

## Acid Rain Effects on Adirondack Streams— Results from the 2003–05 Western Adirondack Stream Survey (the WASS Project)



High flows such as seen in this Adirondack stream tend to have the most acidic stream water.

Traditionally lakes have been the focus of acid rain assessments in the Adirondack region of New York. However, there is a growing recognition of the importance of streams as environmental indicators. Streams, like lakes, also provide important aquatic habitat, but streams more closely reflect acid rain effects on soils and forests and are more prone to acidification than lakes. Therefore, a large-scale assessment of streams was undertaken in the drainage basins of the Oswegatchie and Black Rivers; an area of 4,585 km<sup>2</sup> in the western Adirondack region where acid rain levels tend to be highest in New York State.

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### 💧 Key Findings 💧

- ✓ Acid rain has acidified soils resulting in toxic aluminum in 66 percent of 565 assessed streams.
- ✓ Diatoms, an environmentally sensitive group of algae, were moderately to severely affected by acid rain in 80 percent of assessed streams.
- ✓ Aquatic insects and related organisms referred to as macroinvertebrates were moderately to severely affected in 52 percent of assessed streams.
- ✓ Recovery from acidification has been minimal in 11 of 12 Adirondack streams sampled previously in the early 1980s.
- ✓ The base-cation surplus, a new acidification index developed for this project, indicated that not more than one-third of measured stream acidity was from natural sources.





## Purpose of the Western Adirondack Stream Survey (WASS)

Acidified surface waters were first discovered in the Adirondack region of New York in the 1970s. Comprehensive monitoring and assessment of Adirondack lakes, ongoing since the early 1980s, has identified this region as one of the most affected by acidic deposition in North America. However, assessments of stream acidification in the Adirondack region have been limited to a large survey in the early 1980s and intermittent data collection on a few streams through the 1980s and 1990s.

Lake chemistry and stream chemistry are generally similar within a region, but lake chemistry can be an unreliable indicator of stream chemistry when assessing the effects of acidic deposition. Streams are more prone to acidification than lakes because they receive a larger fraction of water from shallow soils that are often ineffective at neutralizing acidity. Lakes are also able to buffer the acidity of stored water by in-lake processes.

Stream acidification is most prevalent during periods of high flow. The transient nature of high flow, which can last from a few hours to a few weeks, results in episodic acidification that is difficult to measure. The chemistry during base flow (periods between storms or rapid snowmelt when chemical concentrations tend to be relatively stable) is easier to measure, but underestimates the extent of the problem. For example, in a Catskill Mountain watershed, the total length of acidified streams was found to increase from 16 percent at base flow to 82 percent at high flow (Lawrence, 2002). Harmful effects on aquatic life from episodic acidification can be similar or worse than those from chronic acidification (McComick and Leino, 1999; Passy and others, 2006).

To assess the current chemical and biological conditions of streams in the region of the Adirondacks considered most affected, the Western Adirondack Stream Survey (WASS) was conducted by the U.S. Geological Survey (USGS) in collaboration with the Adirondack Lakes Survey Corporation, the New York State Department of Environmental Conservation, and the University of Texas at Arlington, with funding support from the New York State Energy Research and Development Authority. This project is the first regional assessment of Adirondack streams since the early 1980s and the only assessment conducted in the United States to characterize episodic acidification on a regional level.

## Project Objectives

- Develop an improved method for distinguishing between the chemical effects of acidic deposition and the effects of acidity from natural sources.
- Determine the current extent of effects of acidic deposition on stream chemistry and aquatic life in this region.
- Evaluate the role of soil chemistry as a control of stream chemistry.
- Determine to the extent possible changes in stream chemistry over the past two decades.

## Study Approach

The study was undertaken in the drainage basins of the Oswegatchie and Black Rivers, an area of 4,585 square kilometers (km<sup>2</sup>) in the western part of the Adirondack region of New York. A total of 200 streams representing a population of 565 accessible streams were randomly selected for sampling. The population of streams had minimal upstream influences from lakes and ponds.



Five surveys were conducted during spring snowmelt, summer low flow, and fall high flow to account for variations in chemistry that occurred both episodically and seasonally. All samples for each survey were collected within 3 days (with a few exceptions) during periods when flows were either elevated or remained low. Buck Creek (drainage area 3.1 km<sup>2</sup>), the only stream in the study region monitored year-round for flow and chemistry, was used as an index stream to place results within the context of variations throughout the study (fig. 1).



**Figure 1.** Collection of a water sample from Buck Creek, Inlet, NY, during spring snowmelt. Ongoing monitoring of flow and water chemistry at this site provided valuable data on how variations in flow affected stream chemistry.

