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Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990

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Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990

U.S. Environmental Protection Agency
Office of Research and Development
National Health and Environmental Effects Research Laboratory
Research Triangle Park, NC 27711

Notice

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Dear Reader:

EPA's Office of Research and Development and collaborators are issuing a report, "Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990," EPA/620/R-02/004. This report suggests that a market-based approach to pollution control works. The positive results are a product of the 1990 Clean Air Act Amendments (CAAA), which utilize the successful market-based cap and trade program on which President Bush's Clear Skies Initiative is modeled.

The report concludes that the CAAA regulations have resulted in a large and widespread decrease in the deposition of wet sulfur. The amount of wet sulfur deposited in lakes and streams declined by approximately 40 percent in the 1990s for all of the regions. Regional declines in surface water sulfate can be directly linked to declines in emissions and deposition of sulfur that have occurred since the 1990 CAAA.

The 1990 CAAA required control measures for coal-fired power plants, industries, and other sources in an effort to reduce sulfur emissions that contribute to the development of acid rain. EPA and collaborators have conducted extensive monitoring and scientific assessment since 1990 to determine whether control measures have reduced levels of acidity in lakes and streams in five regions of the Northern and Eastern United States most affected by acid rain.

In three regions, one-quarter to one-third of lakes and streams previously affected by acid rain are no longer acidic. That's good news for the environment and good news for the market-based approach.

Sincerely,

Paul Gilman

Paul Gilman, Ph.D.
Assistant Administrator

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Table of Contents

List of Figures

List of Tables

EXECUTIVE SUMMARY

Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990

Purpose of this report. Title IV of the 1990 Clean Air Act Amendments (CAAA) set target reductions for sulfur and nitrogen emissions from industrial sources as a means of reducing the acidity in deposition. One of the intended effects of the reductions was to decrease the acidity of low alkalinity waters and thereby improve their biological condition. *The purpose of this report is to assess recent changes in surface water chemistry in the northern and eastern U.S., in response to changes in deposition.* The regions covered in this report are New England (sites in Maine, New Hampshire, Vermont and Massachusetts), the Adirondack Mountains of New York, the Northern Appalachian Plateau (New York, Pennsylvania and West Virginia), the Ridge and Blue Ridge provinces of Virginia, and the Upper Midwest (Wisconsin and Michigan). The data covered in this report are from 1990 through 2000, the period since the last major science review by the National Acidic Precipitation Assessment Program (NAPAP).

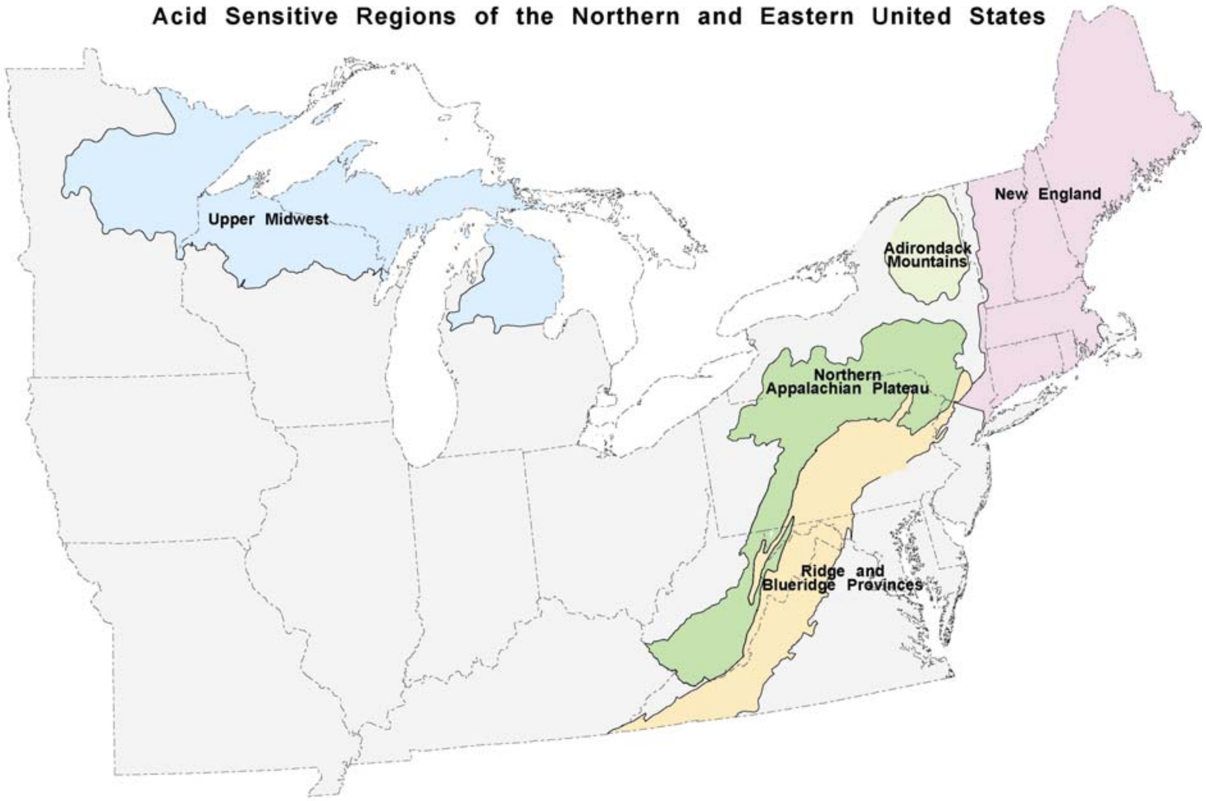


Figure A. Acid sensitive regions of the northern and eastern United States; this report assesses trends in surface waters in each of these regions.

Substantial reductions in emissions of sulfur have occurred in the past 30 years, with the rate of decline accelerated by Phase I of the 1990 CAAA, implemented in 1995. Modest reductions in nitrogen emissions have occurred since 1996. The key questions are (a) whether the declines in emissions translate into reductions in acidic deposition; and (b) whether biologically relevant water chemistry has improved in acid sensitive regions. The measures of expected recovery include decreased acidity, sulfate, and toxic dissolved aluminum concentrations.

Anthropogenic acidity in atmospheric deposition. NO_x and SO_x from the combustion of fossil fuels react with water in the atmosphere to produce acid rain, a dilute solution of nitric and sulfuric acids. This acidity (and the acid anions sulfate and nitrate) may travel hundreds of miles before being deposited on the landscape. The northern and eastern U.S. receives precipitation with mean pH that ranges from 4.3 in Pennsylvania and New York, to 4.8 in Maine and the Upper Midwest. The acidity (hydrogen ion concentration) in precipitation in the eastern U.S. is at least twice as high as in pre-industrial times. Atmospheric deposition is one of the most ubiquitous non-point sources of chemicals to ecosystems.

Acid-base status of surface waters. The 1984-86 EPA National Surface Water Survey (NSWS) estimated the number of acidic waters at 4.2% of lakes and 2.7% of stream segments in acid-sensitive regions of the North and East. Acidic waters are defined as having acid neutralizing capacity (ANC) less than zero (i.e., no acid buffering capacity in the water), corresponding to a pH of about 5.2.

This report addresses the recent chemical responses in the surface waters in five regions of the North and East that are considered sensitive to acidic deposition. The data in this report are largely from the EPA Long Term Monitoring (LTM) and the EPA Temporally Integrated Monitoring of Ecosystems (TIME) projects, part of EMAP (Environmental Monitoring and Assessment Program). The regions include lakes in the Adirondacks, central and northern New England, and the upper Midwest. Sensitive regions with small streams are found in the mid-Atlantic region, including the northern and central Appalachian Plateau and the Ridge and Blue Ridge provinces. Surface waters in most other regions are not sensitive to the impacts of acidification due to the nature of the local geology.

Recent changes in atmospheric deposition. We evaluated the changes in atmospheric deposition from the five regions during 1990-2000, using National Atmospheric Deposition Program (NADP) data. Sulfate declined significantly at a rate between -0.75 and -1.5 µeq/L/year. There was a sharp drop in sulfate concentrations in 1995 and 1996, followed by a modest increase in 1997-2000, in parallel with emissions. Nitrogen (nitrate + ammonium) declined slightly in the Northeast, and increased slightly in the Upper Midwest; most of these changes can be attributed to changes in nitrate deposition. Base cations in deposition, which are important for the neutralization of acidity in precipitation and in watersheds, showed no significant changes during the decade in the East, and increased slightly in the Upper Midwest. These changes in deposition are a continuation of trends that pre-date the 1995 implementation of Phase I of the CAAA, and are consistent with other recent published analyses of changes in regional deposition patterns.

Recent changes in acid base status in surface waters. All regions except the Ridge/Blue Ridge province in the mid-Atlantic showed significant declines in sulfate concentrations in surface waters, with rates ranging from -1.5 to -3 µeq/L/year (Figure B). These declines were consistent with the decline in sulfate in precipitation. Nitrate concentrations decreased in two regions with the highest ambient nitrate concentration (Adirondacks, Northern Appalachian Plateau) but were relatively unchanged in regions with low concentrations. Dissolved Organic Carbon (DOC) increased in each region, potentially contributing natural organic acidity to offset the recovery from decreased acidity and sulfate in deposition.

Acid neutralizing capacity is a key indicator of recovery, as it reflects the capacity of watersheds to buffer inputs of acidity. We expect increasing values of either ANC or pH (or both) in response to decreasing deposition of sulfur and nitrogen from the atmosphere. ANC increased in three of the regions (Adirondacks, Northern Appalachian Plateau and Upper Midwest) at a rate of +1 µeq/L/year, despite a decline in base cations (calcium + magnesium) in each region (Figure B). The decline in base cations offsets some of the decline in sulfate, and thus limits the increase in ANC or pH. In the Adirondacks and Northern Appalachians, surface water ANC and pH both increased significantly in the 1990s; toxic aluminum concentrations also declined slightly in the Adirondacks. Regional surface water ANC did not change significantly in New England or in the Ridge/Blue Ridge.

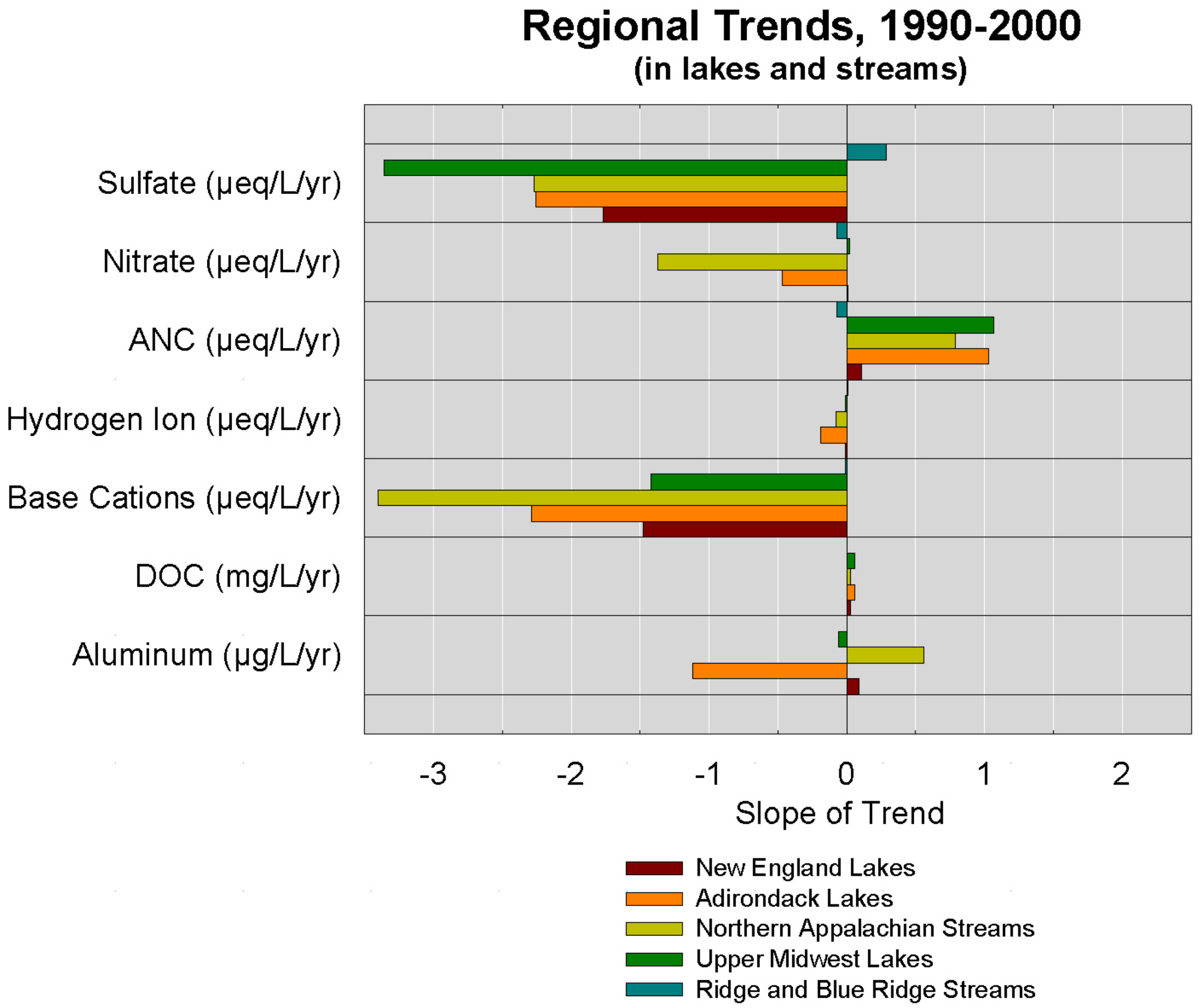


Figure B. Summary of regional trends in surface water chemistry in regions covered by this report.

Has the number of acidic waters changed? Modest increases in ANC have reduced the number of acidic lakes and stream segments in some regions. We estimate that there are currently 150 Adirondack lakes with ANC less than 0, or 8.1% of the population, compared to 13% (240 lakes) in the early 1990s. In the Upper Midwest, an estimated 80 of 250 lakes that were acidic in mid-1980s are no longer acidic. TIME surveys of streams in the northern Appalachian Plateau region estimated that 5,014 kilometers of streams (ca. 12%) were acidic in 1993-94. We estimate that 3,600 kilometers of streams, or 8.5%, remain acidic in this region at the present time. *In these three regions, approximately one-quarter to one-third of formerly acidic surface waters are no longer acidic, although still with very low ANC.* We find little evidence of a regional change in the acidity status of New England or the Ridge/Blue Ridge regions and infer that the numbers of acidic waters remain relatively unchanged. There is no evidence that the number of acidic waters have increased in any region, despite a general decline in base cations and a possible increase in natural organic acidity.

Do changes in deposition translate into changes in surface waters? A major goal of this assessment is to evaluate the effectiveness of emission reductions in changing surface water chemistry. We only make this assessment for sulfate because changes in the deposition of nitrogen have been minor. In New England, the Adirondacks and the Northern Appalachians, the percent declines in sulfate concentrations in precipitation were generally steeper than in surface waters. This is largely as expected and suggests that for a majority of aquatic systems, sulfate recovery exhibits a somewhat lagged response. However, the lakes and streams with the steepest declines in sulfate had very similar rates to those in deposition, indicating that the *most responsive* watersheds responded directly and rapidly to the sulfate decrease in deposition. As expected, there was little correspondence between rates of sulfate decline in streams and deposition in the Ridge and Blue Ridge provinces due to the adsorptive capacity of the soils in the region. In the upper Midwest, the rate of decline in lakes was *greater than* the decline in deposition, probably reflecting the residual effects of the drought of the late 1980s. Longer term, we expect the chemistry of seepage lakes in the Upper Midwest to mirror the decline in deposition, similar to the pattern seen in seepage lakes in New England that did not experience the 1980s drought.

Complications for assessing recovery. Declines in atmospheric deposition of sulfate have led to nearly universal declines in sulfate concentrations in surface waters. This response is one simple measure of the intended recovery in surface waters and marks a success of the CAAA and efforts by industry in reducing SO_2 emissions. However, the anticipated decrease in acidity corresponding to the decline in sulfate has been modest.

It is important to recognize that *recovery will not be a linear process*. Moreover, the changes in surface water chemistry reported here have occurred over very short periods relative to the implementation of the CAAA emission reductions in 1995. The decline in sulfate is without question due to the decline in emissions and deposition, but mechanisms producing other changes are much less clear. Other responses in surface waters may be partially attributable to factors other than atmospheric deposition, such as climate change and forest maturation. In particular, some of the observed increase in ANC may result from decreases in nitrate concentrations (e.g., in the Adirondacks and Northern Appalachian Plateau); changes in nitrate are unrelated to changes in nitrogen deposition and are not expected to continue. If the trend toward lower nitrate in surface water reverses, some of the gains in ANC may be lost.

We can identify at least five factors that are important in determining the recovery, or lack of recovery, in surface waters of the northern and eastern U.S. Continued long-term research and monitoring will be necessary to understand the causes, effects, and trends in these processes.

1) Base cations. We report declining surface water concentrations of base cations (e.g., calcium, magnesium) in all of the glaciated regions in this report (the Ridge and Blue Ridge region is the only non-glaciated region). At some individual sites, further acidification has occurred because base cations are declining more steeply than sulfate. While decreases in base cation loss from watersheds probably indicates slower rates of soil acidification, they nonetheless limit the magnitude of surface water recovery. Continued long-term research at acid-sensitive sites is needed to determine the cause and effect of the relationship between base cations and sulfate and the effects of cation loss on soil and surface water recovery.
2) Nitrogen. Continued atmospheric loading of nitrogen may be influencing the acid-base status of watersheds in yet undetermined ways. Unlike sulfate, concentrations of nitrogen in deposition have not changed substantially in 20 years. Also unlike sulfate, most nitrogen deposited from the atmosphere is retained in watershed soils and vegetation; nitrogen sequestration is not expected to continue *ad infinitum* (Stoddard 1994, Aber et al., in press). We report that surface water nitrate concentrations are largely unchanged, except in two regions characterized by high nitrate concentrations a decade ago (Adirondacks, Northern Appalachian Plateau). The mechanisms behind these decreases in nitrate are not understood and could include climate change, forest recovery from disturbance, and the effects of land-use history. Future increases in nitrate concentrations in all regions are not improbable and would retard recovery if other factors remain constant.
3) Natural organic acidity. Increases in dissolved organic carbon in acid-sensitive waters may have contributed additional natural organic acidity to surface waters, complicating our interpretation of the response in acidity. This factor is an important long-term research question that is probably linked to complex issues including climate change and forest maturation.
4) Climate. Climatic fluctuations induce variability in surface water chemistry and thus obscure changes that we expect to result from declining acidic deposition. Climate or climate-related processes may counteract recovery by producing declines in base cations to offset a decline in sulfate or by inducing an increase in natural organic acidity. These interactions of factors underscore the need to continue monitoring a subset of sensitive systems so as to understand the full suite of drivers and responses in ecosystems.
5) Lag in response. Documentation of the response of watersheds to changes in atmospheric deposition may take longer than the timeframe of available data. Recovery itself may have an inherent lag time beyond the time scale of currently available monitoring data. Moreover, the changes observed are not unidirectional. Uncertainty with respect to timeframes can only be resolved with continued long-term data.

Indicators of recovery. A main goal of the Title IV of the CAAA is to decrease the acidity of affected surface waters. Although decreases in acidity have occurred in several regions, additional factors appear to point toward recovery, *forecasting* an improvement in biologically relevant surface water chemistry. It is not yet clear if further reductions in emissions and deposition will be necessary for widespread recovery to occur. These factors forecast the onset of recovery:

a) Sulfate is an increasingly smaller percentage of total ion concentration in surface waters.

b) ANC has increased modestly in three of the five regions.

c) Dissolved Organic Carbon has increased regionally, perhaps toward a more natural pre-industrial concentration as acidity decreases in surface waters.

d) Toxic aluminum concentrations appear to have decreased slightly in some sensitive systems.

Expectations for recovery. An important consideration for measuring the success of the CAAA is to have appropriate expectations for the *magnitude* of potential recovery. Lakes inferred to have been measurably acidified by atmospheric deposition were already marginally acidic, typically with pH less than 6, before anthropogenic atmospheric pollution began more than 100 years ago. Therefore, full recovery of acidic lakes will not yield neutral pH. However, there is evidence that DOC will increase during recovery, and both increasing DOC and increasing pH values will lower the toxicity of aluminum. This change may allow recovery of fish populations to historical conditions even if pH remains low.

Recommendations. In the North and East, there is evidence of recovery from the effects of acidic deposition. The complexities of ecosystem response – effects of forest health, soil status, natural organic acidity, the relative importance of sulfur vs. nitrogen deposition, future emission/deposition scenarios – make predictions of the magnitude and timing of further recovery uncertain. The results of this trend analysis suggest two recommendations for environmental monitoring:

1) Deposition monitoring: The analyses in this report depended heavily on the long-term NADP/NTN program for monitoring the chemistry of precipitation. The future assessment of deposition and aquatic trends will depend heavily on these data, and therefore our recommendation is to maintain a national precipitation chemistry network.

2) Surface water monitoring: The effectiveness of current or future amendments to the Clean Air Act can best be determined by monitoring the response of subpopulations of sensitive surface waters through time. Long-term records provide the benchmark for understanding trends in ecological responses. The reviewers of early drafts of this report strongly urged the authors to recommend the continuation of the long-term research programs upon which this report is based and the addition of biological monitoring to begin documenting potential biotic recovery.

Future research. The data from these long-term sites will be invaluable for the evaluation of the response of forested watersheds and surface waters to a host of research and regulatory issues related to acidic deposition, including soil and surface water recovery, controls on nitrogen retention, mechanisms of base cation depletion, forest health, sinks for sulfur in watersheds, changes in DOC and speciation of aluminum, and various factors related to climate change. As one reviewer of this report noted, *"...these sites have irreplaceable long-term data that should constitute a 'research infrastructure' akin to an EPA laboratory. These sites will help address many basic science issues in which EPA ORD has a continuing interest...."* Moreover, as several of the reviewers observed, long-term data serve as the foundation for ecological research and modeling. Without such data, our ability to ask the right questions is reduced, and our ability to base the answers to these questions on actual data is likewise compromised.

INTRODUCTION

The existence of acid rain, more properly called acidic deposition, has been known for more than 100 years (Smith 1872). Documentation of acidification of surface waters began in Scandinavia (e.g., Oden 1968), although reports of acidic lakes date back to the 1950s in North America (Gorham, 1957). Recognition of the issue became common in the U.S. in the early 1970s (Likens et al., 1972), with identification of impacts on fish by the mid-1970s (e.g., Schofield 1976).

Acidic deposition is a dilute solution of sulfuric acid and nitric acids derived from emissions of SO_2 and NO_x, by-products of the combustion of fossil fuels. The regions most impacted by acidic deposition are downwind of the documented sources of industrial sulfur emissions in the Midwestern states, *and* located in geologically sensitive areas in the Northeast, Mid-Atlantic and Upper Midwest regions. Lake and stream chemical data from these regions are the subject of this report.

The potential and documented effects of acidic deposition include damage to building materials, impacts to forests or crops, leaching of soil nutrients, acidification of surface waters, direct impacts on aquatic or amphibious biota, and indirect impact on other organisms in the same foodweb. The effects of the precursor emissions that lead to acidic deposition also include human respiratory stress and decreased visibility, both effects that would be reduced if sulfur and nitrogen emissions were reduced.

This report assesses the responses of surface waters in the five acid-sensitive regions of the northern and eastern states: New England (lakes); the Adirondack Mountains (lakes); the northern Appalachian Plateau (streams); the Ridge/Blue Ridge province (streams); and the Upper Midwest (lakes). With the exception of Florida, these regions include the vast majority of acidic surface waters in the U.S. Florida lakes are not addressed in this report because the majority of the acidity there is due to natural organic acidity (Baker et al*.,* 1990) and because data have not been systematically collected there for more than a decade.

There have been major changes in emissions during the past century. Emissions of SO_2 are inferred to have increased from 9 million metric tons in 1900 to a peak of 29 million metric tons in 1973 (Husar et al., 1991), declining to 18 million metric tons by 1998. NO_X emission are inferred to have increased from 2.5 million metric tons in 1900 to 22 million metric tons around 1990, remaining relatively constant for more than a decade. As a result of the changes in emissions, the ratio of S to N *in deposition* in the North and East has changed from 2:1 to 1:1, with a minor decrease in acidity. It is within the context of these changes in deposition that this report evaluates the responses in surface waters since 1990.

Aquatic Effects Research in the U.S. A consortium of federal agencies mobilized to address the issues of acidic deposition effects in 1980, creating the National Atmospheric Precipitation Assessment Program (NAPAP). The NAPAP effort spent more than $500 million in the 1980s, one of the major environmental research efforts in U.S. history. The ecological research under NAPAP greatly enhanced our understanding of ecological and hydrological processes relevant to acidification, and set the stage for the NAPAP assessment report, and the CAAA, in 1990.

This report makes no attempt to summarize NAPAP research results from the 1980s because many such efforts exist (e.g., the State of Science and Technology series from 1990, including reports 9 through 15 on surface water status, trends, and processes in watersheds). Instead, this report presents results as they relate to the patterns and trends found in the data in the 1990s.

Title IV, Clean Air Act Amendments of 1990. Despite the complication of long-range transport across political boundaries, legislative actions in the United State and Canada have resulted in reductions in acidic emissions and deposition. The purpose of Title IV (the Federal Acid Deposition Control Program) of the Clean Air Act Amendments of 1990 (Public Law 101-549, amending the Clean Air Act of 1970) were to reduce the adverse effects of acidic deposition through reductions in emissions of N and S acid precursors (National Acid Precipitation Assessment Program 1998). The 1990 CAAA enhanced the trend toward decreased sulfur emissions and deposition that had been underway since the early 1970s.

Title IV largely targets the emissions of electric utilities that are estimated to account for 70% of S emissions and 30% of N emissions (Government Accounting Office 2000). These reduction targets were implemented with Phase I in 1995, and Phase II in 2000 (Figure 1). The goal is a 10 million ton reduction in SO_2, and 2 million ton reduction in NOx, by 2010, compared to the baseline year of 1980. Emissions of SO_2 from utilities were 10.6 million tons per year in 2001, compared to the baseline years of 1980 (17.3 m tons) and 1990 (15.7 m tons). The target decrease in S emissions represents a 40% permanent cap compared to 1980 emissions. The target decrease in N is 10% compared to 1980.

Phase I affected 263 units at 110 mostly coal-burning electric utility plants located in 21 eastern and mid-western states. An additional 182 units joined Phase I of the program as substitution or compensating units, bringing the total of Phase I units to 445. Phase II tightened the annual emissions limits imposed on these large, higher-emitting plants and also set restrictions on smaller, cleaner plants fired by coal, oil, and gas, encompassing over 2,000 units in all. In 2001, program sources emitted 10.6 million tons of SO_2 — nearly 7 million tons below 1980 levels, representing a reduction of approximately 40%.

Title IV focuses on NOx-emitting coal-fired electric utility boilers. As with the SO_2 emission reduction requirements, the NOx program was implemented in two phases, beginning in 1996 and 2000. The NOx program embodies many of the same principles of the SO_2 trading program, with flexibility in the method to achieve emission reductions. However, it does not cap NOx emissions as the SO_2 program does, nor does it utilize an allowance trading system. There has been a reduction in NOx emissions from Title IV affected sources from 5.5 million tons in 1990 to 4.7 million tons in 2001.

Linkages to other environmental stressors. Although the evaluation of the effectiveness of the Clean Air Act Amendments is important for understanding the direct link to surface water chemistry and fisheries, there are ancillary advantages to controlling emissions and deposition. For example, coastal eutrophication is a problem of increasing importance for estuarine ecosystems and marine productivity (Jaworski et al., 1997, Paerl 2002, Nielsen and Kahl, in press).

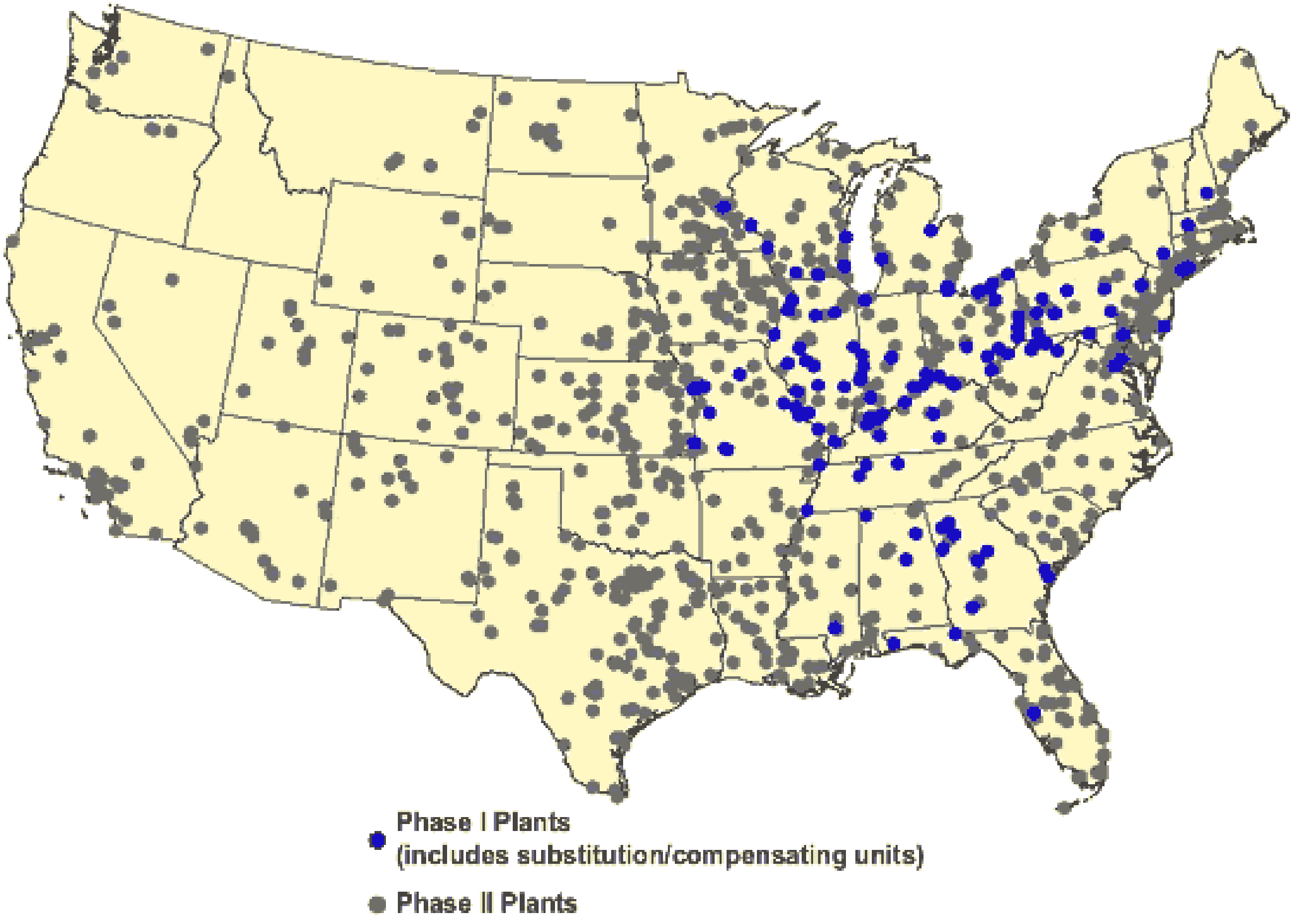


Figure 1. Emission sources affected under the EPA Acid Rain Program.

