Results from the 2003-2005 Western Adirondack Stream Survey

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List of Acronyms

ACI: acidity index
acidBAP: Acid Biological Assessment Profile index
ALTM: Adirondack Long-Term Monitoring Program
ATI: Acid Tolerant Index
ANOVA: analysis of variance
BCS: base cation surplus
ANC: acid-neutralizing capacity
ANC_G: acid-neutralizing capacity by Gran titration
DEC: Department of Environmental Conservation
DOC: dissolved organic carbon
ERP: Episodic Response Program
PMR: percent mayfly richness
RDA: redundancy analysis
USGS: U.S. Geological Survey
USEPA: U.S. Environmental Protection Agency
WASS: Western Adirondack Stream Survey

EXECUTIVE SUMMARY

Purpose of the Western Adirondack Stream Survey (WASS)

Assessment of stream acidification in the Adirondack region has been limited to a stream survey in the early 1980s and intermittent data collection on selected streams to support toxicity studies of stream biota. In contrast, comprehensive monitoring and assessment of Adirondack lakes has been ongoing since the early 1980s. In the absence of sufficient stream data for either regional assessments or trends analysis, lake data have served to represent Adirondack surface waters for over two decades.

Lake chemistry and stream chemistry are generally similar within a region, but lake chemistry can be an unreliable indicator of stream chemistry when assessing effects of acidic deposition. Streams are more prone to acidification than lakes because they receive a larger fraction of water from shallow flow paths that are often ineffective at neutralizing acidity. Furthermore, streams are not able to attenuate acidic inputs during high flows with stored water that can be neutralized by in-lake processes. Therefore, the decreasing acidity observed in lakes over the past two decades (Driscoll et al. 2007) may or may not be occurring in streams, and evidence of decreased base saturation of soils (Sullivan et al. 2006) suggests that streams have become more susceptible to episodic acidification (Lawrence 2002).

There is insufficient information to assess the current status of Adirondack streams with regard to acidification, and without this information neither past nor future changes in stream chemistry can be assessed. Therefore, the Western Adirondack Stream Survey (WASS) was conducted to assess the current chemical and biological conditions of streams in the region of the Adirondacks considered most impacted.

Because regional stream assessments that included episodic acidification had not been previously conducted, this project was implemented as a pilot study to evaluate methods for possible use in other regional stream assessments. The WASS was designed with the following objectives:

(1) Develop an improved method for distinguishing between the chemical effects of acidic deposition and those of naturally-derived acidity.

(2) Determine the current extent of acidic deposition effects on stream chemistry and biota in this region.

(3) Evaluate the role of soil chemistry as a control of stream chemistry;.

(4) Determine, to the extent possible, changes in stream chemistry over the past two decades.

Scientific Approach

The study region was defined as the Black River and Oswegatchie River drainages that lie within the Adirondack Ecological sub region (McNab and Avers 1994), which is approximated by the boundaries of the Adirondack Park. All streams within the 4,585 km^2 study region that fit the following criteria were identified for possible sampling: 1) the stream was mapped on a U.S. Geological Survey (USGS) 1:24,000 quadrangle map as a solid blue line, 2) the stream was accessible by hiking to and from the sampling location within 1 hour, and 3) the stream did not contain upstream lakes or ponds that drained more than 25 % of the total drainage area defined by the sampling point. From the 565 streams that fit these criteria, 200 were randomly selected for sampling. The total drainage area of the 200 selected streams was 284 km^2; the total

drainage area of streams in the potential sampling population was 825 km^2. Stream order of the sampled streams ranged from one to three, but most were first order.

The stream water sampling was designed to account for variations in chemistry that occurred both episodically and seasonally. The goal was to collect all samples within three days during periods when flows were expected to be either elevated or remain low. Buck Creek (drainage area 3.1 km^2), the only stream in the study region monitored for year-round flow and chemistry, was used as an index stream to place results within the context of variations throughout the year. To address seasonal variation, sampling surveys were conducted twice during spring snowmelt (March 29-31, 2004 and March 29-31, 2005), twice during summer base flows (August 25-28, 2003 and August 16-18, 2004), and once during fall storms (October 27-29, 2003). Samples for all surveys were collected within three consecutive days, with a few exceptions.

