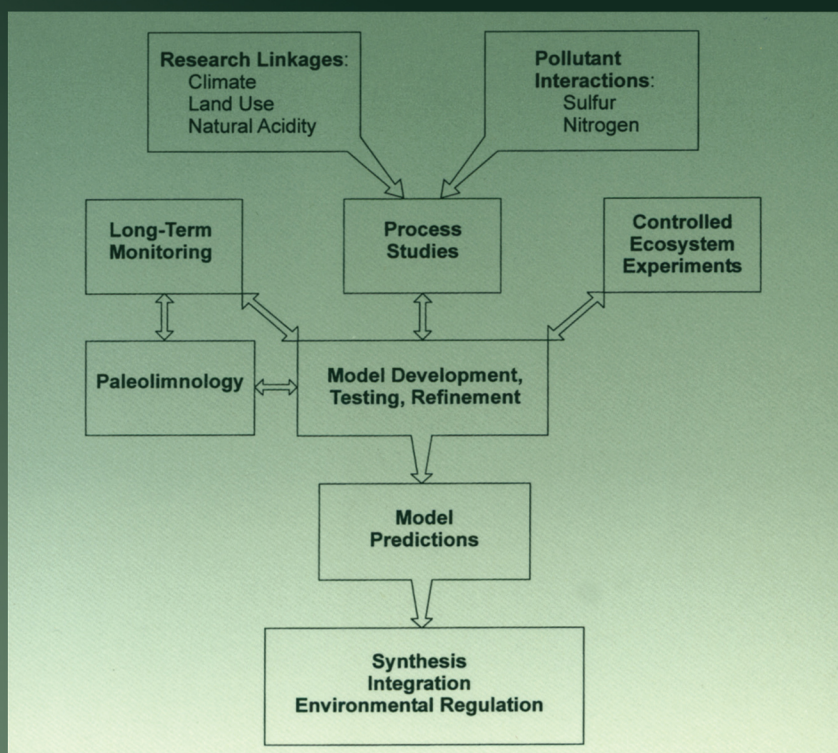


AQUATIC EFFECTS OF ACIDIC DEPOSITION



Timothy J. Sullivan



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To Debbie, Laura, and Jenna



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Acronyms

ABW	Absaroka-Beartooth Wilderness
AERP	Aquatic Effects Research Program
ALSC	Adirondack Lakes Survey Corporation
ALTM	Adirondack Long-Term Monitoring Program
ANC	Acid neutralizing capacity
ANC _G	ANC as measured by Gran titration in the laboratory
AQRV	Air quality related values
ASI	Acidic stress index
BMW	Bob Marshall Wilderness
CAAA	Clean Air Act Amendments
CALK	Calculated ANC
CCA	Canonical correspondence analysis
CEC	Cation exchange capacity
CLIMEX	Climate Change Experiment
DDF	Dry deposition factor
DDRP	Direct Delayed Response Project
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
ELS	Eastern Lake Survey
ELS-I	Phase I of the Eastern Lake Survey
ELS-II	Phase II of the Eastern Lake Survey
EPA	Environmental Protection Agency
ERP	Episodic Response Program
EXMAN	Experimental Manipulation of Forest Ecosystems in Europe Program
FADS	Florida Acid Deposition Study
FISH	Fish in Sensitive Habitats Project
FLAG	Federal Land Managers AQRV Group
FLM	Federal Land Manager
GLAC	Glacier National Park
GLEES	Glacier Lakes Ecosystem Experiment Site

GRTE	Grand Teton National Park
HBEF	Hubbard Brook Experimental Forest, NH
HUMEX	Humic Lake Acidification Experiment
IA	Integrated Assessment
IAG	Internal Alkalinity Generation Model
IAM	Integrated Assessment Model
ILWAS	Integrated Lake–Watershed Acidification Study
IWS	Integrated Watershed Study
LAC	Limits of acceptable change
LTM	Long-term monitoring program
LTRAP	Long Range Transboundary Pollution Program
MAGIC	Model of Acidification of Groundwater in Catchments
MAGIC-WAND	Model of Acidification of Groundwater in Catchments with Aggregated Nitrogen Dynamics
MERLIN	Model of Ecosystem Retention and Loss of Inorganic Nitrogen
MPCA	Minnesota Pollution Control Agency
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NDDN	National Dry Deposition Network
NIICCE	Nitrogen Isotopes and Carbon Cycling in Coniferous Ecosystems Model
NITREX	Nitrogen Saturation Experiments Program
NIVA	Norwegian Institute for Water Research
NLS	National Lake Survey
NPP	Net primary production
NPS	National Park Service
NSS	National Stream Survey
NSWS	National Surface Water Survey
NTN	National Trends Network
NuCM	Nutrient Cycling Model
OTA	Office of Technology Assessment
OWLS	Object Watershed Link System
PIRLA	Paleoecological Investigation of Recent Lake Acidification

PIRLA-II	Continuation of Paleoecological Investigation of Recent Lake Acidification
PRL	Proton reference level
PSD	Prevention of significant deterioration
QA/QC	Quality assurance/quality control
RADM	Regional Acid Deposition Model
RAIN	Reversing Acidification in Norway Project
RIA	Randomized intervention analysis
RILWAS	Regionalized Integrated Lake Watershed Acidification Study
RMSE	Root mean square error
ROMO	Rocky Mountain National Park
SAMI	Southern Appalachian Mountains Initiative
SBW	Selway-Bitterroot Wilderness
SNSF	Sur Nedbørs Virkning på Skog og Fisk (Acid Precipitation—Effects on Forest and Fish)—acidic deposition research program in Norway
SOS/T	State-of-Science/Technology Report
SWAP	Surface Water Acidification Program
TAF	Tracking and Analysis Framework
TOC	Total organic carbon
UN/ECE	United Nations/Economic Commission for Europe
USGS	U.S. Geological Survey
VTSSS	Virginia Trout Stream Sensitivity Study
VWM	Volume weighted mean
WACALIB	Weighted-averaging calibration
WLS	Western Lake Survey
WMP	Watershed Manipulation Project
WY	Water year
YBP	Years before present
YELL	Yellowstone National Park



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Acknowledgments

Aquatic Effects of Acidic Deposition covers a wide range of topics and scientific disciplines in which I have been involved in my own research over the last two decades. My interest in these areas of research has been stimulated by a large number of colleagues, many of whom are specialists in the various elements and fields of study covered in this book. This state-of-the-science summary was made possible by the concerted efforts of a great many scientists who provided the research foundation that I have summarized and by my interactions with them to enhance my understanding of the key elements that are discussed.

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Preface

In 1990, the U.S. National Acid Precipitation Assessment Program (NAPAP) completed the initial phase of what was then the largest environmental research program ever conducted. NAPAP research investigated the causes and effects of, and mitigation strategies for, acidic atmospheric deposition throughout the U.S. This massive environmental research and assessment effort took 10 years to complete, involved hundreds of scientists, engineers, and economists, and cost in excess of \$500 million. The scientific culmination of this research was embodied in a series of 27 State of Science and Technology (SOS/T) Reports that were published in 1990. In addition, a policy report was published in 1991 as the NAPAP Integrated Assessment. After 1990, research funding for work on acidic deposition effects decreased suddenly and substantially. However, many significant research programs were still in progress and/or not yet published, especially in the areas of aquatic effects of nitrogen and sulfur deposition. Results from these efforts appeared in the scientific literature during the early 1990s. In addition, a suite of research projects was initiated post-1990, albeit with somewhat lower funding levels than were common during the heyday of the NAPAP research program. These latter projects took advantage of the significant knowledge gains of the 1980s and, therefore, tended to be more focused and productive than earlier research efforts. Many addressed significant knowledge gaps that had been identified in the SOS/T reports, particularly regarding the interactions between acidic deposition and other sources of natural and anthropogenic acidity. As a consequence, a large body of scientific information related to aquatic effects of atmospheric nitrogen and sulfur deposition has been produced since publication of the SOS/T series of reports. New findings have added support to the state of scientific understanding in some areas, modified it in others, and led to the development of new paradigms and perspectives in still other areas of research.

