

**AN ASSESSMENT OF RECOVERY AND KEY
PROCESSES AFFECTING THE RESPONSE
OF SURFACE WATERS TO REDUCED
LEVELS OF ACID PRECIPITATION IN THE
ADIRONDACK AND CATSKILL MOUNTAINS**

**FINAL REPORT 05-03
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**NEW YORK STATE
ENERGY RESEARCH AND
DEVELOPMENT AUTHORITY**





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Prepared for the
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PREFACE

The New York State Energy Research and Development Authority (NYSERDA) is pleased to publish “An Assessment of Recovery and Key Processes Affecting the Response of Surface Waters to Reduced Levels of Acid Precipitation in the Adirondack and Catskill Mountains.” This project was funded as part of the New York Energy SmartSM Environmental Monitoring, Evaluation and Protection (EMEP) program and represents one of several studies focusing on the response of New York State’s ecosystems to pollution associated with the generation of electricity. More information on the EMEP program may be found in NYSERDA’s website at: www.nyserdera.org/programs/environment/emep/.

ABSTRACT

Recovery from recently reduced levels of acid deposition was examined and compared in 17 surface waters in the Adirondack Mountains and Catskill Mountains of New York through trend analysis, and future water chemistry was simulated at 5 sites by the model PnET-BGC. Additionally, the role of sugar maple in the nitrogen (N) cycle across these two regions was examined. Precipitation pH has increased an average of about 0.02 units in these two regions from 1984 to 2001; three-fourths of this increase has resulted from decreases in SO_4^{2-} concentrations and about one-fourth from decreases in NO_3^- concentrations. These changes in precipitation chemistry are paralleled by, and are assumed to result from, similar decreases in sulfur (S) and nitrogen oxide (NO_x) emissions largely from power plants in the predominant source region of acidic precipitation to the State. During 1992 to 2001, sulfate (SO_4^{2-}) concentrations decreased significantly at every surface water site by an average of $3.3 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in Adirondack lakes and $2.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in Catskill streams. These decreases in SO_4^{2-} concentrations in surface waters were highly synchronous among surface waters and in surface water–precipitation comparisons, which demonstrates the tight link between atmospheric deposition and the sulfur cycle in these watersheds. Nitrate (NO_3^-) showed significant decreasing trends at most surface-water sites, however, the decreases ranged from three- to ten-fold less than those of SO_4^{2-} . The trends in NO_3^- were generally not synchronous across the two regions or within the Adirondacks, a result of the numerous factors other than atmospheric N deposition including sugar maple that affect the N cycle and surface water NO_3^- concentrations. Other factors that affect the N cycle include land-use history, long-term climate variability, and short-term climate disturbances such as soil freezing, wind storms, ice storms, and floods, insects and pathogens, and aquatic processes.

Overall, hydrogen ion (H^+) concentrations decreased significantly at about 60% of surface water sites. ANC increased significantly at about 50% of surface-water sites, and these increases averaged $14 \mu\text{eq L}^{-1}$ in 7 of the 12 Adirondack lakes with significant trends, and $5 \mu\text{eq L}^{-1}$ in 1 of the 5 Catskill streams with significant trends during 1992-2001. Inorganic monomeric Al, a metal that is toxic to many acid-sensitive species, also decreased at most surface-water sites during 1992-2001. The trends in base cation concentrations (C_B), ANC, and H^+ were not generally synchronous in surface waters within and among these regions, nor in precipitation–surface water comparisons. Thus, the myriad complexities that affect the cycles of N and C_B partially mask the otherwise strong relation between precipitation and surface-water SO_4^{2-} concentrations, an indication that trends in acid-base chemistry (ANC and H^+) respond in part to factors such as climate variation that are independent of the acidity of precipitation.

The PnET-BGC model results indicate that current clean air laws will result in little additional change in surface water ANC in these two regions, but that a future scenario in which sulfur dioxide (SO_2) emissions were reduced by 50% and NO_x emissions by 30% would increase surface-water ANC by an average of $24 \mu\text{eq L}^{-1}$ from 2001 to 2050 in the 5 water bodies that were modeled. These changes were sufficient to increase ANC to $> 0 \mu\text{eq L}^{-1}$, a critical value for many surface-water biota, in the most acidic of the surface waters that were modeled.

The results of this study indicate that surface waters are slowly recovering due to reduced levels of acid precipitation, but that additional recovery may require reductions in SO_2 and NO_x emissions greater than are mandated under current clean air laws*. Although reduced SO_4^{2-} concentrations in precipitation are the major cause of increased ANC and pH and decreased Al concentrations in sensitive surface waters in New York, future changes in climate and ecosystem disturbance that may affect the cycling rates of N, DOC, and C_B should be closely monitored over multi-year periods because these constituents also affect pH and ANC, and have the potential to negate recovery due to decreased SO_4^{2-} concentrations in precipitation and surface waters. A quantitative understanding of the factors other than acid precipitation that may affect surface-water pH and ANC is necessary to separate the effects of clean air laws and atmospheric deposition from natural variability and disturbance.

* As of 2003.

KEY WORDS

Acid precipitation, recovery, trends, Adirondack Mountains, Catskill Mountains, sugar maple, PnET-BGC, sulfur, nitrogen

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EXECUTIVE SUMMARY

The Adirondack Mountains and Catskill Mountains of New York are among the most sensitive regions in North America to the effects of acid precipitation. These regions have probably been receiving acid precipitation with a pH of less than 5 since the early- to mid-20th century, although there are no precipitation chemistry data prior to the 1970s to confirm this. Precipitation in New York was most acidic in the 1970s, and since that time, pH has increased and sulfate (SO₄²⁻) concentrations have decreased significantly. These changes are believed to largely result from decreases in sulfur (S) emissions as mandated by the Clean Air Act of 1970 and subsequent Amendments to the Act in 1990. The reasoning of the Clean Air Act and Amendments regarding acid precipitation was that increases in precipitation pH would result in increases in surface water pH and acid-neutralizing capacity (ANC), and decreases in SO₄²⁻, nitrate (NO₃⁻), and aluminum (Al) concentrations. This would be followed by a recovery of species diversity in aquatic biological communities (and terrestrial communities as well), which were affected by surface-water acidification in the 20th century.

Sufficient historical surface-water chemical data are now available to evaluate whether the intent of clean air legislation has been realized. The study described in this summary report addressed the effects of acid precipitation within the context of several questions that are commonly asked by policy makers regarding recovery of sensitive surface waters:

- **Is there evidence of chemical recovery from reduced levels of acid precipitation in sensitive regions of New York?**
- **If so, then how much recovery has occurred?**
- **Can changes or trends in surface water chemistry be attributed solely to acid precipitation, or do other factors complicate a simple cause and effect interpretation?**
- **What do model results tell us about the likely future of surface-water chemistry given likely future scenarios of precipitation chemistry?**

These questions were addressed by performing statistical trend analysis on long-term (10 years or more) chemistry data from six precipitation-chemistry sites near the Catskill and Adirondack regions, five streams in the Catskills, and 12 lakes in the Adirondacks (Figure S1). Additionally, soil chemistry and vegetation data were compiled from stands of sugar maple in the Catskills and Adirondacks to examine the extent to which the dynamics of tree species affect the nitrogen (N) cycle and the perceived effects of nitric acid from precipitation. Finally, PnET-BGC, a model that simulates biogeochemical processes and the water cycle in forested ecosystems was calibrated to match the current effects of acid precipitation and to predict likely future effects.

