic lakes and streams. Observations of increased or unchanged growth in acidified surface waters, however, suggest that adverse effects of acidity on fish metabolism and physiology are counterbalanced, in part or totally, by changes in food availability.

Acidification is associated with substantial changes in the structure and, in some cases, the function of lower trophic levels (Sections 5.3 and 5.5). Despite the fact that some important prey organisms are sensitive to acidic conditions and, as a result, fish may be required to shift their predation patterns, still in most acidic lakes food does not seem to be a significant limiting factor for adult fish (Beamish et al. 1975, Hendrey and Wright 1976). Possibly, with decreased fish density resulting from recruitment failures or fish kills, decreased interspecific and/or intraspecific competition for food supplies may lead to increased food availability for the fish remaining. Increased food availability may balance any negative effects of acid-induced metabolic stress.

Detailed studies of effects of food availability on fish, at all life history stages, in acidic waters are not, however, available. Therefore, the conclusion that shifts in food availability with acidification have no adverse effects on fish survival or production is preliminary. The growth response for any particular species may depend on its sensitivity to acidic conditions relative to the sensitivity of desirable prey items. As a group, aquatic invertebrates appear more tolerant than fish. Therefore, fish that feed primarily on invertebrates often experience increases in growth with acidification. However, fish that require or prefer prey intolerant of acidification may be adversely affected by reduced food supplies.

5.6.2.4 Episodic Fish Kills--Observations of dead and dying fish in acidifying waters are not common. Mechanisms of population extinction (e.g., recruitment failure) are often too subtle to be easily detected. However, instances of massive acute mortalities of adult and young fish have occurred, typically associated with rapid decreases in pH resulting from large influxes of acid into the system during spring snowmelt or heavy autumn rains. Chemical characteristics and occurrence of these short-term acid episodes are described in Chapter E-4, Section 4.4.2. In general, organisms are less tolerant of rapid increases in toxic substances than they are of chronic exposure and gradual changes in concentration. As a result, the rapid fluctuations in acidity associated with short-term acidification (defined in Chapter E-4, Section 4.2.3) may be particularly lethal to fish and may play an important role in the disappearance of fish from acidified lakes and streams.

Fish kills apparently associated with acid episodes have been reported numerous times in the streams and rivers of southern Norway (Jensen and Snekvik 1972, Muniz 1981). The first records of mass mortality of Atlantic salmon date from 1911 and 1914, and coincide closely with the sharp drop in salmon catch recorded for rivers in southern Norway over the years 1910-17 (Figure 5-7). Additional observations of mass mortality were reported in 1920, 1922, 1925, 1948, and 1969, in each case following either heavy autumn rains or rapid snowmelt, particularly in May to June. In 1948, a massive mortality of salmon and sea trout (Salmo trutta) occurred in the Frafjord River. At least 200 dead salmon and sea trout were collected, some of the salmon weighing more than 20 kg. pH measurements (colormetric) taken when dead fish first appeared were 3.9 to 4.2. One month later the pH was 4.7 to 4.8.

A similar episode occurred in the Tovdal River (Norway) in the spring of 1975 (Leivestad et al. 1976). Dead fish were first observed at the end of March. During the first weeks of April thousands of dead trout covered a 30 km stretch of the river. The Tovdal River valley is sparsely populated and has no industry. Veterinary tests failed to find signs of any known fish diseases. The pH of the river was about 5.0. In March, at two stations downstream, a drop in water pH was recorded apparently associated with a period of snowmelt at altitudes below 400 m. At higher altitudes, no dead fish were found, and temperatures probably never rose above freezing.

Leivestad and Muniz (1976) observed the physiological response of fish to this acid episode in the Tovdal River. Trout surviving within the affected 30 km area of river had substantially lower levels of plasma chloride and plasma sodium than did fish from apparently unimpacted reaches of the river. In the upper reaches of the river, the snow started to melt on April 21 and continued at a moderate rate until May 6. The pH dropped from 5.2 to a minimum of 4.65. Blood samples from fish collected in this area on May 15 had significantly lower plasma sodium and/or chloride compared to samples from fish from the same area taken before and after snowmelting. Leivestad and Muniz (1976) proposed that increased acidity interferred with osmoregulation via perhaps impairment of the active transport mechanism for sodium and/or chloride ions through the gill epithelium. Additional evidence for the adverse effects of acidity on ionic balance in fish is available from laboratory bioassays (Section 5.6.4.1.5).

Fish kills attributed to short-term acidification have been reported for only one water outside of Norway. During each spring 1978 to 1981, coincident with spring run-off, dead and dying fish, especially pumpkinseed sunfish, were observed in Plastic Lake, LaCloche Mountain region, Ontario (Harvey 1979, Harvey and Lee 1982). Measured pH levels were 5.5 at the lake surface and 3.8 in the major inlet. Field experiments to verify these toxic conditions in Plastic lake were completed in 1981 and are described in Section 5.6.3.3.

In addition to these observations of mass mortalities of fish attributed to acid episodes under natural field conditions, several instances of unusually heavy fish mortality have been reported within fish hatcheries receiving water directly from lakes or rivers. In Norway, poor survival of eggs and newly-hatched larvae of Atlantic salmon, attributed to water acidity, were reported as early as 1926 in hatcheries on rivers in Sørlandet (Muniz 1981). In Nova Scotia, 19 to 38 percent mortality of Atlantic salmon fry occurred in 1975 to 1978 at the Mersey River hatchery (Farmer et al. 1981). In Norway and Nova Scotia, neutralization of the water by passage through limestone alleviated the problem. In the Adirondacks, adult, yearling, and larval brook trout, which had been maintained without incident over the winter 1976-77 in water from Little Moose Lake, experienced distress and mortality during the first major winter thaw in early March (Schofield and Trojnar 1980). The minimum pH measured was 5.9 on March 13 (with 0.39 mg Al ℓ^{-1}). Mortalities occurred over a 5-day period March 13 to 17. Deaths included three adult brook trout, 25 yearlings (132 to 167 mm), and an undetermined number of recently hatched fry. Eyed brook trout eggs exposed to the same water did not experience significant mortality.

All of the above observations of fish kills were associated with episodic increases in acidity. Grahn (1980), however, recorded fish kills in two lakes in Sweden associated with decreases in acidity. In June 1978 in Lake Ransjon and in June 1979 in Lake Amten, large numbers of dead ciscoe (Coregonus albula) were discovered. A weather pattern of heavy rainfall, decreasing pH levels, and increasing aluminum

concentrations in the lakes, followed by a long period of dry, sunny weather preceded fish kills in both lakes. pH levels in the lake epilimnion increased from approximately 4.9 and 5.4 to 5.4 and 6.0, respectively. Grahn (1980) hypothesized that the increase in pH level precipitated aluminum hydroxide, and that ciscoe, migrating into the epilimnion to feed, were exposed to these lethal conditions. Laboratory experiments (Section 5.6.4.2) have also noted that aluminum is particularly toxic to fish as it precipitates out of solution. Dickson (1978) reported that acidic lake waters immediately after liming (pH values increased to 5.5 and above), were toxic to trout. Concentrations of aluminum were still high and, presumably, aluminum would be actively precipitating out of solution.

5.6.2.5 Accumulation of Metals in Fish--An indirect result of acidification of surface waters may be accumulation of metals in fish. Evidence for this relationship is derived from correlations between metal concentrations in fish and lake and stream pH levels, and evaluations of metal chemistry and availability in oligotrophic, acidic waters. Data are presented in Chapter E-6, Section 6.2.3. Elevated levels of mercury in fish from acidic waters have been measured in Sweden, Ontario, and the Adirondack region of New York. (Almer et al. 1978, Schofield 1978, Bloomfield et al. 1980, Hakanson 1980, Jernelov 1980, Suns et al. 1980). There is no evidence that this bioaccumulation has adverse effects on the fish, although it may represent a hazard for human health. Other metals in addition to mercury occur at elevated concentrations in acidified waters and potentially may accumulate in fish and other biota. Data on these accumulations and their effects on fish are, however, very limited.

5.6.3 Field Experiments

Correlations between fish population status and acidity of surface waters, and field observations of declines in fish populations concurrent with acidification of a lake, river, or stream, strongly imply that acidification has serious detrimental effects on fish. Such observations, however, rarely prove cause-and-effect. In experiments, one variable is changed, and the response to that change is recorded. Thus, the cause and its effect are clearly delineated.

Whole-ecosystem acidification experiments have been carried out at two locations: Lake 223 in the Experimental Lakes Area, Ontario and Norris Brook in the Hubbard Brook Experimental Forest, New Hampshire. In both cases, acid was added directly to the water and pH levels were held fairly constant. Despite these deviations from the process of acidification in nature, results from these two experiments demonstrate important biological changes associated with increased water acidity.

5.6.3.1 Experimental acidification of Lake 223, Ontario--Lake 223 is a small, oligotrophic lake on the Precambrian Shield of western Ontario. Prior to acidification, surface waters had an average alkalinity of about 80 $\mu eq\ \ell^{-1}$ and pH of 6.5 to 6.9. Five species of fish were present: lake trout, white sucker, fathead minnow (Pimephales promelas),

pearl dace (Semotolus margarita) and slimy sculpin (Cottus cognatus). Beginning in 1976, additions of sulfuric acid to the lake epilimnion gradually reduced lake pH. Early in each ice-free season, lake pH was decreased to a predetermined value and then maintained at that value through the following spring, at which time pH was again reduced. Mean pH values were 6.8 in 1976, 6.1 in 1977, 5.8 in 1978, 5.6 in 1979, 5.4 in 1980, and 5.1 in 1981. Biological responses to this acidification have been described in Schindler et al. 1980b, Schindler 1980, Malley et al. 1982, Schindler and Turner 1982, Mills 1982, NRCC 1981, and U.S./Canada MOI 1982, and are summarized in Table 5-10.

A number of important biological changes occurred at pH values of 5.8 to 6.0, notably the disappearance of the opossum shrimp (Mysis relicta), a benthic/planktonic crustacean (Section 5.5.3), and the collapse of the fathead minnow population. Although both these species were important prey for lake trout in the lake, no effects on trout populations were detected. Lake trout density and population structure remained stable, and year-class recruitment failures were not detected until 1981 at a pH of 5.1. At the onset of acidification (1976), fathead minnows were abundant while pearl dace were rare. With the collapse and eventual extinction of the fathead minnow population as the pH declined to 5.5, pearl dace abundance increased dramatically (perhaps in response to the loss of its closest competitor). The increased abundance of pearl dace and a succession of strong year classes of white suckers in 1978 to 1980 apparently provided adequate food alternatives for the lake trout.

Despite many changes in lower trophic levels, lake trout and white sucker populations showed no definite indications of stress until 1981, pH about 5.1, when reproductive failures occurred. During the early years of acidification, population numbers of both species increased and growth rates were relatively unchanged. The primary food source for white suckers, benthic dipterans, increased in abundance. Although types of prey available to lake trout changed dramatically, suitable food remained abundant. Both species spawned successfully all years of study prior to 1981, and there were no indications of egg resorption or skeletal malformations.

The population of bottom-dwelling slimy sculpin gradually declined throughout the acidification 1976 to 1981. Potential reasons for the decline include direct adverse effects of increased acidity and/or increased trout predation, associated with an increase in water clarity.

Among the fish, fathead minnow seemed to be most sensitive to acidification. Fathead minnows are ubiquitous in lakes in northern North America and form an important part of aquatic food chains. The population in Lake 223 disappeared extremely quickly, probably as a result of two factors: its particular sensitivity to acidity and its short life span. Recruitment failure occurred initially at pH 5.8 in 1978. Prior to acidification, fathead minnow in Lake 223 typically lived only three years. Natural mortality rates during their second and third years of life were extremely high, over 50 percent per year,

TABLE 5-10. BIOLOGICAL CHANGES IN LAKE 223 IN RESPONSE TO EXPERIMENTAL ACIDIFICATION (MILLS 1982, SCHINDLER AND TURNER 1982)

pH	Recorded change
Below 6.5	Increased bacterial sulfate reduction partially neutralize acid additions
	Increased abundance of Chlorophyta (green algae)
	Decreased abundance of Chrysophyceans (golden brown algae)
	Increased abundance of rotifers
	Increased dipteran emergence
5.8-6.0	Disappearance of the opossum shrimp (*Mysis relicta*)
	Reproductive impairment of the fathead minnow (*Pimephales promelas*)
	Possible increased embryonic mortality of lake trout (*Salvelinus namaycush*)
	Inhibition of calcification of exoskeleton of crayfish (*Orconectes virilis*)
	Disappearance of the copepod *Diaptomus sicilis*
5.3-5.8	Increased hypolimnetic primary production
	Development of *Mougeotea* algal mats along shoreline
	Increased infestation of crayfish with a parasite *Thelohania* sp.
	Collapse of the fathead minnow population
	Increased abundance of the pearl dace minnow (*Semotilus margarita*)
	Decreased abundance of the slimy sculpin (*Cottus cognatus*)
	Decreased abundance of crayfish
	Increased abundance of white sucker (*Catostomus commersoni*)
	Increased abundance of lake trout
	Disappearance of copepod *Epischura lacustris*
	First appearance of the cladoceran *Daphnia catawba* x *schoedleri*
Below 5.3	Recruitment failure of lake trout
	Recruitment failure of white sucker

presumably as a result of heavy trout predation. Few individuals remained after the second year of life. Year-class failure in 1978, therefore, left few spawning adults (age 2 and 3) the following year. Successive year-class failures in 1978 and 1979 assured the rapid disappearance of this species from Lake 223.

In summary, experimental acidification of Lake 223 resulted in severe changes in fish populations at pH values as high as 5.8 to 6.0. Adverse effects on fish and loss of populations occurred primarily as a result of recruitment failures rather than as a result of increased mortality of adult fish or reductions in food supplies.

5.6.3.2 Experimental Acidification of Norris Brook, New Hampshire--Norris Brook, a third order stream in the Hubbard Brook Experimental Forest, New Hampshire, was experimentally acidified to pH 4.0 from April to September 1977 (Hall et al. 1980, Hall and Likens 1980a,b). Brook trout were observed in the study section before and after acid addition. Small numbers of trout confined in the study section during low water in June, July, and August were exposed continuously to water at pH 4.0 to 5.0 and total aluminum levels up to about 0.23 mg ℓ^{-1}. Trout captured at pH 4.0, 5.0 and 6.4 in August showed no evidence of pathological changes in gill structure. Most of the trout, however, moved downstream to areas of higher pH at the onset of acid addition in the spring. No mortality was observed, only a general avoidance reaction. Potential effects on young-of-the-year trout and reproductive success were not included in this study.

5.6.3.3 Exposure of Fish to Acidic Surface Waters--In addition to the above field experiments involving acidification of an entire ecosystem, smaller scale field experiments have been conducted involving the transfer of fish into acidic lakes and streams. It is important to distinguish these small-scale field experiments from similar exposures of fish to acid waters in laboratory experiments for two reasons: (1) water quality conditions in field experiments may undergo substantial natural fluctuations while conditions are usually held rather constant in laboratory experiments, and (2) many laboratory experiments create acidic water by diluting strong acids (H_2SO_4, HNO_3, HC) into nonacidic background water. These artificially acidic waters may not precisely mimic acidified surface waters, and, as a result, fish responses recorded in laboratory bioassays may not always accurately represent what would occur in the field. In this section, in situ exposures of fish to acidic surface waters are reviewed in addition to experiments that, although conducted in a laboratory or hatchery, used unmodified acidic water taken directly from an acidic lake(s) and/or stream(s).

Excessive mortality of adult fish has been observed in a number of in situ experiments with fish held in cages in acidic waters. Following observation of fish kills in Plastic lake (LaCloche Mountain region, Section 5.6.2.4) in 1979 and 1980, during the spring of 1981 rainbow trout (Salmo gairdneri) were held in cages at four locations in Plastic Lake and at four locations in a control, nonacidic lake (Harvey et al.

1982). No mortality occurred at any of the cage sites in the control lake (pH 6.09 to 7.34). In Plastic Lake, however, mortality ranged from 12 percent at the lake outlet (pH 5.0 to 5.85) to 100 percent at the inlet (pH 4.03 to 4.09). At the inlet, mortalities commenced on the first day and all fish were dead within 48 hr. Aluminum accumulated rapidly on the gills of fish tested in Plastic Lake.

During the winter (December to April) 1971-72, Hultberg (1977) placed seatrout and minnows (Phoxinus phoxinus), both with a mean length of 6.5 cm, at ten test stations ranging in pH from 4.3 to 6.0 within the watershed of Lake Alevatten, Sweden. At all but three of the test stations native minnow populations had disappeared within the ten years preceding the experiment. Fifty-three percent of the seatrout and 91 percent of the minnows died during the four-month test. Most of the mortalities (68 percent of the seatrout total mortality; 59 percent for minnows) coincided with periodic drops in pH level.

Several Norwegian laboratory experiments with adult fish have used acidic stream waters (Leivestad et al. 1976, Grande et al. 1978). During simultaneous exposure to water from an acidic brook, pH 4.4 to 4.7, all yearling rainbow trout, Atlantic salmon, and brown trout died within 32 days. Brook trout were more tolerant, with 30 percent survival of one-year-old trout after 80 days. Similarly, in tests with fingerling age 0+ fish in acidic stream water, rainbow trout and Atlantic salmon were least tolerant (all dead within 12 days), brown trout intermediate (all dead within 32 days), and brook trout substantially more tolerant (50 percent survival after 42 days). By comparison, in stocking experiments at Lake Langtjern, Norway (mean pH 4.95), 24 and 61 percent (age 0+ and age 1+ fish, respectively) of brook trout stocked were recaptured, as compared to 0.6 and 19 percent of the brown trout and none of the rainbow trout (Grande et al. 1978). Long-term exposure of brook trout to acidic stream water (mean pH 4.6, range 4.2 to 5.0) resulted in decreased growth and reductions in plasma sodium and chloride levels.

A number of studies have also examined survival of fish eggs incubated in waters from acidic lakes and streams (Table 5-11). Hatching success and egg survival of brook trout ova decreased sharply between pH levels 5.0 and 4.6. For brown trout, hatching was near 100 percent at pH levels 6.2 and 6.5, but 0 percent at pH 4.8 and 5.1. The critical pH for hatching of Atlantic salmon eggs appears to be 5.0 to 5.6; for walleye about pH 5.4; for roach, something above pH 5.7.

In three studies, results from in situ incubation experiments were compared with concurrent surveys of occurrence of fish species within the same waters. Leivestad et al. (1976) reported that no brown trout eggs hatched and few trout fry were found (by electrofishing) in an acidic tributary (pH 4.8), formerly an important spawning ground. By contrast, in a second tributary with inferior spawning conditions but pH 6.2, numerous trout fry were collected. Harriman and Morrison (1982) reported no survival of Atlantic salmon eggs incubated in acidic streams (pH 4.2 to 4.4) draining forested catchments in Scotland and the absence

TABLE 5-11. SUMMARY OF FIELD EXPERIMENTS WITH FISH EGGS EXPOSED TO ACIDIC SURFACE WATERS

Species	Location	pH	% Survival	Comments	Reference
Brook trout[g]	Hatchery with water from Honnedaga Lake plus 6 tributary streams	4.5 4.6 5.0 5.1 5.3 5.4 5.6	25 60 90 95 80 85 85	0.10 mg Zn ℓ^{-1} 0.05 0.002 0.002 0.04 0.03 0.02 Exposure from eyed stage	g
Brown trout[d]	In situ in 2 Norwegian streams	4.8 ~ 7	0 ~ 100		d
Brown trout[f]	In situ in 2 Norwegian streams	5.13 6.55	0 90	Spawning observed in acidic brook	f
Atlantic salmon[d]	In situ in acidic Mandal River and a near-neutral tributary, Norway	4.9 ~ 7	< 1 80		d
Atlantic salmon[b]	In situ at several rivers in Sørlandet Norway	5.0 - 5.5		Critical pH for hatching	b
Atlantic salmon[a]	In situ in streams, Scotland	4.2 4.4 4.9 5.8	0 0 54 30	Comparison of forested vs non-forested catchments	a

TABLE 5-11. CONTINUED

Species	Location	pH	% Survival	Comments	Reference
Perch[e]	In situ in Lakes Stensjon, Trehorningen, and Malaren, Sweden	4.7 5.7 7.5	28 50 89		e
Roach[e]	As above	4.7 5.7 7.5	0 14 100		e
Walleye[c]	In situ in series of small streams in LaCloche Mt. area, Ontario	4.6 6.7	-	Hatching success significantly reduced at pH	c

References

[a]Harriman and Morrison 1982
[b]Hendrey and Wright 1976; Muniz and Leivestad 1980a
[c]Hulsman and Powles 1981
[d]Leivestad et al. 1976
[e]Milbrink and Johansson 1975
[f]Muniz and Leivestad 1980a
[g]Schofield 1965

of fish from the same streams in an electrofishing survey. Finally, Milbrink and Johansson (1975) incubated perch (Perca fluviatilis) and roach eggs in situ in Lakes Malaren (pH 7.5), Stensjon (pH ~ 5.7), and Trehorningen (pH ~ 4.7) in Sweden. While some perch eggs hatched in all three lakes (89, 50, and 28 percent, respectively), very few or no roach eggs hatched in the two acidic lakes (14 percent in Lake Stensjon, 0 percent in Trehorningen). Likewise, perch populations occurred in all three lakes, although extremely few perch were collected in the most acidic lake, Trehorningen. Roach, on the other hand, have apparently disappeared from Lake Trehorningen. Roach are still prevalent in both Lake Stensjon and Malaren.

5.6.4 Laboratory Experiments (J. P. Baker and P. G. Daye)

One of the best ways to prove cause and effect is to conduct experiments in a carefully controlled environment, i.e., the laboratory. Experimental conditions and fish response can be clearly quantified and dose-response relationships developed with a minimum of time and effort. Unfortunately, laboratory experiments have several drawbacks. For one, the simplified, controlled environment of the laboratory may differ from the natural environment in essential attributes. Factors that cannot be easily incorporated into laboratory experiments include: (1) the temporal and spatial variability in the field environment; and (2) the potential for compensatory mortality, i.e., shifts in the efficacy of natural mortality factors (e.g., predation, starvation) resulting from the addition of acid-induced mortality and/or stress. Consequently, results from laboratory experiments cannot be translated automatically into an expected response in the field.

Serious gaps exist in the understanding of how to use laboratory results in a quantitative assessment of field observations. It has never been definitely demonstrated that "X" conditions that yield "Y" response in the laboratory (e.g., 40 percent mortality) will also yield "Y" response in the field. Laboratory results are, however, useful in firmly establishing cause-and-effect, that increasing acidity has adverse effects on fish, and a qualitative estimate of the levels of acidity of concern.

The more closely the laboratory environment simulates the field experience, the more realistic the observed response. Laboratory bioassays conducted to date vary substantially in their use of conditions appropriate to the problem of acidification of surface waters. Most laboratory experiments concerned with acidification have focused on the effects of low pH on fish. With acidification, however, other factors also change in association with decreasing pH (Chapter E-4, Section 4.6). Increased aluminum concentrations in acidic waters, in particular, have been shown to affect fish adversely (Section 5.6.4.2). Unfortunately, most of the bioassay results to date have failed to include aluminum. Thus, these results must be interpreted with caution. In addition to aluminum concentration, other factors change with acidification, e.g., increased manganese and zinc concentrations and perhaps a decrease in dissolved organic carbon

(Chapter E-4, Section 4.6). The importance of these other changes to fish populations in acidified waters has yet to be delineated in either laboratory or field experiments.

Within the discussion of laboratory experiments, Section 5.6.4.1 considers effects of low pH on fish. Section 5.6.4.2 examines combined effects of both low pH and elevated aluminum (and other metals). Because of the large number of experiments dealing with low pH, Section 5.6.4.1 is subdivided into experiments dealing with survival, reproduction, growth, behavior, and physiological responses. Reproduction is arbitrarily defined as including data on survival of fish larvae and fry in acidic water. Section 5.6.4.1.1 (Survival) therefore considers only data for fish approximately aged 4 months (fingerlings) and older. Questions related to acclimation to acidic waters and differences in tolerances among fish strains, as related to possible mitigation of effects of acidification, are discussed in Section 5.9. Interpretation of laboratory results must also consider that fish response in a bioassay is a function of testing conditions (e.g., temperature, flow-through or static water supply), background water quality (e.g., water hardness, concentrations of dissolved gases), and characteristics of the fish tested (e.g., prior exposures and stress, size, age, condition).

5.6.4.1 Effects of Low pH--

5.6.4.1.1 Survival. The majority of laboratory experiments designed to determine the direct toxicity of elevated hydrogen ion concentrations to fish have been short-term, acute bioassays involving principally pH levels 4.0 and below (Table 5-12). If 2 days is arbitrarily selected as the length of an acid episode, laboratory experiments suggest that a 50 percent fish kill would occur at approximately pH 3.5 for brook trout, pH 3.8 for brown trout, pH 3.8 to 3.9 for white suckers, and pH 4.0 for rainbow trout. In contrast, field observations of fish kills (Section 5.6.2.4 and 5.6.3.3) indicate mortality of: (1) Atlantic salmon and sea-run brown trout in Frafjord River, Norway in 1948 at pH 3.9 to 4.2; (2) brown trout in the Tovdal River, Norway in 1975 at pH 5.0; (3) rainbow trout in Plastic Lake, Ontario at pH 4.0 to 4.1; (4) brook trout in Little Moose hatchery, Adirondacks, NY, at pH 5.9; and (5) brook trout in Sinking Creek, PA, at pH 4.4 and below.

A few experiments have considered survival of fish following longer-term exposure to low pH levels (Table 5-13). Apparently, adult fish can survive quite low pH levels for fairly long time periods. For periods up to 11 days, brook trout were able to withstand pH levels as low as 4.2 with only small reductions in survival. During even longer periods of exposure (65 to 150 days), however, a pH level of 4.4 to 4.5 was severely toxic, and only at pH levels of 5.0 and above was brook trout survival unaffected. Long term experiments (> 100 days) with adult rainbow trout, brown trout, arctic char, and fathead minnow indicated no substantial reductions in survival at the lowest pH levels tested, 5.0, 4.8 and 4.6, respectively.

TABLE 5-12. MEDIAN SURVIVAL TIME (HR) FOR FISH EXPOSED TO pH LEVELS

Species		Age/ size	PH level 2.0-2.5	2.6-2.8	3.0-3.1	3.2-3.3	3.4-3.5	3.6-3.7	3.8-3.9	4.0-4.1	4.2-4.3	4.4-4.5	Reference
Brook trout	*	10-60 g	< 1			7							a
		fngl†			2-3	3-6	6-18	10-38	14-51	20-270			b
		2 g	1	2	3-6	12-14	45						c
		90 g	1	4	9	18	61-66	334					c
		60-130 g	< 1		1		5-9						d
		50 g					25	66-70					e
		50-90 g					10-32						f
								8		37			g
Rainbow trout	*	1 g							23				
	*	130 g		1-4	4	8	18						g
	*	200-300 g	2	2	5								h
		2-5 g			1	2	3	6	17	83	117	133	i
	*	2-5 g			< 1	1	2	6	27	133			i
	*	5-15 cm			1		2	3	8	22	70		j
		5-15 cm			2		3	7	18	55			j
										120			k
Brown trout	*	1-5 g					25	40		2-4			
	*	6 g	1-2		3-7								l
	*	60-80 g	3	4	9								h
				3									
Arctic char	*	100-170 g	3		4								h
White sucker		7 mo			1	2	5	10	30-200	350	1000		m
Roach		7-13 cm			< 1	1		3					j

*Experiments using low alkalinity water.

†fngl = fingerling, age 0+, weight usually < 50 g.

References -

a. Daye and Garside 1975
b. Johnson 1975
c. Robinson et al. 1976
d. Packer and Dunson 1972
e. Swarts et al. 1978
f. Falk and Dunson 1977
g. Kwain 1975
h. Edwards and Hjeldnes 1977
i. McDonald et al. 1980
j. Lloyd and Jordan 1964
k. Brown 1981 with 0.1 mM Ca
l. Edwards and Gjedrem 1979
m. Beamish 1972

TABLE 5-13. PERCENT SURVIVAL OF FISH FOLLOWING CHRONIC EXPOSURE TO LOW pH LEVELS

Species	Age/Size	Length of Exposure (days)	3.2	3.6	4.2-4.4	4.5-4.6	4.8-5.0	5.2-5.6	5.9-6.2	6.5-6.8	7.0-7.5	Reference
Brook trout	100-300g	5			60-90		100				100	a
*	10-60g	7	0	85	100		100	100		100		b
*	5g	11			100							c
	50g	65			0-36	0	75					d
	150-360g	150								75	100	e
Rainbow trout*	200-300g	100					93	96	97			f
Brown trout*	60-80g	100					94 90	98	95			f
Arctic char*	100-170g	100					86	100	100			f
Fathead Minnow	1 yr	400				80		75	85	75	85	g
Flagfish*	Mature Adult	20				36		79	100	93		h

*Experiments using low alkalinity water.

References

[a]Dively et al. 1977
[b]Daye and Garside 1975
[c]Baker 1981
[d]Swartz et al. 1978
[e]Menendez 1976
[f]Edwards and Hjeldnes 1977
[g]Mount 1973
[h]Craig and Baksi 1977

An important objective of many of these experiments was not solely to determine fish mortality at low pH levels but also to evaluate factors that influence fish tolerance to low pH. For example, Lloyd and Jordan (1964) and Kwain (1975) concluded that as fish grow older they became more acid tolerant. Higher temperatures (5 to 20 C) tended to decrease fish survival at low pH (Kwain 1975, Edwards and Gjedrem 1979, Robinson et al. 1976). Water hardness also affected fish tolerance. Lloyd and Jordan (1964) and McDonald et al. (1980) noted that at low pH levels (pH $\leq$ 4.0), the resistance of rainbow trout to acids increased with increasing hardness of water. As a result, experiments conducted in high alkalinity, hard water (see Tables 5-12 and 5-13) are relatively inappropriate for assessing effects of acidic deposition on fish, a phenomenon confined to dilute, poorly buffered surface waters. Brown (1981) suggested that higher calcium levels (more so than higher sodium, potassium, or magnesium levels) in harder water may be responsible for the increase in resistance. Within even dilute, low alkalinity waters, small changes in calcium concentration (0 to 2 mg ℓ^{-1}) have been shown to have a significant influence on survival times of fish (Brown 1982). Similarly, in the field (in Norway) the number of fishless lakes was correlated with both pH level and calcium level, with the greatest number of fishless lakes having both low pH and low calcium (Wright and Snekvik 1978; Section 5.6.2.1.3.1). The sensitivity of fish to low pH obviously interacts with a number of other stress and condition factors.

5.6.4.1.2 Reproduction. As discussed in Section 5.6.2.2, loss of fish populations with acidification is in many lakes and rivers preceded by successive recruitment failures. These field observations suggest that fish reproductive processes are particularly sensitive to acidic conditions. This conclusion is supported by laboratory experiments on effects of low pH on spawning behavior, egg production, and egg and fry survival. Tolerance to low pH varies considerably among the early development stages and reproductive processes. At the same time, many fish reproduce during the spring season, a period of large fluctuations in water chemistry. Information on the timing of these fluctuations in water quality and the occurrence and sensitivity of various reproductive processes and stages has yet to be tied together in an analysis of which reproductive process(es) and/or stage(s) may play key roles in the success or failure of recruitment and survival of the population.

Studies on the effect of low pH on the entire reproductive cycle have been completed only for brook trout (Menendez 1976), fathead minnow (Mount 1973), flagfish (Jordanella floridae) (Craig and Baksi 1977), and desert pupfish (Cyprinodon n. nevadensis) (Lee and Gerking 1981) (Figure 5-12). pH level had some effect on all stages (processes) tested, with the exception of number of eggs spawned by brook trout. However, sensitivity varied among both life history stages (processes) and species. For brook trout, survival of eggs and fry appeared to be the phase most sensitive to low pH levels, with survival significantly ($p < 0.05$) reduced at pH 6.1 and below. For fathead minnow, flagfish and desert pupfish, on the other hand, egg production appeared particularly sensitive to low pH, with reductions in eggs produced per female at pH levels between 6.0 and 7.0. Lee and Gerking (1981) concluded that

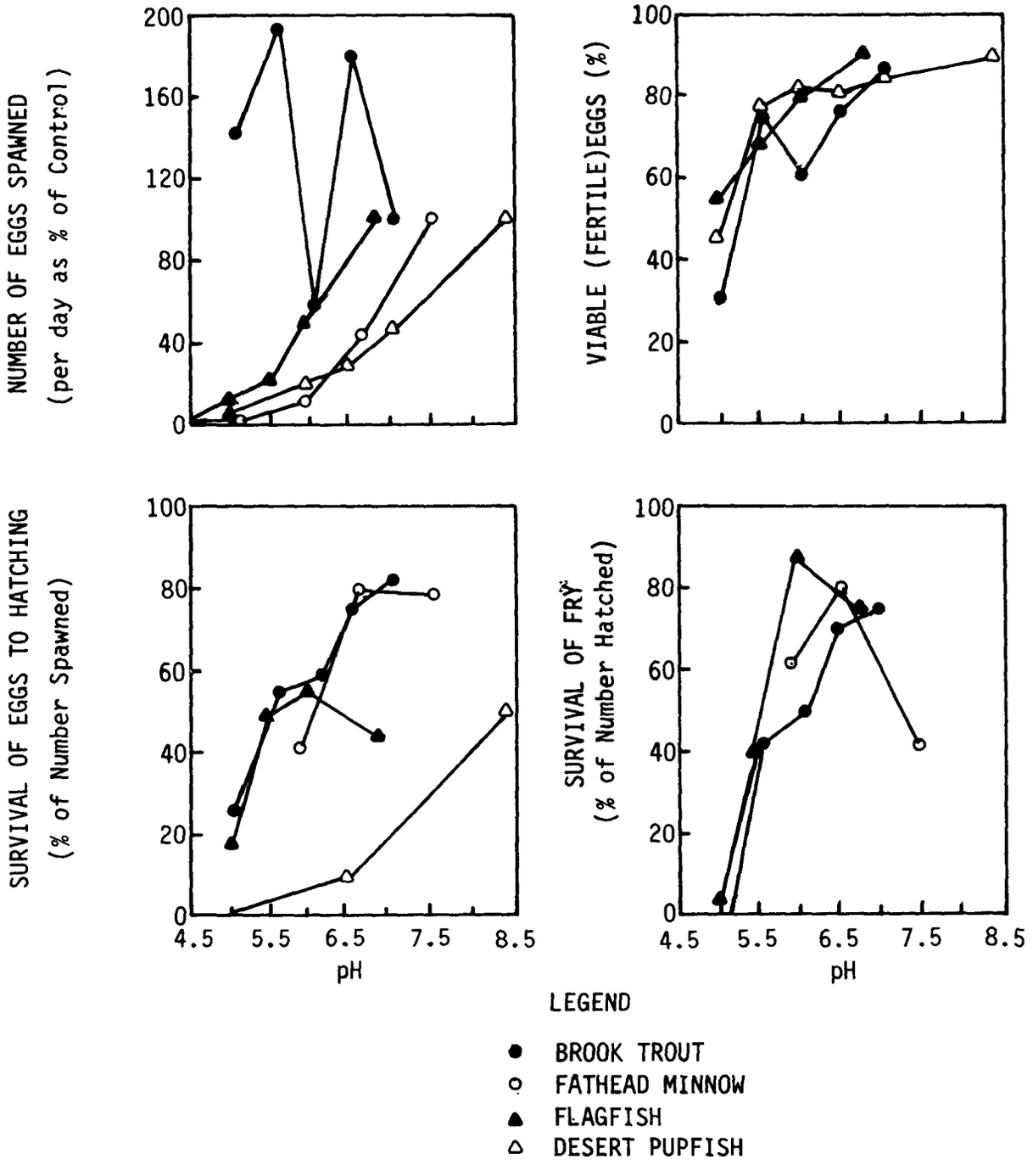

Figure 5-12 Effect of low pH on the reproductive cycle of fish (Menendez 1976, Mount 1973, Craig and Baksi 1977, Lee and Gerking 1981).

reduced egg production at low pH levels resulted primarily from inhibition of oogenesis (rather than interference with normal spawning activity). Ruby et al. (1977, 1978) also observed retarded oocyte growth (and reduced sperm production) for flagfish exposed to pH 6.0 relative to the control of pH 6.8.

Unfortunately three of these four experiments (all except Craig and Baksi 1977) were conducted in hard water (alkalinity > 500 $\mu eq\ \ell^{-1}$ and two used fish species that do not occur in surface waters sensitive to acidic deposition. Conclusions, therefore, must be interpreted cautiously. Results for brook trout (Menendez 1976), in particular, differ markedly from results from other researchers using low alkalinity water (Figures 5-13 and 5-14) and/or naturally acidic surface waters (Section 5.6.3.3). Life cycle experiments with both fish species and conditions appropriate to acidification of dilute surface waters are not yet available. Thus, the relative sensitivities of reproductive stages to low pH cannot be accurately assessed at this time.

Data on survival of fish embryos at low pH levels in laboratory experiments are summarized in Figure 5-13. In each case, hatching was reduced at low pH levels. Among North American freshwater species, brook trout was the most tolerant. Excluding results from Menendez (1976), numbers of brook trout embryos surviving through hatching were reduced substantially (< 50 percent hatching) only at pH levels below 4.5. Hatchability of white sucker eggs, on the other hand, dropped off sharply at pH levels 5.0 to 5.2. Number of fathead minnow embryos hatching declined at pH 5.9. In experiments conducted in Scandinavia and Great Britain, survival through hatching was reduced below approximately pH 4.4 for sea-run brown trout and below pH 4.6 for roach. Experiments with perch and Atlantic salmon yielded inconsistent results. These pH values for effects on egg survival are distinctly higher than values noted as acutely toxic to adults (pH 3.5 for brook trout; pH 3.8 to 3.9 for white suckers; pH 3.8 for brown trout) (Section 5.6.4.1.1).

A number of studies have noted that the hatching process itself appears pH sensitive (Runn et al. 1977; Peterson et al. 1980a,b; Baker 1981). For eggs exposed to low pH either throughout their development or just during hatching, a large proportion of embryos hatch incompletely, with fry remaining partially encapsulated for days following hatching. Delay or prevention of hatching can be induced by transfer of eggs into low pH water just prior to hatching, and normal hatching may occur if eggs are transferred just prior to hatching from low pH water into control water. Thus, mechanisms involved in the hatching process especially may be key factors limiting embryo survival in low pH water (disintegration of the chorion, facilitating mechanical rupture of the chorion by embryo trunk movements at hatching; Bell et al. 1969, Yamagami 1973, 1981). Mechanisms proposed involved: (1) the relationship between pH and activity of the hatching enzyme (Yamagami 1973), (2) thicker, more rigid egg capsules at lower pH, with increased resistance to degradation (Runn et al. 1977, Peterson et al. 1980b), and (3) reduction in body movements inside eggs at low pH (Peterson et al. 1980b).

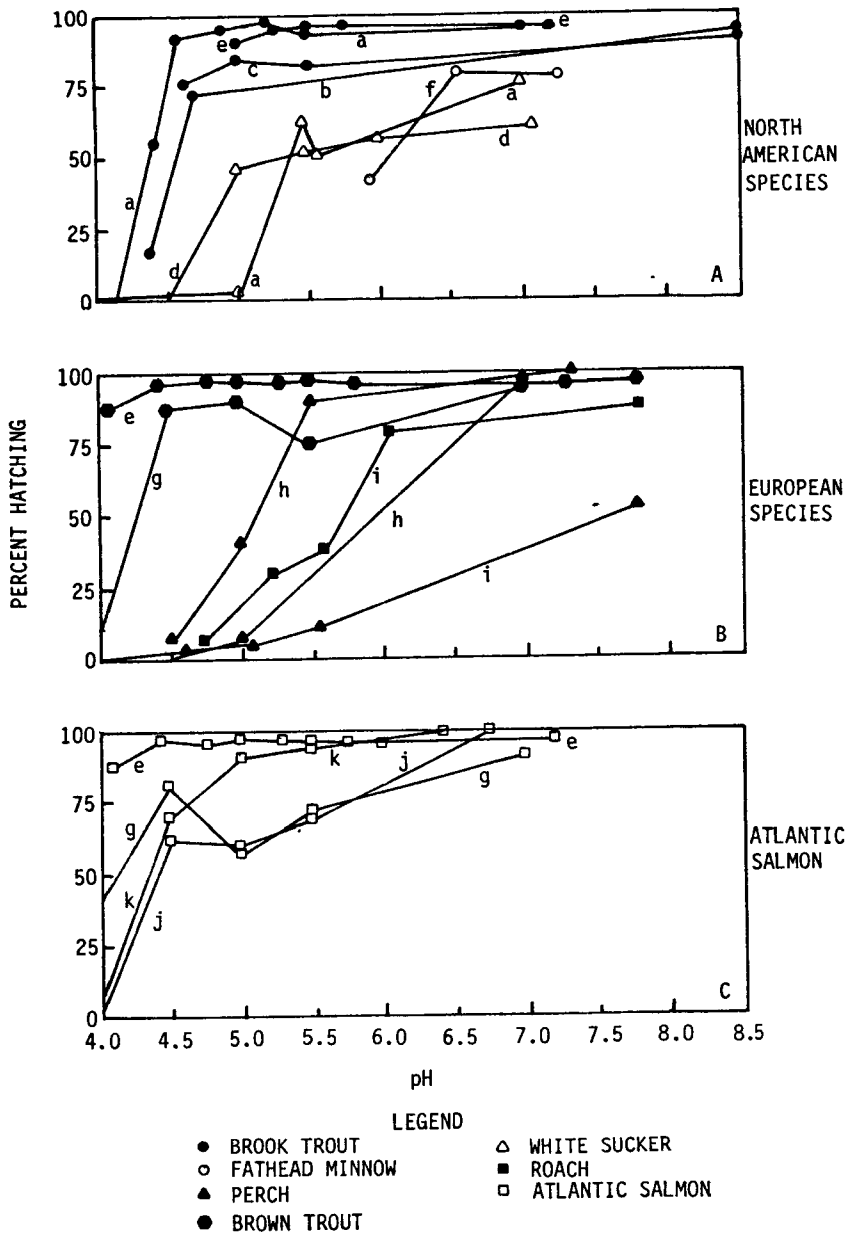

Figure 5-13. Effect of low pH on survival of fish through hatching.

References:

a	Baker and Schofield	1982	g	Carrick	1979
b	Swarts et al.	1978	h	Runn et al. (in 1975)	1977
c	Trojnar	1977a	i	Johansson and Milbrink	1976
d	Trojnar	1977b	j	Peterson et al.	1980a
e	Johansson et al.	1977	k	Peterson et al.	1980b
f	Mount	1973			

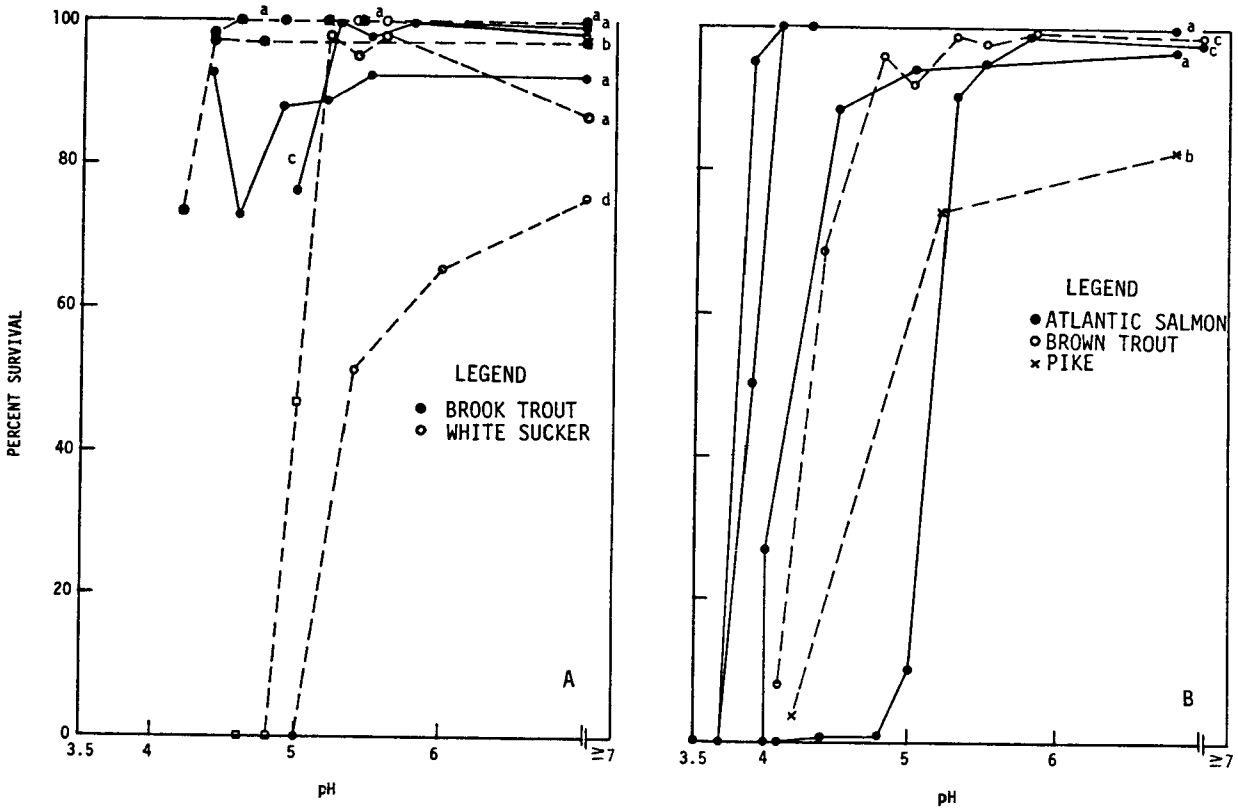

Figure 5-14. Effect of low pH on survival of fish as sac fry. Solid line, sac fry survival through swin-up following development of eggs and hatching of larvae in low pH water (expressed as percent normal hatch); Dashed line, sac fry survival without previous exposure to low pH.

PART (A)	References		PART (B)		
a	Baker and Schofield	1982	a	Daye and Garside	1975
b	Swarts et al.	1978	b	Johansson and Kihlstrom	1975
c	Johansson et al.	1977	c	Johansson et al.	1977
d	Trojnar	1977b			

Exposure of embryos to low pH levels during early stages of development (particularly within the first day after fertilization or during water hardening) also adversely affected survival, although to a lesser extent than did exposure during hatching (Johansson et al. 1973, Johansson and Milbrink 1976, Daye and Garside 1977, Lee and Gerking 1981, Baker 1981). For roach eggs exposed to pH 7.7 throughout their development, 89 percent hatched successfully. After exposure to pH 4.7 for the first 24 hr and then to pH 7.7 from 24 hr to hatch, 52 percent hatched. With exposure to pH 7.7 for 24 hr followed by pH 4.7 to hatch, 20 percent hatched. Finally with exposure to pH 4.7 throughout development, only 6 percent hatched successfully (Johansson and Milbrink 1976).

The egg changes its character rapidly after being spawned. Permeability decreases and the chorion hardens during the first few hours after release, allowing the egg to become more resistant with time (Lee and Gerking 1981). Zotin (1965) noted that teleost eggs exchange water with the surrounding solution primarily immediately after fertilization and just before hatching. Exchange of water and ions between the egg and external medium during intermediate periods of development occurs but is limited (Kalman 1959, Zotin 1965).

Given the evidence that timing of exposure substantially affects the sensitivity of embryos to low pH, it is obvious that to determine the impact of acidification on embryo survival, the occurrence of particularly susceptible stages must be evaluated in relation to the timing of fluctuations in pH level in acidified surface waters. As with the toxicity of low pH to adult fish, the effect of low pH on fish embryos was also found to be a function of temperature (Kwain 1975).

At intermediate pH levels, between those recorded to have no consistent adverse effect on embryo survival and pH levels that result in near 100 percent mortality, some researchers (Mount 1973, Runn et al. 1977, Trojnar 1977b) have observed increased incidence of deformities in larvae after hatching. Runn et al. (1977) suggest that these malformations result, at least in part, from the prolongation of the non-hatching period. Peterson et al. (1980a), in contrast, reported no increase in deformities of Atlantic salmon fry hatched at low pH levels (5.5 to 4.5).

Finally, pH may determine recruitment success for fish populations in acidic waters by influencing the survival of young fish larvae (or fry) after hatching. The direct effect of low pH on fry survival has been examined in laboratory experiments. Fry survival in field situations would also be strongly influenced by food availability, predation, temperature, and a large number of other environmental factors. In general, survival of fry in laboratory bioassays decreased below pH 4.0 to 4.5 for Atlantic salmon; pH 4.2 to 4.4 for brook trout; pH 4.8 for brown trout; pH 5.0 to 5.5 for white suckers; and pH 5.2 for pike (Figures 5-14 and 5-15).

