Changes in Stream Chemistry and Aquatic Biota in Response to the Decreased Acidity of Atmospheric Deposition in the Neversink River Basin, Catskill Mountains, New York, 1987 to 2003

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CHANGES IN STREAM CHEMISTRY AND AQUATIC BIOTA IN RESPONSE TO THE DECREASED ACIDITY OFATMOSPHERIC DEPOSITION IN THE NEVERSINK RIVER BASIN, CATSKILL MOUNTAINS, NEW YORK, 1987 TO 2003

FINAL REPORT

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PREFACE

The New York State Energy Research and Development Authority (NYSERDA) is pleased to publish "Changes in Stream Chemistry and Aquatic Biota in Response to the Decreased Acidity of Atmospheric Deposition in the Neversink River Basin, Catskill Mountains New York, 1987 to 2003." This project was funded as part of the New York Energy $mart[SM] 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 on NYSERDA's website at: www.nyserda.org/programs/environment/emep/ .

ABSTRACT

The decreased acidity of atmospheric deposition in New York State and the northeastern United States since the 1970s has resulted in small increases in pH, acid-neutralizing capacity (ANC), and small decreases in inorganic monomeric aluminum (Al_{IM}) concentrations since monitoring began in the acid-sensitive upper Neversink River basin in the Catskill Mountains of southeastern New York during the 1980s. Temporal trends as shown by Seasonal Kendall analyses, indicate that stream pH increased by 0.01 units yr^{-1} from 1987 to 2003 at three stream sites in the Neversink basin, consistent with an increase in precipitation pH of 0.01 units yr^{-1}. Twelve sites in the Neversink River were sampled during summer 2003 for water chemistry, macroinvertebrates, fish, and periphytic diatoms for comparison with a similar data set collected during summer 1987 to assess the biological effects of this observed decrease in precipitation and stream acidity. Metrics and indices that reflect sensitivity to stream acidity were calculated from these biological data to discern whether changes in stream biota over the intervening 16 years paralleled those of stream chemistry. Statistical comparisons of the 1987 data with the 2003 data on stream chemistry and acid biological assessment profiles (Acid BAP) derived from macroinvertebrate data, showed no significant difference between the years. The pH and ANC values of 2003 were generally lower than those of 1987, however, probably because flow in the summer of 2003 was greater. Despite these probable flow-induced changes in the summer of 2003, an ordination and cluster analysis of relative abundances of macroinvertebrate taxa for 2003 indicated that the four headwater sites formed a significantly different cluster from that of 1987. The 2003 cluster had a lower mean Acid BAP value, that denotes generally lower stream acidity at those sites in 2003. This finding indicates the return of some acid-sensitive invertebrate species to the most acidic upstream reaches of the river, but additional improvement in stream chemistry is required before this conclusion can be confirmed. Fish data from 2003 indicate that the acid-intolerant slimy sculpin had not expanded its habitat into upstream reaches, in which it was also absent in 1987. Additionally, an acid-tolerance index based on periphytic diatom data from 2003 indicated high acid impact throughout middle and headwater reaches.

KEY WORDS

Acid precipitation; aluminum; pH; fish; macroinvertebrates, diatoms, trends; recovery; Catskill Mountains