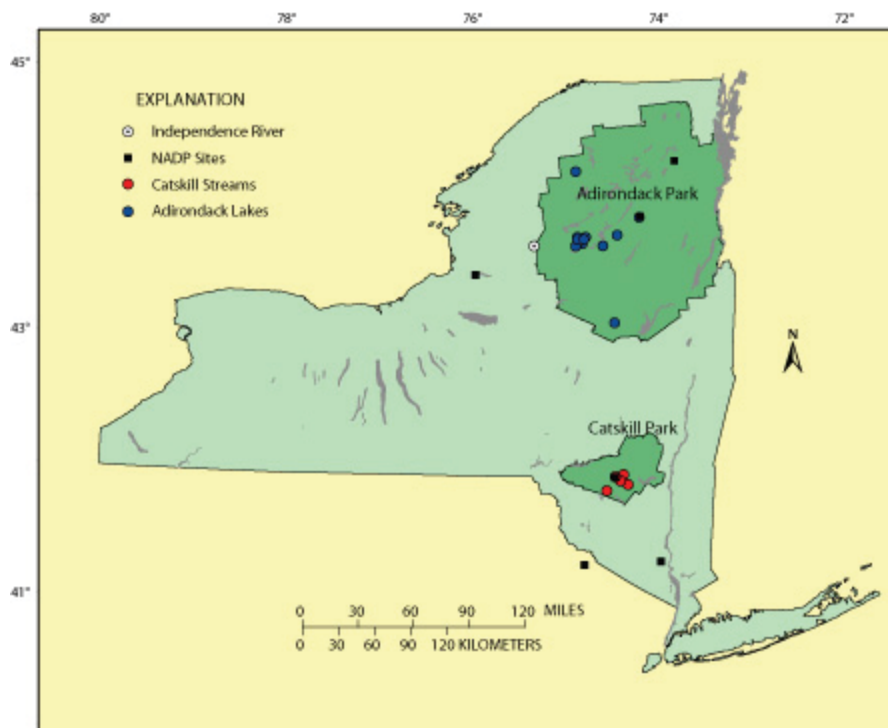


Figure S1. Map of New York showing location of Adirondack and Catskill State Parks, six NADP sites located near the two study regions, and 17 streams and lakes for which trends were evaluated.

Is there evidence of chemical recovery from reduced levels of acid precipitation in sensitive regions of New York? If so, then how much recovery has occurred? Yes, there is evidence of limited recovery of surface water chemistry at about half the sites examined in these two regions, and a greater proportion of Adirondack lakes than Catskill streams showed evidence of recovery. This recovery has not likely been great enough, however, to result in widespread biological recovery in these sensitive waters.

Precipitation: Precipitation pH has increased on average by about 0.02 units in these two regions from 1984 to 2001. Three-fourths of this increase has resulted from decreases in SO_4^{2-} concentrations and about one-fourth from decreases in NO_3^- concentrations. These changes in precipitation chemistry are paralleled by, and are assumed to result from, similar decreases in S emissions largely from power plants in regions southwest of New York that are the predominant source of acidic precipitation in the State. Only a modest decrease has been measured in nitrogen oxide (NO_x) emissions from these same stationary sources; however, about half of the NO_x emissions that produce acidic precipitation are believed to originate from vehicles. Fewer significant precipitation-chemistry trends were found when a shorter time period (1992-2001) was examined. This finding probably reflects both the shorter record and a flattening of previous trends during 1995-2001 (Figure S2). Precipitation-chemistry trends were more synchronous in the Catskills than in the Adirondacks suggesting more diverse acid sources in the Adirondacks, which means that a greater number of precipitation-chemistry sites than are currently operated by the National Atmospheric Deposition Program (NADP) may be needed to accurately assess trends in this region.

However, an NADP site was recently added (2003) in the Adirondacks at Moss Lake, and the New York State Department of Environmental Conservation operates three precipitation-chemistry sites in the Adirondacks, all of which could be included in future studies.

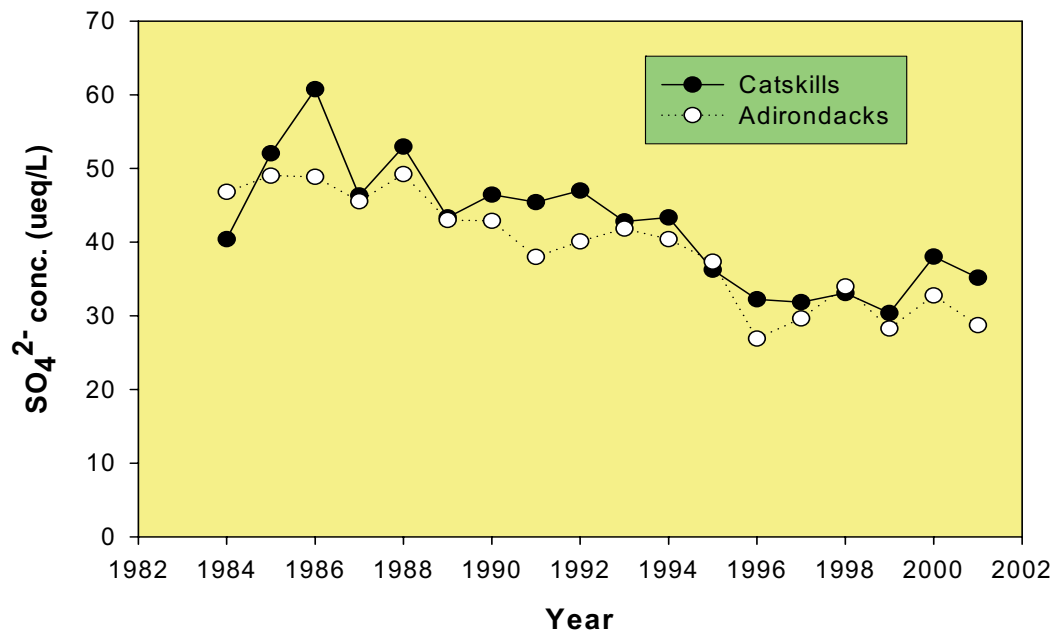


Figure S2. Mean annual volume-weighted mean SO₄²⁻ concentrations in precipitation 1984-2001 at three NADP sites located in each of the Catskill and Adirondack study regions. This figure illustrates the flattening of precipitation chemistry trends during 1995-2001 at the sites that were examined, which may explain in part why there were fewer significant trends during 1992-2001 than during 1984-2001.

