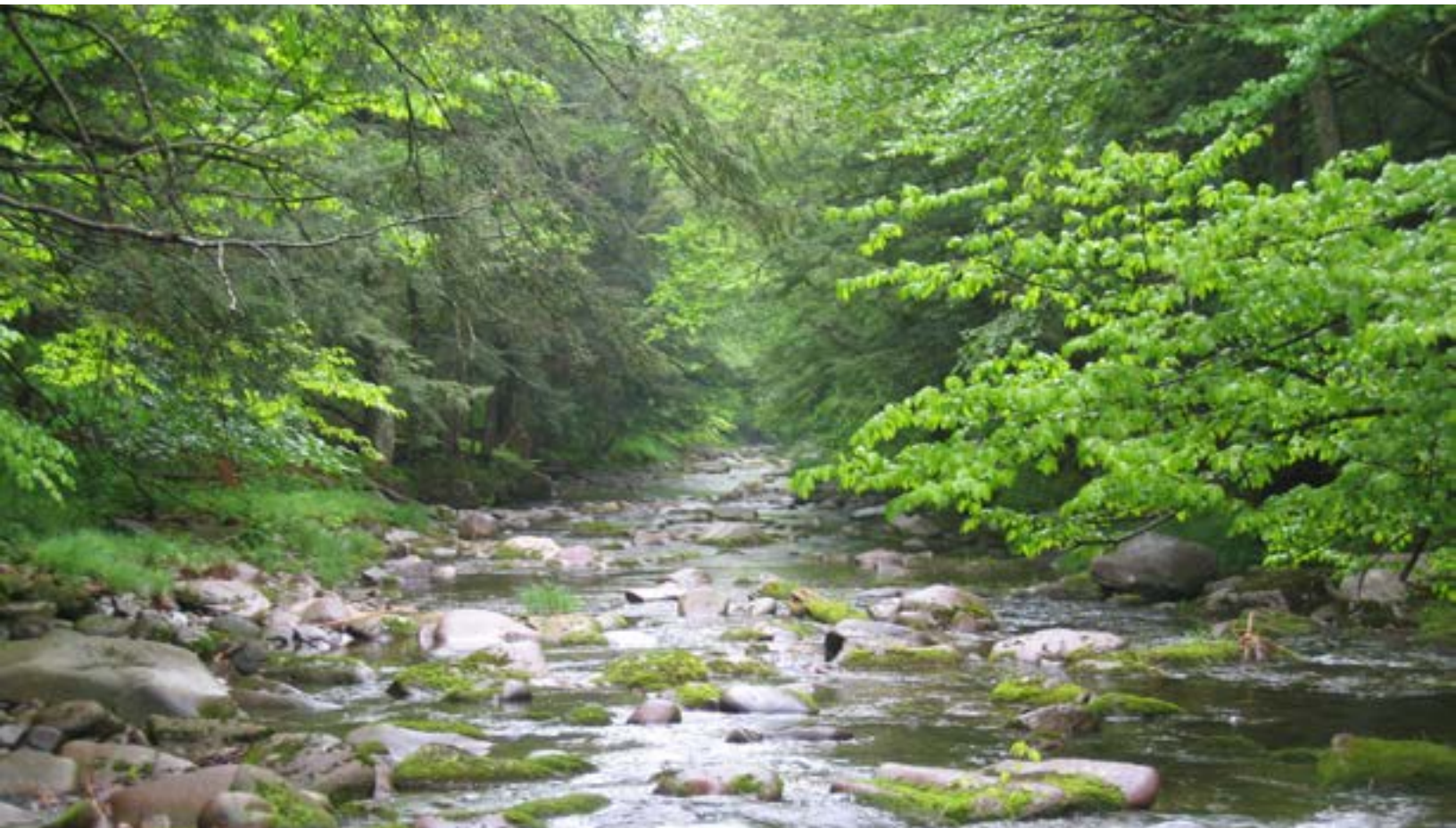


The Response of Soil and Stream Chemistry to Decreases in Acid Deposition in the Catskill Mountains, New York



Final Report | Report Number 18-19 | March 2019

NYSERDA's Promise to New Yorkers:

NYSERDA provides resources, expertise, and objective information so New Yorkers can make confident, informed energy decisions.

Mission Statement:

Advance innovative energy solutions in ways that improve New York's economy and environment.

Vision Statement:

Serve as a catalyst – advancing energy innovation, technology, and investment; transforming New York's economy; and empowering people to choose clean and efficient energy as part of their everyday lives.

The Response of Soil and Stream Chemistry to Decreases in Acid Deposition in the Catskill Mountains, New York

Summary Report

Prepared for:

New York State Energy Research and Development Authority

Albany, NY

Gregory Lampman
Program Manager

Prepared by:

U.S. Geological Survey

Troy, NY

Michael R. McHale
Douglas A. Burns
Jason Siemion
Michael Antidormi
Project Managers

Notice

This report was prepared by the U.S. Geological Survey in the course of performing work contracted for and sponsored by the New York State Energy Research and Development Authority (hereafter “NYSERDA”). The opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York, and reference to any specific product, service, process, or method does not constitute an implied or expressed recommendation or endorsement of it. Furthermore, NYSERDA, the State of New York, and the contractor make no warranties or representations, expressed or implied, as to the fitness for particular purpose or merchantability of any product, apparatus, or service, or the usefulness, completeness, or accuracy of any processes, methods, or other information contained, described, disclosed, or referred to in this report. NYSERDA, the State of New York, and the contractor make no representation that the use of any product, apparatus, process, method, or other information will not infringe privately owned rights and will assume no liability for any loss, injury, or damage resulting from, or occurring in connection with, the use of information contained, described, disclosed, or referred to in this report.

NYSERDA makes every effort to provide accurate information about copyright owners and related matters in the reports we publish. Contractors are responsible for determining and satisfying copyright or other use restrictions regarding the content of reports that they write, in compliance with NYSERDA’s policies and federal law. Please email print@nyserda.ny.gov if you are the copyright owner and believe a NYSERDA report has not properly attributed your work or has used it without permission.

Information contained in this document, such as web page addresses, are current at the time of publication.

Funding

This research was supported by the New York State Energy Research and Development Authority (no. 40509), the Environmental Protection Agency’s Office of Air and Radiation through the Long-Term Monitoring Network, the New York City Department of Environmental Protection, and the United States Geological Survey’s Hydrologic Benchmark Network. Although this work was partially funded by the U.S. Environmental Protection Agency, the report has not been subjected to agency review; therefore, no official endorsement should be inferred.