Similarly, the linkage to climate change is impossible to ignore. Reductions in S and N emissions may be coupled to reduced emissions of greenhouse gases and mercury, especially if the reductions are the result of increased efficiency or conservation. In addition, potential climate change may have an impact on the response of ecosystems and complicate interpretation of data collected for purposes of evaluating the effectiveness of the CAAA (Webster and Brezonik 1995, Norton et al., in press).

OBJECTIVES

The overarching objective of this report is to evaluate the chemical response of lakes and streams in the northern and eastern U.S. during the past decade. This response will be evaluated relative to the well-documented status and trends in precipitation chemistry. For purposes of this report, we define the northern and eastern U.S. as including all of the acid sensitive regions north of the Virginia/North Carolina border and east of the Rocky Mountains. The time period of our focus is 1990 to 2000.

Our specific objectives are to:

1) Identify trends and regional patterns in surface water chemistry using:
    a. Statistical population assessments from the U.S. EPA Environmental Monitoring and Assessment Program (EMAP), and the Temporally Integrated Monitoring of Ecosystems (TIME) project – these data result from repeated probability surveys of lakes in the Adirondacks and New England and of streams in the Mid-Atlantic and can be expanded statistically to the population(s) of surface waters in each region;
    b. Data from lakes and streams identified to be the indicator systems most responsive to changes in deposition chemistry, including the U.S. EPA Long-Term Monitoring (LTM) project – these data are from specially selected sensitive surface waters, and represent the behavior of the most affected systems.
2) Evaluate linkages in changes in surface waters, if any, to changes in deposition that are related to regulatory goals.

These two objectives will assist in providing the foundation for setting targets for future emission reductions, based on goals and expectations for future changes in aquatic chemistry. The results of analyses reported here will inform debates about re-authorization of the current CAAA and about any future emissions regulation.

Evaluating the response: a multi-aquatic system approach. A key issue for the evaluation of the CAAA is the relationship between trends in deposition and trends in surface water chemistry. *Have regulatory changes produced the intended results in surface waters?* The data may indicate a direct relationship between variables, a delayed response, or no apparent relationship. The more direct the apparent relationship and the more types of aquatic systems in which the relationship occurs, the more confidence we have that the trends in deposition are the causal factor.

The data in this report represent many locations and types of surface waters in the North and East (Table 1, Figures 2, 3); we group these sites into regions based on similarities in their acid sensitivity and the rates of acidic deposition to which they have historically been exposed. Consistent recovery across a regional population of streams or lakes provides the strongest evidence that trends are directly related to acidic deposition controls. The regions covered here contained 95% of the acidic lakes, and 84% of the acidic streams, in the 1980s (Linthurst et al., 1986a, Landers et al., 1988). We are therefore confident that we have both represented the bulk of aquatic ecosystems affected by acidic deposition and that we report regionally significant results.

Acidic or acidified? In an assessment of recovery, it is important to distinguish between *acidic* waters and *acidified* waters. Acidic describes a condition that can be defined and documented (i.e., Gran ANC ≤ 0) and may be due either to the effects of acidic deposition or to natural causes such as organic acidity or the weathering of sulfur-containing minerals in the watershed. In contrast, acidified refers to the *process* of acidification (an increase in acidity observed through time) and does not require that the water body be acidic. The process of acidification has been observed in many long-term monitoring records (e.g., Lake Langtjern in Norway; Henriksen and Grande 2002), in short-term studies of episodic acidification (e.g., Wigington et al., 1996), and experimental manipulations of aquatic ecosystems (Schindler 1988, Kahl et al., 1993a, Wright et al., 1993). Chronic acidification can also be inferred from reconstructions of pH based on the remains of diatoms or chrysophytes collected in lake sediment cores (Charles et al., 1990, Smol et al., 1998). The term anthropogenically-acidified implies that acidic deposition was responsible for any increase in acidity; the term acidified does not imply the cause.

Table 1. Sources of data and sample sizes for datasets used in this report, along with estimates of the condition of surface waters in each region in the 1980s. Statistical survey data are from the EMAP and TIME projects. Sensitive surface water data are from the LTM project, as well as other contributed studies.

Sources of Data	No. of sites[1]	Size of Population[2]	Percent acidic in 1980s[3]
Statistical Surveys			
New England Lakes[4]	30	4,327 lakes	5%
Adirondack Lakes[4]	43	1,290 lakes	14%
Appalachian Plateau Streams	31	72,000 stream miles	6%
Sensitive Surface Waters			
New England Lakes	24	N.A.	5%
Adirondack Lakes	48	N.A.	14%
Northern Appalachian Streams	9	N.A.	6%
Upper Midwest Lakes	38	N.A.	3%
Ridge/Blue Ridge Streams	69	N.A.	5%

[1] Number of monitoring sites with data available for this report (1990-2000); locations of sites are illustrated in Figures 2 and 3.

[2] Total number of lakes, or stream length, for which statistical survey results can be inferred. Site selection for LTM (sensitive surface waters) is not statistically based, and results cannot be expanded to population level.

[3] Estimates of extent of acidification, based on National Surface Water Survey results (Linthurst et al., 1986b, Kaufmann et al., 1988).

[4] Estimates are for lakes with surface areas $\geq$ 4 ha; estimates based on populations including smaller lakes are likely to be higher, due to the increased incidence of acidification in small lakes.

***What is* recovery?** Recovery from anthropogenic acidification can be defined in several ways. The most easily documented is a biologically relevant decrease in acidity, measured as an increase in pH or Gran ANC, a measure of the buffering capacity of the water. However, an expectation of large increases in pH is unrealistic based on historical information for sensitive lakes. Today's acidic lakes were marginally acidic in pre-industrial times (typical pH less than 6, inferred ANC probably less than 20 µeq/L; Charles and Norton 1986, Smol et al., 1998). Progress toward recovery should be considered to be progress toward pre-industrial chemical conditions, rather than progress toward pH 7.

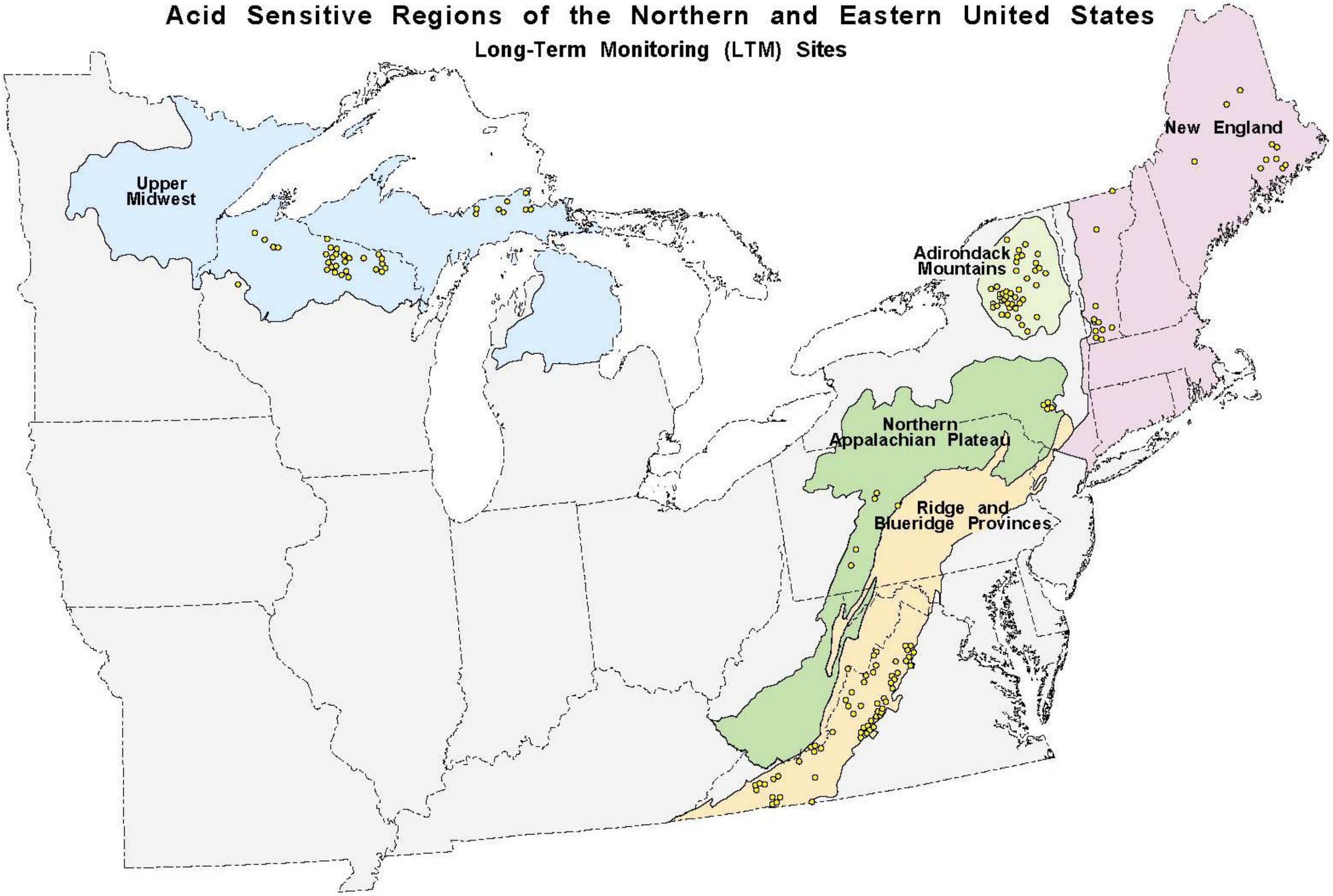


Figure 2. Location of acid-sensitive regions of the northern and eastern U.S. covered in this report and locations of individual LTM sites used in trend analysis.

Other indicators of recovery may be *forecasting* recovery, although it is not clear if further reductions in emissions and deposition will be necessary for widespread recovery to occur. These indicators of recovery include decreased sulfate concentrations which constitute an increasingly smaller percentage of total ion concentration in surface waters and decreased aluminum concentrations. Higher dissolved organic carbon (DOC) concentrations have been reported ubiquitously in surface waters of the northern hemisphere in the past decade (Evans and Monteith 2001, Skjelkvåle et al., 2001, Jeffries et al., 2002; this report). Higher DOC may be an indicator of recovery, due to a decline in the protonation and precipitation of DOC from acidification (Krug and Frink 1983, Davis et al., 1985), or may be driven by climate change. These factors will be discussed later in the context of trends results for DOC and aluminum.

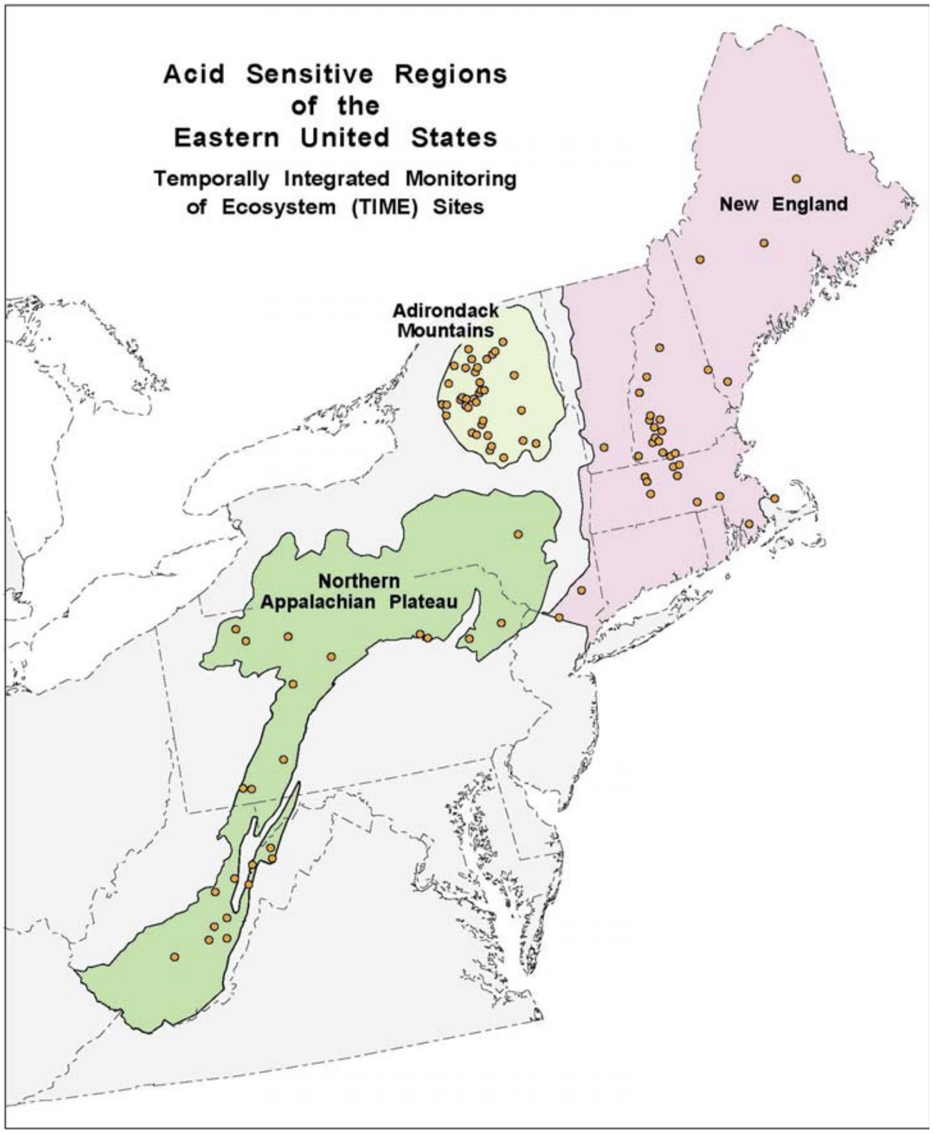


Figure 3. Location of acid-sensitive regions of the northern and eastern U.S. for which statistical survey data are available in the 1990s, and locations of individual TIME sites used in trend analysis.

BACKGROUND

Precipitation chemistry. Acid rain has received much media coverage and research attention since widespread recognition in the late 1970s. Acidic deposition refers to deposition of dilute acids from the atmosphere to the landscape. The source of the acids is the largely the combustion of fossil fuels that produce waste by-products including gases such as oxides of sulfur and nitrogen. Ammonia (NH_3) is a by-product of some natural processes, as well as agricultural sources (e.g., application of nitrogen fertilizers; confined animal feedlots). In its dissolved form (NH_4^+) it contributes acidity to surface waters through the process of nitrification (Stoddard 1994). Oxidized sulfur and nitrogen gasses are acid precursors in the atmosphere. For example, SO_2 reacts with water in the atmosphere to yield sulfuric acid:

$$SO_2 + H_2O + \frac{1}{2}O_2 \rightarrow H_2SO_4$$

An analogous reaction of water with nitrogen oxides, symbolized as NO_x, yields nitric acid (HNO_3).

In addition to *wet deposition* (rain, snow, and fog), acidic deposition includes the deposition of dry, particulate, and gaseous acid precursors that become acidic in contact with moisture. This *dry deposition* is difficult to quantify and expensive to measure. Inferential methods indicate that dry deposition represents 20% to 80% of the total deposition of acids to the landscape, depending on factors such as location, season, and total rainfall (Sisterson et al., 1990, Government Accounting Office 2000).

Natural sources can also contribute additional acidity to precipitation (Likens et al., 1983, Keene and Galloway 1984, Lindberg et al., 1984). Natural emissions of sulfuric, nitric, and hydrochloric acids occur from wetlands and geologic sources. Major natural sources of NO_x include lightning and soil microbes. Organic acidity may arise from freshwater wetlands and coastal marshes. It is these natural sources that lead to the inference that pre-industrial precipitation in forested regions had a pH around 5.0 (Charlson and Rodhe 1982). If true, then modern precipitation in the North and East is two to three times more acidic than pre-industrial.

The acidity of precipitation is still subject to misunderstanding. Even in pristine environments, precipitation pH is rarely controlled by the CO_2 reaction that has an equilibrium pH of 5.6:

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Because of the many sources of acidity in precipitation, pH 5.6 is not the benchmark normal pH against which the acidity of modern precipitation should be compared. Precipitation is a variable and complex mixture of particulates and solutes derived from local sources and long-range transport. For example, in arid or partly forested regions, dust from soil and bedrock typically neutralizes both the natural and human sources of acidity in precipitation, yielding a solution that may be quite basic (pH greater than 7). In the northeastern U.S. and eastern Canada, annual precipitation pH ranges from 4.3 in Pennsylvania, New York, and Ohio, to 4.8 in Maine and maritime Canada (National Atmospheric Deposition Program/National Trends Network 2002).

Effects of acidic deposition. Acidic deposition and emissions of acid precursors have been implicated as a risk to human health, including lung and cardiovascular system impacts (National Acid Precipitation

Assessment Program 1998). These effects are typically associated with air pollution events and poor visibility caused by high ozone or sulfate haze. Acidic deposition is also known to cause degradation of building materials and monuments, such as those constructed from marble (National Acid Precipitation Assessment Program 1998). At the ecosystem-scale, impacts may occur to the terrestrial portions of both forested and agricultural landscapes. The most severe and widespread ecosystem effects are recognized to occur in surface waters, where both long-term chronic acidification and short-term temporary episodic acidifications are of concern. The issue of surface water acidification is the main subject of this report.

Why do we care about lake and stream chemistry? Surface water chemistry is a *direct* indicator of the potential deleterious effects of acidification on biotic integrity. Because surface water chemistry integrates the sum of processes upstream in a watershed, it is also an indicator of the *indirect* effects of watershed-scale impacts, such as nitrogen saturation, forest decline, or soil acidification. Admittedly, we do not always know how to interpret the potentially complex interactions of upstream processes based solely on surface water chemistry, but their dual interpretive nature makes them invaluable in tracking surface water and watershed recovery.

Chronic acidification. Surface waters become acidic when the supply of acids from atmospheric deposition and watershed processes exceeds the capacity of watershed soils and drainage waters to neutralize them (Charles 1991). Surface waters are defined as acidic if their acid neutralizing capacity (ANC, analogous to alkalinity) is less than 0, corresponding to pH values less than about 5.2. We are not addressing the impacts of acid-mine drainage in this report, and the sites used in this assessment exclude those with significant sources of geologic sulfur. The chemical conditions that define acidity are that acid anion concentrations (sulfate, nitrate, organic acids) are present in excess of concentrations of base cations (typically calcium or magnesium), the products of mineral weathering reactions that neutralize acidity in soil or rock.

The National Surface Water Survey (NSWS) documented the status and extent of chronic acidification during probability surveys conducted from 1984 through 1988 in acid sensitive regions throughout the U.S. (Linthurst et al., 1986b, Landers et al., 1987, Kaufmann et al., 1988). By using statistical techniques to select representative lakes and streams in each region surveyed, the NSWS estimated the chemical conditions of 28,300 lakes and 56,000 stream reaches in all of the major acid-sensitive regions of the U.S. (Baker et al., 1990). The data collected by the NSWS have allowed us to focus our monitoring efforts on those areas that contain the vast majority of anthropogenically acidified waters in the U.S. and that are most likely to respond to changes in deposition as a result of the CAAA.

The NSWS concluded that 4.2% of lakes larger than 4 hectares and 2.7% of stream segments in the acid-sensitive regions were acidic. The regions represented in this report (Table 1) are estimated to contain 95% of the lakes and 84% of the streams that have been anthropogenically acidified in the U.S. The Adirondacks had the largest proportion of acidic surface waters (14%) in the NSWS; the Adirondack Lake Survey Corporation sampled 1469 Adirondack lakes greater than 0.5 ha in size in 1984-87, and estimated that 26% were acidic (Driscoll et al., 1991). The proportions of lakes estimated by NSWS to be acidic were smaller in New England and the Upper Midwest (5% and 3%, respectively), but the large numbers of lakes in these regions translate to several hundred acidic waters in each region.

The Valley and Ridge province and Northern Appalachian Plateau had 5% and 6% acidic sites, respectively. The only acid-sensitive region not assessed in the current report is Florida, where the high proportion of naturally acidic lakes, and a lack of long-term monitoring data, make assessment problematic.

Episodic acidification. Short-term decreases in pH and Gran ANC, lasting on the order of hours to weeks, can occur during high flow events in both lakes and streams. Severe episodes can produce conditions that are as deleterious to biota as chronic acidification (Baker et al., 1996). The mechanisms that produce acidic episodes include dilution, and flushing of NO_3^-, SO_4^{2-} and/or organic acids from forest soils (Kahl et al., 1992, Wigington et al., 1996, Wigington 1999, Lawrence 2002). Acidic deposition may contribute to episodic acidification both by supplying nitrogen to sensitive watersheds (producing pulses of NO_3^- during high flow events), producing hydrologically mobile stores of SO_4^{2-} through dry deposition and by lowering baseline pH and ANC so that smaller episodes are sufficient to produce acidic conditions.

Biologically relevant Surface Water Chemistry. The main cause for concern over the effects of surface water acidification in the U.S. and elsewhere is the potential for detrimental biological affects (Baker and Christensen 1991, National Acid Precipitation Assessment Program 1998). Typically, there is concern for biological impact if the pH is less than 6. At low pH values, aluminum may be present at concentrations that are toxic to biota, including sensitive life stages of fish and sensitive invertebrates. Aluminum is an abundant and normally harmless component of rocks and soils. However, it leaches from silicate minerals when they come in contact with low pH waters. While much of the aluminum present in surface waters is organically bound and relatively non-toxic, certain inorganic species are highly toxic. The best indicator of recovery in biologically relevant chemistry would be a decrease in concentrations of *inorganic monomeric* aluminum, the most toxic form. Decreases in *total* aluminum would also suggest recovery, although the actual magnitude of the improvement in chemical conditions for biota would be unknown because we would not know how much of the decrease is due to inorganic vs. organic forms of aluminum.

Biological effects. The biological effects of acidification have been demonstrated in laboratory and field bioassays (e.g., Baker et al., 1996), with whole-ecosystem acidification experiments (e.g., Schindler et al., 1985), and through field surveys (e.g., Baker and Schofield 1982, Gallagher and Baker 1990). A number of the species, especially of fish and macro-invertebrates, that commonly occur in surface waters susceptible to acidic deposition cannot survive, reproduce or compete in acidic waters. Sensitive species may be lost even at moderate levels of acidity. For example, some important zooplankton predators are not found at pH levels below 5.6; sensitive mayfly species (e.g., *Baetis lapponicus*) are affected at pH levels near 6.0; and sensitive fish species, such as the fathead minnow, experience recruitment failure and extinction at pH 5.6 to 5.9 (Baker and Christensen 1991).

Unfortunately, there are very few examples of long-term monitoring data for biological assemblages in acid-sensitive surface waters (e.g., Henriksen and Grande 2002), and none in the U.S. Therefore, many of our conclusions about the effect of acidic deposition on the distribution of sensitive species are based on relationships like the one shown in Figure 4. This relationship represents the sum total of the effects of acidification, lake size, and other complex interactions between the survival of fish species and the quality of their habitat. Research in the Adirondacks has shown that many lakes have always had marginal spawning habitat for Eastern Brook Trout (Schofield 1993), and at least some of the currently fishless acidic lakes in the Adirondacks may never have supported fish. Given the multiple lines of evidence available, it is very likely that acidic conditions, both natural and anthropogenic, limit the distribution of fish, benthic invertebrate, and zooplankton species, but a lack of historical data make it difficult to infer the magnitude of biological recovery (if any) from acidic deposition in individual lakes or streams.

Ecological response: is sulfate or nitrate more deleterious? The NAPAP research effort of the 1980s was focused largely on sulfur as the problem behind the ecological impacts of acidic deposition (Baker et al., 1990, Church et al., 1990, Turner et al., 1990). Conceptual models were developed to understand regional responses (e.g., Galloway et al., 1983, Wright 1983). Computer models of watershed geochemistry enhanced our understanding of sulfate in watersheds (Christophersen and Wright 1981, Chen et al., 1984, Cosby et al., 1985). As a result, sulfur biogeochemistry

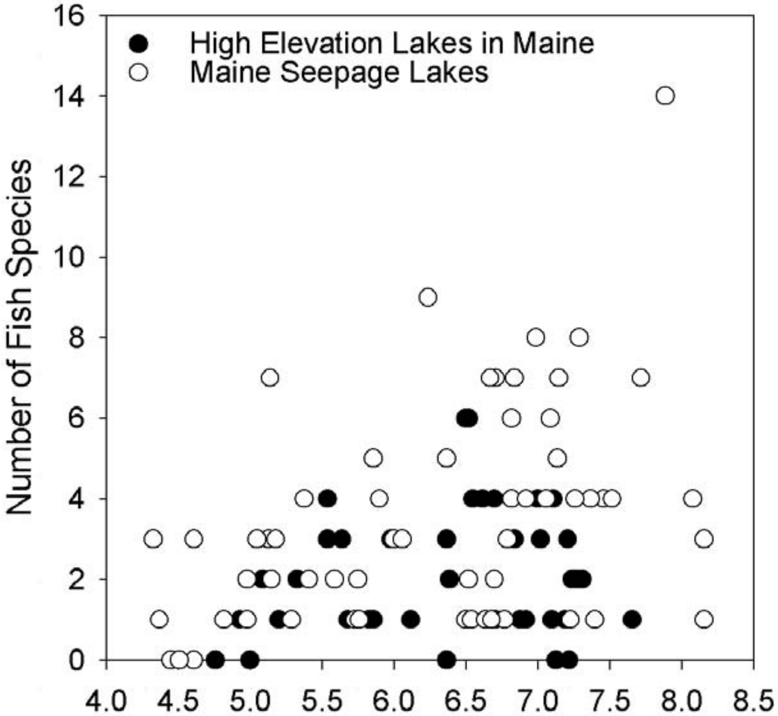


Figure 4. Distribution of fish species by lake pH in high elevation and seepage lakes in Maine (Kahl and Scott 1994). Y-axis represents the number of fish species found in each lake.

is relatively well understood qualitatively. However, a decade after NAPAP, it is clear that we cannot predict sulfate quantitatively in most instances due to the complications of other, less well understood, factors.

One of the key factors still the subject of much research and scientific debate is the role of nitrogen in watershed responses to acidic deposition. The concept of *nitrogen saturation* (Aber et al., 1989, Stoddard 1994) received increasing attention in the 1990s (Murdoch and Stoddard 1992, Mitchell et al., 1996, Williams et al., 1996, Aber et al., 1998). Nitrogen saturation is defined as deposition of N to a watershed in excess of the assimilative capacity of soils and vegetation, resulting in the export of NO_3^-. Nitrate export can contribute to acidification (especially episodic acidification), mobilization of aluminum, and leaching of cations from soils (Aber et al., 1998, Fenn et al., 1998).

In the U.S., nitrogen saturation has received the most attention in the eastern states, although it is not clear if chronic N-saturation has occurred. Several forest manipulation studies in New England show increased mortality and declining growth of softwoods in response to N additions, leading to the suggestion that the widespread spruce decline in the eastern U.S. may be related to long-term N deposition (Aber et al., 1995). Nitrate concentrations in streams draining forests in the Northeast are higher than in any other forested region in the country and have increased by a factor of 3 to 4 since 1970 (Murdoch and Stoddard 1992, Aber et al., in press), although these concentrations have begun to decrease based on analyses in this report.

Our understanding of nitrogen cycling in forested watersheds is complicated by nitrogen's response to climatic variation, land use history, forest disturbances (e.g., fire and insect defoliation) and drought (Mitchell et al., 1996, Aber and Driscoll 1997, Goodale et al., 2000). Indeed, under most conditions, nitrogen from deposition functions as a fertilizer for N-limited forests. Despite the complexities of the nitrogen cycle in forested watersheds, the scientific consensus seems to be that, in the absence of substantial declines in nitrogen deposition, future increases in surface water NO_3^- concentrations, particularly in the Northeast and Mid-Atlantic U.S., are likely (Stoddard 1994, Aber et al., in press). The difficulties inherent in controlling N emissions further complicate this issue—emissions are from both combustion sources (NO_x) and agricultural sources (NH_3 and NO_x), and unlike S emissions, mobiles sources play a much larger role than stationary sources. An assessment of current status and trends, like the one presented here, can serve as the starting point for any future discussions of future effects and regulations concerning nitrogen.

DATA USED IN THIS REPORT

National Atmospheric Deposition Program/National Trends Program (NADP/NTN). This report relies heavily on long-term records of wet deposition from the NADP/NTN program (http://nadp.sws.uiuc.edu). The NADP/NTN network has collected data on rates of atmospheric deposition (rainfall, snowfall and major ion chemistry) since the early 1980s. The network currently consists of 245 sites and is an excellent example of grass roots scientific cooperation creating an enormously useful source of data.

In order to characterize deposition trends with adequate confidence, we chose to use at least nine NADP/NTN locations for each region. None of the regional boundaries shown in Figure 2 encloses an adequate number of sites with long data records. We therefore expanded the regional boundaries slightly to include deposition monitoring stations within close enough proximity to have a high probability of exhibiting trends similar to those actually within the boundaries. The list of NADP/NTN sites used in this exercise are shown in Table 2.