The primary aim of this book is to summarize and synthesize major advancements since 1990 in the state of scientific understanding of the aquatic effects of atmospheric deposition of nitrogen and sulfur. It is intended to emphasize advancements in those aspects of aquatic effects research that are of direct policy relevance. Thus, topics concerning quantification of the magnitude of effects and recent developments in the area of predictive modeling capabilities are deemed to be of great importance, for the purposes of this book. Special attention is given to those aspects of aquatic effects research that had either been poorly studied pre-1990 or for which major research efforts have been completed in recent years. Topics of special interest include virtually all aspects of nitrogen effects research, as well as the importance of

natural sources of acidity, the influence of land use and landscape change on the chemistry of drainage waters, and the role of short-term episodic events.

This book is intended as a teaching resource and reference source. It provides a comprehensive update on the state of scientific understanding regarding an important environmental topic. It also illustrates the progression and refinement of the scientific knowledge base as research in this field has evolved from general basic research to more narrowly focused efforts aimed at answering specific questions. The target audience includes advanced students of environmental science and engineering and applied environmental practitioners. The latter group includes federal and state land managers and environmental stewards, many of whom are tasked with protecting sensitive natural resources from air pollution degradation and overseeing and prioritizing efforts to mitigate past damage. The wealth of recent knowledge gains summarized here will assist environmental professionals in making informed judgments regarding air pollution sensitivities, effects, and remediation.

The effects of atmospheric nitrogen and sulfur inputs to watershed systems, and the interactions between such inputs and other natural and anthropogenic features and stressors, provide an ideal framework for the study of upland hydrobiogeochemistry. Such study requires understanding of the key aspects of myriad disciplines and ecosystem compartments. Major components include mass balance input–output calculations, the study of hydrological flowpaths as water moves through the watershed system, and a wide range of interactions between drainage water and soils, geological substrates, and both terrestrial and aquatic biota. Understanding how hydrobiogeochemical processes and cycles govern the response of the entire watershed to atmospheric inputs and the associated interactions with natural features of the landscape, climate, and human disturbance aids our understanding of global ecosystems and the influence of human activities on ecosystem function and integrity.

Timothy J. Sullivan

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1

Introduction

1.1 1990 NAPAP Reports and Integrated Assessment

It is well known that emissions of sulfur and nitrogen from power plants, industrial facilities, and motor vehicles are linked to acidic deposition in many parts of the world. The potential effects of acidic deposition on human health and the environment became a major concern in the U.S. during the 1970s. Published reports linked acidic deposition with surface water acidification, fish kills, damage to crops and materials, and adverse effects on human health. The U.S. Congress considered actions to limit the emissions into the atmosphere of acid-forming precursor materials, including sulfur and nitrogen oxides, but information was limited regarding key processes and cause/effect relationships.

In order to provide sufficient scientific information with which to make the policy and regulatory decisions thought to be necessary for the protection of the environment and public welfare, Congress mandated a 10-year research program. The study was initiated under the Acid Precipitation Act of 1980 (PL 96-294, Title VII). An Interagency Task Force was established and the National Acid Precipitation Assessment Program (NAPAP) was started. NAPAP set out to answer important questions regarding the distribution of acid-sensitive natural resources and their degree of sensitivity, emissions and deposition of sulfur and nitrogen, source-receptor relationships and processes, the probable extent of damage and potential need for mitigation, and the availability of emission control technologies and mitigation options. Over the next 10 years, NAPAP was to spend over \$500 million and became, at the time, what was the largest environmental research program ever conducted.

NAPAP developed a complex research and assessment process that involved many hundreds of scientists throughout the U.S., Canada, and Europe. Major objectives were to identify the causes and extent and magnitude of the effects of acidic deposition. The culmination of the NAPAP process in 1990 included two major elements. A series of 27 State of Science and Technology (SOS/T) Reports was prepared to summarize NAPAP's technical findings. The SOS/T reports addressed the full spectrum of acidic deposition

issues, from emissions (SOS/T 1) through valuation (SOS/T 27). Of these reports, six covered aspects of acidic deposition aquatic effects (SOS/T 9 through 15) that were thought to comprise the most significant components of environmental impacts. The second major element that culminated the NAPAP effort was the Integrated Assessment (IA), a policy report to Congress that was published in 1991.

In 1990, as the NAPAP research program was winding down, Congress passed the Federal Acid Deposition Control Program as Title IV of the Clean Air Act Amendments. The objective of Title IV was to reduce the adverse effects of acidic deposition by reducing the emissions of sulfur dioxide in particular and to a lesser extent nitrogen oxides. Title IV stated that "reduction of total atmospheric loading of sulfur dioxide and nitrogen oxides will enhance protection of the public health and the environment." An annual 10 million ton reduction in SO₂ emissions below 1980 levels was mandated and targeted to electric utilities. In addition, a reduction in the emissions of nitrogen oxides of about 2 million tons from 1980 levels was specified. Upon full implementation of the control program, reductions of about 40% in SO₂ emissions and 10% in NO_x emissions from the 1980 base year are anticipated. There will be a national cap on the utility and industrial emissions of SO₂ at this level, but a national cap on the emissions of NO_x is not legislated, and NO_x emissions are projected to rise in the 21st century (NAPAP 1992). The Federal Acid Deposition Control Program includes an innovative market-based approach for achieving emissions reductions. Electric utilities have been given considerable flexibility in achieving reductions in efficient, cost-effective ways. Emissions allowances were issued to affected utility units based on their historic fuel consumption and rate of SO₂ emissions. Each allowance entitles a unit to emit 1 ton of SO₂ during or after the year specified on the allowance. Once allocated, allowances are marketable, allowing affected utilities to buy, sell, or bank allowances for future use (NAPAP 1992).

The first phase of implementation of the control program began January 1, 1995. About 260 units at the 110 highest emitting electric-utility plants in the eastern U.S. were allocated emissions allowances. Phase II began January 1, 2000, and will affect about 2300 electric generating units throughout the U.S., serving generators with capacities of 25 megawatts or greater. When the program is fully implemented in 2010, the annual allocation of emissions allowances will result in a national emissions cap of 8.9 million tons of SO₂ from utility units. Nonutility SO₂ emissions will be capped at 5.6 million tons per year.

NAPAP expected a number of environmental benefits in response to implementation of Title IV. Lakes and streams acidified by acidic deposition were expected to recover and support fish life. The risks of long-term soil degradation, ecosystem change, and loss of biological diversity were expected to be reduced. Average visibility was expected to improve, allowing for increased enjoyment of scenic vistas throughout the nation. Stresses on forest health were expected to decrease, particularly in red spruce forests along the ridges of the Appalachian Mountains (NAPAP 1991).