Preferred Citation

New York State Energy Research and Development Authority (NYSERDA). 2017. “The Response of Soil and Stream Chemistry to Decreases in Acid Deposition in the Catskill Mountains, New York,” NYSERDA Report Number 18-19. Prepared by U.S. Geological Survey. nysesda.ny.gov/publications

Abstract

Acid deposition has adversely affected the Catskill Mountains for many decades. In 1990, the United States Congress passed amendments to the Clean Air Act; one of the amendments was designed to address the issues related to acid deposition. Since that time, emissions and deposition of sulfur and nitrogen have been greatly reduced. From 1991 through 2014 the U.S. Geological Survey in cooperation with the U.S. Environmental Protection Agency have monitored stream water chemistry at five small forested watersheds and soil chemistry in two locations within the Neversink River watershed to measure the effect of the reductions in acid deposition in the region. In general, there were significant improvements in stream-water quality in the five watersheds, but no improvements in soil chemistry were detected. The most significant trends were for sulfate concentrations (mean trend of -2.5 micro-equivalents per liter per year). Hydrogen ion and inorganic monomeric aluminum also decreased significantly (mean trends of -0.3 micro-equivalents per liter per year for hydrogen ion and -0.1 micromoles per liter per year for inorganic monomeric aluminum for the three most acidic sites). There was a mean increase in acid neutralizing capacity of 0.65 micro-equivalents per liter per year for all five sites, although that increase was four times smaller than the decrease in sulfate concentrations. There was a decrease in base cation concentrations during the same time period (-1.3 micro-equivalents per liter per year for calcium + magnesium) that limited the increase in acid neutralizing capacity. Nitrate is another strongly acidic anion that can contribute to watershed acidification and although the nitrate concentration of wet-only precipitation decreased significantly during the study (-0.70 micro-equivalents per liter per year; $p < 0.01$) there was no significant decrease in stream water nitrate concentrations.

Additional trend analyses focused on water chemistry during April of each year (April is the month of the peak of spring streamflow in the region). The April concentration trends generally paralleled the annual trends, but there were fewer significant trends during April. Comparisons of flow-weighted mean chemical concentrations for low and high flow from the beginning of the study period to the end of the study period showed that much of the reduction in stream acidity occurred during high flow conditions. These results indicate that there have been improvements in chronic stream water acidity (all flow

conditions) and episodic acidification (high flow conditions). There was no indication of recovery in watershed soil chemistry during the study period. The lack of significant changes in soil chemistry is likely attributable to an initially low soil buffering capacity because of the chemical composition of the parent material (silica-based sedimentary bedrock) that was further depleted by decades of acid deposition. However, we also detected no indications of marked soil acidification in that the soils did not show signs of recovery during the study, but they also did not show signs of further acidification. The soils in this base-poor region may take several decades to show signs of recovery and continued monitoring is necessary to detect that change.

Keywords

acid rain; soil monitoring; chemical trends; sulfate; nitrate; Catskill Mountains

Acknowledgements

We would like to thank Tom Suleski for years of fieldwork collecting streamflow and stream water samples that were used for this research. We would also like to thank Deb Horan-Ross, Hannah Ingleston, and Trish Lincoln for more than two decades of chemical analyses that made this research possible.

Table of Contents

Notice	ii
Funding	ii
Preferred Citation	iii
Abstract	iii
Keywords	iv
Acknowledgements	iv
List of Figures	v
1 Introduction	1
2 Scope	3
3 Principal Findings	5
3.1 Emissions and Deposition Chemistry	5
3.2 Trends in Stream Water Chemistry.....	6
3.3 Changes in Episodic Acidification	9
3.4 Changes in Soil Chemistry.....	13
4 Conclusions	14
5 References Cited	16

List of Figures

Figure 1. Map Showing Locations of Stream-Sampling Stations	4
Figure 2. EPA Acid Rain Program Estimates	6
Figure 3. Results from Seasonal Kendall Trend Analyses	8
Figure 4. Results from Mann-Kendall Trend Analyses.....	10
Figure 5. Change in Volume-Weighted Mean Concentrations on the Neversink River	12

1 Introduction

Acid deposition in New York State is mainly a result of emissions of sulfur dioxide and nitrogen oxides that originate largely from fossil-fuel combustion (Driscoll et al., 2001). Acid deposition has caused acidification of soils and surface waters in the Catskill Mountains resulting in negative effects to fish and other aquatic life as well as forests. Acid deposition generally peaked in New York State in the late 1970s and has declined by about 75% since the 1980s (Driscoll et al., 2016). Regulation of emissions implemented as part of the U.S. Clean Air Act have largely driven these declines in acid deposition. The watersheds discussed in this report are part of the Long-Term Monitoring (LTM) Program of the U.S. Environmental Protection Agency (EPA), designed to monitor the response of surface water chemistry to the implementation of Title IV of the 1990 Clean Air Act Amendments in regions such as the Catskills with high sensitivity to acid rain.¹

The Catskill Mountains are particularly sensitive to acid rain because the bedrock and soils have little ability to buffer acidity. The Catskill Mountains are composed of sedimentary rock (mostly sandstone, siltstone, and conglomerate) which do not contain large amounts of base cations (calcium, magnesium, potassium, and sodium) needed to neutralize the acidity in acid rain. As a result, acid rain in the region has acidified surface waters and caused harmful effects to aquatic biota (Baldigo and Lawrence, 2001; Siemion et al., 2014; Stoddard and Murdoch, 1991). The Neversink River and its headwaters are the most sensitive part of the Catskills with streams that are acidic at low flow and become more acidic during high flow such as annual snowmelt (Baldigo and Lawrence, 2001; Wigington et al., 1996a). Past investigations have failed to find strong evidence of improvement (often termed “recovery”) in stream water chemistry or in biodiversity of aquatic organisms in the Neversink River basin, despite sharp decreases in acid deposition (Burns et al., 2006; Burns et al., 2008). Stream sulfate concentrations have declined in parallel with declines in precipitation sulfate concentrations (Murdoch and Stoddard, 1993; Stoddard and Murdoch, 1991), but stream nitrate concentrations have not shown a parallel decline with those of decreasing nitrate concentrations in precipitation (Burns et al., 2006). Base-cation concentrations have shown decreasing trends in Catskill surface waters, whereas dissolved organic carbon

¹ <https://www.epa.gov/airmarkets/clean-air-markets-monitoring-surface-water-chemistry>

concentrations increased from 1992–2001 (Burns et al., 2006). These trends in base cations and dissolved organic carbon contributed to the lack of recovery in a measure called acid-neutralizing capacity in Catskill streams through 2001. Acid-neutralizing capacity is a measure of the amount of acidity a solution (for example stream water) can buffer (or neutralize); acid-neutralizing capacity is higher in waters with more base cations and lower in waters with less base cations.

Rainstorms and snowmelt cause increases in streamflow and concurrent sharp decreases in acid neutralizing capacity in Catskill Mountain streams (Wigington et al., 1996a). These decreases in acid neutralizing capacity are often termed “episodic acidification” and are associated with pulses of nitrate and inorganic monomeric aluminum. Inorganic monomeric aluminum is mobilized under acidic conditions and has negative effects on biota that live in surface waters. Therefore, even as streams recover from long-term acidification, episodic acidification may continue to affect Catskill streams (Lawrence, 2002).