Surface Waters: The minimum length of data record available at all 17 surface-water sites examined in this study was 10 years, from 1992 to 2001. During this time, SO₄²⁻ concentrations decreased significantly at every site by an average of 3.3 μeq L⁻¹ yr⁻¹ in the Adirondack lakes and 2.5 μeq L⁻¹ yr⁻¹ in the Catskill streams. These decreases were 2 – 3 times greater than declines in precipitation SO₄²⁻ concentrations, which mainly reflect the concentrating effects of evapotranspiration on the steepening of trends. These decreases in SO₄²⁻ concentrations in surface waters were highly synchronous (Table S1) among surface waters and in surface water–precipitation comparisons, which demonstrates the tight link between atmospheric deposition and the biogeochemical cycle of S in these watersheds. Nitrate showed significant decreasing trends at most surface-water sites, however, the decreases were three- to ten-fold less than those of SO₄²⁻. The trends in NO₃⁻ were generally not synchronous across the two regions or within the Adirondacks (Table S1), a result of the numerous factors other than atmospheric N deposition that affect the N cycle and surface water NO₃⁻ concentrations.

Table S1. Regional and Inter-regional mean temporal coherence of surface-water chemistry during 1992-2001 at 5 Catskill streams and 12 Adirondack lakes as indicated by the p value, the Pearson Product Moment Correlation Coefficient. Values of p greater than 0.602 indicate significant correlation at p = 0.05, represent high synchronicity of trends, and are indicated in bold red type.

Chemical Constituent	Catskills	Adirondacks	Inter-regional
SO ₄ ²⁻	0.93	0.69	0.69
NO ₃ ⁻	0.52	0.41	0.15
C _B	0.55	0.64	0.34
ANC	0.42	0.37	0.38
H ⁺	0.30	0.39	0.28

Overall, hydrogen ion (H⁺) concentrations decreased significantly at about 60% of surface water sites, and ANC increased significantly at about 50% of surface-water sites that were examined in this study. The increases in ANC averaged 14 µeq L⁻¹ in the seven of 12 Adirondack lakes with significant trends, and 5 µeq L⁻¹ in the 1 of 5 Catskill streams with significant trends during 1992-2001. These ANC trends reflect decreases in base cation (C_B) concentrations that were less than those of the acid anions SO₄²⁻ and NO₃⁻. Inorganic monomeric Al, a metal that is toxic to many acid-sensitive species, also decreased at most surface-water sites during 1992-2001 by an average of -0.12 and -0.13 µmol L⁻¹ yr⁻¹ for the Catskill streams and Adirondack lakes, respectively. The trends in C_B, ANC, and H⁺ were not generally synchronous in surface waters within and among these regions, nor in precipitation–surface water comparisons. Thus, the myriad complexities that affect the N cycle and that of base cations partially mask the otherwise strong relation between precipitation and surface-water SO₄²⁻ concentrations. The net result is that trends in the key indicators of acid-base chemistry (ANC and H⁺) are responding in part to factors such as climate variation that are independent of the acidity of precipitation.

Additionally, a surprising significant increase in surface water DOC concentrations was found in both these regions. The cause of this increase is uncertain, but bears further study because DOC affects surface-water acidity and in turn DOC concentrations are affected by pH.

Comparisons of non-flow-weighted to flow-weighted trends indicate that flow-weighting did not change the direction of any trend; however, three NO₃⁻ concentration trends and four ANC trends shifted from significant to non-significant when chemistry data were corrected for variation with flow. These results indicate that the accuracy of future trend-analysis studies for flow-sensitive species such as NO₃⁻ and ANC may be affected by climate change and would be more accurate if more streamflow data were available from the outlets of these Adirondack lakes.

Can changes or trends in surface water chemistry be attributed solely to acid precipitation, or do other factors complicate a simple cause and effect interpretation? The analysis of the effects of sugar maple on increasing rates of nitrification and NO_3^- leaching relative to other common northern hardwood species suggests that trends in surface water chemistry cannot be attributed solely to trends in acid deposition. For example, beech bark disease that favors sugar maple over American beech may cause increases in NO_3^- concentrations and decreases in pH and ANC that are independent of trends in acid precipitation. Sugar maple stands generally have higher rates of NO_3^- production by soil bacteria than those of other common tree species such as American beech and yellow birch, and therefore, higher NO_3^- concentrations in drainage waters. The presence and abundance of sugar maple in a watershed is but one factor that may strongly affect the N cycle. Other factors that have been identified in previous studies and in the PnET-BGC modeling simulations include land-use history, long-term climate variability, and short-term climate disturbances such as soil freezing, wind storms, ice storms, and floods, insects and pathogens, and in-lake processes, which are important when comparing lakes in the Adirondacks to streams in the Catskills.

The calculations of trend synchronicity also provide insight about the cause and effect relation between precipitation acidity and stream water chemistry. Trends in SO_4^{2-} concentrations in surface waters showed high synchronicity, consistent with modeling results that indicate little within-watershed retention of SO_4^{2-} . These calculations indicate a strong link between rates of SO_2 emissions, SO_4^{2-} concentrations in precipitation, and SO_4^{2-} concentrations in surface waters. However, trends in NO_3^- and C_B concentrations and ANC were less synchronous, indicating that (1) SO_4^{2-} concentration trends are only partly responsible for ANC trends, and (2) that temporal patterns in NO_3^- , C_B , ANC, and pH vary greatly among watersheds and are strongly affected by changes in the rates of processes that affect the rates of N and C_B cycling. Model results confirm that biogeochemical processes such as cation exchange and mineral weathering that affect rates of C_B cycling are important sources of ANC; thus, changes in the rates of processes such as Ca^{2+} depletion from soil exchange sites and chemical weathering rates affect the rate of recovery of surface water pH and ANC.

What do model results tell us about the likely future of surface-water chemistry given likely future scenarios of precipitation chemistry? The PnET-BGC model results indicate that current clean air laws¹ will result in little additional change in surface water ANC in these two regions, but that a future scenario in which sulfur dioxide (SO_2) emissions were reduced by 50% and NO_x emissions by 30% would increase average annual volume-weighted surface-water ANC by an average of $24 \mu\text{eq L}^{-1}$ from 2001 to 2050 in the five water bodies examined in this part of the study. These changes were sufficient to increase ANC to $> 0 \mu\text{eq L}^{-1}$, a critical value for many surface-water biota, in the most acidic of the surface waters that were modeled.

¹ As of 2003

In conclusion, the results of this study indicate that surface waters are slowly recovering due to reduced levels of acid precipitation during the past two decades, but that additional recovery may require further reductions in SO_2 and NO_x emissions than are mandated under current clean air laws. Although reduced SO_4^{2-} concentrations in precipitation (and possibly in dry deposition as well) are the major cause of increased ANC and pH and reduced Al concentrations in sensitive surface waters in New York, future changes in climate and ecosystem disturbance that may affect the cycling rates of N, DOC, and C_B should be closely monitored because these constituents affect pH and ANC. Disturbances have the potential over multi-year periods to negate the recovery due to decreased SO_4^{2-} concentrations in precipitation and surface waters. Historical land use in a watershed has the potential to suppress NO_3^- concentrations in surface waters for decades to more than a century as N is sequestered in vegetation and soil, and to mask expected responses to changes in NO_3^- concentrations in precipitation. A quantitative understanding of the factors other than acid precipitation that may affect surface-water pH and ANC is necessary to separate the effects of clean air laws and atmospheric deposition from natural variability and disturbance.