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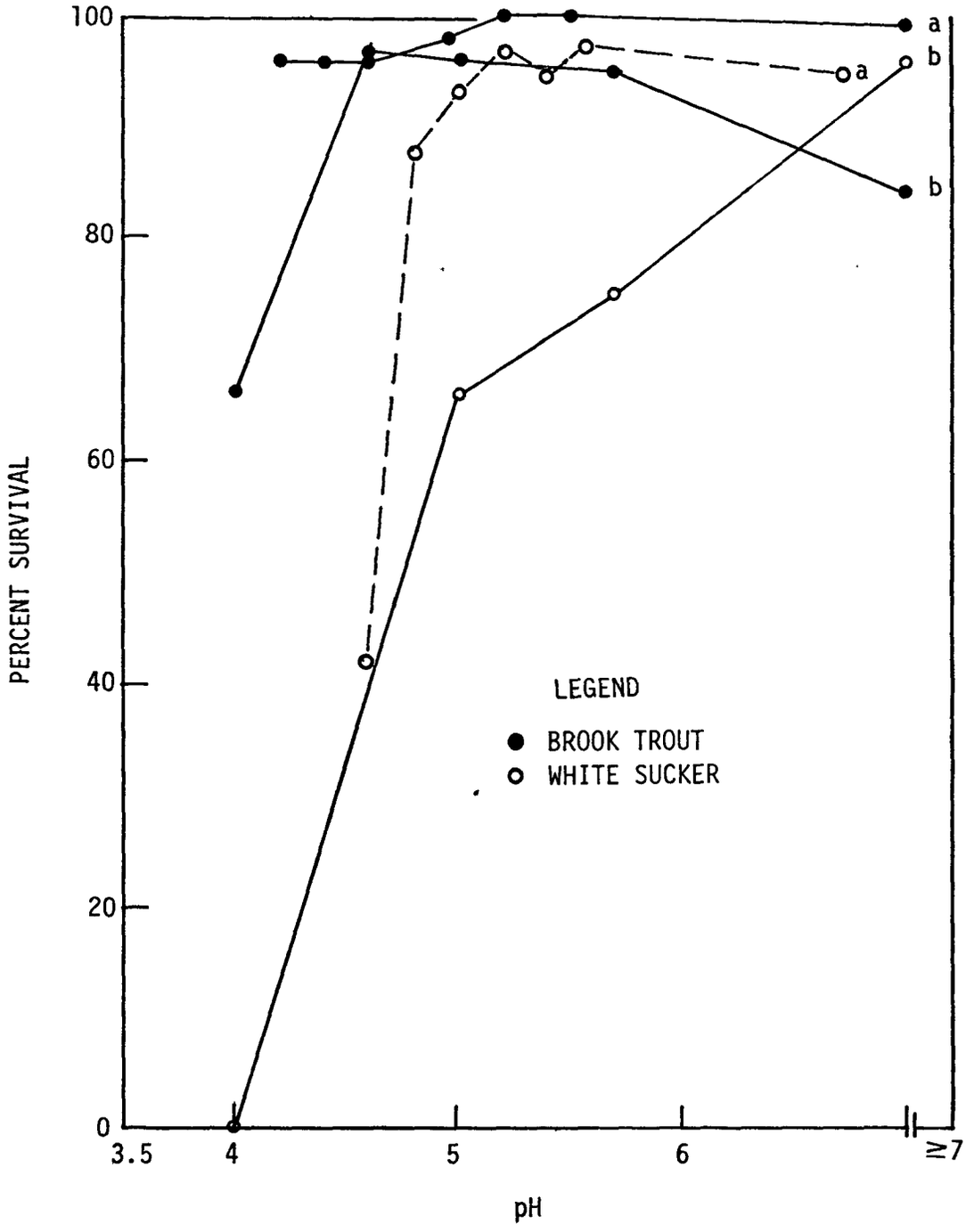

Figure 5-15. Effect of pH on survival of fry exposed for 14 days after swim-up and initiation of feeding.

[a]Baker and Schofield 1982
[b]Trojnar 1977a; previous exposure during development at pH 8.0 (o); previous exposure at pH 4.6 to 5.6 (•).

Evaluations of the relative sensitivities of eggs, sac fry (fish larvae after hatching but prior to initiation of feeding and swim-up), and fry (after initiation of feeding) have been inconsistent among experiments, perhaps reflecting differences in species response. Baker and Schofield (1982) and Swarts et al. (1978) found in successive experiments with brook trout and/or white sucker that sensitivity to low pH decreased with age. Also, a high proportion (> 75 percent) of embryos alive at hatching survived through swim-up with continued exposure to the same low pH level (Trojnar 1977a, Craig and Baksi 1977, Baker and Schofield 1982). Daye and Garside (1977, 1979), on the other hand, concluded that Atlantic salmon fry were more sensitive to low pH than were eggs. Likewise, Johansson et al. (1977) observed that Atlantic salmon and brown trout (and to a lesser extent brook trout) that survived through hatching at low pH levels (pH 4.1 to 5.0) subsequently suffered substantial mortality (10 to 100 percent) during the four weeks after hatching until just prior to full resorption of the yolk sac.

Therefore, while some researchers have concluded that fry are relatively (as compared with fish eggs) tolerant of low pH, other researchers considered fry to be a particularly sensitive stage in the reproductive cycle of fish. Because as fry emerge from the nest, "redd," or spawning tributary upon swim-up they may be subjected to an environment and water quality distinctly different from that to which the eggs (and sac fry) were previously exposed, an understanding of these relative tolerances is important.

5.6.4.1.3 Growth. The direct effect of low pH on fish growth has been examined in several laboratory experiments. Although field observations of changes in growth with acidification indicate a variable response to increased acidity (Section 5.6.2.3), reflecting the large number of variables determining growth in natural situations, in the laboratory low pH has consistently resulted in decreased growth. These decreases in growth often occur at pH levels above those producing substantial fish mortality. Edwards and Hjeldnes (1977) observed a significant ($p < 0.001$) decrease in growth (relative to the control at pH 6.0) of yearling rainbow trout, brown trout, and arctic char held at pH 4.8 for 3.5 months; mortality levels were less than 10 percent. Jacobsen (1977) found no significant decrease in growth of 18 month old brown trout after 48 days, but tested pH levels only down to 5.0. Swarts et al. (1978) and Baker (1981) noted delayed development of brook trout sac fry hatched at pH 4.6 and below. For brook trout embryos reared at pH 6.5, 6.0 and 5.5, fry were significantly ($p < 0.05$) shorter after 3 months than were fry in control water at pH 7.1 (Menendez 1976). Likewise, flagfish surviving through embryo development and 45 days after hatching weighed significantly less at pH 6.0, 5.5, and 5.0 than did fry at pH 6.8 (Craig and Baksi 1977) and rainbow trout reared at pH 4.3 to 4.8 were shorter ($p < 0.001$) than controls at pH 7.0 to 7.2 (Nelson 1982).

The decrease in growth at low pH represents a sublethal response to elevated hydrogen ion concentrations and suggests that fish are

physiologically stressed at pH levels above those that produce acute or chronic mortality.

5.6.4.1.4 Behavior. Behavioral responses of fish to low pH probably play an important role in determining the effect of surface water acidification on fish populations. Within a given aquatic system at any time, water quality may vary substantially (Driscoll 1980). If fish can detect regions of low pH and by behavioral adaptation avoid exposure to these toxic conditions, the impact of acidification may be, in part, mitigated. Muniz and Leivestad (1980a) reported observations of trout concentrated into "refuge areas" during acid incidents. In the acidic river Gjor in Norway during spring snow melt, hundreds of brown trout from the river crowded into a tiny tributary with a higher pH. If experimentally restrained within the river, fish died within a week. Information on the presence of such "refuge" areas and the ability of fish to detect and use these areas are necessary for a complete assessment of the impact of acidification.

Unfortunately, laboratory (and field) data on behavioral responses of fish to low pH are very limited. Jones (1948) tested sticklebacks (Gasterosteus aculeatus) in a sharp concentration gradient in a laboratory apparatus. Fish were able to detect and avoid waters with pH < 5.4, a value slightly above the lethal level of pH 5.0. Hoglund (1961) concluded that Atlantic salmon fingerlings avoid water at pH 5.3 and below, roach at pH 5.6 and below. Johnson and Webster (1977) investigated the effect of low pH on spawning site selection of brook trout. Female trout clearly avoided areas of water upwelling at pH 4.0 and 4.5. Discrimination was not evident at pH 5.0. Preference by adult brook trout for spawning in areas receiving neutral or alkaline aquifer water may protect eggs and sac fry from adverse water quality conditions. Decreased spawning activity at low pH (discussed in Section 5.6.4.1.2) may therefore partially reflect a behavioral response rather than an adverse effect on reproductive physiology.

5.6.4.1.5 Physiological responses. In the laboratory a decrease in pH level has been demonstrated to result in a wide diversity of physiological responses in fish. Some of these observed responses may reflect only a general response of fish to stress; others appear to be specifically related to low pH. The following does not represent a complete review of the extensive and varied literature available on fish responses to acidity; only major topics are summarized. Fromm (1980) and Wood and McDonald (1982) have provided a thorough critique of the literature on physiological and toxicological responses of freshwater fish to acid stress.

The best documented physiological response, and probably the response most widely accepted as the physiological basis for the toxicity of low pH, involves interference of elevated hydrogen ion levels with osmoregulatory mechanisms and impaired body salt regulation. Freshwater fish maintain a higher salt concentration in their tissues than is in the water that surrounds them, and must actively take up ions from the surrounding water through the gill epithelium. Sodium in the

water is exchanged for hydrogen ions or ammonium ions, and chloride for bicarbonate (Maetz 1973, Evans 1975). Increased hydrogen ion activity in the surrounding medium may impede the active uptake of sodium. 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, Section 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 nervous conductions and enzymatic reactions.

Laboratory experiments have also found decreased plasma (or whole body) sodium and/or chloride levels as a result of exposure of organisms to low pH levels (Packer and Dunson 1970, 1972; Leivestad and Muniz 1976; McWilliams and Potts 1978; Jozuka and Adachi 1979; Leivestad et al. 1980; McWilliams et al. 1980; McDonald et al. 1980; McDonald and Wood 1982; Ultsch et al. 1981). The exact mechanisms behind these effects are not, however, fully understood. A major influence on branchial ion fluxes is the transepithelial potential (TEP) across the gills. The TEP of brown trout has been shown to be strongly dependent on the pH of the external medium, being negative in neutral solutions but positive in acid solutions (McWilliams and Potts 1978). At near neutral pH, the influx and efflux of sodium were similar, indicating that trout were in sodium balance. As the pH in the external medium declined, sodium influx decreased and sodium efflux increased until, at pH 4.0, the rate of loss of sodium amounted to about 1 percent of the total body sodium per hr.

These processes are influenced by the content of dissolved salts in the water, particularly calcium and sodium (McDonald et al. 1980; Brown 1981, 1982). Calcium is essential in the maintenance of ionic balance in freshwater fish, probably as a result of its influence on the permeability of gills to certain ions (McWilliams and Potts 1978, McWilliams 1980a). Increased calcium concentrations (from near zero to about 40 mg ℓ^{-1}) decreased membrane permeability and thus decreased the rate of passive sodium efflux from fish. At the same time, calcium appeared to have no significant effect on sodium influx (McWilliams 1980a, 1982). The result was a decrease in the overall rate of sodium loss from fish exposed to low pH in waters with higher calcium content. Gill permeability also varied between species and populations of fish (McWilliams 1982), and sodium loss rates declined with acclimation of fish to acid waters (McWilliams 1980b). These results help explain the observed correlation between low calcium levels and loss of fish populations in Norwegian Lakes (Section 5.6.2.1.3; Wright and Snekvik 1978) and imply that small changes in calcium availability in natural waters (e.g., during spring snowmelt, see Chapter E-4, Section 4.3.2.6) and previous exposure of fish to high acidity are crucial factors in determining the response of fish exposed to sudden acid episodes.

A decrease in blood pH levels (by 0.2 to 0.5 pH units) is often associated with the drop in plasma sodium levels in fish exposed to low pH waters (Lloyd and Jordan 1964, Packer and Dunson 1970, Packer 1979, Jozuka and Adachi 1979, Neville 1979a, McDonald et al. 1980, McDonald and Wood 1982, Ultsch et al. 1981) and is possibly a result of flux of hydrogen ions across gill membranes into the blood. McDonald et al. (1980) noted that in moderately high alkalinity waters (calcium 30 to 50 mg ℓ^{-1}), fish exposed to a pH of 4.3 developed a major blood acidosis (drop in blood pH) but exhibited only a minor depression in plasma ion levels. In acidified, low alkalinity water (calcium 6 mg ℓ^{-1}), only a minor acidosis occurred, but plasma ion levels fell and mortality was substantially greater. Possibly the nature of the mechanism of acid toxicity varies with the nature of the ionic environment.

A drop in blood pH level would affect a large number of pH-sensitive metabolic reactions. The oxygen carrying capacity of fish blood drops sharply below a blood pH level of 7.0 (Green and Root 1933, Prossner and Brown 1961). Decreased oxygen consumption by fish exposed to acid waters has been found by Packer and Dunson (1970, 1972), Packer (1979), and Ultsch (1978). Carrick (1981), however, observed no significant differences in oxygen uptake by brown trout fry at pH 7.0 vs pH 4.0. Neville (1979b) concluded that an observed increase in serum erythrocyte concentration offset the reduced capacity of the hemoglobin to transport oxygen brought about by acidosis. The increase in hemoglobin level, maintenance of arterial oxygen tension (pO_2), and constancy of blood lactate levels in rainbow trout exposed to pH 4.0 suggested that there was no oxygen stress despite the acidosis.

At critically low pH levels ($\leq$ 3.5), where death occurs within hours rather than days, a failure of oxygen delivery to the tissues may be of primary importance. A marked reduction in blood oxygen capacity due to massive acidosis, combined with impaired branchial oxygen diffusion as a result of accumulation of mucous on the gills and a sloughing of gill epithelial tissue (e.g., Plonka and Neff 1969, Daye and Garside 1976, Ultsch and Gros 1979), may result in eventual cellular anoxia. However, such low pH levels are rarely encountered by fish in natural situations. At more moderate pH levels, mucous accumulation on the gills has not been observed and blood gas levels remain normal, indicating acid-base and/or ion regulatory failure are more probable mechanisms of toxicity (McDonald et al. 1980, Fromm 1980).

Finally, Nelson (1982) reported that ossification, amount of calcium deposited in bone, in rainbow trout fry varied significantly ($p < 0.005$) as a function of pH of the medium (pH 4.3, 4.8, and 7.3). After calcium stores from the yolk sac are exhausted, fry must accumulate calcium from the surrounding water and from food intake. A decrease in skeletal ossification at low pH level could be partially responsible for increased incidence of skeletal deformities observed in some laboratory bioassays at low pH (e.g., Beamish 1972, Mount 1973, Trojnar 1977b) and in white suckers from acidic George Lake, LaCloche

Mountain region, Ontario (Beamish et al. 1975). Nelson (1982), however, noted no increase in deformities despite decreased ossification.

5.6.4.2 Effects of Aluminum and Other Metals in Acidic Waters--Increases in certain metal concentrations can be associated with deecreasing pH levels in acidified surface waters (Chapter E-4, Section 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. Critical values for survival of fish populations developed only on the basis of pH level may therefore be misleading.

Muniz and Leivestad (1980a) noted that naturally acidified water is generally more toxic to fish than are dilute sulfuric acid solutions of the same pH. Brown trout exposed to soft waters acidified by additions of sulfuric acid (a pure hydrogen ion stress) demonstrated physiological stress (impaired regulation of body salts) only at pH levels below 4.6 (Leivestad et al. 1980). When tests were performed in water from acidified brooks and rivers in southern Norway, water with a pH of 4.6 resulted in significant physiological stress, rapid salt depletion, and mortality after 11 days (Leivestad et al. 1976; Section 5.6.3.3). For Atlantic salmon, Daye and Garside (1977) found lower limits for survival of fry to be around pH 4.3 and pH 3.9 for eggs exposed from fertilization through hatching (Section 5.6.4.1.2). Bua and Snekvik (1972), on the other hand, used water from the acidic Mandal River, Norway and found lower limits for survival to be pH 5.0 to 5.5. Schofield observed stress and heavy mortality among adult, yearling, and sac fry of brook trout held in an Adirondack hatchery receiving lake water from Little Moose Lake at pH 5.9 during spring snowmelt in 1977 (Schofield and Trojnar 1980; Section 5.6.2.4). In contrast, in laboratory experiments (Sections 5.6.4.1.1 and 5.6.4.1.2) critical pH levels for brook trout were generally between pH 3.5 and 4.5. These and other comparisons strongly imply that acidified lake and river water must contain toxic agents in addition to hydrogen ions (Muniz and Leivestad 1980a).

Metals consistently exhibiting increased concentrations in acidic surface waters, apparently as a result of increased solubility with decreasing pH level, are aluminum, manganese, and zinc (Chapter E-4, Section 4.3.4.1). In some regions, concentrations of cadmium, copper, lead, nickel, and other metals are also elevated in acidic lakes. High concentrations of these metals, however, probably result primarily from increased atmospheric loading and deposition and occur principally in surface waters in close proximity to pollutant sources (e.g., Sudbury, Ontario). As such, they are not specifically a result of acidic deposition but may still interact additively or synergistically with toxic effects of low pH, aluminum, manganese, or zinc. Unfortunately, with the exception of aluminum, data are not sufficient for a thorough evaluation of possible adverse effects of metals on fish in acidic waters. Spry et al. (1981) and Baker (1982) have reviewed the available literature.

Total zinc concentrations measured in acidic surface waters in the Adirondack region, in southern Norway and in southwestern Sweden ranged up to 0.056 mg ℓ^{-1} (Schofield 1976b, Henriksen and Wright 1978, Dickson 1980). Although laboratory bioassays examining effects of zinc on fish are numerous (Taylor et al. 1982), none of these studies considered low alkalinity water with pH levels below 6.0, and results should not be automatically extrapolated to conditions in acidified surface waters. For the most part, however, lethal concentrations of zinc in bioassays are 10 times zinc concentrations found in acidic waters (Spry et al. 1981, Taylor et al. 1982). Sinley et al. (1974) estimated that the maximum acceptable toxicant concentration (MATC) for rainbow trout exposed to zinc in low alkalinity circumneutral water was between 0.14 and 0.26 mg ℓ^{-1}. Benoit and Holcombe (1978) determined that the threshold level for significant adverse effects on the most sensitive life history stage of fathead minnows was between 0.078 and 0.145 mg ℓ^{-1}. Taylor et al. (1982) concluded from a review of the available literature that concentrations of zinc that could be tolerated by aquatic organisms lie between 0.026 and 0.076 mg ℓ^{-1}.

Manganese has been considered a relatively nontoxic element; thus toxicological data are very limited. Total manganese concentrations measured in acidic surface waters ranged up to 0.13 mg ℓ^{-1} in the Adirondacks (Schofield 1976b) and up to 0.35 mg ℓ^{-1} in southwestern Sweden (Dickson 1975). Lewis (1976) determined that manganese concentrations up to 0.77 mg ℓ^{-1} had no effect on survival of rainbow trout in soft waters with pH levels of 6.9 to 7.6.

Relationships between pH and levels of cadmium, copper, lead, and nickel vary markedly between regions. Excluding lakes within 50 km of Sudbury, concentrations of cadmium, copper, lead, and nickel measured in acidic Ontario surface waters ranged up to about 0.6, 9, 6, and 48 µg Ni ℓ^{-1}, respectively (Spry et al. 1981). In southwestern Sweden, concentrations of cadmium in acidic waters were measured up to 0.3 µg ℓ^{-1}; lead up to 5 µg ℓ^{-1} (Dickson 1980). Spry et al. (1981) reviewed available bioassay data and noted no significant adverse effects on survival and reproduction at concentrations up to 0.7 to 11 µg Cd ℓ^{-1}, 9.5 to 77 µg Cu ℓ^{-1}, 13 to 253 µg Pb ℓ^{-1}, and 380 µg Ni ℓ^{-1}.

In general, all of these reported toxic concentrations and/or maximum acceptable concentrations for zinc, manganese, cadmium, copper, lead, and nickel are above the highest levels of these metals measured in acidic surface waters of Scandinavia and eastern North America (unless a local source of metal emissions exists). However, the lack of sufficient bioassay data collected in low alkalinity, acidic waters makes this statement tentative. In addition, sublethal and additive or synergistic effects with other toxic components in acidified surface waters cannot be ruled out.

Aluminum, on the other hand, has been found to be toxic to fish at concentrations as low as 0.1 to 0.2 mg ℓ^{-1} (Schofield and Trojnar 1980, Muniz and Leivestad 1980b, Baker and Schofield 1982), a level within the range of concentrations measured in acidic surface waters.

Total aluminum levels measured ranged up to 1.4 mg ℓ^{-1} in the Adirondack region, New York (Schofield 1976b), 0.76 mg ℓ^{-1} in southwestern Sweden (Dickson 1975, Wenblad and Johansson 1980), 0.6 mg ℓ^{-1} in southern Norway (Wright et al. 1980), and 0.8 mg ℓ^{-1} in the Pine Barrens of New Jersey (Budd et al. 1982). In addition, analysis of survival of brook trout stocked into 53 Adirondack lakes as a function of 12 water quality parameters indicated aluminum to be a primary chemical factor controlling trout survival (Schofield and Trojnar 1980; Section 5.6.2.1.2.1).

Baker (1981, 1982), Baker and Schofield (1982), and Driscoll et al. (1980) examined the effect of aluminum complexation on aluminum toxicity to fish in laboratory experiments. Complexation of aluminum with organic chelates appeared to eliminate aluminum toxicity to fry, and survival of brook trout and white sucker fry in acidic Adirondack waters correlated most accurately with inorganic aluminum concentrations and pH. The toxicity of a given inorganic aluminum concentration varied at different pH levels and with different life history stages. At low pH levels (4.2 to 4.8), the presence of aluminum was beneficial to egg survival. In contrast, in experiments with sac fry and fry, aluminum concentrations of 0.1 mg ℓ^{-1} (for white suckers) or 0.2 mg ℓ^{-1} (for brook trout) and greater resulted in measurable reductions in survival and growth at all pH levels (Schofield and Trojnar 1980, Baker and Schofield 1982, Muniz and Leivestad 1980a).

The toxic action of aluminum seems to be a combined effect of impaired ion exchange and respiratory distress caused by mucous clogging of the gills (Muniz and Leivestad 1980a). Muniz and Leivestad (1980b) observed rapid loss of sodium and chloride from the blood of brown trout exposed to aluminum concentrations as low as 0.19 mg ℓ^{-1} at pH 5.0. Schofield and Trojnar (1980) noted moderate to severe gill damage at aluminum levels of 0.5 and 1.0 mg ℓ^{-1} at pH 4.4 and higher. Aluminum was particularly toxic in solutions over-saturated with aluminum at pH levels 5.2 to 5.4 (Baker and Schofield 1982).

The pH level in acidic waters therefore affects fish survival both as a direct toxicant and by controlling the concentration of inorganic aluminum.

5.6.5 Summary

5.6.5.1 Extent of Impact

Loss of fish populations associated with acidification of surface waters has been documented for five areas--the Adirondack region of New York State, the LaCloche Mountain region of Ontario, Nova Scotia, southern Norway, and southern Sweden. The following summarizes major points from Section 5.6.2.1:

- The best evidence that the loss of fish has occurred in response to acidification is derived from observations of lakes in the LaCloche Mountain region, Ontario (Section 5.6.2.1.2.1).

Twenty-four percent of 68 lakes surveyed had no fish present. Fifty-six percent of the 68 lakes are known or suspected to have had reductions in fish species composition (Harvey 1975). Based on historic fisheries information, 54 fish populations are known to have been lost, including lake trout populations from 17 lakes, smallmouth bass from 12 lakes, largemouth bass from four lakes, walleye from four lakes, and yellow perch and rock bass from two lakes each (Harvey and Lee 1982). The principal source of atmospheric acidic inputs to the LaCloche area is sulfur dioxide emitted from the Sudbury smelters located about 65 km to the northeast. Large acidic inputs have resulted in relatively rapid acidification of many of the region's lakes. For some lakes the development of increased lake acidity and the simultaneous decline of fish populations have been followed and recorded by a single group of researchers (Beamish and Harvey 1972, Beamish et al. 1975, Harvey and Lee 1982) from the mid-1960's to the present.

- In Norway (Section 5.6.2.1.3.1), sharp drops in catch of Atlantic salmon in southern rivers began in the early 1900's and are associated with current low pH levels and a recorded doubling of the hydrogen ion concentration in one of these rivers from 1966 to 1976 (Jensen and Snekvik 1972, Leivestad et al. 1976). For almost 3000 lakes in Sørlandet (southernmost Norway) data on the status of brown trout has been recorded since about 1940 (Sevaldrud et al. 1980). Today, more than 50 percent of the original populations have been lost, and approximately 60 correlated with acidity, acidification, and/or inputs of acidic deposition (Wright and Snekvik 1978).

- Extensive surveys of fish population status and acidity of surface waters in Sweden have not been completed (Section 5.6.2.1.3.2). However, for 100 lakes in southern Sweden with historic records on fish populations, loss of fish was correlated with present-day low pH levels in lakes (Almer et al. 1978). Forty-three percent of the minnow populations, 32 percent of the roach, 19 percent of the char, and 14 percent of the brown trout populations had disappeared.

- In Nova Scotia, records of angling catch of Atlantic salmon in rivers date back, in some cases, to the early 1900's (Section 5.6.2.1.2.3). Of 10 rivers with current pH < 5.0 and historic catch records, 9 have had significant declines in angling success over the time period 1936 to 1980. For 12 rivers with pH > 5.0, only one experienced a significant decrease in salmon catch. Decrease in salmon catch over time is correlated with present-day pH values 5.0 and below. In addition, 6 former salmon rivers with current pH < 4.7 have no long-term catch records, but surveys in 1980 indicated they no longer support salmon runs. Acidification of rivers in the area between 1954 and 1974 has been reported (Chapter E-4, Section 4.4.3.1.2.2). The high organic content in many of the low pH waters

(especially pH < 4.7) suggests, however, that these rivers are naturally somewhat acidic, and perhaps always had fairly low pH values and low fish production (Farmer et al. 1981). The estimated lost or threatened Atlantic salmon production potential represents 30 percent of the Novia Scotia resources but only 2 percent of the total Canadian potential (Watt 1981).

- Finally, fish populations in Adirondack lakes and streams have also declined over the last 40 to 50 years (Section 5.6.2.1.1.1). The New York State Department of Environmental Conservation reports that about 180 lakes (2900 ha) out of a total of 2877 lakes (114,000 ha) in the Adirondacks have lost their fish populations (especially brook trout) (Pfeiffer and Festa 1980). The absence of fish in Adirondack lakes and streams is clearly correlated with low pH levels (Schofield 1976b), although several factors may confound this relationship, e.g., lake size dystrophic conditions. Records of pH and other information have not, however, been published to substantiate that loss of fish in these 180 lakes resulted from acidification. For very few individual lakes are historical data available that suggest both lake acidification and simultaneous loss of fish. Acidification probably contributed to the disappearance of fish for at least some surface waters, but exactly how many lakes and streams (perhaps substantially less than or more than 180) have been impacted cannot be satisfactorily evaluated at this time.

- In other regions of the world with low alkalinity waters and receiving acidic deposition (e.g., Muskoka-Haliburton area of Ontario and Maine) (Sections 5.6.2.1.1.1 and 5.6.2.1.2.2) acidification of surface waters does not appear to have progressed to levels clearly detrimental to fish (Schofield 1982). No damage to fish populations has been reported.

5.6.5.2 Mechanism of Effect--Three major mechanisms for the disappearance of fish populations with acidification have been proposed: (1) decreased food availability and/or quality; (2) fish kills during episodic acidification; and (3) recruitment failure. Each probably plays some role, although recruitment failure has been hypothesized as the most common cause of population loss (Schofield 1976a, Harvey 1980, NRCC 1981, Overrein et al. 1980, Haines 1981b). The following summarizes major points from Sections 5.6.2.2 through 5.6.2.4, and 5.6.3.1:

- The influence of food chain effects on decreases in fish populations in acidified waters has received little attention to date, but available information suggests it plays a relatively minor role (Beamish 1974b, Hendrey and Wright 1976, Muniz and Leivestad 1980a, Rosseland et al. 1980). With acidification, or in comparisons between acidic and circumneutral lakes, fish

growth is often unaffected or increased with increasing acidity (Section 5.6.2.3). Some important prey organisms are sensitive to acidic conditions and disappear with acidification yet fish seem capable of shifting to other suitable prey. During the experimental acidification of Lake 223 (Section 5.6.3.1), lake trout production remained unchanged in spite of the loss of fathead minnows, a major prey item prior to acidification (Mills 1982). Few studies, however, have examined the potential effect of reduced food quantity and/or quality on survival of early life history stages of fish or on fish production at pH levels above those that result in recruitment failures and reduced population size.

- Fish kills have been observed during episodic acidification of surface waters (Section 5.6.2.4), and in certain instances may play an important role in the disappearance of fish from acidified surface waters. For example, in the Tovdal River, Norway, in 1975 thousands of dead adult trout were observed in association with the first major snow melt in spring (Leivestad et al. 1976). Dead and dying fish are, however, seldom reported in acid-stressed waters relative to the large number of lakes, streams, and rivers with fish populations apparently impacted by acidification. In contrast, a substantial portion of fish populations examined in acidified lakes lack young fish (Section 5.6.2.2) and apparently have experienced recruitment failure.

- Recruitment failure may result either from acid-induced mortality of eggs and/or larvae or because of a reduction in numbers of eggs spawned. The number of eggs spawned could be reduced as a result of disruption of reproductive physiology and ovarian maturation or inhibition of spawning behavior. Evidence exists that supports each one of these proposed mechanisms (Sections 5.6.2.2, 5.6.4.1.2, 5.6.4.1.4, and 5.6.4.1.5). For example, Johnson and Webster (1977) demonstrated experimentally that brook trout avoid spawning in waters with pH below 5.0. Beamish and Harvey (1972) observed that recruitment failure in several acidic lakes in the LaCloche Mountain region, Ontario was associated with a failure of the female fish to spawn. Lockhart and Lutz (1977) hypothesized that a disruption in normal calcium metabolism, induced by low pH, had adversely affected the reproductive physiology of female fish in these lakes. Adverse effects of low pH levels and elevated aluminum concentrations on survival of fish eggs and larvae have been demonstrated in numerous laboratory and field experiments (Sections 5.6.3.3 and 5.6.4.1.2). In Norway, total mortality of naturally spawned trout eggs was observed in an acidic stream a few weeks after spawning (Leivestad et al. 1976).

- It is likely that each one of these factors plays some role in recruitment failure but the importance of each factor probably varies substantially among aquatic systems, depending on the particular circumstances.

- More research is necessary to define clearly the specific mechanism for population decline in a given water. However, many studies in the United States and Scandinavia (Schofield 1976a, Muniz and Leivestad 1980a) emphasize increased mortality of eggs and larvae in acidic waters as the primary cause of recruitment failures, and recruitment failure as a common cause for the loss of fish populations with acidification of surface waters.

5.6.5.3 Relationship Between Water Acidity and Fish Population Response--To assess the impact of acidification on fish resources quantitatively, the functional relationship between acidification and fish population response must be understood. Unfortunately, loss of fish populations from acidified surface waters is not a simple process and cannot be accurately summarized as "X" pH (or aluminum concentration) yields "Y" response. The mechanism by which fish are lost (Section 5.6.5.2) seems to vary between aquatic systems and probably within a given system from year-to-year.

The water chemistry within a given aquatic system is likewise extremely variable both spatially and temporally, and these variations are very important to the survival or decline of fish populations. Lakes with seemingly identical water quality may show marked differences in fish response, perhaps reflecting, in part, the existence or lack of water quality "refuge" areas for fish survival (Muniz and Leivestad 1980a). A circumneutral tributary or small segment of a lake may provide an area for successful fish reproduction for a number of years following acidification of the main body of a lake.

Fish species differ not only in their ability to tolerate acidic conditions but also in their ability to exploit these chemical variations in their environment (e.g., spawning time and location). Within a given fish species, sensitivity to acidity varies with life history stage, age, condition, previous exposures to acidity, associated water quality conditions (e.g., aluminum and calcium concentrations, temperature), and other parameters. In addition, for reasons discussed at the beginning of Section 5.6.4, results from laboratory experiments cannot be translated automatically into an expected response in the field. Serious gaps exist in the understanding of how to use laboratory results in a quantitative prediction of fish response in the field and in the analysis of the complexity of the natural environment and the significance of this complexity in determining the impact of acidification. It is therefore not surprising that development of an accurate functional relationship between acidification and fish response is impossible at this time.

First steps, however, in developing such a relationship are to: examine in a semi-quantitative manner all of the available information connecting acidity and fish (summarized in Table 5-14), produce an initial approximation of the dose-response relationships (Figure 5-16), and then assess patterns and reasons for deviations from this initial

TABLE 5-14. SUMMARY OF FIELD OBSERVATIONS, FIELD EXPERIMENTS, AND LABORATORY EXPERIMENTS RELATING WATER pH TO FISH RESPONSE

	Brook Trout	Lake Trout	Arctic Char	Brown Trout	Rainbow Trout	Atlantic Salmon	White Sucker	European Perch	Walleye	Fathead Minnow	Roach	Northern Pike	Slimy Sculpin	Brown Bullhead
FIELD OBSERVATIONS														
Recruitment failure	5.0-5.5[a]	5.2-5.5[b] 6.9[e] 5.7[i]	5.2[c]	< 5.0[c] 4.7-5.1[f]		4.7-5.0[d]	5.2[a] 4.7-5.2[b] 5.0[e]	4.4-4.9[c] 5.0-5.5[g] <4.7[h]	5.5-6.0[b] 5.4[e] 6.5[i]		5.5[e] 5.1[f]	5.0[e] 5.0[f] 4.4-4.9[c] 4.7[h]		4.7-5.2[b] 4.9[e] 5.2[i]
Population loss	5.0[a] 4.5-4.8[j]	5.0-5.5[a] 4.4[e]		4.5-4.8[j] 4.5-5.0[l] 5.1[h] 4.9-5.1[m]	5.5-6.0[j]	5.1[k]	5.1[a] 4.3[e]		5.2[e] 5.5[f]		4.7[i]	4.3[e]		4.7-5.0[a] 4.7[e]
Fish kill	5.9[n]			4.6[m] 5.0[l]		3.9-4.2[o] 5.0[n]								
FIELD EXPERIMENTS														
Recruitment failure		5.1-5.3[q]					5.1-5.3[t]			5.8-6.0[q]			5.3-5.8[q]	
Population extinction										5.3-5.8[q]				
Adult mortality	4.8-5.2[n] 4.7-5.1[s] 4.4-4.6[t]				4.0-5.0[r]									
Embryo mortality	4.5-4.6[s]			4.5[o] 4.8[k] 5.1[w]		4.5-5.0[l] 5.0-5.5[o] 4.9[k]		4.7-5.7[u]	5.4[v]		5.7[u]			
LABORATORY EXPERIMENTS														
Adult mortality-acute (2 day)	3.8[x] 3.5[bb] 3.6[dd]			3.8[y]	4.0[z] 3.8-4.8[cc] 4.0-4.2[ee]		3.9[aa]			< 4.6[h]				
Adult mortality-chronic (> 20 day)	4.4[ff] 4.5[ii]		< 4.8[gg]	< 4.8[gg]	< 5.0[gg]			5.0[g] 5.6[ll]		5.9[hh]	5.6[ll]			
Embryo mortality	*4.1[jj] 6.1[ii] 4.4[dd] <4.6[pp] <4.0[kk]			4.1[kk] 4.0-4.5[mm]		4.1[kk] 5.5[nn] 5.5[mm] 4.5[qq]	*> 5.6[jj] 5.2[oo]							
Fry mortality	*4.4-4.9[n] *4.5-4.8[jj] 6.1[ii] 4.2[dd] <4.4[kk] 4.0-5.0[pp]			4.4[kk]		3.7-4.0[rr] 5.0[kk]	*5.4-5.6[jj] 5.0-5.4[oo]			< 5.9[hh]		4.2-5.2[ss]		
Reduced production of viable eggs	5.1[ii]									6.6[hh]				
Reduced growth	6.5[ii]		4.8[gg]	4.8[gg] < 5.0[xx]	4.8[gg] 4.3-4.8[uu]						5.3[ww]			
Avoidance	4.5[vv]					5.3[ww]								

	Lake Herring	Lake Whitefish	Smallmouth Bass	Largemouth Bass	Rock Bass	Pumpkinseed Sunfish	Bluegill	Yellow Perch	Common Shiner	Bluntnose Minnow	Lake Chub	Creek Chub	Trout Perch	Gadidae Burbot
FIELD OBSERVATIONS														
Recruitment failure	4.5-4.7[b]	5.0[f]	5.5-6.0[b] 5.0[c]	5.1[c] 5.0[d]	4.7-5.2[b] 5.0[c]	5.0[d]		4.5-4.7[b] 4.4[c]	5.5-6.0[f] 5.7[c]		4.5-4.7[b]		5.2-5.5[b]	5.5-6.0[b]
Population loss	4.4[c]	4.4[c]	4.4[c]	4.4[c] 6.0[d]	4.8-5.0[r] 4.3[c]	4.3[c]	4.4[c]	4.4-5.0[s] 4.3[c]		5.7[b]	4.5-5.0[a]	5.0[a]		5.4[d]

REFERENCES

a Schofield 1976c
b Beamish 1976
c Almer et al. 1978
d Watt et al. 1983
e Harvey 1979
f Hultberg 1977
g Runn et al. 1977
h Grahn et al. 1974
i Beamish et al. 1975
j Grande et al. 1978
k Leivestad et al. 1976
l Harriman and Morrison 1982
m Overrein et al. 1980
n Schofield and Trojnar 1980
o Jensen and Snevik 1972
p Farmer et al. 1981
q Mills 1982
r Harvey et al. 1982
s Schofield 1965
t Dunson and Martin 1973
u Milbrink and Johansson 1975
v Hulsman and Powles 1981 as reported in MOI 1982
w Muniz and Leivestad 1980
x Johnson 1975
y Brown 1981
z Kwain 1975
aa Beamish 1972
bb Robinson et al. 1976
cc McDonald et al. 1980
dd Swarts et al. 1978
ee Lloyd and Jordan 1964
ff Swartz et al. 1978
gg Edwards and Hjeldnes 1977
hh Mount 1973
ii Menendez 1976 (e from Table 5-22)
jj Baker and Schofield 1982
kk Johansson et al. 1977
ll Johansson and Milbank 1976
mm Carrick 1979
nn Peterson et al. 1980a
oo Trojnar 1977b
pp Trojnar 1977b
qq Peterson et al. 1980b (conf)
rr Daye and Garside 1976
ss Johansson and Kihlstrom 1975
tt Jacobsen 1977
uu Nelson 1982
vv Johnson and Webster 1977
ww Hoglund 1961
xx Ryan and Harvey 1977
yy Ryan and Harvey 1980

*Refers to laboratory experiments taking into account both low pH and inorganic aluminum (at the expected concentration for that pH based on Driscoll 1980).

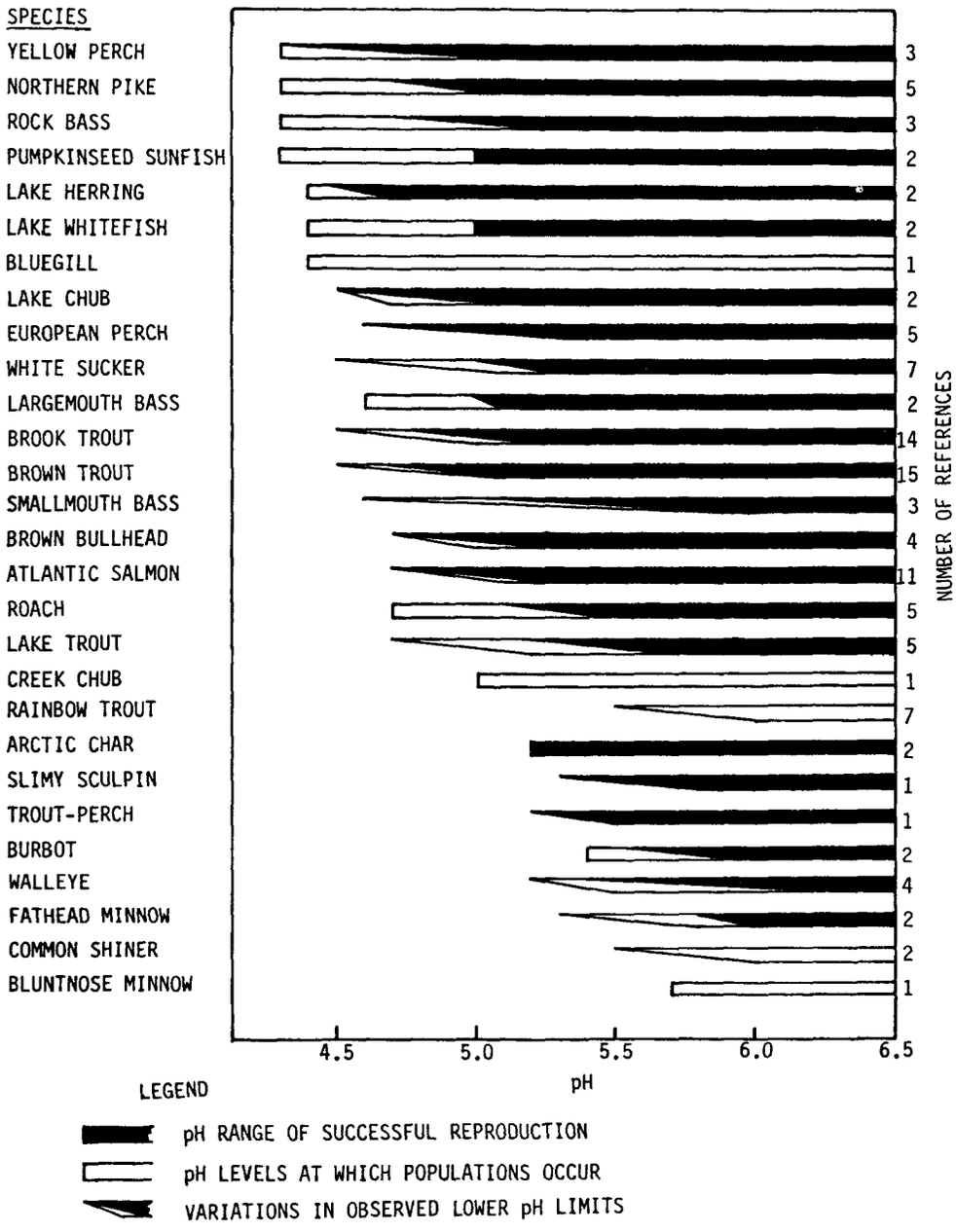

Figure 5-16. Initial estimates of relationship between acidity and fish response, based on references in Table 5-14.

approximation. In large part, the analysis of deviations and variations must be done on a lake-by-lake, population-by-population basis, and is the subject for further research. Several points are, however, obvious. Acidification adversely affects fish populations. Sensitivity of fish to acidity is species-dependent, and determined by aluminum and calcium concentrations, in addition to pH values. Loss of fish populations need not be associated with large declines in annual average pH, but could result from indirect effects on aluminum chemistry or episodic acidification.

5.7 OTHER RELATED BIOTA (R. Singer and K. L. Fischer)

5.7.1 Amphibians

Direct effects of acidity on vertebrates have been demonstrated only on fish (Section 5.6) and amphibians. Amphibians are particularly sensitive because many frogs, toads, and salamanders breed in vernal pools filled by acidic snowmelt and spring rains. The salamanders Ambystoma maculatum and A. jeffersonianum breed in shallow hilltop ponds that have pH values 1.5 pH units less than nearby permanent ponds in New York State (Pough and Wilson 1977). Spotted salamander (A. maculatum) egg mortality increased to > 60 percent in water less than pH 6.0, a substantial rise from the normal mortality of < 1 percent at pH 7.0. In contrast, the Jefferson salamander, A. jeffersonianum, was most successful at pH 5.0 to 6.0 (Pough 1976). The preference for neutral water by adult spotted salamanders may be a result of the absence of their preferred prey, the stickleback (Eucalia), from acidic water (Bishop 1941). When a stretch of stream was artificially acidified to pH 4.0, "salamanders" were reported (Hall and Likens 1980a) to leave the water. Elsewhere in its range in central Ontario, the number of egg masses of the spotted salamander positively correlated with pH (Clark and Euler 1980). Adults are not as sensitive to pH stress, but given a choice, adult spotted salamanders (A. maculatum) preferred neutral substrates (Mushinsky and Brodie 1975).

The contribution of salamanders to the energy flow of a forest aquatic ecosystem is considerable. In one study (Burton and Likens 1975a), 20 percent of the energy available to birds and mammals passed through salamanders, and these amphibians represented twice as much standing crop of biomass as did birds and an amount equal to that of small mammals (Burton and Likens 1975b). Most (94 percent) of the salamanders were terrestrial, but all salamanders are aquatic as larvae. Not only do amphibians provide energy for birds and mammals, but they represent the top predators in many temporary ponds (Orser and Shure 1972).

The species specific tolerance of amphibians to low pH was confirmed by a survey of newts in England (Cooke and Frazer 1976). Smooth newts (Triturus vulgaris) were rarely encountered in water with pH < 6.0, but the palmate newt (T. helveticus) was routinely captured in bogs at pH 4.0 to 3.8. The distributions of these species were correlated most strongly with potassium and calcium concentrations, both of which co-varied with pH. The variable sensitivity of newts to

acid-stress is demonstrated by the american red-spotted newt, Notophthalamus viridescens, which one of us (RS) has observed at 6 m in acidic (pH 4.9) Woods Lake. This same species has been reported at 13 m in neutral (pH 7.4) Lake George, also in the Adirondacks (George et al. 1977).

Many anurans are sensitive to acidity, too. Calling densities (an estimate of population size) of spring peepers (Hyla crucifer) were positively correlated with the pH of water in which they occurred (Clark and Euler 1980). Bullfrogs (Rana catesbeiana) (Clark and Euler 1980, Cecil and Just 1979, Saber and Dunson 1978), wood frogs (R. sylvatica) (Clark and Euler 1980) the common frog (R. temporaria) (Hagstrom 1977), and the leopard frog (R. pipiens) (Noble 1979) have all been reported to be sensitive to acidity below pH 5.0. Evidence from counts of dead and moldy egg masses in the Netherlands (Strijbosch 1979) supports the relationship between acidity and mortality of frogs. The most serious effects occur in the immature stages (Gosner and Black 1957). Cricket frog (Acris gryllus) and spring peeper (Hyla crucifer) embryos exposed to pH 4.0 for a few hours suffered 85 percent mortality. Noble (1979) reported embryonic mortality in the leopard frog (R. pipiens) at pH < 4.7, and Schlichter (1981) observed sub-lethal reductions in sperm mobility in this species below pH 6.5 and some embryonic mortality at pH < 6.3. In spite of the sensitivity of R. pipiens to acidity in the laboratory, one of us (RS) has seen adult leopard frogs in an acidic (pH 4.8) Adirondack lake. The larvae may have been breeding in ponds that provided refuge near the lake. Reports of only adult amphibians are of questionable value because of the much greater sensitivity of the larval forms.

Toads, although terrestrial as adults, are also sensitive to acidity as larvae and embryos. The common toad (Bufo bufo) was not reported below pH 4.2 in Sweden (Hastrom 1977), and the natterjack toad (Bufo calamita) was not found below pH 5.0 (Beebee and Griffin 1977) in England.

The mechanism by which acidity effects amphibians is not known. Huckabee et al. (1975) suggest that the aluminum, manganese, and zinc mobilized by low pH (Chapter E-4, Section 4.6) may be toxic agents for the shovel-nosed salamander (Leurognathus marmoratus) larvae in the Great Smokey Mountains National Park. Another mechanism may be the inability to control ion fluxes across membranes against strong H^+ gradients. This has been indicated in fish (Section 5.6), invertebrates (Sections 5.3 and 5.5), and frogs (Fromm 1981).

5.7.2 Birds

5.7.2.1 Food Chain Alterations--Direct effects of acidity on birds are not expected, but indirect effects by alterations in food resources and bioaccumulation of toxic metals is possible. Waterfowl that feed on fish are likely to avoid lakes devoid of prey. Indeed, species richness of fish-eating birds such as mergansers, loons, and gulls is positively correlated with pH (Almer et al. 1978, Nilsson and Nilsson 1978). The

diet of the common loon, Gavia immer, is approximately 80 percent fish, the remainder consisting of crustaceans, molluscs, aquatic insects, and leeches (Barr 1973). The range of the loon includes the sensitive areas of Canada's Precambrian Shield (Godfrey 1966) and the Adirondack Mountains. Populations have declined in the Adirondacks (Trivelpiece et al. 1979), but no causal relationship between acidification and declining bird populations was implied (McIntyre 1979) but habitat restriction unrelated to acidification is important in. In Quebec, the common merganser (Mergus merganser) and the kingfisher (Megaceryle alcyon) were observed only on those lakes where the summer pH is higher than 5.6 (DesGranges and Houde 1981). The distribution of the black duck (Anas rubripes) has been restricted in some lakes in Maine because of the lack of their preferred invertebrate prey (Reinecke 1979) but habitat restriction unrelated to acidification is important in this area. Some waterfowl may prefer acidic lakes if they can prey on the large predatory insects which are often very common in these lakes (Section 5.3.2.5). Goldeneye ducks (Bucephala clangula) were shown to favor acidic fishless lakes that had large insect populations (Eriksson 1979) and to feed in larger numbers around a lake after the fish were experimentally removed (Eriksson et al. 1980a). Birds are opportunistic feeders. The alteration of a food resource from a number of lakes may reduce the population but not cause a total loss of population as the birds switch to other resources and to other lakes in the region.