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EXECUTIVE SUMMARY

Precipitation and stream-chemistry data from long-term monitoring sites in the Neversink River basin in the Catskill Mountain region of southeastern New York indicate that pH increased by 0.16 units during 1987 through 2003, an average of 0.01 units yr^{-1}. Twelve stream reaches were sampled for chemistry, macroinvertebrates, fish, and diatoms in summer 2003 for comparison with a similar dataset collected in summer 1987 to discern whether long-term decreases in stream acidity and in the concentrations of associated chemical constituents resulted in measurable increases in species of acid-sensitive stream biota. An index based on acid-sensitive macroinvertebrate taxa showed no significant difference in a grouped comparison between the 1987 data and 2003 data, except for four headwater sites, that showed a significant difference consistent with decreased stream acidity. These headwater sites formed a separate, statistically significant cluster that corresponded with results of an ordination and cluster analysis. These macroinvertebrate data indicate no widespread increase in acid-sensitive species throughout the basin, but indicate a small increase in the most acidic headwater reaches. This limited improvement in the summer of 2003 was insufficient to allow the return of slimy sculpin to headwater reaches from which they were also absent in the summer of 1987. Adult brook trout were found in 2003 but not in 1987 at the most upstream and acidic reach of the West Branch Neversink River, suggesting an expansion upstream of habitat consistent with less acidic conditions. An acid-tolerance index based on diatoms indicated adverse effects of acidity at all headwaters and many middle reaches in the summer of 2003. Current regional model projections (Chen and Driscoll, 2004) indicate little expectation for measurable expansion of slimy sculpin habitat and improvement in the diatom index by 2050. Collection of macroinvertebrates, fish, and diatoms, and consequent development of metrics and indices of acid sensitivity, provides a multi-organism approach to studying the recovery of aquatic ecosystems from decreased atmospheric acid loads. These summer 2003 data can provide a benchmark that will allow comparisons of future changes in the aquatic biological community as stream acid/base conditions change.

Section 1
INTRODUCTION

Acidic atmospheric deposition affects ecosystems in New York by acidifying soils and surface waters. That change mobilizes inorganic forms of aluminum, and depletes base cations from soils (Lawrence et al., 1999; Driscoll et al., 2001). The strong mineral acidity in precipitation in New York consists mainly of sulfuric and nitric acids derived largely from the burning of fossil fuels, primarily coal and oil. Precipitation in New York has become less acidic since the late 1970s, largely in response to implementation of the Clean Air Act and subsequent Amendments to the Act in 1990 (Lynch et al., 2000). Several recent studies have evaluated the extent of recovery or improvement of acid-sensitive surface waters in New York, and throughout the eastern U.S., from these reduced levels of acid deposition (Stoddard et al., 1999; Driscoll et al., 2003; Burns et al., 2006). The extent of recovery is commonly evaluated by comparing trends in pH, acid-neutralizing capacity (ANC), and sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations in surface waters with those in precipitation. Indicators that have been less commonly evaluated are changes in aquatic communities toward a condition that likely existed before the advent of acid precipitation in the first half of the 20th century. Little work has thus far examined changes in aquatic communities in the U.S., but recent studies in Scandinavia and Canada, some of which involved liming studies or monitoring recovery from artificial acidification, have documented recovery of acid-intolerant species of aquatic macroinvertebrates, zooplankton, and eplilithic algae (Halvorsen et al., 2003; Raddum and Fjellheim, 2003; Vinebrooke et al., 2003; Sandin et al., 2004).

The Catskill Mountains are located in an upland region of southeastern New York that receives among the highest loads of atmospheric acid deposition in North America (Stoddard and Murdoch, 1991). This region consists of steep slopes with rapid subsurface drainage, thin till cover, and bedrock that weathers slowly. The effect of these factors is an abundance of surface waters that are sensitive to the effects of acid deposition (Stoddard and Murdoch, 1991). The acidity of precipitation in this region has decreased since at least 1983 (when data collection began), as in other regions of eastern North America. Recent studies indicate that stream-water SO_4^{2-} concentrations have declined sharply since the 1980s along with small decreases in NO_3^- concentrations and significant increases in pH and ANC at many sites (Murdoch and Shanley, in press; Burns et al., 2006). Within the Catskill region, the Neversink River basin shows the most widespread and severe effects of acid deposition on surface waters and terrestrial ecosystems (Stoddard and Murdoch, 1991).

The objective of this study was to document the extent of biological change within the Neversink River basin since the 1980s. To assess change, we collected chemical and biological data from several sites in 1987 to compare with a similar set of data collected in 2003. Most of the sites sampled in 1987 were sampled in 2003 by similar methods to facilitate data comparison. We also evaluated weekly to monthly stream-chemistry data collected at three of these sites during 1987-2003 and a weekly precipitation chemistry data set collected at one site during the same period to provide a more temporally detailed assessment of chemical change in this basin.