Several previous studies in the northeastern U.S. have suggested that the recovery of surface waters from acid deposition has been limited by the depletion of soil base cations (Lawrence et al., 2015; Likens et al., 1996; Warby et al., 2009). Mineral soils in the Catskills are generally highly acidic with a limited supply of base cations that help to neutralize acid deposition (Siemion et al., 2014). The long-term depletion of soil base cations coupled with little or no change in stream water nitrate concentrations may delay the recovery of stream water from decreases in acid deposition. However, some recent evidence of increases in soil base cations across the northeast may signal the beginning of a more robust recovery from stream acidification (Lawrence et al., 2015; Lawrence et al., 2012).

The purpose of this study was to examine the response of stream water and soil chemistry to decreases in acid deposition in five Catskill Mountain watersheds. Although previous work has documented decreases in stream water sulfate concentrations in the region, decreases in base cations, increases in dissolved organic carbon, and little change in nitrate (NO_3^-) concentrations have resulted in only a minimal increase in stream water pH (a measure of relative acidity that generally varies from about 4 to 9 in most natural waters) and acid-neutralizing capacity (Burns et al. 2006). We evaluated the recovery of five Catskill streams by examining year-round temporal trends as well as those for April each year when snowmelt typically causes episodic acidification. Soil resampling was used to determine whether soils were recovering, which could indicate a more robust, ecosystem-scale recovery.

2 Scope

This report summarizes data collected as part of the Long-Term Monitoring Network funded and managed by the EPA. The purpose of the network is to monitor the response of surface water chemistry to implementation of Title IV of the 1990 Clean Air Act Amendments. The full results of this research are published in the scientific journal *Environmental Pollution* (McHale et al., 2017). The study examined 23 years of atmospheric and stream water chemistry data from 1992 through 2014. The five study watersheds are located in the southeastern Catskill Mountains in southeastern New York State (Table 1; Figure 1). These watersheds have been included in previous studies of stream acidification and recovery during the last three decades (Baldigo and Murdoch, 1997; Burns et al., 1998; Burns et al., 2006; Lawrence, 2002; Lawrence et al., 2000; Murdoch and Stoddard, 1992; Stoddard and Murdoch, 1991; Wigington et al., 1996b).

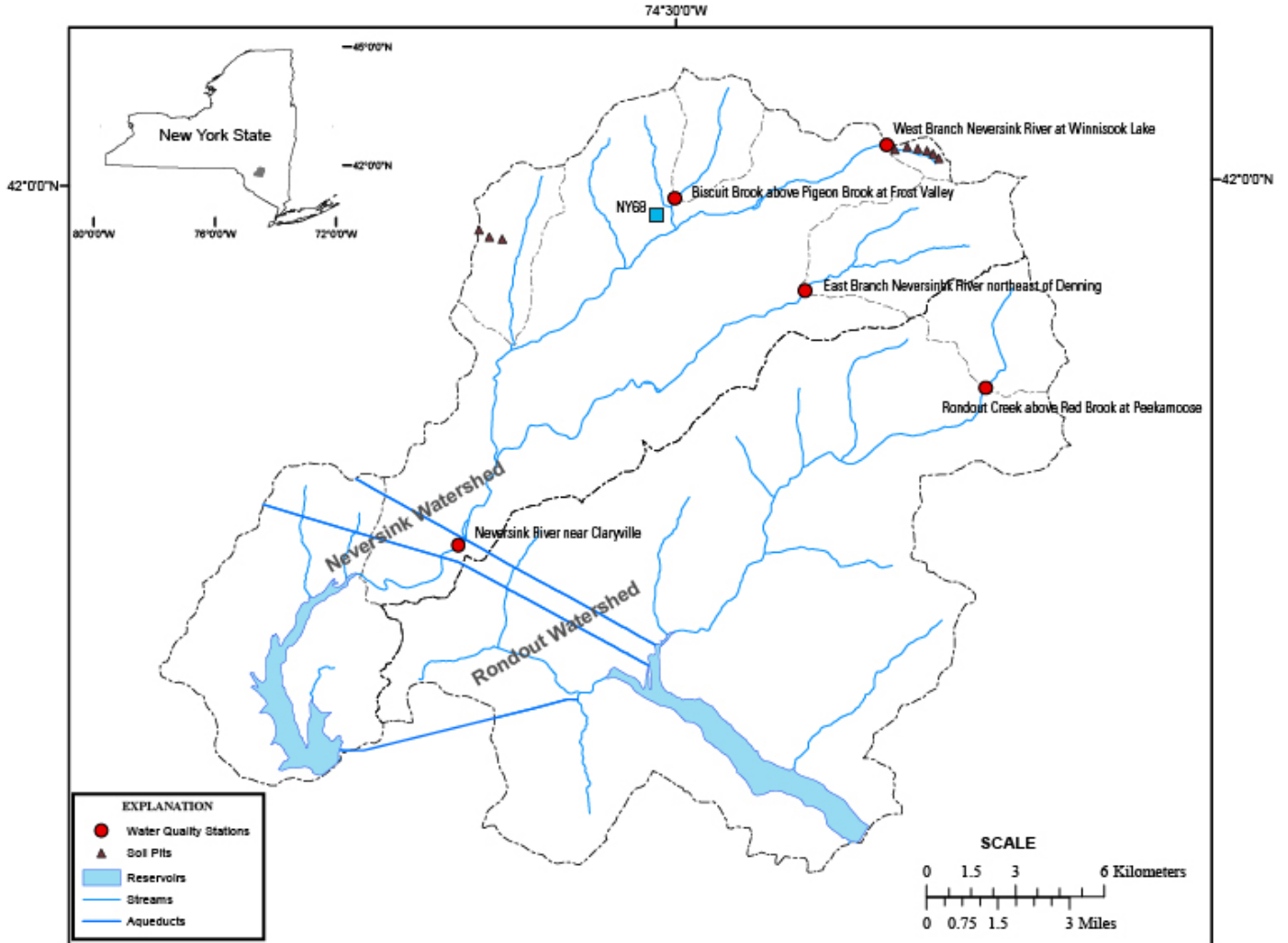
Table 1. Site Characteristics

Percentage of forest was calculated using the 2014 National Land Use and Land Cover Data Set
ha = hectares

Station Name	USGS gaging station #	Short Name	Site Abbreviation	Latitude	Longitude	Area (ha)	Elevation (meters)	% Forest
West Branch Neversink River at Winnisook Lake	01434021	Winnisook	WN	42°00'40" N	74°24'53" W	199	817	100
East Branch Neversink River northeast of Denning	0143400680	Tisons	TS	41°58'01" N	74°26'54" W	2,313	652	100
Rondout Creek above Red Brook at Peekamoose	01364959	Rondout	RC	41°56'13" N	74°22'30" W	1,388	530	100
Biscuit Brook above Pigeon Brook at Frost Valley	01434025	Biscuit Brook	BS	41°59'43" N	74°30'05" W	963	628	100

Figure 1. Map Showing Locations of Stream-Sampling Stations

The sampling stations are represented by circles, the National Atmospheric Deposition Program (NADP) station, NY68 by a square, and soils sampling locations by triangles.