Birds such as swallows, flycatchers, and kingbirds that feed on the aerial adult form of aquatic insects are forced to find alternative food sources if the insect populations upon which they normally feed are depleted (Section 5.3.2.5). In early spring when many aquatic insects emerge, acid runoff to lakes and ponds is at a peak. It is also in early spring that the birds depend heavily on a supply of food to prepare for nesting and raising young. This may be the explanation for the observation in southern Quebec, where the tree swallow (Iridoproene bicolor) was more common during the breeding season around the less acid lakes studied (DesGranges and Houde 1981). Blancher (1982) observed that weight gain of kingbirds was related to insect emergence, not lake pH. Lake pH was not correlated with densities of red-winged blackbirds (Agelaius phoniceus) and barn swallows (Hirundo rustica).

5.7.2.2 Heavy Metal Accumulation--Alterations of food resources may not be the only mechanism by which birds may be inhibited by acidity. The mobilization of metals at low pH (Chapter E-4, Section 4.6) may result in increased body burdens in higher trophic levels. Studies by Nyholm and Myhrberg (1977) and Nyholm (1981) have implicated aluminum in the impaired breeding of four species of passerines in Sweden. Aluminum is quite insoluble in the alkaline conditions characteristics of vertebrate intestines, but it might be actively transported across the intenstinal barrier if calcium is in short supply. Effects were manifested by reductions in breeding success; formation of thin, porous eggs; small clutch size; and lower egg weight near acidic lakes. The causal link with lake pH was suggested to be the high aluminum content of the insects near the acidic lakes (Nyholm 1981). A laboratory study (Gilani and Chatzinoff 1981) proved that aluminum is toxic to bird embryos but

results from Al injected into eggs are not comparable to field responses to dietary Al. Similar findings of decreased egg size and weight were found for the eastern kingbird (Tyranus tyranus) in Ontario (Blancher 1982). Mercury levels were found to be elevated in the eggs of goldeneye ducks (Bucephala clangula) near acidic Swedish lakes (Eriksson et al. 1980a,b). Across eastern North America where extensive pesticide use has occurred, the mobilization of pesticides and heavy metals by acidification may have even more serious effects, but these considerations have not been researched. This whole area concerning how acidification may affect metal and pesticide toxicity requires more research.

5.7.3 Mammals

Mammals that feed on aquatic plants and animals, such as muskrats, minks, otters, shrews, and raccoons, will be affected variously by acidification, depending on the sensitivity of their food organisms to acidity and their ability to choose alternate food sources and suitable habitats in acidified areas. While many species are not directly affected, they are likely to experience major changes in availability of food and habitat quality. An increase in the concentration of heavy metals in the diet of certain species of wildlife may occur (Newman (1979). Raccoons (Procyon lotor) from the sensitive Muskoka area of Ontario contain mercury levels of 4.5 ppm in their livers, a level five times greater than in raccoon livers from an area with non-acidic waters (Wren et al. 1980). Metal contamination of roe deer (Capreolus capreolus) resulted in reduced weight and antler size in an industrialized region in Poland (Sawicka-Kapusta 1978, 1979; Jop 1979), but this metal deposition is not related to the long-range deposition characteristic of North America. In remote areas of Sweden, however, cadmium accumulated in the body tissues of roe deer and moose (Alces alces) (Frank et al. 1981, Mattson et al. 1981).

The long-term effects of anthropogenic acidification on caribou (Rangifer tarandus caribou) are potentially severe. The primary source of winter browse for caribou (Thompson and McCourt 1981), the lichen Cladina stellaris is very sensitive to acidity (Chapter E-3, Section 3.2.2). Exposure of this lichen to simulated acidic rain at pH 4.0 reduced photosynthetic rates by about a quarter (Lechowicz 1982). Recovery time from drying was also impaired. The caribou/caribou lichen relationship is very sensitive, as the lichen normally grows only 6 mm per year (Scotter 1963) and an adult caribou eats 5 kg of lichen per day (Hanson et al. 1975). Any impairment of lichen growth rate may have a serious impact on the winter range of caribou, but it will take years for this effect to be noticeable as normal regeneration of lichen communities requires in excess of 30 years.

Acidic deposition may affect mammals by causing changes in soil chemistry that can sequester important nutrients (Chapter E-2, Section 2.3.3.3). One mineral that is likely to be made less available to herbivorous animals is selenium. The solubility of selenium in soil pore water declines with pH (Geering et al. 1968, C. M. Johnson 1975),

and uptake by grasses is inhibited by SO_x (Davies and Watkinson 1966, Gissel-Nielsen 1973), so concentrations of selenium in forage are reduced in areas of sensitive soils receiving acidic deposition (Gissel-Nielsen 1975, Shaw 1981). Furthermore, excess sulfur in the diet of animals can scavenge selenium from tissues (Harr 1978). Dietary deficiency of selenium leads to degeneration of the liver, kidney, and heart (Schwarz and Foltz 1957, Harr 1978). Selenium deficiency leads to muscular dystrophy ("white muscle disease") in sheep, cattle, swine, and horses (Muth et al. 1958, Muth and Allaway 1963, Hidiroglou et al. 1965, Harr 1978). Many soils in eastern North America are naturally low in selenium and produce forage with concentrations below the 0.1 ppm level recognized as essential (Kubota et al. 1967, Levesque 1974, Winter and Gupta 1979). Incidence of white muscle disease has been related to the use of sulfur-containing fertilizers in areas naturally deficient in selenium (Davies and Watkinson 1966, Allaway and Hodgson 1964, Allaway 1970). Effects on the availability of other essential minerals, like molybdenum (Chapter E-2, Section 2.3.3.3), may be equally important but have not yet been considered.

5.7.4 Summary

Effects of acidification on vertebrate animals, not including fish (Section 5.6) are still largely speculative. The potential effects are diverse and research is at an early stage. These data are summartized in Table 5-15. Many of the effects are expected to take many years to appear; therefore long term monitoring will be essential. The following tentative conclusions can be drawn:

- Direct effects are most severe on the embryos and larvae of amphibians, including salamanders, newts, frogs, and toads. Sensitivity to acidity varies widely within closely related taxa, but total amphibian biomass may decline in areas exposed to acidic rainfall and snowmelt.

- Fish-eating birds (e.g., loons, mergansers) will be unable to rear young in areas where fish populations are limited, resulting in smaller population sizes for portions of the breeding range.

- Some insectivorous bird populations may be limited by the reduced availability of preferred prey (flycatchers, swallows, kingbirds) around acidic lakes, but others (goldeneye ducks) seek out the species of aquatic insects found in acidic lakes and may actually prosper in impacted areas.

- Mammals that feed on plants and animals in acidic lakes may accumulate higher than normal body burdens of heavy metals, but population losses have not yet been demonstrated.

- The large North American herds of caribou may be affected in the long-term due to the sensitivity of the caribou lichen upon which they depend for winter browse.

TABLE 5-15. SUMMARY OF EFFECTS OF ACIDITY ON NON-FISH VERTEBRATES

Taxa	Common name	Observation	Mechanism	Evidence	References
AMPHIBIA					
Ambystoma maculatum	Yellow-spotted salamander	Reproductive failure at pH < 6.0	Embryonic mortality	Field obs.	Mushinsky and Brodie 1975, Pough and Wilson 1977
		Egg number correlated with pH	?	Field obs.	Clark and Euler 1980
A. jeffersonianum	Jefferson salamander	No effect of pH 5.0	?	Field obs.	Pough 1976
Trituris vulgaris	Smooth newt	Not observed < pH 6.0	Cation concentration	Field correl.	Cooke and Frazer 1976
T. helveticus	Palmate newt	Tolerant to pH 3.8	?	Field obs.	Cooke and Frazer 1976
Motophythalamus viridescens	Red-spotted newt	Tolerant of pH 7.4-4.8	?	Field obs.	George et al. 1977, pers. obs. (RS)
	"Salamanders"	Leave water at pH 4.0	Behavior change	Field pH manip.	Hall and Likens 1980a,b
Hyla crucifer	Spring peeper	Population density correlated with pH	?	Field obs.	Clark and Euler 1980
		Mortality at pH 4.0	Embryonic mortality	Lab study	Gosner and Black 1957
Rana catesbeiana	Bullfrog	Mortality below pH 5.0	?	Field obs.	Clark and Euler 1980
		Mortality below 5.0	Embryonic mortality	Lab study	Saber and Dunson 1978
R. sylvatica	Wood frog	Mortality below 5.0	?	Field obs.	Clark and Euler 1980
R. temporaria	Common frog	Mortality below 5.0	?	Field obs.	Hagstrom 1977
R. pipiens	Leopard frog	Mortality below 4.7	Embryonic mortality	Lab study	Noble 1979
		Reduction in sperm mortality at pH < 6.5	?	Lab study	Schlicter 1981
		Adults observed at pH 4.8	?	Field obs.	pers. obs. (RS)
Acris gryllus	Cricket frog	Mortality at pH 4.0	Embryonic mortality	Lab study	Gosner and Black 1957
Bufo bufo	Common toad	Not observed < pH 4.2	?	Field obs.	Hagstrom 1977

TABLE 5-15. CONTINUED

Taxa	Common name	Observation	Mechanism	Evidence	References
B. calamita	Natterjack toad	Not observed < pH 5.0	?	Field obs.	Beebee and Griffin 1977
BIRDS					
Gavia immer	Common loon	Habitat restriction in sensitive areas	Land use changes, fish losses?	Field obs.	Trivelpiece et al. 1979 McIntyre 1979
Mergus merganser	Common merganser	Avoidance of acid lakes	Fish losses	Field obs.	DesGranges and Houde 1981
Megaceryle alcyon	Kingfisher	Avoidance of acid lakes	Fish losses	Field obs.	DesGranges and Houde 1981
Iridoprocne bicolor	Tree swallow	Avoidance of acid lakes	Fish losses	Field obs.	DesGranges and Houde 1981
Anas rubripes	Black duck	Avoidance of acid lakes	Aquatic insect losses	Field obs.	DesGranges and Houde 1981
Eucephala clangula	Goldeneye duck	Preference for acidic lakes	Abundance of predatory insect food items	Field obs.	Eriksson 1979
		Elevated (Hg) in eggs	From Hg in insects	Lab analysis	Eriksson et al. 1980a
Tyranus tyranus	Eastern kingbird	Decreased egg weight near acidic lakes	Aluminum toxicity?	Lab analysis	Blancher 1982
Passerines	Songbirds (4 sp)	Breeding failure, thin, porous eggs	Aluminum in insect prey	Lab analysis	Nyholm 1981, Nyholm and Myhrberg 1977
MAMMALS					
Procyon lotor	Raccoon	5 x normal (Hg)	Bioaccumulation	Lab analysis	Wren et al. 1980
Capreolus capreolus	Roe deer	Cd accumulation	Bioaccumulation	Lab analysis	Frank et al. 1981
Alces alces	Moose	Cd accumulation	Bioaccumulation	Lab analysis	Frank et al. 1981, Mattson et al. 1981
Rangifer sp.	Caribou	Loss of winter browse over a long period	Sulfur sensitivity of caribou lichen	Lab study	Lechowicz 1982

- Other grazing animals, including some domestic cattle, may be subject to mineral deficiencies, particularly selenium, if high SO_x deposition continues for extended periods. The seriousness of this impact is difficult to quantify and is highly speculative at this time.

- Mechanisms of impact include disrupted ionic balances in amphibians, metal toxicity in higher trophic levels of wildlife, alterations in food chains, and nutrient deficiencies.

5.8 OBSERVED AND ANTICIPATED ECOSYSTEM EFFECTS (J. P. Baker, F. J. Rahel, and J. J. Magnuson)

Acidification may produce changes in either ecosystem structure or function. Effects on structure involve changes in species composition caused by species declines, extinctions or replacements. Effects on ecosystem function refer to changes in such processes as primary production, energy transfer between trophic levels, detrital decomposition and rates of nutrient cycling. Most studies have described the response of individual taxa to the acidification process. Thus most of our knowledge about the ecosystem-level effects of acidification concern changes in structure. Little is known about how these structural changes influence ecosystem function. The object of this section is to note the ecosystem changes which have been observed in acidic habitats and to suggest potential ecosystem responses that need to be examined in future studies.

5.8.1 Ecosystem Structure

Acidification produces changes in the basic structure of aquatic ecosystems (Figure 5-17). Certain taxa (e.g., fish and Daphnia) disappear apparently as a direct result of acid toxicity. Direct effects of acidity or aluminum are, however, complicated by interactions among a complex web of consumers and their food resources (Section 5.10.2.3). Important components of upper trophic levels-fish populations decline or disappear. As a result, large-bodied acid-tolerant invertebrates become top predators in the system (5.3.1.5). Shifts in the importance of invertebrate predators may alter zooplankton community structure which, in turn, may alter the phytoplankton community structure. The reduction of grazers (snails, amphipods, etc.) may allow periphyton to accumulate, while the inhibition of detritivores and decomposers apparently causes detritus to accumulate. Within benthic and planktonic communities the number of species generally decreases. The overall result is a general decrease in ecosystem complexity.

Woodwell (1970) considered simplification a system response common to all types of environmental pollution and also to natural sources of environmental stress. It is possible that simplification increases system instability (e.g., Woodwell 1970, Van Voris et al. 1980), although the relationship between system complexity and system stability

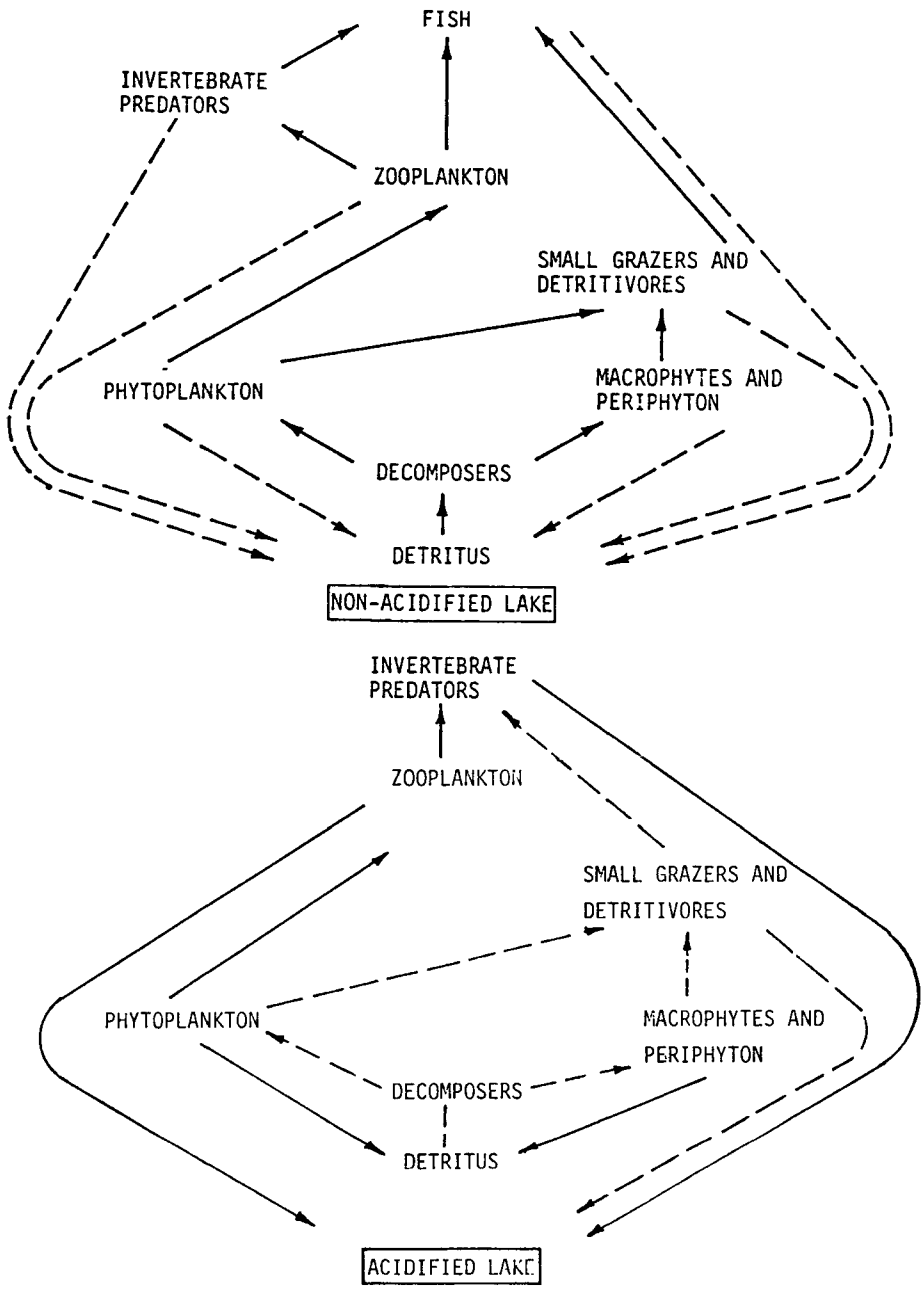

Figure 5-17. Trophic interactions in a neutral pH, oligotrophic lake compared to those in an acidified lake. Dotted lines indicate trophic interactions which may be particularly affected by acidification. Note the replacement of fish by invertebrates as the top-level predators.

is disputed (Allen and Starr 1982). Marmorek (1983) and Yan et al. (1982) observed in field experiments that acidification indirectly reduced the short-term stability and reslience of the plankton community to nutrient additions.

The physical structure of the aquatic system may also be slightly altered with acidification. The correlation between increasing acidity and increased water clarity has been well established (Chapter E-4, Section 4.6.3.4). With an increase in light penetration, some shift in the thermal budget and patterns of thermal stratification may occur as has been demonstrated for Lake 223 in the Experimental Lakes Area of Ontario (Schindler and Turner 1982).

5.8.2 Ecosystem Function

5.8.2.1 Nutrient Cycling--It has been suggested that nutrient cycling and nutrient availability to primary producers are reduced in acidic aquatic environments. The rate of nutrient cycling is thought to be slowed primarily because of inhibition of bacterial decomposition and a sealing-off of mineral sediments from the overlying water column with the accumulation of detritus and periphyton on the lake bottom (Section 5.3.2.1). Grahn et al. (1974) speculated that acidification stimulated lake oligotrophication as a result of these changes but definite confirmation of this hypothesis is lacking.

Nutrient availability could also be affected by chemical changes in the water. Of particular importance may be decreased phosphorus availability because of aluminum-phosphorus interactions (Chapter E-4, Section 4.6.3.5), decreased levels of dissolved inorganic carbon due to the decrease in pH (Section 5.5.2.3.2), and also precipitation of organics (Chapter E-4, Section 4.6.3.3) and increased displacement of these materials into benthic habitats. Although all of these postulated chemical changes are theoretically plausible and potentially very significant, effects on nutrient cycling in acidic waters have not yet been experimentally demonstrated.

5.8.2.2 Energy Cycling--Previous sections have discussed four types of possible reactions to acidification that are relevant to energy cycling in aquatic systems: 1) a potential decrease in primary productivity, 2) decreased growth efficiencies, 3) decreased energy transfer between trophic levels and 4) elimination of upper trophic levels. The evidence or lack of evidence for these hypotheses is discussed below.

Biological productivity in aquatic ecosystems is supported by both allochthonous organic carbon imported from sources external to the system plus autochtonous production of organic carbon by primary producers within the aquatic system. As a result of decreased nutrient availability, water column primary productivity in acidic waters may be altered. Limited observations from field studies reviewed in Section 5.5.2.1.2 indicate, however, that in most cases acidification has no consistent adverse effect on primary productivity. Adverse effects of decreased nutrient availability on water column primary productivity may

be counterbalanced by other changes (especially increased light penetration) that stimulate primary production. Although acidification does not consistently decrease primary productivity, increased light penetration apparently does, to a certain extent, increase the importance of benthic primary producers relative to planktonic primary producers. The effects of acidification on total primary production (including periphyton, macrophytes and phytoplankton) have not been studied.

Energy transfers within aquatic systems can be examined both within a given trophic level and between trophic levels. Growth efficiency usually refers to within stratum transfer; the fraction of a given quantity of energy (food or light energy) consumed that is manifested as production (growth and reproduction). Organisms that inhabit acidic waters may be inherently less efficient or may be less efficient because of acid-induced stress, but examination of this phenomenon has been limited. Fish have been observed in laboratory experiments to grow more slowly at lower pH levels (Section 5.6.2.8). Primary producers in some acidic waters (Sections 5.5.2.1.2 and 5.3.2.2.3) have lower instantaneous rates of production per unit biomass. Possible reasons for this lower production are numerous, however, and have not been clearly defined. No studies of growth efficiencies for zooplankton, benthos, or other aquatic organisms have been completed. If growth efficiencies are reduced in acidic environments, transfer of energy through the food chain would be reduced.

Energy transfers between trophic levels involve the percentage of available food actually used by consumers, or relative productivities in successive trophic levels. In Section 5.5.3.3, it is postulated that the transfer of energy between phytoplankton and zooplankton may be inhibited by the inedible nature of many of the phytoplankton species common in acidic lakes. In stream systems, a reduction in populations of benthic invertebrate grazers apparently decreases conversion of primary production into secondary production (Section 5.3.2.5.4). Processing of detrital particles may also be affected. Again, some evidence suggests there may be inhibition of energy cycling and energy transfer through the food chain.

One of the best documented changes associated with acidification is the decline and loss of fish populations which represent major components of upper trophic levels in aquatic ecosystems. Loss of fish populations results in a shortened aquatic food chain (Section 5.7).

5.8.3 Summary

Structural changes in acidified aquatic ecosystems have been well documented and include the loss of fish populations, reductions in the number and diversity of benthic and planktonic invertebrates, and accumulations of periphyton and detritus. How these structural changes affect ecosystem processes such as primary production, energy transfers between trophic levels, or nutrient cycling is largely unknown. To date, the limited evidence available suggests that ecosystem functions

are relatively robust, but additional research is required before final conclusions can be reached.

5.9 MITIGATIVE OPTIONS RELATIVE TO BIOLOGICAL POPULATIONS AT RISK (C. T. Driscoll and G. C. Schafran)

The concept of surface water neutralization as a result of base, carbon, and phosphorus additions is discussed in Chapter E-4, Section 4.4. The biological response to these additions and other mitigative options for fish populations at risk from acidification of surface waters follows.

5.9.1 Biological Response to Neutralization

In lakes where neutralization has resulted in large, rapid pH changes (e.g., $Ca(OH)_2$ addition, see Chapter E-4, Section 4.7.1), phytoplankton concentrations have been observed to decline drastically This phenomena may be either the result of stress associated with a drastic change in pH ("pH shock") or removal of algal biomass with metals through flocculation and precipitation processes (Scheider and Dillon 1976, Scheider et al. 1975). Yan and Dillon (1981) noted that a small pH change, or a large pH change initiated gradually, resulted in no change in biomass of lake phytoplankton.

After base addition, phytoplankton undergo a taxonomic shift. Certain species will disappear while others appear. Species dominance has been observed to shift, and total number of species has been observed to increase. Species dominance/composition are lake-specific, so response of the phytoplankton population cannot be generalized for all lakes. Subsequent to liming, Scheider et al. (1975) observed a shift in dominance to the genera Dinobryon and an unidentified chrysomonad. The appearance of diatoms (Bacillariophycae--mostly Navicula and Nitzschia) and blue-green algae (Cyanophyta-Oscillatoria) was also noted. Yan and Dillon (1981) observed an increase in the contribution of dinoflagellates, while cryptomonads declined. Among many species changes noted in a Swedish liming experiment were the increase in small cryptomonads, diatoms, and chrysophyceans and the disappearance of Merismopedia sp. (Hultberg and Andersson 1982).

After a population has been depleted by base addition, within a few months phytoplankton biomass will increase and approach preneutralization levels. The rapid recovery after base addition appears to be due to the short life cycle of phytoplankton and decreased predation due to decreases in zooplankton population.

Zooplankton populations are affected in much the same way as phytoplankton. Additions of base that drastically increase lake pH immediately reduce standing stocks of zooplankton. In three Canadian lakes where the most frequently observed species were Cyclops vernalis, Chydorus sphaericus, and Bosmina longirostris, the addition of base, which quickly increased pH more than two units, caused immediate and drastic reductions in zooplankton standing stock. Base additions that

have resulted in smaller pH changes have not affected the population negatively (Scheider et al. 1975, Dillon et al. 1979). Swedish lakes that have undergone a gradual increase in pH through base application show a substantial increase in zooplankton biomass, shifts in species composition, and increases in species diversity (Hultberg and Andersson 1982).

Recovery of zooplankton populations is much slower than that observed for phytoplankton. For two full years following base addition, zooplankton biomass was observed not to recover to pretreatment levels (Yan and Dillon 1981). This relatively slow recovery from base addition stress may be due to slow life cycles and recolonization difficulties.

The literature is not consistent with respect to the response of benthic fauna to base addition. In the first year following large pH increases due to base addition, Scheider et al. (1975) observed numbers of benthic organisms decrease substantially. Chironomids, which were observed to be dominant prior to neutralization (Scheider et al. 1975, Yan and Dillon 1981), contributed significantly to this decline. This was attributed to an interruption of a life cycle in response to the sudden pH change. However, this is not consistent with Swedish observations. Hultberg and Andersson (1982) observed that the groups Orthocladinae and Tanypodinae increased, while no change was evident in trichopteran populations. With benthic fauna constituting an important food source for fish, population perturbations resulting from neutralization may affect fish positively or negatively.

In some regions, a feltlike structure of algal filaments, detritus, and Sphagnum completely cover lake sediments and deplete normal populations of submerged vegetation like Isoetes and Lobelia (Grahn et al. 1974, Hendrey and Vertucci 1980). Hultberg and Andersson (1982) indicate that liming appears to have a profound effect on Sphagnum. After base addition, Sphagnum was rapidly eliminated from the littoral region where $CaCO_3$ was spread. Populations were slowly depleted (1 to 2 years) in the remainder of the treated lakes. The few plants that survived neutralization exhibited very slow growth rates (~1 cm x yr^{-1}) as compared to acidic lake populations (8 to 10 cm x yr^{-1}) (Hultberg and Andersson 1982). In lakes that were allowed to reacidify, Sphagnum was observed to recolonize the benthic region.

Neutralization to improve the water quality of acidified waters has both a long- and short-term effect on fish. Immediately following base addition and subsequent pH rise, aluminum hydrolysis generally occurs. This perturbation, as previously described, may be detrimental to the existing fish population (Baker and Schofield 1980). Mortality of fish may be lessened by incremental addition of base, resulting in small pH changes. In some lakes this may not be deemed necessary as the fish population may be negligible.

The long-term consequence of lake neutralization, provided reacidification is not allowed to occur, is a much more hospitable environment for fish. An immediate response (improvement) in

reproduction and survival has been observed in one-year-old fry (Hultberg and Andersson 1982). An increase in recruitment and fish survival tends to increase the biomass of the younger fish where previously the population had been dominated by older fish (Dickson 1978). If pH is maintained, fish reproduction and survival will show marked improvement over acidified conditions and possibly restore the population to pre-acidification levels. Restocking of native species, lost because of acidification, may be necessary in some waters.

5.9.2 Improving Fish Survival in Acidified Waters

Three major approaches for improving fish survival in acidified waters deal directly with the fish. They are 1) screening existent fish strains to determine which strains exhibit high acid tolerance, 2) selectively breeding a given strain for improved tolerance to low pH, and 3) acclimating a group of fish to increase their resistance to acidic water.

5.9.2.1 Genetic Screening--Several studies have shown differences in acid tolerance between different strains within the same species (Johnson 1975, brook trout; Gjedrem 1976, brown trout; Robinson et al. 1976, Swarts et al. 1978, Edwards and Gjedrem 1979, Rahel and Magnuson 1980, yellow perch; and Schofield et al. 1981).

Edwards and Gjedrem (1979) determined that the method used for screening different strains was important in determining the hierarchy of tolerance among strains. They screened brown trout fingerlings (5.8 + 0.8 g) in water synthetically acidified to pH values of 2.5, 3.0, and 4.0 and brown trout eggs and fry in naturally acidic water (pH 4.7) and in water adjusted from pH 4.7 to 5.2 with sodium hydroxide. They found a high correlation of ranking among strains tested at low pH values, indicating that the pH level used within this range was unimportant. However, when they compared ranking obtained from the fingerlings tested at very low pH values and those determined from the eggs and fry tested in the naturally acidic water, they found a low rank correlation between strains. They concluded that the two different procedures were apparently testing for different traits and thus could not be used interchangeably.

The results of Edwards and Gjedrem (1979) indicate that a standardized screening procedure is very important in determining the relative tolerance of strains within species. Their results also indicate that the life cycle stage screened is important in determining relative strain tolerance. Thus, it is important to develop a screening procedure consistent with the goals of the project. Edwards and Gjedrem (1979) concluded that a screening program aimed at reestablishing viable populations in acidified waters must select for strains with acid-resistant egg and larval stages because the major cause of trout population losses is thought to be poor recruitment caused by egg and fry mortality (Beamish and Harvey 1972, Jensen and Snekvik 1972, Leivestad et al. 1976, Schofield 1977). However, if the goal of a screening program is to find a strain to be used in maintaining stocked

populations, the screening procedure should target the life cycle stages that will be stocked.

5.9.2.2 Selective Breeding--The logical extension of a genetic screening program is to select for acid tolerance within a few superior strains and improve their acid tolerance through selective breeding. Gjedrem (1976) and Edwards and Gjedrem (1979) found high heritabilities (ratio of genetic variance to total variance) for acid tolerance in eggs and alevins of brown trout. They concluded that there was a good possibility of producing acid-tolerant strains of brown trout through selective breeding.

Selective breeding tests with brook trout have produced mixed results. Swarts et al. (1978) performed a single selection with NYSV strain brook trout (selecting to 80 to 90 percent loss of equilibrium at pH 3.4 to 3.5) and found no increased tolerance in their offspring in field or laboratory tests. Schofield et al. (1981) selected yearling (1977 year class) domestic strain brook trout to 50 percent, using naturally acidified runoff water. They then challenged the offspring (1979 year class) of the resistant and non-resistant cohorts as fry in naturally acidified water. The offspring of the resistant cohort were significantly more resistant (mean LT_{50} 195.5 hr) than those of the non-resistant cohort (LT_{50} 72.0 hr; $P < 0.001$). However, when an identical test was performed on the 1980 year class offspring of the 1977 year class resistant and non-resistant cohorts, the offspring of the resistant cohort exhibited inferior performance to that of the offspring of the non-resistant cohort (LT_{50} values 76.6 and 77.1 hr vs 84.7 hr, respectively). Included in the 1980 year class tests were tests of hybrid crosses between resistant and non-resistant cohorts and two wild strains from Canada (Assinica and Temiscamie). In these tests the resistant X Assinica and resistant X Temiscamie always performed better than the non-resistant X Assinica and non-resistant X Temiscamie. From these results Schofield et al. (1981) hypothesize that genetically inherent physiological acid tolerance may be fixed within the selected cohorts.

In a preliminary field trial, Schofield et al. (1981) separated Assinica X domestic yearlings into resistant and non-resistant cohorts in March of 1979, stocked them in equal numbers in an acidified lake in May, and sampled them in July. They observed a 3:1 return of resistant over non-resistant fish. However, more extensive field trials performed in 1980 produced a resistant/non-resistant ratio not significantly different from the expected 1:1 ratio of the no difference case. Schofield et al. (1981) attributed the lack of an unbalanced ratio to the relatively good water quality conditions in the spring of 1980 caused by low snowfall during the winter of 1980. This study appears to give some evidence of improved acid tolerance of brook trout through selective breeding, but it is far from conclusive.

Hybrid vigor with regards to acid tolerance has been observed in several studies. Robinson et al. (1976) found heterosis (hybrid vigor) in 66 percent of the strain crosses tested. Edwards and Gjedrem (1979)

observed mean percent survival in hybrid crosses of brown trout to be twice that of the parental strains. From this they suggest that the most efficient way to produce acid-tolerant strains for restocking acidified waters would be to identify the best strain crosses and then maintain just a few pure bred strains in the hatchery. These strains could be improved by selective breeding while hybrid fish for stocking could be routinely produced by crossing a brood fish of the pure bred lines.

5.9.2.3 Acclimation--A conceivable method for improving the success of stocked populations in acidified waters would be to acclimate the fish to the acidic conditions before stocking. The question of whether fish can acclimate to acidic conditions has been addressed by numerous authors, with mixed results. Most of the studies in which fish were acclimated to sublethal pH values and then tested for increased survival at lethal pH values have produced negative results. Lloyd and Jordan (1964) acclimated rainbow trout to pH values of 6.55, 7.50, and 8.40 and found no difference in survivorship when the fish were tested at pH values from 3.0 to 4.0. Robinson et al. (1976) held brook trout at pH 3.75 for one week and then tested them for survival at pH 2.5 and 3.0. They found that survival time was 20 to 25 percent less in acclimated fish than in fish not previously exposed to acidic water. Falk and Dunson (1977) exposed brook trout to sublethal pH values of 5.0 and 5.8 for two or 24 hours prior to testing for survival at pH 3.15 or 3.5. They found significant differences in survival time between acclimated and non-acclimated fish in only three of nine tests. Swarts et al. (1978) performed laboratory and field acclimation trials with brook trout. In the laboratory they acclimated the fish to pH 4.25 for 10 days or 4.8 for 28 days and then tested them for improved survival at pH 3.25 or 3.6 respectively. They found no consistent differences between acclimated and non-acclimated fish in their laboratory trials. In three field trials in which fish were held in an acidified stream (pH 4.8 to 5.8) and then tested in an acidic river (pH 4.2), the acclimated fish performed better than non-acclimated fish in only one trial.

In a study with embryos and alevins of Atlantic salmon and rainbow trout which had been incubated at pH values ranging from 4.5 to 6.8 for variable time periods, Daye (1980) could find no difference in tolerance between the different groups and thus concluded no acclimation had occurred. In a similar study, performed by Trojnar (1977b), brook trout eggs were incubated at pH 4.6, 5.0, 5.6, and 8.0 and then tested at swim-up for survival at pH values from 4.0 to 7.86. He found that fish incubated at pH 5.6 and below showed greatly increased survival at low pH as compared with fish incubated at pH 8.0. He attributed the difference to acclimation.

Physiological evidence for acclimation in brown trout exposed to acidified water was provided by McWilliams (1980b), who suggested that acclimation might occur through a progressive decrease in the diffusional permeability of the gills to sodium. However, actual resistance to lowered pH levels, in terms of increased survivalship, was not determined in this study.

In all of the aforementioned studies, the acclimation procedure consisted of holding the fish at a single sublethal pH for a fixed time period and then transferring them to the test pH levels. Guthrie (1981) used a different method. He hypothesized that previous acclimation attempts had failed for three major reasons. First, if the acclimation pH was too high the fish might not need to adjust physiologically to maintain homeostasis. The study by Lloyd and Jordan (1964) might be an example of this. Second, if the acclimation pH is too low then it might constitute a major stress in itself, to which the fish are unable to adjust. The study by Robinson et al. (1976), where the fish were acclimated to a pH of 3.75 before being tested at a lower pH, is probably an example of this. Third, if the test pH is very low and the adaptive response of the fish is overwhelmed, then no amount of previous acclimation will improve survival. This probably occurred in the studies where the test pH was below 4.0 (Lloyd and Jordan 1964, Robinson et al. 1976, Swarts et al. 1978, Falk and Dunson 1977).

To avoid these problems, Guthrie (1981) developed a gradual acclimation procedure in which the acidity and aluminum concentration were increased from control conditions to test conditions over a period of 4 to 5 days. He used test pH values of 5.0, 4.5, and 4.0 with nominal aluminum concentrations of 0.2 and 0.4 mg Al ℓ^{-1}. In acclimation tests on brook trout sac-fry and swim-up fry, Guthrie (1981) found significantly improved survival at pH 5.0 and 4.5 at both aluminum levels, but no difference in survival between acclimated and non-acclimated fish at pH 4.0. This lends credence to the hypothesis that pH values below 4.0 are too low for testing for acclimation. Guthrie also acclimated brook trout parr (55.7 $\pm$ 6.8 mm) to naturally acidic water (pH 4.9, 0.32 mg Al ℓ^{-1}) by gradually changing water from non-acidified lake water (pH 6.5) to acidic brook water. After 6 days in the acidic brook water, 80 percent of the acclimated fish remained alive while only 40 percent of the non-acclimated fish (transferred into the acidic brook water at the same time that the acclimation procedure was completed) were still alive. In experiments with advanced fry (28 to 36 mm) and yearlings at pH 5.0 with 0.4 mg Al ℓ^{-1}, dramatic improvements in the survival of the acclimated fish were also observed. However, at pH 4.5 with the same aluminum level, acclimation did not improve survivorship in these life history stages.

The studies performed by Guthrie (1981) clearly demonstrate the ability of brook trout to resist increased acidity and aluminum levels, within specific limits of water quality and developmental sensitivities, as measured by improved survival of fish in short term gradual acclimation treatments. These results indicate it may be possible, through acclimation prior to stocking, to improve initial survival in hatchery-reared brook trout destined for stocking in waters of low pH and high Al levels.

5.9.2.4 Limitations of Techniquest to Improve Fish Survival--In the future it appears that a combination of these three techniques could be a feasible strategy for maintaining a sport fishery in waters where the extent of acidification is such that a natural fishery is no longer

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possible. This could be accomplished by screening for the most acid resistant strains of fish, selectively breeding those strains and acclimating them to the acid water before stocking.

This strategy would probably be successful in allowing the maintenance of a sport fishery where none could exist otherwise, however it would not be a solution. It is doubtful that these techniques could ever be used to re-establish a naturally reproducing population where one had been lost due to acidification. Also since these techniques all require a great deal of propagation work and clearly defined genetic strains, it would only be possible to use game fish. The reestablishment of non-game fish in acidified waters using these techniques would not be feasible.

When these techniques are used to re-establish sport fisheries in acidified waters there is one foreseeable contraindication. Toxic metals such as mercury may be mobilized as a result of acidification. This could result in a hazardous situation if stocked fish accumulated these contaminants before they were caught. Thus it is important that fish stocked in acidified waters be closely monitored for toxic metals contamination.

5.9.2.5 Summary--All three techniques for producing the fish better able to survive in acidified waters--genetic screening, selective breeding, and acclimation--show promise as ameliorative strategies. However, all are still in the early stages of development and require more laboratory and field testing before they will be well enough defined to be useful as fish management tools.

5.10 CONCLUSIONS (J. J. Magnuson, F. J. Rahel, J. P. Baker, R. Singer, and J. H. Peverly)

Although the literature regarding the response of aquatic biota to acidification is sometimes conflicting, some effects have been well documented. These are summarized below (Section 5.10.1). Emphasis is placed on those biological changes which are supported by a combination of field observations, field experiments and laboratory experiments. Together, these species declines, extinctions and replacements represent major changes in the structure of acidified aquatic ecosystems. The next section (5.10.2) focuses on the mechanisms by which acidification affects aquatic ecosystems. Although mechanisms by which acidification may affect processes such as primary production, energy transfer between trophic levels, and nutrient cycling have been hypothesized, few have been critically evaluated using field and laboratory experiments. The major conclusion is that many of these mechanisms are speculative and need to be examined in future research. Section 5.10.3 describes potential mitigative options from a biological perspective. The final section (5.10.4) presents an overview of biological changes expected if current rates of acidic deposition continue in the northeastern United States and southeastern Canada.

5.10.1 Effects of Acidification on Aquatic Organisms

The effects of acidification on aquatic organisms that are supported by numerous observations and experimental studies are summarized in Table 5-16 and in the following statements.

Benthos

- The bottom community, which provides substrates for many organisms and is the principal site of nutrient recycling, is severely altered in clear waters low in pH, as compared to otherwise similar, but neutral pH waters.

- Bacterial metabolic rates are decreased, between pH 6.0 and 4.0, and shredding invertebrate populations are reduced in numbers, bringing about an increased accumulation of undecomposed organic materials.

- Most substrates are covered with an encrusting mat of algae and detritus in acidic lakes and streams below pH 5.0.

- Many predatory insects (beetles, true bugs, dragonflies) increase in numbers below pH 6.0 in lakes and streams. Their effect on the plankton and on benthic detritivores is not known.

- Several preferred food sources for game fish (e.g., Gammarus snails, many mayflies and stoneflies) do not survive below pH 5.0, but fisheries impacts due to food shortages have not been observed.

Macrophytes

- Dominant macrophyte species are the same in both acidified (pH less than 5.6) and nonacidified (pH 5.6 to 7.5) North American lakes.

- Shifts to Sphagnum-dominated macrophyte communities have been documented in six Swedish lakes acidified for at least 15 years. However, this does not seem to be a general property of acidified lakes as there is currently no trend toward dominance of macrophyte communites by Sphagnum spp. in 50 oligotrophic, soft-water lakes surveyed in North America.

- Standing crops of macrophytes vary widely (5 to 500 g dry wt m^{-2}) in soft-water, oligotrophic lakes, and acidification produces no consistent changes in standing crop. In Lobelia dortmanna, a common plant in soft-water, oligotrophic lakes, oxygen production was reduced 75 percent at pH 4.0 vs pH 4.3 to 5.5 in one flow-through laboratory experiment.

TABLE 5-16. EFFECTS OF INCREASING ACIDITY ON AQUATIC ECOSYSTEMS. "NUMEROUS" REFERS TO MANY OBSERVATIONS OR EXPERIMENTS, WHICH ARE DESCRIBED IN THE SECTIONS INDICATED

Taxa or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
Benthos				
Molluscs (most species except fingernail clams, family sphaeriidae)	Numerous (Section 5.2 and 5.3)			The calcareous shell of these animals is soluble under acidic conditions making this group highly sensitive to low pH. Few species present below pH 6.0 except for several species of fingernail clams which may persist down to pH 4.5- 5.0.
Crayfish	Almer et al. 1978	Mills 1982	Malley 1980	In soft water lakes, calcium uptake and exoskeleton formation inhibited in the pH range 5.0-5.8. Reproduction impaired at pH 5.4.
Amphipods (Gammarus)	K. Okland 1980c Sutcliffe and Carrick 1973		Costa 1967 Borgstrom and Hendrey 1976	Absent below pH 6.0, in the laboratory avoids pH 6.2 and lower.
Mayfly larvae (Ephemeroptera)	Numerous (Section 5.3)	Hall et al. 1980	Bell and Nebeker 1969, Bell 1971	Most species decline or are absent in the pH range 4.5 to 5.5.
Water striders (Gerridae), backswimmers (Notonectidac), water boatmen (Corixidae), beetles (Dytiscidae, Gyrinidae), dragonflies (Odonata)	Numerous (Section 5.3)			Tolerant of acidity. Increase in abundance in acidified lakes (below pH 5.0) after other invertebrate groups and fish have been eliminated.
Benthos community structure	Numerous (Section 5.2 and 5.3)	Hall et al. 1980	Bell and Nebeker 1969, Bell 1971, Malley 1980	With increasing acidity, species richness declines. Entire groups of aquatic organisms are absent or poorly represented below pH 5.0 (e.g., molluscs, amphipobs, crayfish, mayflies). Other taxa become dominant, particularly after the loss of fishes (e.g., predacious beetles and true bugs).
Benthic algae (periphyton)	Numerous (Section 5.3)	Hall et al. 1980 Schindler 1980	Hendrey 1976	Algal mass overgrow rooted plants and cover bottom subtrates in acidified lakes below pH 5.0

TABLE 5-16. CONTINUED

Taxa or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
Macrophytes				
Eriocaulon sp. Lobelia sp.	Grahn 1977, Best and & Peverly 1981, Miller et al. 1982		Laake 1976	Rosette plant communities may become overgrown by algal mats. Tissue aluminum concentrations increase as pH decreases photosynthesis of rosette species decreases by 75% as pH declines from 5.5 to 4.0.
Plankton				
Daphnid	Numerous (Section 5.5)		Davis and Ozburn 1969 Parent and Cheetham 1980	Most species are acid-sensitive and absent below pH 7.0 to 5.5
Zooplankton community structure	Numerous (Section 5.2 and 5.5)			The number of species declines as acidity increases. Taxa characteristic of acid conditions include certain genera of rotifers (Keratella, Kellicottia, Polyarthra); cladocerans (Bosmina); and copepods (Diaptonus).
Phytoplankton community structure	Numerous (Section 5.2 and 5.5.)	Yan and Stokes 1978		The number of species declines as acidity increases. Dinoflagellates (Phylum Pyrrophyta) frequently dominate acidified lakes (pH 4.0-5.0). Dinoflagellates are a less palatable food source for zooplankton compared to the phytoplankton they frequently replace.
Fishes				
Fatheal Minnow (Pimephales promelas)	Rahel and Magnuson 1983	Mills 1982	Mount 1973	One of the most acid-sensitive fish species. Reproductive failure occurs near pH 6.0. Generally absent in waters below pH 6.5.

TABLE 5-16. CONTINUED

Taxa or Process	Type of Evidence: Field Observation	Field Experiment	Lab Experiment	Observed Effects
Darters (Etheestoma exile, E. nigtum, Percina capnodes) and Minnows (several Notropis spp. Pimephales notatus)	Harvey 1980 Rahel and Magnuson 1983		Rahel and Magnuson 1983	Very acid-sensitive. Generally absent below pH 6.0 in both naturally acidic and anthropogenically acidified waters.
Smallmouth Bass (Micropterus dolomieui)	Beamish 1976, Harvey 1980, Rahel and Magnuson 1983			Reproduction ceases and populations become extinct below pH 5.2-5.5
Lake Trout (Salvelinus namayeusch)	Beamish 1976, Beamish et al. 1976	Mills 1982	Beamish 1972 Trojnar 1977a	Experiences reproductive failure near pH 5.0. Generally absent below pH 5.0 in both naturally acidic and anthropogenically acidifed waters.
White Sucker (Catostomus commersoni)	Harvey 1980, Rahel and Magnuson 1983	Mills 1982		
Rainbow Trout (Salmo gairdneri)	Numerous (Section 5.6)		Numerous (Section 5.6)	Adversely affected by pHs below 5.0-5.5
Atlantic Salmon (Salmo salar)	Numerous (Section 5.6)		Numerous (Section 5.6)	Adversely affected by pHs below 5.0.
Brown Trout (Salmo trutta)	Numerous (Section 5.6)		Numerous (Section 5.6)	Lower pH limit between 4.5 to 5.0.
Brook Trout (Salvelinus fontinalis)	Numerous (Section 5.6)	Hall et al. 1980	Numerous (Section 5.6)	Lower pH limit between 4.2 to 5.0.
Sunfishes (Ambloplites rupestris, Micropterus salmoides, Lepomis spp.)	Harvey 1980, Rahel and Magnuson 1983	Smith 1957		Lower pH limit near 4.5.
Yellow Perch (Perca flavescens)	Svardson 1976, Keller et al. 1980, Harvey 1980, Rahel and Magnuson 1983		Rahel 1983	Lower pH limit 4.2 to 4.5. May become very abundant after other species have become extinct.
Decomposition	Hendrey 1976, Leivestad et al. 1976	Scheider et al. 1976, Gahnstrom et al. 1980, Hall et al. 1980	Leivestad et al. 1976	Bacterial decomposition is signifi-significantly reduced in the pH range 4.0 to 5.0. In many cases, fungi replace bacteria as the primary decomposers

- In the two published studies of metal concentrations in macrophytes from acidic lakes, tissue concentrations of iron, lead, copper and especially aluminum are higher, while cadmium, zinc and manganese are lower compared to tissue concentrations in plants from nonacidic lakes.

Plankton

- Changes in species composition, standing crop, and productivity of the plankton community with acidification are complex and probably result from not only lower pH levels and higher metal concentrations, but also decreased fish predation, increased water clarity, and perhaps decreased nutrient availability.

- The structure of the plankton community in acidic lakes (pH 4.0 to 6.0) is markedly different from that in nonacidic lakes within the same region. With increasing acidity, the total number of species decreases (by 30 to 70 percent) and biomass is dominated by fewer species.

- Comparisons between acidic and nonacidic lakes within the same region and experimental acidification of a lake indicate no consistent change in water column primary productivity with increased acidity.

- Data on zooplankton productivity are not available. In three studies, the biomass and/or numbers of zooplankton were lower in more acidic lakes (pH 4.0 to 5.0).

Fish

- The clearest evidence for impacts of acidification on aquatic biota is adverse effects on fish.

- Loss of fish populations associated with acidification of surface waters has been documented in the LaCloche Mountain range of Ontario, Nova Scotia, and southern Norway. Available data for these regions include historic records of declining fish populations coupled with historic records of increasing water acidity. Additional evidence for loss of fish populations is available from the Adirondack region of New York State and southern Sweden.