It is too early to judge the extent to which reductions in acid deposition in response to implementation of Title IV have or have not affected aquatic chemistry or biology. Chemical effects owing to changes in atmospheric deposition exhibit lag times of one to many years. Lags in measurable effects on aquatic biota can be longer. Continued monitoring of water quality for several years or more will be required to assess potential improvements that may occur as a consequence of emissions reductions already realized. It is clear that the concentrations of sulfate have decreased substantially in surface waters in many areas of the eastern U.S. It is expected that the concentrations of sulfate in surface waters will continue to decline in many areas, especially in the Northeast. However, the extent to which surface water acidity may be reduced in response to the expected continued decreases in sulfate concentrations as well as the extent to which biological recovery may be realized remains uncertain.

NAPAP was reauthorized under the 1990 Clean Air Act Amendments (PL 101-549, Title IX). Although the research activities of NAPAP have been completed, additional assessment efforts have continued (e.g., NAPAP 1992, 1998). Since 1990, aquatic effects research has also continued, albeit at a much lower level of effort than was seen during the 1980s. The recent research has been more heavily focused, however, and has benefitted from the substantial progress in understanding that was made during the heyday of acid deposition research funding of the previous decade. In many ways, the post-1990 research has been more efficient, and great strides have been made through relatively modest levels of research funding. Many of the knowledge gaps identified by NAPAP in 1990 have been filled in large part by a series of narrowly focused, carefully designed studies. This book attempts to bring together the key findings of these recent research efforts. By summarizing advancements in the state of the science of aquatic effects since 1990, this book contributes to NAPAP's ongoing assessment activities.

1.2 Scope

The scope of this book is limited mainly to the aquatic effects of acidic deposition. The NAPAP SOS/T reports included technical summaries for six major areas of aquatic effects research:

SOS/T 9 Current Status of Surface Water Acid-Base Chemistry (Baker et al., 1990a).

SOS/T 10 Watershed and Lake Processes Affecting Surface Water Acid-Base Chemistry (Turner et al., 1990).

SOS/T 11 Historical Changes in Surface Water Acid-Base Chemistry in Response to Acidic Deposition (Sullivan, 1990).

SOS/T 12 Episodic Acidification of Surface Waters Due to Acidic Deposition (Wigington et al., 1990).

SOS/T 13 Biological Effects of Changes in Surface Water Acid-Base Chemistry (Baker et al., 1990c).

SOS/T 14 Methods for Projecting Future Changes in Surface Water Acid-Base Chemistry (Thornton et al., 1990).

SOS/T 15 Liming Acidic Surface Waters (Olem, 1990).

This book summarizes recent advancements in scientific understanding that pertain mainly to areas addressed in the SOS/T Reports 9, 11, 12, and 14, with lesser treatment of areas addressed in the SOS/T Reports 10 and 13. Liming issues (SOS/T 15) are not addressed. The greatest attention is focused on recent findings in the U.S. Research elsewhere, especially in Europe, is discussed to the extent that it has complemented research in this country. An effort is made to summarize what is new in the understanding of the science of aquatic effects of acidic deposition, particularly in those research areas that have direct bearing on policy-relevant assessment activities. Research completed and published between 1990 and 1998 receives the greatest attention.

1.3 Goals and Objectives

The major goal of this book is to summarize important scientific findings regarding the aquatic effects of acidic deposition subsequent to publication of the State of Science and Technology Reports by NAPAP in 1990. Because the focus is on advancements in the science that are of direct policy relevance, improved modeling capabilities and improved understanding of acidification responses are of greater interest than specific advancements with respect to the understanding of acidification processes.

Specific objectives of the analyses reported here are to

1. Clarify current understanding of the extent to which lake and stream systems in the U.S. have experienced chronic acidification owing to acidic deposition.
2. Quantify acidification dose-response relationships for sensitive surface waters and recent advancements regarding specification of the critical loads of acidifying compounds required to protect sensitive aquatic receptors from adverse effects.
3. Describe improvements in predictive capabilities for aquatic effects and the results of model testing efforts.
4. Clarify current understanding regarding the relative importance of various causes of surface water acidification.

5. Describe recent advancements in the understanding of episodic acidification of surface waters.
 6. Describe the results of ecosystem manipulation experiments that have involved short-term increases or decreases in the levels of acidic deposition to forested plots or small catchments.
-

1.4 Outline of State of Science Update

Chapter 2 provides background material on acidic deposition, the major response variables of concern, and methods for evaluating acidification. Chapters 3 through 9 comprise a state of science update on advancements in acidic deposition aquatic effects research since 1990. The focus is on aspects of aquatic effects that have direct relevance to public policy. Special emphasis is given to advancements in the science that enhance our predictive capabilities and shed light on dose–response relationships and the establishment of critical loads of S and N for the protection of sensitive aquatic resources. Chapters 10 and 11 comprise case studies of two important acid-sensitive regions, one heavily impacted (Adirondack Mountains) and one highly sensitive but only minimally impacted to date (high-elevation portions of the Rocky Mountains and Sierra Nevada).

Chapter 3 covers advancements in the understanding of chronic acidification. The characteristics of sensitive systems are described. Causes of chronic acidification are reviewed and summarized, including an assessment of the relative importance of each.

Current understanding of the extent and magnitude of chronic surface water acidification is reviewed in Chapter 4 for the major acid-sensitive regions of the U.S. An assessment is provided of the sensitivity of aquatic resources to acidification from acidic deposition in each of the regions. Quantitative data are presented regarding the extent of acidification to date.

Chronic acidification chemical dose–response relationships are summarized in Chapter 5 for those sites for which such data are available. Recent steps toward the establishment of deposition standards or critical loads are described.

Chapter 6 addresses issues related to episodic acidification, short-term (hours to weeks) decreases in pH and ANC of surface waters in response to increased hydrologic discharge associated with snowmelt or rain events. Although less is known about episodic acidification than chronic acidification, it is thought that the biological impacts of acidification are most often first manifested as episodic, rather than chronic, processes. The characteristics of aquatic systems that are sensitive to episodic acidification are presented. The extent and magnitude of episodic acidification are summarized

to the extent that they are known. Finally, the major causes of episodic acidification and their relative importance are described.

Chapter 7 provides a summary of recent advancements in the scientific understanding of N dynamics and the aquatic effects associated with elevated N deposition. The N cycle is described, with particular emphasis on recent results from experimental field studies conducted during the past decade in Europe.

Chapter 8 summarizes the results of recent selected examples of whole-ecosystem experimental acidification and de-acidification studies. Many such experiments have been conducted in Europe and a few in the U.S. during the past decade. The results of these experimental manipulation studies provide invaluable quantitative dose-response data as well as a basis for extensive testing of predictive models.

Chapter 9 covers aspects of acidification modeling of aquatic effects. Selected new models are described for N effects modeling. Results of model testing activities for S effects modeling are described, including recent modifications to the MAGIC model, the principal modeling tool used thus far in the U.S. and Europe to predict chronic acidification responses on a regional as well as site-specific basis.

In Chapters 10 and 11, detailed case studies are presented for Adirondack Park, NY, and for national parks and wilderness areas of the West, with particular emphasis on Sequoia National Park, CA, and Rocky Mountain National Park, CO. A great deal of aquatic effects research has been conducted within these three parks during the last one to two decades. Discussion of major findings in these areas provides an excellent overview of recent scientific developments in this research field as well as important insights into key acidification processes.

Finally, in Chapter 12, major conclusions of the book are highlighted and topics for future work are considered. Significant remaining knowledge gaps in the state of scientific understanding are underscored. Major research and assessment needs are described.