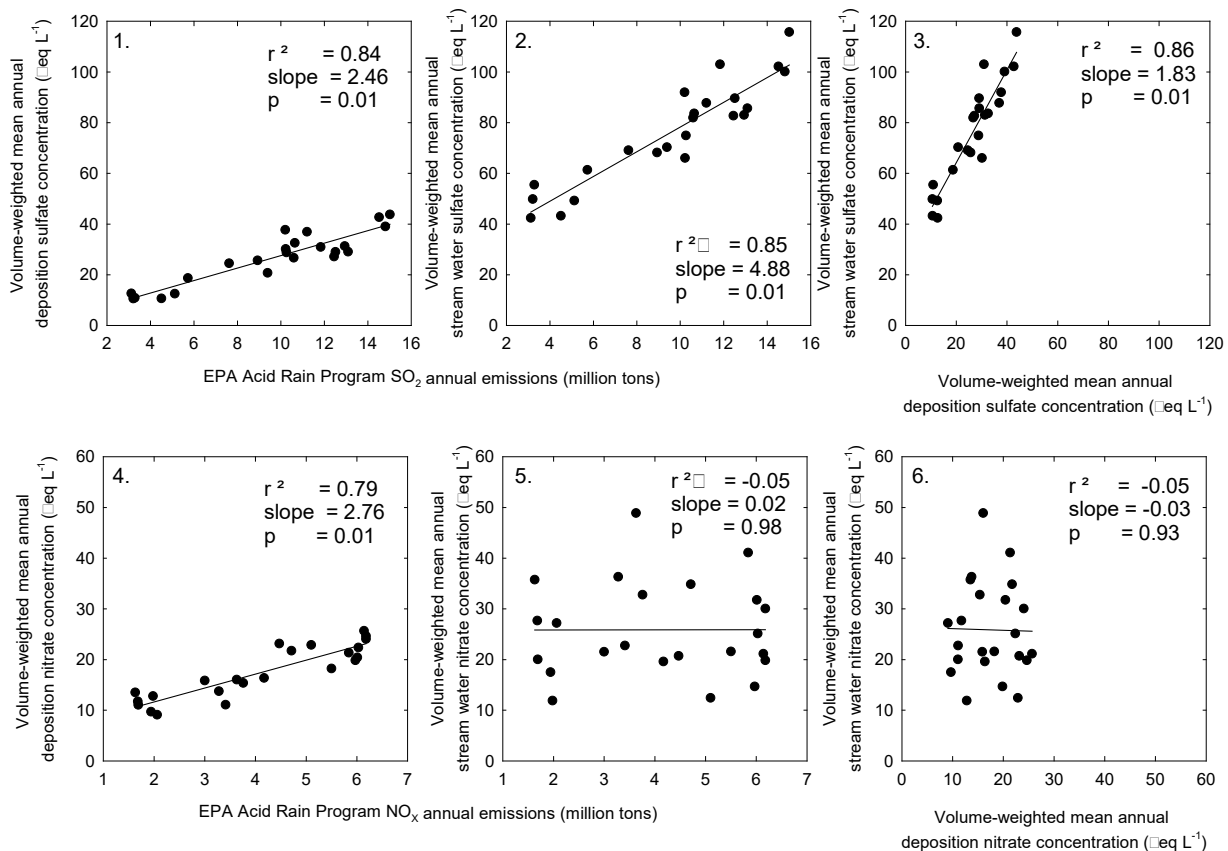
3 Principal Findings

3.1 Emissions and Deposition Chemistry

The chemistry of atmospheric deposition is altered as it moves through watershed soils, and in-turn, watershed soil chemistry is altered by atmospheric deposition. Decreases in annual sulfur dioxide emissions as tracked by the EPA Acid Rain Program have resulted in parallel decreases in annual sulfate loads in wet deposition (rain and snow) at a deposition collector operated by the National Atmospheric Deposition Program (NADP) and decreases in sulfate concentrations in Biscuit Brook (Figure 2). Although the relation between annual nitrogen oxide emissions and mean annual nitrate concentrations in wet deposition was significant, there was no relation with either nitrogen oxide emissions or mean annual nitrate concentrations in wet deposition and annual stream water nitrate concentrations (Figure 2). In other words, decreases in emissions of sulfur have resulted in decreases in sulfur deposition and stream sulfate concentrations and although decreases in nitrogen emissions have resulted in decreases in nitrogen deposition, they have not resulted in decreases in stream water nitrate. This difference in the response to decreases in emissions between sulfur and nitrogen is likely caused by two primary factors (1) historically there is more sulfate than nitrate in these streams so there is more of it to decrease and (2) nitrogen is an essential nutrient for both aquatic and terrestrial organisms so the interaction of nitrogen with all types of watershed organisms make the relation between precipitation chemistry and stream chemistry for nitrogen much more complicated than it is for sulfur.

Figure 2. EPA Acid Rain Program Estimates

The relation between (1) annual SO₂ emissions and annual mean SO₄²⁻ deposition at the NADP station at Biscuit Brook, (2) annual SO₂ emissions and annual mean stream water SO₄²⁻ concentration at Biscuit Brook, (3) annual mean SO₄²⁻ deposition and annual mean stream water SO₄²⁻ concentration at Biscuit Brook, (4) annual NO_x emissions and annual mean NO₃⁻ deposition, (5) annual NO_x emissions and annual mean stream water NO₃⁻ concentration at Biscuit Brook, (6) annual mean NO₃⁻ deposition and annual mean stream water NO₃⁻ concentration at Biscuit Brook.



3.2 Trends in Stream Water Chemistry

The five study watersheds spanned a range in pH and acid-neutralizing capacity. Winnisook is the smallest area, highest elevation watershed, and is also the most acidic, whereas the Neversink River at Claryville is the largest, lowest elevation, and least acidic watershed included in the study. The three most acidic watersheds (Winnisook, Tisons, and Rondout) all experienced significant decreases in hydrogen ion concentrations and significant increases in acid-neutralizing capacity during the study period (Figure 3). The largest trends (positive or negative) of any constituent measured were those for sulfate, which accounts for the majority of the acidity in these watersheds (Figure 3). There were no

statistically significant trends in stream water nitrate concentrations at any of the five streams. There has been a significant decrease in the main base cations—calcium and magnesium—in stream water (Figure 3). Acid-neutralizing capacity trends were statistically significant in four of the five study watersheds with the largest increases at the most acidic watersheds, even though the decreases in base-cation concentrations diminished the increasing trends in acid-neutralizing capacity to some extent.

Stream water inorganic monomeric aluminum is a particular concern in these watersheds because it is toxic to brook trout at concentrations greater than $2.0 \mu\text{mol L}^{-1}$ (Baldigo et al., 2007). There were small but statistically significant decreases in inorganic monomeric aluminum in the Winnisook, Tisons, and Rondout streams (Figure 3) and although the trends were small relative to those of other solutes, they may be ecologically significant in terms of toxicity. The flow-weighted mean concentration of inorganic monomeric aluminum at the Winnisook stream was $9.9 \mu\text{mol L}^{-1}$ during the first three years of the study period and had only decreased to $6.9 \mu\text{mol L}^{-1}$ during the last three years of record, still well above the $2.0 \mu\text{mol L}^{-1}$ toxicity threshold. The flow-weighted mean inorganic monomeric aluminum concentration in the stream at Tisons decreased more than half from the first three years of the period ($5.3 \mu\text{mol L}^{-1}$) to the last three years ($2.4 \mu\text{mol L}^{-1}$).