- In the United States, only in the Adirondack region have adverse effects of acidification on fish populations been observed. The presence of fish in Adirondack lakes and streams is correlated with pH level. Particularly below pH 5.0, the occurrence of fish is reduced. Loss of fish populations has been documented for about 180 Adirondack lakes (out of a total of approximately 2877), although historic records are not available at this time to relate each loss specifically to acidification or acid deposition.

- Fish kills have been observed during episodic acidification of surface waters in Norway and Ontario. In addition, in hatcheries receiving water directly from lakes or rivers, unusually heavy mortalities of adult and young fish have occurred in the Adirondack region, Nova Scotia, and Norway. These mortalities are typically associated with rapid decreases in pH (generally to pH levels below 4.5 to 5.0) during snowmelt.

- Many fish populations in acidic waters (pH 4.5 to 5.0) lack young fish, implying that failure to reproduce is a common, although not the only, cause for extinction of fish populations with acidification. In Sweden, neutralization through lake liming resulted in the recurrence of young fish.

- Field observations of growth of adult fish in acidic (pH 4.0 to 6.0) versus nonacidic waters, or through time with acidification, typically indicate no change or increased growth with increased acidity. In some cases, increased growth may be a result of reduced competition for food as fish populations decline.

- Experiments in the laboratory and the field have established a direct cause-and-effect between acidification and adverse effects on fish. In the field, acid additions to Lake 223 in the Experimental Lakes Area of Ontario produced pH declines from pH 6.5 to 5.9 in 1976 to pH 5.1 in 1981 and resulted in reproductive failures and/or extinction of several fish populations. In laboratory bioassays, pH and aluminum levels typical of acidified surface waters were toxic to fish.

Other Related Biota

- Effects of acidification on amphibians, birds, and mammals are still largely speculative. Research is at an early stage. Decreased pH levels have been demonstrated in the laboratory to decrease amphibian reproductive success, but the significance and extent of breeding habitats acidified or sensitive to acidification have not yet been evaluated.

Ecosystem Effects

- Changes in ecosystem structure have been well-documented in acidified aquatic habitats and include species declines, local extinctions and reduced species richness in many taxonomic groups. In some cases, acid-tolerant taxa which formerly were rare, may become abundant.

- The effects of acidification on ecosystem processes such as primary production, energy transfer between trophic levels and nutrient cycling have not been well-studied and should be addressed in future research efforts.

5.10.2 Processes and Mechanisms by Which Acidification Alters Aquatic Ecosystems

5.10.2.1 Direct Effects of Hydrogen Ions--Effects of low pH on aquatic organisms are the best studied aspect of the acidification process. Numerous laboratory bioassays have documented both the toxicity of hydrogen ions to aquatic organisms and differences in sensitivity to acid stress among taxonomic groups. These studies provide insight into physiological mechanisms of toxicity and offer guidelines for predicting effects of various pH levels on aquatic biota. Mechanisms by which various taxa are affected by low pH have been discussed elsewhere (Section 5.3 through 5.6, Fromm 1980) and include disruptions in ion transport, acid-base balance, osmoregulation and enzyme function. Low pH stress seldom exists alone in acidified waters and thus its effect on aquatic organisms will be influenced by other stresses (Sections 5.10.3.2, 5.10.3.4, 5.10.3.7) and biological interactions (Section 5.10.3.3).

5.10.2.2 Elevated Metal Concentrations--The acidification process has resulted in elevated concentrations of aluminum and other metals in many waters (Chapter E-4, Section 4-6). Aluminum leached from the soil in response to acidic deposition has been implicated in fish kills in field observations, field experiments, and laboratory studies (Section 5.6.4.2). The interaction of acidity and aluminum is especially important as fish may be killed by aluminum at a pH value not considered harmful by itself. The toxicity of aluminum is greatest in the pH range 4.5 to 5.5.

In laboratory experiments, aluminum precipitates phosphorus from water, with the greatest effect occurring in the pH range 5.0 to 6.0 (Almer et al. 1978). Phosphorus is the nutrient that typically limits plant growth in oligotrophic lakes. While increased aluminum due to acidification would be expected to reduce phosphorus concentrations and thereby reduce productivity, this process has not been confirmed by in-lake studies.

Aluminum concentrations are higher in macrophytes from acidified lakes than in macrophytes from nonacidified lakes. The biological significance of these higher aluminum concentrations is not known.

High mercury concentrations in fish are correlated with low pH levels for lakes in Sweden, Ontario and the Adirondack Mountains of New York (Section 5.6.2.5). In laboratory experiments, bological uptake of most metals is enhanced at low pH but whether lake acidification will significantly enhance bioaccumulation of mercury has not been definitively demonstrated. Furthermore, there is considerable variation in fish mercury concentrations between lakes and not all acidified lakes contain fish with elevated mercury concentrations. Other factors, in addition to pH, which may contribute to between-lake variability in fish mercury concentrations include dissolved organic carbon, conductivity, bioproductivity and watershed geology.

Other metals which consistently exhibit increased concentrations in acidic surface waters are manganese and zinc (Chapter E-4, Section 4.6.1). Currently available toxicity data indicate that concentrations of these metals in acidic surface waters (unless local sources of metal emissions exist) are below toxic levels. However, a lack of sufficient bioassay data collected in soft, acidic waters and the potential for additive or synergistic effects with other toxic components make this statment tentative.

5.10.2.3 Altered Trophic-Level Interactions--The loss of fish from acidified lakes has been documented in Scandinavia, Canada and the United States (Section 5.6.2.1). As the top predators in aquatic habitats, fish are known to exert control over trophic structure, trophic dynamics and nutrient cycling in lakes (Brooks and Dodson 1965, Shapiro et al. 1975, Kitchell et al. 1979, Clepper 1979, Zaret 1980). For example, zooplanktivorous fish, by influencing the species composition and size distribution of zooplankton, can alter the rate of primary production in lakes (Shapiro et al. 1975).

Changes in aquatic ecosystems following the loss of fish populations are evident in nonacidified lakes where fish have been intentionally removed (Stenson et al. 1978, Eriksson et al. 1980b, Henrikson et al. 1980a,b). Large invertebrate predators (e.g., corixids, dytiscid beetles, Chaoburus) normally kept at low abundance by fish predation become abundant. Zooplankton community composition changes and dinoflagellates become dominant among the phytoplankton. Many of these same changes have been observed in lakes which have lost their fish populations as a result of acidification. Thus biological and limnological changes in a complex aquatic ecosystem undergoing acidification may be difficult to ascribe directly to the toxicity of increased acidity or metal concentration. Understanding the role of trophic-level interactions in producing biological changes during acidification will require holistic, manipulative studies of consumer regulation of ecosystem dynamics.

5.10.2.4 Altered Water Clarity--Water clarity typically increases with increased acidity (Section 5.5.2.3.2 and Chapter E-4, Section 4.6.3.4). This may be due to a reduction in algal biomass in the water column, the precipitation of dissolved organics by aluminum or changes in the light-absorption capacity of aquatic humic materials. Increased light penetration would allow macrophyte and phytoplankton growth at greater depths and would warm the water to a greater depth.

5.10.2.5 Altered Decomposition of Organic Matter--Decomposition of organic material releases nutrients for reuse by plants. Reductions in decomposition rates have been reported in some acidified lakes as a result of decreased bacterial metabolic rates and declines in populations of shredding invertebrates. It has been suggested that decreases in nutrient recycling as a result of decreased decomposition would lead to decreased productivity at all trophic levels, but this hypothesis has not been adequately tested nor have consistent decreases in productivity been observed.

5.10.2.6 Presence of Algal Mats--Algal mats which cover the lake bottom down to the limit of light penetration are characteristic of acidified lakes. While these mats would be expected to interfere with water column-sediment interactions important in the recycling of nutrients, this hypothesis has not been experimentally tested. The degree to which the physical alteration of the bottom substrate affects benthic invertebrates and fish is unknown.

5.10.2.7 Altered Nutrient Availability--Increased aluminum concentrations could decrease the concentration of phosphorus via precipitation of aluminum-phosphorus complexes. Reducing phosphorus availability should decrease biological production but this result needs to be quantitatively evaluated. Nitrogen added via acidic deposition is used as a nutrient, but overall biological effects on production would be negligible since phosphorus is the limiting nutrient in most oligotrophic waters.

5.10.2.8 Interaction of Stresses--Predicting the response of a particular lake or stream to acidification is difficult because acidification results in many limnological changes besides increased acidity. These changes interact with biotic responses in complex and often counterbalancing ways. This is illustrated by the response of the phytoplankton to acidification. Phytoplankton biomass and productivity have shown increases, decreases, or no change with respect to decreasing pH (Section 5.8). Certain types of algae (dinoflagellates) are frequently dominant in acidic lakes, yet exceptions are not uncommon. Alga species that are rare one year may dominate a lake the following year (Yan and Stokes 1978). Variation in the response of plankton communities to acidification may result from the interaction of many factors. Acidification eliminates sensitive algal species, may decrease phosphorus and inorganic carbon concentrations, and may depress nutrient cycling. These changes would tend to decrease phytoplankton biomass and productivity. Yet acidification may increase water clarity, allowing light to penetrate into the thermocline and hypolimnion, where nutrient levels are generally higher. This would tend to increase productivity. Zooplankton are similarly affected by numerous factors besides pH, including changes in their food supply and the loss of fish predators.

The response of fish to acidification is likewise complicated. Aluminum and hydrogen ions interact to cause fish mortalities. Yet this interaction may be most important during short time periods (e.g., spring snowmelt) and may not be detected during stream or lake surveys done at other times of the year. Laboratory experiments predict decreased fish growth in acidified waters (Section 5.6.4.1.3), yet increased fish growth has been observed in the field. The reason may be that the increased metabolic demands at low pH are outweighed by the greater abundance of forage organisms available to a continually dwindling fish population. Reproductive failures, not decreased growth, the loss of food items, or adult mortality, appear responsible for most fish extinctions.

Contradictory responses should not be interpreted as evidence that acidification has no effect, but rather as an indication that poorly understood interactions among stresses may be involved. The infrequency of manipulative, whole-system experiments has contributed to this lack of resolution.

5.10.3 Biological Mitigation

Techniques for mitigating the effects of acidification on aquatic organisms include base additions to neutralize the acidity (Section 5.9.1 and Chapter E-4, Section 4.7.1) and development of acid-tolerant fish strains (Section 5.9.2). Immediately after base addition dramatic reductions in phytoplankton, zooplankton and benthic fauna have been reserved. However, the long-term consequence of lake neutralization, provided that reacidification is not allowed to occur, is repopulation by aquatic organisms and an environment that is more hospitable for fish.

Fish survival in acidic waters may be enhanced by genetic screening, selective breeding and acclimation. These techniques appear to be a feasible strategy for maintaining a sport fishery in waters acidified to the point where a natural fishery is no longer possible. It is doubtful, however, that they could be used to reestablish naturally reproducing fish populations and they do not address the problem of restoring other components of the biota to preacidified conditions. Because of the potential for increased metal concentrations in fish from acidified waters (Section 5.6.2.5), fish stocked in such waters should be monitored for toxic metal accumulation.

5.10.4 Summary

Biological effects due to acidification become apparent as alkalinities decline to 65-35 $\mu eq\ \ell^{-1}$ and pH's decline to between 6.5 to 6.0 (Table 5-16). Since the biological response to acidification is a graded one, continuing pH declines below this range will result in escalating biological changes. In Chapter E-4 it was concluded that, under current rates of acidic deposition, a long-term pH of $\leq$ 4.9 can be expected in low-alkalinity lakes and streams in the northeastern United States and southeastern Canada that have pH levels in the mid 5's prior to acidification (Section 4.4.4). Episodic depressions down to pH 4.3 to 4.9 will occur during periods of snowmelt and heavy rainfall and can affect systems with a pH as high as 7.0 (Section 4.4.2). These pH levels, along with other changes associated with the acidification process (e.g., increased aluminum clarity, accumulation of detritus and algal mats), will have significant harmful effects on aquatic organisms. In waters where pH values average 4.9 or lower, most fish species, virtually all molluscs, and many groups of benthic invertebrates will be eliminated. Increased aluminum concentrations may eliminate fish species otherwise tolerant of low pH. The plankton community will be simplified and dominated by a few acid-tolerant taxa. Benthic algal mats will often cover the lake bottom, and water clarity may increase. These represent the best documented effects of acidification. Effects on ecosystem processes remain largely unconfirmed and are an important area for future research efforts.

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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-6. INDIRECT EFFECTS ON HEALTH

6.1 INTRODUCTION (T. W. Clarkson)

Indirect health effects that may be causally related to acidic deposition have not been demonstrated in human populations. This lack of documented effects may mean that no such effects exist in individuals or populations. On the other hand, interest in the pheomenon of acidic deposition is recent and few investigations, if any, have been made into the possibility of indirect health effects. In principle, acidic deposition may influence human exposure to toxic chemicals via two main pathways: the accumulation of chemicals in food chains leading to man and the contamination of drinking water. The format of this chapter is organized according to these exposure pathways, i.e., Food Chain Dynamics (Section 6.2) and Ground, Surface and Cistern Waters (Section 6.3).

The substances requiring special attention are methyl mercury, due to its accumulation in aquatic food chains, and lead, due to the potential for contaminating drinking water. Aluminum is a special case where its presence at elevated concentrations in water used in dialysis therepy may be a cause of brain damage. Other elements and chemicals will only be briefly mentioned as information is limited. These include arsenic, asbestos, cadmium, copper, nickel, and the nitrosamines. Furthermore, reference will be made to other metals and elements that may interact with mercury, lead, and aluminum to modify human exposure and toxicity.

6.2 FOOD CHAIN DYNAMICS (T. W. Clarkson)

6.2.1 Introduction

Human exposure could result from bioaccumulation processes. Aquatic organisms, particularly predatory fish at the top of the food chain, may concentrate certain toxic elements, leading to substantial human exposure as in the case of mercury. Accumulation may occur in wildlife in contact with the contaminated water or consuming aquatic organisms. Water used for irrigation could lead to contamination of edible vegetation. Concentrations of toxic elements in meat, eggs, and diary products could be produced by contamination of livestock. This could occur from drinking water or from contamination of livestock food.

Each of these potential bioaccumulation pathways to humans should be considered in light of possible health hazards. Data, however, are very limited with regard to measurement of the toxic elements and to the kinetics of transfer and uptake in bioaccumulation processes. This discussion will, therefore, be limited to only a few toxic elements and the major pathways of exposure.

6.2.2 Availability and Bioaccumulation of Toxic Metals

Mercury and its compounds have been extensively studied in terms of availability and bioaccumulation. The impetus for this work came from a discovery made in the late 1960's (see below) that inorganic mercury may be methylated in the aquatic environment to the highly neurotoxic species - methyl mercury - and thereby accumulate in aquatic food chains leading to man. Mercury is the most dramatic example of a change in speciation produced in the environment that ultimately leads to increased levels in human food. Alkylation of certain other toxic metals may also occur in the environment (Wood 1974). Organic forms of arsenic are known to accumulate in shellfish but organic arsenic is much less toxic to man and animals than the inorganic species. Cadmium accumulates in plants and certain marine crustacea, although the role of aquatic acidification in these accumulation processes is not well documented. In short, this section will deal primarily with our knowledge concerning the bioaccumulation of methyl mercury in aquatic food chains and the possible role of acidification. Other metals and elements will be discussed briefly as a group.

6.2.2.1 Speciation (Mercury)--The different chemical and physical forms of mercury each have their own distinctive biological activity (for a detailed review, see Carty and Malone 1979). Each differs from the others in the extent of bioaccumulation in food chains and in toxicity to humal life. The speciation of mercury in natural bodies of water is, therefore, an important consideration in assessing potential hazard to man.

Mercury exists in a variety of physical and chemical forms. The inorganic forms have three oxidation states: Hg° or "metallic" mercury is in the zero oxidation state. It is a liquid metal ("quicksilver") and possesses a high vapor pressure. The vapor is a monatomic gas, is highly diffusible, and possesses a low solubility in water. It is commonly referred to as "mercury vapor" despite the fact that certain other forms of mercury (e.g., dimethyl mercury) also readily vaporize. If Hg° is produced in aquatic bodies of water, it will readily diffuse into the atmosphere.

Mercury vapor in the presence of water and oxygen is readily oxidized to the first oxidation state Hg_2^{2+}, called mercurous mercury and to the second oxidation state, Hg^{2+}, known as mercuric mercury. Indeed, the interconversion of these three oxidations states via the disproportionation reaction

$$Hg_2^{2+} \rightleftarrows Hg^{2+} + Hg^{\circ}$$

is an important reaction in the environmental transport of mercury (Wood 1974). The direction of the reaction is affected not only by the relative concentrations of the three species of mercury but by the ambient redox potential and by certain microorganisms capable of reducing Hg^{2+} to Hg° (Wood 1974).

Most mercurous salts of mercury possess a low solubility in water. Furthermore, the mercurous action disproportionates to Hg° and Hg^{2+} in the presence of protein and other substances containing ligands having a high affinity for Hg^{2+}. Thus, inorganic mercury in the environment tends either to be present as Hg° (usually as the vapor) or Hg^{2+}.

The mercuric cations are capable of forming a wide variety of chelates and complexes with electron donating groups (ligands). For example, four complexes are formed with chloride anions--$HgCl^{+}$, $HgCl_2$, $HgCl_3^{-}$, and $HgCl_4^{2-}$. The mercuric cation possesses such high affinities for many organic ligands expected to be present in sediments, water, and aquatic biota that it is unlikely that the free cations, Hg^{2+}, will ever be detected in measurable quantities. Its highest affinity is for sulfur anions S^{2-}, S-H and the sulfhydryl anion in proteins and amino acids--$R\text{-}S^{-}$ where the affinity constants are usually in the range of 10 to 20. It is not surprising, therefore, that the naturally occurring ore of mercury, cinnabar, is the sulfide complex HgS. The reaction of Hg^{2+} with sulfide ions is important in the geochemical cycles of mercury (see below). Mercuric sulfide is highly insoluble in water, (solubility product 10^{-53} M), so reaction of mercury with sulfides in water and sediments leads to immobilization of the metal. However, in the presence of well-oxygenated water (Jensen and Jernelov 1972) and also in the presence of aerobes, HgS can be oxidized to the much more soluble sulfite and sulfate salts, thus leading to remobilization of mercury (see below).

Mercuric mercury can form a wider variety of organometallic compounds in which the mercuric atom is linked covalently with at least one carbon atom. These organometallic compounds are usually referred to as "organic mercury." Examples of two organic forms of mercury are depicted in Table 6-1. Phenyl mercury has long been used as a fungicide in the paint industry and as a slimicide in the paper pulp industry. The latter use led to contamination of many bodies of fresh water in Europe and North America, and its use has now been banned. Phenyl mercury may be broken down rapidly to inorganic mercury (Hg^{2+}) by microorganisms present in the aquatic environment and by enzymes in mammalian tissues. It has a low toxicity to man.

Methyl mercury possesses unique environmental and toxicological properties that make it the most dangerous mercury compound to human health and one of the most hazardous chemicals found in the natural environment. Methyl mercury is known to be produced by methylation of inorganic (Hg^{2+}) mercury by methanogenic bacteria present in sediments in natural bodies of water (for review, see Wood 1974). It is avidly accumulated by fish and attains the highest concentration in species of predatory fish. Like Hg^{2+}, it has a high affinity for organic ligands, prticularly the sulfhydryl anion in proteins. It appears to have a low toxicity to fish and other aquatic species but is highly toxic to the human central nervous system (see Section 6.2.4.2).

Dimethyl mercury $(CH_3)_2Hg$ is also produced by methanogenic bacteria. Like mercury vapor, it possesses a low solubility in water

TABLE 6-1. SOURCES OF MERCURY IN THE ENVIRONMENT 1971
(WHO 1976, NRIAGU 1979)

Source	Amount Metric tons yr^{-1}
Natural	
degassing of earth's crust	~ 30,000
Anthropogenic	
worldwide mining	10,000
combustion of coal	3,000
combustion of oil	400-1500
smelting of metal sulfide ores	1,500
steel cement phosphates	500

and has a high vapor pressure. Thus, dimethyl mercury tends to escape from the aquatic system into the atmosphere, where it may be broken down by sunlight to Hg° and methyl free radicals.

6.2.2.2 Concentrations and Speciations in Water (Mercury)--The early findings of Stock and Cucuel (1934) that rain water contains mercury between 50 to 500 ng Hg ℓ^{-1} is generally supported by more recent findings. Brune (1969) reported average values of approximately 300 ng Hg ℓ^{-1} in Sweden, and Eriksson (1967) also in Sweden found most samples of rain water in the range of 0 to 200 ng ℓ^{-1}.

Values for snow depend greatly on the collection conditions and how long the snow has laid on the ground. Straby (1968) found values of 80 ng g^{-1} in fresh snow, but values as high as 400 to 500 ng Hg g^{-1} were found in snow samples that had partly melted and evaporated over the winter. Analysis of the samples deposited in Greenland prior to the 1900s yielded values of 60 ng g^{-1} (Weiss et al. 1971).

Bodies of fresh water for which there is no known source of contamination generally yield values less than 200 ng ℓ^{-1}. Most values fall in the range of 10 to 40 ng ℓ^{-1} and drinking water usually has values less than 30 ng ℓ^{-1} (WHO 1976).

Few reports exist on the speciation of mercury in water, probably because of analytical difficulties. A recent review by McLean et al. (1980) found that methyl mercury accounted for a small fraction of the total - of the order of 1 percent. However, a more recent report by Kudo et al. (1982) found that methyl mercury accounted for about 30 percent of total mercury in samples taken from Canadian and Japanese rivers. Mercuric mercury (Hg^{2+}) accounted for about 50 percent.

Two important conclusions may be drawn from these data. First, that precipitation is an important source of mercury to fresh water (see next section), and second, that mercury in drinking water offers no health threat. Concentrations on the order of a few hundred nanograms per liter would result in a negligible intake of mercury on the assumed intake of two liters per day (U.S. EPA 1980a). This intake, less than 2 µg day^{-1}, is well below the advised maximum safe intake of 30 µg Hg day^{-1} (WHO 1972b); thus, additional mobilization of mercury into water by acidic deposition should not pose a health threat in terms of contaminated drinking water.

6.2.2.3 Flow of Mercury in the Environment--This topic has been the subject of a number of reviews (WHO 1976, NAS 1978, U.S. EPA 1980a) and will be briefly summarized here. The subject is one of intensive research, particularly by the Coal-Health-Environment Project (KHM 1981) in Sweden. This topic's development is hampered by the need for more sensitive and more specific methods for measuring the various physical and chemical species of mercury believed to be present at extremely low concentrations in the atmosphere and in bodies of natural water.

6.2.2.3.1 Global cycles. The global cycles of mercury have recently been reviewed by Nriagu (1979) and by the National Academy of Sciences (1978). The global cycle of mercury involves degassing of the element from the earth's crust and evaporation from natural bodies of water, atmospheric transport believed to be mainly in the form of mercury vapor, and deposition of mercury back onto land and water. Mercury ultimately finds its way to sediments in water, particularly to oceanic sediments where the carry-over is very slow. The ocean and oceanic sediments are believed to be the ultimate destination of mercury in the global cycle.

Andren and Nriagu (1979) have indicated that mercury's residence time in the atmosphere may vary from approximately 6 to 90 days. Residence times of mercury in soils are on the order of 1000 years, oceans on the order of 2000 years, and sediments on the order of millions of years.

Estimates of the quantities of mercury entering the atmosphere from degassing of the surface of the planet vary widely, but a commonly quoted figure is 30,000 tons yr^{-1} (Table 6-1). Estimates of the proportion of the mercury in the atmosphere due to anthropogenic sources vary greatly; figures from 10 percent to 80 percent of atmospheric mercury have been credited to man. Estimates of the yearly amount of mercury finding its way to the ocean indicate that atmospheric deposition accounts for the major amount, approximately 11,000 tons yr^{-1}, with land runoff accounting for about 5,000 tons yr^{-1}.

The measurement of mercury in extremely low environmental concentrations is frequently close to the limit of detection of many current methods. With this caveat, it would appear that the vastly predominant reservoir for mercury is the ocean water, containing on the order of 40 million tons (Table 6-2). In contrast, the atmosphere and fresh water contain much less. As one might expect, therefore, the impact of man-made release of mercury is much greater on these smaller reservoirs, especially those to which man-made release is direct. Thus, the impact on levels of atmospheric mercury and mercury in fresh waters is appreciable, whereas it is estimated that oceanic concentrations have not appreciably changed in recent history. For example, it is estimated that the mercury content of lakes and rivers may be increased by a factor of 2 to 4 due to man-made release (Nriagu 1979).

6.2.2.3.2 Biogeochemical cycles of mercury. This overall global cycle of mercury results from extremely complex physical, chemical, and biochemical processes occurring in the main reservoirs and interfaces between these reservoirs. Most of these processes are poorly understood; nevertheless, certain very import fundamental discoveries have been made in recent years and are summarized below.

The most important single discovery in understanding the chemical and biochemical cycles of mercury in the environment was made by Swedish investigators in the 1960s (for a review see NAS 1978, Nriagu 1979). An intensive investigation into the source of the methyl mercury compound

TABLE 6-2. THE AMOUNT OF MERCURY IN SOME GLOBAL RESERVOIRS (NAS 1978).

Reservoir	Mercury Content (metric tons)
Atmosphere	850
Fresh water	2,000
Freshwater biota	400
Ocean water	41,000,000
Oceanic biota	200,000

in freshwater fish revealed that microbial activity in aquatic sediments can result in the methylation of inorganic mercury (Jensen and Jernelov 1967). The most probable mechanism involves the non-enzymatic methylation of mercuric mercury ions by methyl-carboning compounds (Vitamin B_{12}) that are produced as a result of bacterial synthesis. However, other pathways both enzymatic and nonenzymatic may play a role (Beijer and Jernelov 1979).

The methylation of ionic mercury in the environment appears to occur under a variety of conditions: in both aerobic and anaerobic waters; in the presence of various types of microbial populations, both anaerobes and aerobes; and in different types of freshwater bodies such as both eutrophic and oligotrophic lakes.

The methylation of mercury can result in a formation of either monomethyl or dimethyl mercury compounds (Figure 6-1). The monmethyl mercury compound is avidly accumulated by fish and shellfish, whereas the dimethyl compound, having a low solubility and high volatility, tends to vaporize from the water phase to the atmosphere where it may be subjected to photolytic decomposition (Figure 6-1).

However, these reactions are not understood in detail and there does not appear to be general agreement in the literature as to those conditions that favor the formation of monomethyl or the dimethyl form; neither is there complete agreement as to the extent that the dimethyl species actually vaporizes from the water phase into the atmosphere.

Methyl mercury compounds are subject to decomposition in the water phase probably by the action of a variety of microorganisms. These demethylation microbes appear to be widespread in the environment, occuring in water sediments and soils and in the gastrointestinal tract of mammals, including humans. This biogeochemical cycle involving bacterial methylation and demethylation is part of a more general cycle of mercury that describes global transport of mercury. Professor Brosset and colleagues (KHM 1981) have described a large-scale cycle that has the following aspects.

1) Mercury is introduced to the atmosphere from the ground and water surfaces. It occurs primarily in the form of mercury vapor (Hg°).

2) The total concentration of mercury diminishes while the proportion of water soluble mercury increases as a function of height over the ground. The origin of the soluble mercury is not yet completely understood.

3) Water soluble mercury is deposited in wet and dry forms in the water phase of terrestrial and aquatic systems and probably in other phases if the mercury compounds are soluble in those phases.

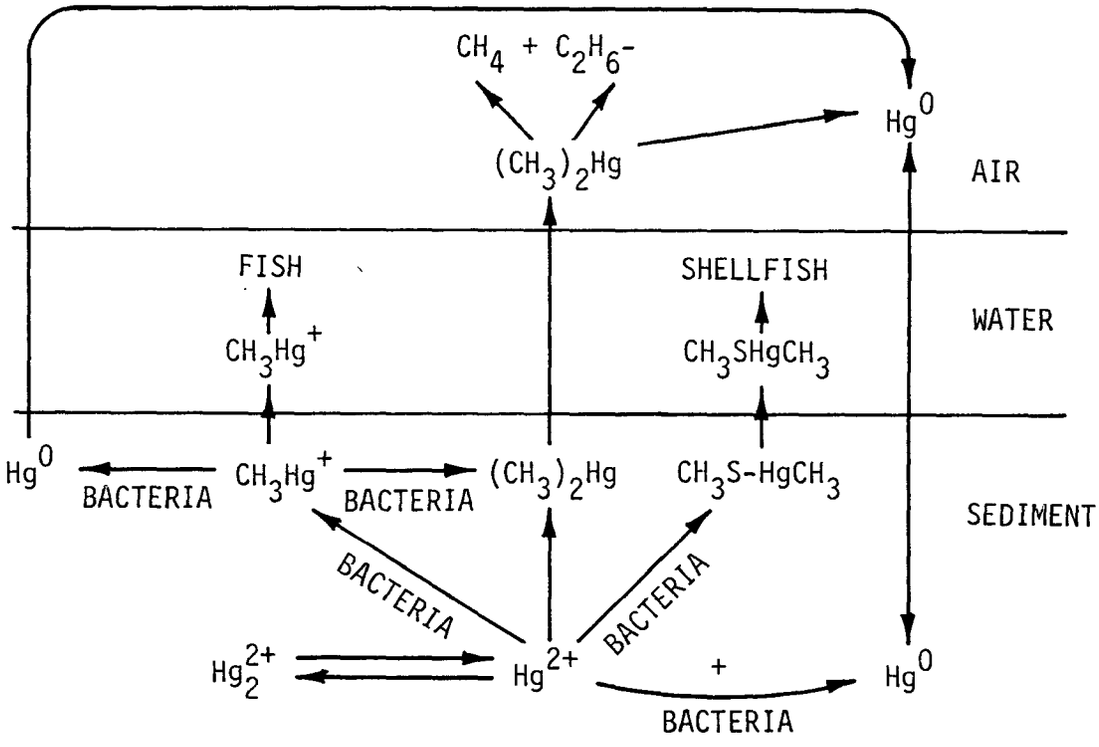

Figure 6-1. The mercury cycle, demonstrating chemical transformation by chemical and biological processes and the accumulation of monomethyl mercury by fish. Adapted from NAS (1978).

4) The deposited forms of water soluble mercury, once in the water or terrestrial phase, partly undergo reduction to Hg°, and are partly absorbed temporarily or permanently on sediments.

5) The rates of deposition into and removal from the water phases determine the steady state levels of each mercury species in water.

6) The concentration of each mercury species in the water phase determines the concentration on the sediment in contact with the water phase.

7) The reduction product Hg° returns (i.e., is re-emitted) to the atmosphere.

Neither the detailed chemical mechanisms nor the kinetics of these processes are understood at this time; for example, the extent to which mercury may be deposited and remitted from water or land surfaces to the atmosphere is still not understood in quantitative terms. Nevertheless, the general picture that emerges is one in which long distance transport of mercury in the vapor phase is possible, its deposition in water and remission probably occurs extensively, and the chemical conversion of mercury from the elemental to the ionic and to the organic forms is much more extensive than was originally believed. Therefore, methyl mercury may occur not only as a result of microbial action in aquatic sediments as indicated in Figure 6-1 but may have a more general source, including the atmosphere.

6.2.3 Accumulation in Fish (T. W. Clarkson and J. P. Baker)

Once methyl mercury enters the water phase as a soluble compound, it is rapidly accumulated by most aquatic biota and attains highest concentrations in the tissues of large carnivorous fish. Indeed, it is generally believed that the major amount of methyl mercury compounds in bodies of water are contained in the biomass of the system. The bioconcentration factors, that is, the ratio of the concentration of methyl mercury in fish tissue to concentrations in fresh water can be extremely large, usually of the order of 10,000 to 100,000 (U.S. EPA 1980a).

In principle, fish can accumulate methyl mercury both directly from water and from the food supply. Hultberg and Hasselrot (1981) have reviewed available data and suggested that pike obtain virtually all their methyl mercury from their food supply. Methyl mercury concentrations correlate well between different trophic levels of fish and other aquatic organisms, implying the importance of the food chain. In a survey of several lakes, levels of methyl mercury in pike were closely correlated ($r = 0.92$) with methyl mercury concentration in plankton (Hultberg and Hasselrot 1981). Thus factors that affect bioaccumulation of methyl mercury at this early stage of the food chain should also affect methyl mercury levels at the highest level (e.g., in predatory fish).

The concentration of methyl mercury in fish tissue is of special interest in terms of human exposure. Bioaccumulation of methyl mercury in fish is the main if not the sole source of human exposure, barring episodes of accidental discharge or misuse of man-made methyl mercury compounds. Thus, factors that affect concentrations of methyl mercury in edible fish tissue are of considerble importance in assessing potential human health risks from this form of mercury.

6.2.3.1 Factors Affecting Mercury Concentrations in Fish--In general, for any body of water one might expect to see an eventual steady-state distribution of methyl mercury--a balance of synthetic and degradation reactions. Concentrations of methyl mercury in sediment, water, and biomass at steady-state are influenced by a wide variety of experimental conditions, perhaps only a few of which have so far been identified. No detailed review will be given in this chapter, but the reader is referred to other references that give a more specific treatment of this topic (Nriagu 1979).

Theoretical considerations, experimental data, and observations in field studies have indicated or suggested that methyl mercury concentrations in fish are affected by: (1) the species of fish, (2) the age of the fish, (3) concentrations of mercury in surface sediments and/or in water, (4) the biomass or biomass production index, (5) salinity, (6) concentrations of dissolved organics, (7) the microbial activity associated with sediments, (8) the degrees of oxygenation of water and redox potential, (9) the pH and/or alkalinity of water (Hultberg and Hasselrot 1981, Jensen and Jernelov 1972, Fagerstrom and Jernelov 1971, Jernelov 1980). This list is not exhaustive and, indeed, recent evidence suggests that other as yet unknown factors are involved (for discussion see Hultberg and Hasselrot 1981). In view of the current interest in the relationship between the use of fossil fuels, particularly coal, and possible acidification of large bodies of fresh water, the influence of aquatic pH on levels of methyl mercury in fish will be given special attention here.

An indirect result of acidification of surface waters may be increased accumulation of mercury (and perhaps other metals) in fish. Evidence for this relationship derives from correlations between metal concentrations in fish and lake and stream pH levels, and evalutions of metal chemistry and availability in oligotrophic, acidic waters.

Elevated levels of mercury in fish from acidic waters have been measured in Sweden, Norway, Ontario, and the Adirondack region of New York (Hultberg and Hasselrot 1981, Overrein et al. 1980, Suns et al. 1980, Jernelov 1980, Schofield 1978). In each case, although fish mercury content was statistically correlated with pH level, the data points still exhibit significant scatter. At any particular pH level, for a given age and species of fish, the range observed between lakes in values of mg Hg kg^{-1} flesh was considerable, even to the extent that not all lakes with low pH exhibited elevated mercury concentrations in fish and some lakes without low pH had fish with high mercury content. Obviously, other factors in addition to pH control the accumulation of

mercury in fish as noted above. Waters of low productivity (oligotrophic lakes) and low alkalinity tend to be more sensitive to mercury contamination and mercury accumulation in fish. Because these conditions are also strongly associated with low pH levels, the effect of pH on mercury bioaccumulation may be somewhat confounded. The correlation between pH and fish mercury content may in part be a result of the observation that low pH waters tend to be oligotrophic, soft waters with low alkalinities. On the other hand, the association between low alkalinity and elevated mercury accumulation and low pH waters have low alkalinities. Results from these correlations must be interpreted carefully.

The most extensive studies on factors controlling mercury levels in fish have been carried out in Sweden. In the 1960's pike and other edible fish were found to have unacceptably high levels of mercury (greater than 1 μg Hg g^{-1}). For some lakes, local industrial "mercury emitters" with direct outlets to the lakes were identified as the cause. Many lakes, however, had inexplicably high mercury levels in fish. This led to extensive studies in Sweden on the dynamics of mercury chemistry and uptake by fish and the role of acidity in these processes.

Data collected by Jernelov et al. (1975), Grahn et al. (1976), Landner and Larsson (1972), and Hultberg and Jernelov (1976), as reported by Jernelov (1980), all indicated an overall strong correlation between mercury levels in fish and pH values of lakes. Jernelov (1980) concluded that in Swedish lakes in general, extremely few lakes with pH values below 5.0 have pike (weighing 1 kg) with mercury concentrations of less than 1 mg kg^{-1}. At a pH value of 6.0, the normal level for the same pike would be approximately 0.6 mg kg^{-1}.

Hultberg and Hasselrot (1981) reviewed ten years of Swedish work on factors affecting mercury in fish. In a study involving over 152 Swedish lakes mercury level in pike muscle was inversely correlated with water pH (Figure 6-2). Water samples collected during the fall overturn were analyzed for pH, humic material (water color at an adjusted pH) and specific conductivity (salt content). Multiple linear regression analysis (Table 6-3) suggested that a one unit decrease in pH would elevate mercury in the muscle tissue of pike (weighing 1 kg) by 0.14 ppm. The influence of pH on fish mercury content was generally greater than that associated with humic content or conductivity.

Hakanson (1980), also using the Swedish data base, developed (based on a combination of statistics and deductive reasoning) a quantitative model expressing mercury content in a 1-kg pike as a function of pH, the mercury content in the top one cm of lake sediments, and a bioproduction index. The model was validated using an independent data set from 107 Swedish lakes. The correlation coefficient between observed and predicted mercury content was 0.79.

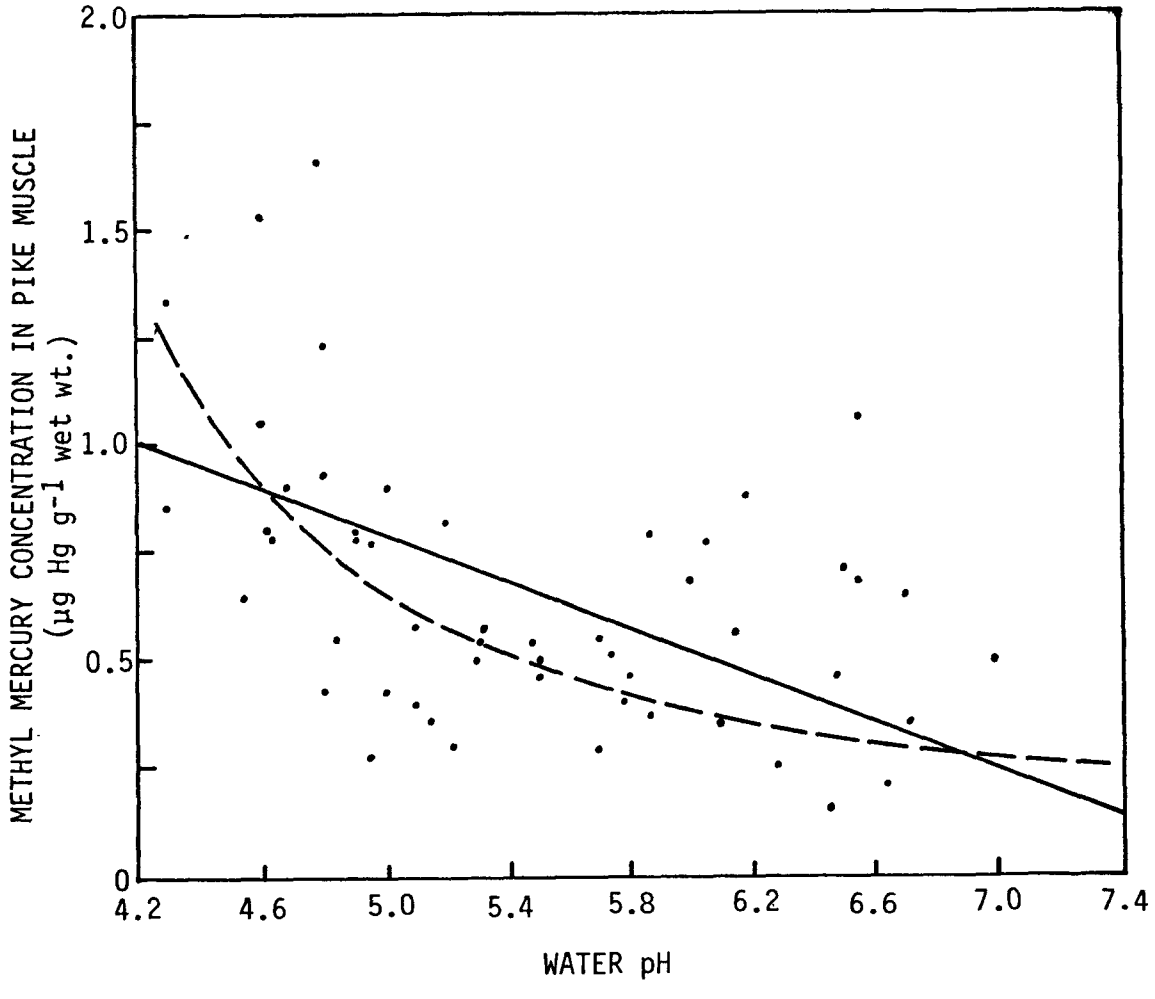

Figure 6-2. Variations in methyl mercury concentrations in pike muscle as a function of pH. The study was conducted in lakes in the Halland-Smaland of Sweden. These lakes have no known local source of mercury. The straight line was drawn by linear least-squares regression analysis and the curved broken line according to a hyperbolin function. Data are from Hultberg and Hasselrot (1981).

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TABLE 6-3. THE RESULTS OF A STATISTICAL ANALYSIS INDICATING THE CONTRIBUTION OF pH, HUMIC CONTENT AND SPECIFIC CONDUCTIVITY TO METHYL MERCURY CONCENTRATIONS IN THE MUSCLE TISSUE OF 1 KG PIKE (ADAPTED FROM HULTBERG AND HUSSELROT 1981)

Change in water pH	Change in mercury concentration mg Hg kg^{-1}
one pH unit	0.14
two pH units	0.28
three pH units	0.42
Color increase	
10 mg Pt ℓ^{-1}	0.015
50 mg Pt ℓ^{-1}	0.075
100 mg Pt ℓ^{-1}	0.150
Change in specific conductivity	
5 mS m^{-1}	0.075
10 mS m^{-1}	0.150
20 mS m^{-1}	0.300

Hakanson's formula was as follows:

$$F(Hg) = \frac{4.8 \times \log\left(1 + \frac{Hg_{50}}{200}\right)}{(pH-2) \times \log(BPI)}$$

where

F(Hg) = the concentration of methyl mercury in a 1 kg pike in $\mu g\ g^{-1}$ wet weight,

Hg_{50} = the weighted mean mercury content of surface sediments, 0 to 1 cm, in ng Hg g^{-1} ds (ds = dry substance),

pH = the mean pH of the water system, i.e., the mean of at least five measurements of which two should be obtained at different seasons, and

BPI = Bioproduction Index - for details, see Hakanson (1980).

Calculations based on the Hakanson formula yield results similar to those from Hultberg and Hasselrot (1981). For example, if it is assumed that a 1 kg pike at pH 6.0 contains 0.75 ppm Hg (e.g., Figure 6-2), then a pH change from 6.0 to 5.0 would increase fish mercury concentration by approximately 0.13 ppm. Overlap in the data bases used by both Hakanson and Hultberg-Hasselrot may have occurred, however, accounting in part for this close agreement.

If the Hakanson formula is valid, then a question might be raised on the appropriateness of linear regression analyses relating pH to mercury concentration (e.g., in Figure 6-2 and the multilinear analysis used for Table 6-3). The Hakanson formula has the general form of a rectangular hyperbole:

$$FHg = \frac{\alpha}{pH - \beta}$$

where Hg_{50} and BPI are constant.

Regression analysis of the data in Figure 6-3 according to a hyperbolic equation yielded a value of the correlation coefficient ($r^2 = 0.81$) appreciably higher than that obtained by linear regression analysis ($r^2 = 0.3$). Thus, for the Swedish study, change in pH accounted for about 80 percent of the total variance in methyl mercury concentrations in 1 kg pike. The hyperbolic aspects will become more pronounced at lower pH values and will be discussed later with regard to apparent scatter of points around linear regression lines.

Additional and as yet unknown factors seem to be operative in determining mercury concentrations in fish. For example, Hultberg and

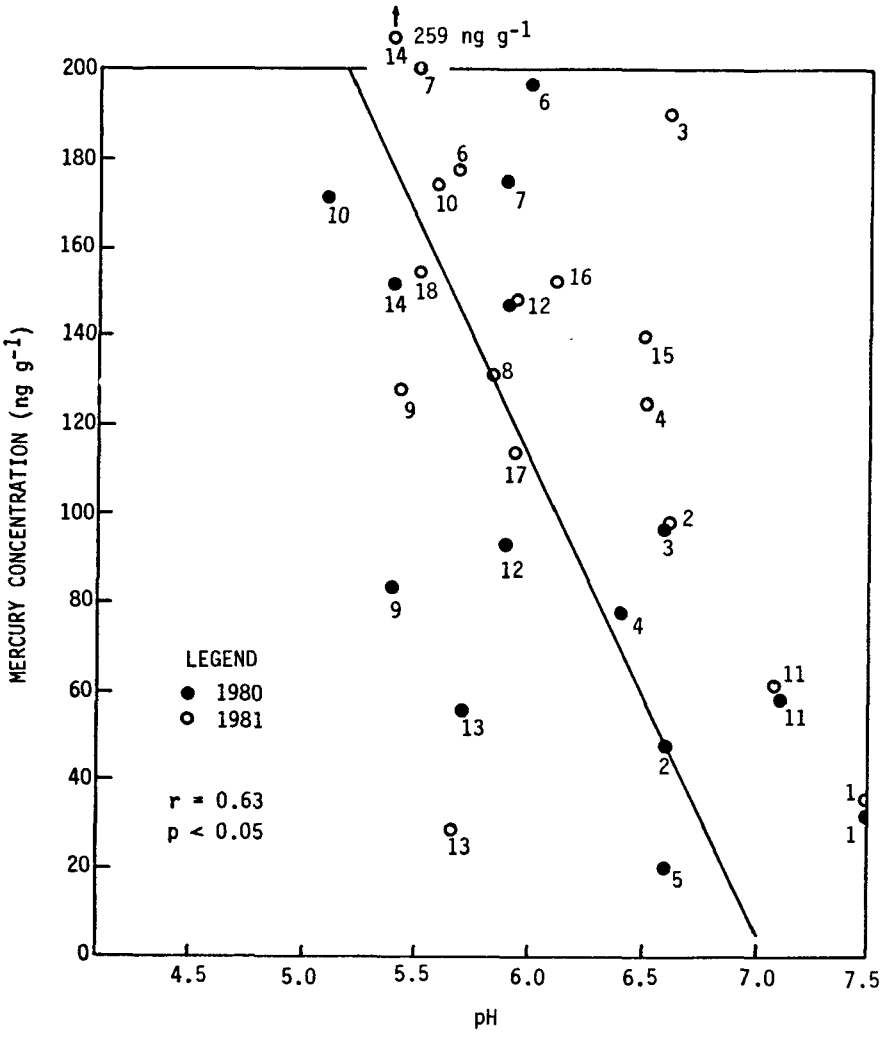

Figure 6-3. Mercury concentrations in yearling yellow perch and epilimnetic pH in lakes in the Muskoka-Haliburton area of Ontario (Suns et al. 1980, U.S./Canada 1983).

Hasselrot (1981) noted that lakes in more northern regions of Sweden tend to have higher concentrations of mercury in pike. Possible explanations include 1) the impact of snow on water quality during the spring melt, 2) loss of sensitive prey species (in this case roach, Rutihis rutilis) adversely affected during acid episodes during spring melt and a shift to predation on higher trophic levels (in this case perch, Percas gluvicotilis) that contain greater amounts of mercury, 3) the importance of snow itself as a source of mercury including methyl mercury (Brouzes et al. (1977) and 4) lower water temperature and salinity generally associated with northern latitudes.

In Norway, concentrations of mercury in muscle of trout, perch, char, and pike were studied by Muniz, Rosseland, and Paus (Overrein et al 1980). Again, fish populations in acidic waters generally had higher levels of mercury than did reference populations from areas without acidified lakes.

Studies in Canada (Suns et al. 1980) have also found a statistically significant ($r = 0.65$, $p < 0.05$) inverse correlation between water acidity and mercury levels in fish, for yearling perch in 14 pre-cambrian lakes in Ontario (Figure 6-3). For lakes with similar pH, mercury levels were higher in fish from lakes with a higher drainage area/lake volume ratio.

Suns et al. (1980) failed to see a relationship between mercury in fish and water alkalinity, whereas Scheider et al. (1979) reported that for walleye (Stigostedion vitreum) of equal length, caught in Ontario lakes with alkaline water ($\leq$ 15 mg $CaCO_3$ ℓ^{-1}) had significantly higher mercury levels than walleye caught in lakes with high alkalinity ($>$ 15 mg $CaCO_3$ ℓ^{-1}). Comparisons based on fish length may, however, be somewhat misleading. If fish from waters with lower alkalinity grow slower (possibly as a result of lower primary prooductivity or lower temperatures), than the higher mercury content at a given length may actually only reflect the older age of the fish.