Section 1

INTRODUCTION

The sensitivity of an ecosystem to acidic atmospheric deposition is dependent on the load, timing, and form of deposition to the landscape and the interaction of atmospherically deposited acids with the vegetation, soils, and waters that drain the landscape. Characteristics such as the relative weathering rate of the bedrock, the age of the soils, the climate, the steepness of slopes, and the dominant tree species all contribute to the sensitivity of a landscape to acid deposition. The Adirondack Mountains and Catskill Mountains of New York are two regions in North America that are among the most sensitive to the effects of acid deposition (Omernik and Powers, 1983; Brakke et al., 1988). These effects include soil and surface-water acidification, which has likely reduced the habitat of acid-sensitive aquatic and terrestrial species (Baker and Christensen, 1991; Baker et al., 1993; Baldigo and Lawrence, 2000).

Precipitation is naturally acidic in northeastern North America with a pH of 5.0 – 5.6, primarily the result of carbonic acid from carbon dioxide in the atmosphere, but is also affected by emissions from volcanoes, forest fires, and biogenic sources (Bates et al., 1992). Precipitation with a pH less than about 5.0 is typically defined as acid precipitation, which most often results from the presence of sulfuric and nitric acid derived from emissions of sulfur dioxide and nitrogen oxides that originate from the burning of fossil fuels (Patrinos, 1985; Venkatrim and Pleim, 1985). The Adirondacks and Catskills have probably been receiving acid precipitation since the early- to mid-20th century (Cogbill and Likens, 1974; Husar et al., 1991). Limited data from the 1950s suggests precipitation pH values of less than 5.0 (Cogbill and Likens, 1974), and continuous measurements of precipitation chemistry in New York that began in the late 1970s and early 1980s can be used to determine temporal trends in precipitation pH, and sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations (<http://nadp.sws.uiuc.edu>). These data generally indicate that pH has increased and SO_4^{2-} concentrations have decreased since the 1970s (Husar et al., 1991; Sirois, 1993), paralleled by and largely resulting from decreases in sulfur (S) emissions from coal-fired power plants in the Ohio River valley (Lynch et al., 2000), which is an important source area of precursors for acid precipitation in New York. These historical decreases in S emissions, and more recent slight decreases in nitrogen (N) emissions are believed to largely result from provisions in the Clean Air Act of 1970 and subsequent amendment of that Act in 1990 (Stoddard et al., 1999; Lynch et al., 2000). Other factors such as energy conservation, the closing or downsizing of many smokestack industrial facilities, and decreases in average automobile emissions also likely contributed to reductions in acid precipitation in the eastern United States during the past three decades. One expected outcome of clean air legislation, particularly Title IV of the Clean Air Act Amendments of 1990, is reduced effects of acid precipitation in sensitive ecosystems such as the Adirondack and Catskill Mountains of New York, and subsequent recovery of affected biological communities to “pre-acid precipitation” conditions (Kahl et al., 2004). Previous studies have indicated limited recovery in these two regions and across the eastern United States (Driscoll et al., 2003; Lawrence et al., 2004; Kahl et al., 2004), however, no previous investigation has provided a detailed comparison of

the extent of recovery in these two regions, examined the key factors that affect recovery, and modeled surface-water chemistry to predict future recovery according to potential future acid-deposition scenarios. The goal of this study was to determine and compare acid-precipitation related trends in surface-water chemistry in the Catskills and Adirondacks, examine a key factor that affects the production of nitrogen-related acidity in forested ecosystems of these two regions, calibrate a model to surface-water chemistry data from these two regions, and predict precipitation-driven surface-water chemistry under various future acid-deposition scenarios.

WHAT IS RECOVERY?

The term recovery as applied to studies of the effects of acid precipitation usually implies a return of water and soil chemistry to values comparable to the time before precipitation became more acidic due to human activities in the early- to mid-20th century. Chemical recovery is generally assumed to drive biological recovery of the terrestrial and aquatic communities that existed in sensitive ecosystems prior to the onset of acid precipitation. Recovery is difficult to quantify because scientists are uncertain about the chemical and biological conditions that existed prior to the onset of acid precipitation. Generally, only indirect or historic data that used methods no longer practiced are available such as measurements of diatom communities in lake sediments and chemical measurements and fish population inventories that pre-date the recognition of acid deposition in North America in the mid-1970s (Schofield, 1982; Charles et al., 1990). The most widely available data to examine recovery are chemical data from precipitation and surface waters that have been collected regularly in the Adirondacks and Catskills since the 1980s such as those analyzed in the current study. If these data indicate increases in the pH of precipitation that are paralleled by increases in the pH and acid-neutralizing capacity (ANC) of sensitive waters, then the waters can be viewed as “recovering” and by inference that soil chemistry and pH-sensitive biota such as mayflies and fish are recovering as well. Although biological recovery in surface waters may lag chemical recovery by several years, evidence collected to date indicates that macroinvertebrate, zooplankton, and phytoplankton populations recover fairly quickly when chemistry changes to a favorable pH range for various species (Findlay, 2003; Raddum and Fjellhiem, 2003). Ideally, soil chemical and biological data would be used to evaluate recovery as well, but these data are generally either not collected frequently enough or not in sufficient detail to allow such an evaluation. An additional complication is that many other factors such as climate change, extreme climatic events, pest infestations, and forest harvesting can also affect the acid-base chemistry of soil and waters, and resident biological communities.

Section 2

STUDY AREA

The study regions are within the Adirondack and Catskill State Parks in New York (Figure 1). The Adirondack State Park consists of 2.4×10^6 ha of predominantly forested land in northern New York, and is the largest publicly protected area in the contiguous United States. The Adirondacks contain an estimated 1,290 lakes with surface area greater than 4 ha (Brakke et al., 1988) and abundant wetlands and streams. Wide variability exists in the landscape and climate across the Adirondacks, but the region is generally underlain by granitic gneiss and metasedimentary rock with acidic Spodosol soils developed in glacial till that is 12,000 to 18,000 years old (Driscoll et al., 1987). The climate is described as humid continental, with short cool summers and long cold winters (Trewartha, 1954).