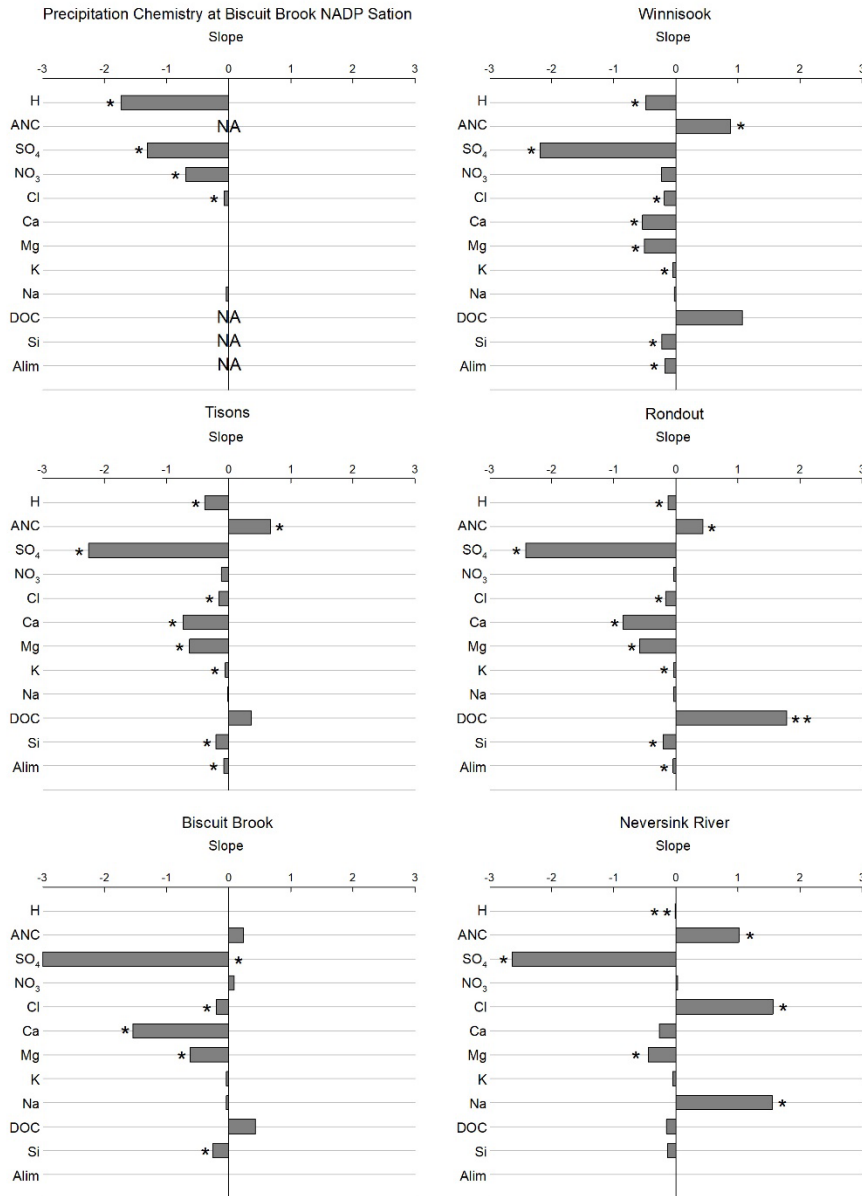
Brook trout were absent from reaches in the Winnisook watershed near and upstream from the U.S. Geological Survey (USGS) gage during 1991–1993 fish surveys (Baldigo and Lawrence, 2000) when inorganic monomeric aluminum concentrations were about $9.9 \mu\text{mol L}^{-1}$. Several wild brook trout individuals were observed in this stream during 2003 (Burns et al., 2008) and many mature wild brook trout were collected during surveys in 2014–2016 (Barry Baldigo, personal communication), although the volume weighted inorganic monomeric aluminum concentration remained high at $6.9 \mu\text{mol L}^{-1}$ during the last three years of this study. There is no known stocking of brook trout in this stream.

Figure 3. Results from Seasonal Kendall Trend Analyses

The following are results from seasonal Kendall trend analyses for stream chemistry from five Catskill streams during water years 1992 through 2014 (a water year is defined as October 1 through September 30). The slope is given in micro-equivalents per liter for all solutes except dissolved organic carbon and inorganic monomeric aluminum which are shown in micromoles per liter.