We chose not to use dry deposition estimates from programs such as the Clean Air Status and Trends Network (CASTNet; U.S. Environmental Protection Agency 2002) for several reasons. Perhaps the most important of these is the need to compare directly the concentrations of ions in surface waters with the concentrations in deposition. At present there is no straightforward method to produce deposition concentrations (e.g., SO_4^{2-} in μeq/L) from dry deposition data. In addition, the limited spatial and temporal coverage, and the high spatial variability of CASTNet data, make them difficult to use with any confidence in the sort of regional analysis presented here. There are, for example, no CASTNet sites currently operating in the Adirondack Mountains, and only two useable sites in the Upper Midwest region, as we define it here.

Table 2. Location of NADP/NTN wet deposition sites in each region.

Region	NADP/NTN Site Code	State	NADP/NTN Site Name
New England	MA01	Massachusetts	North Atlantic Coastal Lab
	MA08	Massachusetts	Quabbin Reservoir
	MA13	Massachusetts	East
	ME02	Maine	Bridgton
	ME09	Maine	Greenville Station
	ME98	Maine	Acadia National Park
	NH02	New Hampshire	Hubbard Brook
	VT01	Vermont	Bennington
	VT99	Vermont	Underhill
Adirondacks	NY08	New York	Aurora Research Farm
	NY20	New York	Huntington Wildlife Refuge
	NY52	New York	Bennett Bridge
	NY68	New York	Biscuit Brook
	NY98	New York	Whiteface Mountain
	NY99	New York	West Point
	VT01	Vermont	Bennington
	VT99	Vermont	Underhill
Northern Appalachians	NY08	New York	Auroroa Research Farm
	NY65	New York	Jasper
	NY68	New York	Biscuit Brook
	NY99	New York	West Point
	PA15	Pennsylvania	Penn State
	PA29	Pennsylvania	Kane Experimental Forest
	PA42	Pennsylvania	Leading Ridge
	PA72	Pennsylvania	Milford
	WV18	West Virginia	Parsons
Upper Midwest	MI09	Michigan	Douglas Lake
	MI98	Michigan	Raco
	MI99	Michigan	Chassell
	MN16	Minnesota	Marcell Experimental Forest
	MN18	Minnesota	Fernberg

Region	NADP/NTN Site Code	State	NADP/NTN Site Name
Upper Midwest	MN23	Minnesota	Camp Ripley
	MN27	Minnesota	Lamberton
	WI09	Wisconsin	Popple River
	WI25	Wisconsin	Suring
	WI28	Wisconsin	Lake Dubay
	WI36	Wisconsin	Trout Lake
	WI37	Wisconsin	Spooner
	WI98	Wisconsin	Wildcat Mountain
	WI99	Wisconsin	Lake Geneva
Ridge and Blue Ridge	KY22	Kentucky	Lilley Cornett Woods
	MD03	Maryland	White Rock
	NC45	North Carolina	Mt. Mitchell
	PA15	Pennsylvania	Penn State
	PA29	Pennsylvania	Kane Experimental Forest
	PA42	Pennsylvania	Leading Ridge
	PA72	Pennsylvania	Milford
	TN11	Tennessee	Great Smoky Mountains National Park
	VA00	Virginia	Charlottesville
	VA13	Virginia	Horton's Station
	VA28	Virginia	Shenandoah National Park
	WV04	West Virginia	Babcock State Park
	WV18	West Virginia	Parsons

Lake and stream monitoring programs. The core of the acid rain aquatic effects monitoring effort in the eastern U.S. has been two EPA programs: the Temporally Integrated Monitoring of Ecosystems (TIME) project (Stoddard 1990) and the Long-Term Monitoring (LTM) project (Ford et al., 1993, Stoddard et al., 1998b). Both projects are operated cooperatively with numerous collaborators in state agencies, academic institutions and other federal agencies. Augmenting these core programs are ongoing surveys of lake sub-populations especially sensitive to acidification or recovery. These programs all have slightly different objectives and structures, outlined below.

TIME project: At the core of the TIME project is the concept of a probability sample where each sampling site is chosen statistically to be representative of a target population. In the Northeast (New England and Adirondacks), this target population consists of lakes likely to be responsive to changes in rates of acidic deposition (i.e., those with Gran ANC < 100 µeq/L). In the Mid-Atlantic, the target population is upland streams with a high probability of responding to changes in acidic deposition (i.e., Northern Appalachian Plateau streams with Gran ANC < 100 µeq/L).

Each lake or stream is sampled annually (in summer for lakes, in spring for streams), and results are extrapolated with known confidence to the target population(s) as a whole (Larsen and Urquhart 1993, Larsen et al., 1994, Stoddard et al., 1996, Urquhart et al., 1998). TIME sites were selected using the methods developed by EMAP (Paulsen et al., 1991, Herlihy et al., 2000). The TIME project began sampling Northeast lakes in 1991; for the purposes of this report, we group these lakes into two acid-sensitive regions, the Adirondacks and New England. Data from 43 Adirondack lakes can be extrapolated to the target population of low ANC lakes in the region (there are ca. 1000 low ANC Adirondack lakes, out of a total population of 1830 lakes with surface area > 1 ha). Data from 30 lakes (representing ca. 1500 low ANC lakes, out of a total population of 6,800) form the basis for our trend analysis in New England. Probabilistic monitoring of Mid-Atlantic streams began in 1993; this report utilizes data from 30 low ANC streams in the Northern Appalachian Plateau (representing ca. 42,000 km of stream length, of which ca. 24,000 km are considered low ANC). In the Ridge and Blue Ridge provinces, the sample coverage from TIME was not sufficient to conduct regional trend analysis; all of our conclusions about this region (ca. 5,500 km of low ANC streams, out of a total population of 23,000 km) are therefore based on the non-probabilistic Virginia Trout Stream Survey described below. There are no sample survey data available from the Upper Midwest in the 1990-2000 time period. The ultimate goal of having a probability program like TIME is to determine not just how a representative sample of lakes and/or streams is changing through time, but to know whether the proportion of the population that is acidic has changed.

LTM project: As a complement to lake and stream sampling in a statistical population of lakes in TIME, the Long-Term Monitoring project samples a subset of sensitive lakes and streams with long-term data, most dating back to the early 1980s. These sites are sampled 3 to 15 times per year. This information is used to characterized how the most sensitive of aquatic systems in each region are responding to changing deposition, as well as giving information on seasonal chemistry and episodic acidification. In most regions, a small number of higher ANC (e.g., Gran ANC > 100 µeq/L) sites are also sampled and help separate temporal changes due to acidic deposition from those attributable to other disturbances (e.g., climate change, landuse change). Because of the long-term records at most LTM sites, their trends can also be placed in a better historical context than those of TIME sites, where data are only available from the 1990s. The details of data from each region are given below.

New England lakes: The LTM project collects quarterly data from lakes in Maine (sampled by the University of Maine; Kahl et al., 1991, Kahl et al., 1993b) and Vermont (data collected by the Vermont Department of Environmental Conservation; Stoddard and Kellogg 1993, Stoddard et al., 1998a). Data from 24 New England lakes are available for the trend analysis reported here (time period 1990-2000). In addition to quarterly samples, a subset of these lakes have outlet samples collected on a weekly basis during the snowmelt season; these data are used to characterize spring episodic chemistry. The majority of New England LTM lakes have mean Gran ANC values ranging from –20 to 100 μeq/L; two higher ANC lakes (100< Gran ANC < 200 μeq/L) are also monitored.

Adirondack lakes: Our trend analysis includes data from 48 Adirondack lakes, sampled monthly by the Adirondack Lake Survey Corporation (Driscoll and Van Dreason 1993, Driscoll et al., 1995); a subset of these lakes are sampled weekly during spring snowmelt to help characterize acidic episodes. The Adirondack LTM dataset includes both seepage and drainage lakes, most with Gran ANC values in the range –50 to 100 μeq/L; 3 lakes with Gran ANC > 100 μeq/L (but less than 200) are also monitored.

Appalachian Plateau streams: Stream sampling in the Northern Appalachian Plateau is conducted roughly 15 times per year, with the samples spread evenly between baseflow (e.g., summer and fall) and high flow (e.g., spring) seasons. Data from four streams in the Catskill mountains (collected by the U.S. Geological Survey; Murdoch and Stoddard 1993), and five streams from Pennsylvania (collected by Pennsylvania State University; DeWalle and Swistock 1994) are used in this report. All of the Northern Appalachian LTM streams have mean Gran ANC values in the range -25 to 50 μeq/L.

Upper Midwest lakes: Roughly 40 lakes in the Upper Midwest were originally included in the LTM project, but funding in this region was terminated in 1995. The Wisconsin Department of Natural Resources (funded by the Wisconsin Acid Deposition Research Council, the Wisconsin Utilities Association, the Electric Power Research Institute and the Wisconsin Department of Natural Resources) has continued limited sampling of a subset of these lakes, as well as carrying out additional sampling of an independent subset of seepage lakes in the state. The data used in this report consist of 16 lakes (both drainage and seepage) sampled quarterly (Webster et al., 1993), and 22 seepage lakes sampled annually in the 1990s. All of the Upper Midwest data exhibit mean Gran ANC values from -30 to 80 μeq/L.

Ridge/Blue Ridge streams: Data from the Ridge and Blue Ridge provinces consist of a large number of streams sampled quarterly throughout the 1990s as part of the Virginia Trout Stream Survey (Webb et al., 1989, Webb et al., 1994) and a small number of streams sampled more intensively (as in the Northern Appalachian Plateau). A total of 69 streams, all located in the Ridge section of the Ridge and Valley province, or within the Blue Ridge province, and all within the state of Virginia, had sufficient data for the trend analyses reported here. The data are collected cooperatively with the University of Virginia and the National Park Service. Mean Gran ANC values for the Ridge/Blue Ridge data range from –15 to 200 μeq/L, with 7 of the 69 sites exhibiting mean Gran ANC > 100 μeq/L.

Supplemental datasets: Lake surveys conducted in the 1980s revealed that 70% of the known acidic lakes in the state of Maine were either in seepage lakes or high elevation lakes (Kahl et al., 1991). We have used data from these two sets of lakes, as well as from the control stream at the Bear Brook Watershed Manipulation Project (Norton et al., 1994, Church 1999), in some of the supplementary analyses presented in this report.

Maine Seepage lakes: This dataset includes data from 120 of the estimated 150 lakes in Maine meeting the following criteria: 1) location in a sand and gravel area mapped by the U.S.G.S. or Maine Geological Surveys; 2) depth at least 1 meter; and 3) area at least 0.4 hectare (1 acre). Sampling was conducted in 1986-87 and 1998-2000 and included at least one fall index sample for each lake. The population was reduced to 87 lakes for this report by screening for lakes with Gran ANC less than 100 µeq/L.

Maine High Elevation lakes: Data from 90 high elevation lakes (above 600 meters elevation), available annually for the periods 1986-88 and 1997-99, represent the vast majority of lakes in Maine meeting this criteria: 1) depth at least 1 meter; and 2) area at least 0.4 hectare (1 acre). The population was reduced to 64 lakes for this report by screening for lakes with Gran ANC less than 100 µeq/L.

Surface water classification. For purposes of analysis and illustration, the surface water data contained in this report were classified according to average Gran ANC and DOC values. For the period of record, *acidic* waters were those with mean Gran ANC less than or equal to zero. *Low ANC* waters were those with Gran ANC greater than 0 but less than or equal to 25 µeq/L. *Moderate ANC* waters were those with Gran ANC greater than 25. The site selection process or the definition of the statistical population eliminated high ANC waters. The vast majority of sites included here all have mean Gran ANC less than 100 µeq/L.

Sites were also classified by dissolved organic carbon (DOC), with the intent to evaluate the contributions of natural organic acidity to the response of systems. Waters with mean DOC less than or equal to 5 mg/L were classified as *low DOC*. Sites with DOC greater than 5 mg/L were *high DOC*. The highest DOC lake (a seepage lake in Wisconsin) had a mean DOC concentration of 17 mg/L.

Additionally, seepage lakes were also evaluated by silica concentration in order to classify systems as *perched* or *flow-through*. Seepage lakes with mean silica less than 1mg/L were considered perched. The significance of this classification is that perched lakes are disconnected hydrologically from groundwater (they supply water to the local groundwater) and have minimal watershed contributions to their chemistry. Such lakes are expected to be more responsive to changes in atmospheric deposition. Seepage lake data are available from Maine, the Adirondacks, and Wisconsin.

Analytical methods and quality assurance. The specific field protocols, laboratory methods, and quality assurance procedures are specific for each investigator. This information is contained in the cited publications of each research group and are compiled in Newell et al., (1987). The EMAP and TIME protocols and quality assurance methods are generally consistent with those of the LTM cooperators and are detailed in Peck (1992) and in Table 3.

The data used in this report have been screened for internal consistency among variables including ion balance and conductance balance. Samples with unexplained variation in these variables have been deleted. Sites with mean Gran ANC greater than 200 µeq/L were deleted. We excluded sites with chloride values that were outliers in their region because high Cl^- is typically associated with human development in the watershed. The Cl^- and associated Na^+ would alter normal soil ion exchange relationships, thus obscuring the response to acidic deposition.

Sea-salt corrections. We did not systematically correct surface water chemistry for contributions from marine aerosols in large part because the marine influence was minor for most regions. The exception was stream data from the Bear Brook Watershed Manipulation which is of close proximity to the Gulf of Maine and where the detailed analyses of relationships between SO_4^{2-} and base cation behavior required the greater precision provided by sea salt correction. For these streams, and in a few other instances as noted in the text we corrected surface water chemistry by assuming all chloride was of marine origin and correcting sulfate and base cations based on the ratios found in seawater (Riley and Chester 1971).

Table 3. Typical analytical methods used for samples reported here. Samples are filtered before analysis, except in Adirondack LTM.

Variable	Technique	Protocol reference
pH, closed cell	Electrode	Hillman, et al.[6], EPA 19.0[5]
pH, aerated	Electrode	Hillman, et al.[6], EPA 5.0[5]
Specific conductance	Wheatstone bridge	EPA 120.1[2],EPA 23.0[5]
True color	Spectrophotometer, 457.5 nm	EPA 110.2[2]
Gran ANC	Gran Titration	Hillman et al.[6], EPA 5.0[5]
Anions: Cl^-, NO_3^-, SO_4^{2-}	Ion chromatography	EPA 300.0[1]
Calcium	AAS with N_20-acetylene flame	EPA 215.1[2]
Magnesium	AAS with N_20-acetylene flame	EPA 242.1[2]
Sodium	AAS with air-acetylene flame	EPA 258.1[2]
Potassium	AAS with air-acetylene flame	EPA 273.1[2]
Aluminum, total	AAS with graphite furnace	EPA 200.9[4]
Dissolved Organic Carbon	IR C analyzer, persulfate oxidation	EPA 415.1[2]
Dissolved Inorganic Carbon	IR C analyzer, direct injection	EPA 13.0[5], OI, 1990[8]
Ammonium	Autoanalyzer	EPA 9.0[5] and Bran & Luebbe 780-86T[7]
Silica	Autoanalyzer	EPA 22.0[5] and Bran & Luebbe 785-86T[7]

AAS=atomic absorption spectrophotometry
IR=Infrared Spectrophotometry
Method references:

[1] Methods for the Determination of Inorganic Substances in Environmental Samples, EPA 600/R-93/100, 1993.

[2] Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79/020, 1979, Revised 1983.

[3] Standard Methods for Examination of Water and Wastewater, 18th ed. 1992.

[4] Methods for the Determination of Metals in Environmental Samples, EPA 600/4-91/010, 1991, Supplement 1, EPA 600/R-94/111, 1994.

[5] Handbook of Methods for Acid Deposition Studies: Laboratory Analysis For Surface Water Chemistry, EPA 600/4-87/026, 1987.

[6] Hillman,D.C., J. Potter, and S. Simon, 1986. Analytical methods for the National Surface Water Survey, Eastern Lake Survey. EPA/600/4-86/009, EPA Las Vegas.

[7] Bran & Luebbe Manual

[8] OI Analytical Manual, 1990

We did not correct NADP/NTN data for marine aerosols. Air masses move west to east, meaning that marine contributions to precipitation chemistry will be minor, with the exception of seasonal effects in coastal New England. Other sources are more likely to contribute chloride than seawater, and thus correction of sulfate and base cations based on a seawater-source assumption will likely lead to erroneous corrections. In the instance of base cation data that are important for watershed function, there is no point in mathematically removing cations presumed to arise from marine aerosols because the source of the cations is irrelevant to watersheds.

Statistical analyses. Numerous statistical techniques are available to analyze trends in time series like those presented here. For trends at single monitoring sites, the Seasonal Kendall Tau (SKT) test (Hirsch et al., 1982, Hirsch and Slack 1984) is often the method of choice because it deals well with censored data and with data collected at irregular intervals with marked seasonality (Loftis and Taylor 1989). One weakness of the SKT is that it does not compute a slope. The regional analyses we present in this report depend on the ability to calculate a robust estimator of slope for each site. Rather than utilizing a Sen estimator (Sen 1968), as is often done with the SKT, we have chosen to use simple linear regression (SLR) to calculate a trend slope for each monitoring site. This has the added advantage of allowing us to use identical methods for detecting regional trends in both the LTM and TIME data; the probability data from TIME are not of sufficient sample size (for individual sites) or sampling frequency to make the choice of SKT appropriate. While the significance of individual tests conducted with SLR are questionable (especially when repeated tests are conducted within each region), the slopes calculated for multiple sites within a region represent a distribution of results which can in turn be examined and analyzed for patterns. Within each region, we test for a significant regional trend by calculating confidence limits about the median value in the slope distribution (SAS Institute, Inc., 1988, Altman et al. 2000) and testing whether these confidence limits include zero. For a distribution in which all of the slopes are negative, for example, the median value would be significantly less than zero, indicating a significant regional downward trend.

TRENDS IN EMISSIONS AND DEPOSITION

Overview of Emissions and Deposition Changes: Sulfate emissions declined substantially in the 1990s (Figure 5); plants regulated under Phase I of the CAAA reduced emissions by 50%, while total emissions nationwide were reduced by 30% over 1980 levels.

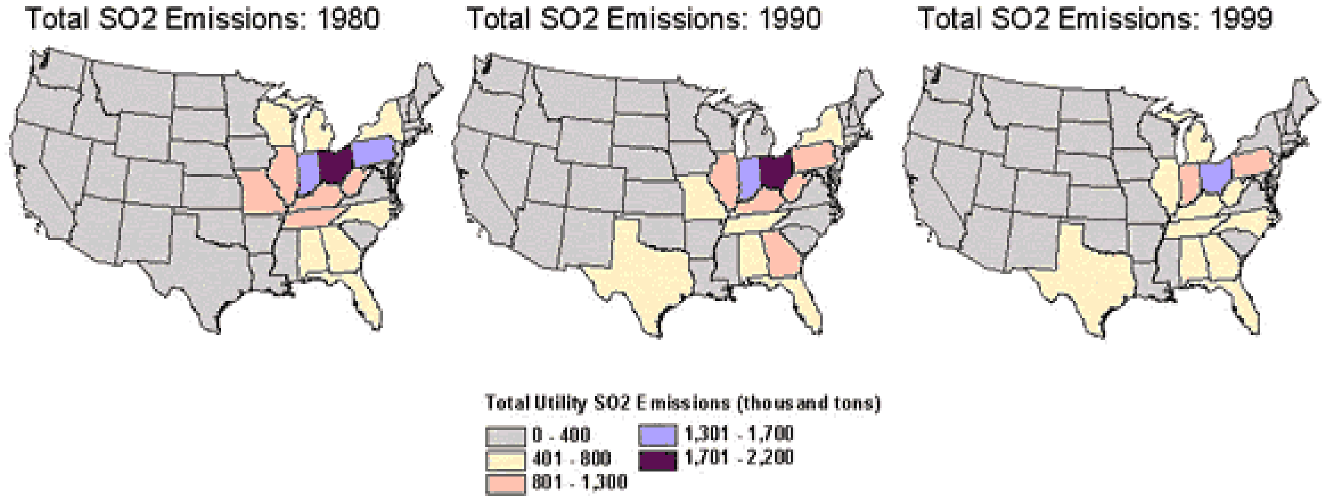
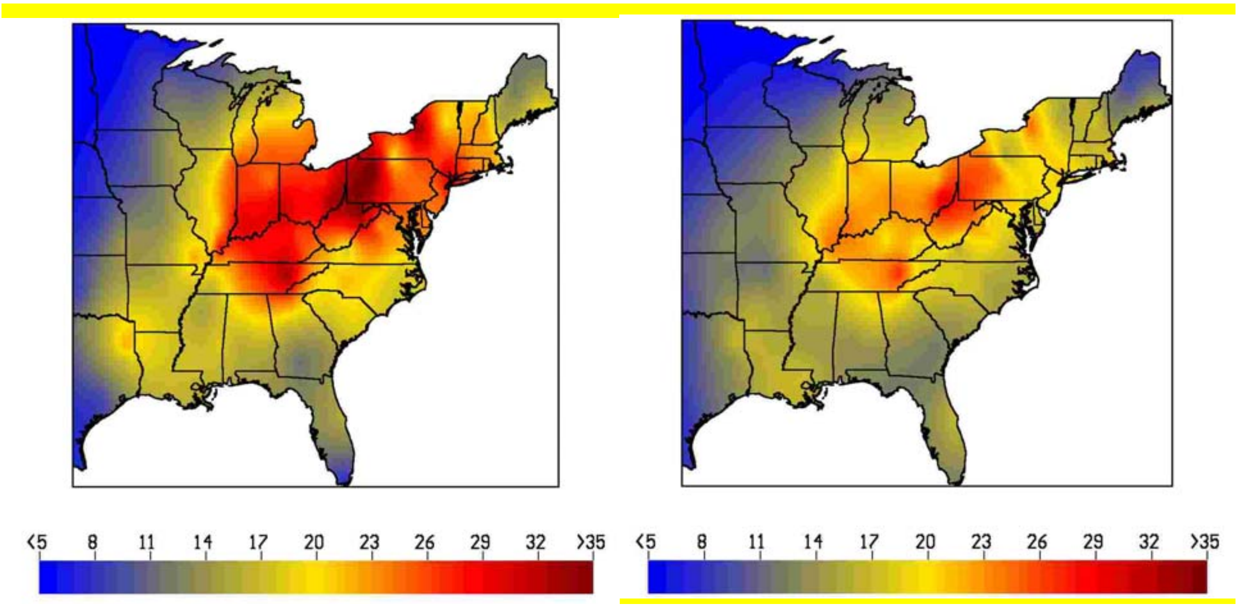


Figure 5. Trends in sulfur dioxide emissions following implementation of Phase I of the Acid Rain Program: Total state-level utility SO_2 (1980, 1990, 1999).

Data from NADP/NTN indicate that sulfur emissions declines have contributed to a continuation of the long-term decline in sulfur deposition (Figure 6) from the previous decade (Holland et al., 1999, Shannon 1999, Government Accounting Office 2000, Lynch et al., 2000). Many NADP/NTN sites exhibit declines in excess of 45% since 1980. Compared to trends from 1983-94, the decline in wet deposition sulfate accelerated after 1995 at 74% of NADP sites in the eastern U.S. presumably as a result of Phase I of Title IV of the CAAA (Lynch et al., 2000).


1989-1991

1995-1998

Figure 6. Trends in wet sulfate deposition in the eastern United States from NADP/NTN data (1989-1991 vs. 1995-1998). Data are in kg/ha.

Power plant SO_2 emissions increased after 1996, perhaps because utilities overshot the CAAA targets in 1995 (Government Accounting Office 2000). This increase translated into a measurable increase in deposition in many NADP/NTN stations in the regions of interest for surface water response (Figure 7). The lowest SO_4^{2-} concentration in precipitation occurred in 1995 or 1996, depending on the station (Figure 7; Government Accounting Office 2000, National Atmospheric Deposition Program/National Trends Network 2002). Since 1980, total U.S. SO_2 emissions have decreased by about 5.5 million tons.

Decreases in NO_x emissions were more modest than those of sulfur with declines noted in several states in the northeastern corridor (Figure 6). Since 1990, total utility NO_x emissions (Phase I and II sources) were reduced an average of 23% nationally following implementation of Phase I of the Acid Rain Program. However, electric utilities contribute only about one-third of total NO_x emissions. Since total NO_x emissions from other sources have remained relatively constant (motor vehicles and other industrial sources also contribute significantly), the reductions achieved under the Acid Rain Program have not resulted in a significant change in total NO_x emissions.

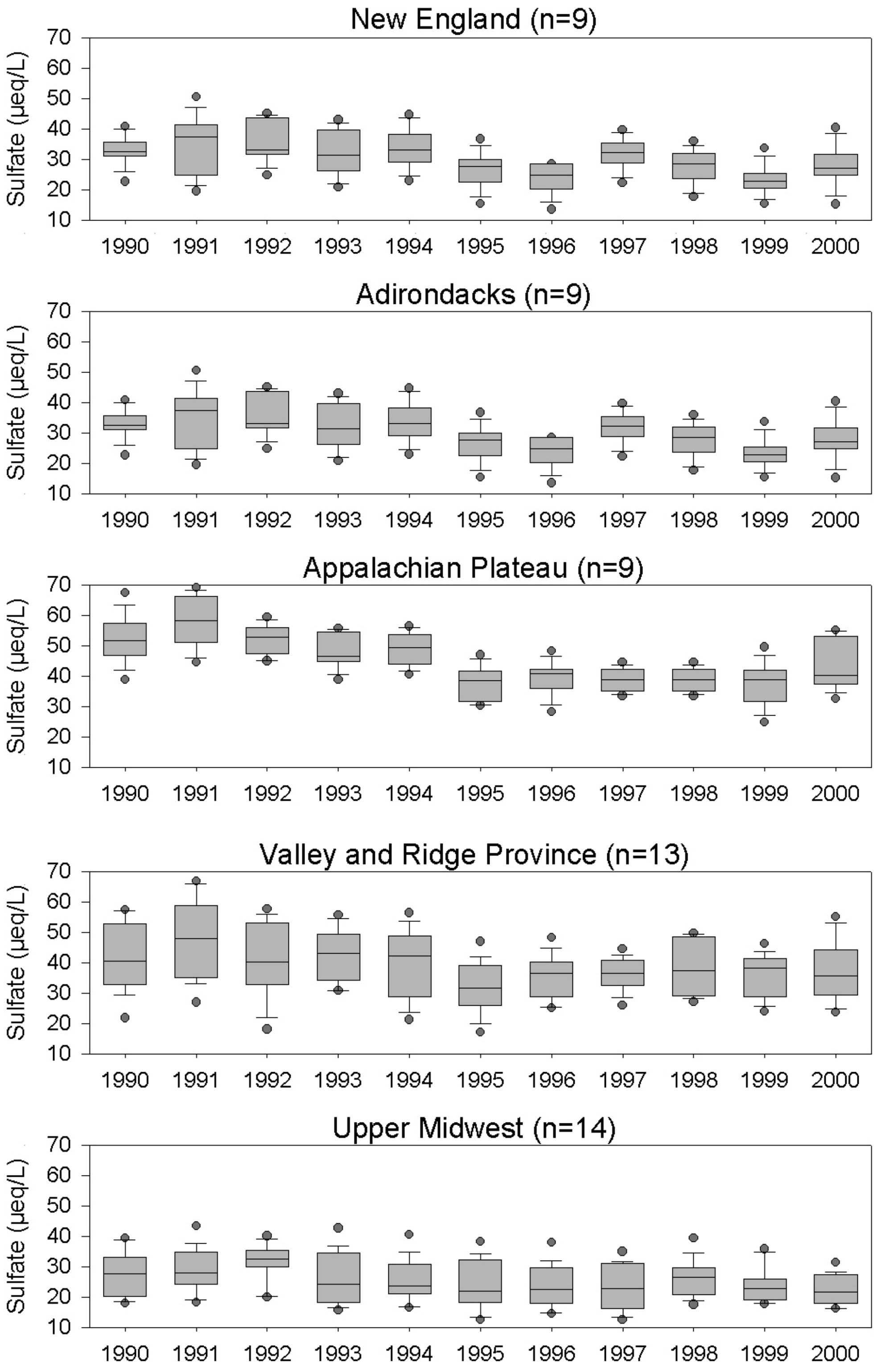


Figure 7. Trends in wet deposition concentrations of SO_4^{2-} during 1990 – 2000 (NADP, 2002). Boxes indicate the interquartile range in SO_4^{2-} for each region in each year; caps indicate the 10th and 90th percentiles; median concentration is indicated by line in box; dots enclose the range.

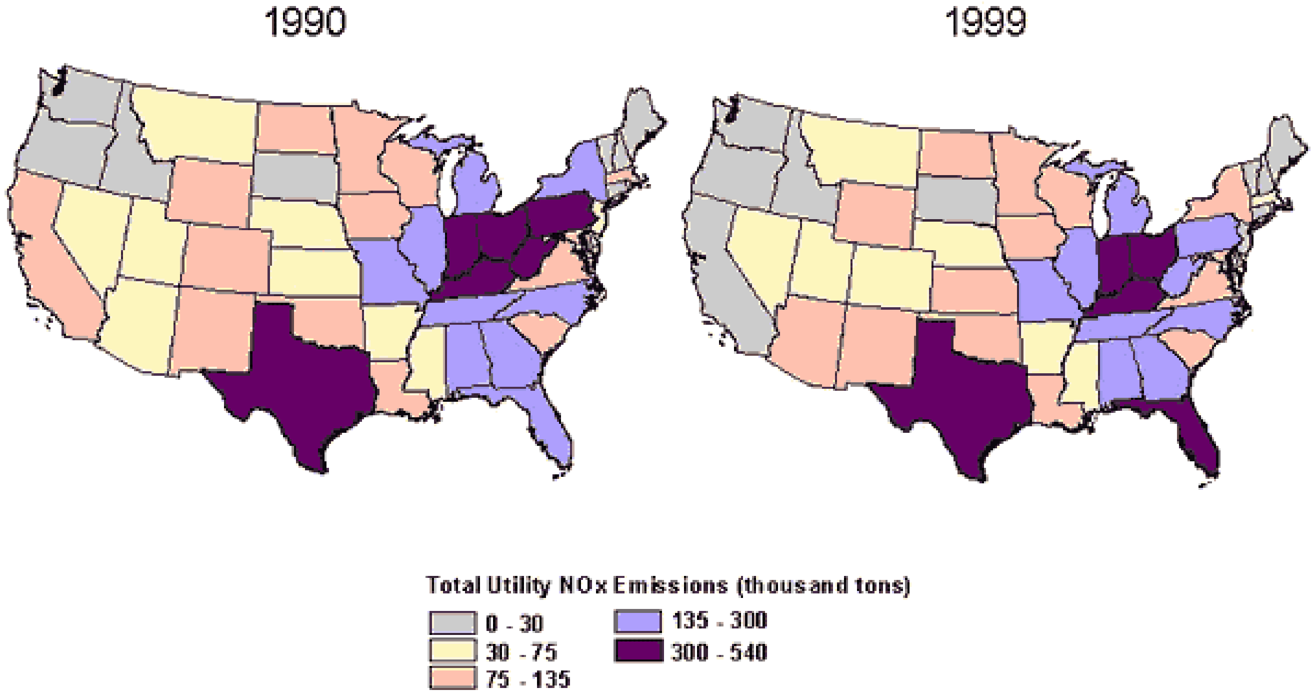


Figure 8. Trends in nitrogen oxide emissions following implementation of Phase I of the Acid Rain Program: Total state-level utility NO_x (1990 vs. 1999).