The Catskill State Park consists of 2.4×10^5 ha of predominantly forested land in southeastern New York. The Catskills consist of a plateau of sedimentary rock that rises about 1,000 m above the surrounding

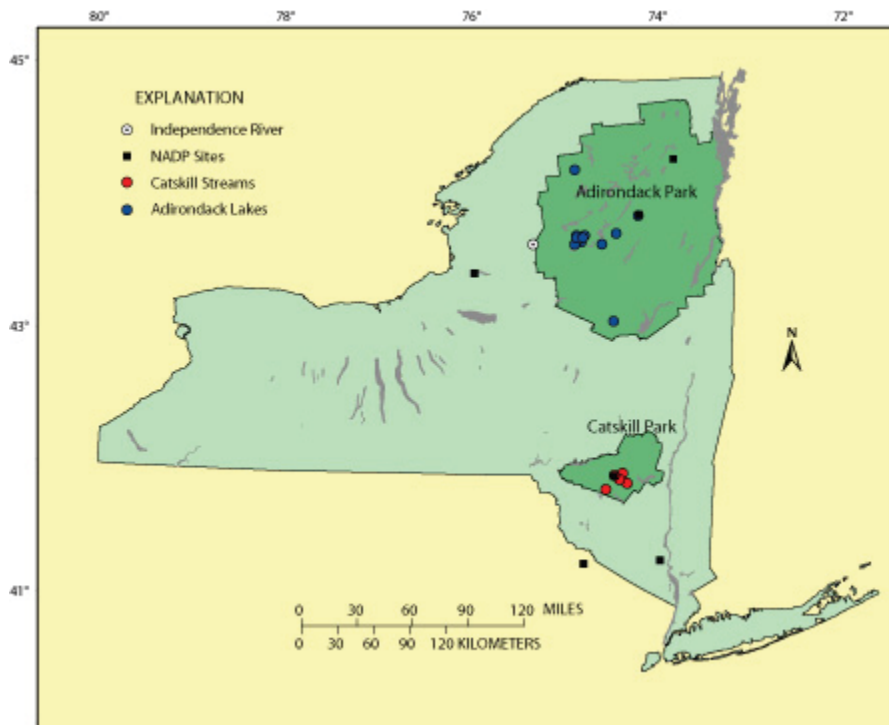


Figure 1. Map of New York showing location of Adirondack and Catskill State Parks, 6 NADP sites located near the 2 study regions, and 17 streams and lakes for which trends were evaluated.

terrain, and has been dissected by streams and rivers; lakes in the region are much less numerous than in the Adirondacks. The Neversink River and Rondout Creek Basins contain the greatest number of acid-sensitive waters in the region and are largely underlain by sandstone and conglomerate with some

interbedded shale. Soils in the region are generally Inceptisols that have developed in glacial till that is of a similar age to that in the Adirondacks. The climate is similar to that of the Adirondacks, except with slightly milder winter temperatures and greater precipitation amounts at an equivalent elevation. Levels of acidic atmospheric deposition, which are driven foremost by precipitation amount, are similar in the Catskills and western Adirondacks, where most of the study surface waters are located (Ollinger et al., 1993).

HOW TRENDS WERE DETERMINED

One of the methods through which scientists evaluate recovery related to acid deposition is by use of trend analysis. Nearly everyone has an idea of what constitutes a temporal trend - a line drawn through data points that shows some variable increasing or decreasing through time (Figure 2). Many temporal trends, however, are subtle and not obvious when viewing a graph of data. For example, in the data shown for SO_4^{2-} concentrations at the Milford, PA precipitation chemistry site near the Catskills (Figure 3), there is a statistically significant trend during 1984-2001, but the trend during 1992-01 is not statistically significant. Many different approaches have been used to evaluate temporal trends, however, the consensus is that Seasonal Kendall trend analysis with flow correction is the most robust for studying temporal trends in water-chemistry data assuming a uniform trend direction in the data, and this is the analysis method used in this study. The Seasonal Kendall trend method first corrects for changes in concentrations of flow-sensitive chemical species like NO_3^- , accounts for seasonality that is common in water chemistry data, and uses the ranks rather than the actual data to disallow undue influence by the occasional small or large “outlier” values. Other methods should be used when a sudden “step change” is evident in the temporal data.

Section 3

KEY STUDY FINDINGS AND POLICY RELEVANCE

The study findings described in this report are discussed in greater detail in four papers that were written based on this work (Lovett and Mitchell, 2004; Chen et al., 2004; Chen and Driscoll, 2004; Burns et al., in press). A web site (<http://ny.cf.er.usgs.gov/nyserdaproject/nyserda.cfm>) developed for the project describes the objectives, provides surface-water data used in analyses, and also provides complete references to study publications.

TRENDS IN PRECIPITATION CHEMISTRY

Precipitation-chemistry trends were evaluated at six sites close to or within the Adirondack and Catskill regions. These sites are part of the National Acid Deposition Program (NADP) and all data are available at the Program web site (<http://nadp.sws.uiuc.edu>). Dry deposition, the other key component of acid deposition, was not evaluated in this study. The resulting trends are summarized as follows:

- Long-term data (1984-2001) at the six study sites show significantly decreasing trends in SO_4^{2-} , NO_3^- , H^+ , and the sum of base cation (C_B) concentrations at all sites. Decreases in SO_4^{2-} concentrations were 1 to 1.5 $\mu\text{eq L}^{-1} \text{yr}^{-1}$, and were approximately balanced by decreases in H^+ concentrations. Decreases in NO_3^- concentrations were only about one-third those of SO_4^{2-} . The decreases in H^+ concentrations were equivalent to an increase of 0.01 to 0.02 pH units yr^{-1} .
- Ten years of data (1992-2001) from these sites show only two decreasing trends in SO_4^{2-} concentrations, four increasing trends in H^+ concentrations, and no significant trends in NO_3^- concentrations or C_B concentrations. The fewer number of trends partly reflects the shorter time period - statistical significance of a trend is more difficult to demonstrate with a shorter data series - but also reflects that the greatest changes in precipitation chemistry were prior to the mid-1990s. The trends leveled off between 1995 and 2001, which had a greater effect on the trend analysis of the shorter data series (Figure 2).

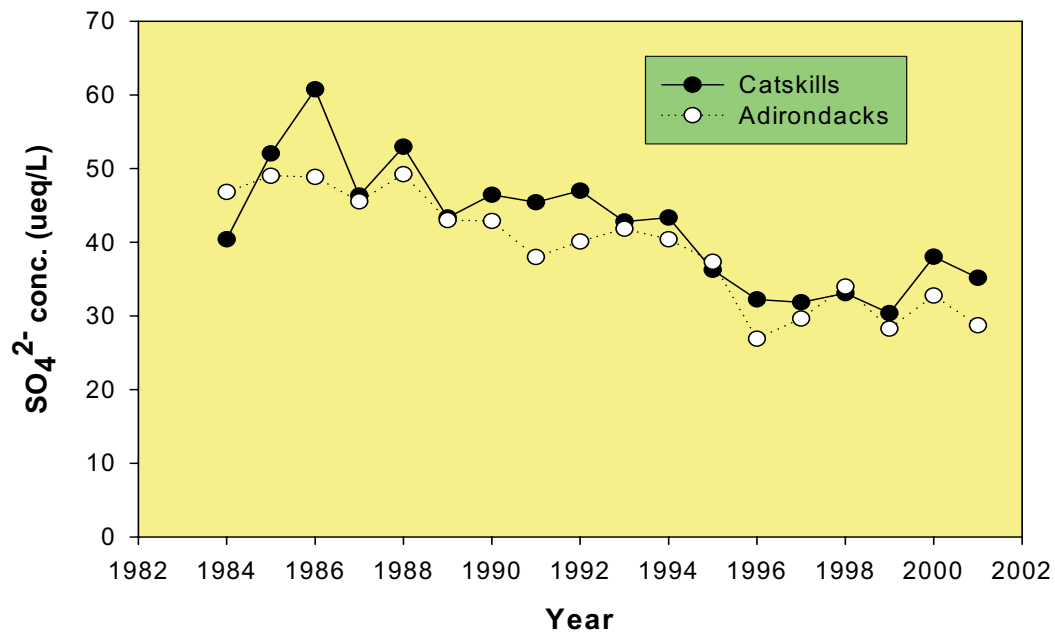


Figure 2. Mean annual volume-weighted mean SO_4^{2-} concentrations in precipitation 1984-2001 at three NADP sites located in each of the Catskill and Adirondack study regions. This figure illustrates the flattening of precipitation chemistry trends during 1995-2001 at the sites that were examined, which may explain in part why there were fewer significant trends during 1992-2001 than during 1984-2001.