It is hoped that the recently completed and ongoing research highlighted in this book will aid in the preparation of much improved NAPAP assessments in the years 2000 and 2010. Acidic deposition research developments provide an excellent example of the interconnections between environmental research and public policy. Formulation of sound environmental policy requires the kind of iterative research and modeling program that has been implemented for acidic deposition.

2

Background and Approach

2.1 Overview

2.1.1 Atmospheric Inputs

The approach taken for this book has been to review and summarize important results of aquatic effects research efforts undertaken or completed since 1990. The major emphasis is on the results presented in peer-reviewed publications in the scientific literature, although results of some agency reports are also discussed. Conclusions are drawn on the basis of a variety of assessment tools, using a weight-of-evidence approach, as followed by Sullivan (1990) and NAPAP (1991). Emphasis is placed on studies conducted in regions that contain large numbers of acid-sensitive aquatic systems. Regions in which aquatic resources are either not very sensitive or are primarily influenced by environmental perturbations other than acidic deposition receive less coverage.

The natural cycling of S, N, and C has been fundamentally altered by human activities across large areas of the earth since the last century. Both S and N have the capacity to acidify soils and surface waters. Nitrogen can also lead to eutrophication of lakes, streams, estuaries, and near-coastal ocean ecosystems and can cause reduction in visibility. Disruptions of the carbon cycle have caused increasing concerns about global climate change. A need has therefore arisen to develop a more complete scientific understanding of key processes that regulate elemental transport of S, N, and C among the various environmental compartments: atmosphere, soils, water, and biomass.

The term acidic deposition refers to deposition from the atmosphere to a surface of the hydrosphere, lithosphere, or biosphere (i.e., any portion of a watershed) of one or more acid-forming precursors. The latter can include oxidized forms of S and oxidized or reduced forms of N. Such atmospheric deposition occurs in several forms, the best understood of which is wet deposition, or deposition as dissolved SO_4^{2-} , NO_3^- , and NH_4^+ in rain or snow. A sizable component of the acidic deposition to a watershed can also occur in

dry form, when gaseous or particulate forms of S or N are removed from the atmosphere by contacting watershed features, especially vegetative surfaces. In some environments, particularly at high elevation, a substantial component of the total deposition of S and N occurs as cloudwater intercepts exposed watershed surfaces. Thus, the total deposition of S and N to a watershed includes wet, dry, and cloudwater (occult) deposition. The wet component is most easily measured of the three, and in most (but not all) cases it makes up the largest fraction of the total.

This chapter includes discussion of the primary chemical variables of concern in acidification research, historical water quality assessment techniques, and predictive models. It is important that each of these topics is understood in order to make sense of the state-of-the-science summary presented in Chapters 3 through 12.

We have a general idea of wet deposition levels of S and N throughout the U.S. on a regional basis, largely by virtue of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) of monitoring sites. However, few data are available from high-elevation sites where many of the most sensitive aquatic and terrestrial resources are located. In addition, knowledge is limited of the amounts of deposition other than wet deposition.

Some aspects of measuring air pollution and air pollution effects are evolving, and scientists remain divided with respect to appropriate assessment techniques. Among these topics is the measurement or estimation of atmospheric deposition in remote areas. The estimation of deposition of atmospheric pollutants in high-elevation areas is problematic, in part because all components of the deposition (e.g., rain, snow, cloudwater, dry-fall, and gases) have seldom been measured concurrently. Even measurement of wet deposition remains a problem because of the logistical difficulties in operating a site at high elevation. Portions of the deposition have been measured by using snow cores (or snow pits), bulk deposition, and automated sampling devices such as those used at the NADP/NTN sites. All of these approaches suffer from limitations that cause problems with respect to developing annual deposition estimates. The snow sampling includes results for only a portion of the year and may seriously underestimate the load for that period if there is a major rain-on-snow event prior to sampling. Bulk deposition samplers are subject to contamination problems from birds and litterfall and automated samplers have insufficient capacity to measure snowfall events.

Cloudwater, dryfall, and gaseous deposition monitoring further complicate the difficult task of measuring total deposition. Cloudwater can be an important portion of the hydrologic budget in forests at some high-elevation sites, and failure to capture this portion of the deposition input could lead to substantial underestimation of total annual deposition. Furthermore, cloudwater chemistry has the potential to be much more acidic than rainfall. Dryfall from wind-borne soil can constitute a major input to the annual deposition load of some constituents, particularly in arid environments. Aeolian inputs can provide a major source of acid neutralization, not

generally measured in other forms of deposition. Gaseous deposition is calculated from the product of ambient air concentrations and estimated deposition velocities. The derivation of deposition velocities is subject to considerable debate. In brief, there is great uncertainty regarding current deposition of atmospheric pollutants throughout much of the mountainous regions of the U.S.

Dry and/or occult (i.e., fog) deposition of major anions and cations can be extremely important components of the total atmospheric deposition to a watershed. At some locations, total deposition of S or N may be only slightly higher (e.g., less than 50%) than the measured wet deposition. This often seems to be the case in areas remote from major emission sources. Such a situation is not universally generalizable, however. The Bear Brook watershed in Maine provides a good example of particularly high levels of S deposition above what is recorded in precipitation. Rustad et al. (1995) calculated average water yields, after evapotranspiration, of 65 and 70%, respectively, for the East and West Bear Brook catchments. The volume-weighted average concentration of SO_4^{2-} in precipitation was about 26 $\mu\text{eq/L}$ from 1987 to 1991, and this should account for about 39 $\mu\text{eq/L}$ in runoff after adjusting for the water yield. However, the average SO_4^{2-} concentration in discharge actually measured 105 $\mu\text{eq/L}$ in both streams prior to the chemical manipulation of the West Bear Brook watershed. Rustad et al. (1995), Norton et al. (1999), and Kahl et al. (in press) concluded that the additional SO_4^{2-} was not from weathering of S-bearing minerals because there were no identified sources of sulfide in the watershed and because the $^{34}\text{S}/^{32}\text{S}$ ratio in streamwater was approximately the same as in the incoming precipitation (Stam et al., 1992). Furthermore, the watershed soils appeared to be generally adsorbing, rather than desorbing, S. Thus, Norton et al. (1999) concluded that dry and occult deposition delivered at least an additional 150% S to the watershed. This conclusion was further supported by the chemistry of fog samples collected at the watershed summit, which averaged 127 to 160 $\mu\text{eq/L}$ SO_4^{2-} during three years of study. Input/output data for other first order streams in Maine also suggested quite high levels of dry and occult deposition of S (Norton et al., 1988).

Dry and occult deposition of N are also undoubtedly high at the Bear Brook watershed. Norton et al. (1998) reported average fog concentrations of NO_3^- ranging from 56 to 64 $\mu\text{eq/L}$ and average concentrations of NH_4^+ ranging from 28 to 53 $\mu\text{eq/L}$ in 1989, 1990, and 1991. Mass balance calculations for N do not allow quantification of dry and occult inputs, however, because the forest canopy actively takes up deposited N.

Lovett (1994) summarized the current understanding of atmospheric deposition processes, measurement methods, and patterns of deposition in North America. National monitoring networks for wet and dry deposition, such as NADP/NTN and CASTNET, provide data for regional assessment. Model formulations are available for estimating deposition at sites where direct measurements are not available. The reader is referred to the review of Lovett (1994) for further details.