The full suite of chemical measurements typically used to assess acidification was used for all stream samples. This included acid-neutralizing capacity by Gran titration (ANC_G), the most commonly used measure of acidification effects. However, ANC_G does not distinguish between natural organic acidity and that derived from acidic deposition. This is a particular problem for Adirondack surface waters because high concentrations of dissolved organic carbon (DOC) are common and have been changing in some Adirondack lakes (Driscoll et al. 2007). Therefore, for the purpose of this assessment, a new approach was developed to better discriminate between acidic deposition effects and natural acidity derived from natural ecosystem processes.

Headwater streams have generally been observed to become more acidic in the upstream direction (Palmer et al. 2005). To confirm this tendency within the study

region, longitudinal sampling was done along the reaches of 10 streams. In six of these streams, all upstream sampling sites were similarly acidic or more acidic than the lowest site. In the remaining four streams, some sites were less acidic than the lowest site, but none showed any trends over the stream reaches. Based on these results, the length of acidified stream reaches was estimated from a single sampling point on each stream.

In the summer of 2004, soil samples also were collected in 10 first-order watersheds to identify links between soil chemistry and stream chemistry. Samples were removed from the Oe, Oa, and upper 10 cm of the B horizon at three locations within each of five plots chosen to represent landscape variability within the watershed (15 total sampling locations per watershed). Previously collected soil data from the north and south tributary watersheds of the Buck Creek watershed also were used in this analysis.

Diatoms and macroinvertebrates were used as biological indicators in this study. In each of the 200 survey streams, diatoms were collected from rock surfaces, moss beds, and fine-grained sediment surfaces in four of the five surveys (March 2005 was omitted). Macroinvertebrates also were collected in 36 of the 200 survey streams that represented the full range of acidification, between August 11 and September 1, 2004. The standardized traveling kick method was used to collect macroinvertebrate samples (Bode et al. 2002).

Historical measurements of ANC_G, pH, and specific conductance were available over several years in the early 1980s for 18 Adirondack streams and lake outlets within the study region. The historical sampling was replicated in this study during 2003-2004 to determine if there were differences in water chemistry between the two periods. These streams were located in the southern part of the Black River drainage, with the exception of a single site that was located in the Oswegatchie River drainage. Because stream

water chemistry is strongly influenced by flow, variations in flow were accounted for with flow data from the U.S. Geological Survey (USGS) stream gage on the Independence River at Donnattsburg, which were available for both sampling periods.

This project was the first regional assessment of Adirondack streams since the early 1980s and the only assessment conducted in the U.S. to characterize episodic acidification on a regional level. All water samples were analyzed for the full suite of major ions needed to assess the effects of acidic deposition. The study also included the development of a new chemical index, termed the base cation surplus (Lawrence et al. 2007), which was compared with the widely used ANC_G. This study, which included only about 20 % of the Adirondack region, also served as a pilot project to demonstrate the effectiveness of this new approach for regional stream assessment.

Findings

A New Index for Assessing Chemical Effects of Acidic deposition. Assessments of acidic deposition effects and recovery have relied on acid-neutralizing capacity by Gran titration (ANC_G) as the primary chemical indicator for over two decades (Driscoll and Newton 1985, Stoddard et al. 2003). However, measurements of ANC_G can be substantially influenced by naturally produced organic acidity associated with dissolved organic carbon (DOC), which is abundant in many Adirondack streams. Furthermore, in the past 10-15 years, concentrations of DOC have increased in Adirondack Lakes (Stoddard et al. 2003), while sulfur deposition has been decreasing (Driscoll et al. 2003). To better distinguish between acidic deposition and natural organic acidity, chemical relations involving inorganic Al mobilization were investigated. Results showed that

when inorganic Al concentrations were plotted against the quantity referred to as ANC (the sum of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} minus the sum of SO_4^{2-}, NO_3^{-}, and Cl^{-}), a distinct threshold for Al mobilization became apparent. This value of ANC, at which this threshold occurred, varied with the concentration of DOC. However, if the concentration of strongly acidic organic anions was included as a negative component of ANC, the threshold occurred at an ANC value of approximately 0, which is the value expected from theoretical charge balance constraints. This adjusted ANC, termed the base-cation surplus (BCS), proved to be more effective as a chemical indicator of human-induced acidification than pH, ANC_G, or ANC in waters with substantial concentrations of DOC.