* = trend is significant at $p < 0.01$

** = trend is significant at $p < 0.05$



3.3 Changes in Episodic Acidification

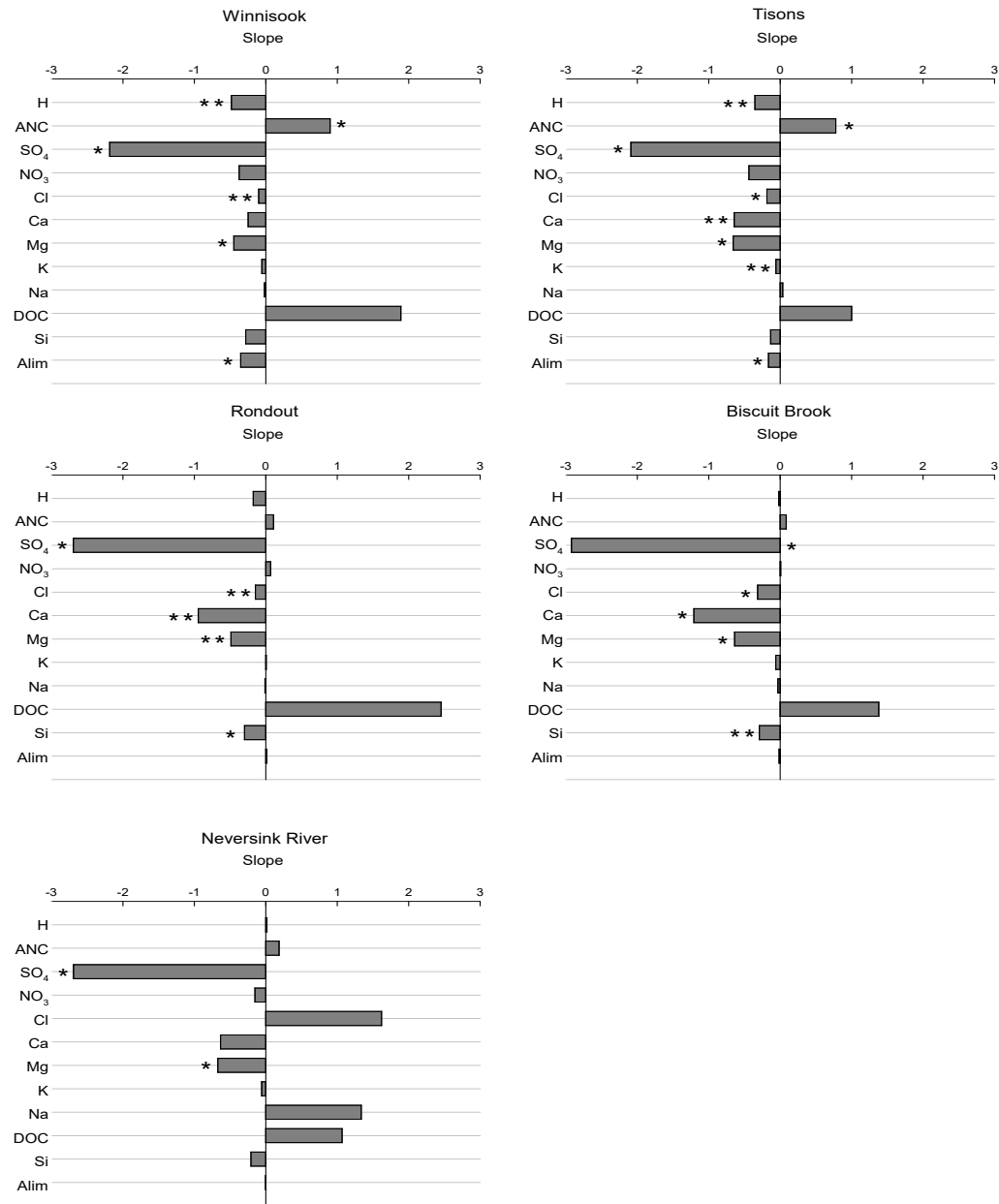
Episodic acidification is associated with large storms and particularly with snowmelt in the northeastern United States (Wigington et al., 1996a). Studies of episodic acidification have shown that even in streams that are not chronically acidic (acidic during low flow and high flow), episodic acidification can have deleterious effects on stream ecosystems (Baker and Christensen, 1991; Baker et al., 1996; Baldigo and Lawrence, 2000; Wigington et al., 1996a). Initially we focused on episodic acidification related to spring snowmelt; we computed Mann-Kendall trends for stream chemistry during April of each year because this is the month during which peak spring streamflow is measured in the region. Sulfate trends were of similar magnitude and direction in April as they were for the annual trends and the most acidic streams (Winnisook and Tisons) showed the largest decreases in acidification during spring melt (Figure 4). Trends in acid-neutralizing capacity and hydrogen ion during April were similar to annual trends at all five watersheds (Figure 4). In general, fewer significant trends in chemistry were observed during April than during the entire year at every stream, and none of the significant trends changed direction when comparing April to the annual trends (Figures 3 and 4).

Figure 4. Results from Mann-Kendall Trend Analyses

The following are results from Mann-Kendall trend analyses for April stream chemistry from five Catskill streams during water years 1992 through 2014 (a water year is defined as October 1 through September 30). The slope is given in micro-equivalents per liter for all solutes except dissolved organic carbon and inorganic monomeric aluminum, which are shown in micromoles per liter.