Statistical evaluations of mercury in fish and water acidity have not been published for fresh water fish caught in the United States. A graph of mercury levels in brook trout muscle as a function of fish length for Adirondack lakes indicated that fish from acid drainage lakes (pH < 5.0) in general had higher mercury levels (for a given length) than fish from limed, seepage, or bog lakes (Schofield 1978). However, high mercury level in fish were also found in some lakes without low pH, indicating that the unusual mercury bioaccumulation may be, in part or in total, independent of pH level. From 1969 to 1972, over 3500 fish from New York State lakes and streams were collected and analyzed for mercury content. Two Adirondack Mountain reservoirs, Cranberry Lake and Stillwater Reservoir, yielded fish with particularly high mercury levels, despite the undeveloped nature of their watersheds (Bloomfield et al. 1980) (Figure 6-4). The highest mercury levels in the New York State survey were recorded for Onondaga Lake fish and caused, for the most part, by mercury contributions from a chlor-alkali plant during the 1960s. Other areas, such as Lake Ontario, Lake Champlain, and the St.

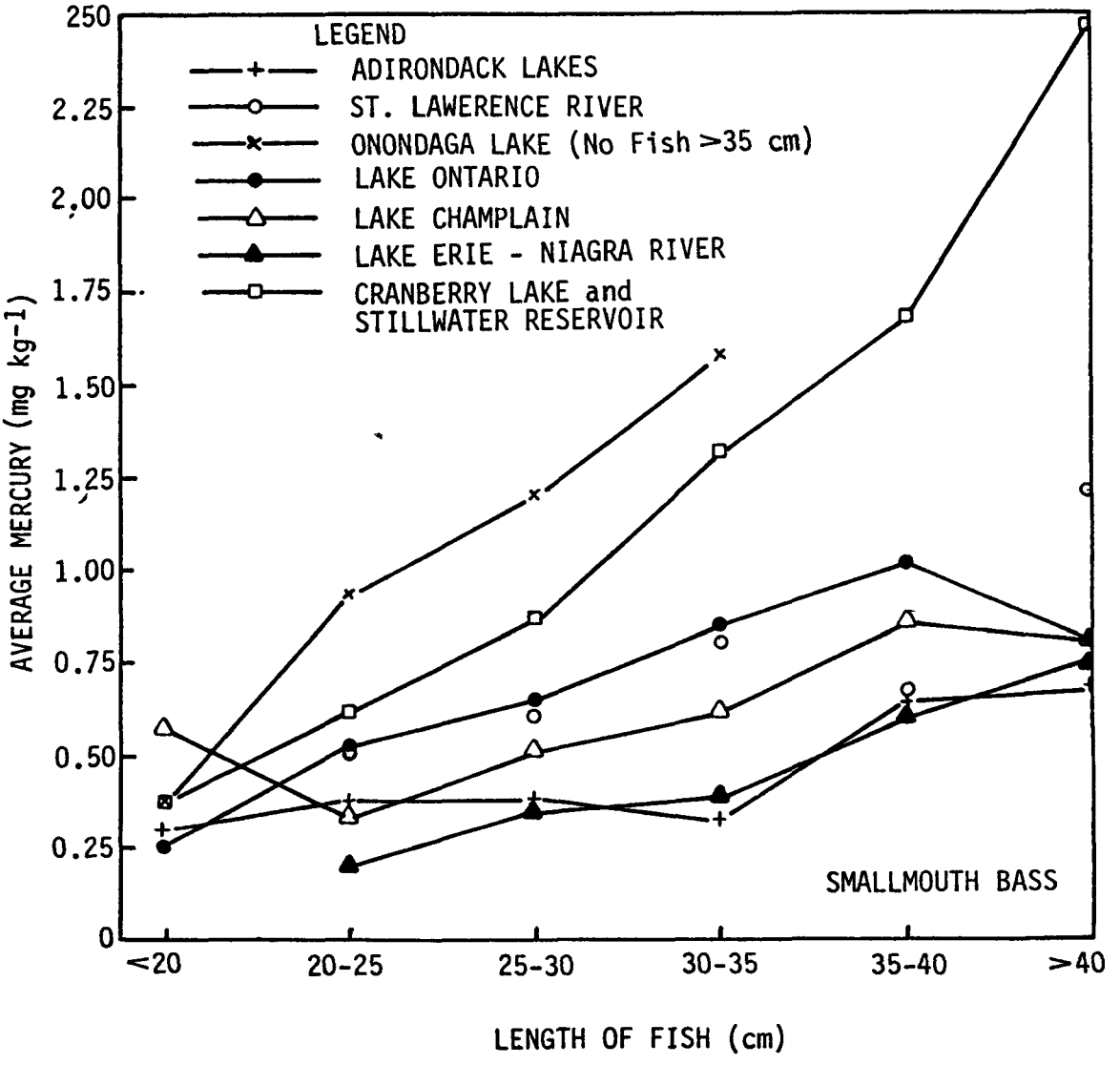

Figure 6-4. Average mercury concentration vs length class in New York State smallmouth bass. Adapted from Bloomfield et al. (1980).

Lawrence River also either have or have had in the past sources of direct contamination, yet mercury levels found in fish from these areas were lower than in fish from Stillwater Reservoir and Cranberry Lake. Other Adirondack lake samples also tended to have lower fish mercury levels. The source of mercury to Cranberry Lake and Stillwater Reservoir remains unresolved. Stillwater Reservoir is an acidic (pH < 5.0) clear water lake. Cranberry Lake, on the other hand, had a mean pH of 6.90 in the fall of 1978 (Bloomfield et al. 1980). Cranberry Lake waters are, however, relatively highly colored with high concentrations of humic organics.

In summary, field studies in Sweden, Norway, and Canada have identified several factors that correlate (positively or negatively) with mercury levels in fish. This includes fish species and age (length and weight are frequently used instead of age), mercury levels in surface sediments, the biomass or bioproductivity of the lake, the salinity (specific conductivity) and pH. Other factors may also be operative, such as morphometric parameters (drainage area/lake volume ratios) and geographic (northern latitude). However, in virtually all such studies published to date, elevated mercury levels in fish muscle (most notably the pike and the perch) have been statistically associated with higher levels of acidity.

However, a number of factors influencing mercury levels in fish may also change in parallel with acidity. Thus, a true cause-effect relationship between acidity and elevated mercury in fish has not been established by the available data. Absolute proof may be unattainable in field studies, given the large number of variables and the probability that, in any given field study, not all of these will be controlled or even measured.

To resolve whether correlations observed between lake pH level and mercury content in fish actually reflect a cause-and-effect relationship and whether acidification will enhance bioaccumulation of mercury, the effects of pH and acidity on mercury chemistry, mobilization, and uptake must be understood. Field and laboratory research on mercury cycles have resulted in several proposed mechanisms (Jernelov 1980, Wood 1980, Haines 1981):

1) Acidic precipitation may scavenge mercury from the atmosphere more effectively than nonacidic precipitation.

2) The rate of methylation of inorganic mercury by microorganisms is pH-dependent, the maximum occurring at pH 6.0--methylation is higher from pH 5.0 to 7.0 than above 7.0. Thus, at lower pH more methyl mercury would be present and, because methyl mercury is the form most rapidly taken up by fish, bioaccumulation presumably would be enhanced.

3) Low pH levels favor the formation of monomethyl mercury rather than dimethyl mercury. Dimethyl mercury is unstable and volatile and thus more quickly lost from the aquatic system (Figure 6-1).

4) Under aerobic conditions, inorganic mercury is more soluble at reduced pH and thus more available for methylation reactions. Retention of mercury in the water column is enhanced with increased acidity (Jackson et al. 1980), thus increasing the exposure of fish to mercury.

5) Since the biomass of fish is often lower in acidic lakes, the available mercury is concentrated in a smaller biomass, resulting in higher body burdens per fish. Also, if growth rate is reduced, fish in an acidic lake would be older than fish of an equivalent size in a nonacidic lake and would have been accumulating mercury longer.

Laboratory experiments will be useful, if not essential, in order to unravel mechanisms associating pH change with mercury accumulation in fish. Laboratory experiments have shown that, for a given amount of total mercury in an aquatic ecosystem, higher levels of mercury were found in fish at low pH values than at high pH values (for review, see Jernelov 1980).

Miller and Akagi (1979) presented experimental evidence that low pH levels mobilize methyl mercury absorbed on sediments. Natural water from the Ottawa River was incubated with various types of sediment materials for periods of approximately three weeks. Irrespective of the type of sediment, a reduction in water pH shifted, by a factor of 2 for each unit change in pH, the distribution of methyl mercury from the sediment to the water phase (Figure 6-5). Miller and Akagi (1979) asserted that the effect of pH on the equilibrium of methyl mercury between water and sediment, may be the principal factor responsible for higher levels of mercury in fish in low pH aquatic environments.

That acidification of surface waters will significantly enhance bioaccumulation of mercury has not been definitively demonstrated. The chemistry and environmental sampling of mercury are extremely complex. More research is needed to identify all factors that affect mercury accumulation in fish and the relative importance of each. The significance of a one unit pH decrease (or a decline in alkalinity by 100 $\mu eq\ \ell^{-1}$) relative to the effects of the large number of other factors that influence bioaccumulation has not been quantified. This need is especially urgent in the United States, where few data are available at this time.

Other metals in addition to mercury occur at elevated concentrations in acidic waters and potentially may accumulate in fish and other biota. Data on these accumulations are, however, very limited. Dickson (1980) reported that concentrations of cadmium in pike increased with increased acidity. Harvey et al. (1982) determined

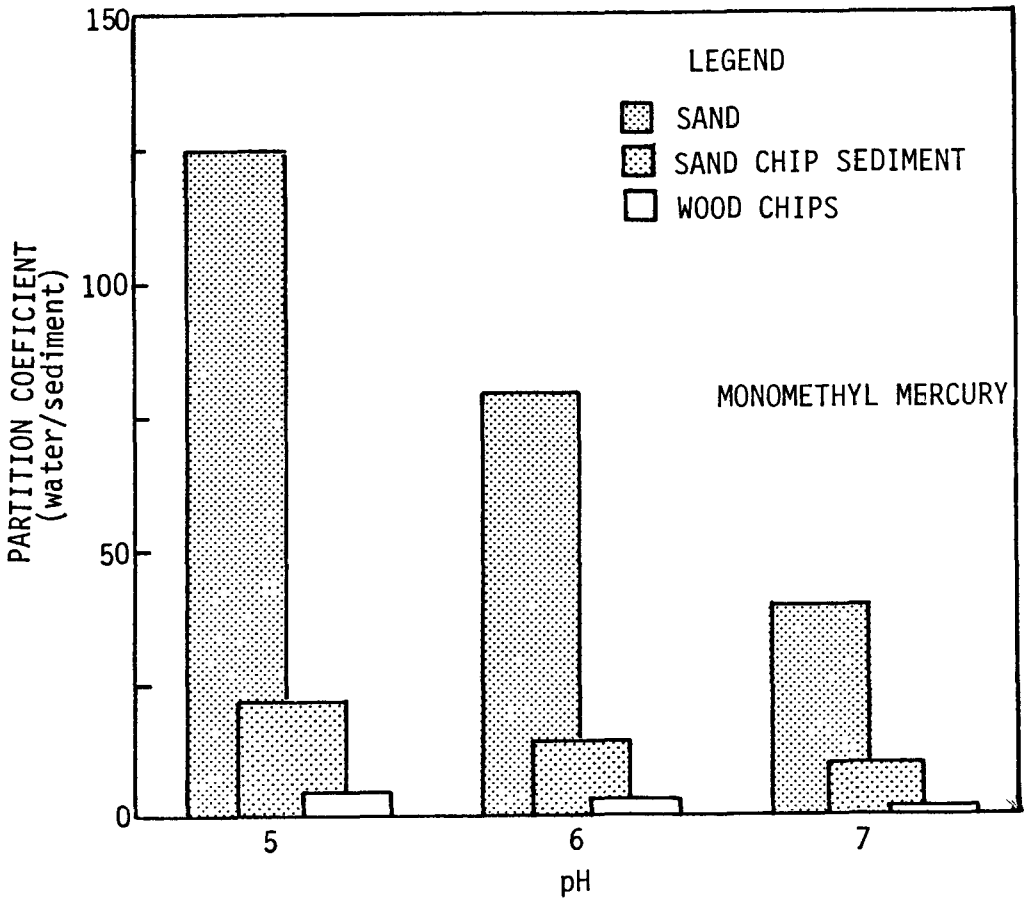

Figure 6-5. The partition coefficient of methyl mercury between water and three different types of sediments. The units of the ordinate have been multiplied by a factor of 10,000. The data are taken from Miller and Akagi (1979).

manganese concentrations in the vertebrae of white suckers from six lakes in sourthern Ontario. Fish from the most acidic lake, George Lake (pH 4.65) had particularly high manganese content. The remaining five lakes had pH levels from 5.02 to 6.59, and fish manganese level appeared relatively independent of pH. George Lake also had aqueous manganese concentrations that were 50 percent greater than in any of the other lakes. The Ontario Ministry of Environment (U.S./Canada 1983) analyzed yearling yellow perch for body burdens of lead, cadmium, aluminum, and manganese in 14 Ontario lakes (Figure 6-6). Lead ($p < 0.01$) and cadmium ($p < 0.05$) were significantly correlated with lake pH level. No data are available to evaluate the environmental significance of these accumulations. No correlations between lake acidity and body levels of aluminum or manganese were evident. Aluminum has, however, been observed to accumulate on gills of fish during fish kills in Plastic Lake, Ontario, and in two lakes in Sweden. Grahn (1980) measured 40 to 47 μg Al g^{-1} wet weight of tissue on gills from dead ciscoe from lakes Ransjon and Amten, Sweden, but only 6 μg Al g^{-1} for fish from reference lakes without fish kills. Aluminum concentrations on fish gills from dead and moribund pumpkinseed and sunfish from Plastic Lake ranged from 83 to 250 mg g^{-1} dry weight (Harvey et al. 1982).

6.2.3.2 Historical and Geographic Trends in Mercury Levels in Freshwater Fish--Presently it is difficult to assess quantitatively the contribution of acidic deposition to elevations of mercury concentrations in freshwater fish. The problem in part is a lack of data showing temporal and regional changes in mercury as related to water pH and in part due to the operation of other processes affecting mercury levels in fish.

Bloomfield et al. (1980) have reviewed the results of an extensive mercury screening involving some 3500 freshwater fish collected in New York State from 1960 to 1972. Less than 10 percent of the fish had mercury levels in excess of the current federal guideline of 1.0 ppm. A sizeable portion of the high mercury fish came from Onondaga Lake--known to be polluted by a local industrial source of mercury. Predatory species of fish such as walleye, pike, and smallmouth bass had levels sometimes exceeding 1 ppm in certain Adirondack Lakes remote from known sources of mercury. Bloomfield et al. (1980) quote unpublished work indicating that concentrations in smallmouth bass were still high in 1975, and Armstrong and Sloan (1980) reported elevated mercury levels in predatory fish species collected in certain Adirondak Lakes (Cranberry, Great Sacandaga, Raquette) in 1978. In contrast, fish from rivers and lakes previously contaminated with mercury now show declining fish levels (Armstrong and Sloan 1980). For example, following cessation of mercury discharge, levels of mercury in smallmouth bass in Lake Onondaga declined by 55 percent over the period 1972 to 1978. The Ontario Ministry of Environment (1977) has reported substantial declines in mercury in fish caught in Lake St. Clair following curtailment of industrial discharge of mercury.

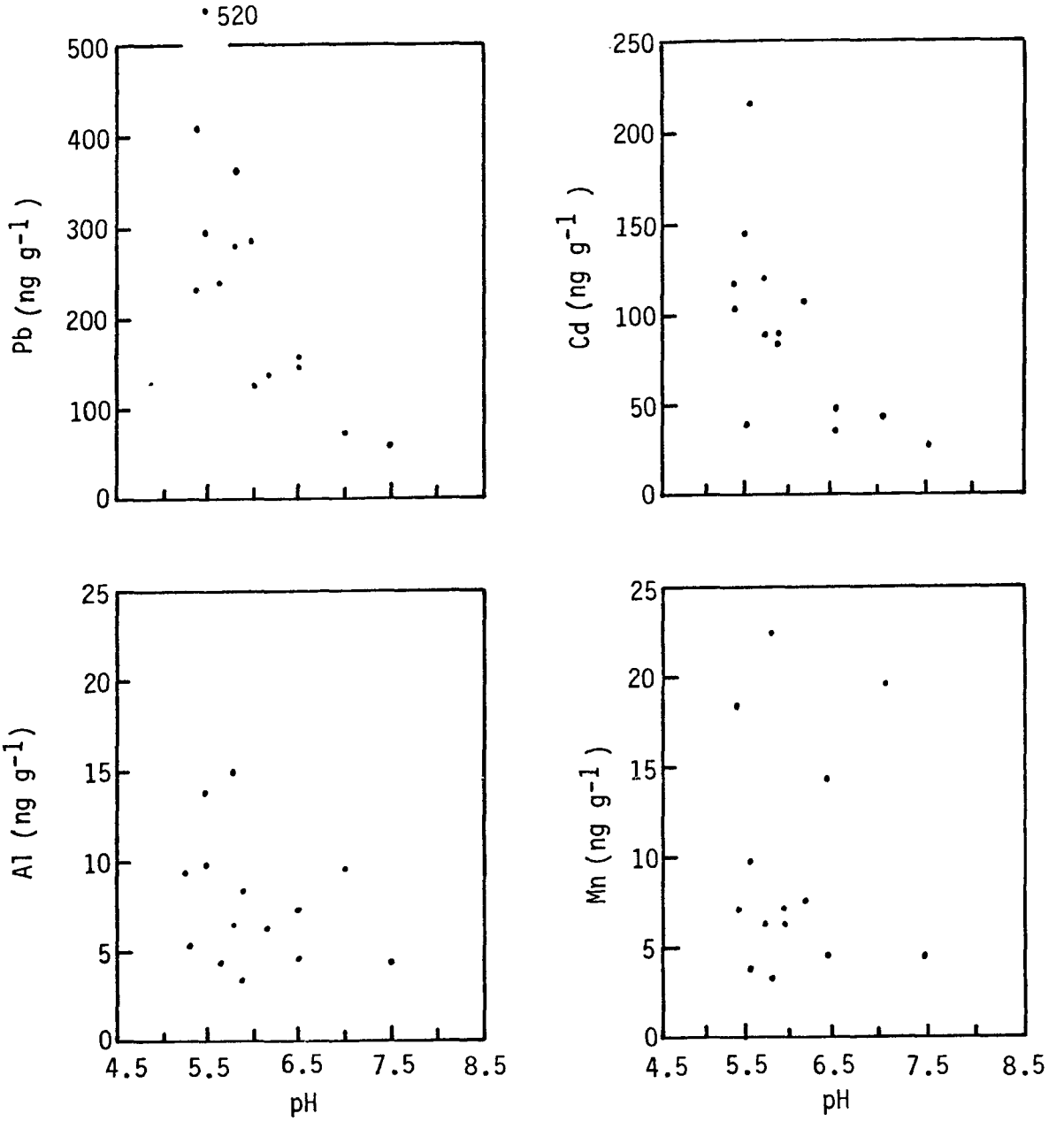

Figure 6-6. Metal concentrations in yearling yellow perch and epilimnetic pH in 1981 in lakes in the Muskoka-Haliburton area of Ontario (U.S./Canada 1983).

Based on very limited data in the United States, a general picture emerges of declining mercury levels in freshwater fish caught in areas where direct discharge of mercury has been curtailed but of continued high levels of mercury in certain lakes remote from industrial activity. Reasons for these high mercury levels are being investigated (Section 6.2.2.3). Wet deposition of mercury from the atmosphere has been shown to occur in several Adirondack Lakes. These lakes, in general, are characterized by low pH and low alkalinity. The role of long distance transport of mercury and lake acidification merits careful investigation.

6.2.4 Dynamics and Toxicity in Humans (Mercury)

6.2.4.1 Dynamics in Man (Mercury)--The U.S. EPA (1980a) has reviewed information on uptake, distribution, and excretion of methyl mercury in man. Methyl mercury is almost completely absorbed from the diet (90 to 100 percent, i.e., between 90 to 100 percent of the amount ingested is absorbed). After absorption in the gastrointestinal tract, methyl mercury passes into the bloodstream and is distributed to all organs in the body. Approximately 5 percent of the absorbed dose goes to the blood compartment and 10 percent to the brain--the target organ for toxic effects.

After the initial distribution is completed, usually a matter of a few days in man, the brain to blood concentration ratio is roughly constant, having value between 5:1 to 10:1. Methyl mercury is accumulated in growing hair. At the time of formation of the head hair, the ratio of the concentration of mercury in hair to the simultaneous concentration in blood is roughly constant and has an average value of about 250:1. Once incorporated into the hair, the mercury concentration remains constant. Because human head hair grows about 1 centimeter per month, analyzing centimeter segments of hair can recapitulate average monthly concentrations of methyl mercury in blood. Measurements of mercury in samples of blood or hair are now routinely used to assess the body burden of methyl mercury in humans and as an indicator of brain concentrations.

Methyl mercury is excreted from the body mainly in feces. Before excretion in the feces, methyl mercury is converted into inorganic mercury. The site of this conversion is not known, but microflora in the lower gut are known to possess this capability. The rate of elimination from the body is directly proportional to the body burden. It is well described by a single exponential function characterized by a half-time of about 70 days. An important conclusion from this kinetic information is that it will take about one year for humans to attain a state of balance, i.e., to attain maximum steady body burden of methyl mercury for any given daily intake in the diet. After cessation of given exposure, it will take one year for the body burden to fall to pre-exposure levels. Thus, dietary intake of methyl mercury from fish should be evaluated over a matter of months. Intake on any one single day does not normally make an important contribution to the overall body burden.

Considerable individual differences exist in biological half-times in man although the average value is 70 days with a range of 30 to 180 days. The distribution is bimodal with 90 percent of the values distributed about an average value of about 65 days and 10 percent distributed about an average value of 120 days. The reasons for this wide range of biological half-times are not known, except that lactating women have a short half-time averaging about 40 days.

Methyl mercury readily crosses the placental barrier and enters the fetus. It distributes to all tissues in the fetus, including the fetal brain, which is the principal target for prenatal toxicity of methyl mercury. Levels of methyl mercury in cord blood are usually higher than the maternal blood concentrations.

Methyl mercury is secreted in milk. Thus body burdens of methyl mercury acquired by the infant before birth may be maintained by breast feeding if the nursing mother continues to be exposed to methyl mercury.

The rate of elimination of methyl mercury from the human fetus and suckling infant is not known. Experiments on animals indicate that elimination in suckling animals is much slower than in adults. The adult rate of excretion appears to commence at the end of the suckling period.

In brief, methyl mercury accumulates in the human body over a period of about one year. Blood and hair analyses may be used as indicators of human absorption of mercury. In assessing hazard to human health, chronic exposure over weeks or months is important.

6.2.4.2 Toxicity in Man--Methyl mercury damages primarily the human central nervous system. When ingested in sufficient amounts, methyl mercury destroys neuronal cells in certain areas of the brain, the cerebellum and the visual cortex, resulting in permanent loss of function. Symptoms of damage include loss of sensation, constriction of the visual fields, and impairment of hearing. Coordination functions of the brain are also damaged, leading to ataxia and dysarthria. Severest damage causes mental incapacitation, coma, and death. The mildest and earliest effect in adults is usually a complaint of paresthesia, an unusual sensation in the extremities and around the mouth. In the Japanese population poisoned by methyl mercury from contaminated fish, paresthesia was usually permanent. In the Iraqi population, paresthesia was frequently reported to be transient. This population had consumed homemade bread from wheat contaminated with a methyl mercury fungicide.

The effects on the fetal brain differ qualitatively from those seen in adults. Methyl mercury interferes with the normal growing processes of the brain. It inhibits migration of neuronal cells to their final destination, thus affecting the brain's architecture. This damage manifests itself as diminished head size (microcephaly) and gross neurological manifestations such as cerebral palsy. The mildest effects are delayed achievement of developmental milestones in children and the presence of abnormal reflexes and mild seizures.

Brain concentrations associated with the onset of human methyl mercury poisoning are in the range of 1 to 5 μg Hg g^{-1} wet tissue. Blood concentrations for the onset of the mildest effects have been established to be between 200 and 500 ng Hg m^{-1} whole blood. Corresponding hair concentrations would be 50 to 125 μg Hg g^{-1} hair (Table 6-4). The chronic daily intake of methyl mercury that would lead to a miximum blood level of 200 ng m^{-1} has been established to be 300 μg Hg. However, in the mother during pregnancy, the blood level associated with the earliest damage to the fetus has not yet been determined.

The conclusions reported in Table 6-4 were based on observations of affected populations in outbreaks of poisoning in Niigata, Japan and in Iraq (the 1971-72 outbreak). In effect, the numbers in Table 6-5 refer to the lowest effect levels observed in an outbreak of poisoning from methyl mercury contaminated fish in Niigata, Japan (Swedish Expert Group 1971) and lowest effect levels estimated from an affected population in the Iraqi outbreak of 1971-72 (Bakir et al. 1973). With such low observed effect levels on humans, it is usual to apply a safety factor of ten (WHO 1972a) to arrive at an acceptable "safe" body burden or "allowable daily intake."

A direct estimation of absolute risks associated with a given long-term daily intake of methyl mercury was reported by Nordberg and Strangert (1976, 1978). In their approach they combined the data from dose-response relationship published in the Iraqi outbreak (Bakir et al. 1973) with the range of biological half-times, also obtained in the Iraqi outbreak (Shahristani and Shihab 1974) to calculate the relationship depicted in Figure 6-7.

Their calculations indicated that an intake of 50 μg day^{-1} in an adult gives a risk of about 0.3 percent of the symptom of paresthesia, whereas an intake of 300 μg day^{-1} would give a risk of about 8 percent of symptoms of paresthesia. As pointed out by Nordberg and Strangert (1976), the background frequency of these non-specific symptoms such as paresthesia plays a key role in determining the accuracy of the estimates of response of low frequencies. They estimated from the same Iraq data the background frequency of paresthesia of 6.3 percent. However, there is considerable uncertainty in determining the precise value of the background frequency, and this uncertainty becomes the dominant cause of error at low rates of response.

Since the studies on the Iraqi outbreak, a major epidemiological study has been carried out in Northwestern Quebec on Cree Indians exposed to methyl mercury in freshwater fish (Methyl Mercury Study Group 1980). The authors claim to find an association in men over age 30 and women over age 40 of a set of neurological abnormalities and the estimated exposure to methyl mercury. However, it should be pointed out that this association has been seen by only four of seven observers who

TABLE 6-4. THE CONCENTRATIONS OF TOTAL MERCURY IN INDICATOR MEDIA AND METHYL MERCURY ASSOCIATED WITH THE EARLIEST EFFECTS IN THE MOST SENSITIVE GROUP IN THE ADULT POPULATION[a] (ADAPTED FROM WHO 1976)

Concentrations in indicator media		
Blood ($ng\ ml^{-1}$)	Hair ($\mu g\ g^{-1}$)	Equivalent long-term daily intake ($\mu g\ kg^{-1}$ body weight)
200 to 500	50 to 125	3 to 7

[a]The risk of the earliest effects can be expected to be between 3 to 8 percent, i.e., between 3 to 8 percent of a population having blood levels in the range 200 to 500 mg ml^{-1}, or hair levels between 50 to 125 $\mu g\ g^{-1}$ would be expected to be affected (for further details, see text).

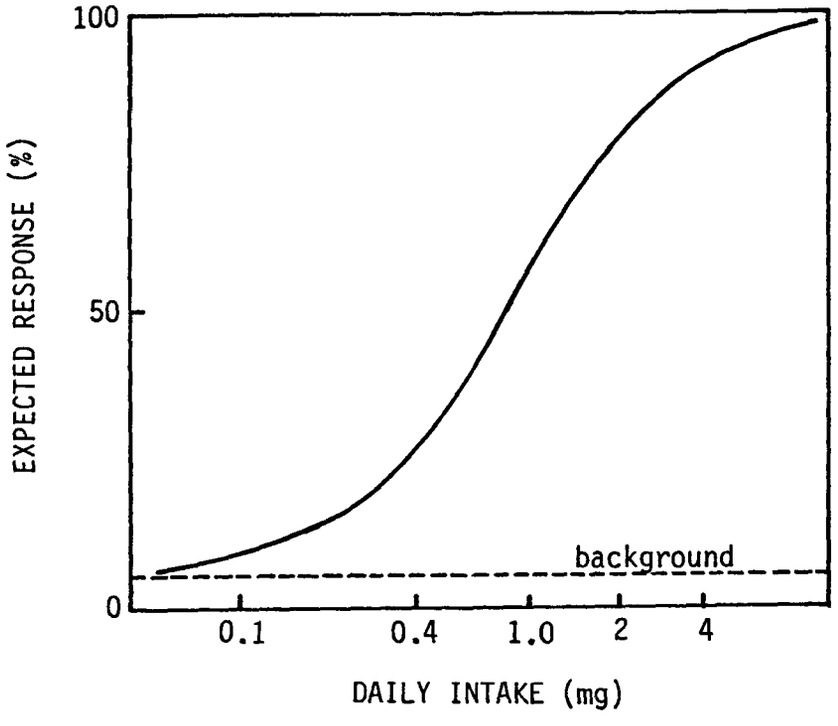

Figure 6-7. The calculated relationship between frequency of paresthesia in adults and long-term average daily intake of methyl mercury. The calculations were performed by Nordberg and Strangert (1978). The broken line is the estimated background frequency of paresthesia in the population. Data are taken from publications on the Iraqi outbreak of methyl mercury poisoning (Bakir et al. 1973; Shahristani & Shihab 1974).

reviewed video taped recordings of the neurological screening tests. The severity of these neurological abnormalities was assessed by neurologists as mild or questionable. It was not possible to estimate any threshold body burden or hair levels because this population had been exposed possibly for most of their lives; therefore peak values in previous years are unknown. However, observations on this population over several years indicate that maximum blood concentrations are below 600 ppb and most below 200 ppb (Wheatley 1979). A WHO expert group (1980), on examining the reports from these studies, raised the possibility that this might be the first example of an endemic disease due to exposure to methyl mercury in freshwater fish. However, another epidemiological and clinical study of the same population of Cree Indians failed to find any effects associated with methyl mercury (Kaufman, personal communication to EPA).

The safety factor of ten applied to the lowest effect levels in Table 6-4 was intended to take into account inter alia the greater sensitivity of the fetus. Since the WHO evaluation of 1976, data have been published relating methyl mercury levels in the mother during pregnancy to effects such as psychomotor retardation in the offspring (Marsh et al. 1980). These data were the basis of a recent risk estimate (Berlin 1982) relating concentrations of mercury in maternal hair to risk of mental retardation in prenatally exposed infants (Figure 6-8). Berlin calculated a background frequency in the Iraqi children of approximately 4 percent as compared to a background frequency of mental retardation in Sweden of 2 percent. He also noted that in the case of adults that the error in determining background frequency is probably the major source of error when researchers look at low rates of responses. Berlin calculated that there was a risk of doubling the background frequency of mental retardation at methyl mercury levels in the mother on the order of 20 ppm in hair and a risk of a 50 percent increase in background frequency at hair concentrations of about 10 ppm.

The McGill Group (Methyl Mercury Study Group 1980) in their study of Cree Indians exposed to methyl mercury in fish, found an association "... between findings on examination of tone and reflexes in Cree boys and the concentration of methyl mercury in the mothers' hair during pregnancy. This association was shown at levels of methyl mercury exposure which are very low in relationship to those previously reported to be associated with effects of methyl mercury in utero.... These findings were isolated and the variation from normal was mild." The highest range of maternal hair concentration was 13 to 23.9 g g^{-1}.

These hair levels overlap the range estimated by Berlin associated with the earliest detectable effects in Iraq. However, the association noted in the McGill study may have been due to chance as their observations on tone and reflexes were part of a number of observations, the rest of which did not correlate with mercury levels.

These observations on human infant-mother pairs agree with animal data indicating the greater sensitivity of prenatal life to methyl mercury (for review, see Clarkson 1983). However, the risk

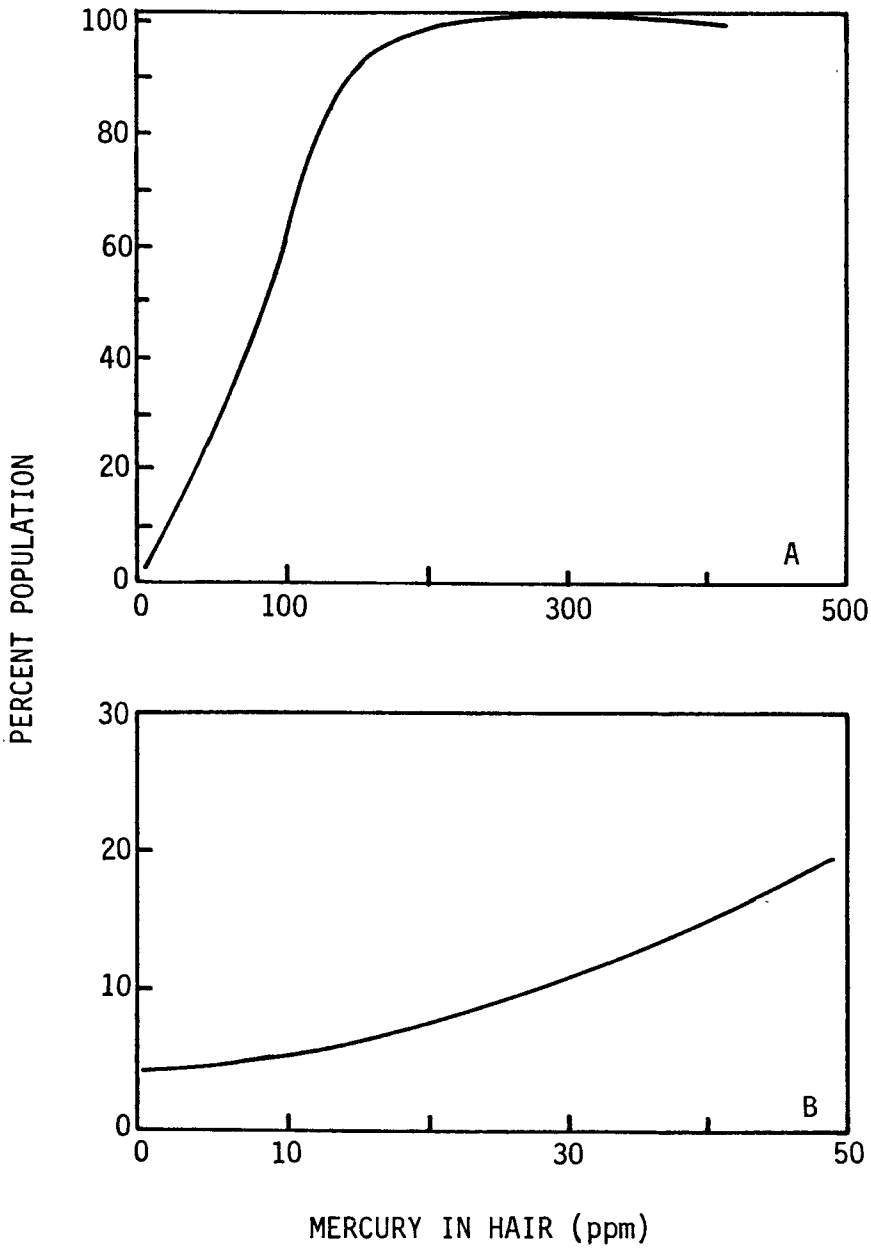

Figure 6-8. A dose-response relationship between the frequency of mental retardation in a population of children prenatally exposed to methyl mercury and the maximum hair concentrations of the mothers during pregnancy. The maximum hair concentrations in the mothers during pregnancy was used as a measure of the prenatal dose. The curves are drawn according to logit analysis, assuming the presence of a background frequency. Figure 6A gives the complete dose-response curve and the logit equation. Figure 6B gives the low frequency end of the dose-response relationship, indicating the presence of a background frequency, i.e., the vertical intercept at zero mercury concentration in the mothers' hair. The analysis was carried out by Berlin (1982) on data from the Iraqi outbreak (Marsh et al. 1980).

estimation described in Figure 6-7 should only be regarded as approximate, as they are based on small numbers. We greatly need to obtain more precise estimates of human health risks associated with prenatal exposure to methyl mercury.

6.2.4.3 Human Exposure from Fish and Potential for Health Risks--Dietary intake accounts for the greatest fraction of total mercury intake by man (Table 6-5). Methyl mercury intake is exclusively from the diet and almost entirely from fish and fish products. The evidence comes from dietary studies showing close correlation of blood levels with fish consumption (Swedish Expert Group 1971) and from large-scale analyses of food items in several countries, indicating that significant concentrations of methyl mercury are found only in fish and fish products (U.S. EPA 1980a).

Based on data from the National Marine Fisheries, Cordle et al. (1979) have reported a ranking of species of fish according to annual consumption in the United States (Table 6-6). The table clearly demonstrates that oceanic fish, especially tuna, account for the major amount consumed. However, when consumption is expressed according to the consumer use, a different picture emerges. On this basis, freshwater fishes dominate the rankings, with northern pike consumed at 17.4 g day^{-1}, followed by freshwater trout at 12.3 g day^{-1}, bass (freshwater) and catfish at 12.1 g day^{-1}. The highest user consumptions of seafood are crabs and lobster at 10.6 g day^{-1}, with tuna down to 6.1 g day^{-1}.

The highest average mercury concentrations are also found in freshwater fish - pike at 0.61 µg Hg g^{-1} and trout at 0.42 µg Hg g^{-1}. Thus a pike consumer would have a daily average intake of methyl mercury of 10.4 µg exclusively from pike, and a trout consumer would have had an average intake of 5.2 µg Hg. These average values are well below the recommended maximum safe intake of 30 µg day^{-1}.

The National Marine Fisheries developed an extensive data bank on fish consumption by individuals according to fish species (U.S. Department of Commerce 1978). These data were based on a Diary Panel Survey of approximately 25,000 individuals chosen to be representative of the U.S. population. These data, along with additional information on mercery concentration of edible tissues of various fish species, allowed a calculation of the number of individuals who would be expected to exceed the maximum safe daily intake of 30 µg. It was calculated that 47 individuals would exceed this limit by a small margin from consumption of fish and that 23 of these were consumers mainly of freshwater fish. According to calculations by Nordberg and Strangert (Figure 6-7) the risk at this level of intake will be small--on the order of 0.3 percent.

The risk of prenatal poisoning cannot be estimated with any precision, given the small number of cases used in Figure 6-8. The daily intake of about 30 µg Hg roughly corresponds to a hair concentration of 6 to 10 ppm. The dose-response data in Figure 6-8

TABLE 6-5. ESTIMATES OF AVERAGE AND MAXIMUM DAILY INTAKES OF MERCURY BY THE "70 kg MAN" IN THE UNITED STATES POPULATION (ADAPTED FROM U.S. EPA 1980a)

Media	Mercury intake μg day^{-1} 70 kg^{-1} (average)	Predominate form
Air	0.3	Hg°
Water	0.1	Hg^{2+}
Food	3.0	CH_3Hg^{+}

TABLE 6-6. ESTIMATED FISH AND SHELLFISH CONSUMPTION IN THE UNITED STATES RANKED ACCORDING TO ANNUAL CONSUMPTION FOR THE PERIOD SEPTEMBER 1973 TO AUGUST 1974 (ADAPTED FROM U.S. EPA 1980a AND CORDLE ET AL. 1979)

	Rank	Amount 10^6 lb yr^{-1}	Percent of total by weight	Number of actual users (millions)	Mean Amount per user, (g day^{-1})	Average conc. of mercury μg Hg g^{-1}[a]
Total		2957	100.0	197.0	18.7	
Tuna (mainly Canned)	1	634	21.4	130.0	6.1	0.14[b] 0.27
Unclassified (mainly breaded, including fish sticks)	2	542	18.4	68.0	10.0	0.35 c
Shrimp	3	301	10.2	45.0	8.3	0.05
Ocean Perch[d]	4	149	5.0	19.0	9.7	0.13
Flounder	5	144	4.9	31.0	8.6	0.10
Clams	6	113	3.8	18.0	7.6	0.05
Crabs/lobsters	7	110	3.7	13.0	10.6	0.07-0.14[e]
Salmon	8	101	3.4	19.0	6.7	0.08
Oysters/scallops	9	88	3.0	14.0	7.8	0.03
Trout[f]	9	88	3.0	9.0	12.3	0.42
Cod[d]	11	78	2.7	12.0	8.1	0.14
Bass[f]	12	73	2.5	7.6	12.0	c
Catfish[f]	12	73	2.5	7.5	12.1	0.15
Haddock[d]	12	73	2.5	11.0	8.6	0.11
Pollock[d]	15	60	2.0	11.0	6.8	0.14
Herring/smelt Sardines	16	54	1.8	10.0	6.7	0.02
Pike[f]	17	35	1.2	2.5	17.4	0.61
Halibut[d]	18	32	1.1	5.0	8.0	0.19-0.53
Snapper	18	32	1.1	4.3	9.3	0.45-36[g]
Whiting	20	25	0.9	3.2	9.7	c
All other classified		152	5.1			c

[a]U.S. Chamber of Commerce (1978).
[b]Average values for skipjack, yellow fin, and white tuna, respectively.
[c]Data not available.
[d]Mainly imports.
[e]King crab - all others, respectively.
[f]Fresh Water.
[g]Red Snapper - other.

would indicate that the background frequency of mental retardation would be increased by less than 50 percent.

Estimates of increased rates risks due to acid precipitation would depend upon a number of assumptions, including whether increases in freshwater acidity would elevate levels of methyl mercury in freshwater fish and by how much, the effect of acidity on the supply of freshwater fish, as well as actions taken by local state and Federal agencies to limit fishing and sales of fish if methyl mercury levels increase. Nevertheless, information on methyl mercury is now reaching the point where rough estimates can be made of health risks in this country for consumption of methyl mercury from freshwater fish, and information may be forthcoming on the impact of acidity on methyl mercury levels in fish. At least the direction of future research is now more clear--to obtain more quantitative information on human dose-response relationship and to further test hypotheses on cause-effect relationship between pH and methyl mercury levels in freshwater fish.

6.3 GROUND SURFACE AND CISTERN WATERS AS AFFECTED BY ACIDIC DEPOSITION (W. E. Sharpe and T. W. Clarkson)

For reasons given in Section 6.1, this section will deal only with those metals whose concentrations and/or speciation in drinking water may be affected by acidic deposition. As discussed in the previous section, mercury concentrations, including any potential changes due to pH, should not offer any conceivable threat to human health. Lead is the one metal of greatest concern and will be given special attention in this section. Other metals such as aluminum, cadmium, and copper, will be discussed briefly.

6.3.1 Water Supplies

An understanding of the modes of hydrologic interactions between acid deposition and various types of water supplies is essential to assessing the potential indirect health effects to users of drinking water obtained from such systems. In addition, the physical facilities used to store, treat, and distribute water are of primary importance, as are the chemical methods used to treat water prior to use. Principal water sources in continental North America are usually either surface or groundwater, with other sources such as direct use of precipitation of much lesser importance. Health risk is directly related to the source of drinking water.

Health risk in drinking water supplies is also closely related to the management of the drinking water supply. Risks are generally greater the smaller the water supply, with small privately owned water systems serving a single dwelling at greatest risk. These systems typically do not routinely monitor water quality nor do they provide even rudimentary water treatment. Data on the impacts of atmospheric deposition on drinking water quality are extremely scarce; however, by using available information on the impacts to surface water aquatic ecosystems, we may assess impacts.

6.3.1.1 Direct Use of Precipitation (Cisterns)--The direct use of precipitation by collection in artificial catchments is one of the oldest forms of water supply, having been used widely by ancient civilizations. The Romans used lead-lined cisterns for the storage of water, and it has been reported that plumbism (chronic lead poisoning) was a major reason for the fall of the Roman Empire (Gilfillan 1965, Nriagu 1983).

Direct use of precipitation has been practiced in North America from very early times and is still common where there are no other water supply alternatives. Island communities in the equatorial regions of the world still rely heavily on rainwater cisterns to supply their freshwater needs, and this method of water supply is being seriously considered as appropriate technology for the developing counties of the world.

Roof catchments consist of an impervious surface, usually a house or auxiliary building roof, connected by means of conventional roof gutters and downspouts to a below ground concrete or cinder block cistern. Water is pumped from cistern storage to points of use within the house. Since, in most systems, precipitation is used directly with no treatment, the quality of precipitation and the amount of dry deposition on the catchment between precipitation events are of paramount importance to the quality of drinking water at the user's tap. The major impacts are twofold. First, direct deposition of atmospheric pollutants such as lead and copper may occur and, second, the acid components of atmospheric deposition may cause increased corrosion of metallic plumbing system components.

In a study of 40 roof-catchment cistern systems in western Pennsylvania, Young and Sharpe (1983a) report that lead in atmospheric deposition accumulates in the sediments that collect at the bottoms of cisterns and that this particulate lead could appear in the drinking water of cistern users when conditions allowing the suspension of this material in cistern water are present. They did not report on the frequency of such conditions, but they did point out that in the systems they studied there were no safeguards to prevent the ingestion of lead contaminated cistern sediments. However, cistern systems with gross particulate filters for incoming catchment runoff had much lower lead concentrations in sediments.

Young and Sharpe (1983a) also report accumulations of cadmium in cistern sediments, although such accumulations were less frequent than lead. The cadmium concentrations in atmospheric deposition in the Young and Sharpe study are generally very low, indicating that some other source such as corrosion of galvanized gutters and downspouts might be present.

Young and Sharpe (1983a) found that precipitation was highly corrosive as measured by the Langelier Saturation Index (LSI) and that cistern water, although still corrosive in all but a few systems, was less corrosive than bulk precipitation. The decreased corrosion

potential of cistern water was attributed to dissolution of the calcium carbonate building materials in the cistern, a fact confirmed by the much higher LSI's of cisterns with impermeable vinyl liners.

Young and Sharpe measured the concentrations of copper and lead in tapwater that had stood in the plumbing system overnight. In nine of the 40 systems studied (22 percent) average lead concentrations exceeded drinking water limits (U.S. EPA 1979b), copper exceeded drinking water standards (U.S. EPA 1979b) in 11 of the 40 systems. All of the systems (100 percent) having all copper plumbing showed an increase in copper concentration in standing tapwater as compared to cistern water, indicating that corrosion was taking place.

Young and Sharpe (1983b) attempted to establish a relationship between the corrosivity of precipitation and the concentration of copper in the tapwater of cistern systems. Their basic premise was that although atmospheric deposition is more so, and this increased corrosivity has caused an increase in the concentration of copper in the tapwater of the cistern systems studied. Table 6-7 contains a comparison of pH, corrosivity (as indicated by the Ryznar Index) and corresponding tapwater copper concentrations. The potential impact of increasing the corrosivity of atmospheric deposition on tapwater copper concentrations is obvious. If the relationship proposed by Young and Sharpe is valid, increasingly polluted atmospheric deposition would appear to be responsible for tapwater copper concentrations in excess of drinking water standards. Unpolluted atmospheric deposition (pH 5.6) would appear to result in tapwater copper concentrations within drinking water standards for roof catchment cisterns.

The actual number of roof-catchment cisterns in those areas of the country impacted by polluted atmospheric deposition is unknown. Kincaid (1979) estimated that there were 67,000 cistern systems in the state of Ohio, although there is good reason to believe that this figure may be too high. Determination of the population at risk is difficult, but these data indicate that it is likely to be substantial.

Cistern systems can be modified to minimize the risk (Young and Sharpe 1982). However, these modifications are likely to be expensive with minimum estimated costs of $500 to $1000 per household for water treatment equipment and the necessary changes to plumbing systems (Sharpe 1980).

Young and Sharpe (1983a) conclude that "The Presence of lead and copper in the tapwater of cistern water supplies in western Pennsylvania was sufficient to constitute a hazard to users of such systems. Users involved in the study were advised to discontinue use of cistern water for drinking purposes until such time as proper safeguards were employed to reduce the hazards implicit from this study."

6.3.1.2 Surface Water Supplies--Very little work has been done on the specific effects of atmospheric deposition on surface water supplies, although quite a bit can be inferred from the surface water quality work

TABLE 6-7. COMPARISON OF BEST AND WORST CASE AND MEAN RYZNAR STABILITY INDEX (RI) OF BULK PRECIPITATION COLLECTED WEEKLY DURING 1979, 1980 AND 1981 IN CLARION AND INDIANA COUNTIES, PA (FROM YOUNG AND SHARPE 1983b)

Parameter	Best case	Mean[a]	Worst case
pH	5.29	3.87	3.40
Alkalinity (mg ℓ^{-1} $CaCO_3$)	2.22	0	0
Specific conductance (mhos cm^{-1})	127	70	220
Calcium (mg ℓ^{-1})	12.8	1.14	0.23
RI @ 20 C	14.73	18.76	19.58
Predicted Cu conc. (μg ℓ^{-1})	922	2724	3299

[a]Based on 138 samples collected over three years.

done to determine impacts on aquatic biota. In most regions where atmospheric deposition is of concern the same types of surface water are used for both water supply and fish propagation; consequently, the water quality changes reported for one are applicable to the other. The chief area of concern is for surface water supplies providing drinking water for humans.