- The 10-year trends were highly synchronous for the three Catskill sites, but less so for the three Adirondack sites and in a comparison across both regions. Greater divergence in temporal trends among the three Adirondack sites probably indicates greater variation in sources and atmospheric transport among these three Adirondack sites. On the basis of this analysis, a greater number of precipitation chemistry sites probably are needed in the Adirondacks than were available during 1992-2001 to adequately account for regional variation. However, an NADP site was added in the Adirondacks at Moss Lake during 2003, and additionally, the New York State Department of Environmental Conservation operates five precipitation chemistry sites within or near the Adirondack Park (collected with slightly different methods than those used by NADP; <http://www.dec.state.ny.us/website/dar/baqs/acidrain>), which may be adequate to account for regional spatial variation in precipitation chemistry.

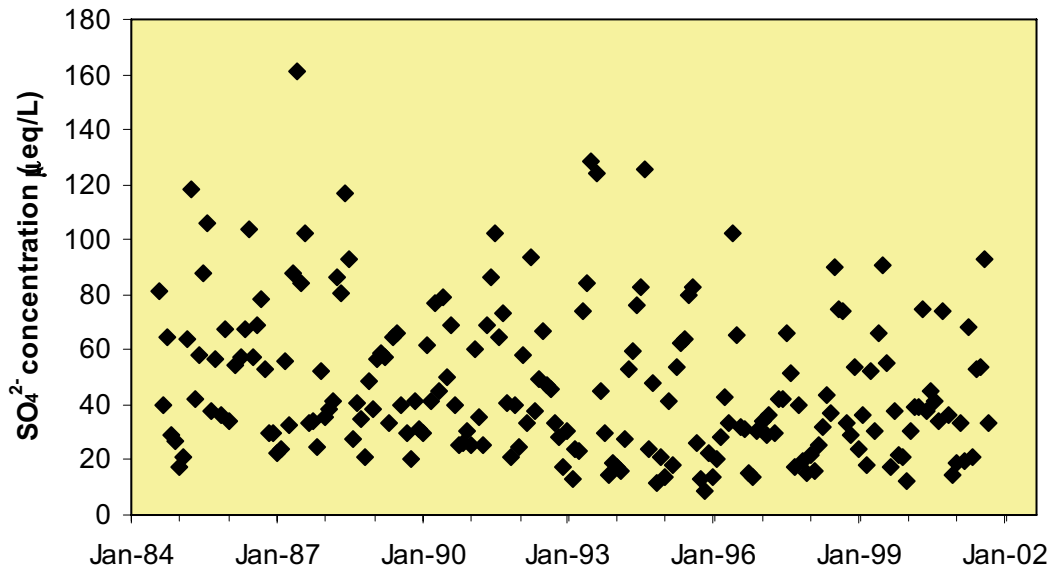


Figure 3. Monthly volume-weighted mean SO_4^{2-} concentrations in precipitation 1984-2001 at the NADP site in Milford, PA near the Catskills. This figure provides evidence of the “noise” inherent in precipitation and surface-water chemistry data, and the subtleness of trends that should be determined using an objective and statistically rigorous method.

THE MEANING OF TREND SYNCHRONICITY

Coherence or synchronicity of trends in chemical constituents in precipitation and surface waters can reveal whether common processes seem to be affecting atmospheric deposition and the cycles of S and N through watersheds. For example in this study, high synchronicity was found among trends in precipitation and surface water SO_4^{2-} concentrations in surface waters reflecting tight cycling of atmospherically deposited S and watershed S cycling processes. In contrast, only weak synchronicity was found among trends in precipitation and surface water NO_3^- concentrations reflecting the complexity of the N cycle and the likelihood that changes in N deposition will not be immediately reflected in surface waters.

TRENDS IN SURFACE-WATER CHEMISTRY

Trends in surface-water chemistry were derived for five Catskill streams and 12 Adirondack lakes with residence times less than 6 months during 1992-2001, the minimum length of record that includes all sites. The resulting trends are summarized as follows:

- Significant decreasing trends in SO_4^{2-} concentrations were present at all sites. The mean trend was two to three times steeper than the mean trend in precipitation, which can be mostly accounted for by the concentrating effects of evapotranspiration.

- Nitrate and inorganic monomeric Al concentrations have decreased significantly at more than half the sites, and ANC and H^+ concentrations have increased significantly at about half the sites. However, a greater proportion of the Adirondack lakes (about 67%) than Catskill streams (20%) showed trends in ANC and H^+ concentrations that indicate recovery.
- Dissolved organic carbon (DOC) concentrations are increasing at most of the sites by a mean of $4.7 \mu\text{mol L}^{-1} \text{yr}^{-1}$ in the Catskill streams and $7.6 \mu\text{mol L}^{-1} \text{yr}^{-1}$ in the Adirondack lakes. These large increases may be caused by the effects of increased pH on the solubility of DOC, or may result from climate variability between the beginning and end of the data record. Changes in DOC are of interest because of the role DOC plays in (1) the recovery of surface-water acid-base chemistry, (2) aquatic light penetration and productivity, and (3) the possible formation of disinfection by-products in the New York water supply, which is largely derived from the Catskills.
- Sulfate concentrations show high synchronicity in surface waters and in precipitation – surface water comparisons in both regions. All other chemical constituents showed marginally significant to weak synchronicity. These results demonstrate the strong connection of atmospheric S deposition and watershed S cycling processes, and further indicate that watershed-cycling processes of N and C_B , which affect pH and ANC, are less coherent within each region and are only weakly linked to NO_3^- , C_B , and H^+ concentrations in precipitation.
- Most previous trend studies in the Adirondacks, Catskills, and throughout the northeastern United States, have not used flow-weighting prior to performing trend calculations (Stoddard et al., 1999; Driscoll et al., 2003; Kahl et al., 2004). Comparisons of non-flow-weighted to flow-weighted trends indicate that flow-weighting did not change the direction of any trend; however, three NO_3^- concentration trends and four ANC trends shifted from significant to non-significant when chemistry data were corrected for variation with flow. These results indicate that the accuracy of future trend-analysis studies for flow-sensitive species such as NO_3^- and ANC may be affected by climate change and would be more accurate if more streamflow data were available from the outlets of these Adirondack lakes.