2.1.2 Sensitivity to Acidification

Surface waters that are sensitive to acidification from acidic deposition of S or N typically exhibit a number of characteristics. Such characteristics either predispose the waters to acidification and/or correlate with other parameters that predispose the waters to acidification. Although precise guidelines are not widely accepted, general ranges of parameter values that reflect sensitivity are as follows (Peterson and Sullivan, 1998):

Dilute—Waters have low concentrations of all major ions and, therefore, specific conductance is low (less than 25 $\mu\text{S}/\text{cm}$). In areas of the West that have not experienced substantial acidic deposition, highly sensitive lakes and streams are often ultradilute, with specific conductance less than 10 $\mu\text{S}/\text{cm}$.

Acid neutralizing capacity—ANC is low. Acidification sensitivity has long been defined as $\text{ANC} < 200 \mu\text{eq}/\text{L}$, although more recent research has shown this criterion to be too inclusive (Sullivan, 1990). Waters sensitive to chronic acidification generally have $\text{ANC} < 50 \mu\text{eq}/\text{L}$, and waters sensitive to episodic acidification generally have $\text{ANC} < 100 \mu\text{eq}/\text{L}$. Throughout the acid-sensitive regions of the western U.S., where acidic deposition is generally low and not expected to increase dramatically, ANC values of 25 $\mu\text{eq}/\text{L}$ and 50 $\mu\text{eq}/\text{L}$ probably protect waters from any foreseeable chronic and episodic acidification, respectively.

Base cations—Concentrations are low in non-acidified waters, but increase (often substantially) in response to acidic deposition. The amount of increase is dependent on the acid-sensitivity of the watershed. In relatively pristine areas, the concentration of ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+ + \text{Na}^+$) in sensitive waters will generally be less than about 50 to 100 $\mu\text{eq}/\text{L}$.

Organic acids—Concentrations are low in waters sensitive to the effects of acidic deposition. Dissolved organic carbon (DOC) imparts substantial pH buffering and causes water to be naturally low in pH and ANC, or even to be acidic ($\text{ANC} < 0$). Waters sensitive to acidification from acidic deposition in the West generally have DOC less than about 3 to 5 mg/L .

pH—pH is low, generally less than 6.0 to 6.5 in acid-sensitive waters. In areas that have received substantial acidic deposition, acidified lakes are generally those that had pre-industrial pH between 5 and 6.

Acid anions—Sensitive waters generally do not have large contributions of mineral acid anions (e.g., SO_4^{2-} , NO_3^- , F^- , Cl^-) from geological or geothermal sources. In particular, the concentration of SO_4^{2-} in drainage waters would usually not be substantially higher than could be attributed reasonably to atmospheric inputs, after accounting for probable dry deposition and evapotranspiration.

Physical characteristics—Sensitive waters are usually found at moderate to high elevation, in areas of high relief, with flashy hydrology and minimal contact between drainage waters and soils or geologic material that may contribute weathering products to solution. Sensitive streams are generally low order. Sensitive lakes are generally small drainage systems. An additional lake type that is often sensitive to acidification is comprised of small seepage systems that derive much of their hydrologic input as direct precipitation to the lake surface.

2.2 Chemical Response Variables of Concern

An important objective of this book is to quantify change in the principal chemical constituents that respond to atmospheric deposition of S and N. In order to standardize the voluminous information available from a variety of sources (e.g., paleolimnology, historical data, measurements of recent trends, empirical distributions, modeling, surveys, manipulation experiments), changes are typically presented proportionally, on an equivalent basis (e.g., the equivalent change in ANC \div the equivalent change in SO_4^{2-}). Such an approach facilitates quantification and intercomparison.

Several watershed processes control the extent of ANC consumption and rate of cation leaching from soils to drainage waters as water moves through undisturbed terrestrial systems. Of particular importance is the concentration of anions in solution. Naturally-occurring organic acid anions, produced in upper soil horizons, normally precipitate out of solution as drainage water percolates through lower mineral soil horizons. Soil acidification processes reach an equilibrium with acid neutralization processes (e.g., weathering) at some depth in the mineral soil (Turner et al., 1990). Drainage waters below this depth generally have high ANC. The addition of strong acid anions from atmospheric deposition allows the natural soil acidification and cation leaching processes to occur at greater depths in the soil profile, thereby allowing water rich in mobile anions to emerge from mineral soil horizons. If these anions are charge balanced by hydrogen and/or aluminum cations, the water will have low pH and could be toxic to aquatic biota. Thus, the mobility of anions within the terrestrial system is a major factor controlling the extent of surface water acidification.

2.2.1 Sulfur

Sulfate has been the most important anion, on a quantitative basis, in acidic deposition in most parts of the U.S. Consequently, sulfate and the controls on its inputs and processing have received the greatest scientific and policy

attention to date (Turner et al., 1990). Virtually all of NAPAP's major aquatic modeling and integration efforts leading up to the Integrated Assessment (NAPAP, 1991) focused predominantly on the potential effects of S deposition (e.g., Church et al., 1989; Turner et al., 1990; Baker et al., 1990a; Sullivan et al., 1990a). The response of S in watersheds, and to a lesser extent its chronic effects on surface water quality, are now reasonably well understood. This understanding has been developed largely through the efforts of three large multidisciplinary research efforts: the Norwegian SNSF program (Acid Precipitation Effects on Forests and Fish, 1972–1980), NAPAP (1980–1990), and the British-Scandinavian Surface Water Acidification Program (SWAP 1984–1990).

2.2.2 Nitrogen

The second important acid anion found in acidic deposition, in addition to sulfate, is nitrate. Nitrate (and also ammonium that can be converted to nitrate within the watershed) has the potential to acidify drainage waters and leach potentially toxic Al from watershed soils. In most watersheds, however, N is limiting for plant growth and, therefore, most N inputs are quickly incorporated into biomass as organic N with little leaching of NO_3^- into surface waters. A large amount of research has been conducted in recent years on N processing mechanisms and consequent forest effects, mainly in Europe (cf., Sullivan, 1993). In addition, a smaller N research effort has been directed at investigating effects of N deposition on aquatic ecosystems. For the most part, measurements of N in lakes and streams have been treated as outputs of terrestrial systems. However, concern has been expressed regarding the role of NO_3^- in acidification of surface waters, particularly during hydrologic episodes, the role of NO_3^- in the long-term acidification process, and the contribution of NH_4^+ from agricultural sources to surface water acidification (Sullivan and Eilers, 1994).

Until quite recently, atmospheric deposition of N has not been considered detrimental to either terrestrial or aquatic resources. Because most atmospherically deposited N is strongly retained within terrestrial systems, atmospheric inputs of N have been viewed as fertilizing agents, with little or no N moving from terrestrial compartments into drainage waters. More recently, however, N deposition has become quantitatively equivalent to S deposition in many areas owing to emissions controls on S, and biogeochemical N cycling has become the focus of numerous studies at the forest ecosystem level. It has become increasingly apparent that, under certain circumstances, atmospherically deposited N can exceed the capacity of forest and alpine ecosystems to take up N. This N saturation can lead to base cation depletion, soil acidification, and leaching of NO_3^- from soils to surface waters. Aber et al. (1989) provided a conceptual model of the changes that occur within the terrestrial system under increasing loads of atmospheric N. Stoddard (1994) described the aquatic equivalents of the stages identified by Aber et al. (1989),

and outlined key characteristics of those stages as they influence seasonal and long-term aquatic N dynamics. The N-saturation conceptual model was further updated by Aber et al. (1998).