The Extent of Stream Acidification. The streams sampled in this study showed considerable variability in BCS values that were linked to season and flow. In the March 2004 survey, the most acidic of the five surveys, 124 of 188 streams (66%) had BCS values less than 25 $\mu eq\ L^{-1}$. This criterion was used to classify streams as prone to acidification, defined as likely to have had BCS values less than 0 during the study period. Values of BCS below 0 indicate that toxic inorganic Al has moved from the soil into streams. In the August 2003 survey, when conditions were least acidic, 25 of 129 streams (19%) had values less than 25 $\mu eq\ L^{-1}$. Stream chemistry during the August 2004 and March 2005 surveys was intermediate with respect to the March 2004 and August 2003 surveys. The % of acidified streams during the October 2003 survey was similar to the March 2004 survey (63%), although flows were considerably higher than in the March 2004 survey.

To compare the role of acidic deposition effects to natural sources of acidity in the mobilization of inorganic Al, the total concentration of strongly acidic anions resulting from acidic deposition (SO_4^{2-} plus NO_3^-) and natural organic matter (strong organic anions) were expressed as a percentage of the total concentration of strongly acidic anions. The percentage attributable to acidic deposition ranged from 62 to 80 for the five surveys. The percentage attributable to natural sources of acidity ranged from 16 to 34 and was positively related to concentrations of DOC. Although the number of streams in the October 2003 survey with a BCS value less than 0 μeq L^{-1} was similar to that of the March 2004 survey, the contribution of natural acidity was 13% greater in the fall than during spring snowmelt. These results indicate that acidic deposition is the major factor in mobilizing the toxic form of Al in these streams throughout the year, and that natural sources of acidity contributed a maximum of 34% of the total strong acidity in stream water during periods of elevated DOC such as fall rain storms.

To evaluate the relative extent of chronic and episodic acidification, results of the March 2004 survey were chosen to represent high-flow, or episodic conditions, and the results of the August 2004 survey were chosen to represent base flow, or non-episodic conditions. Of the 189 streams in this comparison, 67 (35%) were chronically acidified, 57 (30%) were episodically acidified, and 65 streams (34 %) were not acidified. Episodic decreases in BCS values tended to be highest in streams with the highest BCS values at base flow. The mean BCS value in episodically acidified streams in March 2004 was 104 μeq L^{-1} less than in August 2004. The mean BCS value in non-acidic streams in March 2004 was 209 μeq L^{-1} less than in August 2004.