Relatively constant NO_x emissions translate to little change in wet NO_3^- deposition in the 1990s (Figure 8). The relative lack of change in NO_3^- deposition, relative to the decline in SO_4^{2-}, has changed the ratio of S:N from 2:1 in 1980 to 1:1 in 2000 (Lynch et al., 2000). This long-term flat trend in nitrate deposition may have begun to shift downward after the implementation of Phase I for nitrate in 1996. Nevertheless, the geographic pattern of nitrate deposition has not changed substantially (Figure 9), in contrast to the changing pattern for sulfate (Figure 6).

Regional deposition trends for SO_4^{2-} and nitrogen: We evaluated the trends in wet deposition in each region for which we report trends in surface water response. Our analysis uses precipitation concentrations as reported by NADP/NTN (National Atmospheric Deposition Program/National Trends Network 2002).

Throughout this report, we illustrate the range of trend behaviors in each region (for both deposition and surface waters) through the use of cumulative frequency distributions (e.g., Figure 10). These plots show the range of trend slopes in each region with the minimum slope shown as the value of the x-axis corresponding to the left side of the regional curve and maximum slope value equivalent to the x-value at the right end of the curve. The median value for each region which is the value generally reported in the text and for which statistical significance is calculated can be estimated by finding the 50th percentile value for the region (from the y-axis) and estimating the corresponding value on the x-axis. For example, the median change in SO_4^{2-} concentration in wet deposition in the Northern Appalachian Plateau region (Figure 10a) is ca. -1.6 µeq/L/year.

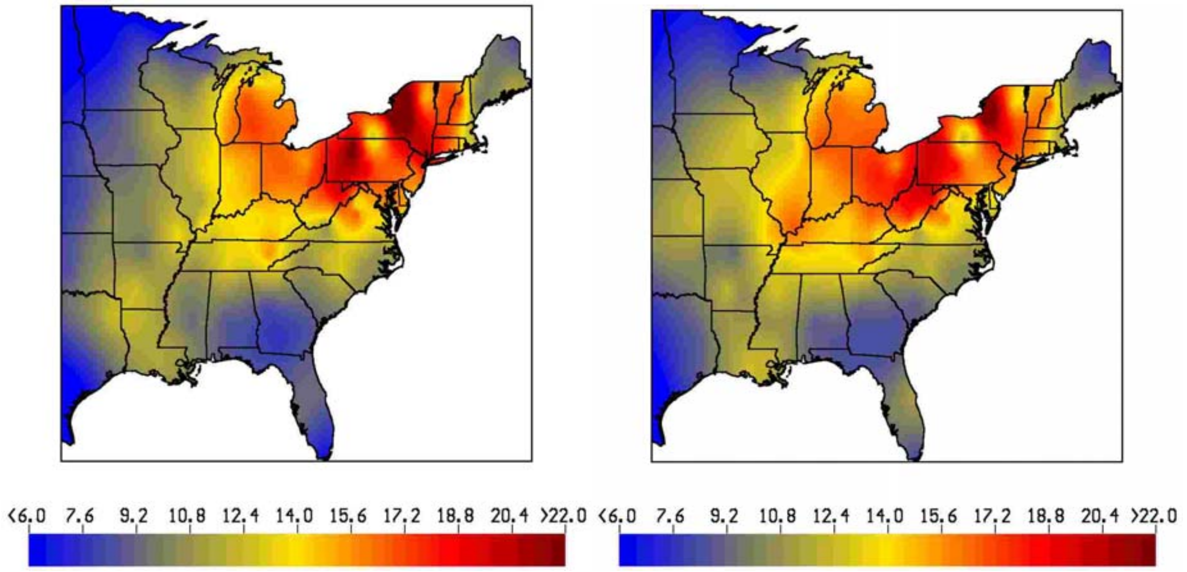


Figure 9. Trends in wet NO_3^- deposition in the eastern United States from NADP/NTN monitoring data (1989-1991 vs. 1995-1998). Data are in kg/ha.

Sulfate concentrations declined substantially in each of the regions at a median rate between -0.8 and -1.5 µeq/L/year for the period 1990 to 2000 (Figure 10a). Nitrogen (NO_3^- plus NH_4^+) declined slightly in the Northeast and Northern Appalachian Plateau and was essentially unchanged in the Ridge and Blue Ridge provinces. The median change in wet deposition of nitrogen in the Upper Midwest during the 1990s was upward (Figure 10b); this was the only region to exhibit an increase in concentrations of either SO_4^{2-} or nitrogen consistent with results reported by Lynch et al., (2000).

An immediate goal of the Title IV of the CAAA is to decrease atmospheric deposition of SO_4^{2-} by reducing sulfur emissions. Wet deposition of SO_4^{2-} declined significantly in every region assessed (Table 4), with median slopes of -0.8 and -1.5 µeq/L/year for the period 1990-2000.

Nitrogen and NO_3^- concentrations also declined significantly in every eastern region with the exception of the Ridge and Blue Ridge provinces where declines were not significant. These trends appear to be driven by a decline in NO_3^- in deposition after 1995. Nitrogen and NO_3^- wet deposition actually increased significantly in the Upper Midwest.

Regional deposition trends for acidity and base cations. It is clear from the emission and deposition data that deposition closely follows emissions for sulfur and perhaps for nitrogen. This is a positive result for evaluating the effectiveness of the CAAA. The expectation is that these declines in acid anions should result in a decline in acidity in precipitation. However, most studies have failed to find a commensurate decline in acidity (hydrogen ion) corresponding to the decline in SO_4^{2-} deposition although the declines in hydrogen ion are statistically significant at many NADP stations (Lynch et al., 2000). Some investigators have attributed the lower than anticipated response in hydrogen ion to decreased deposition of base cations that can offset declines in the wet deposition of sulfate (Hedin et al., 1994, Lynch et al., 2000).

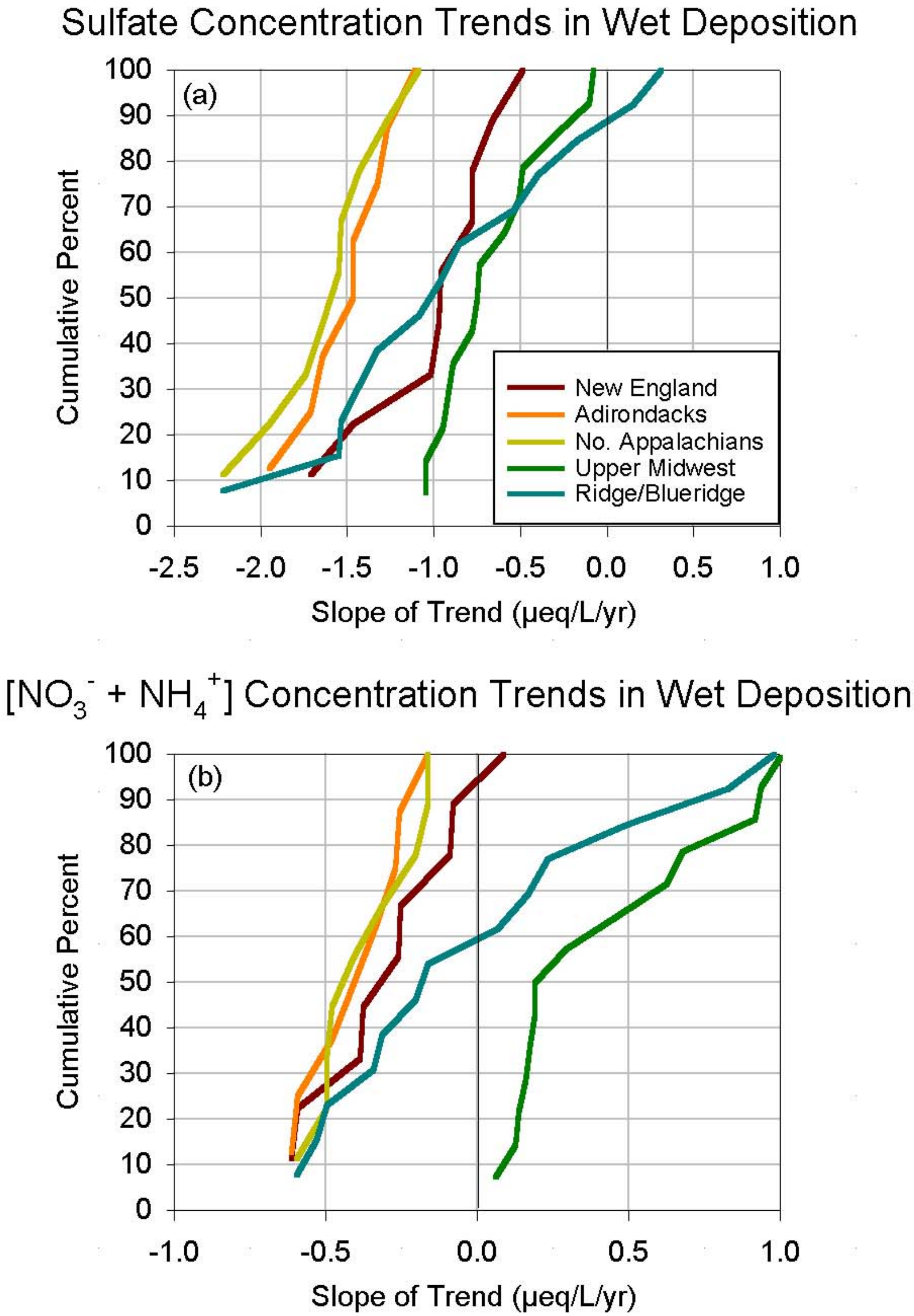


Figure 10. Cumulative frequency distribution of slopes for SO_4^{2-} (panel a, top) and nitrogen (panel b, bottom) trends in wet deposition, from regional NADP/NTN data for the period 1990-2000. The x-axis is the slope (rate of change in µeq/L/yr). The y-axis is the cumulative percent of the population; the median rate of change for each region corresponds to the value of the x-axis at the 50th percentile of the curve.

Table 4. Regional trend results (1990-2000) for atmospheric deposition (wet-only annual concentration data from NADP/NTN network) in acid sensitive regions. All units are µeq/L/yr. Values are the median slopes for each region with significance determined by calculating confidence intervals around each regional median.

Region	SO_4^{2-}	Nitrogen	NO_3^-	Base Cations	Hydrogen
New England	-0.96**	-0.26*	-0.20**	+0.02 ^{ns}	-0.81**
Adirondacks	-1.47**	-0.37**	-0.38**	+0.01 ^{ns}	-1.48**
Appalachian Plateau	-1.55**	-0.41**	-0.37**	+0.01 ^{ns}	-1.54**
Ridge/Blue Ridge Province	-0.96**	-0.16 ^{ns}	-0.13 ^{ns}	+0.05 ^{ns}	-0.94 ^{ns}
Upper Midwest	-0.75**	+0.24**	+0.21**	+0.18**	-0.57**

^{ns} regional trend not significant ($p > 0.05$)

* $p < 0.05$

** $p < 0.01$

We evaluated the deposition patterns for base cations (Ca^{2+} plus Mg^{2+}) and hydrogen ion in each region. In watersheds, base cations are weathering by-products of the neutralization reactions that produce ANC. It is not well understood if base cation deposition from the atmosphere contributes quantitatively important amounts of cations to soils or to the neutralization capacity of the watershed. A long-term decline in the deposition of base cations (Hedin et al., 1994) has been suggested as a possible cause of declining base cation concentrations in surface waters (Driscoll et al., 1989). Widespread declines in surface water base cations have offset decreases in SO_4^{2-} concentrations, and minimized or prevented recovery in ANC in many waters (e.g., Stoddard et al., 1999). While median slopes for base cation deposition trends were positive in every eastern region (Figure 11b), only in the Upper Midwest did wet deposition concentrations of base cations increase significantly.

The combination of significantly decreasing SO_4^{2-} deposition (and to a lesser extent declining nitrogen) and largely unchanged base cations deposition, as reported in this analysis, leads to an expectation of declining acidity in wet deposition as well. In fact, wet deposition of hydrogen ion has decreased in every region (Figure 11a) and is significant in every region except the Ridge and Blue Ridge provinces (Table 4). This is contrary to previous analyses (e.g., Lynch et al., 2000) using data through 1997, and can be attributed to the lack of trend in base cation concentrations for the period 1990-2000.

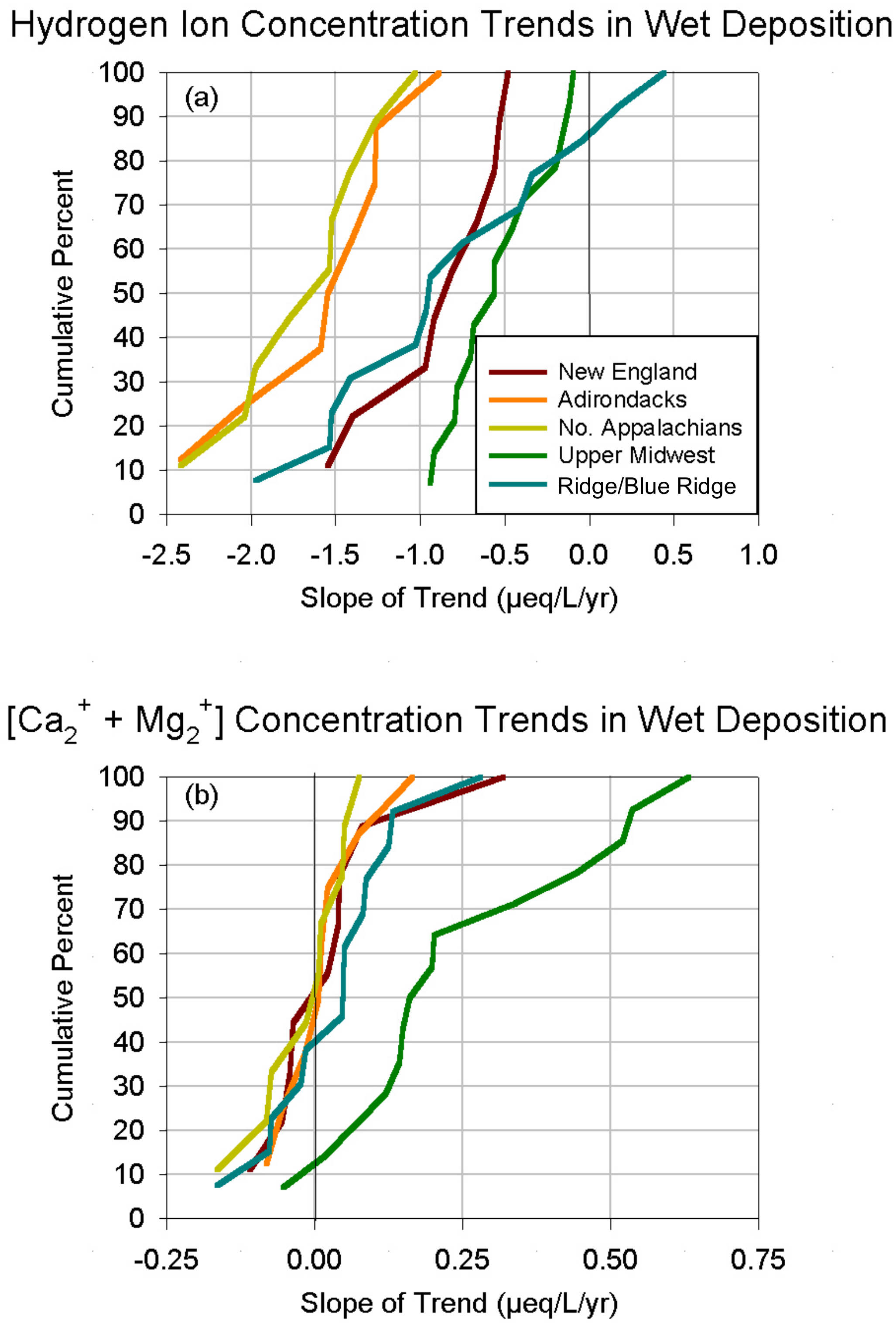


Figure 11. Distribution of slopes for acidity (hydrogen ion; panel a, top) and base cations (Ca^{2+} +Mg^{2+}) (panel b, bottom) trends in regional NADP/NTN data, by region, for the period 1990-2000.

What is background precipitation chemistry? Miller (1999) analyzed the relationship between NADP/NTN SO_4^{2-} wet deposition and sulfur emission inventories for the period 1980-98, using data from New England. We used his equations for the relationship at inland NADP/NTN stations to extrapolate SO_4^{2-} deposition to a hypothetical condition of zero SO_2 emissions. The predicted range of precipitation SO_4^{2-} concentrations at zero SO_2 emission was 1.9 to 4.4 kg/ha at the six stations for which Miller developed equations. The mean SO_4^{2-} deposition intercept (i.e., at zero emissions) was 2.9 kg/ha. Assuming consistent climatic conditions, this deposition would equate to 6 to 10 µeq/L SO_4^{2-} in precipitation as background based on current concentration-deposition relationships.

A background concentration of 6 to 10 µeq/L can be compared to the present range of 20 to 60 µeq/L of wet SO_4^{2-} at NADP/NTN sites in the eastern U.S., and 5 to 20 µeq/L in the western U.S. The precipitation pH represented by this background SO_4^{2-} would be pH 5.0 to 5.2 not including acidity from nitrate or organic acids. This analysis supports the inference of Charlson and Rodhe (1982) that the pre-industrial background precipitation pH in the eastern U.S. was around 5.0 setting the baseline against which to compare modern chemistry. When other sources of acidity are included, it is unlikely that regulatory actions will be able to increase precipitation pH in the eastern U.S. to mean values greater than pH 5.0.

Regional trends in precipitation amount. Climatic variation can be a major complication for interpreting chemical changes in surface waters. In particular, more dilute concentrations of both acid anions and base cations can be expected to occur in wet years, and lower concentrations may result during periods of drought, at least in streams and drainage lakes. In Midwestern seepage lakes, drought may have the effect of isolating lakes from base-rich groundwater, essentially creating temporarily perched seepage lakes, and short-term acidification (Webster et al., 1990). During the period investigated in this report, annual rainfall was relatively uniform in all of the regions (Figure 12). None of the trends in precipitation amount was significant for the 1990-2000 time period, and we have not considered trends in rainfall as part of our analysis of surface water trends. Seasonal wet and dry spells may nonetheless impart extra noise to the data, but we assume that the length of the data record smoothes the noise relative to seasonal variation. In short, we do not consider that climate variation is a major factor affecting the trends in the east and northeast with one exception: recovery from the drought of the 1980s in the Upper Midwest (Webster and Brezonik 1995) is believed to have influenced lake chemistry in the early 1990s and is discussed later in this document.

RESPONSE OF SURFACE WATERS, 1990-2000

Important response variables. Our analysis of surface water response to changing deposition focuses on the key variables that play major roles in acidification and recovery:

1) **SO_4^{2-}** and **NO_3^-**, the acid anions that, when found in surface waters, are often the indicators of acidic deposition. Trends in the concentrations of these anions are inferred to reflect recent trends in deposition (especially SO_4^{2-}) and in ecosystem response to long-term deposition (e.g., NO_3^-).

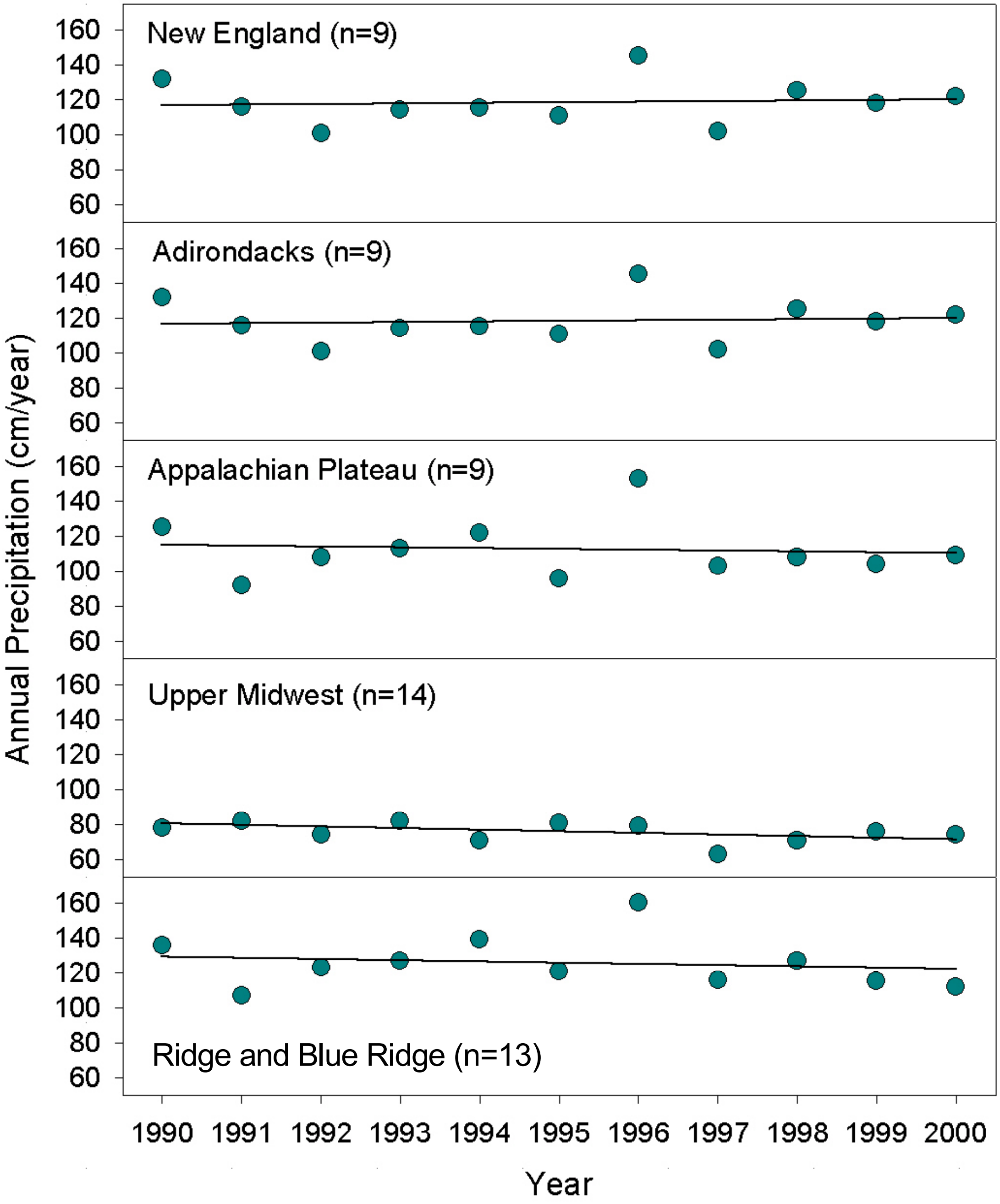


Figure 12. Annual precipitation in the study regions (National Atmospheric Deposition Program/National Trends Network 2002). Symbols represented mean values for sites in each region. Locations of NADP/NTN sites in each region listed in Table 2.

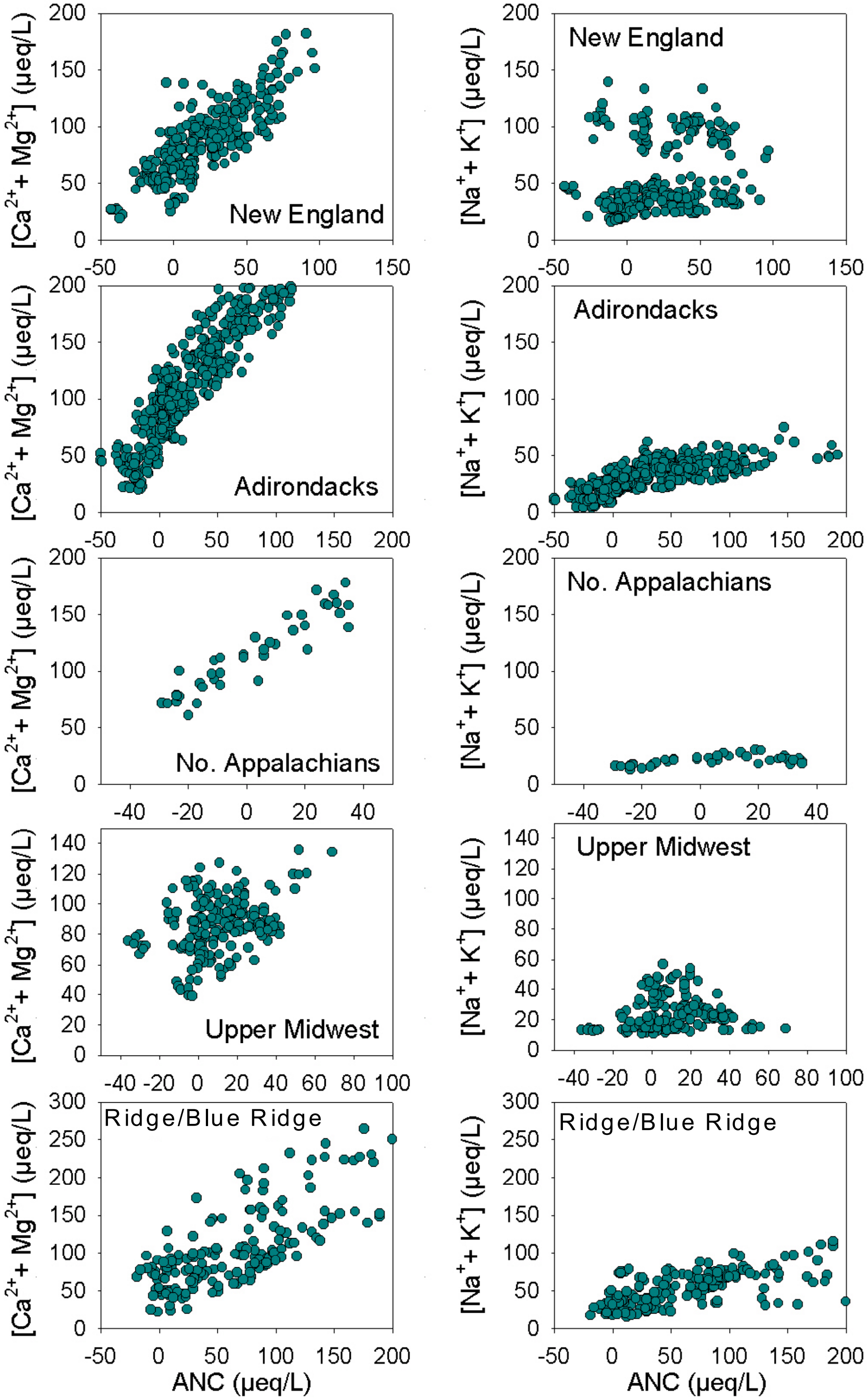


Figure 13. The relationships between Gran ANC and $[Ca^{2+} + Mg^{2+}]$, and between Gran ANC and $[K^{+} + Na^{+}]$ in acid-sensitive regions.

2) **Base cations**, the by-products of the weathering reactions that neutralize acids in watersheds. We have chosen to evaluate the response of the two divalent cations, calcium and magnesium (henceforth [Ca^{2+} + Mg^{2+}]) because of the nature of their behavior in soils; these two cations are quantitatively the most important for generation of Gran ANC (Figure 13). In most regions, the relationship between [Ca^{2+} + Mg^{2+}] and Gran ANC is much stronger than between potassium (K^+) plus sodium (Na^+). The addition of [K^+ + Na^+] to the cation-ANC relationship imparts extra variability to the interpretation of base cation response although the patterns differ by region.
3) **pH** and **Gran ANC**, the measures of acidity. These variables reflect the outcome of interactions between changing acid anions and trends in base cations.
4) **Aluminum**, one of the most important variables for biological impacts due to its toxicity in the ionic form. Changes in concentrations and forms of aluminum are largely driven by changes in pH and DOC with lower and less toxic aluminum concentrations resulting from high pH values and DOC concentrations.
5) Concentrations of **Dissolved Organic Carbon** (DOC), as a surrogate for organic acidity. Organic acids are additional, largely natural, sources of acidity in surface waters.

Representative data from the regions. The trends we report below are for the period of focus for this report, 1990-2000. Many of the monitoring sites for which we report data have been operating since the early 1980s, and examining the entire period of record helps to put current trends into a longer-term context. As detailed earlier, SO_4^{2-} deposition has been declining in the northern and eastern U.S. since the 1970s, and changes produced by the CAAA of 1990 overlay the changes already underway. In order to illustrate this historical context, we have chosen representative sites from each region and present time series of the important response variables outlined above. Representative in this case refers to the observed time trends; each site exhibits trends in the 1990s that are typical of the region.

Salmon Pond in eastern Maine (Figure 14) is one of 24 drainage lakes sampled as part of the LTM project in New England which operates sites in Maine and Vermont. Salmon Pond has been sampled since early 1982 pre-dating the beginning of the LTM project by a year. It is sampled quarterly – in the spring, summer, and fall.

Sampling at Darts Lake (Figure 15) in the Adirondacks began with the RILWAS project (Gherini et al., 1989) in 1982; it became part of the LTM project in 1983 and has been sampled monthly through the 1980s and 1990s.