Section 2
STUDY AREA AND METHODS

The upper Neversink River basin drains an area of 172.5 km^2. The basin originates at the summit of Slide Mountain (elevation 1274 m) and flows along two principal branches—the East and West Branches of the Neversink River—that join upstream of the Neversink Reservoir (elevation 450 m), part of New York City's water supply. The region is underlain by near flat-lying Devonian age sedimentary bedrock overlain by till deposits and alluvium (Rich, 1934; Buttner, 1977). The bedrock is primarily coarse sandstone and conglomerate with interbedded shale and siltstone (Way, 1972) and stands as a dissected plateau approximately 1000 m higher than the surrounding terrain. The till is derived largely from local bedrock and was deposited during the most recent glaciation ~14,000 years ago. Soils of the region are classified as Inceptisols in the Arnot-Oquaga-Lackawanna series (Tornes, 1979). These soils range from 0.1 to 1.5 m in thickness, are excessively to moderately well drained, and are predominantly very steep and medium textured on the uplands.

Vegetation is mainly northern hardwood forest, dominated by American beech, sugar maple, red maple, and yellow birch. Red spruce and balsam fir dominate above elevations of 1100 m, (Kudish, 2000). Timber below 850 m elevation was harvested extensively during the 19th century; logging above 850 m was generally minimal and these forests remain relatively undisturbed by human activity.

The upper Neversink River basin has a population of less than 1000, with scattered homes and little agriculture; therefore, surface-water chemistry principally reflects the progressive neutralization of acid precipitation through biogeochemical processes during transit through the basin. The headwaters of both branches of the river have pH values < 5.0, that progressively increase to ~ 6.5 at Claryville, just below the confluence (Baldigo and Lawrence, 2000). The distribution of pH in the river determines the inorganic monomeric aluminum (Al_{IM}) concentrations, that are highly correlated with brook trout mortality and fish-species richness (Baldigo and Murdoch, 1997; Baldigo and Lawrence, 2000). The acid/base chemistry of the river spans the range observed in sensitive surface waters of eastern North America; the headwaters are among the most acidified, and the reach near Claryville, below the confluence, is among the most pristine, although short-term episodic acidification during spring snowmelt to pH values < 5.2 and ANC < 0 μeq/L has been documented (Baldigo and Lawrence, 2000).

Weekly precipitation-chemistry data were used to establish trends in precipitation acidity during 1987-2003. Precipitation samples were collected at the Biscuit Brook site (NY-68; 634 m elevation; Fig. 1), part of the National Atmospheric Deposition Program (NADP) National Trends Network. Samples are analyzed for major ions according to methods for handling, preparation, analysis, and quality assurance that are described on the NADP web site at http://nadp.sws.uiuc.edu/QA (accessed July 11, 2006).

Stream-chemistry trends during 1987-2003 were determined from data collected at three long-term stream-monitoring sites in the Neversink River watershed (Fig. 1), East Branch Neversink River at Tison (NE-05), West Branch Neversink River at Winnisook (NW-01) and Biscuit Brook (NW-06). Streams

generally were sampled weekly to monthly at base flow and more frequently during high flow. Sites NE-05 and NW-06 were sampled throughout 1987-2003, whereas NW-01 was sampled regularly only during 1991-2003.

Stream-water samples were collected for chemical analysis during July and August 1987 and September 2003. Details of analytical methods and QA/QC procedures used at the USGS laboratory in Troy, New York are provided in Lawrence et al. (1995) and Lincoln et al. (2005).

Macroinvertebrate communities were sampled with standardized traveling kick sample techniques by identical methods in 1987 and 2003. In the laboratory, the macroinvertebrate samples were subsampled for 300 organisms and identified to the species level or lowest possible taxon as in Bode et al. (2002).