THE ROLE OF SUGAR MAPLE IN THE NITROGEN CYCLE

Nitric acid is one of the principal sources of acidity in precipitation, exceeded in concentration only by that of sulfuric acid. Nitrogen, principally in the form of NO_3^- , plays an important role in the acid-base chemistry of Catskill streams and Adirondack lakes (Driscoll et al., 1987; Murdoch and Stoddard, 1992). High NO_3^- concentrations are associated with low ANC in these waters, particularly during rain events and snowmelt. Therefore, understanding the many factors that affect the N cycle in these forested watersheds is important to understanding multi-decadal patterns in acid-base chemistry in these Adirondack and Catskill surface waters and to predicting future recovery of these waters. The relative abundance of various tree

species greatly affects the N cycle in these two regions (Lovett et al., 2000). Sugar maple in particular are important in this regard because this species is the most dominant one in northern hardwood forests of New York and its abundance is associated with higher rates of nitrification (conversion of relatively immobile ammonium to nitrite and mobile NO_3^- by bacteria), and therefore higher NO_3^- concentrations in drainage waters than that of other tree species common to these forests. Key factors affecting the abundance of sugar maple were explored by examining available data from forests in the Adirondacks, Catskills, and elsewhere in the Northeast.

- Sugar maple stands have soils with higher rates of nitrification, and therefore, likely have higher rates of NO_3^- leaching and higher concentrations of NO_3^- in drainage waters than stands of other common hardwood and softwood species such as American beech, red oak, and eastern hemlock. High rates of nitrification in sugar maple may result from low lignin concentrations and low lignin:N ratios in leaf litter, which results in a low C:N ratio in soil organic matter. Other factors such as the preference of sugar maple for soils of high pH and calcium (Ca^{2+}) content, and a difference in the form of mycorrhiza associated with sugar maple relative to other common hardwoods may also play a role in the high rates of nitrification under sugar maple stands.



Figure 4. Examples of organisms that can affect the nitrogen cycle and stream NO_3^- concentrations in forested ecosystems in New York. Pictures of fungal spores indicative of beech bark disease (left) and a female Asian Long-Horned Beetle (right). Beech bark disease is currently widespread in New York, and provides an opportunity for sugar maple to advance into areas formerly occupied by healthy beech trees. The Asian Long-Horned Beetle is currently confined to urban areas, but is known to attack sugar maple, and could pose a problem if containment efforts fail.

- There appears to have been little change in the last few decades in the proportion New York's forests composed of sugar maple. Several factors, however, may affect the future abundance of sugar maple in the Adirondack and Catskill regions, and therefore, NO_3^- leaching and acid-base chemistry. These include: (1) beech-bark disease (Figure 4) and resulting mortality or changes in the age and size structure of American beech, a principal competitor of sugar maple, (2) acid

deposition and resulting loss of Ca^{2+} from soils, (3) climate warming as predicted by models, and (4) invasion of pests such as the Asian long-horned beetle (Figure 4).

- The abundance of sugar maple as well as several other factors that affect the N cycle such as extreme climate events, land disturbance history, and deer browsing should be considered when evaluating long-term changes in the acid-base chemistry of surface waters in the Adirondacks and Catskills.
- If the abundance of sugar maple increases in the future because of the decline of its main competitor, American beech, a general increase in NO_3^- in surface waters would be expected. If sugar maple populations decrease due to climate change, calcium depletion, or other causes, NO_3^- concentrations in surface waters will probably decrease because whatever species replaces the sugar maple will most likely develop soils with lower nitrification rates.

MODELING

The model PnET-BGC was used to simulate the principal biogeochemical processes that affect the acid-base chemistry of four Adirondack lakes (includes three of the lakes for which trends were analyzed) and one Catskill stream (also analyzed for trends), and to predict surface-water chemistry under three different future acid-deposition scenarios (Chen et al., 2004; Chen and Driscoll, 2004). This model was developed specifically to examine the effects of acidic atmospheric deposition on soil and surface water chemistry in northern hardwood forests similar to those found in the Adirondack and Catskill watersheds of the current study. The model originated by linking PnET-CN, a carbon (C), N, and water balance formulation, with a geochemical equilibrium model, BGC to simulate the dynamic cycling of base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), acid anions (SO_4^{2-} , NO_3^- , Cl^-), silica, Al, C, phosphorus, and other forms of S and N in forested ecosystems. Model results are summarized in terms of volume-weighted averages below:

- Model-simulated surface-water SO_4^{2-} and Ca^{2+} concentrations agreed well with measured values (normalized mean error (NME) = 0 to -0.03, a value of 0 indicates exact agreement) at the five study sites.
- Simulated NO_3^- concentrations did not agree with measured values as well as those of SO_4^{2-} and Ca^{2+} (NME = 0.04 to -0.19). The model generally predicted increased NO_3^- concentrations, especially during 1996-2000, whereas the measured values generally decreased during the 1990s. One possible reason for the disagreement between modeled and measured results in the 1990s is that the model fails to accurately account for increasing uptake of N by plants driven by increasing atmospheric CO_2 concentrations (Ollinger et al., 2002). However, this mechanism is controversial (Huntington, 2004) and presently unproven.

- The model also failed to accurately predict a peak in NO_3^- concentrations observed in 1990 at three of the sites; this difference is likely the result of widespread regional soil freezing during December 1989 (Mitchell et al., 1996), and the lack of a soil freezing effects algorithm in the model may explain this discrepancy.
- Model-predicted surface water ANC agreed well with measured values (NME = 1.4 to -1.5), however, the model showed little or no trends during the 1990s whereas the measured ANC values showed an increasing trend at most sites. These differences in trends can be attributed to the failure of the model to accurately capture trends in NO_3^- concentrations.
- Modeled SO_4^{2-} budgets indicated little watershed retention of atmospheric S, and are consistent with the high synchronicity in SO_4^{2-} concentration trends among Adirondack and Catskill surface waters.
- Modeled budgets showed considerable variability in watershed N retention among the sites. These results are consistent with the low synchronicity found in NO_3^- concentration trends among the surface waters in these two regions. Land-disturbance history and in-lake processes were determined to strongly affect NO_3^- fluxes from these watersheds.
- With full implementation of the Clean Air Act Amendments of 1990 by 2010, the model predicted nearly offsetting decreases in surface water SO_4^{2-} , NO_3^- , and C_B concentrations that resulted in a modest increase in ANC from 2006-2050 that averaged $3.4 \mu\text{eq L}^{-1}$, and ranged from 1 to $6 \mu\text{eq L}^{-1}$ (Table 1).
- The moderate emissions-control scenario that was modeled resulted in increases in surface water ANC that averaged $9.4 \mu\text{eq L}^{-1}$, and ranged from 3 to $15 \mu\text{eq L}^{-1}$ (Table 1). Model-predicted ANC increased to greater than $0 \mu\text{eq L}^{-1}$ by 2050 in all but one of the five surface waters.

Table 1. Mean and standard deviation of the mean of the predicted change in surface water ANC values in 2050 relative to 2006 for four Adirondack lakes and one Catskill stream according to three possible future emissions that were modeled with PnET-BGC (Chen and Driscoll, 2004).