Two main drinking water impacts exist. The quality of the source water may be impaired and/or increases in the corrosivity of the water could lead to the same types of tapwater quality problems evident with cistern water supplies. As reported elsewhere in this document (Chapter E-5), aluminum concentrations may be increased in surface waters. In a 1981 study of the surface water quality of a stream (Card Machine Run) feeding a small water supply reservoir, DeWalle et al. (1982) reported that aluminum concentrations in the stream directly above the water supply intake increased from .05 mg ℓ^{-1} to 0.70 mg ℓ^{-1} in response to a February rain and snowmelt event on the watershed. These data are illustrated in Figure 6-9. High concentrations of aluminum have been reported elsewhere by Cronan ahd Schofield (1979) and Herrman and Baron (1980). The health significance of aluminum concentrations of this magnitude are addressed elsewhere in this chapter. Other metals not as readily leached from acidified soils are not likely to increase as dramatically as aluminum.

Increasing corrosivity is probably the most significant potential impact of atmospheric deposition on surface water supplies. The corrosivity of the dilute water often used for surface water supplies in the northeastern United States is mostly controlled by H^+ concentration. As the H^+ concentration increases so does the corrosivity of the water.

Corrosivity in surface water supplies has been widely reported, and its impacts are well documented. Where lead water distribution pipes are in use, clinical lead poisoning of children has been reported as a consequence of corrosive drinking water conveyance. A notable example of such a problem is Boston, Massachusetts. Less well known is the case of Mahanoy City, PA (Kuntz 1983). A case of copper toxicity from a corroded water fountain has also been reported by Semple et al. (1960). Where pipes are of other metals such as copper, iron, or galvanized steel the respective corrosion products of copper, lead, iron, zinc, and cadmium can be problems.

Because these corrosion problems can lead to elevated concentrations of toxic metals in drinking water, the U.S. EPA (1979a) has recommended that all drinking water supplies be noncorrosive and that a minimum pH of 6.5 be maintained. The results of a review of the drinking water standard for corrosivity, which was completed by U.S. EPA in 1980, have not as yet been released. Numerous studies of surface water chemistry have shown dramatic increases in the H^+ concentration of surface waters in response to acidification by atmospheric deposition. In dilute surface waters such increases are almost certain to produce corresponding increase in the corrosivity of that water. If

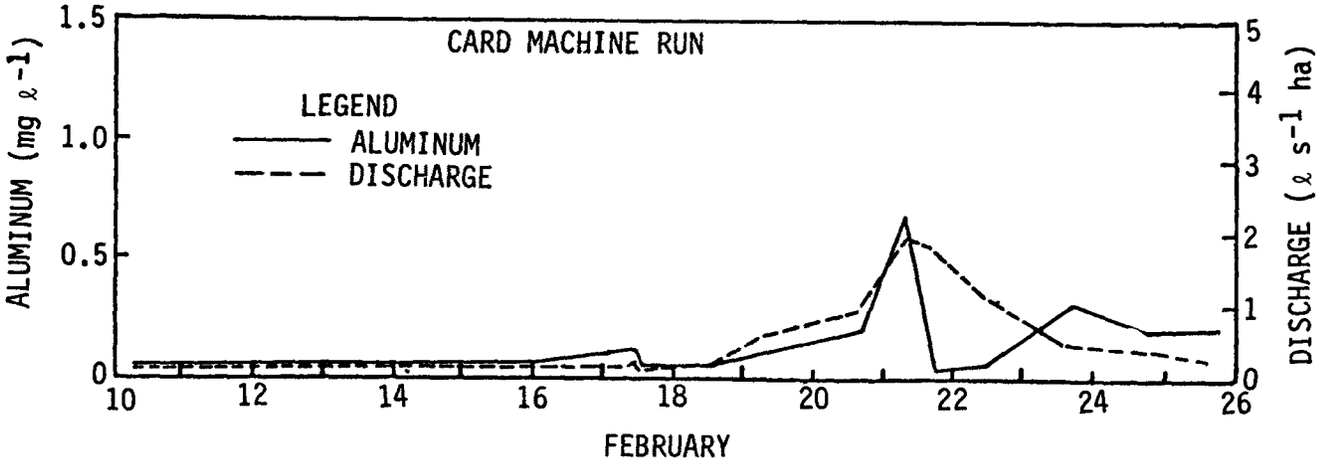

Figure 6-9. Aluminum concentration and discharge for Card Machine Run. Adapted from DeWalle et al. (1982).

the pH and computed Ryznar Stability Index (RI) for the data of DeWalle et al. (1982) are plotted for a rain and snowmelt event on Card Machine Run In February 1981 (Figure 6-10) a strong relationship between the two is identified. Linear regression techniqes were used to quantify the relationship between pH and RI for this runoff event, and a correlation coefficient of $r = -1.00$ was obtained. This indicates that large changes in the pH of dilute surface waters, weakly buffered by $CaCO_3$, are almost certain to produce correspondingly large increases in the corrosivity of such waters.

If RI values are plotted with streamflow (discharge) for the same event on Card Machine Run (Figure 6-11), it is obvious that as streamflow increases as a result of acid snowmelt and rainfall runoff, the corrosivity as indicated by the Ryznar Index also increases dramatically. Regression analysis again yields a very good correlation ($r^2 = .80$) for these two variables.

Although the data presented are limited, there would appear to be strong indications that the corrosviity of raw water entering surface water supplies located in headwater areas of the Laurel Hill is increased substantially as a result of acid snowmelt and rainfall runoff. If the model for the relationship of pH and RI holds true for all dilute surface waters, then increased corrosivity is likely anywhere that the pH of such waters changes dramatically subsequent to acid runoff events. Where surface water storage facilities are small, necessitating the direct use of raw water during stormflow periods, and where corrosion control is not practiced in the water system, populations served are at increased risk of being exposed to higher concentrations of corrosion products such as Cu, Pb, Cd, and Zn.

6.3.1.3 Groundwater Supplies--Acidification of groundwater as a consequence of atmospheric deposition has been reported in Sweden by Hultberg and Wenblad (1980). Such changes have not as yet been well documented in North America. Fuhs (1981) reports that atmospheric deposition in sensitive regions of New York State has decreased the pH and increased the Al concentration of shallow groundwater and indicates that pH of groundwater is significantly correlated with depth, with deeper groundwater sources having higher pH. Fuhs also reports on the concentrations of Pb and Cu in private individual water supplies obtaining water from shallow circulation springs and shallow wells. Fuhs indicates that the Al concentrations measured in these types of water sources would make such water unsuitable for hemodialysis units. Although Fuhs demonstrates that standing tapwater derived from shallow groundwater systems in atmospheric deposition sensitive areas of New York contains high concentrations of Cu and Pb, he does not make a clear case linking these results to the acidity of atmospheric deposition. As Fuhs correctly states, shallow groundwater in these areas would be corrosive even without acid deposition; consequently, the degree to which atmospheric deposition makes these waters more corrosive and the concomitant increases in tapwater metals concentrations must be determined. Neither has yet been demonstrated conclusively.

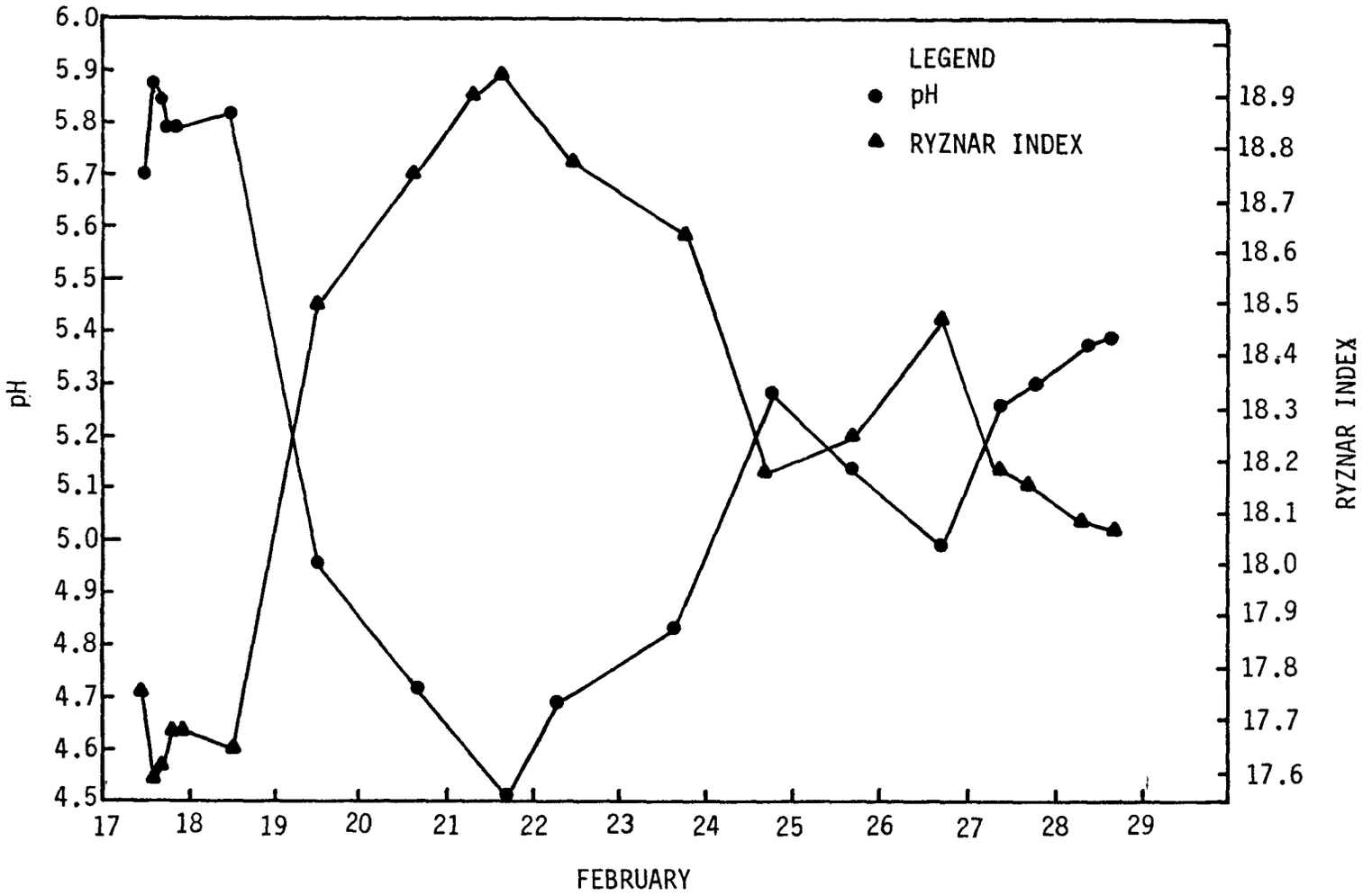

Figure 6-10. pH and Ryznar Index for Card Machine Run.

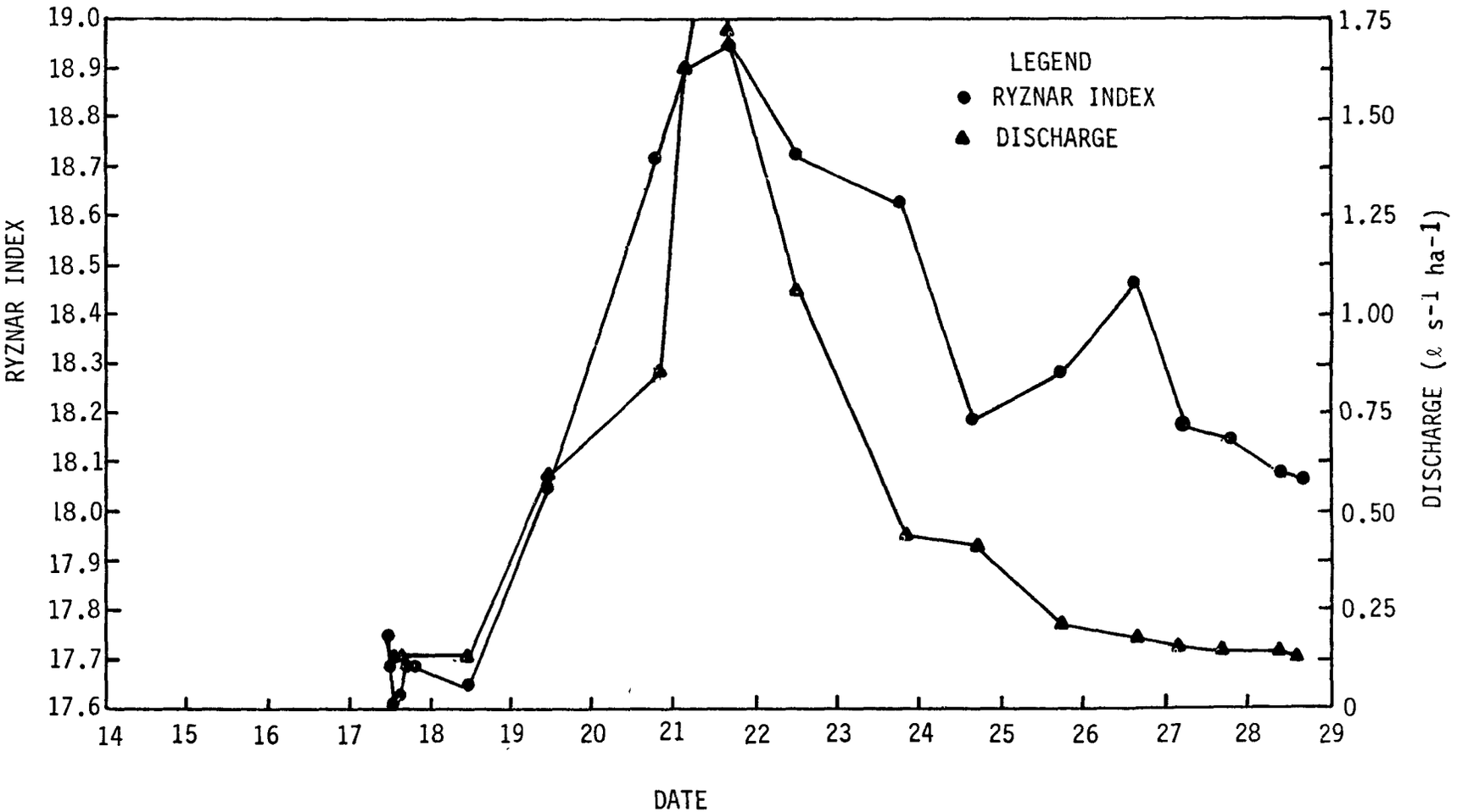

Figure 6-11. Ryznar Index and discharge for Card Machine Run.

Unpublished data collected by Sharpe and DeWalle indicate a probable link between acid recharge water and the decreasing pH and alkalinity of a deep circulation spring on Pennsylvania's Laurel Hill. The data were collected during an acid snowmelt and rainfall runoff event in March of 1982 and are depicted in Figure 6-12. Unfortunately, flow data for the spring are not available; consequently, flow data for Wildcat Run, a stream whose watershed makes up a significant part of the spring's recharge area, are used for comparison. Wildcat Run, at the point of flow measurement, is only several feet from the spring discharge and groundwater is an important component of its total flow. Thus, the run's temporal response to acid runoff recharge is likely to be quite similar to that of the spring. The pH and alkalinity of the spring water appear to drop in concert with the increased streamflow in Wildcat Run, with the most dramatic change occurring in alkalinity.

As discussed in an earlier section of this chapter there is a strong correlation between pH change and corrosivity for dilute waters; therefore, it could be reasonably assumed that the corrosivity of the water in this spring increased during the acid recharge event.

The lack of data is greatest with respect to groundwater impacts from atmospheric deposition. Much additional work is indicated, but preliminary information seems to indicate that adverse impacts to drinking water quality are possible in water supplies using shallow groundwater in areas edaphically and geologically sensitive to atmospheric deposition.

6.3.2 Lead

6.3.2.1 Concentrations in Noncontaminated Waters--The U.S. national interim primary drinking water standard for lead is 50 $\mu g\ \ell^{-1}$. The United States Environmental Protection Agency (U.S. EPA 1979a) summarized data in two surveys on lead in drinking water. The median lead concentration in municipal drinking water supplies is about 10 $\mu g\ \ell^{-1}$. In certain areas, such as Metropolitan Boston, it may contain lead in excess of the 50 $\mu g\ \ell^{-1}$ standard. This is believed to be due to very soft water (low pH) and the presence of lead piping in the domestic water distribution system (The Nutrition Foundation Expert Advisory Committee 1982). Lead piping is no longer used for new potable water systems in the United State (U.S. EPA 1979a).

A recent national survey of Canadian drinking water supplies involving 71 municipalities representing 55 percent of the population, indicated a medial level of lead equal to or less than 1 $\mu g\ \ell^{-1}$ and values ranged from $< 1\ \mu g\ \ell^{-1}$ to 7 $\mu g\ \ell^{-1}$.

Most natural ground waters have concentrations ranging from 1 to 10 $\mu g\ \ell^{-1}$.

6.3.2.2 Factors Affecting Lead Concentrations in Water, Including Effects of pH--In areas where the home water supply is stored in lead lined tanks and where it is conveyed to the household taps by lead

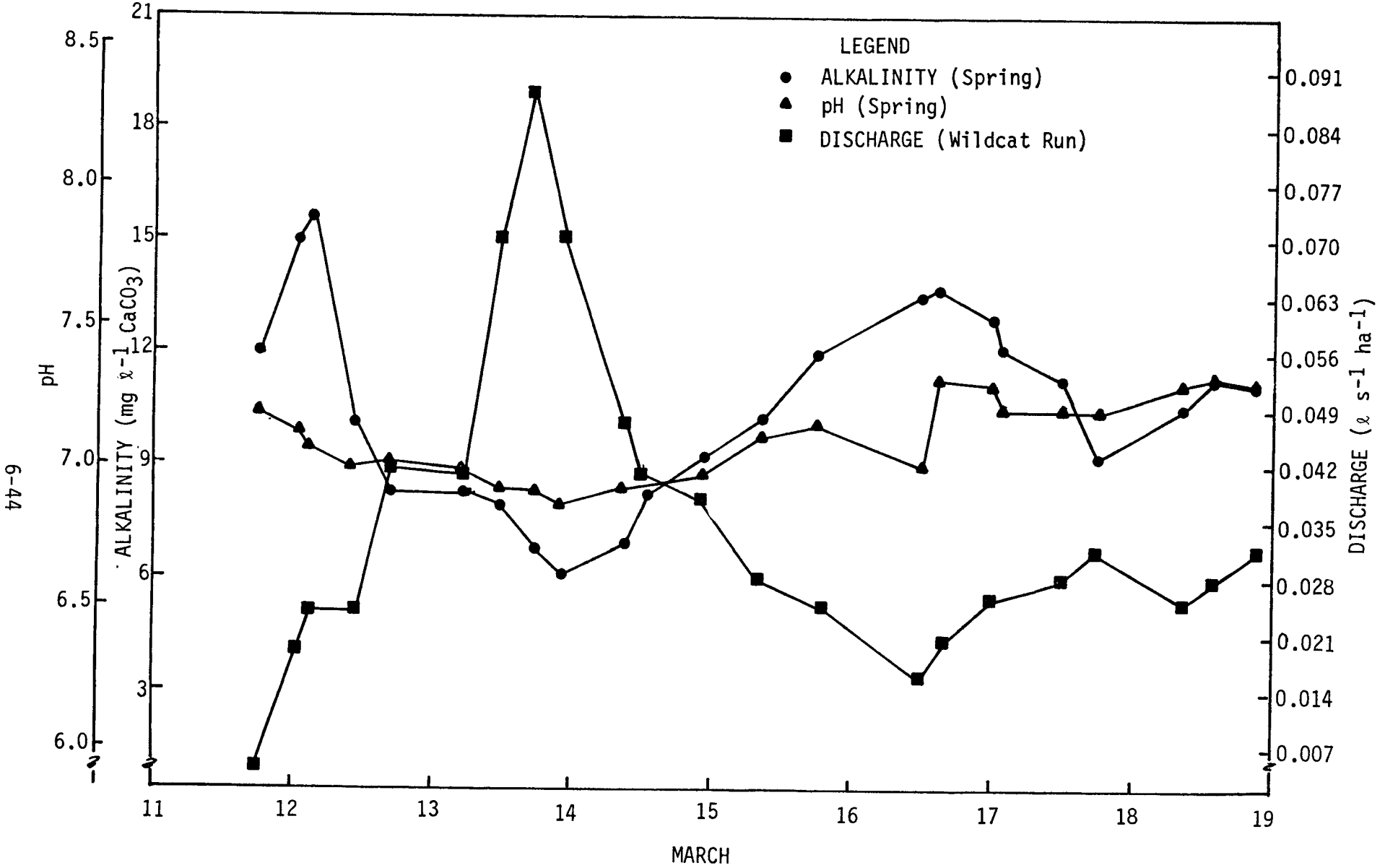

Figure 6-12. Alkalinity, pH, and discharge for Wildcat Run.

pipes, the concentration may reach several hundred micrograms per liter and even exceed 1000 $\mu g\ \ell^{-1}$ (Beattie et al. 1972). The concentration of lead in water conveyed through lead pipes is affected by several factors. The longer the water is held in the pipes, the higher the lead concentrations (Wong and Berrang 1976). The so-called "first flush" sample generally has lead concentrations about three times higher than free-running tap water (Nutrition Foundation Expert Advisory Committee 1982). The lower the pH of the water and the lower the concentration of dissolved salts, the greater the solubility of lead in water.

Leaching of lead from plastic pipes has also been reported (Heusgem and DeGraeve 1973). The source of lead was probably lead stearate, which is used as a stabilizer in the manufacture of polyvinyl plastics.

6.3.2.3 Speciation of Lead in Natural Water--Lead does not present the wide range of chemical and physical forms that mercury does. Metallic lead and its inorganic compounds possess a negligible vapor pressure at room temperatures, so volatile forms of lead are not important in the geochemical cycle. The organometallic forms of lead, such as the tetra-alkyl leads, although synthesized for use as antiknock compounds in gasoline, do not occur naturally as in the case of methyl mercury compounds. The inorganic salts of lead are numerous. The solubility of these compounds differs greatly.

The soluble salts will dissociate in water to liberate the reactive lead cation Pb^{2+}, which will form complexes and chelates with a variety of organic ligands present in water and sediments. Sibley and Morgan (1977) have described different forms of lead in freshwater: complexed ions, lead absorbed to precipitate, solid precipitate, and free lead ions. Lead present as the complexed ion is by far the most predominant species.

No studies have reported on the effect of acidic deposition on the speciation of Pb in natural bodies of water. Lead has been reported to bind to a wide range of organic fractions in river water (Ramanoorthy and Kusher 1975). As pointed out in Chapter E-4 of this document, decreasing water pH will reduce the fraction of heavy metals bound to organic components and increase the concentration of free inorganic metal species. This should increase lead levels in aquatic biota, possibly affecting human dietary intake.

6.3.2.4 Dynamics and Toxicity of Lead in Humans--Excellent reviews of this topic have been published in recent years (WHO 1977, U.S. EPA 1980b, Nutritional Foundation Expert Advisory Committee 1982).

6.3.2.4.1 Dynamics of lead in humans. The uptake, distribution, and excretion of lead have recently been reviewed in detail (U.S. EPA 1980b). Approximately 8 percent of dietary lead is absorbed in the gastrointestinal tract in adults. Children absorb about 50 percent of the ingested lead. Lead in water and other beverages may be absorbed with greater efficiency than lead presented in food.

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Lead is distributed to all tissues in the body and to all compartments within cells. Most of the lead in blood is associated with the red blood cells. The skeleton is the main site of lead storage, with about 95 percent of the total lead in the body in the skeleton of adults. Lead readily crosses the placenta. It also crosses the blood-brain barrier but more readily in children than in adults.

Lead is excreted in urine and feces, with the human urinary route probably being more important. The half-time of lead retention in soft tissues is about six weeks following exposure of a few months. The half-time may be longer following years of occupational exposures to lead. Lead is accumulated in the skeleton throughout most of the human life-span, and the half-time in skeletal tissue is very long.

Lead concentration in whole blood is the most commonly used indicator for assessing the burden of lead in soft tissues. The relative contributions of airborne lead, lead in food, and other sources of lead are often assessed in terms of their contributions to the blood-lead concentration.

A positive correlation exists between the concentration of lead in domestic water supply and the concentration of lead in blood. The United States Environmental Protection Agency, based on a study by Moore et al. (1977), has estimated blood concentrations associated with levels of lead in free-running tap water (Table 6-8).

If the relationship is valid, the impact of lead concentrations in running tapwater is greatest in the lower range of lead in water. According to Table 6-8, the median lead level in U.S. drinking water (10 $\mu g\ \ell^{-1}$) would contribute approximately 3.4 $\mu g\ dl^{-1}$. Assuming the median blood level in the absence of the water contribution to be 11 $\mu g\ dl^{-1}$, the U.S. water supply contributing about 30 percent additional blood lead and lead present in tapwater at the current interim primary drinking water standard would contribute about 10 $\mu g\ dl^{-1}$ to blood lead concentration, i.e., about equal to the lead contribution from all other sources. However, blood levels in the United States are affected by a number of factors such as age, sex, and urban versus non-urban locations. Urinary excretion of lead may be used on a group basis to indicate the soft tissue burden. Lead in hair, unlike the case of methyl mercury, is not a useful indicator because it represents external contamination of the hair sample.

6.3.2.4.2 Toxic effects of lead on humans. Lead damages a variety of human organs and tissues. Damage to the human hemopoietic system is usually the first observable effect of lead (Figure 6-13). The inhibition of enzymes involved in synthesizing hemoglobin results in the accumulation of precursor substances: δ-aminolevulinic acid (δ-ALA) in plasma and urine, and free erythrocyte protoporphyrin (FEP) on the red blood cells. Measuring FEP has become a routine method for checking the earliest effects of lead.

TABLE 6-8. THE ESTIMATED RELATIONSHIP BETWEEN LEAD CONCENTRATIONS IN RUNNING TAP WATER AND HUMAN BLOOD LEAD LEVELS (MOORE ET AL. 1977 IN U.S. EPA 1980b)

Lead in running tap water ($\mu g\ \ell^{-1}$)	Total lead in blood (PbB) ($\mu g\ dl^{-1}$)	Lead in blood due to water ($\mu g\ dl^{-1}$)
0	11	0
1	14.4	3.4
5	16.7	5.8
10	18.4	7.4
25	21.0	10.0
50	23.6	12.6
100	26.8	15.8

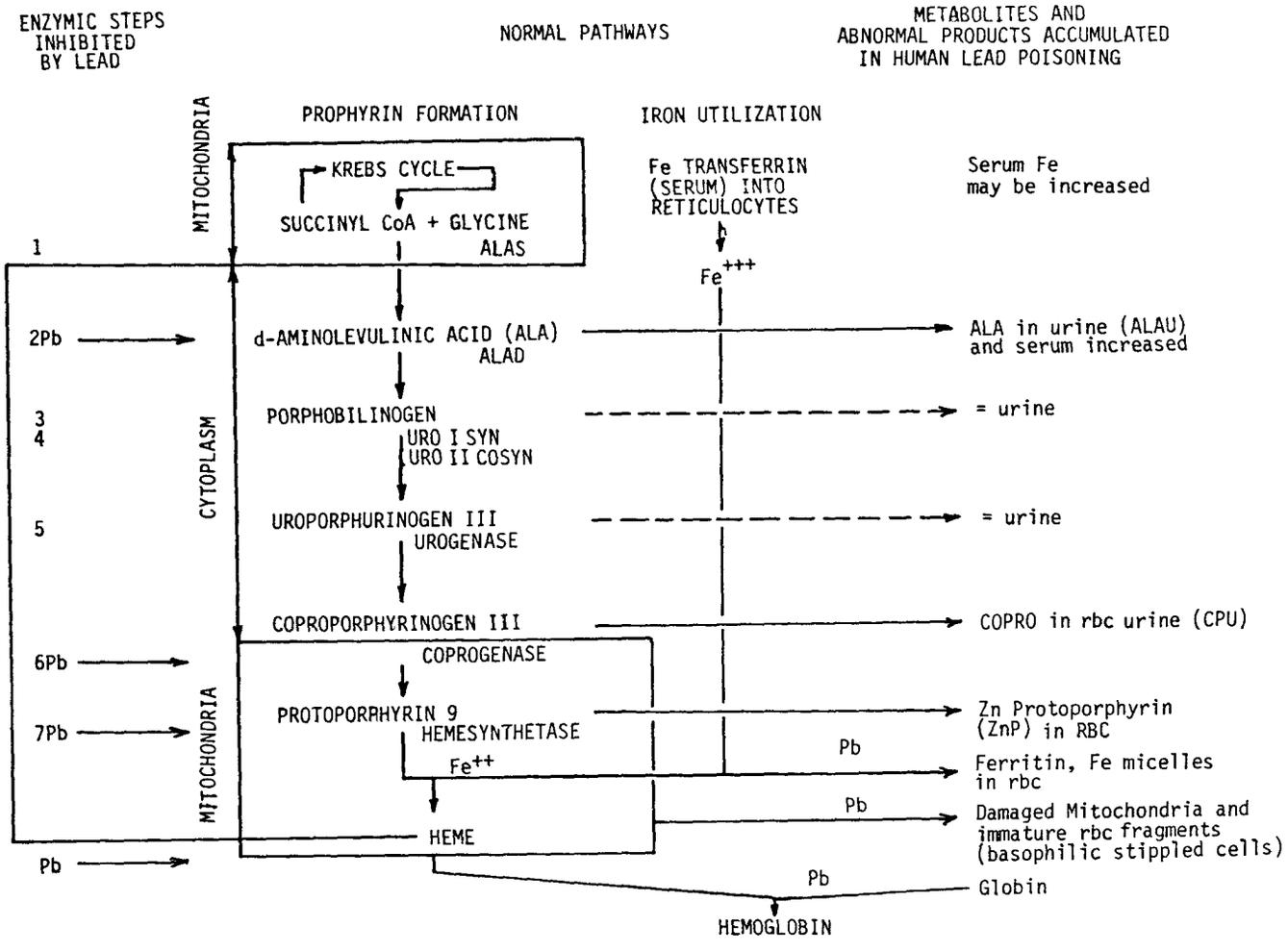

Figure 6-13. The initial and final steps associated with disturbances in the biosynthesis of hemoglobin due to lead are mediated by intramitochondrial enzymes and the intermediate steps by cytoplasmic enzymes. The enzymes most sensitive to lead (steps 2 and 7) are the SH-dependent enzymes, δ-amino-levulinate dehydrase (ALAD) and heme synthetase. Accumulation of the substrates of these enzymes (ALA and FEP) is characteristic of human lead poisoning as is increased urinary coproporhyrin excretion. Although zinc protoporphyrin (ZnP) accumulates in erythrocytes in lead poisoning (and iron deficiency), it is usually measured as "free" erythrocyte protoporphyrin (FEP). Lead reduces the bioavailability of iron for heme formation. A compensatory increase in the activity of the first enzyme in the pathway, δ-amino-levulinic acid synthetase (ALAS), occurs in response to reduced heme formation. Other compensatory responses include erythroid hyperplasia , reticulocytosis and micro-cytosis. Non-random shortening of erythrocyte life span has been demonstrated in lead workers. Amicrocytic, hypochromic anemia results including some morphological features noted above. Adapted from Chisolm (1978).

During recent years, measurement of FEP has come into wide use as the most practical screening tool in both epidemiologic studies and in monitoring populations at high risk for lead toxicity. Figure 6-14 shows the curvilinear relationship between FEP and lead concentration in blood. The curvilinear shape is typical of the relationship between blood lead and other intermediate metabolites of porphyrin synthesis, such as δ-aminolevulinic acid and urinary coproporphyrin. Thus it is difficult to assign a specific blood level of lead at which FEP or other metabolites attain abnormal values. At first, levels of FEP increase slowly with blood lead, but as lead rises about 40 to 50 μg dl^{-1} the rate of increment of FEP rises rapidly. Roels et al. (1978) defined abnormal blood FEP levels as those in excess of the upper 95 percent confidence limit of the controls and published a dose-response relationship relating blood lead levels to the frequency of individuals having FEP values equal to or in excess of their defined abnormal value (Figure 6-11). Children and adult females tend to show a greater response than adult males. This analysis indicates that most of a population having blood leads in the range of 30 to 40 μg Pb dl^{-1} will have abnormally high FEP values.

Higher doses of lead cause anemia and damage to both the peripheral and central human nervous system (Table 6-9). The central nervous system in children appears to be more sensitive than the mature central nervous system. A growing body of knowledge suggests that lower blood levels of lead exposure than those previously recognized are associated with altered neuropsychological function and intelligence deficits. For example,reduced general intelligence quotients, reduced auditory and speech processing, and attention deficits have been reported in children with higher dentine lead than those with lower dentine lead (Needleman et al. 1979). In a study of 166 children whose blood lead levels ranged from 7 to 33 μg 100 ml^{-1}, Yule et al. (1981) reported decreases in attainment scores on tests of reading, spelling, and intelligence as blood lead levels increased. Some, but not all, of this variabliity was removed after influence of the social class of the subject's family was considered.

Piomelli (1980) has reported that heme synthesis si impaired in children with blood levels less than 30 μg Pb 100 ml^{-1} consistent with findings of Roels et al. (1978) reported in Figure 6-15. Several other metabolic changes associated with low level lead exposure of children have been identified. Plasma levels of the vitamin D metabolite, 1,25 dihydroxy vitamin D, which is active in stimulating the gastrointestinal absorption of calcium and phosphorous, decreased as the blood level increased (Rosen et al. 1980). Plasma levels of the vitamin D metabolite exhibited a strong negative correlation with blood lead concentrations in the range of 12 to 120 μg 100 ml^{-1}, with no difference in slope of the regression line from blood lead levels over or under 30 μg 100 ml^{-1} (Mahaffey et al. 1982b).

Lead produces both acute and chronic effects on kidney function (Nutritional Foundation's Expert Advisory Committee 1982). The acute effects manifested as dysfunction of the proximal tubular cell, such as

$$FEP = 0.043 \times (\text{blood lead})^2 + 0.45(\text{blood lead}) - 2.14$$
$r = 0.79$
$n = 1056$

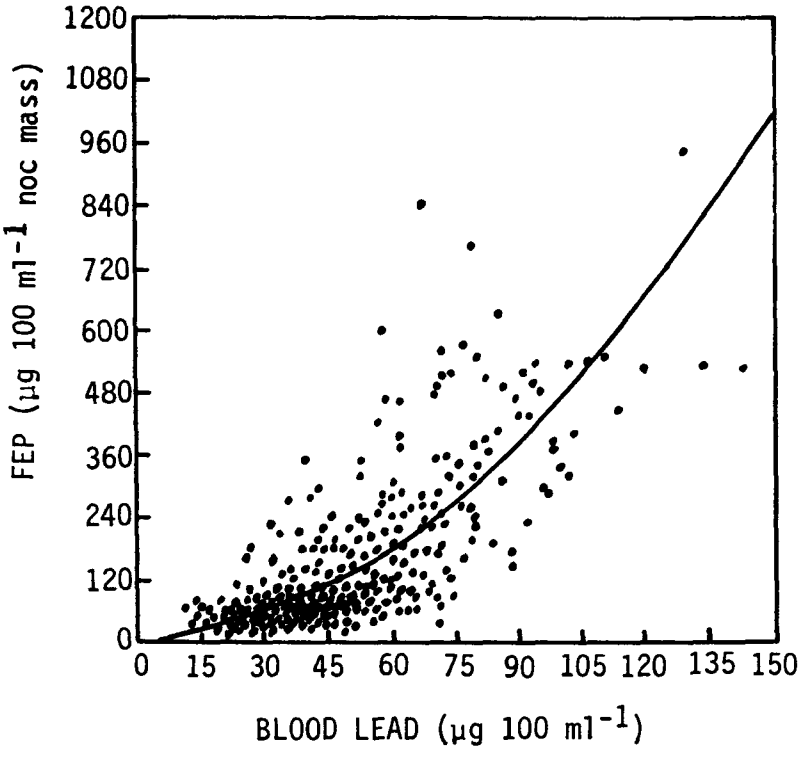

Figure 6-14. Free erythrocyte protoporphyrin (FEP) vs blood level. Shoshone County, Idaho, August 1974. Adapted from Landrigan et al. (1976).

TABLE 6-9. NO DETECTED EFFECT LEVELS IN RELATION TO PbB
(ADAPTED FROM WHO 1977)

No-detected effect level ($\mu g\ 100\ ml^{-1}$)	Effect	Population
< 10	Erythrocyte ALAD inhibition	Adults, children
20-25	FEP	Children
20-30	FEP	Adults, female
25-35	FEP	Adults, male
30-40	Erythrocyte ATPase inhibition	General
40	ALA excretion in urine	Adults, children
40	CP excretion in urine	Adults
40	Anemia[a]	Children
40-50	Peripheral neuropathy	Adults
50	Anemia[a]	Adults
50-60	Minimal brain dysfunction	Children
60-70	Minimal brain dysfunction	Adults
60-70	Encephalopathy	Children
> 80	Encephalopathy	Adults

[a]The term anemia here is used to denote earliest statistically demonstrable decrease in blood hemoglobin. In adult workers a decrease in blood hemoglobin within the normal range has been reported during the first 100 days of employment. Other studies of workers indicate that frank anemia is not statistically demonstrable until PbB > 100 μg, as cited elsewhere in the WHO report. An increased frequency of early anemia has been reported at PbB > 40 μg of groups of children in whom concurrent iron deficiency anemia was not ruled out but is highly likely.

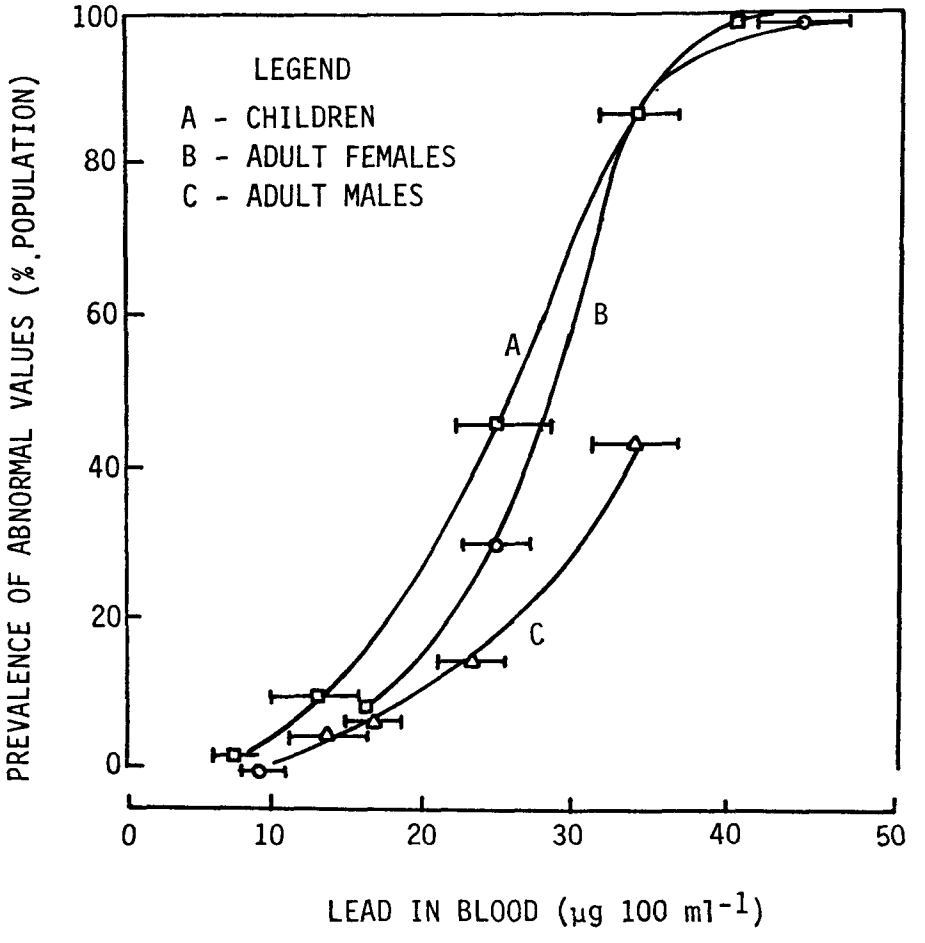

Figure 6-15. The relationship between the percentage of abnormally high free erythrocyte protoporphyrin and average blood lead levels in A, children; B, adult females; and C, adult males. Abnormal values were defined as FEP values in excess of 82, 83, and 63 µg 100 ml^{-1} for children, women, and men, respectively. Adapted from Roels et al. (1978).

amino aciduria, glycoseria, and hyperphosphoturia, usually do not occur until blood levels exceed 70 μg dl^{-1}. Chronic lead nephropathy is not usually recognized in humans until it has reached an irreversible stage. The disease is characterized by the slow development of contracted kidneys with pronounced arterioscelerotic changes, fibrosis, glomerular atrophy and hyaline degeneration of blood levels. These changes portend progressive disease sometimes resulting in acute renal failure. The duration of excessive exposure to lead is believed to play an important role in the development of the disease. Although information on blood levels is inadequate, it is unlikely that the general child and adult populations, even in the upper 2 to 5 percentile of the "normal" U.S. range are sufficient to produce chronic renal effects.

Studies in the 19th and early 20th centuries indicated that occupational exposures to lead (presumably higher than current exposures) caused increased frequency of abortions and stillbirths (Oliver 1911). Indeed, following the publication of Oliver's findings, women have largely been excluded from occupational exposures to lead until very recently.

Lancranjan et al. (1975) have reported reduction in sperm counts and abnormal sperm morphology in occupationally eposed men. The functional significance on fertility is not known.

Prenatal exposure to lead may be associated with mental retardation in children (Moore 1980). The human data are consistent with experimental findings on animals that modestly elevated blood levels, ~ 40 μg dl^{-1}, during prenatal and early postnatal life may be associated with subtle and long lasting adverse consequences to the offspring.

Lead has been shown to be a carcinogen in animal tests, but epidemiologial studies have failed to reveal an association between lead exposure and human cancer. Measurement of precursor metabolite of heme synthesis such as FEP or δ-ALA provide the earliest warning of the effects of lead. If protected against, effect on heme synthesis will protect against the more serious clinical effects of lead, such as anemia and encephalopathy.

6.3.2.4.3 Intake of lead in water and potential for human health effects. Mahaffey (1977) estimated that the daily intake of drinking water ranged from 300 ml for children to as much as 2000 ml for adults. An expert group of the National Academy of Sciences (NAS 1980) stated a value of 1630 ml day^{-1} for water intake of adults (not including amounts used to prepare foods and beverages) and a range of 100 ml to 3000 ml for children.

A study in Canada by Armstrong and McCullough quoted by the Nutrition Foundation's Expert Advisory Committee (1982) indicated that the total daily intake including water used as a food ingredient was 760 ml averaged for 0 to 6 years, and 1140 ml for the 6- to 18-year-old

group. The highest average daily intake was 1570 ml for the 55 and older age group. However, up to 3000 ml total water per day was consumed by some children in the 0- to 6-year-old age group and up to 4300 ml total water was consumed by certain individuals in each of the remaining age groups.

Using the NAS reported range of 100 to 3000 ml for children and a U.S. median level of 10 $\mu g\ \ell^{-1}$, the range of intake for children would be 1 to 30 μg Pb and for adults 16 μg, assuming a water intake of 1600 ml day^{-1} (Table 6-10). If average lead concentrations attained the interim drinking water standard of 50 $\mu g\ \ell^{-1}$, these intake values would be five times greater.

The review of the human toxicity of lead in Section 6.3.2.4.2 identified children as the most susceptible group in the general population. Blood lead levels in children in the United States cover a broad range of values (Mahaffey et al. 1982a). A criterion of 30 μg Pb 100 ml^{-1} whole blood has been used in estimating the prevalence of elevated blood lead (Center for Disease Control 1978). If this concentration of blood lead is accompanied by an erythrocyte protoporphyrin concentration of 50 to 250 μg 100 ml^{-1} of whole blood, the child is thought to have undue lad absorption. Community based lead poisoning prevention programs report that approximately 75 percent of children with blood lead levels of > 30 μg 100 ml^{-1} also have erythrocyte protoporphyrin values of > 50 μg 100 ml^{-1} (Mahaffey et al. 1982a). The review of human toxicity data in Section 6.3.2.4.2 also indicate that blood lead levels in children > 30 μg 100 ml^{-1} indicates a risk of biochemical, if not neuropsychological, dysfunctions.

A survey of blood lead levels in children in the years 1976 to 1980 in the United States indicated that substantial numbers of children have blood leads > 30 μg dl^{-1} (Table 6-11). The prevalence of elevated blood lead values is highest in children of low income families (approximately 11 percent of children in families having an income less than $6000) and in children living in large cities (7.2 percent of children living in cities of population more than one million). However, elevated blood lead is widely distributed in the general population, including children in families earning more than $15,000 annual income (1.2 percent) and in children living in rural areas (2.1 percent).

Section 6.3.1 reviewed available data to indicate that reduced pH increases the corrosivity of water and can mobilize metals such as lead, resulting in increased concentrations in drinking water. Lead piping in home plumbing is rare and no longer used in this country except in certain parts of New England. However, lead can be mobilized from other types of piping where it is used as a solder (copper piping) or in stabilizers (certain types of plastic pipes). Homes using roof-catchment cisterns for collecting drinking water seem especially vulnerable to corrosive rain water. Young and Sharpe (see Section 6.3.1.1) noted that 22 percent of such systems yielded lead

TABLE 6-10. DAILY INTAKE OF LEAD FROM DRINKING WATER

Age Group	Daily Water Intake[a] ml	Daily Lead Intake[b] µg Pb
Children	100 - 3000	1 - 30
Adults	1630	16

[a]National Academy of Science (1980).

[b]Assumes U.S. median concentration of lead in drinking water to be 10 µg Pb ℓ^{-1}.

TABLE 6-11. BLOOD LEAD LEVELS IN CHILDREN 6 MONTHS THROUGH 5 YEARS BY ANNUAL FAMILY INCOME AND DEGREE OF URBANIZATION OF PLACE OF RESIDENCE IN THE UNITED STATES FROM 1976 TO 1980[a]

Demographic variable	Estimated population (thousands)	No. of persons examined	Blood[b] lead $\mu g\ 100\ ml^{-1}$	Revalence of blood lead levels < 30 $\mu g\ 100\ ml^{-1}$ % persons examined
Annual Family Income[c]				
< $6000	2465	448	20 ± 0.6	10.9 ± 1.4
$1000 - 14,999	7534	1083	16 ± 0.5	4.2 ± 0.7
> 15,000	6428	774	14 ± 0.4	1.2 ± 0.4
Degree of Urbanization				
urban > 10^6 persons	4344	544	18 ± 0.5	7.2 ± 0.7
urban < 10^6 persons	6891	944	16 ± 0.7	3.5 ± 0.6
Rural	5627	884	14 ± 0.6	2.1 ± 0.9

[a]Adapted from of Mahaffey et al. (1982a).

[b]Mean ± S.E.M.

[c]All values shown for this variable reflect the exclusion (from analysis and tests of significance) of children in households that declined to reported their income.

concentrations in tap water (having stood overnight) in excess of the drinking water standard of 50 μg Pb ℓ^{-1}.

From the point of view of human health risks, any increases of lead concentrations in drinking water should be viewed as an additional burden of lead. This is especially important with children where substantial numbers already have elevated blood levels. Drinking water at the median concentration of 10 μg Pb ℓ^{-1} already makes an appreciable contribution to blood lead levels (approximately 30 percent add on to other sources of lead; see Section 6.3.2.4.1). Thus the drinking water standard of 50 μg Pb ℓ^{-1} will not provide sufficient protection to those children already having high blood lead from other sources of exposure.

Unfortunately quantitative data are lacking on the contribution of acidic deposition to lead in drinking water. Roof-catchment cistern systems believed to be widely used in rural areas of Ohio and Western Pennsylvania appear to be a probable target for the effect of acidic deposition. Thus, it is of great importance to ascertain the extent of usage of these systems in those areas of the USA subject to acidic deposition and to check the extent to which charged corrosivity of this water affects lead levels in tap water.

6.3.3 Aluminum

Inorganic aluminum is toxic to fish and may be the main cause of fish kills due to acidification of natural bodies of water. Acidic deposition dissolves aluminum in clay materials in soils and sediments, thereby increasing concentrations of the Al^{3+} ions and inorganic salts of aluminum (for details, see Chapter E-2). Fish mortality appears to be due to damage to the gills of the fish. The toxic properties of aluminum are self-limiting with regard to bioaccumulation; when the aluminum levels in water reach toxic levels, the ensuing mortality of fish stops further accumulation in aquatic food chains. The behavior of aluminum is thus in sharp contrast to methyl mercury, which is of lower toxicity to fish and is avidly accumulated.

Aluminum in drinking water, unlike lead, is not directly toxic to humans. However, a special circumstance may lead to human toxicity--that is the use of aluminum containing water in hemodialysis procedures. This is believed to lead to direct entry of aluminum into the blood stream and eventually damage to the central nervous system.