* = trend is significant at $p < 0.01$

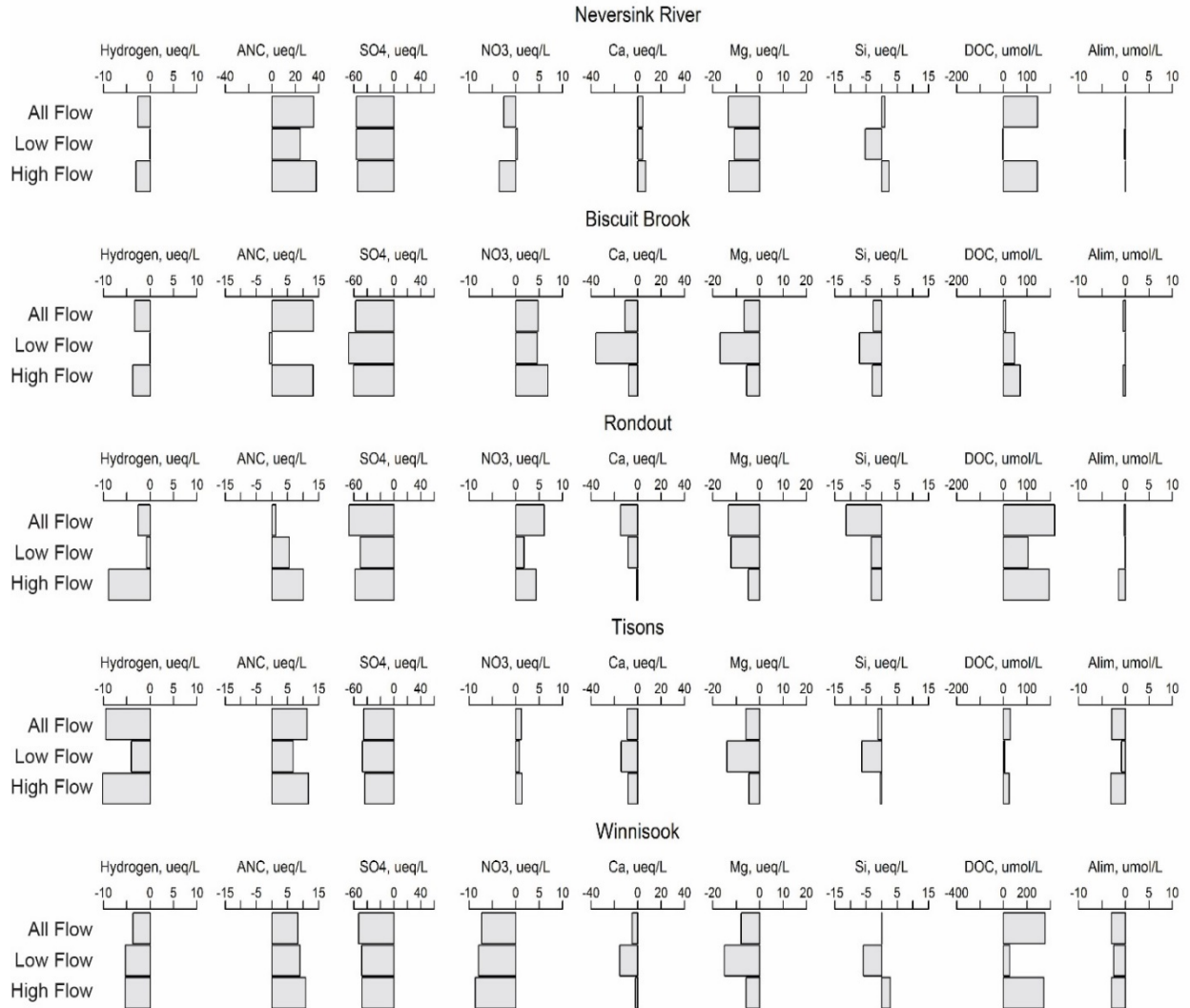
** = trend is significant at $p < 0.05$



We compared annual flow-weighted mean solute concentrations at low-flow, high-flow, and all-flow conditions to examine whether the recovery documented by the annual and April trend analyses was apparent across all flows and during all times of the year (Figure 5). The greatest increases in acid-neutralizing capacity and decreases in hydrogen were measured during high flow, and the response during all-flow conditions was dominated by the high-flow response (Figure 5). Therefore, while improving trends in stream chemistry for all-flow conditions do not equate to improving trends in episodic acidification everywhere, they do in these Catskill watersheds. The decrease in episodic acidification also resulted in a decrease in inorganic monomeric aluminum concentrations at high flow. Our results indicate that there has been a reduction in stream acidity throughout the range in flow conditions at these watersheds, and that while episodic acidification is still a concern at the most acidic streams (particularly Winnisook and Tisons), the acidic episodes measured from 2012–2014 were not as severe as those measured from 1992–1996 (Figure 5). Perhaps the most important finding is that the frequency and magnitude of acidic episodes has decreased dramatically at Winnisook; concentrations of inorganic monomeric aluminum exceeding $7.0 \mu\text{moles L}^{-1}$ were common during the first three years of the study, but there were only two occasions when Al_{im} concentrations exceeded that level during the last three years of the study (one sample during the 2012 snowmelt and one storm during the fall of 2012).

Figure 5. Change in Volume-Weighted Mean Concentrations on the Neversink River

The change in volume-weighted mean concentrations from the first three study years (1992–1994) to the last three study years (2012–2014) during all-flow conditions, high-flow conditions (discharge greater than the 90th percentile), and low-flow conditions (discharge less than the 25th percentile) for five study watersheds (see Figure 1 for site locations).



3.4 Changes in Soil Chemistry

Soils were sampled in two areas of the Neversink River watershed: (1) in the Winnisook watershed, which drains the slopes of Slide Mountain in the headwaters of the Neversink watershed and (2) in the Fall Brook watershed, which is similar to the Biscuit Brook watershed and drains a portion of the northern slopes of the mid-basin of the Neversink watershed. Soils were sampled in 1992 and again in 2012 in the Winnisook watershed and in 2001 and again in 2011 in the Fall Brook watershed. Results from soil resampling show few statistically significant differences in soil chemistry between the 10- or 19-year sampling periods in this study. In the shallow organic horizon soils in Fall Brook, there was a significant decrease in exchangeable sodium and pH and an increase in total carbon. For the Winnisook mineral soils, there was a marginally significant decrease in pH. There were no significant changes in individual exchangeable base cations in the mineral soils of either watershed, although they all decreased resulting in a significant decrease in the total amount of base cations in Winnisook mineral soils (commonly measured as base saturation, or the total amount of exchangeable base cations available in a soil).

The Catskill streams included in this study are showing signs of a strong recovery from decades of acid deposition as evidenced by trends in acid deposition and stream water chemistry. These results are similar to previous trend studies in this region and elsewhere in New York State and the northeastern region of the United States (Burns et al., 2006; Driscoll et al., 2003; Fuss et al., 2015; Sickles and Shadwick, 2015; Strock et al., 2014; Waller et al., 2012). However, Catskill soil chemistry is not showing similar signs of recovery from acid deposition. Lawrence and others (2015) presented promising signs of recovery in soils across the northeastern U.S. that we expected might be detectable in the Catskills. However, decades of acid deposition appear to have leached the small amount of buffering capacity available from these soils and there is little carbonate bedrock present in the Catskill Mountains to replace it (Ver Straeten, 2013). Indeed, these soils probably did not have a lot of base cations before acid deposition began. Nevertheless, there was no evidence of significant acidification in these soils during the study period, so although they do not appear to be improving they are not getting any worse. Continued soil monitoring may reveal a slow recovery of these soils, but the recovery rate remains uncertain.

4 Conclusions

This study reports on 23 years of stream-water quality trends in the southeastern Catskill Mountains of New York State. The area has been an active site of acid deposition, nitrogen cycling, forest harvesting and soil monitoring research for the last 30 years. During this period, there have been large decreases in acid deposition, particularly sulfate, resulting in large decreases in stream sulfate concentrations. The large decreases in acid deposition appear to be in direct response to large decreases in man-made emissions mainly attributable to regulations implemented as part of the Clean Air Act amendments. Although nitrogen emissions and nitrate concentrations in wet deposition have also declined, those changes have not translated into decreases in stream nitrate concentrations. Nitrogen is a nutrient that is sensitive to a variety of factors including disturbances such as insect attacks on trees, and the complexities in the cycle of this nutrient are great enough that a clear signal of decreasing nitrate concentrations is not evident in these Catskill streams. The significant decreases in inorganic monomeric aluminum concentrations measured in the three most acidic streams in this study are promising evidence that recovery is underway; trout have begun to return to even the most acidic of these streams. Nonetheless, the increases in pH and acid-neutralizing capacity are limited by decreases in stream water base-cation concentrations, despite the large decreases in sulfate concentrations.

The decreasing trends in stream water sulfate and inorganic monomeric aluminum and increasing trends in pH and acid-neutralizing capacity were also evident during spring melt which is typically one of the most acidic periods of the year in this region. In fact, we measured improvements in stream water acidity during high-flow conditions throughout the year. Episodic acidification has been a widespread problem in this region even in watersheds that are not chronically acidic such as Biscuit Brook (Lawrence, 2002; Wigington et al., 1996a; Wigington et al., 1996b). Our results indicate that both chronic and episodic acidification are improving at similar rates and that trends were consistent between high-flow and all-flow conditions.

Results from soil monitoring suggest that Neversink watershed soils are not presently showing signs of recovery from acidification. Although there is recent evidence of early signs of recovery of soils from acid deposition in watersheds across the northeastern United States (Lawrence et al., 2015), we found little evidence of soil recovery in the two Catskill watersheds sampled. The bedrock in the Catskills, and particularly in the southeastern Catskills, is characterized by sandstone, siltstone, and conglomerates with little or no limestone. As a result, soils in this region have probably never had much ability to neutralize acidity and decades of acid deposition appear to have depleted much of the capacity that was present. Soil formation is a naturally acidifying process in the soils of the Catskills, so with little potential for replenishing base cations from bedrock, we are unlikely to see substantial soil recovery on a decadal time scale.