Fish surveys were conducted during September, 2003 by electrofishing. An attempt was made to electrofish all types of habitats present and to focus on determining species composition of the reach. This approach was selected to be consistent with the electrofishing sampling during 1987 (Howard Simonin, New York State Dept. of Environ. Conserv., personal communication). Fish collected were identified to the species level, and total length was measured prior to release.

Periphytic diatoms were sampled by a qualitative multi-habitat sampling technique (Passy, 2000; Passy and Bode, 2004). The 1987 diatom sampling and identification procedures were more qualitative than those of 2003; therefore these 1987 data were not evaluated for changes over time and are not discussed in the report.

Trend analysis was performed using the seasonal Kendall test (Hirsch et al., 1982), a modification of the nonparametric Mann-Kendall test (Mann, 1945; Kendall, 1975). Constituents analyzed for trends include pH and calcium in precipitation, and pH, ANC, Al_{IM}, and calcium in stream water. These constituents were chosen for their relevance and possible effects on aquatic organisms (Baldigo and Murdoch, 1997; Baldigo and Lawrence, 2000; Raddum and Fjellheim, 2003).

Diatom, macroinvertebrate, and fish-community metrics or indices known to respond to acidification were used to provide multiple indicators of biological condition. The methods used to develop these indices are described in greater detail in Burns et al. (in press, *Ecological Indicators*).

Section 3

KEY STUDY FINDINGS AND POLICY RELEVANCE

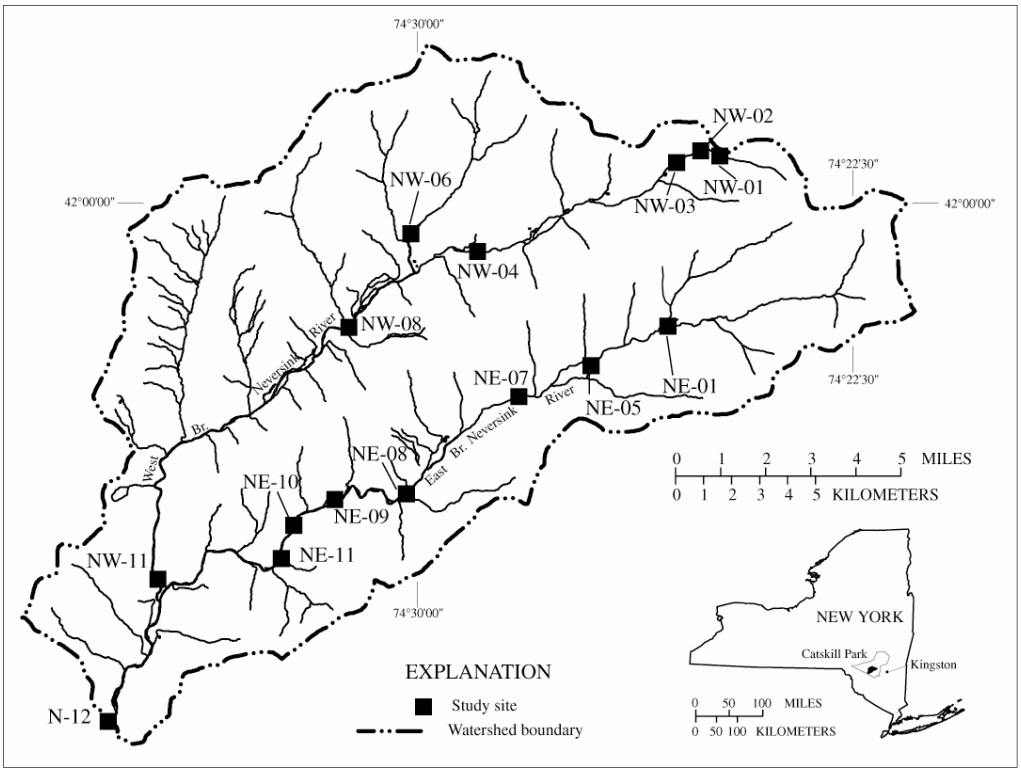

Figure 1 - Map of upper Neversink River watershed showing sites for biological and chemical sampling.