6.3.3.1 Concentrations in Uncontaminated Water--Burrows (1977) has reviewed the literature on concentrations of aluminum in natural bodies of water. He draws attention to two factors that are important in assessing published values. First, many publications do not clearly distinguish between dissolved and suspended aluminum in water. He notes that many investigators now use a 0.45 μm millipore filter to distinguish between dissolved and particulate aluminum. The second factor is that procedures for trace analysis of aluminum have only recently become available and most of the literature data have been

collected without using these techniques. Burrows states that as a general rule all aluminum values reported before 1940 should be regarded with skepticism. Unfortunately, very few analyses have been reported for the most recent times (from 1970). The Maumee River Basin (Ohio) was reported to have a mean value of 0.01 mg ℓ^{-1} for the period 1971-73. A phosphate limestone lake in Florida had a mean value of 0.05 mg ℓ^{-1} at a water pH 7.0 to 9.6. Tributaries to Lake Michigan had mean values of 0.353 in 1972 but pH was not specified. The above values have been taken from Burrows (1977).

6.3.3.2 Factors Affecting Aluminum Concentrations in Water--Burrows (1977) notes a number of factors that influence aluminum concentrations in bodies of natural water:

1) Acidic waters consistently contain much more soluble aluminum than neutral or alkaline waters. Schofield and Trojner (1980) report that in a brook in the Adirondack Wilderness region of New York State, aluminum concentrations rose from about 0.2 mg ℓ^{-1} at pH 5.5 to 6.5 to 0.8 to 1.0 mg ℓ^{-1} as the pH fell to less than 5.0 during the spring snow melt.

2) Highly saline waters contain higher aluminum concentrations than fresh waters.

3) Hot waters (e.g., hot water springs) tend to have higher levels of aluminum than cold water.

4) Moving waters tend to give higher aluminum analysis than quiescent waters. This effect is probably due to mobilization of suspended material.

6.3.3.3 Speciation of Aluminum in Water--The species of aluminum in bodies of natural water have been discussed in Chapter E-4. Most of the dissolved aluminum is present as complexes with organic ligands. The inorganic fractions consist of Al^{3+} and aluminum fluoride, hydroxide, and sulfate complexes. The fluoride complex is probably the predominant inorganic species, according to thermodynamic calculations (Driscoll et al. 1980).

The inorganic monomeric species are more toxic to fish than are the organic complexes of aluminum. Of the inorganic species, the fluoride complex is probably the least toxic because addition of fluoride ion reduces the toxicity of aluminum. Lowering the pH in natural bodies of water increases the labile (inorganic) monomeric aluminum and thereby increases toxicity to fish. Driscoll et al. (1980) found that seasonal variations in organically chelated-aluminum were not affected by seasonal variations in pH in lakes in the Adirondack region of New York State. The organic aluminum correlated with total carbon measurements in water.

6.3.3.4 Dynamics and Toxicity in Humans--This topic has been the subject of a number of reviews (Norseth 1979).

6.3.3.4.1 Dynamics of aluminum in humans. Data on absorption, distribution, and excretion of aluminum compounds in man have been reviewed recently (Norseth 1979). Aluminum is absorbed in the gastrointestinal tract. The fraction of dietary intake absorbed into the blood stream is believed to be small, but precise figures are not available. When aluminum was given as the hydroxide salt to uremic patients, approximately 15 percent of the dose was absorbed, with considerable differences between individuals (Clarkson et al. 1972). Unfortunately, information is not available on the absorption of other forms of aluminum or in people with normal kidney function. Aluminum is distributed to all tissues in the body and has been reported in fetal tissues. When aluminum in food was given to rats, increased levels were reported in blood, brain, liver, and testes (Ondreicka et al. 1966).

Little information on the relative importance of urine versus fecal pathways of excretion is available. Renal clearance of aluminum may be as high as 10 percent of the glomerular filtration rate (creatinine clearance) as indicated in patients with compromised renal function. These data would suggest a high urinary rate of excretion in normal subjects and a correspondingly short biological half-time (on the order of days or hours). Animal experiments indicate that biliary excretion of aluminum contributes to fecal excretion of the metal.

Aluminum is found in both cow and human milk. Normal levels of aluminum in human blood and other biological fluids exhibited a very wide range of values relative to the different laboratories making the analyses. Apparently considerable problems remain, particularly those related to change contamination by the ubiquitous metal, in determining reliable values for the low levels in human plasma.

6.3.3.4.2 Toxic effects of aluminum in man. Toxic effects in terms of fibrosis of lung tissue have been reported in workers inhaling aluminum or its compounds. The situation with regard to toxic effects in humans due to oral intake of aluminum is equivocal. An early claim (Crapper et al. 1973) that Alzheimer's Disease--a chronic degenerative disease of the central nervous system leading to presenile dementia--was associated with accumulation of aluminum in the brain has not been substantiated by later studies (Markesbery et al. 1981). However, a chronic neurological disease "Dialysis Dementia," that develops in a number of patients receiving dialysis therapy may be associated with elevated aluminum intake (Alfrey et al. 1976, McDermott et al. 1978). Intake of aluminum may be directly from the water used in the dialysis fluid or from the aluminum hydroxide compounds given orally to remove phosphate from the uremic patients. Aluminum has been shown to be harmful to the central nervous system in animals when directly administered in brain tissue (Kopeloff et al. 1942) and to damage neuroblastoma cells in culture (Miller and Levine 1974).

6.3.3.5 Human Health Risks from Aluminum in Water--Acute or chronic disease in man has not been related to normal dietary intake of aluminum from food or drinking water. However, a potential risk may exist under the special circumstances of patients with compromised kidney function

who undergo regular therapeutic dialysis. Driscoll et al. (1980) have reported levels of aluminum in natural bodies of freshwater in the Adirondack Region of New York State to attain values as high as 800 μg Al ℓ^{-1} under the influence of acidic deposition. A concentration of 50 μg ℓ^{-1} of aluminum in dialysis water is claimed to be dangerous (Registration Committee, European Dialysis and Transplant Association 1980).

Of the various species of aluminum known to exist in bodies of natural water, only data on aluminum hydroxide are available. This is absorbed across the human gastrointestinal tract. In areas of the country where drinking water is fluoridated or where elevated fluoride concentrations occur naturally, it is likely that aluminum flouride complexes will be present in tap water in substantial amounts. Unfortunately, we know nothing of the gastrointestinal absorption or about its potential toxicity in humans.

6.4 OTHER METALS

A number of other metals such as cadmium, copper, manganese, and zinc have been mentioned with regard to the possibility of indirect heath effects. In general, evidence to justify a detailed report for each metal is lacking. However, it should be noted that this chapter has not considered at least one potential pathway of human intake of environmental chemicals, i.e., the food supply other than fish and fish products. Cadmium is known to be accumulated by plants, including cereals, and the possible effects of acidic deposition have not been considered chiefly because of a lack of studies.

6.5 CONCLUSIONS

Chapter E-6 examines the direct health effects and in doing so mainly discusses lead and mercury availabilities as affected by acidic deposition. The following statements summarize the content of this chapter.

- No adverse human health effects have been documented as being a consequence of metal mobilization by acidic deposition. On the other hand, interest in the phenomena of acidic deposition is recent and few investigations, if any, have been made into the possibility of indirect effects on human health (Section 6.2.1).

- The substances requiring special attention are methyl mercury, due to its accumulation in aquatic food chains, and lead due to the potential for contaminating drinking water (Section 6.2.1).

- In virtually all studies published to date elevated methyl mercury levels in fish muscle (most notably the pike and perch) have been statistically associated with higher levels of acidity in water. However, a number of factors influencing

mercury levels in fish may also change in parallel to acidity (Section 6.2.3).

- More research is needed to identify all the factors that affect mercury accumulations in fish and the relative importance of each. This need is especially urgent in the United States where few data are available at this time (Section 6.2.3).

- The contamination of freshwater fish by direct discharge of mercury has been curtailed in recent years. The role of long-distance transport of mercury merits careful investigation as an explanation for high mercury levels in lakes remote from mercury-related industries (Section 6.2.2).

- Potential impacts in acidic deposition of methyl mercury concentrations in freshwater are of interest for several reasons (Section 6.2).

  a) Fish and fish products are the major if not only sources of methyl mercury for humans.

  b) Consumers of freshwater fish have a greater possibility of exceeding a allowable daily intakes of methyl mercury than do consumers of other forms of fish.

  c) Pike and trout, freshwater fish among the most likely species to be affected by acidic deposition, have the highest user consumption figures and the highest average methyl mercury levels.

- Prenatal life is a more sensitive stage of the life cycle for methyl mercury. More information is needed on fish consumation patterns of women of child-bearing age in order to quantitatively assess the potential impact on human health of elevated methyl mercury levels in freshwater fish (Section 6.2.4).

Data on the impacts of acidic deposition on drinking water quality are scarce. However, by using available information, tentative assessments of impacts on ground and surface water systems were made.

- The lack of data is greatest with respect to groundwater. Preliminary information seems to indicate that adverse impacts to drinking water quality are possible in water supplies using shallow groundwater in areas edaphically and geologically sensitive to acidic deposition (Section 6.3.1.3).

- Increasing corrosivity is probably the most significant potential impact of acidic deposition on surface water supplies. Populations are at increased risk of being exposed to higher concentrations of corrosive toxicants, such as lead and possibly cadmium, where surface water storage facilities

are small, necessitating the direct use of raw water during storm flow periods and where corrosive control is not practiced in the water system (Section 6.3.1.2).

- People receiving drinking water from roof catchment cistern systems should be considered at potential risk of increased intake of lead in areas of acidic deposition and especially if cisterns are used that have no particulate filters (Section 6.3.2).

- From the point of view of human health risks, any increases in lead concentrations in drinking water should be viewed as an additional burden of lead. This is especially important in children where substantial numbers already have elevated blood lead levels (Section 6.3.2.4).

- Acute or chronic diseases in humans have not been related to normal dietary intake of aluminum from food or drinking water. However, a potential threat exists for patients undergoing hemodialysis if aluminum concentrations in the water used in this treatment exceed 50 μg of aluminum per liter (Section 6.3.3).

Generally, the indirect effects on human health attributable to acidic deposition require further study. Data are very limited with regard to measurement of the toxic elements and their speciation and to the kinetics of transfer and uptake by accumulation processes. Studying less toxic essential metals may be important in that elevated concentrations of some or all of them might affect the food chain dynamics or the toxicity of lead or mercury.

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THE ACIDIC DEPOSITION PHENOMENON AND ITS EFFECTS
E-7. EFFECTS ON MATERIALS

(J. E. Yocom and N. S. Baer)

7.1 INTRODUCTION

In the popular press many articles ascribe damaging effects to acidic deposition (LaBastille 1981). Damage to non-living materials and structures is invariably listed as one of the important effects of this phenomenon. Furthermore, damage to irreplaceable historic buildings and monuments, works of art, and other cultural properties is emphasized as one of the most important aspects of such damage. If one narrowly considers the "acid rain syndrome" as precipitation that has been rendered more acidic as a result of long-range transport of acid rain precursors, this mechanism alone probably accounts for only a small fraction of the total damage to materials attributable to the effects of anthropogenic air pollutants.

In general, the distinction between the effects on materials of near or intermediate sources from distant sources is difficult if not impossible to make.[1] If the discussion is broadened to "acidic deposition," which includes all of the mechanisms by which acidic pollutants (gases and solid and liquid particulate matter) may contact and damage surfaces, one is able to point to a considerable body of experimental evidence for damage to materials by acidic deposition. For most cases, in urban areas where most materials are located, the atmospheric load from local sources tends to dominate over the smaller amounts of pollutants arriving from remote upwind sources (U.S.-Canada 1982). This broad definition is used for this chapter.

Damage to materials from acidic deposition takes a variety of forms including 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 to a significant degree as a result of natural environmental conditions, even in unpolluted atmospheres. Moisture, atmospheric oxygen, carbon dioxide, sunlight, temperature fluctuations, and the action of microorganisms all contribute to the deterioration of materials. Quantifying the specific contributions of anthropogenic air pollutants to such damage is a formidable task. Furthermore, distinguishing the relative amount of damage caused by specific

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[1] In Chapter A-9 of this document the following definitions for the scales of acidic deposition transport are given: short range (< 100 km), intermediate range (100 to 500 km), and long range (> 500 km).

pollutant transformation and contact processes (for example, acid precipitation) becomes even more elusive.

This chapter deals with the effects on materials of anthropogenic acidic air pollutants. Later in this chapter several typical broad mechanisms for acidic deposition are discussed. They include adsorption and absorption of acidic primary pollutant gases such as SO_2 and NO_2 on moist surfaces and their conversion to strong acids and the processes in which precipitation is acidified by condensation around acidic particles or washout of acidic primary gases. While this chapter's scope is extremely broad in concept, the literature describing research on any one specific contact-and-effect scenario may be limited or even non-existent.

There is a significant body of literature describing the effects of primary air pollutants on materials as determined by both laboratory and field experiments. This literature has been summarized in detail by the U.S. Environmental Protection Agency in its Criteria Documents supporting the establishment of air quality standards, for example, the document on sulfur oxides and particulate matter (U.S. EPA 1981). Several other reviews have also been published (Yocom and Grappone 1976, Yocom and Upham 1977, Yocom and Stankunas 1980). A recent review in draft form by Haagenrud et al. (1982) deals primarily with effects of sulfur compounds. The draft U.S.-Canada Transboundary Report contains a review of the literature on the effects of acidic deposition on materials (U.S.-Canada 1982).

Among the documented effects of air pollution on materials are many that may broadly be described as associated with acidic deposition. Table 7-1 summarizes the potential damaging effects of air pollutants and other environmental conditions on several classes of materials. One should note that sulfur oxides, other acidic gases, and particulate matter figure prominently among the important, potentially damaging pollutants, and note that moisture (as atmospheric humidity and surface wetness) is an extremely important factor.

7.1.1 Long Range vs Local Air Pollution

Acidic pollutants whether they are present as primary pollutant gases (e.g., SO_2 and NO_x), as fully oxidized acids or salts (e.g., sulfates and nitrates) or in the form of acidified precipitation may, have arrived at a material surface from local pollutant sources or may have been transported many miles from distant sources. Table 7-2 summarizes the characteristics of long-range and local air pollutants and their effects. As the table shows, several mechanisms may be described as acidic deposition. The separation of long-range and local characteristics is somewhat artificial since phenomena associated with long-range transport may be generated by local sources under the appropriate conditions. For example, acidic precipitation may be produced close to sources of primary pollutants under the proper meteorological conditions. The distinction between different acidic

TABLE 7-1. AIR POLLUTION DAMAGE TO 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_2, 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	Moisture, sunlight, ozone, 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 controlled atmosphere 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	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 a controlled atmosphere, 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

TABLE 7-2. CHARACTERISTICS OF LONG-RANGE AND LOCAL AIR POLLUTION

Pollutant or Effect	Long-range	Local
Pollutant Concentration Patterns	Low concentrations and uniform distribution.	High to moderate concentrations and strong gradients in time and space.
Sulfur Oxides	SO_2 tends to be oxidized to particulate sulfates.	Exist primarily as SO_2; however, under light winds and stable atmospheric conditions conversion to particulate sulfate can occur.
Nitrogen Oxides	Significant conversion to particulate nitrates.	Exist primarily as NO and NO_2, but under low wind speed, stable conditions and sunlight, conversion to organic or inorganic nitrates in particulate form is possible.
Particulate Matter (includes aerosols)	Only the smallest primary particle sizes persist. Large component of material converted from gases and vapors to particulate form such as sulfates.	Exists in wide range of sizes which may be bimodal. Particles are capable of producing surface soiling and participates in the formation of corrosion layers (e.g., black crust on stone).
Ozone and Other Oxidants	Ozone and other oxidants are produced from hydrocarbons and NO_x over moderate to long-range transport in presence of sunlight.	The formation of ozone and other oxidants is likely only under low winds and sunlight if precursors are present.
Dry Acidic Deposition	Dry deposition of acidic particles (for example, sulfates) is possible.	Dry deposition of acidic particles is possible, especially under stable conditions, often enhanced by moist surfaces.
Acidic Precipitation	Acidic rain mechanisms may be predominantly through droplet condensation around acidic particles.	Acidic rain formation may be predominantly through rain washout of acidic particles and pollutant gases.
Acidic Fog (includes liquid aerosols)	Acidic fog may be formed by drop condensation around small acidic particles or other acidic condensation nuclei.	Same as for long-range.

deposition scenarios is especially important when the cost of damage related to such deposition is considered and when control strategies to ameliorate such damaging effects are being developed. The transport, deposition, damage, and cost scenarios of greatest economic importance must be defined before the effectiveness of any control strategy can be estimated.

7.1.2 Inaccurate Claims of "Acid Rain" Damage to Materials

The popular literature contains frequent references to "acid rain" damage to cultural property. In most cases no attempt is made to distinguish between local pollution sources and long-range transport. In some cases the damage is caused by factors entirely independent of acidic deposition.

Perhaps the most egregious example is the damage to the granite Egyptian obelisk, "Cleopatra's Needle," located since 1881 in Central Park in New York City. In one account, it was stated that, "The city's atmosphere has done more damage than 3 1/2 millenia in the desert, and in another dozen years the hieroglyphs will probably disappear (New York Times 1978a). " A careful study of the monument's complex history makes it clear that the damage can be attributed to advanced salt decay, high humidity of the New York climate, and unfortunate attempts at preservation (New York Times 1978b, Winkler 1980).

7.1.3 Complex Mechanisms of Exposure and Deposition

The work done to date to measure damage to materials from acidic deposition has not considered to any significant degree the specific mechanisms of exposure, deposition, and subsequent damage. As will be discussed in the next section, most of the studies that have used laboratory chamber exposure or field exposure in the ambient atmosphere are unable to isolate specific deposition mechanisms from the many interrelated chemical and physical processes involved. The following list presents a series of simplified mechanisms that the authors believe occur in one form or another. These mechanisms are based upon the presence of acidic gases such as SO_2 and NO_2, their transformation products, and moisture in some form.

1. Dry Gas, Dry Surface: An acid gas is adsorbed on a relatively dry material surface (for example, building stone) and exposure to moisture forms acids that attack the material.

2. Dry Gas, Wet Surface: An acid is absorbed in moisture (condensed dew or collected precipitation) already on surfaces and results in acid attack.

3. Large, Dry Particle, Dry Surface: Large particles containing acid components fall on the material's surface and lead to damage directly. An example would be acid-containing soot from an oil-fired boiler.

4. Small Particle, Dry or Wet Surface: A small particle containing acidic compounds such as sulfuric or nitric acid salts capable of reacting with moisture to form acids settles on or impacts on a dry or wet surface and subsequently leads to acid attack.

5. Acid Precipitation: Rain or snow containing acidic components falls on the material surface and leads to damage directly.

The above group of simplified mechanisms is not intended to be exhaustive or completely rigorous. They are illustrative of the wide spectrum of processes that operate to produce acidic deposition and each of the listed mechanisms may have one or more variations. For example, in Mechanism 1 (Dry Gas, Dry Surface) it is likely, in the case of SO_2 contact, that some surface oxidation may take place within a relatively dry adsorbed layer or that SO_2 may react directly with a reactive surface to produce a sulfite salt. Nevertheless, as will become apparent later in this chapter, acidic deposition and subsequent damage accelerates in the presence of moisture.

The end result of each of these mechanisms is acidic deposition capable of damaging materials. Yet certain of these mechanisms are undoubtedly more important than others in causing economically significant damage. In large population centers where levels of primary, gaseous pollutants, and total material inventories are high, Mechanisms 1, 2, and 3 may be more important than 4 and 5. In rural areas where the inventory of exposed materials is likely to be different than in urban areas, and the pollutant mix may include a higher portion of secondary, particulate pollutants, Mechanisms 4 and 5 may dominate.

These factors and others such as the distinction between wet and dry deposition mechanisms are important because of the link between pollutant levels and meteorological factors. For example, if a local source has an elevated emission point, the kind of surface inversion associated with radiational cooling and dew formation may also act to keep the pollution from reaching ground level. Thus, Scenario 2 may not be especially important, even though all the critical components (active pollutant, susceptible material, wet surface) are all present on an annual average basis. Conversely, materials on elevated terrain may be subject to pollutant plume impact only rarely, but when they are affected, the conditions (such as wetness) may be such that the maximum degree of damage occurs.

Note in Table 7-2 that Mechanisms 4 and 5 (small particle, dry or wet surface; and acid precipitation) may occur both locally and after long-range transport. Stable atmospheric conditions and low wind speeds may provide the time necessary for atmospheric transformations to create effects on a local scale that would otherwise be associated with long-range transport.

7.1.4 Laboratory vs Field Studies

The effects of acidic deposition on materials have been studied under both laboratory and field conditions. In laboratory studies, the conditions of exposure can be controlled, and the specific effects of a single pollutant or environmental parameter can be isolated. However, to produce measurable material damage in a reasonable time period, the material is often exposed continuously to severe environmental conditions (e.g., extremely high pollutant concentrations and/or high humidity) completely unrepresentative of field conditions. Furthermore, the exposure conditions are programmed through predetermined cycles that may only remotely resemble the complex interactions of temperature, humidity, surface wetness, sunlight, pollutant concentration, and other environmental factors occurring in the ambient atmosphere. In this context, laboratory experiments have thus far been unable to represent a true picture of the effects of pollutants under conditions of long-range transport, where such transformation would have had ample opportunity to take place.

Field studies normally consist of exposing samples of materials to ambient atmospheres representing various combinations of pollutant concentrations and other environmental factors. By comparing damage level (e.g., loss of surface material) with pollutant concentration and other environmental factors (e.g., humidity, "time-of-wetness", or pH of rainwater) statistical models may be developed for the damage. The principle difficulties with this approach are

- Materials exposed may not represent materials in actual use.
- In normal use materials are found in combination. Field studies may not include interactions of other materials in contact with test materials.
- Damage is a complex function of many environmental conditions, and the effect of one condition is difficult to isolate.
- Measured variables may be interrelated (e.g., pH of rain may be dependent upon SO_2 level).

7.1.5 Measurement of Materials Damage

Material damage is usually measured by noting quantitative changes in some physical or chemical feature of the material (e.g., weight or thickness of a sample, surface color or reflectivity, chemical analysis, and identification of corrosion products).

7.1.5.1 Metals--Corrosion of metals may be measured by weight changes resulting from the accumulated corrosion products before and after a predetermined exposure period. However, for long exposures, corrosion products tend to spall or wear off. Thus corrosion products formed during the exposure period are usually removed chemically to determine

damage by weight of metal lost. Another method applicable to metals is measurement of changes in sample thickness, which in some cases may be obtained from the electrical resistance. Mechanical tests involving bending are frequently used to test for stress corrosion.

Physical methods such as scanning electron microscopy, x-ray diffraction, and x-ray fluorescence can be used to characterize the physical and chemical nature of corrosion products.

7.1.5.2 Coatings--Paint and other coatings damaged by environmental exposure usually erode, so measurement is most conveniently done by measuring weight loss of painted panels. Surface darkening by deposits of particulate matter or reactions between pigments and air pollutants are usually measured photometrically.

7.1.5.3 Masonry--Samples of building materials such as stone, mortar, and concrete can be weighed before and after exposure to determine erosion rates. Caution must be exercised in interpreting such data because conversion to new phases may involve weight gain without obvious change in physical appearance. Discoloration of such samples from exposure to dark particulate matter can be measured photometrically. A series of photographs of buildings taken over sufficient time periods may provide a qualitative assessment in the form of soiling and/or loss of surface detail.

7.1.5.4 Paper and Leather--The embrittlement of paper is accelerated by exposure to acidic deposition. Excess acidity can be observed by combination surface electrode pH measurements. Resulting damage may be determined by measuring folding resistance. Weakening of leather caused by acidic deposition can be quantified by means of tensile strength tests.

7.1.5.5 Textiles and Textile Dyes--Certain textile materials are weakened by acidic deposition. Such damage is best determined by measuring loss in tensile strength. Cotton is also weakened by biological processes (e.g., mildew), and methods have been developed to differentiate between acidic deposition and these biological mechanisms by determining the relative molecular weight of the exposed material. Damage from acidic chemical attack causes depolymerization and reduction in average molecular weight, while biological attack causes essentially no reduction in average molecular weight.

Textile dyes are affected by NO_2. Changes in color values from such damage are measured by specially designed colorimeters or spectrophotometers capable of detecting small changes in color within narrow ranges of the visible spectrum.

7.2 MECHANISMS OF ACIDIC DEPOSITION

Acidic deposition damages a wide range of materials. This section will cover some of the principal damage mechanisms for selected classes of materials that are widely used and economically important.

7.2.1 Metals

The atmospheric corrosion of metals is generally an electrochemical process governed by diffusion of moisture, oxygen, and acidic pollutants (e.g., SO_2) to the surface. The EPA Draft Criteria Document for Sulfur Oxides and Particulate Matter (U.S. EPA 1981) provides a review of the primary mechanisms governing the corrosion of metals in the presence of SO_2 and moisture. This review is based on the research of many workers, and it deals primarily with the effects of SO_2 and moisture on metals and other materials. However, most of the scenarios discussed fall within the general definition of acidic deposition.

The rusting of metals is an oxidation process that is accelerated by the presence of acidic pollutants. Barton (1976) has proposed the following set of reactions involving the oxidation of SO_2 to sulfate on iron surfaces:

$$SO_2 + O_2 + 2e^- \rightarrow SO_4^{2-} \qquad [7\text{-}1]$$

or

$$4\ HSO_3^- + 3\ O_2 + 4e^- \rightarrow 4\ SO_4^{2-} + 2\ H_2O. \qquad [7\text{-}2]$$

The electrons are provide by the oxidation of the metal (M):

$$M \rightarrow M^{n+} + ne^- \qquad [7\text{-}3]$$

Barton (1976) noted that rusting of iron occurs first at isolated sites and then spreads across the entire surface. This phenomenon is not well understood but may relate to a variety of factors including differential deposition rates of SO_2 or acidic particulate matter, the influence of rust deposits on subsequent corrosion, and variations in "time-of-wetness" in relation to electrolyte concentrations at various points on the surface. Rice et al. (1982) believe that moisture forms in "clusters" on metal surfaces even in indoor environments and at the site of these clusters, corrosion is initiated. While rust deposits increase the absorption of SO_2, a thin layer of iron oxide on steel will provide some degree of protection from subsequent atmospheric corrosion. In fact, special steel alloys whose iron oxide layers provide considerable protection against further corrosion have been developed for bold, unprotected exposures. The corrosion products on several non-ferrous metals (zinc, copper, and especially aluminum) tend to suppress the absorption of SO_2.

Moisture is always required for metal corrosion, each metal tending to have a critical humidity above which corrosion tends to accelerate. Depending on the specific metal, these critical humidities are in the range of 60 to 80 percent RH. The relative length of time a metal surface is wet ("time-of-wetness") is the single most important variable affecting the acceleration of corrosion by acidic deposition. Some workers (U.S. EPA 1981) have found that hygroscopic corrosion products (e.g., iron sulfate) cause metal surfaces to remain wet at lower RH than if these products were not present.

7.2.2 Stone

Stones composed almost entirely of calcium carbonate (limestone, marble, travertine, etc.) or stones whose cementing material is calcium carbonate are particularly vulnerable to damage from acidic deposition.

The attack of sulfur dioxide on such carbonate stones has been studied for over a century. Yet, no quantitative relationship has been developed between ambient SO_2 levels and resulting materials damage.

The general decay mechanism includes aerodynamic factors controlling delivery of SO_2 to the stone surface, oxidation of SO_2 to sulfate and the subsequent reaction with the carbonate surface, mechanical stress by which reaction products destroy the stone structure, and removal of the stone and its alteration products by rainfall and other weathering phenomena (Livingston and Baer 1983).

Although the primary air pollutants causing damage to stone are sulfur compounds, a comprehensive decay mechanism must include the roles of nitrogen compounds, carbon dioxide, and water. For the carbonate stone/sulfur compound system three general modes of attack pertain:

Gaseous SO_2

$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2 \qquad \text{(Step 1)} \qquad [7\text{-}4]$$

$$CaSO_3 + 1/2O_2 \rightarrow CaSO_4 \qquad \text{(Step 2)} \qquad [7\text{-}5]$$

Wet Deposition

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2O + CO_2 \qquad [7\text{-}6]$$

Dry Deposition is exemplified by the reaction between sulfates in particulate matter and calcium carbonate either in the form of sulfuric acid as in wet deposition, or in the form of ammonium sulfates (Stevens et al 1980).

$$(NH_4)_2SO_4 + CaCO_3 \rightarrow CaSO_4 + (NH_4)_2CO_3 \qquad [7\text{-}7]$$

$$NH_4HSO_4 + CaCO_3 \rightarrow CaSO_4 + NH_4HCO_3 \qquad [7\text{-}8]$$

The anhydrous $CaSO_4$ is hydrated to form gypsum, which is highly susceptible to surface erosion.

Humidity plays a key role in all aspects of the interactions of SO_x with carbonaceous stone. In autoradiographic experiments using sulfur-35, Spedding (1969b) showed surface saturation of oolitic limestone samples by SO_2 at 81 percent RH occurring in less than ten minutes. However, at the same concentrations but at 11 percent RH only a few distinct sites showed reaction after 20 minutes exposure, with approximately 25 percent of the total SO_2 uptake measured for the high humidity case. Tombach (1982) has summarized the factors contributing to stone decay as shown in Table 7-3.

TABLE 7-3. CLASSIFICATION OF MECHANISMS CONTRIBUTING TO STONE DECAY[a]
(ADAPTED FROM TOMBACH 1982)

Mechanism	Rainfall	Fog	Humidity	Temperature	Solar Insolation	Wind	Gaseous Pollutants	Aerosol
External Abrasion								
Erosion by wind-borne particles						●		●
Erosion by rainfall	●							
Erosion by surface ice	●	●		●				
Volume Change of Stone								
Differential expansion of mineral grains				●			o	
Differential bulk expansion due to uneven heating				●	●			
Differential bulk expansion due to uneven moisture content	●	●	●	●	●	o	o	o
Differential expansion of differing materials at joints				●				
Volume Change of Material in Capillaries and Interstices								
Freezing of water	●	●		●				
Expansion of water when heated by sun	●	●		●	●			
Trapping of water under pressure when surface freezes	●	●		●				
Swelling of water-imbibing minerals by osmotic pressure	●	●	●				o	o
Hydration of efflorescences, internal impurities, and stone constituents	●		●				o	o
Crystallization of salts			●	●	●	●	o	o
Oxidation of materials into more voluminous forms	●	●					o	
Dissolution of Stone or Change of Chemical Form								
Dissolution in rainwater	●			●			●	●
Dissolution by acids formed on stone by atmospheric gases or particles and water	●	●	●	●			●	●
Reaction of stone with SO_2 to form water-soluble material	●	●		●			●	
Reaction of stone with acidic clay aerosol particles	●	●		●				●
Biological Activity								
Chemical attack by chelating, nitrifying, sulfur-reducing or sulfur-oxidizing bacteria			●	●			●	
Erosion by symbiotic assemblages and higher plants that penetrate stone or produce damaging excretions	o	o	●	●				

[a]Solid circles denote principal atmospheric factors; open circles denote secondary factors.

7.2.3 Glass

Glass weathering is the process of removing alkali cations (e.g., Na^+ and K^+) from glass by reaction with water or sulfur dioxide. The reaction with water involves the exchange of sodium ions by hydrogen ions with the rate of reaction limited by the diffusion of sodium ions to the surface. The reaction with sulfur dioxide in the range 20 to 100 C in gas saturated with SO_2 involves the same process at approximately the same rate as with water alone (Douglas and Isard 1949).

7.2.4 Concrete

Cement, concrete, and steel reinforced concrete structures are all subject to complex actions reducing their durability. The alkaline nature of cement has led to general neglect of the effects of acid deposition and acidified water runoff on concrete/cement durability although it is recognized that any reaction reducing matrix alkalinity will be harmful. The role of chloride ion as a major contributor to corrosion of reinforced concrete is well established (Browne 1981, Volkwein and Springenschmid 1981). The alkalis in the hardened cement passivate the reinforcing steel while penetrating chlorides depassivate the iron. Other factors in corrosion of the steel include the development of electrolytic corrosion cells and the penetration of atmospheric O_2 through the concrete to the steel. The reaction of SO_2 and SO_4^{2-} with cement involves the formation of calcium sulfate and calcium sulfate aluminum hydrate (ettringite).

7.2.5 Organic Materials

Most organic materials exposed boldly to the atmosphere are quite resistant to the effects of acidic deposition. Deterioration of such materials is determined primarily by the effects of atmospheric oxygen, ultraviolet (UV) light, and atmospheric oxidants such as ozone. Painted surfaces are the most widely employed organic surfaces exposed to the atmosphere and to some degree are susceptible to acidic deposition. However, these effects are relatively minor when compared with natural environmental factors such as sun and precipitation (Haynie et al 1976).

Paint damage from acidic deposition is strongly related to the paint formulation. Such factors as the ratio of pigment and extenders to film forming ingredients determine the hardness, flexibility, and permeability of the surface. It has been shown that the presence of extremely high concentrations of SO_2, a reducing gas, can interfere with the drying process, which is an oxidation-polymerization reaction (Holbrow 1962). However, it is doubtful that SO_2 concentrations at the present time in any area of the United States would be high enough to cause this potential problem.

The most realistic mechanism for damage to paint by acidic deposition is reaction between acidic materials and pigments (e.g., ZnO)

and extenders such as $CaCO_3$. The long-term effect is the loss of paint surface through erosion.

The degradation of paper and textiles is dominated by three factors: light, humidity, and acidity. Paper and other cellulosic materials (e.g., cotton, linen, and rayon) are highly susceptible to acid hydrolysis at the glucosidic linkage in the cellulose chain. Among proteinaceous textile materials silk is most susceptible to damage by light. In bright light silks may lose 60 percent of their strength in as little as 8 weeks of exposure (Leene et al. 1975).

7.2.6 Deposition Velocities

Chemical reaction between exposed surfaces and air pollutants leads to removal of the pollutant from the atmosphere. Deposition rates are quantified using the expression:

$$\text{Flux} = V_g C \ , \qquad [7\text{-}9]$$

which relates the flux of a pollutant gas to a surface to the atmospheric concentration C above the surface. The deposition velocity, V_g, depends on the specific gas/surface combination. Other factors influencing V_g are humidity, surface roughness, air velocity, and turbulence. The determination of V_g is usually made by measuring the change in concentration above the surface or measuring the rate of deposition at the surface. Judeikis (1979) has compiled deposition velocities for various materials in contact with sulfur dioxide and ozone. Table 7-4 presents the deposition velocities for sulfur dioxide. (More extensive discussion of deposition processes can be found in Chapter A-7.)

7.3 DAMAGE TO MATERIALS BY ACIDIC DEPOSITION

A wide range of sensitive materials can be damaged by acidic deposition. However, this chapter will deal only with those choices that are judged to be economically and culturally most important. These material classes are:

- metals
- masonry
- paint and other coatings
- cultural property (historically and culturally valuable structures and objects)
- other materials (paper, photographic materials, textiles, and leather)

7.3.1 Metals

The position of metals in the electromotive series determines their relative reactivity. However, the solubility of the particular metal

TABLE 7-4. MEASURED DEPOSITION VELOCITIES FOR SO_2 ON VARIOUS SURFACES (COMPILED BY JUDEIKIS 1979)

Surface[a]	V_g (m min^{-1})[b]
Cement (5)	0.6 - 1.6
Limestone (6)	$\geq$ 0.021 - 0.63
Copper	$\geq$ 0.001 - 0.26
Leather (18)	> 0.1 - 0.2
Steel	$\geq$ 0.001 - 0.13
Fabric (2)	0.010 - 0.033
Wood (7)	0.016 - 0.031
Aluminum (2)	0.001 - 0.029
Gloss Paint	0.001 - 0.025
Asphalt	0.024
Carpeting (3)	0.005 - 0.014
Wallpaper (17)	0.002 - 0.010
Solid Floor Materials (25)	0.0003 - 0.003

[a]Number in parentheses indicates the number of different materials examined if greater than one.

[b]As defined by Equation 7-9.

salt and the stability of the metal oxide coatings that tend to form in the atmosphere determine metals' abilities to corrode as a result of acidic deposition. For example, aluminum is high in the series, but aluminum oxide coatings that form in the atmosphere resist corrosion even in the presence of significant amounts of acidic deposition. However, even aluminum may be pitted in atmospheres containing sea salt or large, acidic particles.

Thermodynamic considerations governing electrochemical corrosion are conveniently examined with the help of Pourbaix potential-pH diagrams. By plotting electrical potential against solution pH, regions of stability for various chemical species can be indicated. In simplified form, when reactions to form soluble species occur, one has "corrosion;" when the free metal is stable the region is designated "immune" to corrosion; and when a chemically stable oxide or salt film forms on the surface, leaving the metal resistant to subsequent attack, the region is one of "passivation" or mitigation of corrosion. Pourbaix (1966) has developed diagrams that show areas of stability, corrosion, and passivity for various combinations of electrode potential and pH, several of which are presented as Figure 7-1.

In using these diagrams to determine the effect of lowered pH on corrosion one must determine the potential attained by the metal in the natural environment. Moreover, reduced pH tends to increase the solubility of corrosion products. While the corrosion products in unpolluted atmospheres may be relatively insoluble, in polluted atmospheres quite different corrosion products may form which may be considerably more soluble. This potentially synergistic problem is sometimes overlooked in traditional writings on corrosion. The Pourbaix diagram can give much insight into this process. However, caution must be exercised in interpreting these diagrams because kinetic factors with non-equilibrium behavior may govern corrosion.

7.3.1.1 Ferrous Metals--Corrosion of iron and steel in polluted atmospheres has received a great deal of attention over the years. Steel, unless it is an alloy designed for unprotected exposure is usually coated by painting or plating (e.g., zinc) when used in outdoor exposures. Nevertheless, data on iron and steel corrosion provide valuable information on the relative importance of acidic deposition components and the mechanisms causing damage. The Pourbaix diagram for the iron system is presented as Figure 7-2. It illustrates the relationships among normal corrosion products and the equilibrium pH and potential conditions for their stability.

Some of the earliest work on the nature of iron corrosion in atmospheres containing acid gases and moisture was that of Vernon (1935). He showed that in the presence of SO_2 and moisture, iron corrosion proceeds from randomly distributed centers which he associated with the deposition of particulate matter.

As pointed out in Section 7.2.1, many theories have been advanced on the principle chemical reactions that describe iron and steel

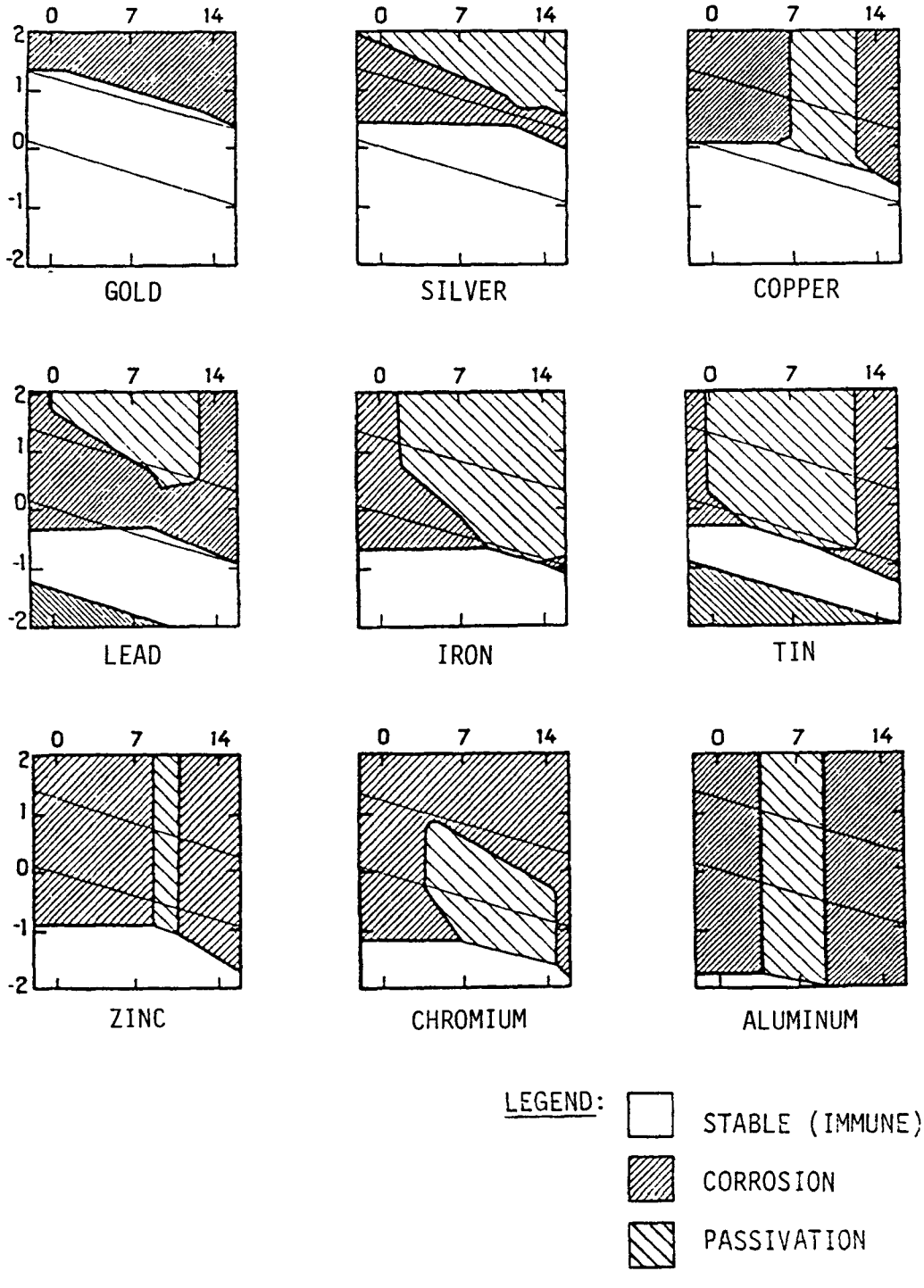

Figure 7-1. Pourbaix diagrams for various metals. The ordinate is in volts (electron potential standard hydrogen electrode) and the abscissa is in units of pH. The upper thin diagonal line is the O_2 evolution line while the lower ine is that for H_2 evolution. Adapted from Pourbaix (1966).

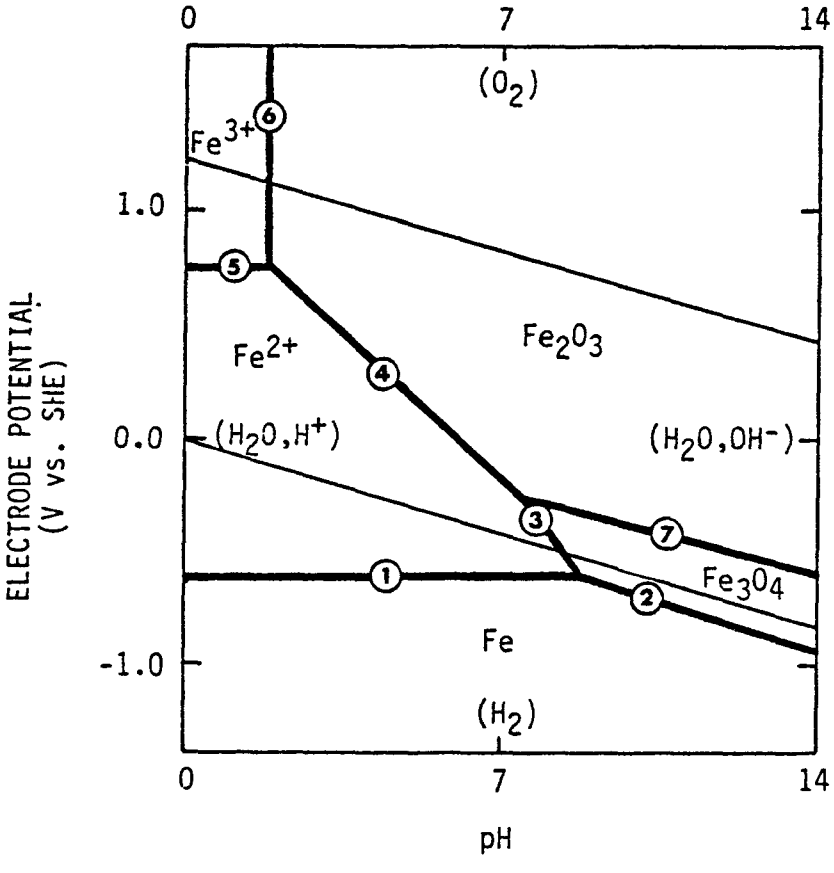

Figure 7-2. Pourbaix diagram for the system Fe, Fe^{2+}, Fe^{3+}, Fe_3O_4, and Fe_2O_3. The thin diagonal lines indicate regions of water stability. Compare with Figure 7-1 for designated regions of "corrosion," "immunity," and "passivation." The reactions considered are:

1) $Fe = Fe^{2+} + 2e^-$
2) $3Fe + 4H_2O = Fe_3O_4 + 8H^+ + 8e^-$
3) $3Fe^{2+} + 4H_2O = Fe_3O_4 + 8H^+ + 2e^-$
4) $2Fe^{2+} + 3H_2O = Fe_2O_3 + 6H^+ + 2e^-$
5) $Fe^{2+} = Fe^{3+} + e^-$
6) $2Fe^{3+} + 3H_2O = Fe_2O_3 + 6H^+$
7) $2Fe_3O_4 + H_2O = 3Fe_2O_3 + 2H^+ + 2e^-$

corrosion in the presence of SO_2 and moisture. Various chemical routes are possible and it is likely that several of them operate in actual atmospheric exposures.

According to Nriagu (1978), once corrosion has been initiated, the progress of the reaction is controlled largely by sulfate ions produced from the oxidation of absorbed or adsorbed SO_2. However, the actual mechanism of SO_2 oxidation on the surface is poorly understood. The work of Johnson et al. (1977) appears to show that sulfur or sulfates are only a minor constituent of the corrosion products of steel. Mild steel samples were exposed to two urban areas near Manchester. One area was heavily polluted, and the other was lightly polluted. Scanning electron microscopy, energy dispersive x-ray analysis, and x-ray diffraction analysis of corrosion products showed them to be predominantly $\gamma \cdot Fe_2O_3 \cdot H_2O$, α-$Fe_2O_3 \cdot H_2O$ and $\alpha \cdot FeOOH$. Some minor amounts of sulfur were found in a few of the samples. While not discussed in the article, the possibility exists that any sulfates formed were soluble and washed away. The relative amount of corrosion produced was strongly dependent on whether the sample was initially wet at the beginning of the exposure.

An iron oxide corrosion layer tends to reduce the rate of further corrosion of iron and steel. Nriagu (1978) and Sydberger (1976) showed that steel samples exposed initially to low concentrations of sulfur oxides were more resistant to further corrosive attack than samples exposed continuously to high concentrations. This suggests that the composition of the initial layer is critical in determining the nature and extent of subsequent corrosion.

7.3.1.1.1 Laboratory studies. Exposing iron and steel samples to SO_2 and moisture under controlled laboratory conditions has two prinicipal advantages:

1. The pollutant concentrations and other influencing factors can be independently controlled in a factorial experiment and permit the quantification of each factor's impact.

2. Exposure conditions can be made more severe than in nature to accelerate the corrosion effect, thereby reducing the duration of the experiment.

While many of the early experiments showed clearly that corrosion rates correlate with both SO_2 and humidity, exposure consisted of SO_2 concentrations many times higher than those found in the ambient atmosphere, or what are referred to as "reflux" conditions, where water and excess SO_2 were continuously flushing the surface of the samples.

The set of laboratory experiments most clearly approximating field conditions was conducted by Haynie et al. (1976). Various materials were exposed to controlled pollutant concentrations and moisture conditions at levels encompassing those found in ambient urban atmospheres. Sunlight and the formation of dew were also simulated.

Steel corrosion was determined in terms of weight loss of the steel panels by chemically removing the corrosion products, and the results showed a strong, statistically significant relationship between steel corrosion and SO_2 concentration, together with high humidity.

7.3.1.1.2 Field studies. A problem inherent with field studies is that iron and steel corrosion occurs even in unpolluted atmospheres, and the impact of specific acidic deposition scenarios is difficult to isolate completely. Therefore, the effects of acidic deposition can only be inferred by statistical treatment of the data.

Upham (1967) exposed mild steel samples in a number of sites in and around St. Louis and Chicago. He showed that corrosion correlated well with sulfur oxide levels and increased with length of exposure. Starting in 1963, Haynie and Upham carried out a five-year progam in which three different types of steel were exposed in eight major metropolitan areas in the United States. Multiple regression analyses showed significant correlations between average SO_2 concentrations and corrosion for all three types of steel. No attempt was made to relate damage to the joint occurrance of SO_2 and moisture (relative humidity or time-of-wetness).

In 1964, Haynie and Upham (1971) exposed steel samples for 1 and 2 years at 57 stations of the National Air Sampling Network. Pollutants of interest were SO_2, total suspended particulate matter, and the sulfate and nitrate content of the particulate matter. An empirical function was developed relating sulfate in particulate matter and humidity to corrosion. However, the authors believed that SO_2 rather than sulfate was the causative agent in producing corrosion, and the relationship was transformed into one based on SO_2 from a linear regression between sulfate and SO_2. The corrosion or damage function is:

$$cor = 325 \sqrt{t}\, e^{[0.00275\ SO_2 - (163.2/RH)]} \qquad [7\text{-}10]$$

where

cor = depth of corrosion, μm,
t = time, years,
SO_2 = SO_2 concentration, μg m^{-3},
RH = average annual relative humidity, percent.