Model Scenario	Reduction in SO_2 Emissions by 2010	Reduction in NO_x Emissions by 2010	Change in ANC
1990 CAAA base case	40	5	$+3.4 \pm 1.8$
Moderate control	55	20	$+9.4 \pm 4.3$
Aggressive control	75	30	$+19.1 \pm 4.9$

- The aggressive future emissions-control scenario that was modeled, resulted in increases in surface water ANC that averaged $19.1 \mu\text{eq L}^{-1}$, and ranged from 12 to $26 \mu\text{eq L}^{-1}$ (Table 1). Model-predicted ANC increased to greater than $0 \mu\text{eq L}^{-1}$ by 2050 in all but one of the five surface waters; the mean increase in ANC relative to full implementation of 1990 CAAA by 2010 was $15.7 \mu\text{eq L}^{-1}$.
- An ANC value of $0 \mu\text{eq L}^{-1}$ is commonly used as a reference to evaluate chemical recovery of surface waters because this value typically occurs at a pH of about 5.2 to 5.4 in most waters, above which Al concentrations decline and significant increases in aquatic species diversity are observed. The model results indicate that only under the aggressive future emissions-control scenario would modest aquatic biological recovery likely be observed, and the most acidic site (Willy's Pond) would still be below this threshold for biological recovery.

Section 4

SUMMARY

Sulfate and NO_3^- concentrations have decreased significantly and at a greater rate than C_B concentrations in precipitation in the Adirondack and Catskill regions during 1984-2001, and therefore, pH has increased by 0.01 to 0.02 units yr^{-1} . From 1992-2001, however, fewer trends were evident; SO_4^{2-} concentrations decreased significantly at only one-third of the six sites examined. Fewer trends in the more recent time series is believed to result from greater decreases in precipitation SO_4^{2-} concentrations and S emissions prior to the mid-1990s and a flattening of trends during 1995-01.

To summarize the analysis of data on surface water recovery, the four questions asked at the beginning of this report are answered:

- (1) Is there evidence of chemical recovery from reduced levels of acid precipitation in sensitive regions of New York? Yes, there is evidence of limited recovery of surface water chemistry at about half the sites examined in these two regions, and a greater proportion of Adirondack lakes than Catskill streams showed evidence of recovery. This recovery has not likely been great enough, however, to result in widespread biological recovery in these sensitive waters.
- (2) How much recovery has occurred? Sulfate concentrations decreased significantly by $2 - 4 \mu\text{eq L}^{-1} \text{yr}^{-1}$ during 1992-2001 at all 12 Adirondack lakes and 5 Catskill streams that were studied. These decreases were 2 – 3 times greater than those in precipitation during 1984-2001, primarily reflecting the steepening of trends by evapotranspiration. Additionally, NO_3^- concentrations decreased significantly at about half the sites studied, though by 3 to 10 times less than those of SO_4^{2-} . Because most sites also showed significant decreasing trends in C_B concentrations that were similar to those of SO_4^{2-} , therefore ANC increased at only about half the sites, and these increases averaged only about $1.5 \mu\text{eq L}^{-1} \text{yr}^{-1}$.
- (3) Can changes or trends in surface water chemistry be attributed solely to acid precipitation, or do other factors complicate a simple cause and effect interpretation? The analysis of the effects of sugar maple on increasing rates of nitrification and NO_3^- leaching relative to other common northern hardwood species suggests that trends in surface water chemistry cannot be attributed solely to trends in acid deposition. For example, beech bark disease that favors sugar maple over American beech may cause increases in NO_3^- concentrations and decreases in pH and ANC that are independent of trends in acid precipitation. The PnET-BGC model results also show that factors such as historic land disturbance, recent forest harvesting, and climate change greatly affect surface water chemistry, and therefore, may affect trends in the acid-base chemistry of surface waters.

The calculations of trend synchronicity also provide insight about the cause and effect relation between precipitation acidity and stream water chemistry. Trends in SO_4^{2-} concentrations in surface waters showed high synchronicity, consistent with modeling results that indicate little within-watershed retention of SO_4^{2-} . These calculations indicate a strong link between rates of SO_2 emissions, SO_4^{2-} concentrations in precipitation, and SO_4^{2-} concentrations in surface waters. However, trends in NO_3^- and C_B concentrations and ANC were less synchronous, indicating that (1) SO_4^{2-} concentration trends are only partly responsible for ANC trends, and (2) that temporal patterns in NO_3^- , C_B , ANC, and pH vary greatly among watersheds and are strongly affected by changes in the rates of processes that affect the rates of N and C_B cycling. Model results confirm that biogeochemical processes such as cation exchange and mineral weathering that affect rates of C_B cycling are important sources of ANC; thus, changes in the rates of processes such as Ca^{2+} depletion from soil exchange sites and chemical weathering rates affect the rate of recovery of surface water pH and ANC.

- (4) What do model results tell us about the likely future of surface-water chemistry given likely future scenarios of precipitation chemistry? Model predictions indicate only slight additional recovery of surface water ANC by 2050 in these two regions under the 1990 CAAA. In the most aggressive scenario considered, with SO_2 emissions reduced by 75% and NO_x emissions reduced by 30% below those levels mandated by the 1990 CAAA by 2010, ANC recovery in the modeled surface waters would increase by 3 to 10-fold by 2050 relative to existing law.

NEW FINDINGS IN THIS STUDY

Other studies cited in this report (Stoddard et al., 1999; Driscoll et al., 2003; Kahl et al., 2004) have examined the recovery of surface water chemistry from the reduced acidity of atmospheric deposition during the past two decades. However, this is the first study to compare the progress of recovery in the Catskills and Adirondacks, the two principal regions in New York State that are sensitive to the effects of acid deposition. The study concludes that limited recovery of surface water chemistry can be observed during 1992-2001, however, the Catskill streams examined have recovered less than the Adirondack lakes. Both regions show higher rates of nitrification and NO_3^- concentrations in drainage waters under sugar maple than in other common tree species, suggesting that changes in sugar maple populations will have a strong effect on trends in surface water NO_3^- concentrations in the future. Modeling results indicate that surface waters in both regions are expected to show only minimal recovery by 2050 according to existing clean air laws. This study was also the first to examine the synchronicity of recovery-related trends in these regions. The lack of strong regional and inter-regional synchronicity in surface water NO_3^- and H^+ concentrations and ANC indicate that these chemical indicators are responding to factors other than changes in precipitation acidity, such as climate change. These results highlight the importance of a strong monitoring network for key

indicators of climate that are likely affecting these trends. This study demonstrated that correcting for flow-related variation in surface water chemistry can affect the statistical significance of trends, particularly those of NO_3^- concentrations and ANC. Since streamflow is a key indicator of climate, and currently, flow is continuously measured on the outlet of only one of the Adirondack lakes (Arbutus) that was analyzed in this study, implementation of additional lake outflow monitoring in the Adirondacks would enhance the ability of future investigations to untangle the effects of flow-related climate variation from those of changes in precipitation chemistry on the chemistry of these lake waters.

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**AN ASSESSMENT OF RECOVERY AND KEY PROCESSES AFFECTING THE
RESPONSE OF SURFACE WATERS TO REDUCED LEVELS OF ACID
PRECIPITATION IN THE ADIRONDACK AND CATSKILL MOUNTAINS**

FINAL REPORT 05-03

STATE OF NEW YORK
GEORGE E. PATAKI, GOVERNOR

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