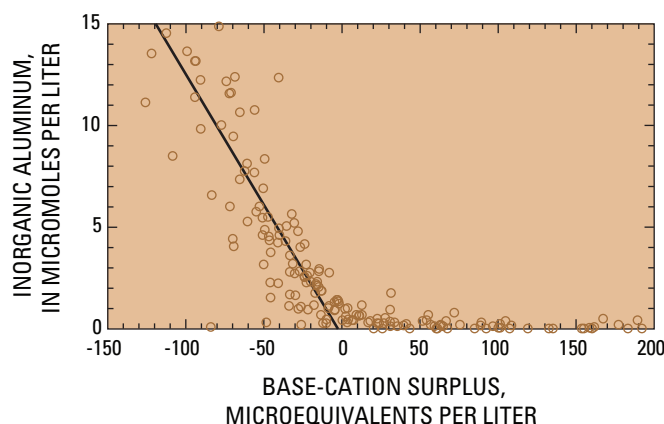
Chemical measurements included pH and acid-neutralizing capacity by Gran titration (ANC<sub>G</sub>), the most commonly used measures of acidification effects. However, pH and ANC<sub>G</sub> do not distinguish between natural organic acidity, which is common in Adirondack waters, and that derived from acidic deposition. Therefore, a new measure, termed the base-cation surplus (BCS), was developed to relate acidic deposition inputs to the buffering threshold of soils below which toxic aluminum is mobilized and enters surface waters. Soil samples also were collected in 11 small watersheds to identify links between soil chemistry and stream chemistry.

Diatoms, a highly diverse group of algae with variable environmental tolerances, and macroinvertebrates (insects and other aquatic life such as worms and crustaceans) were used as biological indicators in this study. Diatom samples were collected in each of the 200 survey streams during the surveys conducted in August 2003, October 2003, March 2004, and August 2004. Macroinvertebrates were collected in 36 streams that represented the range of acidification.

Historical measurements of ANC<sub>G</sub>, pH, and specific conductance were available in the early 1980s for 18 Adirondack streams and lake outlets within the study region. The historical sampling was replicated in this study during 2003–2005 to determine if water chemistry differed between the two periods. Because stream chemistry is strongly influenced by flow, data from the USGS stream gage on the Independence River at Donnattsburg were used to account for flow variations during both sampling periods.

## A New Chemical Index for Measuring Acidification

Assessments of acidic deposition effects and recovery have relied on ANC<sub>G</sub> and pH as the primary chemical indicators. However, both of these measurements can be substantially influenced by naturally produced organic acidity, which is abundant in many Adirondack streams. To better distinguish between acidic deposition and natural organic acidity, a new chemical index, termed the base-cation surplus (BCS), was developed in this project. The BCS is based on the mobilization of inorganic aluminum (the toxic form) within the soil, which does not occur in the absence of acid rain. A BCS value less than 0 microequivalents per liter (μeq/L) in stream water indicates that the soil has become sufficiently acidified by acid rain to enable toxic forms of aluminum to move from the soil into streams (fig. 2). Measurements of the BCS in streams varied seasonally and with changes in flow. Results showed that streams with a BCS value below 25 μeq/L during any of the stream surveys were likely to have negative BCS values at some time over the course of a given year and were therefore defined as prone to acidification.

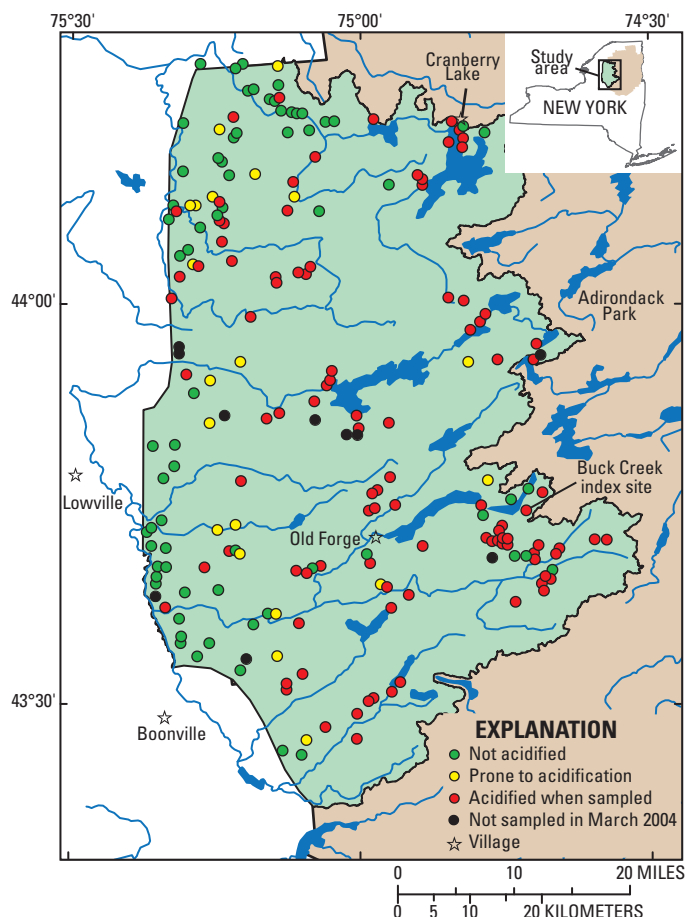


**Figure 2.** Concentrations of inorganic aluminum (the form toxic to aquatic life) plotted against values of the base-cation surplus to illustrate the threshold below which aluminum is mobilized in soils and transported into streams.