Figure 7-3, based on the above damage functions, shows the relationship between pseudocorrosion rate (cor $\sqrt{t^{-1}}$), relative humidity, and SO_2 concentrations. This graph shows that the corrosion rate is much more sensitive to humidity than to SO_2, especially at levels of SO_2 normally experienced in urban areas.

For example, referring to Figure 7-3, if one were comparing relative corrosion at 55 percent relative humidity in two areas with average levels of 100 and 150 μg m^{-3}, a very significant difference in relative air pollutant levels, the difference in relative corrosion

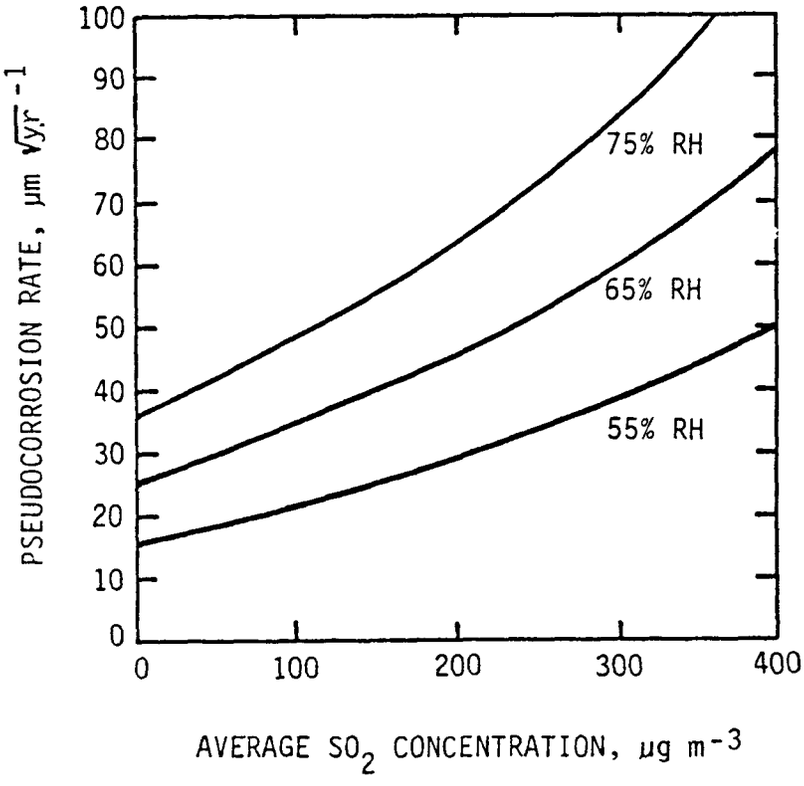

Figure 7-3. Steel corrosion behavior as a function of average sulfur dioxide concentration and average relative humidity. Adapted from Haynie and Upham (1974).

would be approximately three pseudocorrosion units. On the other hand, if one were comparing relative corrosion at a constant SO_2 level of 100 $\mu g\ m^{-3}$ between two areas with a moderate difference in average relative humidity (55 and 65 percent), the difference in relative corrosion rate would be approximately 15 pseudocorrosion units.

This damage function shows that the sensitivity of corrosion to humidity is far greater than that to SO_2, especially at levels of SO_2 normally experienced in urban areas.

A number of other damage functions relating steel corrosion to SO_2 and humidity (or time-or-wetness) have been developed by several other workers which have been summarized by EPA (1981) and Haagenrud et al. (1982). It should be noted that nearly all metal corrosion damage functions have been developed by regression analysis and do not include terms for precipitation.

A recent study of material damage in the St. Louis area in 1974-75 by Mansfeld (1980) included the use of special atmospheric corrosion monitors which measure the length of time that a corrosion panel was wet enough for electrochemical corrosion to take place (time-of-wetness). His sample exposure array included weathering steel, galvanized steel, house paint, and Georgia marble. Concentrations of SO_2 measured in this study were an order of magnitude lower than those measured in Upham's earlier study (Upham 1967). Mansfeld was unable to show any significant correlation between corrositivity and pollutant levels.

Some of the experiments of Vernon (1935) showed that moist air polluted with SO_2 and particles of charcoal produced corrosion much more rapidly than air containing SO_2 and moisture alone. He reasoned that the effect of the particles was primarily physical in that they increase the SO_2 concentration. Sanyal and Singhania (1956) stated that particulate matter had a "profound" effect on corrosion rates. They believed that the influence of particulate matter on corrosion was related to its electrolytic, hygroscopic and/or acidic properties, and its ability to absorb corrosive pollutant gases. While these laboratory studies appear to show a strong influence of particulate matter with corrosion, field studies have not confirmed this effect.

Haynie (1983) has attempted to address the effects of small particles on materials. Lacking a significant body of experimental data, he has approached the question theoretically, using data on deposition velocities. He considered four species of small particles: carbon, sulfuric acid, ammonium sulfates, and ammonium nitrate. He concludes that data from one study (Harker et al. 1980) confirmed the chemical models for damage, and based on calculated pollutant fluxes, SO_2-induced damage will tend to dominate over H_2SO_4 effects in most urban areas.

Measurement of the effects of pollutants associated with long-range transport (e.g., acid precipitation) as compared with locally generated

pollutants (e.g., primary pollutant gases) is just getting under way in the United States. The Scandanavians have been addressing this question for some years. In summarizing several year's work in Norway, Haagenrud (1978) states that monthly corrosion rates for carbon steel are strongly influenced by long-range transport of both acid precipitation and SO_2. However, episodes of precipitation of < pH 4.0 occur so seldom that these episodes do not strongly influence long-term corrosion rates. Similarly, episodes of high SO_2 concentration also affected monthly corrosion rates, but had little effect on long-term values because they occurred so seldom.

7.3.1.2 Nonferrous Metals--The corrosion rates of commercially important nonferrous metals in polluted atmospheres are generally less than those for steel but cover a wide range. Figure 7-4, from the work of Sydberger and Vannenberg (1972), shows adsorption of SO_2 with time at 90 percent relative humidity for iron and three nonferrous metals. Copper and aluminum have relatively low adsorption capacities for SO_2, confirming the lower sensitivity of these metals to attack by SO_2 in the presence of moisture.

These tests were carried out by exposing polished metal surfaces to the test conditions over very short exposure periods. While the results appear to confirm the relative sensitivity of these metals to acidic deposition and attack, the exposure conditions bear little relationship to real life conditions. Rice et al. (1982) point out that a pure metal surface rarely presents itself to the atmosphere for more than a few microseconds. Water is rapidly absorbed in the surface films and may exist as moisture clusters as pointed out in Section 7.2.1. Furthermore, corrosion products and salts from surface contamination (e.g., chlorides) greatly influence corrosion rates, principally through lowering of the critical humidity--the point where corrosion rates begin to accelerate.

Only limited evidence links NO_x with damage to non-ferrous metals, though a number of corrosion problems with telephone equipment have been traced to NO_x and high nitrate concentrations in airborne dust. In a laboratory study of nickel-brass wire springs, stress corrosion cracking was observed when surface concentrations of nitrate reached 2.1 mg cm^{-2} and RH was about 50 percent. To avoid the nickel-brass corrosion problem, zinc has been eliminated from the alloy, and the cooling systems for existing equipment have been modified to keep the RH below 50 percent in NO_x impacted areas (Harrison 1975).

Such damage to components in communications switch gear is an insidious problem because a simple malfunction can put a large system out of service.

7.3.1.2.1 Aluminum. Aluminum is quite resistant to SO_2-related acidic deposition. However, the presence of particulate matter may produce a pitted or mottled surface in the presence of SO_2 and moisture. In view of the reductions in emissions of SO_2 and particulate matter--especially larger particles or agglomerates that

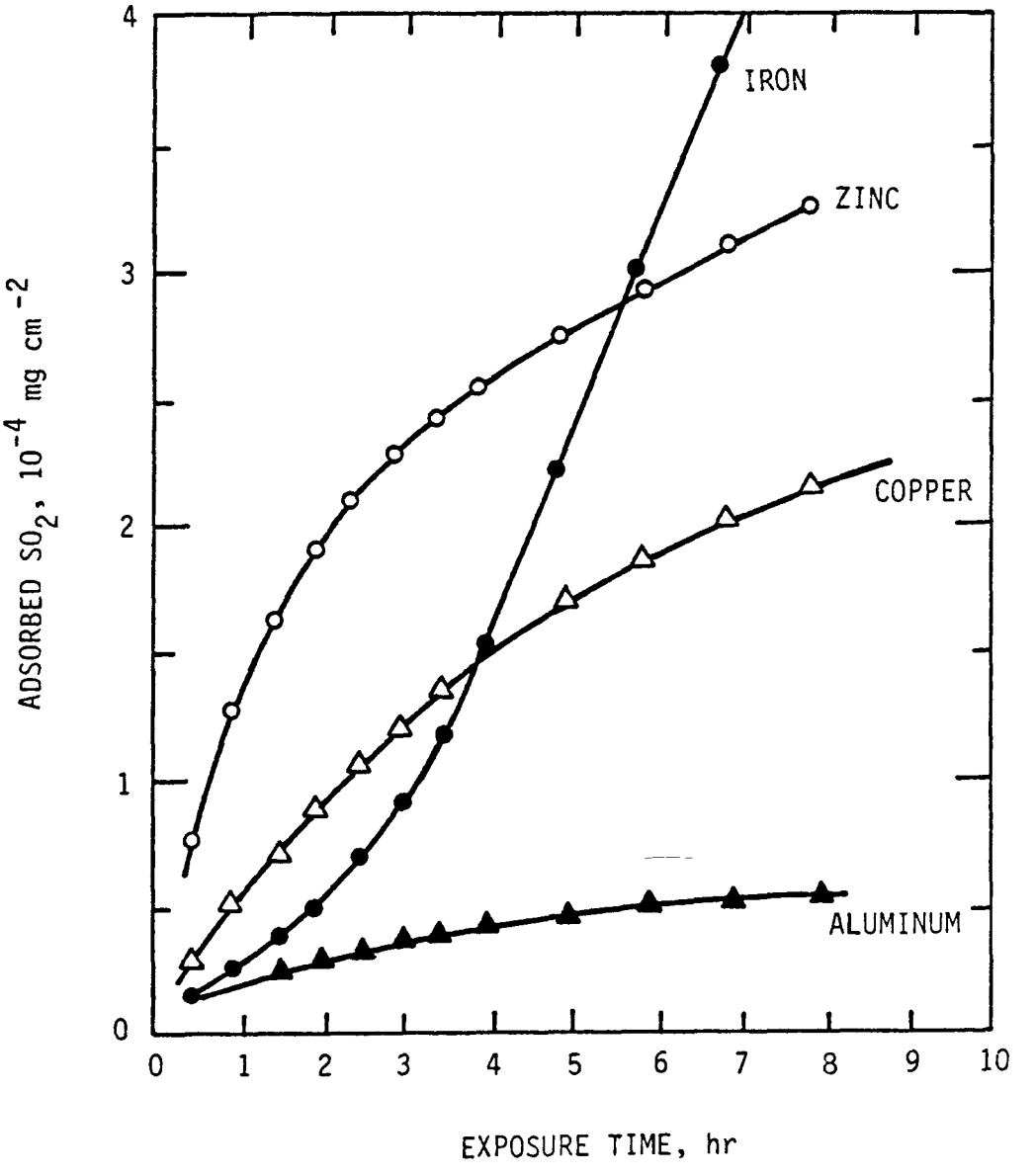

Figure 7-4. Adsorption of sulfur dioxide on polished metal surfaces is shown at 90 percent relative humidity. Adapted from Sydberger and Vannenberg (1972).

could act as centers for corrosion initiation--SO_2 related acidic deposition and surface corrosion of aluminum does not appear to be a significant problem (Fink et al. 1971).

7.3.1.2.2 Copper. Copper and copper alloys in most atmospheres develop thin, stable surface films, which inhibit further corrosion. Initial atmospheric corrosion is a brown tarnish of mostly copper oxides and sulfides that can thicken to a black film. Then in a few years, the familiar green patina forms. Analysis of this film indicates it to be either basic copper sulfate or, in marine atmospheres, basic copper chloride. However, in coastal urban areas, the sulfate may still predominate (e.g., the Statue of Liberty) because of the continuous availability of SO_2 over many years. Nevertheless, both the sulfate and chloride-based patinas are generally resistant to further attack (Yocom and Upham 1977).

7.3.1.2.3 Zinc. Zinc is used primarily for galvanizing steel to make it resistant to corrosion in the atmosphere and as an alloying metal with copper to produce brass. Zinc as a coating on steel is anodic with respect to steel such that when zinc and steel are in contact with eletrolyte, the current flow protects the steel from corrosion at the expense of some oxidation of zinc.

Because of its economic importance, the behavior of zinc in the presence of acidic deposition has been studied intensively by a number of workers. Guttman (1968) carried out long-term measurements of atmospheric corrosion of zinc from which he developed an empirical damage function for zinc corrosion in relation to SO_2 concentrations and time-of-wetness. Time-of-wetness was measured by means of a dew detector. SO_2 was measured by lead peroxide sulfation candles and conductiometric SO_2 measurements. His empirical damage function is

$$Y = 0.005461(A)^{0.8152x}\ (B + 0.02889), \qquad [7\text{-}11]$$

where

Y = corrosion loss, mg for a 3 x 5 in. panel,
A = time of wetness, hr,
B = atmospheric SO_2 content during the periods that the panels were wet, ppm.

Haynie and Upham (1970) carried out an extensive zinc corrosion study in eight cities where zinc panels were exposed, while concurrently collecting data on SO_2, temperature, and humidity. They developed the following empirical damage function relating zinc corrosion to SO_2 levels and relative humidity:

$$y = 0.001028\ (RH - 48.8)\ SO_2, \qquad [7\text{-}12]$$

where

y = corrosion rate, m yr^{-1},
RH = average annual relative humidity,
SO_2 = average SO_2 concentration, $\mu g\ m^{-3}$.

Note that in Equation 7-11 moisture is in terms of time of wetness while in Equation 7-12 annual average relative humidity is used. Time of wetness is a far more relevant indication of surface moisture than average relative humidity when corrosion and other forms of moisture-enhanced material damage are being considered. For example, if Equation 7-12 is applied in an area that has annual average relative humidity significantly less than 48.8 percent, no corrosion is implied. Yet in such areas, surfaces become wet with dew or seasons of high humidity occur and corrosion proceeds even when annual average relative humidity is below the critical value obtained by regression analysis.

The damage coefficients for these two functions plus functions developed from other studies were compiled by EPA (1981). These coefficients are compared in Table 7-5.

7.3.2 Masonry

The term "masonry" is applied to a large number of building and decorative materials exhibiting a broad range of surface activities to physical and chemical stresses imposed by the environment. The importance of acidic deposition to this class of materials may be related to the effect produced directly on a single material (e.g., limestone or marble) or direct or indirect damage to composite masonry systems. An example of direct damage to composite systems involves the rusting of steel reinforcing bars in concrete, which expand and crack the concrete. Indirect damage includes damage to brick-mortar systems in which the relatively reactive mortar is damaged directly by acidic materials and rainfall and then, the salts released by these reactions diffuse into the brick, causing stress and subsequent spalling.

7.3.2.1 Stone--The accelerated decay of stone buildings and monuments in highly industrialized areas has been documented by comparison of current condition with historic photographs and plaster casts. Photographs taken in 1908 and 1969 of a sandstone sculpture carved in 1702 in Westphalia, West Germany demonstrate a dramatic loss of material in the past 60 years with virtual obliteration of the object (Winkler 1982). Similarly, comparison of a plaster cast made in 1802 with a photograph taken in 1938 demonstrates substantial deterioration of a sculpture from the west frieze of the Parthenon (Plenderleith and Werner 1971). A detailed account of the restorations on the Acropolis and measurements of the thickness of gypsum layers formed on its exposed marble surfaces is presented by Skoulikidis (1982). The deteriorating condition of the Caryatids of the Erechthion led to their replacement with replicas and their removal to the controlled environment of the Acropolis Museum (Yocom 1979).

TABLE 7-5. EXPERIMENTAL REGRESSION COEFFICIENTS WITH ESTIMATED STANDARD DEVIATIONS FOR SMALL ZINC AND GALVANIZED STEEL SPECIMENS OBTAINED FROM SIX EXPOSURE SITES

Study	Time of wetness coefficient ($\mu m\ yr^{-1}$)	SO_2 coefficient[a] ($\mu m\ yr^{-1}/\mu g\ m^{-1}$	Number of data sets
Field Studies			
CAMP (Haynie and Upham 1970)	1.15 ± 0.60	0.081 ± 0.005	37
ISP (Cavender et al. 1971)	1.05 ± 0.96	0.073 ± 0.007	173
Guttman 1968	1.79	0.024	< 400
Guttman and Sereda 1968	2.47 ± 0.86	0.037 ± 0.008	136
St. Louis (Mansfield 1980)	2.36 ± 0.13	0.022 ± 0.004	153
Chamber Study			
Haynie et al. 1976	1.53 ± 0.39	0.018 ± 0.002	96

[a] 1 ppm SO_2 = 2620 $\mu g\ m^{-3}$ SO_2.

Few quantative studies of air pollution damage to stone have been reported although the increased rate of erosion for marble tombstones in the urban environment of Edinburgh was observed as early as 1880 (Geike 1880). A study of tombstones in U.S. National Cemeteries (Baer and Berman 1981) has developed methodology for measuring damage to marble headstones exposed to the environment for 1 to 100 years. Their data base consists of measurements of some 3,900 stones in 21 cemeteries distributed throughout the United States. The factors affecting damage rates include grain size, total precipitation, and local air quality.

In the United States, measured rates of marble deterioration have generally been small, on the order of 2.0 mm per 100 years (Winkler 1982). This is substantially below values reported for stones exposed in urban areas in Europe although direct comparison is difficult because the stones exposed in Europe are generally more reactive.

Comparing the condition of similar samples of sandstone exposed in different areas of Germany for about 100 years, Luckat associated large differences in observed deterioration with trends in local air quality (Luckat 1981, Schreiber 1982). These results presented in Table 7-6 describe stones openly exposed to the environment. For similarly reactive test stone specimens protected from the direct action of rain and placed at 20 locations in West Germany, the following functions correlating reaction with SO_2 immission rate were obtained:

Baumberg sandstone $U = 0.54\ D;\ r^2 = 0.92$ [7-13]

Krehnsheim shell limestone $U = 0.22\ D;\ r^2 = 0.72.$ [7-14]

When similar test samples were exposed to the rain the following damage functions were obtained:

Baumberg sandstone $L = 0.03\ D + 0.5;\ r^2 = 0.36$ [7-15]

Krensheim shell limestone $L = 0.018\ D + 0.6;\ r^2 = 0.80$ [7-16]

where:

U = SO_2 immission rate (uptake rate) of the stone in (mg m^{-2} d^{-1}) by weight gain,

D = by weight gain SO_2 immission rate, IRMA measured value (mg m^{-2} d^{-1}),

L = loss in weight, and

r = correlation coefficient.

The high contribution of the non-SO_x factors for stones exposed to rainfall suggests that damage functions for stone must specifically address such variables as other pollutants and rainfall.

TABLE 7-6. DETERIORATION OF SCHLAITDORF SANDSTONE EXPOSED FOR 100 YEARS IN WEST GERMANY (AFTER SCHREIBER 1982)

Monument	Location	Relative SO_2 immission Rate,[a] mg m^{-2}-day	Deterioration
Neuschwanstein Castle	Fussen	6	Practically none
Ulm Cathedral	Ulm	48	Moderate
Cologne Cathedral	Cologne	111	Very severe

[a]Relative immission or uptake rate of SO_2, annual average (August 1973 - July 1974) measured by IRMA method. (See Baer et al. 1983 for details of the technique.)

A series of measurements made at St. Paul's Cathedral, London on the Portland stone (biosparite limestone) balustrade, demonstrate a high rate of weathering (Sharp, et al. 1982). Using lead plugs filled in 1718 in openings in the stone as base level references, a mean rate of lowering of 0.078 mm yr^{-1} was obtained for the period 1718-1980. The balustrades represent conditions of exposed rain flow. Similarly, by use of a micro-erosion meter (dial micrometer gauge mounted on reference studs) a current erosion rate of 0.139 mm yr^{-1} was obtained for six sites on the cathedral. These sites represented drip erosion zones. Though the two sets of data are not strictly comparable, both represent substantially higher rates of loss than observed for marble in the United States.

7.3.2.2 Ceramics and Glass--Although enamels and glasses are quite resistant to chemical attack by air pollutants, in certain circumstances damage has been observed. In a three year exposure study on porcelain enamels placed in seven U.S. cities, some change in surface condition of the enamel was observed although the base metal was protected (Moore and Potter 1962).

Flourides, especially HF, are capable of attack on a wide variety of ceramic materials and glasses. Restrictive legislation on flouride emissions has, for the most part, eliminated fluoride induced damage.

Perhaps the most serious glass damage problems is that associated with the decay of medieval stained glass windows. The unique composition of these glasses combined with their open exposure to the atmosphere makes them particularly susceptible to deterioration. This problem is discussed in detail below.

Properly fired brick is highly resistant to attack by air pollutants while poorly fired brick is highly susceptible to chemical attack. Acidic solutions accelerate such damage, increasing the rate of reaction 10-fold over water alone. Residual sulfates from decay of mortars can combine with other salts to produce failure in brick (Robinson 1982).

7.3.2.3 Concrete--World production of concrete amounts to some 3 billion cubic meters per year. Many important structures, e.g., bridge decks, highways, military installations, and naval shore structures suffer from severe durability problems (NMAB 1980). Similarly, concern has been expressed over leaching of possibly toxic components of cement culverts transporting acidified water.

The highly alkaline nature of cement/concrete leaves such surfaces vulnerable to acidic deposition. Spedding (1969b), reporting on the contamination/decontamination of laboratory surfaces accidentally exposed to sulfur-35/sulfur dioxide, observed that good decontamination was obtained by simple water washing. This suggests that the reaction products of the deposition of SO_2 on concrete are water soluble. The high volume of water flow through rain collecting and distribution

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culverts in drinking water systems raises questions about the possible release of toxic materials leached from the concrete matrix.

Similar concerns have been expressed over the errosive effects of acidified streams on concrete bridge piers. The literature reveals only limited research on the effects of acidified water runoff on concrete durability.

Cements used in dams and culverts require a special formulation for sulfate resistance when exposed to concentrations in excess of 200 ppm in water (Nriagu 1978).

Specialized concretes in which sulfur replaces cement as the binding agent have been developed by the Bureau of Mines for resistance to acid and salt attack and damage to freeze-thaw cycling (Sulphur Institute 1979).

7.3.3 Paint

Paint consists of pigment and vehicle. Pigments, such as titanium dioxide and zinc oxide, provide color, hiding power, and durability. Sometimes fillers such as calcium carbonate or inorganic silicates are also added. The vehicle provides the film-forming properties of the paint and contains resin binders, solvents, and additives. Together, the pigment (along with fillers) and vehicle protect the underlying surface and enhance the appearance of the exposed surface. Air pollution may limit both of these functions by damaging the protective coating, thus exposing the underlying surface to attack and/or spoiling the appearance of the surface. The most important potential effects of SO_2 on paints are interference with the drying process and acceleration of the normal erosion process.

The primary effect of particulate matter on paint is soiling. Soluble salts such as iron sulfate contained in deposited particles can also produce staining. Chemically active large particles such as acid smut (or soot) from oil-fired boilers, mortar dust near building demolition sites, or iron particles from grinding operations can severely damage automotive paint (Yocom and Upham 1977). The effects range from discoloration of the paint film to corrosion of the underlying metal in the vicinity of individual particles. Large particles becoming imbedded in a freshly painted surface can act as wicks to transfer moisture and corrosive pollutants such as SO_2 to the underlying material's surface.

Holbrow (1962) has reported a number of experiments to determine effects of sulfur dioxide on newly applied paints. Drying time for various oil-based paints exposed to extremely high concentrations of SO_2 (1 to 2 ppm) was increased 50 to 100 percent. Thus far no experiments have been carried out on the effect of SO_2 on drying time of water-based latex paints.

Campbell et al. (1974) carried out an extensive study of paint erosion for a variety of paint types and exposure conditions (including SO_2 and O_3). Both chamber and field experiments were conducted. The researchers evaluated four important types of paint:

1. Acrylic latex and oil-based house paints,
2. Urea-alkyd coil coating for sheet metal in coil form,
3. Nitrocellulose-acrylic automotive refinishing paint, and
4. Alkyd industrial maintenance coating.

Table 7-7 presents the principal findings of this work.

Generally, exposures to high concentrations (1 ppm of both SO_2 and ozone) produced statistically significant erosion rate increases compared to clean air (zero pollution) conditions. Oil-based house paint experienced the largest erosion rate increases. The greater susceptibility of oil-based house paint to SO_2 was attributed to the use of extenders such as $CaCO_3$ or metal silicates. Latex and coil coatings experienced moderate increases, and the industrial maintenance coating and automotive refinish experienced the smallest increases. In general, exposures to sulfur dioxide produced higher erosion rates than ozone. Unshaded panels eroded more than shaded panels. Exposures to 0.1 ppm pollutants did not produce significant erosion rate increases over clean air exposures. It should be noted that even these lower concentrations are high when compared with average concentrations found in the ambient air of urban areas.

In the field portion of this same study, painted panels were exposed at four locations with different environments:

1. Rural - clean air (Leeds, North Dakota),
2. Suburban (Valparaiso, Indiana),
3. Urban - sulfur dioxide-dominant (Chicago, Illinois), and
4. Urban - oxidant-dominant (Los Angeles, California).

In most cases, southern exposures produced somewhat larger erosion rates, which agreed with the unshaded versus shaded results of the laboratory study. Oil-based house paint again experienced by far the largest erosion rate increases, followed in order by the urea-alkyd coil coating, latex house paint, industrial maintenance paint, and automotive refinish. Generally, the field exposures showed that the relative paint erosion rate was about the same for the sulfur dioxide-dominant as for the oxidant-dominant location which appeared to contradict the chamber studies. However, the authors believed that differences in the pollutant mix at the two locations and especially the presence of

TABLE 7-7.

PAINT EROSION RATES AND PROBABILITY DATA (T-TEST) FOR CONTROLLED ENVIRONMENTAL LABORATORY EXPOSURES (ADAPTED FROM CAMPBELL ET AL. 1974)

Type of Paint	Mean Erosion Rate (nm hr^{-1} with 95 percent confidence limits) for unshaded panels		
	Clean air control	SO_2 (1.0 ppm)	O_3 (1.0 ppm)
House paint			
oil	5.11 ± 1.8	35.8 ± 4.83[a]	11.35 ± 2.67[a]
latex	0.89 ± 0.38	2.82 ± 0.25[a]	2.16 ± 1.50[b]
Coil coating	3.01 ± 0.58	8.66 ± 1.19[a]	3.78 ± 0.64[b]
Automotive refinish	0.46 ± 0.02	0.79 ± 0.66	1.30 ± 0.33[a]
Industrial maintenance	4.72 ± 1.30	5.69 ± 1.78	7.14 ± 3.56

PAINT EROSION RATES AND PROBABILITY DATA (T-TEST) FOR FIELD EXPOSURES (ADAPTED FROM CAMPBELL ET AL. 1974)

Type of Paint	Mean Erosion Rate (nm hr^{-1} with 95 percent confidence limits) for panels facing south			
	Rural (clean air)	Suburban	Urban (SO_2 dominant), ~60 μg m^{-3}	Urban (oxidant dominant), ~40 μg m^{-3}
House paint:				
oil	109 ± 191	376 ± 124[a]	361 ± 124[b]	533 ± 157[a]
latex	46 ± 13	76 ± 18[a]	97 ± 8[b]	165 ± 142
Coil coating	53 ± 20	254 ± 48[a]	241 ± 20[a]	223 ± 43[a]
Automotive refinish	23 ± 28	58 ± 18[b]	41 ± 10	43 ± 10
Industrial maintenance	91 ± 41	208 ± 361[b]	168 ± 99	198 ± 61[a]

[a]Significantly different from control at p = 0.01.

[b]Significantly different from control at p = 0.05.

Note: 1 ppm SO_2 = 2620 μg m^{-3}

nitrogen oxides at the oxidant-dominant site could have enhanced the erosion rate at this location, bringing it up to the level of damage at the sulfur dioxide-dominated location (Campbell et al. 1974).

It is noteworthy that the oil-based house paint and urea-alkyd coil coating experienced the largest erosion rate increases in both the field and laboratory sulfur dioxide exposures. These coatings were the only ones that contained a calcium carbonate extender--a substance sensitive to attack by acidic materials.

Spence et al. (1975) summarized the results of paint exposure to several gaseous pollutants from the full-scale chamber studies reported by Haynie et al. (1976) and discussed earlier in relation to metal exposures. Four classes of painted surfaces were evaluated: oil-based house paint, vinyl-acrylic latex house paint, vinyl coil coating, and acrylic coil coating. A strong correlation was found between paint erosion for the oil-based house paint and SO_2 and humidity. The vinyl and acrylic coil coating were unaffected, but blistering was noted on the latex house paint. It was not certain if the blistering was the result primarily of SO_2 or moisture.

A multiple regression relationship was developed for the joint influence of SO_2 and relative humidity on the oil-based house paint:

$$E = 14.3 + 0.0151\ SO_2 + 0.388\ RH \qquad [7\text{-}17)$$

Where

E = erosion rate of $\mu m\ yr^{-1}$,
SO_2 = concentration of SO_2 in $\mu g\ m^{-3}$,
RH = means annual relative humidity in percent.

This relationship indicates that paint erosion is significantly more sensitive to changes in humidity than to SO_2. However, one must be careful in using models based on accelerated chamber tests for actual exposures because Equation 7-17 would predict that in an atmosphere with no SO_2 present, with an average relative humidity of 50 percent, the paint erosion rate would be about 34 $\mu m\ yr^{-1}$. Assuming a typical paint thickness of 50 μm, the paint film would be completely eroded away within 1.5 years.

The present understanding of damage to paint from air pollution is based primarily upon two sets of chamber studies and one set of field exposures. Since the field studies were carried out in the early 1970s, further laboratory and field studies are needed to determine the importance of paint damage from present levels of sulfur oxides. Furthermore, these studies should include present formulations (especially water-based paints) that may have a different response to air pollutants than those used earlier.

7.3.4 Other Materials

In addition to coatings, a wide range of organic materials are found to be susceptible to attack by atmospheric pollutants. These materials, including paper, photographic materials, textiles and leather were not considered in the EPA's Criteria Assessment Documents, so they are considered here although the indoor locations in which they are normally found dictate gaseous transport mechanisms for deposition.

7.3.4.1 Paper--The role of sulfur dioxide in the deterioration of paper has been accepted since the 1930's. Early experiments (Langwell 1952, 1953) relied on unrealistically high SO_2 concentrations of 5,000 ppm interacting with damp paper. Hudson and Milner (1961) used sulfur-35 as a radioactive tracer to demonstrate that measureable amounts of SO_2 were rapidly deposited in paper. Working with concentrations of 10 ppm, Grant (1963) showed that SO_2 deposition increased with increasing aluminum sulfate/resin sizing of the paper.

A comparative study of identical copies of twenty-five 17th and 18th century books in two English libraries, one in an unpolluted atmosphere in Chatsworth, the other in the badly polluted urban atmosphere of Manchester, revealed a significant increase in paper acidity in the Manchester library (Hudson 1967). This acidity was greatest at the page edges and decreased greatly toward the center of the page, which might be considered the initial sheet acidity.

Wallpapers form an important part of the indoor surface area available for SO_2 sorption. Spedding and Rowlands (1970) measured the sorption characteristics of PVC and conventional wallpapers on exposure to maximum initial SO_2 concentrations of 150 $\mu g\ m^{-3}$. Sorption depended largely on surface finish and design pattern, with greater sorption by conventional wallpapers. The researchers suggested that SO_2 sorption accelerated the deterioration of wallpaper.

7.3.4.2 Photographic Materials--Under normal conditions of temperature and relative humidity, paper, acetate film, and other photographic materials are oxidized at a very slow rate. One of the most serious factors in the preservation of photographic materials is the presence of large quantities of oxidizing gases: hydrogen sulfide, sulfur dioxide, and to a lesser extent NO_x, peroxides, formaldehyde, and ozone (Eastman Kodak 1979).

The effect of these pollutants is usually yellowing and fading of the silver of the image. The paper base may also be degraded and stained. Acidic gases will degrade gelatin, paper, and the film base of negatives (Eastman Kodak 1979).

Agfa produces a colloidal silver test strip which is 8 to 10 times more sensitive to gaseous pollutants than ordinary photographic materials. In a survey of major libraries and archives using this technique many examples of significant air quality problems were observed (Weyde 1972).

7.3.4.3 Textiles and Textile Dyes--Sulfur oxides are capable of causing deterioration to natural and synthetic fibers. Cotton, like paper, a cellulosic fiber, is weakened by sulfur dioxide. Under circumstances where sulfuric acid comes in contact with a cellulosic surface, the product of reaction is water soluble with little tensile strength (Petrie 1948). In field tests in St. Louis, cotton duck exposed to varying SO_x levels showed a direct relationship between loss in tensile strength and increasing SO_x concentration (Brysson et al. 1967). Zeronian (1970) exposed cotton and rayon fabrics under accelerated aging conditions of light and water spray with and without 0.1 ppm SO_2. Loss in strength was 13 percent in the absence of SO_2 and 22 percent in the presence of SO_2. In a study of nylon fabrics exposed to 0.2 ppm SO_2 under similar conditions, he found that nylon fabrics lost 40 percent of their strength under the SO_2 free conditions and 80 percent of their strength in the presence of SO_2 (Zeronian et al. 1971).

The degradation of nylon 66 by exposure to light and air is increased by the addition of 0.2 ppm of SO_2 to the air. Chemical properties, and yarn tensile properties both reflect this damage (Zeronian et al. 1973). Results demonstrated that the mode of degradation is not changed although SO_2 accelerates the rate of reaction.

Among proteinecous textiles, silk is most vulnerable to the effects of light, acidity, and sulfur dioxide, demonstrating much greater loss in strength than wool (Leene et al. 1975).

Damage to textiles has been attributed to NO_x (Harrison 1975). Such damage has been caused both by loss of fiber strength and fading of textile dyes. Significant reduction in breaking strength and increase in cellulose fluidity were observed for combed cotton yarns exposed in Berkeley, California, to unfiltered air when compared to exposure to carbon filtered air (Morris et al. 1964). Both sets of samples were unshaded and exposed at a 45° angle facing south. Though the authors did not isolate the effects of individual pollutants, they implied that compounds associated with photochemical smog, especially NO_x, were the probable cause of increased damage.

In an EPA chamber study of the effects of individual pollutants on 20 dyed fabrics, it was demonstrated that NO_2 at 0.1 to 1.0 ppm produced appreciable dye fading, and SO_2 at 0.1 to 1.0 ppm caused visible fading on wool fabrics (Beloin 1973). It was also concluded that higher temperatures and relative humidities increase dye fading and that the rate of fading as a function of exposure time appears to be nonlinear.

7.3.4.4 Leather--Michael Farady is attributed (Parker 1955) with having established in 1843 a link between the rotting of leather armchairs in the London Atheneum Club and sulfur dioxide emitted by its gas illumination. Plenderleith (1946), Innes (1948), and Smith (1964)

describe the sequence of chemical deterioration for leather and consider possible mitigative actions.

It has been observed that leather initially free of sulfuric acid will accumulate up to one percent acid by weight per year if exposure to an atmosphere containing SO_2. The mechanism is thought to involve the metal ion catalyzed conversion to sulfuric acid of the SO_2 absorbed by the collagen of the leather. Using sulfur-35 labelled SO_2, Spedding et al. (1971) showed that it is sorbed evenly over the leather surface, with the limiting factor in uptake being gas-phase diffusion to the surface.

7.3.5 Cultural Property

It has been estimated that the United States has over 6,000 museums, historical societies, and related institutions; more than 10,000 entries on the National Register of Historic Places, and in excess of 26,000 libraries and archives of substantial size (NCAC 1976). Light, oxidation, fluctuations in humidity, and chemical pollutants threaten this precious cultural heritage.

Damage to cultural property cannot be quantified in simple-dose-response terms. Just as an electrical component may require replacement due to corrosion of a fraction of its mass or stress-corrosion fracture may lead to failure of a mechanical system, damage to the texture of sculpture or the surface of a fresco exposed to the environment diminishes their aesthetic importance far in excess of the amount of material damage. Still more critical is the circumstance that, for most cultural property, replacement is impossible. What is lost is lost.

7.3.5.1 Architectural Monuments--Historic and artistic structures represent the single most visible aspect of our history and culture. For the United States, legislation providing a mandate for preservation began with the Antiquities Act of 1906, followed most recently by the Historic Preservation Act Amendments of 1980. In Canada, the Archaeological Sites Protection Act and the Historic Sites and Monuments Act were adopted in 1953.

Architectural monuments are universally threatened by the effects of pollution and urbanization as well as by weathering cycles and other natural phenomena (CCMS 1979). Although damage to these monuments is frequently attributed to acid precipitation, no clear evidence providing a cause and effect relationship between acid precipitation and damage to a specific monument exists. In general, it appears that while acidic deposition can effect significant damage to cultural property, the sources are predominantly of local origin.

7.3.5.2 Museums, Libraries and Archives--As discussed above, the sorption of SO_x and NO_x by organic materials in the indoor environment is well established. In some cases, as in paper and leather embrittlement, dye fading, and "red-ox" blemishes on microfilm, a direct

relationship between pollutant sorption and damage has been established. This has led major museums, libraries, and archives to install scrubbers for the removal of acid gases.

Among the systems in use are activated charcoal and Purafil (activated alumina impregnated with $KMnO_4$) dry scrubbers and alkaline wash wet scrubbers. Such systems have been introduced as part of new construction or retrofitted at the National Gallery (London), the Library of Congress (Washington, D.C.), the Newbury Library (Chicago), and the National Gallery (Washington, D.C.). Many other collections of cultural artifacts are preparing for the eventual retrofitting of their air handling systems to use scrubbers for removing air pollutants.

The universal nature of concern for the effects of polluted air on cultural property is reflected in a Japanese study of ambient and indoor SO_x and NO_x concentrations for buildings where important screen and panel paintings are housed (Kadokura and Emoto 1974). Six sites in Kyoto were investigated. Average concentrations for SO_x and NO_x were found to be about one-third of those in Tokyo. Seasonal concentrations for SO_x peaked in winter and were highest for a site near a dyeing factory whose liquid wastes emitted SO_2. The NO_x concentrations were found to be more evenly distributed throughout the city. Tight buildings showed higher NO_x levels indoors than were found for ambient conditions. Although they did not cite specific examples of damage, the authors called for protective measures to prevent air pollution damage to paintings.

7.3.5.3 Medieval Stained Glass--Some evidence exists that medieval stained glass exposed to the atmosphere has deteriorated more rapidly since World War II than in previous centuries. This accelerated deterioration has been attributed to the effects of air pollution (Frenzel 1971, Froedel-Kraft 1971, Korn 1971) because gypsum and syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$) are found in the weathering crust. However, such crusts are found even in locations with low SO_2 concentrations, suggesting that background SO_2 levels are sufficient to produce the sulfates observed. An alternative mechanism of decay suggests that storage of the windows under damp conditions during the war permitted the formation of a fissured hydrated layer that led to enhanced corrosion after reinstallation of the windows. The sulfates found in the weathering crusts are thought to be by-products of the deterioration process (Newton 1973).

A broad range of preservation techniques has been employed, including lamination, coating with inorganic and organic materials, and "isothermal glazing." In the latter process, the ancient glass is moved just inside the building and modern glass is placed in the grooves in the stone.

7.3.5.4 Conservation and Mitigation Costs--Some indication of the problem's magnitude is given by cost for mitigative actions taken for cultural property in West Germany (Table 7-8). Similar cost estimates exist for national preservation programs in the United Kingdom, Greece,

TABLE 7-8. ESTIMATED COSTS ASSOCIATED WITH AIR POLLUTION DAMAGE TO CULTURAL PROPERTY IN WEST GERMANY (AFTER SCHREIBER 1982)

Location	Objects	Measures	Period	Costs DM
Federal Republic of Germany	All municipal bronze monuments and sculptures	Desirable cleaning	Annual	4,000,000
	All metal sculptures in museums and open air	Desirable cleaning, conservation	Annual	1,000,000
	All medieval stained glass	Desirable conservation	10 year cost estimate	200,000,000-300,000,000
	Artifacts in museums	Air conditioning with air improvement	During construction	15% of construction costs
Munster	Castle facade	Cleaning, restoration, conservation	1965-1973	1,000,000
Cologne	Cathedral stained glass windows	Conservation	1978	448,000
Cologne	Cathedral facade	Cleaning, restoration, conservation	Annually 1977-1997	3,000,000-60,000,000 (estimated)
Freiburg	Cathedral stained glass windows	Restoration, conservation	1978	150,000
Ulm	Cathedral stained glass windows	Desirable restoration	Total cost	3,000,000

France, Italy, and the United States. For example, the Italian Parliment designated $200,000,000 in 1980 for a 5-year program to restore and maintain the ancient monuments in Rome (Hofmann 1981) and it is estimated by a British Parliamentary Committee that restoration of the fabric of the Houses of Parliament will cost up to £5,000,000 (International Herald Tribune 1980).

7.4 ECONOMIC IMPLICATIONS

The possibility of determining the economic costs of air pollution's damaging effects has long attracted environmental policy makers. If reliable cost estimates could be developed for such effects in relation to the pollutant levels that produced them, it then might be possible to compare the costs for achieving various levels of air quality control through emission control with the cost savings from reduced damage--a significant step toward developing cost-benefit relationships for air pollution control. The many attempts to estimate costs associated with air pollution-induced material damage have recently been summarized by Yocom and Stankunas (1980). Without exception, all of the generalized estimates of material damage costs related to all types of air pollution existing at the time of this review are of questionable value. The reasons for this include the following:

- As was pointed out earlier, it is usually not possible to isolate the specific portion of damage and therefore the associated costs created by a given air pollution effect.
- Improper assumptions and inaccurate estimates of the quantities of materials in place and exposed to pollutants.
- Unrealistic or improper scenarios of use, repair, and replacement of materials susceptible to air pollution damage, together with improper or inaccurate assignment of costs to the scenarios.
- Incomplete knowledge of substitution scenarios where more expensive material systems may replace more susceptible materials.
- Inadequate knowledge of the exposure conditions of susceptible materials, for example, coexistance of pollutants with other environmental effects such as moisture and temperature, and the physical aspects of exposure such as orientation and degree of sheltering.

A recent study by Stankunas et al. (1981) has addressed many of the above difficulties. In this study the quantities of potentially susceptible materials were determined within 357 randomly selected 100 x 100 foot square areas covering the Boston metropolitan area. Teams of observers using survey techniques determined the areas of various types of exposed painted surface, bare metal of several types, brick, stone, and concrete, and several other types of surfaces. Of the 357 areas

selected, 183 were found to contain manmade structures. The total areas of each material found at the survey sites were extrapolated to the entire Boston metropolitan area. Then, using air quality records for SO_2 in the Boston area, together with humidity data and published air pollution damage functions for given materials, the researchers computed the total damage to a given material for the entire area. In the case of painted surfaces, assumptions were made on the average thickness of typical paint films. Then costs were assigned to the increase in painting frequency, based on the SO_2-related increase in paint erosion, to arrive at a total SO_2-related damage cost to paint in the Boston metropolitan area. The excess painting costs for the Boston metropolitan area attributable to SO_2 damage for the year 1978 were estimated to be $31.3 million. This is equivalent to a per capita cost between $11 and $12. Costs for damage to zinc coated materials were two orders of magnitude lower.

Haynie (1982) estimated costs for damage to zinc-coated transmission towers and to galvanized roofing, siding, and guttering. Different approaches were used for transmission towers than for the other materials. Costs for transmission tower damage were based on a single group of towers serving the Colbert Steam Plant in the TVA system. Measurements were made by TVA of the thickness of the zinc coating at several points on 19 towers likely to be affected by SO_2 from the plant in question. Using SO_2/moisture damage functions for zinc corrosion and an estimate of how height above ground would affect SO_2 deposition velocity (based primarily on changes in wind speed with height), estimates were made of change in zinc thickness with time for the group of towers. Then, using several scenarios of painting, repair, and replacement, researchers estimated annualized costs for mitigating the effects of the damage, based on local SO_2 and humidity levels. Since TVA owned the towers, such costs could be internalized and were estimated to be 0.0028 mills/Kwh $\pm$ 0.0011 to be added to customers' electric bills. These estimates were based on an SO_2 concentration of 17 $\mu g\ m^{-3}$. If SO_2 levels were allowed to reach the ambient air quality standard of 80 $\mu g\ m^{-3}$, the annualized extra maintenance cost would rise to an estimated 0.0132 mills/Kwh $\pm$ 0.0052.

Cost estimates for damage to galvanized roofing, siding, and guttering required estimating the relative quantity of these materials in place. One of the complicating factors in making this determination was the trend in recent years of replacing bare galvanized materials exposed to the outdoor atmosphere with coil coated galvanized steel or bare aluminum. Various models were used to convert data on shipments of the materials in question and anticipated use of alternate materials to a realistic picture of the amount of bare galvanized materials in these categories in 1980. Damage functions for the effects of SO_2 and moisture on zinc, together with estimates for the thickness of zinc coatings and various maintenance scenarios and their costs were used to estimate per capita costs. These costs were computed to be in the range of $0.60 to $1.50 with the best estimate being $1.05 at an annual average SO_2 concentration of 30 $\mu g\ m^{-3}$. At the primary standard of 80 $\mu g\ m^{-3}$, the best estimate of per capita costs would be $1.80.

Such approaches as these should be refined and extended so that realistic estimates may be made of the total costs of damage from acidic deposition.

7.5 MITIGATIVE MEASURES

Assuming that acidic deposition produces significant damage to materials, the primary mitigative measure is to reduce the concentrations of acidic deposition components in the ambient atmosphere. However, as has been implied in the foregoing discussion, the relative amount of damage and associated costs from acidic deposition is not known. Therefore, at present there is no basis for a given degree of control of acidic deposition components and precursors that will eliminate or bring to acceptable levels the potential damage from this source.

Given that there is some degree of damage to materials from acidic deposition, a wide range of mitigative actions may be taken in response to damage. Table 7-1 listed several of these in relation to various material categories. The particular mitigative measure and whether it will be implemented will depend on many factors, including

- Physical and chemical nature of the material,
- Age and state of repair of the materials system,
- Availability and cost of substitute materials,
- Feasibility of isolating the object or surface of concern from the ambient environment,
- The importance of aesthetics in the appearance of the materials,
- The impact of damage on structural integrity, and
- The attitudes of those responsible for the objects made of the materials in question regarding the relative importance of the damage.

As stated earlier, material damage from acidic deposition is generally indistinguishable from damage caused by the natural environment. However, chemical analysis of corrosion or damage products can often distinguish various damage mechanisms. In general, superimposing acidic deposition on these natural phenomena only tends to shorten the time before some mitigative measure must be considered. It does not change the mitigative actions themselves. Thus mitigative measures taken to protect, replace, repair, and maintain materials exposed to the ambient environment will generally not change whether any acidic deposition has an effect. Only the frequency of implementing these measures will change.

7.6 CONCLUSIONS

From a review of the available literature on the effects of acidic deposition on materials the following conclusions are drawn:

- Several senarios and mechanisms exist for damage to materials from acidic deposition including both long-range transport and local source emissions (Section 7.1).

- Without question acidic deposition causes significant incremental damage to materials beyond that caused by natural environmental phenomena (Section 7.1).

- Because very few research efforts have attempted to isolate the effects of specific acidic deposition scenarios, it is presently impossible to determine quantitatively if any one scenario is more important than another in causing material damage. However, based on the juxtaposition of primary acidic pollutant (e.g., SO_2) sources and large quantities of susceptible material surfaces in urban areas, damage to materials from primary pollutants directly or in oxidized form together with surface moisture (e.g., condensed dew) is believed to be more due to acidic deposition than to acidified rain produced from long-range transport of pollutants and their reaction products (Section 7.2)

- Reliable cost estimates for material damage from acidic deposition are at present fragmentary because they deal with only selected material systems or linked geographical areas. Available estimates of total material damage costs on a nationwide basis are unreliable. There is a need for improved inventories of materials in place in various parts of the country (Sections 7.3 and 7.4).

- Damage to cultural property from acidic deposition is a complex problem because of the high value placed upon such objects, their often irreplaceable nature, and the wide range of material types represented. Highest priority should be placed on identifying and quantifying actual and potential damage to such artifacts and developing methods to prevent damage (Section 7.3.5).

- Further research directed at isolating damage caused by specific acidic deposition processes and identifying those processes that are most important and/or amenable to control is needed (Section 7.3).

- Studies that accurately assess damage costs associated with acidic deposition are needed (Section 7.4).

- Further research is needed in the development of mitigative measures such as reliable surface protection systems when damage has already been observed and when protection cannot wait for improvement in air quality (Section 7.5).

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