- Precipitation pH at the Biscuit Brook National Atmospheric Deposition Program site increased by 0.01 units yr^{-1} during 1987 – 2003, and stream pH at three long-term monitoring sites also increased by 0.01 units yr^{-1}. All of these trends were statistically significant.
- Spatial patterns of stream chemistry throughout the Neversink River basin in the summer of 1987 were broadly similar to those of the summer of 2003 (Fig. 2). Stream pH in the headwaters of the two principal river branches varied from 4.6 to 4.8, and increased to about 6.5 at the U.S. Geological Survey gage near Claryville.
- The stream-chemistry data indicated more acidic conditions in 2003 than in 1987 (Fig. 2), the opposite of expectations based on trends of decreasing precipitation and stream acidity in the basin. This qualitative difference was not statistically significant, however. The 2003 chemistry data likely were affected by the greater precipitation amounts and higher flow conditions in the summer of 2003 than in the summer of 1987. Higher streamflow in Catskill streams is associated with decreased pH and ANC and with increased aluminum concentrations (Stoddard and Murdoch, 1991).

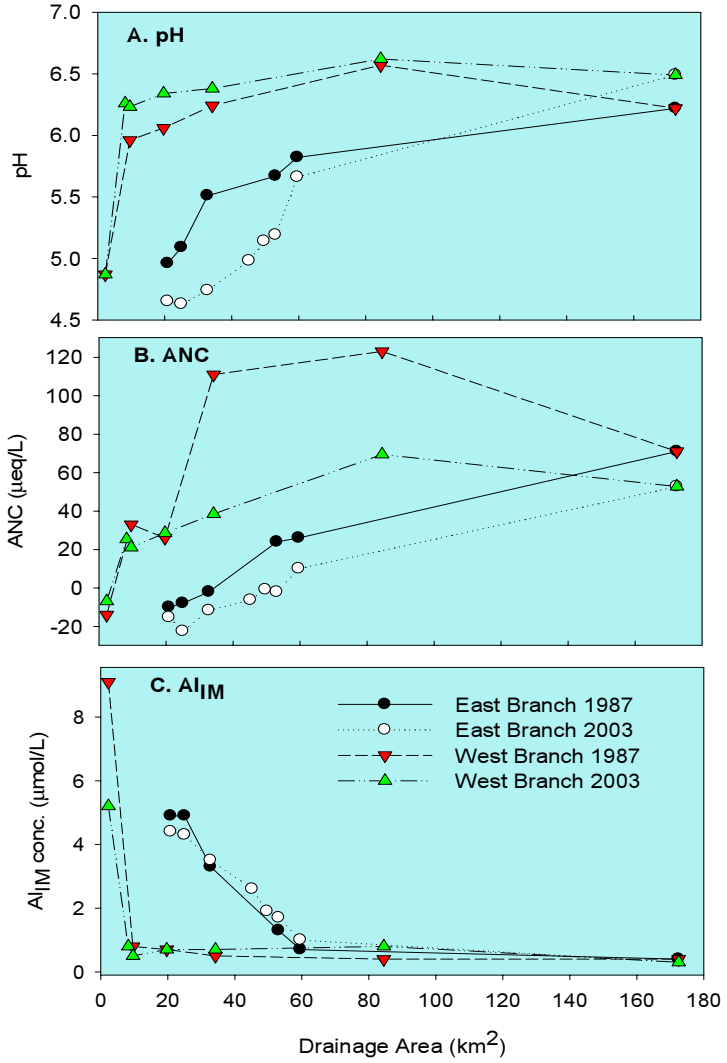

Figure 2 - Values of A. pH, B. ANC, and C. Al_{IM} concentrations as a function of drainage area for samples collected in the upper Neversink River basin during summer of 1987 and summer of 2003.