2.2.3 Acid Neutralizing Capacity

Acid neutralizing capacity (ANC) is the principal variable used to quantify the acid-base status of surface waters. Acidic waters are defined here as those with ANC less than or equal to zero. Acidification is often quantified by decreases in ANC, and susceptibility of surface waters to acidic deposition impacts is often evaluated on the basis of ANC (Altshuler and Linthurst, 1984; Schindler, 1988). In regional investigations of acid-base status, ANC has been the principal classification variable (Omernik and Powers, 1982). Acid neutralizing capacity is widely used by simulation models that predict the response of ecosystems to changing atmospheric deposition (Christophersen et al., 1982; Goldstein et al., 1984; Cosby et al., 1985a,b; Lin and Schnoor, 1986). Historical changes in surface water quality have been evaluated using measured (titration) changes in ANC (c.f., Smith et al., 1987; Driscoll and van Drearon, 1993; Newell, 1993) or estimated by inferring past and present pH and ANC from lake sediment diatom assemblages (Charles and Smol, 1988; Sullivan et al., 1990a; Davis et al., 1994).

ANC is a measure of titratable base in solution to a specified endpoint. It is measured by quantifying the amount of strong acid that must be added to a solution to neutralize this base. The end point of this strong-acid titration would be easily identified except for the presence of weak acids and the relatively small amounts of strong base present in low-ANC waters. Together, these factors obscure the end point. For such systems, the Gran procedure (Gran, 1952) is commonly used to determine the end point and thus the ANC. ANC measured by Gran titration is designated ANC_G .

ANC can be calculated by two distinct methods that have been shown to be mathematically equivalent, using the principles of conservation of charge and conservation of mass (Gherini et al., 1985). In one method (Stumm and Morgan, 1981), ANC is calculated as the difference between the sum of the proton (H^+ -ion) acceptors and the sum of the proton donors, relative to a selected proton reference level:

$$ANC = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] + [\text{other proton acceptors}] - [H^+] \quad (2.1)$$

Here, brackets denote molar concentrations. The other method relates ANC to the total non-hydrogen cation concentrations, the individual uncomplexed cation charges (z_i) at the equivalence point (the point at which, during titration, the concentration of proton donors equals the concentrations of proton acceptors), the total strong-acid anion concentrations, and the individual uncomplexed anion charges (z_j), at the equivalence point (Gherini et al., 1985;

Church et al., 1984; Schofield et al., 1985). Using this approach, ANC is approximated with the following relation:

$$\text{ANC} = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] + [\text{NH}_4^+] + x[\text{Al}_T^{n+}] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-] - [\text{F}^-] \quad (2.2)$$

where brackets indicate molar concentrations. The charges z_i and z_j , and thus the concentration multipliers in Eq. (2.2) are determined by the predominant charges of the uncomplexed constituents at the equivalence point.

For most of the species, there is little uncertainty as to the predominant uncomplexed charge at the equivalence point. For example, the charge of calcium is 2+, and thus the multiplier is 2 in Eq. (2.2). However, because of complexation with OH⁻, F⁻, and organic ligands, the charge of Al, shown as x in Eq. (2.2), is not always obvious. Designation of the charge, however, establishes the proton reference level (PRL). Two PRLs have frequently been used for aluminum, 3+ and 0 (Cosby et al., 1985c; Church et al., 1984; Schofield et al., 1985). These levels have different advantages; the former yields results that are closer to ANC_G values; the latter eliminates the need to include Al in ANC calculations.

Data collected during the Regional Integrated Lake–Watershed Acidification Study (RILWAS; Goldstein et al., 1987; Driscoll and Newton, 1985) from 25 lake–watershed systems in the Adirondack Mountains of New York were used by Sullivan et al. (1989) to estimate the Al PRL. The speciation of Al was calculated using the chemical equilibrium model ALCHEMI (Schecher and Driscoll, 1994), and the equivalent charge on the Al species was determined. The mean charge on Al increases with decreasing pH. However, over the pH range from 4.8 to 5.2 that corresponds to the equivalence point of dilute waters (Driscoll and Bisogni, 1984), an Al charge of 2+ appears more representative than 3+ or 0 (Sullivan et al., 1989). This is equivalent to a PRL species for Al of Al(OH)²⁺ instead of Al³⁺ or Al(OH)₃⁰.

The difference between calculated and measured ANC_G values increases as organic-acid concentration, reflected by DOC, increases. The discrepancy between Gran titration ANC and calculated ANC caused by organic acid influence and/or differences in defining the proton references for Al have major implications for aquatic effects assessment activities. Gran ANC is used primarily for classification, evaluation of current status, monitoring of temporal trends, and calibration of paleolimnological transfer functions. Calculated ANC is used (defined in different ways) for dynamic model predictions (see, e.g., Reuss et al., 1986) and for interpretation of trends data in some instances. Unfortunately, the differences between the various definitions of ANC are seldom considered. These differences can drastically affect interpretation of chemical change (Sullivan, 1990). Both Al and DOC become increasingly important at lower pH and ANC values. For the lakes and streams of greatest interest, the acidic and near acidic systems, the influence of Al and/or DOC on Gran titration results is often considerable.

2.2.4 pH

pH is one of the major controlling variables for chemical and biological response. Biota respond strongly to pH changes and to chemical variables affected by pH (Schindler, 1988). pH (or more appropriately H^+ activity) has a large influence on other important chemical reactions such as dissociation of organic acids (Oliver et al., 1983) and concentration and speciation of potentially toxic Al (Driscoll et al., 1980; Dickson, 1980; Schofield and Trojnar, 1980; Muniz and Leivestad, 1980; Baker and Schofield, 1982). Thus, pH is certainly one of the most important variables to consider in assessing temporal trends in surface water chemistry. A difficulty, however, is that as groundwater emerges to streams and lakes, it is typically oversaturated with respect to CO_2 that combines with water to form carbonic acid and depresses solution pH. As excess CO_2 degasses from solution, the pH rises. Because of this instability in surface water pH, and the strong pH buffering of carbonic acid, ANC is often used preferentially over pH for documenting temporal change.

The previous discussion of ANC and pH illustrates four points, which obfuscate efforts at quantification of historical acidification (Sullivan, 1990):

1. ANC is often the chemical variable of choice for quantification of acidification because pH measurements are sensitive to CO_2 effects (Stumm and Morgan, 1981) and because pH change is not a reliable indication of acidification in waters that have not lost most or all bicarbonate buffering (Schofield, 1982).
2. Gran ANC measurements are easily interpreted, except in dilute waters having elevated concentrations of Al and/or organic acids (Sullivan et al., 1989). Unfortunately, these are often the waters of primary interest with respect to surface water acidification.
3. Mobilization of inorganic monomeric Al (Al_i) from soil to surface waters in response to increased levels of mineral acidity *does not* result in decreased ANC_G , although Al_i is biologically deleterious.
4. Quantification of acidification is routinely accomplished using ANC_G , and/or a variety of definitions of ANC (based on charge balance). These different approaches can yield radically different estimations of acidification for systems having elevated Al and/or DOC.

2.2.5 Base Cations

The ANC (and to a large degree pH) of surface waters lacking high-DOC concentrations is determined primarily by differences between the concentration of base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) and mineral acid anions. The extent to which base cations are released from soils to drainage waters in response to increased mineral acid anion concentrations from acidic deposition is perhaps the most important factor in determining concomitant change in pH,

ANC, Al, and biota. Principal factors that determine the degree of base cation release include bedrock geology, soil characteristics, soil acidification, and hydrologic pathways. The importance of base cation concentrations in regulating surface water ANC is discussed in detail by Baker et al. (1990a, 1991a).