## Effects on the Chemistry of Stream and Soils

Results showed that 66 percent of assessed streams were prone to acidification by acid rain (BCS values less than 25 μeq/L). Of these streams, approximately one-half were chronically acidified and one-half were episodically acidified (acidified during high flows). The prevalence of acidified streams increased from west to east across the study region (fig. 3). Results also showed that 718 kilometers (km) of total stream length was prone to acidification within the study region, although more than 3,000 km of streams in the study region were not assessed due to inaccessibility. Natural sources of acidity were found to contribute only 16 to 34 percent of the acidity measured by the BCS.

Neutralization of acidity is dependent on rapid reactions in the soil that buffer the pH of soil water through the release of bases (mostly calcium) adsorbed to particle surfaces (Lawrence,



**Figure 3.** Acidification categories of sites sampled in the March 2004 survey. Sites not acidified had base-cation surplus (BCS) values greater than 25 microequivalents per liter ( $\mu\text{eq/L}$ ); sites prone to acidification had BCS values greater than 0  $\mu\text{eq/L}$  but less than 25  $\mu\text{eq/L}$ ; acidified sites had BCS values less than 0  $\mu\text{eq/L}$ .

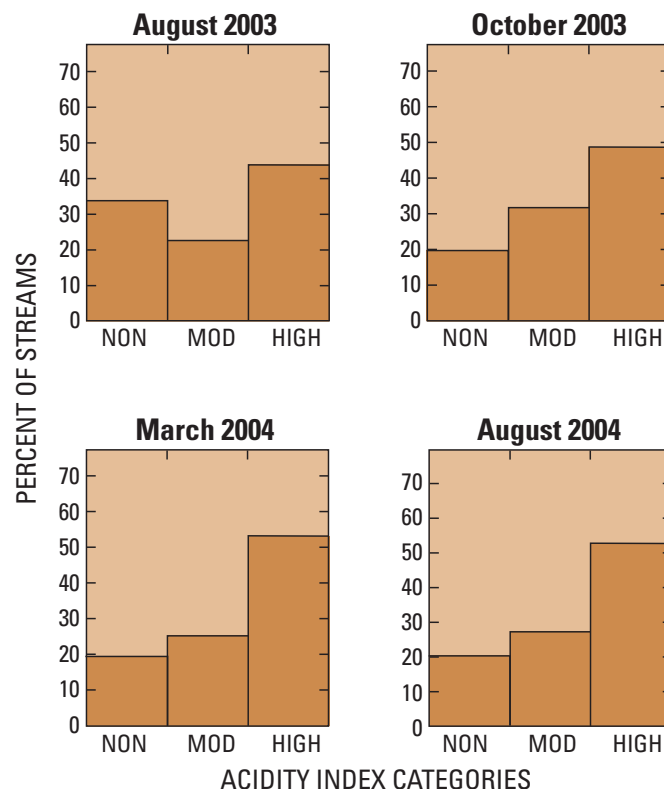


**Figure 4.** A typical upper soil profile in Adirondack soil. The Oa horizon, comprised mostly of humus-like material, lies directly below the litter and decomposing leaves of the forest floor. The upper B horizon, comprised primarily of mineral matter formed from the breakdown of rocks lies directly below the gray, relatively inert E horizon.

2002). If insufficient calcium is available, toxic forms of aluminum are instead released. Soil sampling in selected watersheds showed a close relationship between the availability of bases in the soil, referred to as the base saturation, and the BCS in stream water. Through this relationship, base saturation in the upper B horizon was estimated to be insufficient to prevent aluminum mobilization in 90 percent of the assessed watersheds. The upper B horizon had been generally considered the primary source of calcium for buffering during high flows, but WASS results indicated that the organic soil horizon close to the surface (Oa horizon) plays a greater role than the upper B horizon (fig. 4) in the neutralization of acidity. The neutralizing capacity of the upper B horizon has been lowered by the depletion of calcium from acid rain.