The East Branch of the Neversink River (Figure 16) is a famous trout fishing stream in the Catskill Mountains of New York and exhibits trends typical of the Northern Appalachian Plateau in the 1990s. It has been sampled as part of the LTM project since 1984 with variable sampling frequencies. The Neversink is sampled for both baseflow and episodic chemistry.

Vandercook Lake in Wisconsin (Figure 17) exhibits trends representative of the Upper

Midwest. This seepage lake has been sampled quarterly in the spring, summer, and fall since 1984.

The Staunton River showing trends representative of the Ridge/Blue Ridge region of Virginia (Figure 18) is located in Shenandoah National Park. It became part of the LTM network in 1992 but has been sampled as part of various programs funded by the National Park Service since 1987. It is currently sampled on a schedule similar to the Neversink River.

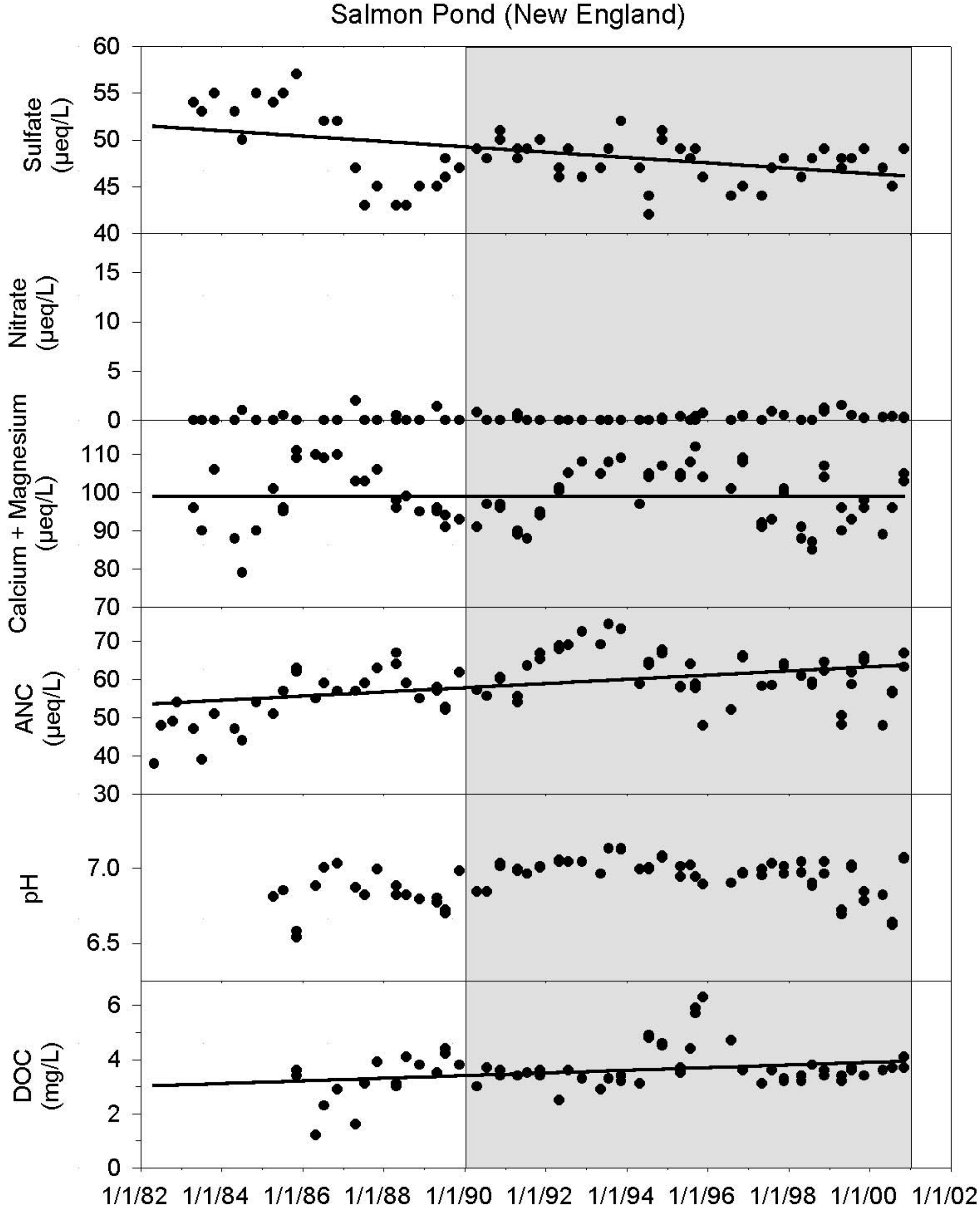


Figure 14. Time series data for SO_4^{2-}, NO_3^-, base cations [Ca^{2+} + Mg^{2+}], Gran ANC, pH, and DOC in Salmon Pond, Maine (New England region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported here.

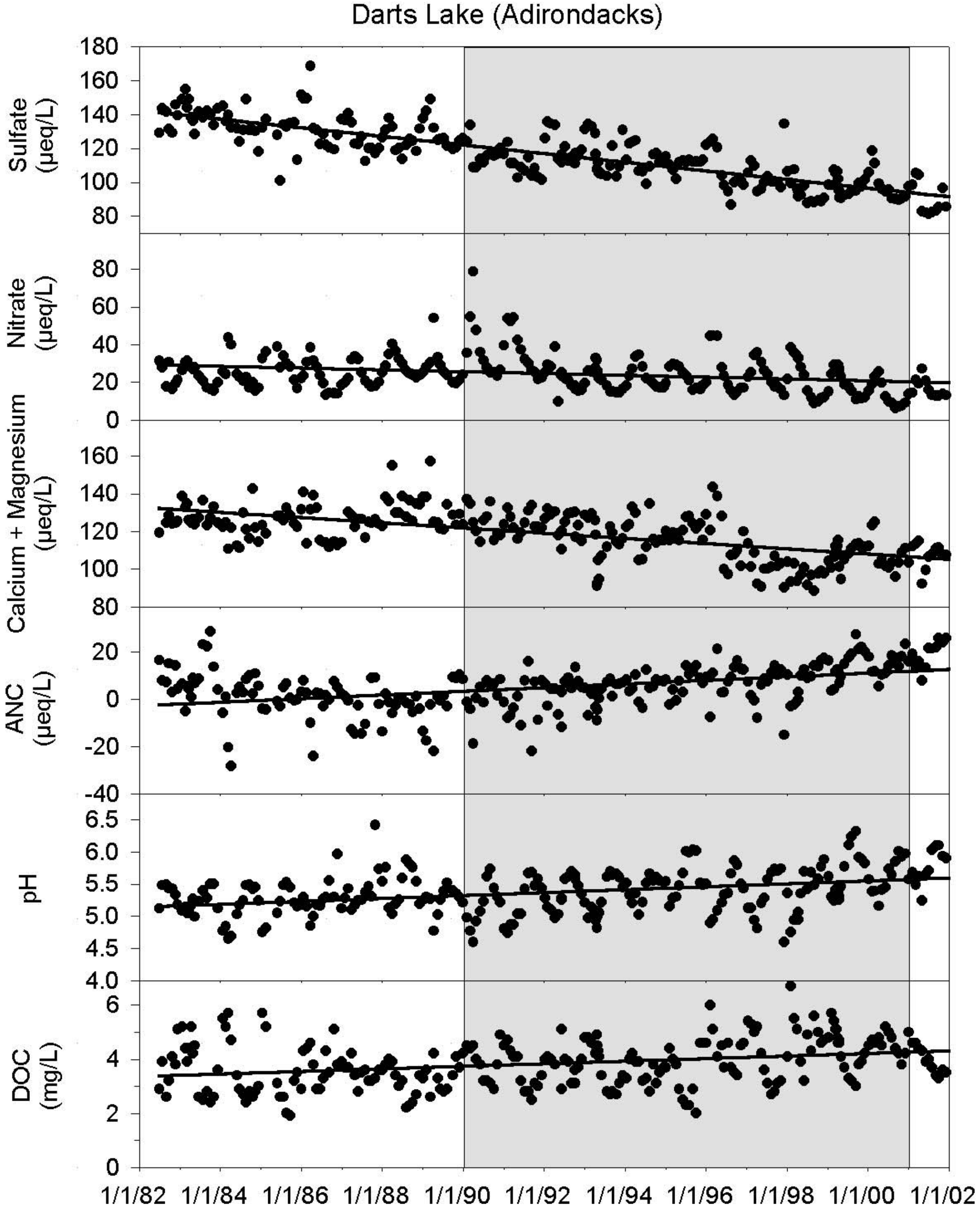


Figure 15. Time series data for SO_4^{2-}, NO_3^-, base cations [$Ca^{2+} + Mg^{2+}$], Gran ANC, pH, and DOC in Darts Lake, NY (Adirondack region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported here.

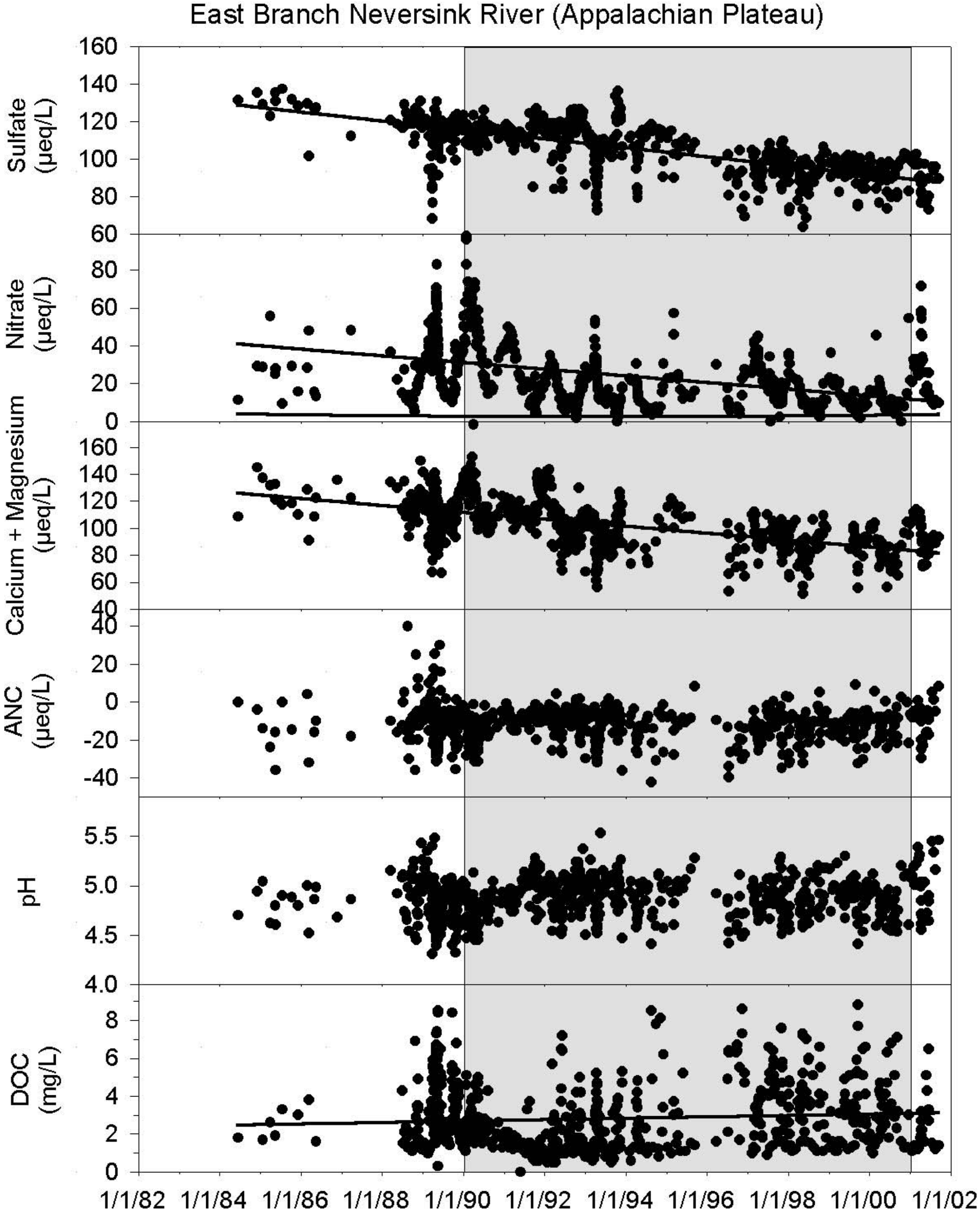


Figure 16. Time series data for SO_4^{2-}, NO_3^-, base cations [Ca^{2+} + Mg^{2+}], Gran ANC, pH, and DOC in the E. Branch of the Neversink River, New York Catskills (Northern Appalachian Plateau region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses.

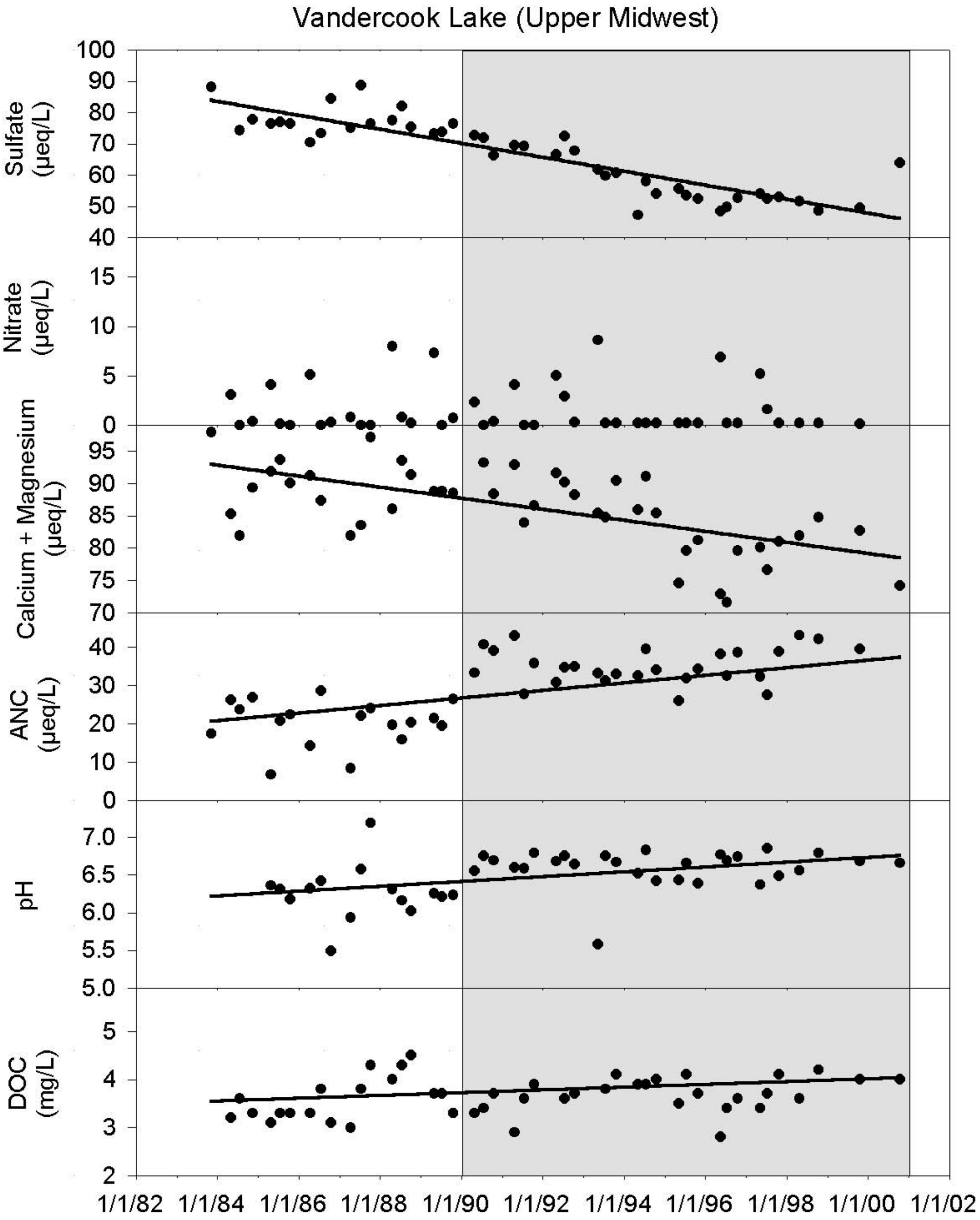


Figure 17. Time series data for SO_4^{2-}, NO_3^-, base cations [Ca^{2+} + Mg^{2+}], Gran ANC, pH, and DOC in Vandercook Lake, Wisconsin (Upper Midwest region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported here.

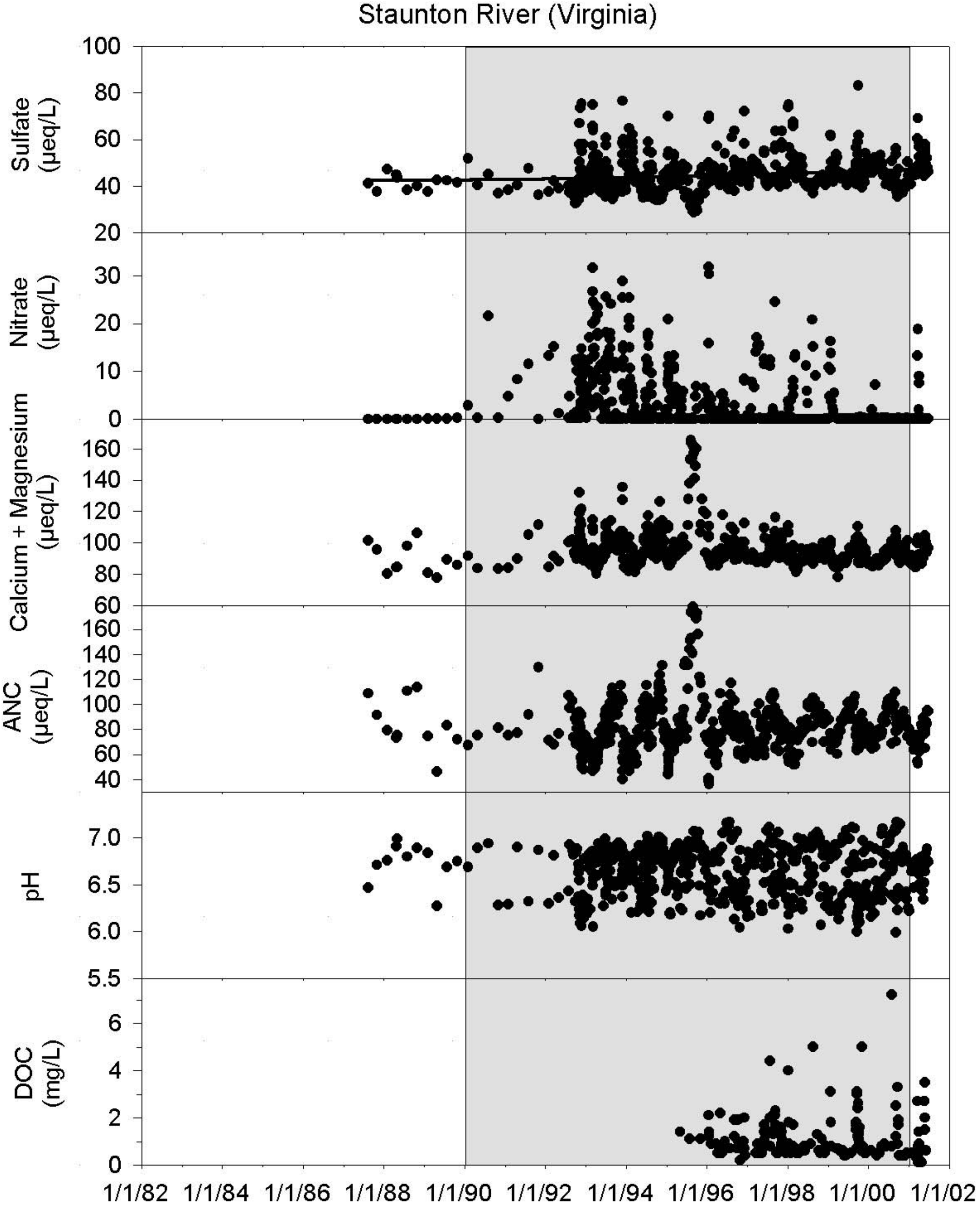


Figure 18. Time series data for SO_4^{2-}, NO_3^-, base cations [Ca^{2+} + Mg^{2+}], Gran ANC, pH, and DOC in the Staunton River, Virginia (Ridge/Blue Ridge region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported here.

Trends in sulfate by region. SO_4^{2-} declined in surface waters in the glaciated regions of the North and East by median values between –2 and –4 µeq/L/year (Figure 19) with the smallest changes in New England and the largest declines in the Upper Midwest. The only exception to the pattern of declining SO_4^{2-} was in the Ridge/Blue Ridge provinces which by virtue of their soil characteristics were not expected to show a rapid response to changes in deposition (Cosby et al., 1986, Church et al., 1989). The median SO_4^{2-} increased slightly in Ridge and Blue Ridge streams. All of the regional SO_4^{2-} trends are highly significant (Table 5) and are consistent with the trends reported previously including other regions of North America and Europe (Mattson et al., 1997, Stoddard et al., 1999, Evans and Monteith 2001, Skjelkvåle et al., 2001).

The marked declines in SO_4^{2-} concentrations in the glaciated portions of the North and East are almost certainly direct responses to declining emissions and SO_4^{2-} deposition in the 1990s and represent the most dramatic effects of Title IV of the CAAA and previous emissions regulations. These changes in emissions and deposition continue the trend in declining SO_4^{2-} that has been occurring for almost three decades (Stoddard et al., 1999).

The small increase in SO_4^{2-} concentrations in the Ridge and Blue Ridge provinces results from the SO_4^{2-} adsorption properties typical of soils found throughout this unglaciated region which have the effect of both decoupling (in time) trends in deposition and surface waters (Tables 4 and 5) and lowering the ambient concentrations of SO_4^{2-} well below those found in deposition (Figure 7). The future response of SO_4^{2-} concentrations in this region will be a critical element in governing any potential recovery in this region.

Table 5. Regional trend results for Long-Term Monitoring sites for the period 1990 through 2000. Values are median slopes for set of sites in each region. Units for sulfate, nitrate, base cations [$Ca^{2+} + Mg^{2+}$], Gran ANC and hydrogen are µeq/L/year. Units for DOC are mg/L/year. Units for aluminum are µg/L/year.

Region	SO_4^{2-}	NO_3^-	Base Cations	Gran ANC	Hydrogen	DOC	Aluminum
New England Lakes	-1.77**	+0.01^{ns}	-1.48**	+0.11 ^{ns}	-0.01 ^{ns}	+0.03*	+0.09 ^{ns}
Adirondack Lakes	-2.26**	-0.47**	-2.29**	+1.03**	-0.19**	+0.06**	-1.12**
Appalachian Streams	-2.27*	-1.37**	-3.40**	+0.79*	-0.08*	+0.03 ^{ns}	+0.56 ^{ns}
Upper Midwest Lakes	-3.36**	+0.02 ^{ns}	-1.42**	+1.07**	-0.01*	+0.06**	-0.06 ^{ns}
Ridge/Blue Ridge Streams	+0.29**	-0.07**	-0.01 ^{ns}	-0.07^{ns}	+0.01 ^{ns}	NA	NA

ns	regional trend not significant ($p > 0.05$)
*	$p < 0.05$
**	$p < 0.01$
NA	insufficient data

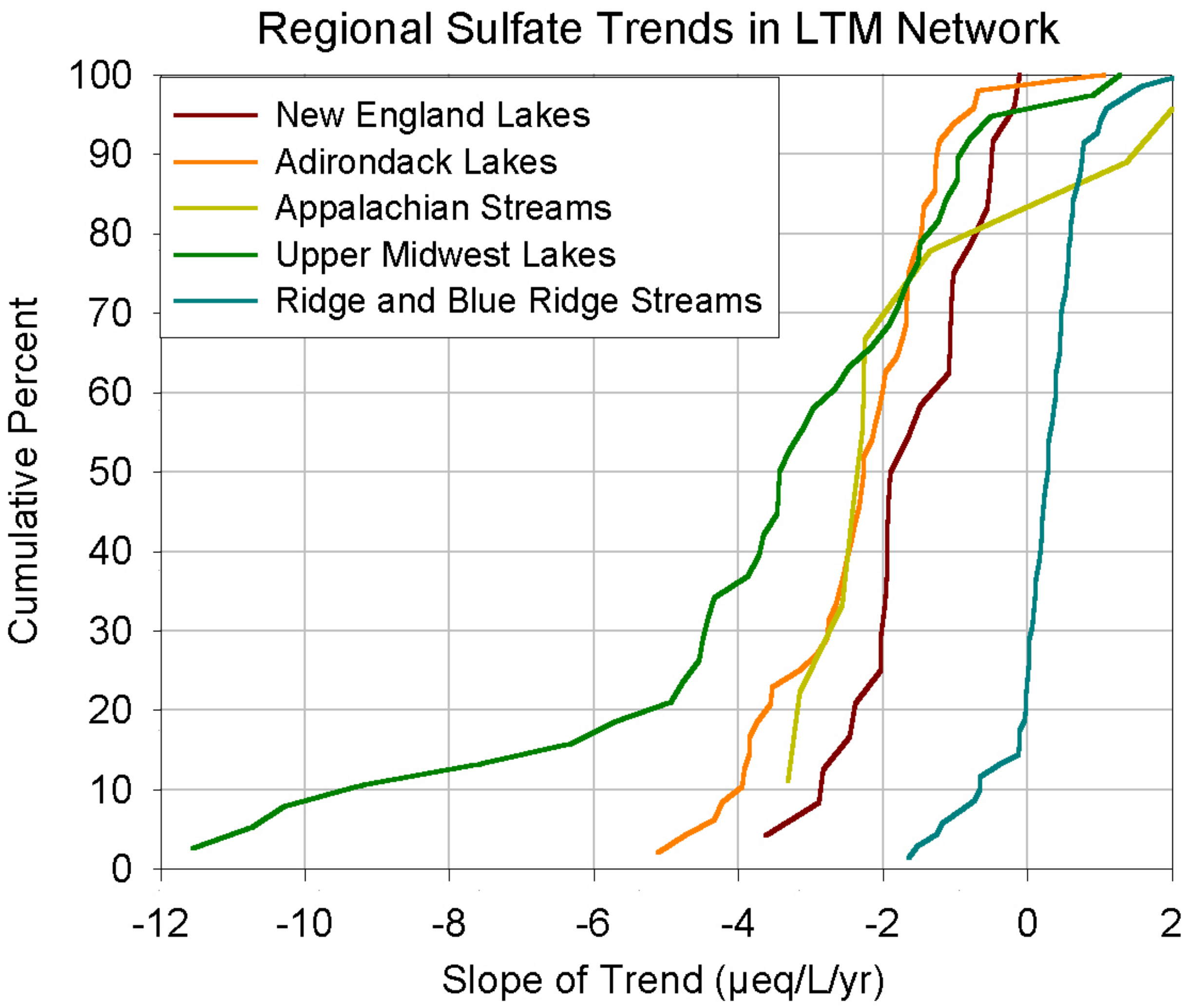


Figure 19. Cumulative frequency diagram (distribution) of slopes (µeq/L/year) for SO_4^{2-} concentrations in surface water monitoring sites, by region for the period 1990-2000.

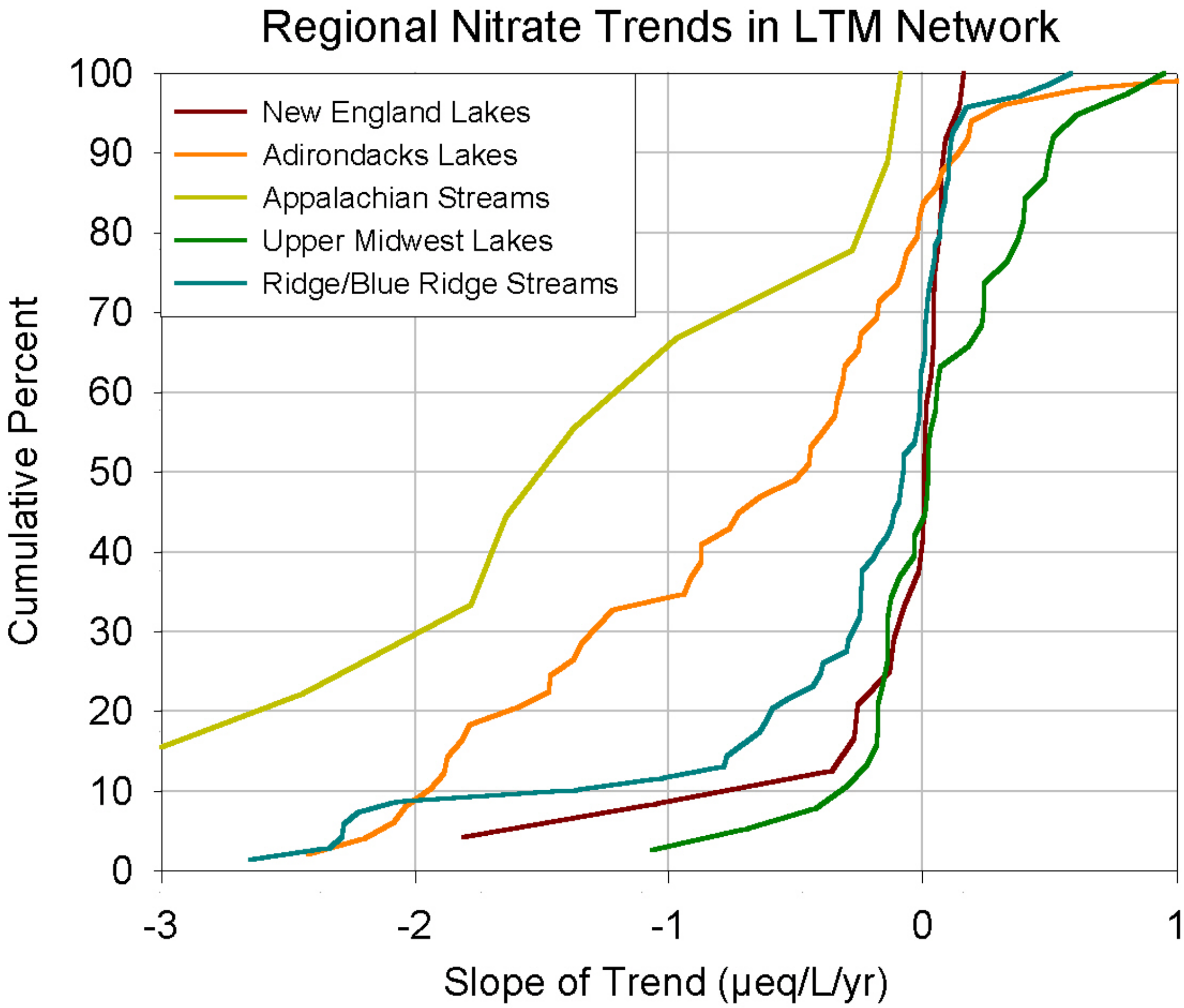


Figure 20. Cumulative frequency diagram (distribution) of slopes (µeq/L/year) for NO_3^- concentrations in surface water monitoring sites, by region for the period 1990-2000.