5 References Cited

- Baker, J.P., Christensen, S.W., 1991. Effects of acidification on biological communities in aquatic ecosystems, in: Charles, D.F. (Ed.), Acid deposition and aquatic ecosystems. Springer-Verlag New York Inc., New York, pp. 83-106.
- Baker, J.P., Van Sickle, J., Gagen, C.J., DeWalle, D.R., Sharpe, W.E., Carline, R.F., Baldigo, B.P., Murdoch, P.S., Bath, D.W., Kretser, W.A., Simonin, H.A., Wigington, P.J., Jr., 1996. Episodic acidification of small streams in the northeastern United States: effects on fish populations. *Ecological Applications* 6, 422-437.
- Baldigo, B.P., Lawrence, G.B., 2000. Composition of fish communities in relation to stream acidification and habitat in the Neversink River, New York. *Transactions of the American Fisheries Society* 129, 60-76.
- Baldigo, B.P., Lawrence, G.B., 2001. Effects of stream acidification and habitat on fish populations of a North American river. *Aquatic Sciences* 63, 196-222.
- Baldigo, B.P., Lawrence, G.B., Simonin, H.A., 2007. Persistent mortality of brook trout in episodically acidified streams of the southwestern Adirondack Mountains, New York. *Transactions of the American Fisheries Society* 136, 121-134.
- Baldigo, B.P., Murdoch, P.S., 1997. Effect of stream acidification and inorganic aluminum on mortality of brook trout (*Salvelinus fontinalis*) in the Catskill Mountains, New York. *Canadian Journal of Fisheries and Aquatic Sciences* 54, 603-615.
- Burns, D.A., Lawrence, G.B., Murdoch, P.S., 1998. Streams in Catskill Mountains still susceptible to acid rain. *Northeastern Geology and Environmental Sciences* 20, 294-298.
- Burns, D.A., McHale, M.R., Driscoll, C.T., Roy, K.M., 2006. Response of surface water chemistry to reduced levels of acid precipitation: Comparison of trends in two regions of New York, USA. *Hydrological Processes* 20, 1611-1627.
- Burns, D.A., Riva-Murray, K., Bode, R.W., Passy, S., 2008. Changes in stream chemistry and biology in response to reduced levels of acid deposition during 1987-2003 in the Neversink River Basin, Catskill Mountains. *Ecological Indicators* 8, 191-203.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001. Acidic deposition in the Northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience* 51, 180-198.
- Driscoll, C.T., Driscoll, K.M., Roy, K.M., Mitchell, M.J., 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. *Environmental Science & Technology* 37, 2036-2042.

- Driscoll, C.T., Driscoll, K.M., Fakhraei, H., Civerolo, K., 2016. Long-term temporal trends and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New York in response to decreases in acidic deposition. *Atmospheric Environment* 146, 5-14.
- Fuss, C.B., Driscoll, C.T., Campbell, J.L., 2015. Recovery from chronic and snowmelt acidification: Long-term trends in stream and soil water chemistry at the Hubbard Brook Experimental Forest, New Hampshire, USA. *Journal of Geophysical Research: Biogeosciences* 120, 2360-2374.
- Lawrence, G.B., 2002. Persistent episodic acidification of streams linked to acid rain effects on soil. *Atmospheric Environment* 36, 1589-1598.
- Lawrence, G.B., Hazlett, P.W., Fernandez, I.J., Ouimet, R., Bailey, S.W., Shortle, W.C., Smith, K.T., Antidormi, M.R., 2015. Declining acidic deposition begins reversal of forest-soil acidification in the northeastern US and eastern Canada. *Environmental Science & Technology* 49, 13103-13111.
- Lawrence, G.B., Shortle, W.C., David, M.B., Smith, K.T., Warby, R.A., Lapenis, A.G., 2012. Early indications of soil recovery from acidic deposition in US red spruce forests. *Soil Science Society of America journal* 76, 1407-1417.
- Lawrence, G.B., Lovett, G.M., Baevsky, Y.H., 2000. Atmospheric deposition and watershed nitrogen export along an elevational gradient in the Catskill Mountains, New York. *Biogeochemistry* 50, 21-43.
- Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272, 244.
- McHale, M.R., Burns, D.A., Siemion, J., Antidormi, M.R., 2017. The response of soil and stream chemistry to decreases in acid deposition in the Catskill Mountains, New York, USA. *Environmental Pollution* 229, 607-620.
- Murdoch, P.S., Stoddard, J.L., 1992. The role of nitrate in the acidification of streams in the Catskill Mountains of New York. *Water Resources Research* 28, 2707-2720.
- Murdoch, P.S., Stoddard, J.L., 1993. Chemical characteristics and temporal trends in eight streams of the Catskill Mountains, New York. *Water, Air, & Soil Pollution* 67, 367-395.
- Sickles, I., Shadwick, D., 2015. Air quality and atmospheric deposition in the eastern US: 20 years of change. *Atmospheric Chemistry and Physics* 15, 173-197.
- Siemion, J., Lawrence, G.B., Murdoch, P.S., 2014. Use of soil-streamwater relationships to assess regional patterns of acidic deposition effects in the northeastern USA. *Hydrological Processes* 28, 3615-3626.
- Stoddard, J.L., Murdoch, P.S., 1991. Acidic deposition and aquatic ecosystems-regional case studies, Catskill Mountains. Springer-Verlag, New York, pp. 237-271.
- Strock, K.E., Nelson, S.J., Kahl, J.S., Saros, J.E., McDowell, W.H., 2014. Decadal trends reveal recent acceleration in the rate of recovery from acidification in the northeastern US. *Environmental Science & Technology* 48, 4681-4689.

Ver Straeten, C.A., 2013. Beneath it all: bedrock geology of the Catskill Mountains and implications of its weathering. *Annals of the New York Academy of Sciences* 1298, 1-29.

Waller, K., Driscoll, C., Lynch, J., Newcomb, D., Roy, K., 2012. Long-term recovery of lakes in the Adirondack region of New York to decreases in acidic deposition. *Atmospheric Environment* 46, 56-64.

Warby, R.A., Johnson, C.E., Driscoll, C.T., 2009. Continuing acidification of organic soils across the northeastern USA: 1984–2001. *Soil Science Society of America journal* 73, 274-284.

Wigington, P., DeWalle, D., Murdoch, P., Kretser, W., Simonin, H., Van Sickle, J., Baker, J., 1996a. Episodic acidification of small streams in the northeastern United States: ionic controls of episodes. *Ecological Applications*, 389-407.

Wigington, P.J., Jr., Murdoch, P.S., Simonin, H.A., Van Sickle, J., McDowell, M.K., Peck, D.V., Barchet, W.R., Baker, J.P., DeWalle, D.R., Kretser, W.A., 1996b. Episodic acidification of small streams in the northeastern United States: Episodic Response Project. *Ecological Abstracts* 6, 374-388

NYSERDA, a public benefit corporation, offers objective information and analysis, innovative programs, technical expertise, and support to help New Yorkers increase energy efficiency, save money, use renewable energy, and reduce reliance on fossil fuels. NYSERDA professionals work to protect the environment and create clean-energy jobs. NYSERDA has been developing partnerships to advance innovative energy solutions in New York State since 1975.

To learn more about NYSERDA's programs and funding opportunities, visit nyserda.ny.gov or follow us on Twitter, Facebook, YouTube, or Instagram.

**New York State
Energy Research and
Development Authority**

17 Columbia Circle
Albany, NY 12203-6399

toll free: 866-NYSERDA
local: 518-862-1090
fax: 518-862-1091

info@nyserda.ny.gov
nyserda.ny.gov



NYSERDA

State of New York

Andrew M. Cuomo, Governor

New York State Energy Research and Development Authority

Richard L. Kauffman, Chair | Alicia Barton, President and CEO