Base cation release from the watershed is not the only aspect of base cation dynamics that is important with respect to acidification from acidic deposition. Significant amounts of base cations also are contributed to the aquatic and terrestrial systems from the atmosphere. Driscoll et al. (1989a) suggested that atmospheric deposition of base cations can have a major effect on surface water response to changes in atmospheric inputs of SO_4^{2-} . They presented a 25-year continuous record of the chemistry of bulk precipitation and stream water at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire. The decline in SO_2 emissions in the northeastern U.S. during that time period (National Research Council, 1986; Likens et al., 1984; Hedin et al., 1987; Husar et al., 1991) was reflected in a decrease in the volume-weighted concentration of SO_4^{2-} in wetfall. Stream-water SO_4^{2-} concentration also declined, but stream-water pH showed no consistent trend. On the basis of generally constant dissolved silica concentrations and net Ca^{2+} export (stream output less bulk precipitation and biomass storage), Driscoll et al. (1989a) concluded that changes in weathering rates were unlikely. The observed decline in atmospheric deposition of base cations explained most of the decline in the concentration of base cations in stream water. The processes responsible for the changes in base cation deposition were unclear, but the potential ramifications of these findings for acidification and recovery of surface waters are important.

Base cations are released from the bedrock in a watershed in amounts and proportions that are determined by the geologic make-up of the primary minerals available in the watershed for weathering. In the absence of acidic deposition or other significant disturbance, an equilibrium should exist between the weathering inputs and leaching outputs of base cations from the soil reservoir. Under conditions of acidic deposition, strong acid anions (e.g., SO_4^{2-} , NO_3^-) leach some of the accumulated base cation reserves from the soils into drainage waters. The rate of removal of base cations by leaching may accelerate to the point where it significantly exceeds the resupply via weathering. Thus, acid neutralization of acidic deposition via base cation release from soils should decline under long-term, high levels of acidic deposition. This has been demonstrated by the results of the experimental acidification of West Bear Brook (c.f., Kahl et al., in press).

Base cation depletion has been recognized as an important effect of acidic deposition on soils for many years and the issue was considered by the Integrated Assessment in 1990. However, scientific appreciation of the importance of this response has increased with the realization that watersheds are generally not exhibiting ANC and pH recovery in response to recent decreases in S deposition. The base cation response is quantitatively more important than was generally recognized in 1990.

As sulfate concentrations in lakes and streams have declined, so too have the concentrations of Ca^{2+} and other base cations. There are several reasons for

this. First, the atmospheric deposition of base cations has decreased in some areas in recent decades (Hedin et al., 1994), likely owing to a combination of air pollution controls, changing agricultural practices, and the paving of roads (the latter two affect generation of dust that is rich in base cations). Second, decreased movement of SO_4^{2-} through watershed soils has caused reduced leaching of base cations from soil surfaces. Third, soils in some sensitive areas have experienced prolonged base cation leaching to such an extent that soils have been depleted of their base cation reserves. Such depletion greatly prolongs the acidification recovery time of watersheds and may adversely impact forest productivity (Kirchner and Lydersen, 1995; Likens et al., 1996).

2.2.6 Aluminum

Aluminum is an important parameter for evaluation of acidic deposition effects in drainage systems because of its influence on ANC, and also because of its toxicity to aquatic biota (Schofield and Trojnar, 1980; Muniz and Leivestad, 1980; Baker and Schofield, 1982; Driscoll et al., 1980). Inorganic Al is mobilized from soils to adjacent surface waters in response to increased levels of mineral acidity (Cronan and Schofield, 1979). Processes controlling Al mobilization, solubility, and speciation are not well understood (Sullivan, 1994). In general, inorganic monomeric Al (Al_i) concentrations in surface waters increase with increasing H^+ concentration (decreasing pH), and are present in appreciable concentrations (greater than 1 to 2 μM) in drainage lakes and streams having pH less than about 5.5. Short-term temporal variations in Al_i concentration and speciation are determined by hydrologic conditions. Partitioning of runoff water between organic and mineral soil horizons and possibly reaction kinetics appear to be the most important determinants of runoff Al_i concentrations (Cronan et al., 1986; Neal et al., 1986; Sullivan et al., 1986; Sullivan, 1994).

Al_i cannot be measured directly, but is estimated based on operationally defined labile (mainly inorganic) and nonlabile (mainly organic) fractions (Driscoll, 1984). One procedure involves measurement of total monomeric Al (Al_m) by complexation with either 8-hydroxyquinoline (Barnes, 1975) or pyrocatechol violet (Seip et al., 1984; Røgeberg and Henriksen, 1985), followed by colorimetric determination, or sometimes in the case of 8-hydroxyquinoline complexation, atomic absorption spectroscopy. Nonlabile monomeric Al (Al_o) is measured in a similar fashion using a sample aliquot that has passed through a cation exchange column. Al_i concentration is then obtained as the difference between the concentrations of Al_m and Al_o .

For drainage lakes in the Adirondack Mountains of New York, an area that has experienced considerable surface water acidification, the concentration of Al_i is highly correlated with H^+ , as would be expected from solubility constraints. Based on analysis of data from Phase II of the Eastern Lake Survey (ELS-II, Herlihy et al., 1991), the relationship between Al_i and H^+ appears to vary seasonally, and Al_i is higher at a given H^+ concentration in the spring

than it is during the fall. This is attributable to seasonal differences in hydrology (e.g., related to spring snowmelt) and contact time of solution in the various soil horizons. It illustrates the limitation of mineral solubility equations for predicting Al_i concentration (Hooper and Shoemaker, 1985; Sullivan et al., 1986). The fall ELS-II data yielded the following relationship (Sullivan et al., 1990a):

$$[\text{Al}_i] = 0.75(0.26) + 0.41(0.02) [\text{H}^+] \quad r^2 = 0.92, \quad n = 33 \quad (2.3)$$

where brackets indicate concentrations, units are in μM , and standard errors of the parameter estimates are given in parentheses. During spring the relationship was equally significant ($p < 0.0001$, $r^2 = 0.94$), but the slope was 0.54 ($\text{SE} = 0.05$), considerably higher than that observed during fall.

Aluminum has also been implicated as a causal factor in forest damage from acidic deposition. The adverse, soil-mediated effects of acidic deposition are believed to result from increased toxic Al in soil solution and concomitant decreased Ca^{2+} or other base cation concentration (Ulrich, 1983; Sverdrup et al., 1992; Cronan and Grigal, 1995). Specifically, a reduction in the Ca/Al ratio in soil solution has been proposed as an indicator reflecting Al toxicity and nutrient imbalances in sensitive tree species. This topic was reviewed in detail by Cronan and Grigal (1995), who concluded that the Ca/Al molar ratio provides a valuable measurement endpoint for identification of approximate thresholds beyond which the risk of forest damage from Al stress and nutrient imbalances increases. Base cation removal in forest harvesting can have a similar effect and can exacerbate the adverse effects of acidic deposition. Based on a critical review of the literature, Cronan and Grigal (1995) estimated that there is a 50% risk of adverse impacts on tree growth or nutrition under the following conditions:

- Soil solution Ca/Al is less than or equal to 1.0.
- Fine root tissue Ca/Al is less than or equal to 0.2.
- Foliar tissue Ca/Al is less than or equal to 12.5.