Trends in nitrate by region. In general, trends in NO_3^- were much smaller than trends in SO_4^{2-} with the only ecologically significant changes occurring in the two regions with the highest ambient NO_3^- concentrations (Figure 20). Both lakes in the Adirondacks and streams in the Northern Appalachian Plateau exhibited small but significant downward trends in NO_3^- in the 1990s (Table 5). Both of these regions are central to the debate over whether nitrogen saturation is a legitimate threat to the health of forests and surface waters (Stoddard 1994, Aber et al., 1998). While declining NO_3^- concentrations in these regions are a positive development for these ecosystems, we clearly do not know if these trends will continue especially since they do not reflect recent trends in emissions or deposition (Table 4, Figures 7-9). The presence of strong *upward* trends in NO_3^- in these same regions in the 1980s (Murdoch and Stoddard 1992, Stoddard 1994) suggests that trends on the scale of a single decade probably represent noise (variability) in a long-term pattern of changing NO_3^- leakage from forested watersheds controlled by factors that will take many years to determine. While great uncertainty exists and the time scales of nitrogen saturation may be longer than previously considered (e.g., centuries rather than decades), the long-term retention of nitrogen deposition in forested regions is unlikely to continue indefinitely (Aber et al., in press).

In New England and the Upper Midwest, where ambient NO_3^- concentrations are much lower than in the Adirondacks and Northern Appalachian Plateau (Figures 14-17), NO_3^- concentrations in surface waters were unchanged. The Ridge/Blue Ridge province registered a small but significant decrease in NO_3^- during the 1990s, but interpretation of trends for NO_3^- in this region is complicated by an outbreak of Gypsy Moths that also occurred during this period. Forest defoliation by Gypsy Moths was the cause of a pulse in NO_3^- export from many streams in this region in the mid-1990s (Eshleman et al., 1998).

Trends in Gran ANC and acidity, by region. In a very real sense, increasing trends in Gran ANC would be the strongest signs of recovery from acidification in response to the CAAA. There was a tendency toward increasing Gran ANC (Figure 21) in all of the glaciated regions of the North and East (i.e., New England, Adirondacks, Northern Appalachian Plateau and Upper Midwest) and decreasing Gran ANC in the Ridge/Blue Ridge province. Only the regional increases in the Adirondacks, Northern Appalachian Plateau, and Upper Midwest were significant (Table 5). Median increases of ca. +1 μeq/L/year in the Northern Appalachian Plateau, Adirondacks and Upper Midwest represent significant ecological recovery from acidification.

Previous regional analyses using data through 1995 have highlighted the lack of ANC recovery in the Adirondacks, Northern Appalachian Plateau and Upper Midwest (Stoddard et al., 1999). In the Adirondacks and Northern Appalachians, many of the sites exhibit the pattern shown for Darts Lake in Figure 15 and the Neversink River in Figure 16 with Gran ANC increasing after an inflection point in the early- to mid-1990s. The current Gran ANC trends (Table 5) in the Adirondacks and Northern Appalachian Plateau appear to have reversed the pattern of lack of recovery with further acidification occurring in some cases that occurred throughout the 1980s and early 1990s in this region.

In the Upper Midwest, the downward Gran ANC trends reported by Stoddard et al., (1999) for the period 1990-95 appear to have been a temporary departure from the long-term recovery of ANC in this region. The trends reported for the 1990s (Table 5) are consistent with the long-term pattern of increasing Gran ANC observed at individual sites.

Stoddard et al., (1999) reported recovery in Gran ANC in the New England region using data through 1995. This trend is no longer evident when all data from the 1990s are examined (Table 5). The temporal pattern for New England lakes appears to be the reverse of that exhibited by lakes in the Adirondacks, with long-term recovery in Gran ANC having fallen off after a similar inflection point in the early 1990s (Figure 14). The slight tendency for Gran ANC to increase in this region is not significant, with nearly as many lakes showing small decreases (11) as show slight increases (13).

Gran ANC showed an insignificant downward trend in the Ridge/Blue Ridge province consistent with the small increases in SO_4^{2-} observed. It is clear that while the evidence for a widespread recovery in ANC in the glaciated North and East is quite strong, no such evidence exists for the unglaciated Ridge/Blue Ridge province.

Widespread changes in Gran ANC translated into some small, but significant, changes in acidity (hydrogen ion; Figure 22). The largest significant decreases in hydrogen ion occurred in the Adirondacks (Table 5), but on an equivalent basis they were less than 20% of the changes observed in Gran ANC in this region. The moderate decrease observed in the Northern Appalachians was likewise small relative to the change in Gran ANC (< 10% of the ANC change). All of the other regions exhibited median slopes near zero, and only the Upper Midwest trend was significant (Table 5). To put these changes in hydrogen ion in context, a decline in hydrogen concentration of 1 μeq/L/year in an acidic lake with pH 4.7 would equate to a of pH 5.00 over 10 years. All of the changes observed here are considerably smaller than this.

Trends in base cations, by region. All of the glaciated regions on the northern and eastern U.S. exhibited declines in base cation [Ca^{2+} + Mg^{2+}] concentrations in the range of –1.5 to –3.4 μeq/L/year (Figure 23), and all of the regional trends were highly significant (Table 5). One of the most universal watershed responses to acidic deposition is the mobilization of base cations from soils (Galloway et al., 1983); as rates of acidic deposition decline in the North and East and the supply of acid anions to watersheds soils decreases, the rates of cation mobilization are also expected to decrease. Lowered rates of cation mobilization translate to downward trends in surface water base cation concentrations, a change widely observed in the northern hemisphere for more than a decade. Keller et al., (2001) suggested that a trend of declining Ca^{2+} has been occurring for more than a century in Ontario lakes.

As a broad generalization, SO_4^{2-} has decreased at a rate of approximately –2.5 μeq/L/year (the mean of regional median slopes), and NO_3^- at a rate of –0.5 μeq/L/year, in surface waters of glaciated terrain. These rates of change set an upper limit to our expectation of ANC recovery of +3 μeq/L/yr (i.e., the sum of SO_4^{2-} and NO_3^- trend magnitudes). The Gran ANC increase is actually about one-third of this maximum, +1 μeq/L/year. The difference between the observed Gran ANC trend and the maximum trend estimated from rates of acid anion change can be almost entirely explained by regional declines in base cations; the average regional median decline in [Ca^{2+} + Mg^{2+}] was about –2.0 μeq/L/year.

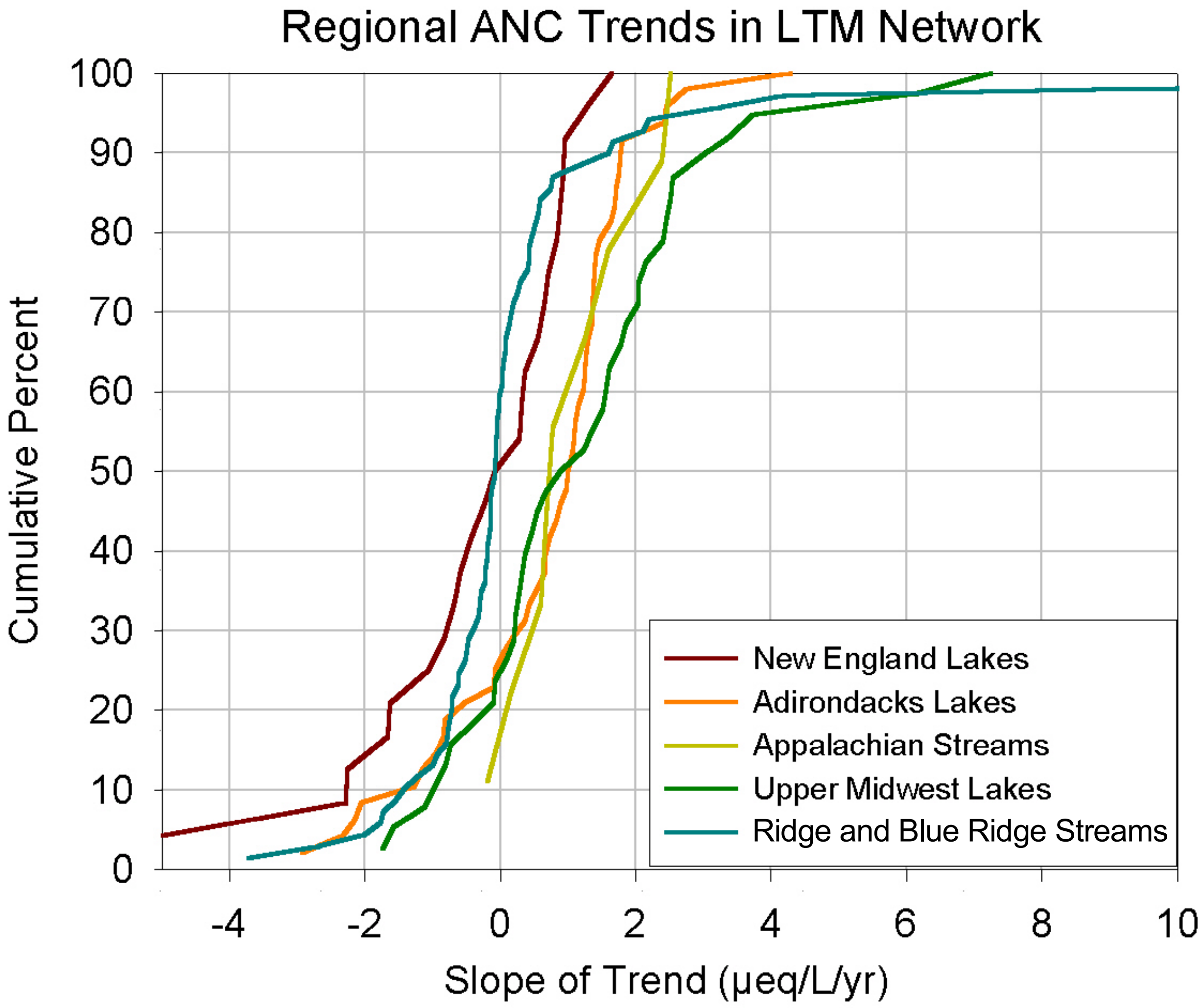


Figure 21. Cumulative frequency diagram (distribution) of slopes (μeq/L/year) for Gran ANC concentrations in surface water monitoring sites, by region for the period 1990-2000.

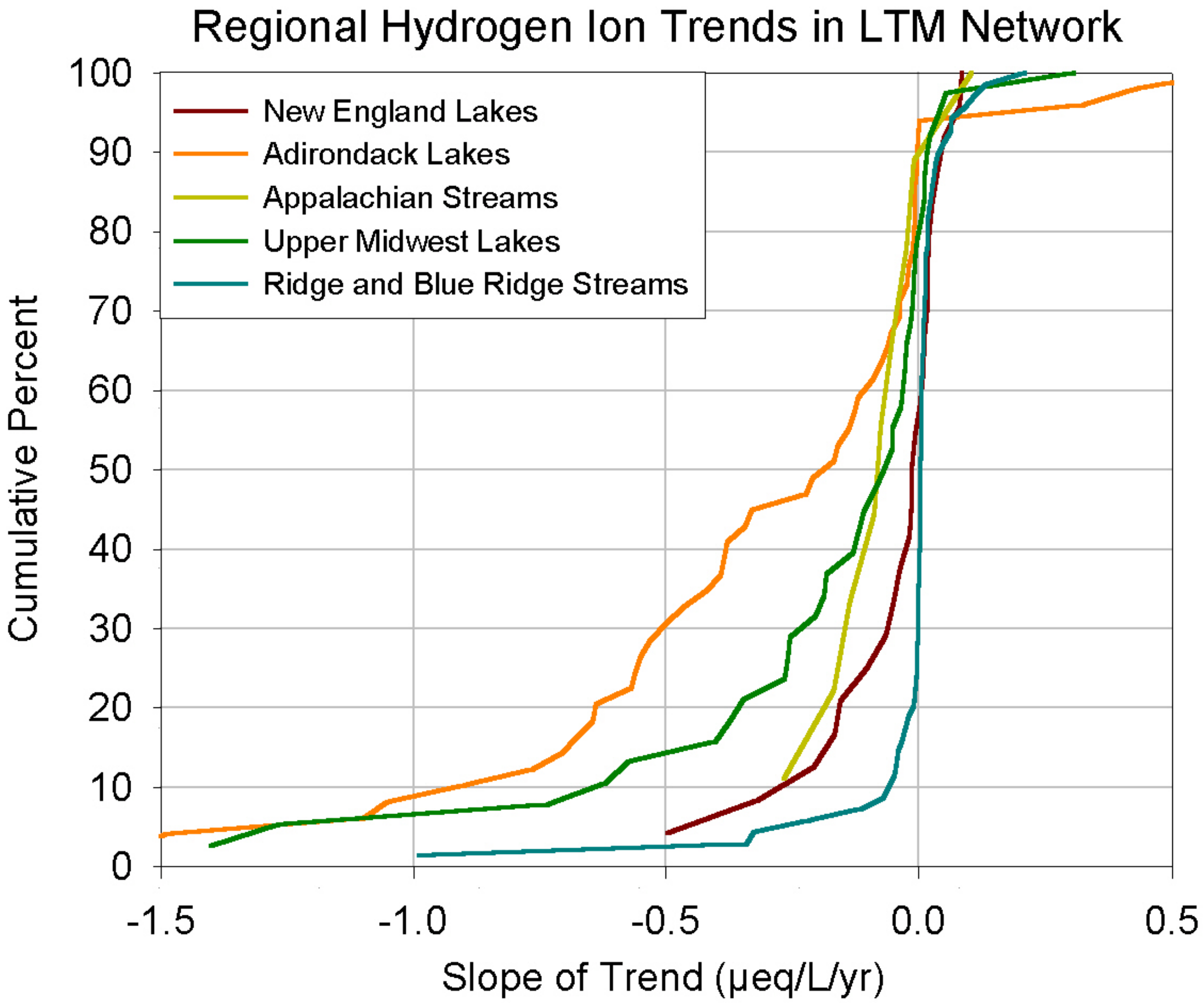


Figure 22. Cumulative frequency diagram (distribution) of slopes (µeq/L/year) for hydrogen ion concentrations in surface water monitoring sites, by region for the period 1990-2000.

The decline in [Ca^{2+} + Mg^{2+}] while not unexpected limits the magnitude of ANC recovery by offsetting some of the decline in SO_4^{2-} and NO_3^{-}. Moreover, if the rate of base cation decline is equal to the rates of decline in acid anions, recovery will be prevented. This is the pattern observed in several regions of North America in previous regional analyses (Stoddard et al., 1998a, Stoddard et al., 1998b) using data through the early 1990s. The observation that acid anions, and particularly SO_4^{2-}, concentrations are decreasing at a faster rate than base cations in most regions (Table 5) leads to an increase in Gran ANC, and is consistent with the pattern that has been observed in northern Europe since about 1990 (Stoddard et al., 1999).

Several researchers (e.g., Likens et al., 1996, Lawrence et al., 1999, Driscoll et al., 2001) have proposed that the recovery of surface waters will be substantially delayed because soil impoverishment induced by decades of base cation leaching by the anions in acidic deposition has reached critical levels. At least one aspect of the current analysis argues against this hypothesis. The regional response of base cations to changing SO_4^{2-} deposition is following expectations (e.g., [Ca^{2+} + Mg^{2+}] is decreasing at lower rates than SO_4^{2-} in glaciated terrain and is unchanged in unglaciated terrain) in every region.

Trends in dissolved organic carbon (DOC), by region. Another potential factor influencing the responsive in ANC and acidity is the general increase in DOC (Figure 24). All regions with sufficient DOC data exhibited increases in concentrations, and all regional trends were significant with the exception of the Northern Appalachian Plateau (the region with the lowest median DOC concentrations). While the character of the DOC found in these watersheds has not been evaluated, some portion of the DOC is organic acid. The median increase of 0.05 mg/L/year corresponds to an increase of about 10% region-wide similar to trends reported elsewhere in the Northern Hemisphere (Evans and Monteith 2001, Skjelkvåle et al., 2001).

It is beyond the scope of an analysis of monitoring data like the one presented here to determine the mechanism for DOC increase unequivocally. However, there are several aspects of the DOC trends that warrant further attention. First, increases in DOC have now been reported from nearly all regions of North America (this report) and Europe (Skjelkvåle et al., 2001). This argues for a large-scale cause, and both climate change (warmer temperatures are expected to increase decomposition and could potentially increase the export of DOC from watersheds) and decreasing acidic deposition are possible hypotheses. Several researchers have proposed that at least part of the increase in mineral acids (e.g., SO_4^{2-} and NO_3^{-}) observed in acidifying watersheds in the past (Rosenqvist 1978, Krug and Frink 1983) resulted from the replacement of natural organic acidity with mineral acidity. They thus propose that the process of acidification was accompanied by a decrease in surface water DOC concentrations. This hypothesis has received some support from paleolimnological studies where reconstructions of historic DOC concentrations show decreases during the period of acidification in the 1900s (Davis et al., 1985, Kingston and Birks 1990, Dixit et al., 2001). David et al., (1999) were also able to measure a decrease in organic anions in response to the experimental whole-watershed acidification experiment at the Bear Brook Watershed in Maine (Norton et al., 1999). In one of the few studies of

DOC behavior during recovery from acidification, Wright et al., (1993) concluded that ANC increases in a small watershed where rates of acidic deposition were experimentally reduced were limited by the increasing role of organic acids and an overall increase in DOC.

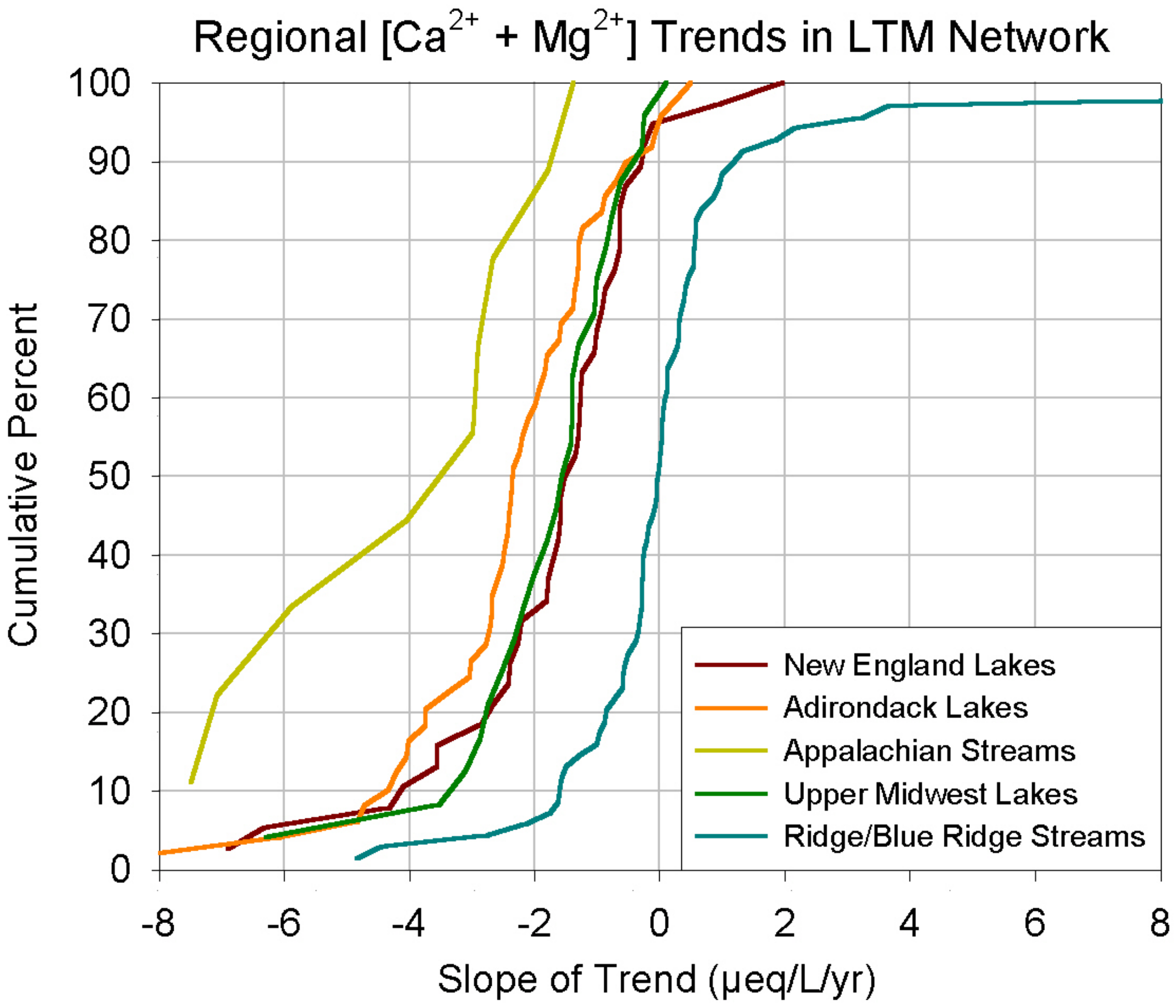


Figure 23. Cumulative frequency diagram (distribution) of slopes (µeq/L/year) for base cations [Ca^{2+} + Mg^{2+}] in surface water monitoring sites, by region for the period 1990-2000.

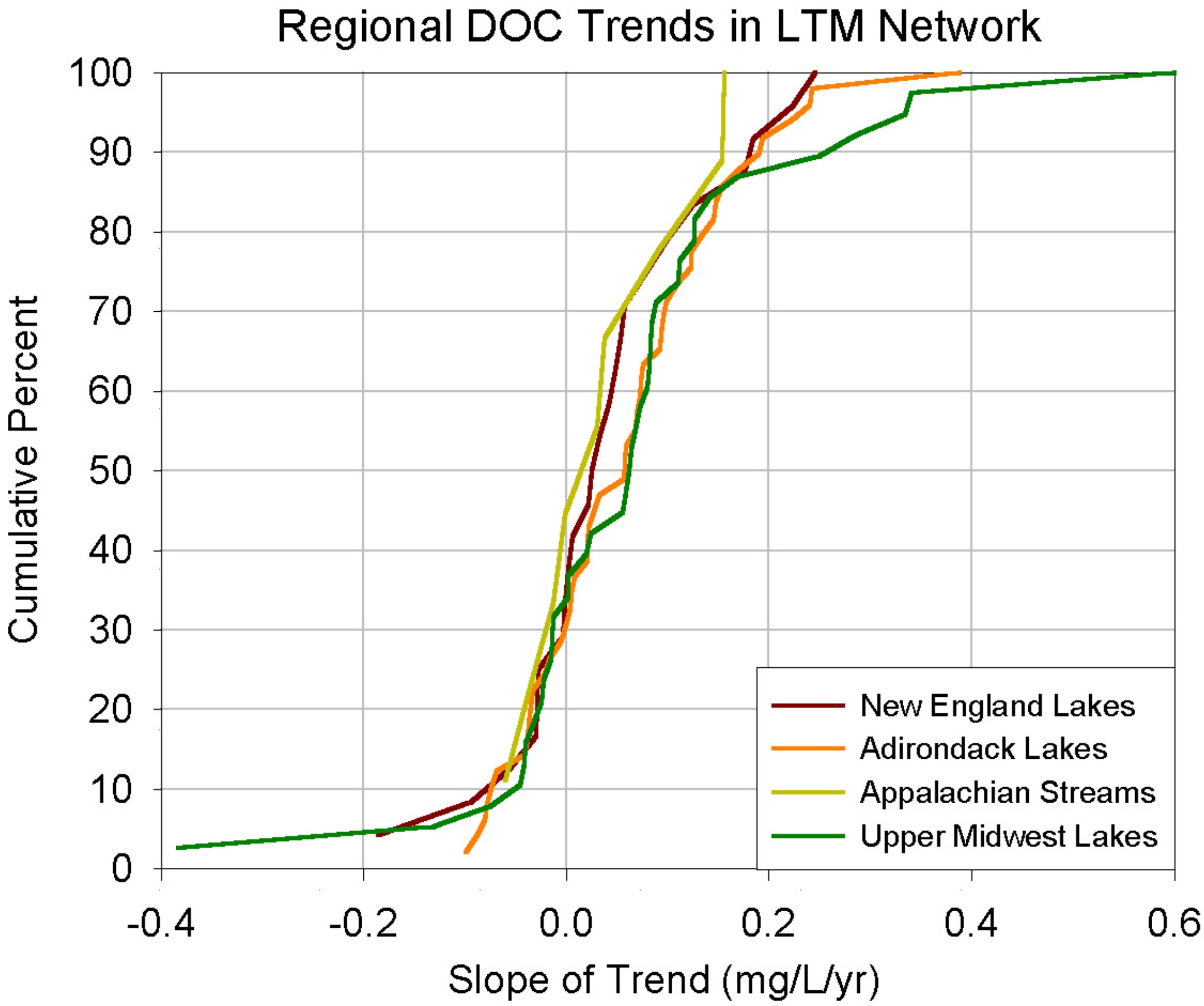


Figure 24. Cumulative frequency diagram (distribution) of slopes (mg/L/year) for DOC concentrations in surface water monitoring sites, by region for the period 1990-2000. The Ridge/Blue Ridge province does not have sufficient DOC data to allow trend analysis.

In a regional study of trends like the one presented here one might predict that if this hypothesis (the replacement of organic acidity by mineral acidity during acidification) is correct, then the current rates of DOC increase should be correlated to rates of SO_4^{2-} decline. This is in fact observed in the trend data for all lake regions (Figure 25). The largest rates of DOC increase are observed at the sites with the strongest declines in surface water SO_4^{2-}. This relationship is strongest in high DOC systems (i.e., those with DOC > 5 mg/L) but is also observed in low DOC lakes.

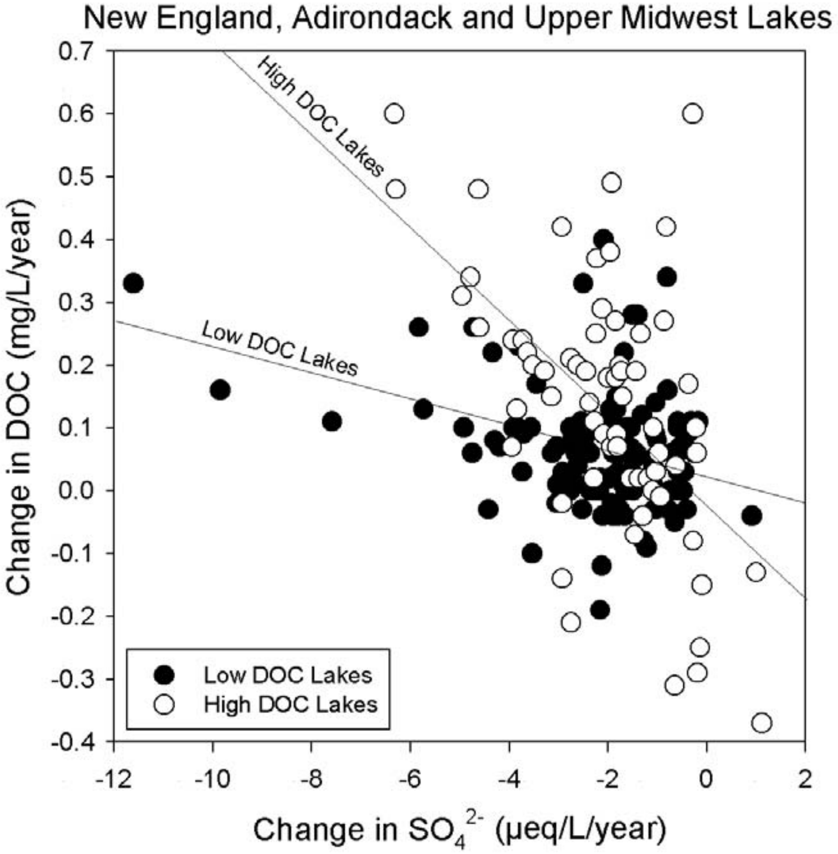


Figure 25. Relationship between trends in DOC and trends in SO_4^{2-} concentrations for lakes. This graph includes data from the Maine high elevation and seepage lakes in order to produce a relationship with sufficient numbers of high DOC in small, responsive lakes.