- An acid biological assessment profile (Acid BAP) was calculated based on taxa richness and relative abundances of 16 macroinvertebrate taxa (genus or species level) that are commonly found in New York streams and that have demonstrated sensitivity to stream acidity and aluminum concentrations. An Acid BAP value of 0 indicates severe acid impact and 10 indicates no acid impact. The Acid BAP was significantly correlated with stream pH and pAl (the negative logarithm of Al_{IM} concentrations) in 1987 and 2003; this indicates that the presence or absence of the macroinvertebrate species studied responded similarly to stream acid/base conditions in 1987 and 2003 (Fig. 3).

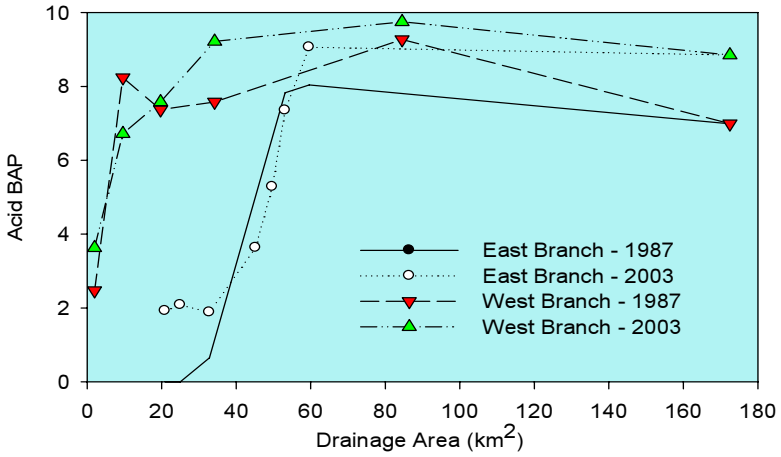

Figure 3 - Acid BAP as a function of drainage area for samples collected in the upper Neversink River basin in the summer of 1987 and the summer of 2003.

- The 1987 Acid BAP values for all sites combined were not statistically different than the 2003 values. This indicates no clear overall change in acid-sensitive macroinvertebrate taxa between the two sampling periods.

- A cluster analysis and an ordination by a multi-dimensional scaling method indicated that the macroinvertebrate communities at four headwater sites in both river branches for 2003 formed a statistically significant separate cluster from that of the 1987 data. This suggests a response in macroinvertebrate community composition and structure that is consistent with a general pattern of decreased stream acidity over the 16-year period.

- Together, the results from these two statistical analyses indicate that despite a lack of significant change in the macroinvertebrate community among all sites sampled in 1987 and 2003, the communities at the four most acidic headwater sites have changed in a manner that is consistent with the observed improvement in stream acid/base chemistry.

- Fish data indicate that slimy sculpin, an acid-intolerant species, have not returned to the headwater sites that show evidence of a slight increase in acid-intolerant macroinvertebrate species.

- Overall, there was little change in brook trout habitat from 1987 to 2003, except adult brook trout were present at the most acidic site (NW-01) in 2003, but not in 1987. This may indicate a slight upstream expansion of brook trout habitat in the West Branch Neversink River that is consistent with the increased macroinvertebrate Acid BAP values found in 2003.

- A diatom acid-tolerance index shows high acid impact at headwater sites, and moderate-to-high acid impact extending downstream throughout the length of the East Branch and in part of the West Branch.

- This multi-organism dataset indicates that despite an increase in precipitation and stream pH of 0.16 units from 1987 through 2003, and some improvement in the acid-intolerant macroinvertebrate community of the headwaters over that period, further increases in stream pH will be necessary before widespread improvement in the macroinvertebrate, fish, and diatom communities become evident. Similar increases in stream pH will depend on future emissions of sulfur and nitrogen oxide air pollutants, as well as local factors such as insect attack, ice storms, climate change, etc.

- Continued increases in stream pH, accompanied by decreases in Al_{IM} concentrations, can be expected to result in favorable changes in Acid BAP values. Changes in the fish community, such as expansion of slimy sculpin into the headwaters and improvement in the diatom acid-tolerance index in middle reaches and in the headwaters, will require a decrease in stream acidity beyond the range predicted for the region by 2050 in a recent modeling study (Chen and Driscoll, 2004).

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