Al toxicity to tree roots and associated nutrient deficiency problems are largely restricted to soils having low base saturation. The Ca/Al ratio indicator was recommended for assessment of forest health risks at sites or in geographic regions where the soil base saturation is less than 15%.

2.2.7 Biological Effects

Matzner and Murach (1995) summarized several of the current hypotheses regarding the impacts of S and N deposition on forest soils and the implications for forest health in central Europe. This region has experienced decades of extremely high levels of both S and N deposition, in many places three- to

five-fold or more higher than deposition levels in the impacted areas of the U.S. Despite needle losses in some areas, there has been a significant increase in forest growth in other areas (c.f., Kauppi et al., 1992). No simple causality between forest damage and air pollution has been identified in areas without large local emission sources. Matzner and Murach (1995) contended that an integrating hypothesis of regional effects of air pollution on forests is almost untestable because of the long-time lags in forest response, large number of natural and anthropogenic stresses that interact with each other, and long history of local forest management. Based on a review of the literature, these authors postulated that:

1. Al stress and low Mg supply in some forests of central Europe cause tree root systems to become more shallow and root biomass to decline.
2. High N deposition reduces fine root biomass and root length.
3. Changes in tree root systems in response to increased soil acidity and N supply will increase drought susceptibility of trees and is a major reason for needle and leaf losses in some areas.

The occurrence of acid stress is restricted to areas where soils are strongly acidified by S and N deposition and where past forest management practices have contributed to base cation depletion. Thus, Matzner and Murach (1995) saw no contradiction between the proposed links between air pollution and forest damage and the finding of Kauppi et al. (1992) that N surplus has resulted in increased forest growth in many areas of Europe.

Concentrations of root-available Ca^{2+} (exchangeable and acid-extractable forms) in forest floor soils have declined in the northeastern U.S. during recent decades (Shortle and Bondietti, 1992; Johnson et al., 1994). Lawrence et al. (1995) proposed that Al, mobilized in the mineral soil by acidic deposition, is transported to the forest floor in a reactive form that reduces Ca^{2+} storage and, therefore, its availability for root uptake. They presented soil and soil solution data from 12 undisturbed red spruce stands and 1 stand that has received experimental treatments of $(\text{NH}_4)_2\text{SO}_4$ since 1989. The stands, located in New York, Vermont, New Hampshire, and Maine, were selected to represent the range of environmental conditions and stand health for red spruce in the northeastern U.S. The Ca/Al molar ratio in B-horizon soil solution ranged from about 1 to 0.06, and was strongly correlated ($r^2 = 0.73$, $p < 0.001$) with exchangeable Al concentrations in the forest floor. Increased Al will potentially slow growth and reduce the stress tolerance of trees by reducing the availability of Ca^{2+} in the primary rooting zone (Lawrence et al., 1995).

Many species of aquatic biota are sensitive to changes in pH and other aspects of surface water acid-base chemistry. Such biological effects occur at pH values as high as 6.0 and above, but become more pronounced at lower pH, especially below 5.0. Individual species and life forms differ markedly in their sensitivity to acidification (Table 2.1). Biological effects on

fish are better understood than are effects on other aquatic life forms, but it is clear that virtually the entire aquatic ecosystem is affected when acidification is pronounced.

The most important chemical parameters that cause or contribute to the adverse effects of acidification on aquatic biota are decreased pH (increased H^+), increased inorganic Al, and decreased Ca^{2+} concentrations. Different species and stages in the life history of a given species differ in their tolerance to variations in these three critical parameters. For example, egg and larval stages are often more sensitive to H^+ and Al stress than are adult life stages. Both H^+ and inorganic Al are toxic to aquatic organisms, in some species at concentrations as low as 1 or 2 μM . Ca^{2+} ameliorates this toxicity.

Assessments of the effects of acidification on aquatic biota can be based on the results of laboratory toxicity studies, *in situ* exposure experiments, and the results of field surveys. Model projections of future changes in surface water chemistry can be evaluated in terms of their likely biological impacts via the use of toxicity models or models based on field distributional data. An assessment must first be made of the expected fish distribution in the absence of acidification. For example, brook trout habitat in the Southern Blue Ridge was defined by Herlihy et al. (1996) as those streams having elevation greater than 1000 m, stream gradient 0.4 to 17%, and Strahler stream order (1 : 24,000 scale) less than 4. Brook trout is considered an important fish species of concern because this species is native to many upland streams in the eastern U.S. that are acid-sensitive. Thus, by using a combination of an acid-base chemistry model and a fish response model, we can estimate the potential long-term effects of changes in acidic deposition on fish communities.

2.3 MONITORING

One of the best ways to study the hydrogeochemistry of forested watersheds has been through carefully designed monitoring programs. Unfortunately, monitoring has long been viewed by many scientists and funding agencies alike as rather routine, not exciting or cutting-edge, perhaps boring. It has not helped the situation that some monitoring programs have operated for years, blindly collecting data, without any critical examination, adherence to quality assurance/quality control (QA/QC) procedures, or consideration of how the resulting data could or should be used. Only recently has the value of high-quality, long-term monitoring become somewhat more widely recognized. Monitoring of the inputs (i.e., atmospheric deposition, precipitation) and outputs (i.e., evapotranspiration, streamflow, groundwater flow) to and from the watershed system provides a means of formulating hypotheses about watershed behavior, quantifying process rates, and testing the behavior of predictive models (Cosby et al., 1996; Church, 1999). The recent results

TABLE 2.1

General Biological Effects of Surface Water Acidification

pH Decrease	General Biological Effects
6.5 to 6.0	Small decrease in species richness of phytoplankton, zooplankton, and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive species (e.g., fathead minnow, striped bass)
6.0 to 5.5	Loss of sensitive species of minnows and dace, such as blacknose dace and fathead minnow; in some waters decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas Visual accumulations of filamentous green algae in the littoral zone of many lakes, and in some streams Distinct decrease in the species richness and change in species composition of the phytoplankton, zooplankton, and benthic invertebrate communities, although little if any change in total community biomass or production Loss of a number of common invertebrate species from the zooplankton and benthic communities, including zooplankton species such as <i>Diaptomus silicis</i> , <i>Mysis relicta</i> , <i>Epsichura lacustris</i> ; many species of snails, clams, mayflies, and amphipods, and some crayfish
5.5 to 5.0	Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass; as well as additional nongame species such as creek chub Further increase in the extent and abundance of filamentous green algae in lake littoral areas and streams Continued shift in the species composition and decline in species richness of the phytoplankton, periphyton, zooplankton, and benthic invertebrate communities; decrease in the total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters Loss of several additional invertebrate species common in oligotrophic waters, including <i>Daphnia galeata mendotae</i> , <i>Diaphanosoma leuchtenbergianum</i> , <i>Asplanchna priodonta</i> ; all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates Inhibition of nitrification
5.0 to 4.5	Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon; few fish species able to survive and reproduce below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters largemouth bass) Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling Substantial decrease in the number of species of zooplankton and benthic invertebrates and further decline in the species richness of the phytoplankton and periphyton communities; measurable decrease in the total community biomass of zooplankton and benthic invertebrates in most waters Loss of zooplankton species such as <i>Tropocyclops prasinus mexicanus</i> , <i>Leptodora kindtii</i> , and <i>Conochilus unicornis</i> ; and benthic invertebrate species, including all clams and many insects and crustaceans Reproductive failure of some acid-sensitive species of amphibians such as spotted salamanders, Jefferson salamanders, and the leopard frog

Source: Baker et al., 1990a.