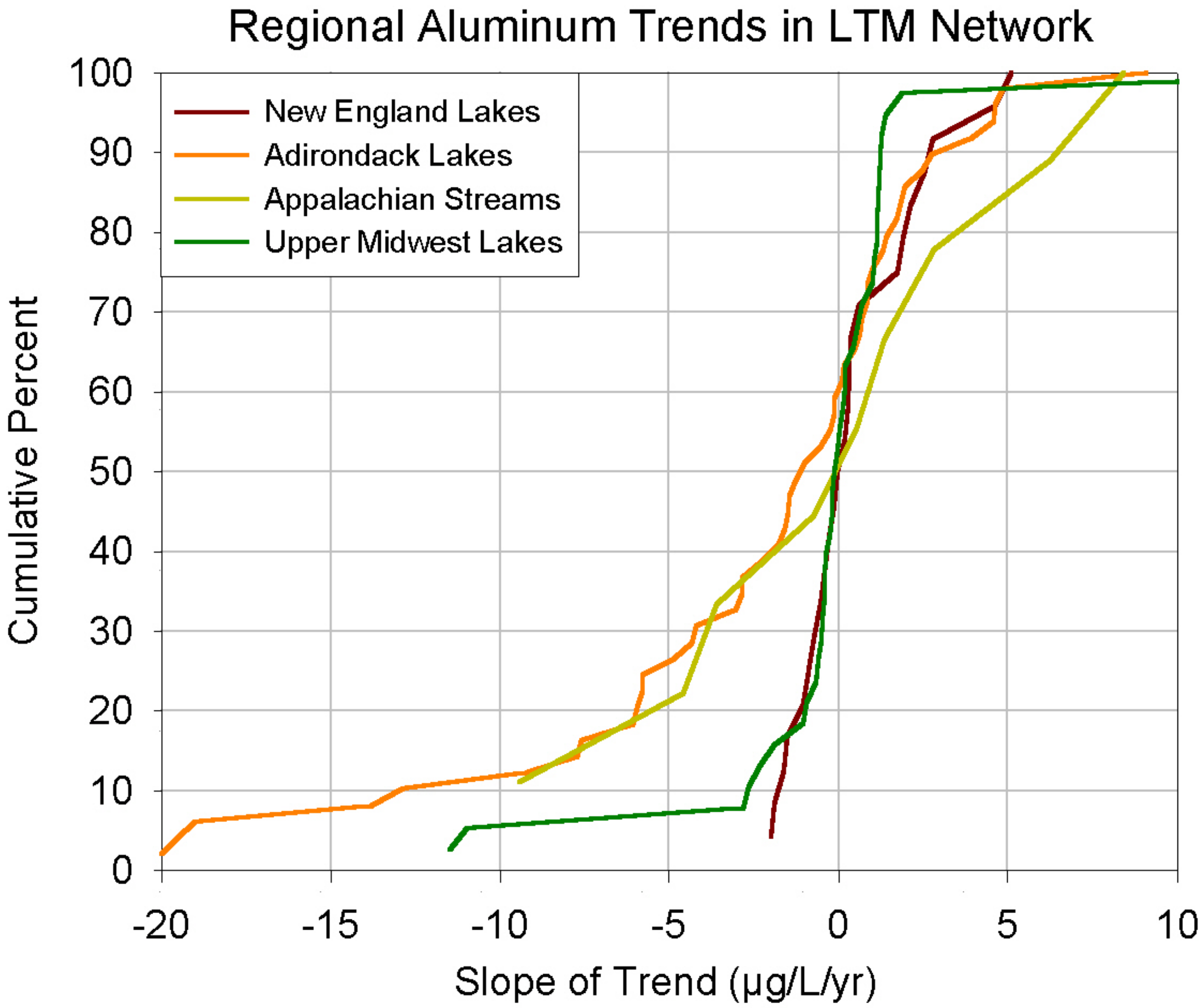


Figure 26. Cumulative frequency diagram (distribution) of slopes (µg/L/year) for aluminum concentrations in surface water monitoring sites, by region for the period 1990-2000. Data from the Adirondacks are for inorganic monomeric aluminum; all others are total dissolved aluminum.

Trends in aluminum by region. Aluminum plays a major role in the biotic impoverishment that often accompanies surface water acidification (e.g., Baker and Schofield 1982, Cleveland et al., 1986). Decreasing trends in aluminum, particularly in the most toxic form of aluminum (inorganic monomeric aluminum), would therefore be a biologically relevant indicator of recovery. Only one of the regions analyzed here exhibited regional decreases in aluminum (Figure 26). In the Adirondacks, the median decline in inorganic monomeric aluminum was approximately –1.0 μg/L/year, a very small number in terms of importance to biota. However, this change is consistent with regional increases in Gran ANC and decreases in hydrogen ion. The Adirondack trends are also consistent with reported decreases in toxic aluminum in soil water samples from the Hubbard Brook Experimental Forest in New Hampshire (Palmer and Driscoll 2002). No regional trends other than the Adirondacks were significant (Table 5).

Our analysis for aluminum is complicated by the fact that the most consistently collected data for aluminum are for total dissolved aluminum which includes both organic forms and polymeric inorganic forms. Small changes in inorganic monomeric aluminum which may make up only a small portion of total dissolved aluminum may be undetectable if the other forms are relatively unchanged, or are highly variable. We do not therefore consider the general lack of trends in regional aluminum concentrations conclusive although they are generally consistent with patterns of unchanged hydrogen ion.

Relationship between ANC trends and ANC class: It is reasonable to expect, based on our conceptual understanding of the process of acidification, that decreasing rates of acidic deposition and decreasing surface water concentrations of acid anions will produce the greatest rates of recovery in the sites that have undergone the most severe acidification. One outcome of this expectation would be larger upward trends in acidic lakes and streams, small upward trends in low ANC sites, and no change in the relatively insensitive sites we classify as moderate ANC. An analysis of Gran ANC trends by ANC class designed to test this expectation is shown in Table 6. Using data from all of the sites in regions where decreases in surface water SO_4^{2-} and/or NO_3^- have occurred, we find that acidic lakes and streams exhibit a highly significant median increase in Gran ANC of +1.3 μeq/L/year. Low ANC sites show a smaller, but nonetheless significant, median ANC increase of +0.8 μeq/L/year. Moderate ANC sites, those with mean ANC values greater than 25 μeq/L, show no significant change in Gran ANC.

Table 6. Slopes of trends in Gran ANC in acidic, low ANC and moderate ANC sites for the period 1990-2000. Analysis includes all sites in New England, Adirondacks, Appalachian Plateau and Upper Midwest; Ridge and Blue Ridge sites excluded.

ANC Class	Number of Sites	Change in Gran ANC (µeq/L/yr)
Acidic (ANC < 0 µeq/L)	26	+1.29**
Low ANC (0 < ANC < 25 µeq/L)	51	+0.84**
Moderate ANC (25 < ANC < 200 µeq/L)	43	$+0.32^{ns}$

ns trend not significant ($p > 0.05$)

* $p < 0.05$

** $p < 0.01$

Regional trends in probability networks. The data described thus far in this report come from the LTM project and from other monitoring networks with similar objectives. The method of site selection utilized for LTM varied among regions and was in part driven by the existence of historical data and/or ongoing data collection rather than statistical frameworks to determine population trends. Stoddard et al., (1998b) placed LTM sites from the Northeast in the lake classification system of Young and Stoddard (1996) and found that they largely covered the range in current status (e.g., current Gran ANC and base cation concentrations) of the most sensitive subpopulation(s) of lakes in the region. The trend results, however, indicated two different classes of response: lakes in New England were increasing in ANC (based on data for the period 1984-94), while those in the Adirondacks were acidifying slightly, even when the current status data indicated they belonged in the same lake subpopulation.

The data in this report offer the first opportunity to extend the analysis of LTM representativeness into the realm of trends, as well as changing population status. By comparing the magnitudes of trends measured from repeated probability surveys (i.e., from the TIME project) with those observed in the same regions through LTM sampling, we have an opportunity to verify the validity of LTM trends.

In both the Adirondacks and New England, population-wide results inferred from TIME data show very similar trends in SO_4^{2-} to those for LTM sites (Figure 27). Both datasets suggest highly significant regional decreases in SO_4^{2-} slightly larger than -2 µeq/L/year in the Adirondacks and -1.8 µeq/L/year in New England (Tables 5 and 7).

Both datasets suggest similar ranges of trend slopes for Gran ANC (Figure 28). In the Adirondacks, regional increases in Gran ANC are significant (Tables 5 and 7) in both the LTM sites and TIME population data. In New England, only the population trend in Gran ANC was significant (Table 7), although both datasets suggest that New England lakes are undergoing slight increases in Gran ANC. The greater response in TIME lakes may be due to the different length of record between the networks. If increases in Gran ANC accelerated in the late 1990s as they did in the Adirondacks, then the TIME data may well estimate a larger rate of change than LTM data.

Table 7. Regional trend results for populations of sites in acid sensitive regions. Results from TIME probability sites are extrapolated to regional target populations. Lake trends in the Adirondacks and New England are for the period 1991-2001. Stream trends in the Northern Appalachian Plateau are for the period 1993-2001. Values are weighted median slopes for all lakes or streams in each region. Units for SO_4^{2-}, NO_3^-, base cations [$Ca^{2+} + Mg^{2+}$], Gran ANC and hydrogen are µeq/L/yr. Units for DOC are mg/L/yr. Units for aluminum (inorganic monomeric) are µg/L/yr.

Region	SO_4^{2-}	NO_3^-	Base Cations	Gran ANC	Hydrogen	DOC	Aluminum
Adirondack Lakes	-2.10**	+0.01^{ns}	-1.22*	+0.56*	-0.09^{ns}	+0.09*	+0.66^{ns}
New England Lakes	-1.88**	+0.02^{ns}	-1.57**	+0.40*	+0.01^{ns}	+0.08*	-1.94^{ns}
Appalachian Streams	-0.64*	+0.04^{ns}	-0.32^{ns}	+0.34*	-0.01^{ns}	+0.01^{ns}	+0.14^{ns}

^{ns} regional trend not significant ($p > 0.05$)

* $p < 0.05$

** $p < 0.01$

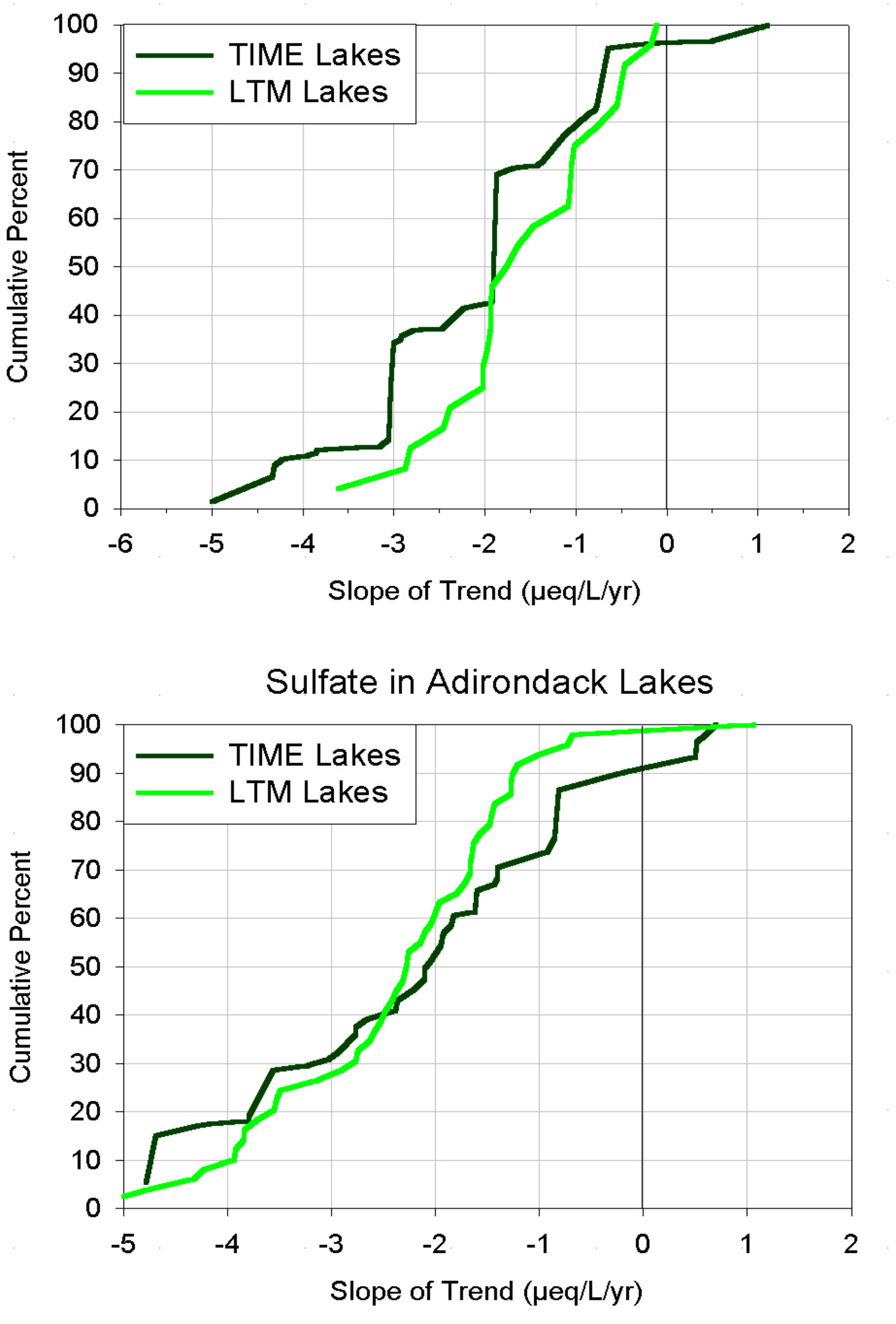


Figure 27. Comparison of trends in SO_4^{2-} in TIME probability sites (expressed as the distribution of slopes in the target population) and LTM sites in New England and the Adirondacks.

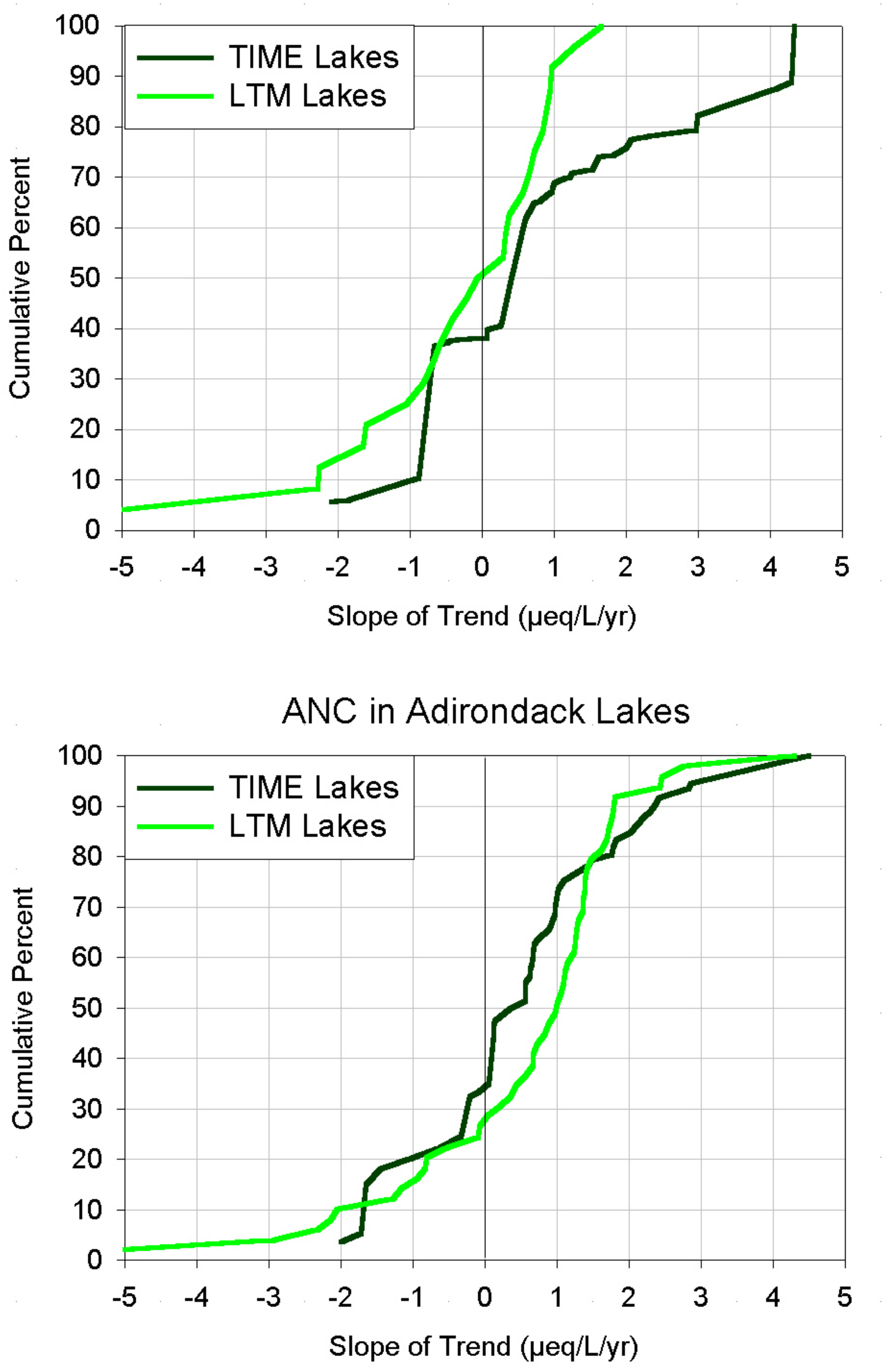


Figure 28. Comparison of trends in ANC in TIME probability sites (expressed as the distribution of slopes in the target population) and LTM sites in New England and the Adirondacks.

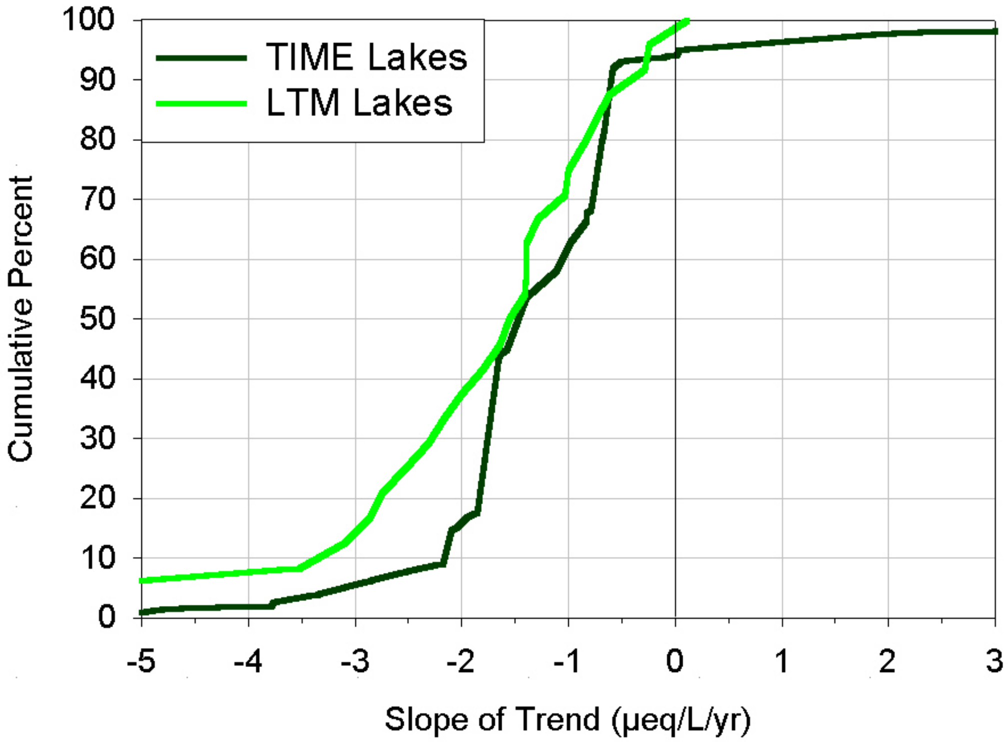
TIME population estimates and LTM data also lead to the same conclusions for regional trends in [Ca^{2+} + Mg^{2+}] concentrations in the two regions (Figure 29). In New England, the distributions of slopes are nearly identical with median decreases of -1.6 μeq/L/year in the TIME population estimate and -1.5 μeq/L/year the LTM data; both regional trends are highly significant (Tables 5 and 7). In the Adirondacks both estimates are significant, but the estimate based on TIME population data (-1.2 μeq/L/year) is only half that of the LTM data (-2.3 μeq/L/year). The reason for this modest discrepancy again may be the different time periods represented by the data.

Overall, the conclusions drawn from either TIME probability sampling and LTM intensive sampling are the same. In New England lakes, SO_4^{2-} is declining only slightly more than base cations, and the result is only a small increase in Gran ANC (significant in the TIME data; insignificant for LTM). In the Adirondacks, base cation declines exceed SO_4^{2-} declines by a large amount, resulting in more substantial recovery in Gran ANC.

Do trends in deposition translate into trends in surface waters? A major goal of this assessment report is to evaluate the changes in surface water chemistry in relation to CAAA reductions in deposition. In particular, did the changes in deposition result in commensurate changes in surface water chemistry in the past decade? There has been discussion in the scientific literature about the recovery response for SO_4^{2-} in surface waters: *would the response be rapid or delayed* (Church et al., 1989, Church 1999)?

It is not possible to compare directly changes in SO_4^{2-} concentrations in surface waters and deposition because of the poorly quantified effects of dry deposition and evapotranspiration. Both dry deposition and the evaporative concentration of ions in surface waters cause SO_4^{2-} concentrations in lakes and streams to be typically 2-3 times higher than in deposition (Sisterson et al., 1990, Rustad et al., 1994). Thus, higher concentrations in surface waters lead to the likelihood of greater downward slopes for SO_4^{2-} concentrations in surface waters than in deposition. In contrast, the *percent change* in SO_4^{2-} should be relatively unaffected by ambient concentrations assuming that dry deposition declines at the same rate as wet deposition. In this section, we present a comparison of the slopes of change in both deposition and surface waters, using the regional NADP/NTN and LTM data already presented.

In New England, the Adirondacks and the Northern Appalachian Plateau, percentage decline in deposition of sulfate (expressed as %SO_4^{2-}) are generally steeper than in surface waters, suggesting that most aquatic systems are exhibiting a lagged response. Apparently watershed soils retain enough atmospheric SO_4^{2-} to reduce the rate declines occurring in deposition (Figure 30). Interestingly, the lakes and streams with the steepest declines in %SO_4^{2-} in these regions have very similar rates to those in deposition, suggesting that the *most responsive* watersheds are acting essentially as flow-through systems. As expected, there is little correspondence between rates of %SO_4^{2-} in streams and deposition in the Ridge and Blue Ridge provinces (Figure 30), due to the adsorptive capacity of the highly weathered soils in the region.



[Ca^{2+} + Mg^{2+}] in Adirondack Lakes

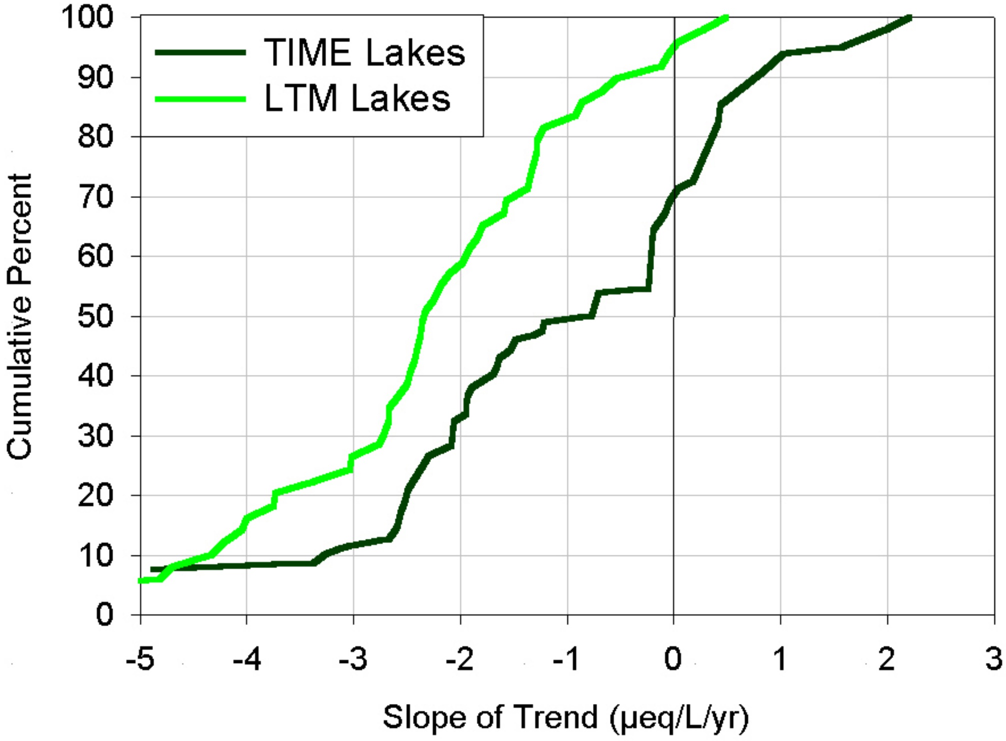


Figure 29. Comparison of trends in base cations [Ca^{2+} + Mg^{2+}] in TIME probability sites (expressed as the distribution of slopes in the target population) and LTM sites in New England and the Adirondacks.

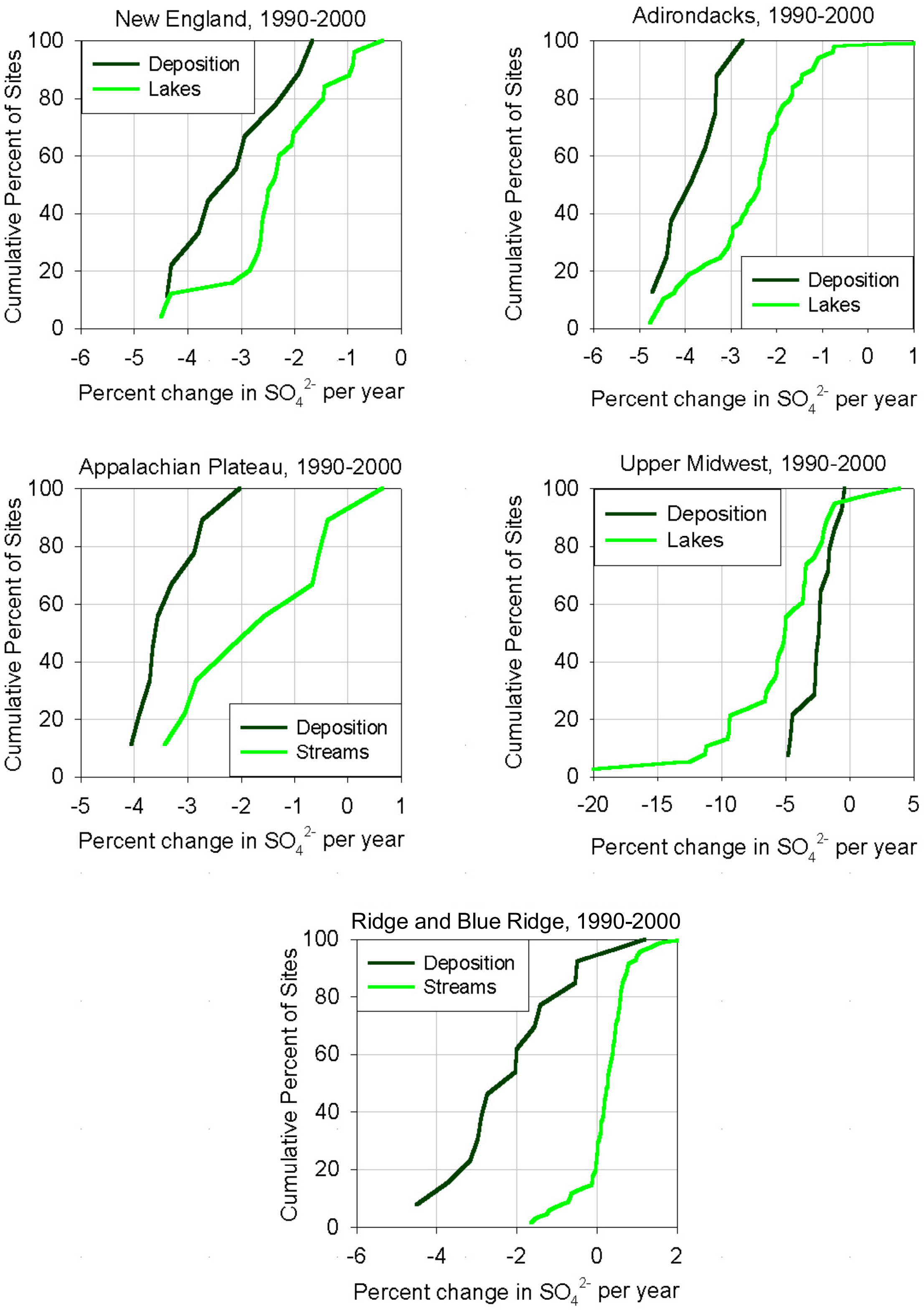


Figure 30. Comparison of % change in SO_4^{2-} concentration in wet deposition and surface waters, by region.

In the upper Midwest, the rate of decline in lakes is *greater than* the decline in deposition, probably reflecting the residual effects of the drought of the late 1980s. All of the lakes with strong negative trends in $\%SO_4^{2-}$ are seepage lakes with long water residence times. These lakes had trends in sulfate that reflected a decline from the evaporative concentration that would have occurred during the drought and the flushing of sulfur likely stored in wetlands during the drought (Dillon et al., 1997, Jeffries et al., 2002). Some SO_4^{2-} may also be stored in the sediments of these lakes via sulfate reduction (Baker et al., 1986), although the rate of sulfate reduction is presumed to decrease as the concentrations decrease.

We conclude that surface waters have responded relatively rapidly to the decline in sulfate deposition. There is reason to expect that additional reductions in deposition would result in additional declines in surface water concentrations of sulfate.

Has there been a decline in the number of acidic waters? Such probability samples such as TIME lakes allow us to estimate the number or proportion of surface waters in each region that are acidic. Because we have time series data in TIME, we have a unique opportunity to assess the changes in the number of acidic systems during the past decade. We have combined analyses of the TIME and LTM datasets to conduct this analysis and have used data from the NSWS, conducted in the mid 1980s, to estimate the extent of acidification in the 1980s in regions where TIME does not operate.

New England Lakes: During 1991-94, TIME population data indicated that there were 386 lakes in New England with Gran ANC<0 µeq/L, or 5.6% of the population. Both TIME and LTM data from this region suggest that only a small increase in Gran ANC has occurred since that time period; combined TIME/LTM results suggest a change of ca. +0.3 µeq/L/year (Tables 5 and 7). If we extend this time trend for 10 years, then sensitive lakes can be expected to have increased in ANC by ca. 3 µeq/L. In the 1991-94 TIME probability survey there were 12 lakes with Gran ANC values between 0 and –3 µeq/L, and only these lakes are estimated to have become non-acidic by the present time (this estimate is for the time period 2001-04, 10 years after the original TIME estimate). We find little evidence of a profound change in the acidity status of this region with the proportion of acidic lakes decreasing only from 5.6% to 5.5% over the previous 10 years (Table 8).