### Effects on Aquatic life

Assessment of diatoms showed that only the most acid-tolerant species were found below a BCS value of 10  $\mu\text{eq/L}$ , which approaches the threshold for mobilization of inorganic aluminum (BCS = 0  $\mu\text{eq/L}$ ). The percentage of streams in which diatom communities were moderately or severely impacted by acidic deposition ranged from 66 to 80 percent (fig. 5). Limited variation was observed in values of the mean diatom acidification index (ACI) among the four surveys despite the considerable variation in flow, season, and water chemistry. Whereas a water sample reflects chemical concentrations at



**Figure 5.** The percent of streams in each of three categories of acid impact, derived from the mean diatom acidification index (ACI) values across the four diatom surveys. ACI represents the proportion of species in a diatom community with preference for acidic conditions. (NON, non-impacted; MOD, moderately impacted; HIGH, highly impacted).



the moment of collection, the presence or absence of a diatom individual reflects environmental conditions, including water chemistry, over the organism's lifespan. The similarity in ACI values for the October 2003 and March 2004 surveys most likely reflects acidification during the several days that the surveys occurred. However, the ACI values for the August 2004 survey, which was similar to the October 2003 and March 2004 surveys, indicates exposure to acidification at some time prior to the survey. The time between the exposure and the survey was too short for recovery of the acid-sensitive diatom species. Therefore, the diatom results reflected variations in stream chemistry over a prior period of up to several weeks, a characteristic that makes diatoms highly valuable in the assessment of stream acidification where water chemistry can vary substantially over a few hours. In the August 2003 survey, 33 of the 162 sample streams were dry due to extremely dry conditions.

Macroinvertebrate sampling of 36 streams (fig. 6) with varying chemistry was used to characterize the range of acidification impacts on macroinvertebrate communities and to define categories of biological impact based on the relationships among BCS, aluminum, and a new Acid Biological Assessment Profile (acidBAP) index that relates the macroinvertebrate community to water chemistry. Using the March 2005 survey results as the median chemical condition, 52 percent of the streams had macroinvertebrate communities that were moderately to severely affected by acid rain.

## Changes in Stream Chemistry Since the Early 1980s

A comparison with historical stream chemistry data showed statistically higher pH values in 2003–2005 than in the early 1980s in 8 of the 12 streams and 4 of the 6 lake outlets, but less than one-half of these streams and outlets had a higher

ANC<sub>G</sub> in 2003–2005 than in the early 1980s. The amount of change was relatively small, and nearly all the streams and outlets exhibited episodic acidification during periods of high streamflow in 2003–2005.

The results indicated that recovery from acidification in these Adirondack streams and outlets has been minimal, with the exception of Bald Mountain Brook and Fly Pond Outlet. However, even in these waters, BCS values during the most acidic sampling conditions in 2003–2005 approached 0 µeq/L; the threshold for mobilization of toxic aluminum. The overall increase in ANC<sub>G</sub> for the 12 streams was 13 µeq/L over 23 years. The degree of chemical recovery observed in this historical comparison probably resulted in little or no biological recovery in most of the streams and outlets.

## Conclusions

The WASS, the largest stream survey conducted in the United States to characterize episodic acidification, has substantially expanded our knowledge of the current conditions of Adirondack surface waters. Current efforts to model changes in soil and water chemistry in response to changes in atmospheric deposition will benefit from the data collected in this study, but additional data will be needed to document the effects of environmental changes. Future trends in atmospheric deposition are uncertain, and upward trends in temperature and precipitation in the study region (Dello, 2007) are expected to continue (Hayhoe and others, 2007). WASS results will be valuable in this regard because the study can be repeated to evaluate future changes in stream chemistry and biota under both base flow and episodic conditions.

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**Figure 6.** Collection of macroinvertebrates in an Adirondack stream by a scientist in the Stream Biomonitoring Unit of the New York State Department of Conservation.

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### **Additional information on the Western Adirondack Stream Survey can be found in the following publications:**

- Baldigo, B.P., Lawrence, G.B., Bode, R.W., Simonin, H.A., Roy, K.M., and Smith, A.J., 2009, Impacts of acidification on macroinvertebrate communities in streams of the western Adirondack Mountains, New York, USA: *Ecological Indicators*, v. 9, p. 226–239.
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By Gregory B. Lawrence<sup>1</sup>, Karen M. Roy<sup>2</sup>, Barry P. Baldigo<sup>1</sup>, Howard A. Simonin<sup>3</sup>, Sophia I. Passy<sup>4</sup>, Robert W. Bode<sup>3</sup>, and Susan B. Capone<sup>5</sup>

<sup>1</sup> U.S. Geological Survey.

<sup>2</sup> New York State Department of Environmental Conservation.

<sup>3</sup> Retired, formerly New York State Department of Environmental Conservation.

<sup>4</sup> The University of Texas at Arlington.

<sup>5</sup> Adirondack Lakes Survey Corporation.



For additional information write to:  
New York Water Science Center  
U.S. Geological Survey  
425 Jordan Road  
Troy, NY 12180

Information requests:  
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