Adirondack Lakes: TIME population estimates from 1991-94 indicate that 13.0% of lakes, or 238 lakes, were acidic in the early 1990s. If we apply an approximate rate of change in Gran ANC of +0.8 µeq/L/year to these estimates (based on trend slopes for TIME and LTM data in this region, Tables 5 and 7), then sensitive lakes could be expected to have increased their ANC values by 8 µeq/L during the 1990s. We estimate that at the present time there are ca. 149 Adirondack lakes with Gran ANC<0, or 8.1% of the population. This represents a decrease of nearly 5%; roughly 38% of lakes that were acidic in the early 1990s are estimated to be non-acidic a decade later.

Northern Appalachian Plateau streams: Population estimates from TIME surveys of streams in the Northern and Central Appalachian Plateau ecoregions (synonymous with the northern Appalachian Plateau region covered by the LTM project) indicate that 5,014 kilometers of streams were acidic in 1993-94 (at the beginning of TIME sampling); this represents 11.8% of the stream length. The approximate rate of change in Gran ANC in the region (Tables 5 and 7) is +0.7 µeq/L/year and extrapolated for a 10-year period amounts to an increase in sensitive streams of +7 μeq/L. We estimate that roughly 3,600 kilometers of stream (or 8.5%) remain acidic in this region at the present time. This represents a ca. 28% decrease in acidic stream length over the decade.

Upper Midwest Lakes: The TIME project has not operated in the Upper Midwest, so the best population estimates for this region come from the 1984 Eastern Lake Survey (Linthurst et al., 1986b). ELS sampling in the Upper Midwest estimated that 251 lakes, or 2.9% of the population, were acidic in 1984 (Baker et al., 1991). LTM data suggest a rate of change of +1 μeq/L/year in this region (Table 5); extrapolated to the present, this represents an increase of +18 μeq/L of Gran ANC in sensitive lakes between 1984 and 2002. In 1984, 80 lakes had Gran ANC values less than -18 μeq/L, and all of these are now estimated to be non-acidic. This represents a change from 2.9% acidic in 1984, to 0.9% in 2002, an overall reduction in the number of acidic lakes of 68%.

Ridge/Blue Ridge Province streams: While we do not have adequate data from TIME to calculate trends in this region, the data are adequate to estimate the number of acidic streams. TIME data indicate that fewer than 400 km of streams (< 1%) were acidic in the Ridge and Blue Ridge region in 1993-94. Because we have no evidence of a significant change in Gran ANC in this region (Table 5), we estimate that <1% of Ridge/Blue Ridge streams remain acidic in 2002. There has probably been no change in the number of acidic waters in this region in the past decade.

Two important caveats in this analysis should be noted. First, as shown in Table 6, the rates of ANC increase (outside of the Ridge and Blue Ridge provinces) are more rapid in acidic lakes and streams than in low ANC sites. Due to sample size constraints (it is not possible to do the ANC class analysis by region), the changes in Gran ANC used in the analysis in Table 8 are based on the median change in all sites in a region. If acidic sites are recovering more rapidly than the population of sites as a whole, then the estimates of change in the number of acidic lakes and streams presented here will be conservative.

It is also important to realize that the trends we report here are for recovery from chronic acidification. Our regression analysis focuses on the central tendency of sites (e.g., their median or mean ANC over time) and whether this central tendency is increasing or decreasing. We know that most sites exhibit seasonally lower ANC and pH values than would be captured by the trend analysis. In many cases, sites that are not chronically acidic nonetheless undergo short-term episodic acidification during spring snowmelt or during intense rain events. In order to estimate the relative importance of episodic acidification in the regions we cover in this report, we examined the mean summer Gran ANC at each site and compared it to the average minimum ANC experienced each spring during the period 1990-2000. The results of this analysis are shown in Figure 31. On average, spring ANC values in New England, the Adirondacks and Northern Appalachian Plateau are 30 μeq/L lower than summer values. This implies that lakes and streams in these regions would need to recover to Gran ANC values above 30 μeq/L before they could be expected not to experience acidic episodes.

Estimating the magnitude of historical lake acidification. It is widely established that many present-day acidic lakes were at least marginally acidic in pre-industrial times (Davis and Anderson 1985, Sullivan 1990, Cumming et al., 1994, Smol et al., 1998). The main method for determining pre-historical pH is using siliceous fossil remains of diatom and chrysophyte algal species in lake sediment cores. Cumming et al., (1994) describes a classification system for the low ANC lakes with four types of response: 1) lakes that have not acidified; 2) lakes that acidified in the mid-1900s; 3) low pH lakes that acidified around 1900; 4) naturally acidic lakes that only acidified slightly. Two examples of these acidification responses are shown (Figure 32) from New England. Little Long Pond, with a present Gran ANC of 10 μeq/L, acidified by about 0.2 pH units after 1920. Its neighbor Mud Pond (Gran ANC today of –20 μeq/L) acidified from about pH 5.4 to 4.9, beginning early in the century.

The estimates of the *magnitude* of lake acidification range from fractions of a pH unit to about 2.0 depending on the lake and the region. Chrysophyte analyses tend to infer a lower pH because they are most abundant in the spring and therefore reflect the lower pH spring condition and because they may respond to episodic acidifications (Cumming et al., 1994). The average diatom-inferred pH decline in New England lakes is about 0.3 pH units (Davis et al., 1994). Sullivan et al., (1990) inferred similar average changes for the Adirondacks. Cumming et al., (1994) examined 14 Adirondack lakes that had acidified since 1900 (mean pre-industrial pH = 5.6, range 4.9 to 6.2) and inferred a mean chrysophyte-inferred pH decline of about 1.1 pH units. Kahl et al., (1989, 1991) observed that no clearwater (low DOC) lakes in Maine had pH less than 5 and concluded that organic acidity was necessary to acidify lakes to less than pH 5 at levels of acidic deposition in the 1980s.

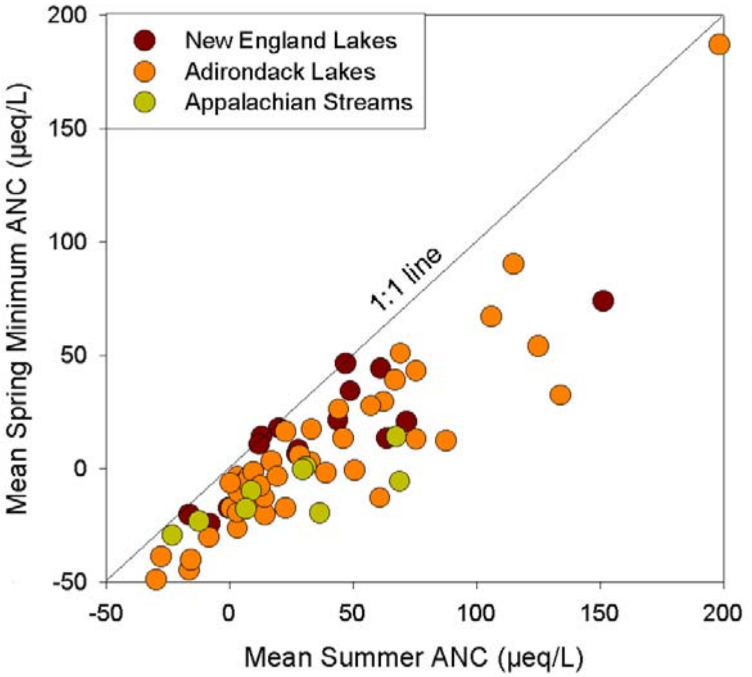


Figure 31. Relationship between summer and spring ANC values at LTM sites in New England, the Adirondacks and Northern Appalachian Plateau. Values are mean summer values for each site during the period 1990-2000 (horizontal axis) and mean spring minima for each site for the same time period. On average, spring ANC values are 30 μeq/L lower than summer values.

Table 8. Estimates of change in number and proportion of acidic surface waters in acid-sensitive regions of the North and East, based on applying current rates of change in Gran ANC to past estimates of population characteristics from probability surveys.

Region	Population Size	Number Acidic[1]	% Acidic[2]	Time Period of Estimate	Current Rate of ANC change[3]	Estimated Number Currently Acidic	Current % acidic	% Change in Number of Acidic Systems
New England	6,834 lakes	386 lakes	5.6%	1991-94	+0.3	374 lakes	5.5%	-2%
Adirondacks.	1830 lakes	238 lakes	13.0%	1991-94	+0.8	149 lakes	8.1%	-38%
No. Appalachians	42,426 km	5,014 km	11.8%	1993-94	+0.7	3,600 km	8.5%	-28%
Ridge/Blue Ridge	32,687 km	1,634 km	5.0%	1987	-0.0	1,634 km	5.0%	0%
Upper Midwest	8,574 lakes	251 lakes	2.9%	1984	+1.0	80 lakes	0.9%	-68%

[1] Number of lakes/streams with Gran ANC<0 in past probability survey (data collected at “Time Period of Estimate,” in column 5)

[2] Percent of population (from Column 2) with Gran ANC<0 in past probability survey (data collected at “Time Period of Estimate,” in column 5)

[3] Based on regional trends presented in this report, in µeq/L/year

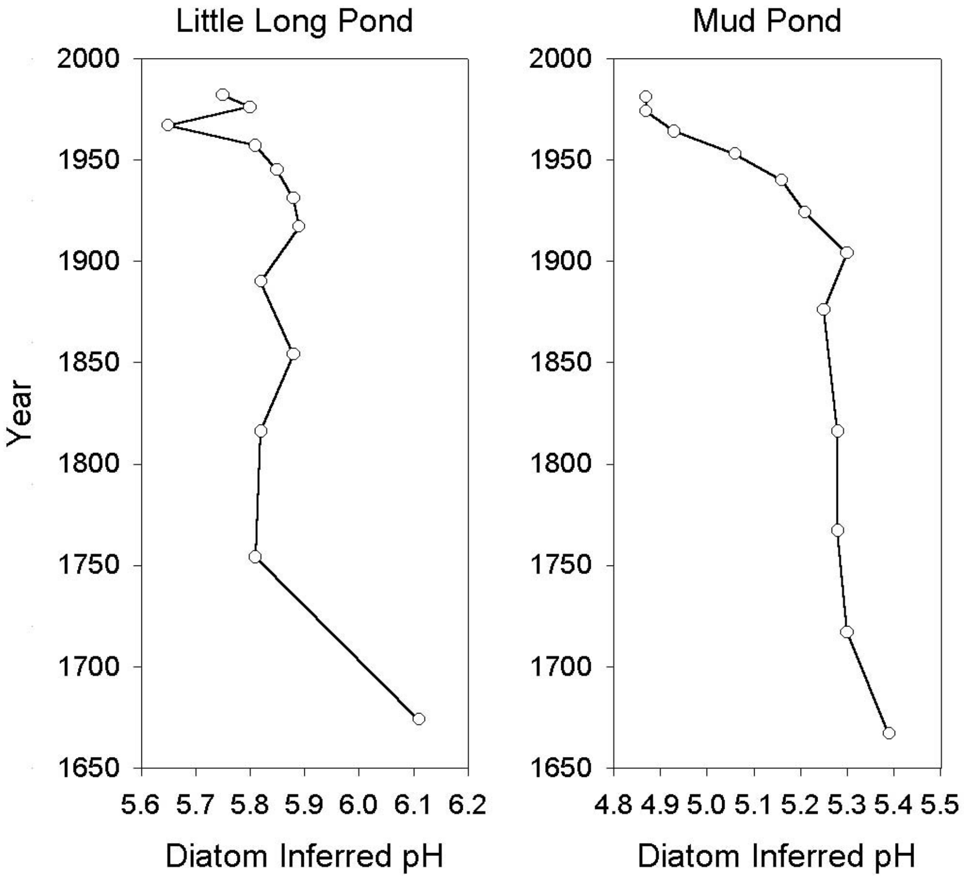


Figure 32. Paleolimnological reconstruction of historical pH change in two New England LTM lakes, as inferred from diatom remains (from Davis et al., 1994).

With the exception of lakes in the heavily impacted region around the Sudbury, Ontario, studies of pre-industrial lake pH agree that the pH of presently acidified lakes was less than pH 6 with rare exceptions before the onset of acidic deposition. Therefore, we propose that pH 6 is an upper limit for *recovery* of acidified lakes equivalent to an Gran ANC of about 20-30 µeq/L in all regions.

The interaction of S, N, and cations. Interactions between trends in SO_4^{2-}, NO_3^- and $[Ca^{2+} + Mg^{2+}]$ govern the magnitude of trends in Gran ANC. At East Bear Brook in Maine (Norton et al., 1999), both SO_4^{2-} and NO_3^-have declined significantly since sampling began in 1998. If the main regional change in surface water chemistry had been a decline in SO_4 without any other changes in major ion chemistry or DOC, then regional increases in ANC would have followed. Instead of a simple ANC response, there have been substantial declines in base cations and modest increases in DOC (Figure 33).

The relationship among these changes is illustrated in the response of East Bear Brook at BBWM (Figure 33). Concentrations of SO_4^{2-} and NO_3^- have declined in parallel which is presumably coincidental (Figure 33a). The rate of decline in base cations is faster than the decline in SO_4^{2-} (Figure 33b). The large decline in base cations apparently results from a change in soil ion exchange processes or from an increase in biomass uptake because there is no corresponding change in concentrations of silica, an indicator of mineral weathering rates (Figure 33c). Silica concentrations in the LTM and TIME networks were also statistically unchanged during the 1990s.

The trend in ANC can also be estimated from:

$$\text{ANC} = [\text{Ca}^{2+} + \text{Mg}^{2+}\ \text{Na}^{+} + \text{K}^{+}]\ \text{minus}\ [\text{SO}_4^{2-} + \text{NO}_3^{-} + \text{Cl}^{-}]$$

In this low DOC stream, the estimated and measured Gran ANC agree closely suggesting that acid anion inputs and buffering by base cations are indeed the likely controlling processes for ANC. It is also possible to calculate the ANC change that would have occurred if NO_3^- had not declined in 1990s (Figure 33d) by using the equation above but holding NO_3^- constant. The resulting calculated ANC in 1998 would be -20 µeq/L instead of zero. It is possible that the observed regional decline in NO_3^- during the 1990s prevented additional acidification in sensitive systems.

CONCLUSIONS

Trends in deposition and surface water chemistry. The CAAA has been successful in reducing the emissions of SO_2 and deposition of SO_4^{2-} accelerating the trend in place since about 1970. There was little change in NO_x emissions and deposition until the late 1990s when a slight decrease occurred due to Phase I controls on nitrogen emissions beginning in 1996. In response, SO_4^{2-} concentrations in surface waters declined across all the glaciated regions of the North and East (Figure 34). South of the glaciated limit, SO_4^{2-} concentrations have increased slightly due to the re-equilibration of SO_4^{2-} retaining soils with changing deposition. Nitrate concentrations exhibited few significant trends: NO_3^- decreased slightly in regions with high NO_3^- and was unchanged in regions with low ambient NO_3^- concentrations.

Base cations, which are important for neutralization of acidity in precipitation and in watersheds, increased non-significantly in atmospheric deposition during 1990-2000. However, the 20-year decline in base cations in surface waters continued, offsetting some of the decline in surface SO_4^{2-}. As a result, Gran ANC and pH have increased less than might be expected from SO_4^{2-} trends alone. Significant increases in Gran ANC were recorded in the Adirondack Mountains, the Northern Appalachian Plateau, and in the Upper Midwest (Figure 34). Lakes in New England show little sign of recovery in the 1990s, and streams in the Ridge/Blue Ridge province may even be acidifying slightly.

Expectations for recovery. While the widespread declines in SO_4^{2-} reported here for sensitive surface water regions (exclusive of the Ridge/Blue Ridge region) are important signs of the success of emission control programs, the true test of Title IV's effectiveness is a reduction in the acidity, and the eventual biological recovery, of lakes and streams in the U.S. We report here that in some regions the number of acidic lakes and streams has declined significantly in the past 10 years (Table 8). In particular, many lakes in the Adirondacks and Upper Midwest, and streams in the Northern Appalachian Plateau, have achieved positive Gran ANC values since implementation of the CAAA. It is important to recognize, however, that despite a roughly one-third reduction in the number of acidic systems in these regions, 8% of Adirondack lakes and 8% of Northern Appalachian streams remain acidic. It is beyond the scope of this report to forecast whether continued emissions reductions will substantially reduce these numbers or whether further additional regulations may be necessary.

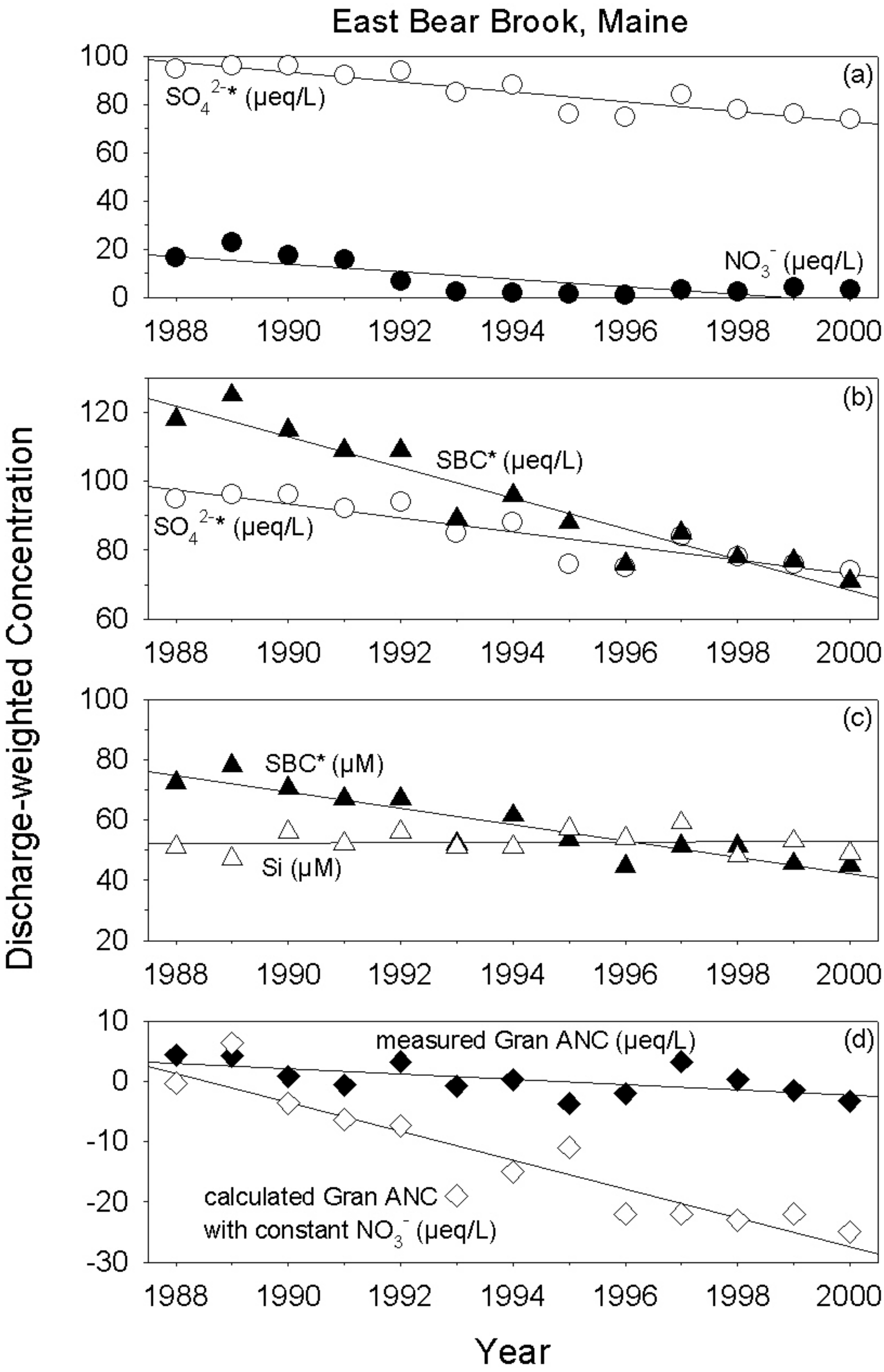


Figure 33. The interaction of SO_4^{2-}, NO_3^- and base cations in East Bear Brook, the reference watershed at the Bear Brook Watershed in Maine.

Uncertainties in the future behavior of NO_3^- and base cations make it very difficult to say how long the current recovery trends will continue.

It is also important to note that one region, the Ridge/Blue Ridge province, has yet to show any signs of recovery, either in SO_4^{2-} concentrations or in acidity. The proportion of streams in this region that are acidic is currently less than 1%, but this region has the highest likelihood of undergoing further acidification as the capacity of regional soils to adsorb atmospheric SO_4^{2-} reaches capacity. The small increase is surface water SO_4^{2-} we report for this region should be a red flag to regulators that this region deserves further research and assessment.

Research needs. Scientists and regulators have long noted the frustrations associated with dealing with complex environmental issues without long-term baseline data. With the continuing evolution of the chemistry of atmospheric deposition, data such as are represented in the TIME and LTM programs will be the only method of assessing recovery of surface water chemistry. LTM and TIME will also provide baseline sites for future biological assessments of recovery.

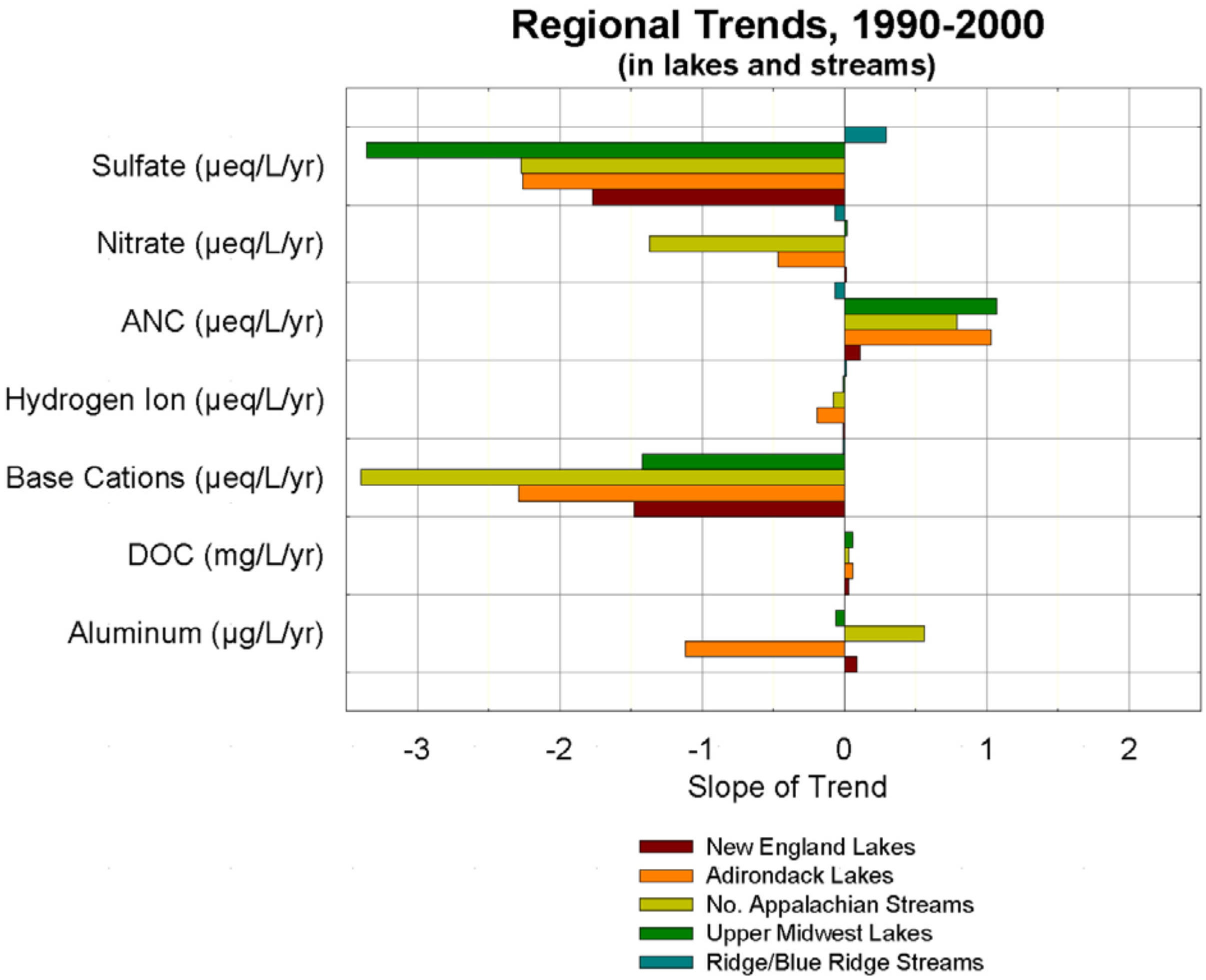


Figure 34. Summary of surface water trends in SO_4^{2-}, NO_3^- , Gran ANC, base cations [Ca^{2+} + Mg^{2+}], DOC and aluminum, by region.

Importantly, these data will also prove useful for other relevant environmental management issues such as base cation depletion, nitrogen saturation, effects of drought, forest health, and the myriad potential ecosystem-level effects of climate change. Increases in dissolved organic carbon in most lake populations may have contributed natural organic acidity to surface waters, further complicating our interpretation of the response to the CAAA. This factor is an important long-term research question that is not well understood. These LTM and TIME sites are core research locations that will provide essential information for a number of present and future research questions faced by EPA. Their long-term data serve as the foundation for other ecological research to be conducted using the locations and their data. Without such data, our ability to ask the right questions is reduced, and our ability to base the answers to these questions on actual data is seriously compromised. It is not possible to re-create or replace long-term data once the data record is interrupted. The more long-term data we accumulate, the better we can differentiate competing controls on surface water chemistry, and the better we can identify slow and subtle emerging trends, like the increased contribution of DOC in surface waters.

TERMS AND ACRONYMS USED IN THIS REPORT

acidic	describes lake or stream water with Gran ANC less than zero, corresponding to pH values less than ca. 5.5.
acidified	describes lake or stream water with sufficient historical information, or appropriate chemical relationships, to justify classification as a water that was historically less acidic than shown by recent measurement. The term may also apply to stream water which is temporarily acidified during a hydrologic episode.
ANC	Acid Neutralizing Capacity – a theoretical estimate of the ability of water to buffer acid (similar to buffering capacity or alkalinity). ANC may be either calculated ('calculated ANC' = sum of cations – sum of anions) or measured (Gran ANC) by titrating a sample of lake or stream water with a known concentration of acid.
anion	a negative charged ion, especially sulfate (SO_4^{-2}) and (nitrate NO_3^-) of importance to this report. Also see *cation*.
alkalinity	See ANC
ALSC	Adirondack Lake Survey Corporation
BBWM	Bear Brook Watershed in Maine. The original EPA Watershed Manipulation Project location for a paired-watershed experiment of enhanced S and N deposition (in eastern Maine) begun in 1987, with the experimental treatment continuing since 1989.
CaPMon	The Canadian equivalent to the U.S. NADP.
cation	A positively charged ion, especially hydrogen (H+), and the base cations calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^+) and sodium (Na^+). See *anion.*
DOC	Dissolved organic carbon
CAA	Federal Clean Air Act of 1970.
CAAA	Federal Clean Air Act Amendments of 1990.
CASTNet	Clean Air Status and Trends Network, the U.S. EPA-operated dry deposition network located primarily in the eastern U.S.
ELS	Eastern Lake Survey. The 1984 EPA program which established the baseline chemical condition of lakes in the eastern U.S. using a statistical survey of lake subpopulations.
EMAP	Environmental Monitoring and Assessment Program. The U.S. EPA monitoring program begun in 1991, which includes TIME and LTM.
EMAP-SW	EMAP-Surface Waters. The aquatic module within the larger environmental monitoring mission of EMAP.
GAO	General Accounting Office

Gran ANC	Gran Acid Neutralizing Capacity – a measured estimate of ANC, based on using the Gran technique to find the inflection point in an acid-base titration of a water sample (Gran 1952).
HELM	High Elevation Lakes in Maine. The 90 lakes higher than 600 meters which, as a population, are as acidified as lakes in the Adirondack NY region.
LTM	The U.S. EPA Long-Term Monitoring project. This EPA monitoring program began in 1983 and included low ANC lakes in Maine, New York (Adirondacks) and Vermont, and low ANC streams in New York (Catskills), Pennsylvania and Virginia. Before 1995 it also included lakes in Colorado and the Upper Midwest (Wisconsin, Michigan and Minnesota).
NADP/NTN	National Atmospheric Deposition Program/National Trends Network, the U.S.G.S.-led entity that operates the 200+ site network of wet-only precipitation collectors in the U.S.
NAPAP	National Acidic Precipitation Assessment Program, the program under which federally sponsored acid rain research was funded in the 1980s. NAPAP was responsible for the 1990 assessment report and has continued a integrative role into 2002.
NSS	U.S. EPA National Stream Survey.
NSWS	U.S. EPA National Surface Water Survey. Consisting of the Eastern Lake Survey (see ELS), the Western Lake Survey (see WLS) and National Stream Survey (see NSS).
PIRLA	Paleolimnological Investigations of Recent Lake Acidification – a project conducted in the 1980s using diatom remains in lake sediment cores to reconstruct historic chemistry trends.
recovery	A return to a more pre-industrial condition, in chemistry or biology. Chemically, recovery would be considered an increase in alkalinity (ANC) and/or an increase in pH, both equivalent to a decrease in acidity in surface water.
TIME	The U.S. EPA Temporally Integrated Monitoring of Ecosystems project. TIME is the component of EMAP targeted at monitoring subpopulations of lakes (Northeast) and streams (Mid-Atlantic) that are most likely to respond to changes in acidic deposition. TIME and EMAP both use probability techniques to select sites so that the results can be statistically inferred to represent the population of interest (e.g., acid sensitive lakes and/or streams in the targeted region).
USGS	U.S. Geological Survey, Department of the Interior.
WLS	Western Lake Survey. The 1986 EPA program which established the baseline chemical condition of lakes in the western U.S. using a statistical survey of lake subpopulations.
WMP	U.S. EPA Watershed Manipulation Project. See BBWM.

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