Results of the March 2004 survey (Figure A) showed a distinct spatial pattern

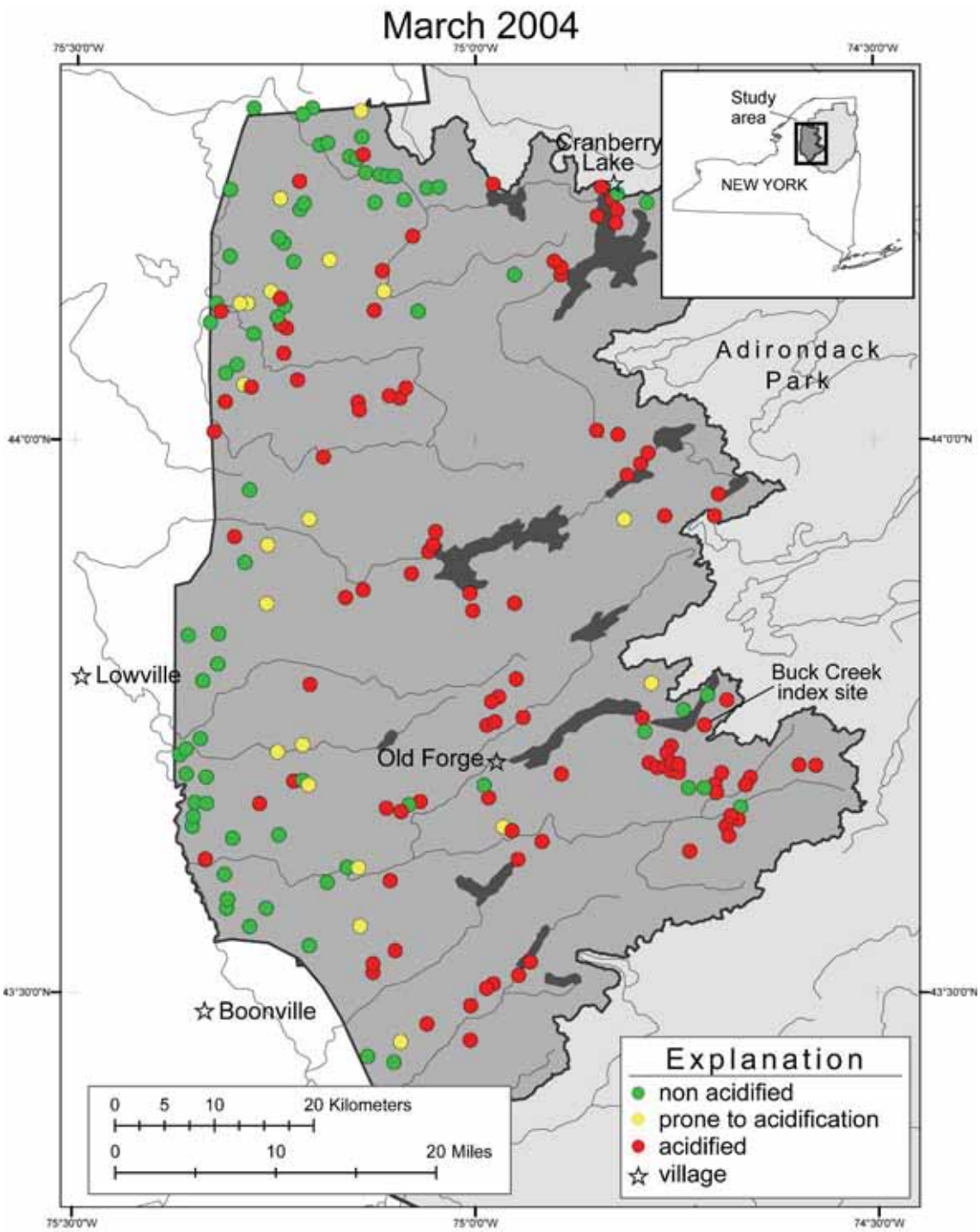


Figure A. Acidification categories of sites sampled in the March 2004 survey. Non acidified sites had base cation surplus (BCS) values > 25 μeq L^{-1}; sites prone to acidification had BCS values > 0 μeq L^{-1}but < 25 μeq L^{-1}; acidified sites had BCS values < 0 μeq L^{-1}.

when stream locations were related to BCS values. Most of the streams not at risk of episodic acidification (BCS > 25 μeq L^{-1}) were located near the western edge of the study region where deep deposits of lacustrine sand and gravel underlie the soil (Roy et al. 1997). The March 2004 survey also showed that 718 km of stream reaches were found to be prone to acidification within the study region—58% of the total stream length assessed. A remaining 3,085 km (72% of the total stream length) within the study region could not be assessed because of inaccessibility. It is uncertain if the percentage of inaccessible streams prone to acidification was similar to that of the accessible streams, but we have no evidence to suggest that this percentage would be different than that of the accessible streams.

Assessment of Soil Acidification. Through relations established between stream chemistry and soil chemistry, base saturation values were estimated to be less than 20% in the upper B horizon of 90% of the WASS watersheds. Base saturation values below 20% indicate that this horizon buffers the acidity of soil water (H^+) primarily through the release of Al, whereas in less acidified soils, buffering is accomplished through release of calcium and other base cations (Reuss 1983). Furthermore, the acidification of the B horizon has likely increased exchangeable Al concentrations in the Oa horizon, which is currently providing more buffering of stream water during high flow than the B horizon (Figure B). Movement of Al into the Oa horizon will continue without reductions in acidic deposition. If base saturation of the B horizon is to increase, acidic deposition will need to be reduced to levels at which Ca^{2+} leaching rates become less than the rate at which Ca^{2+} is released from mineral weathering. Because estimates of weathering rates

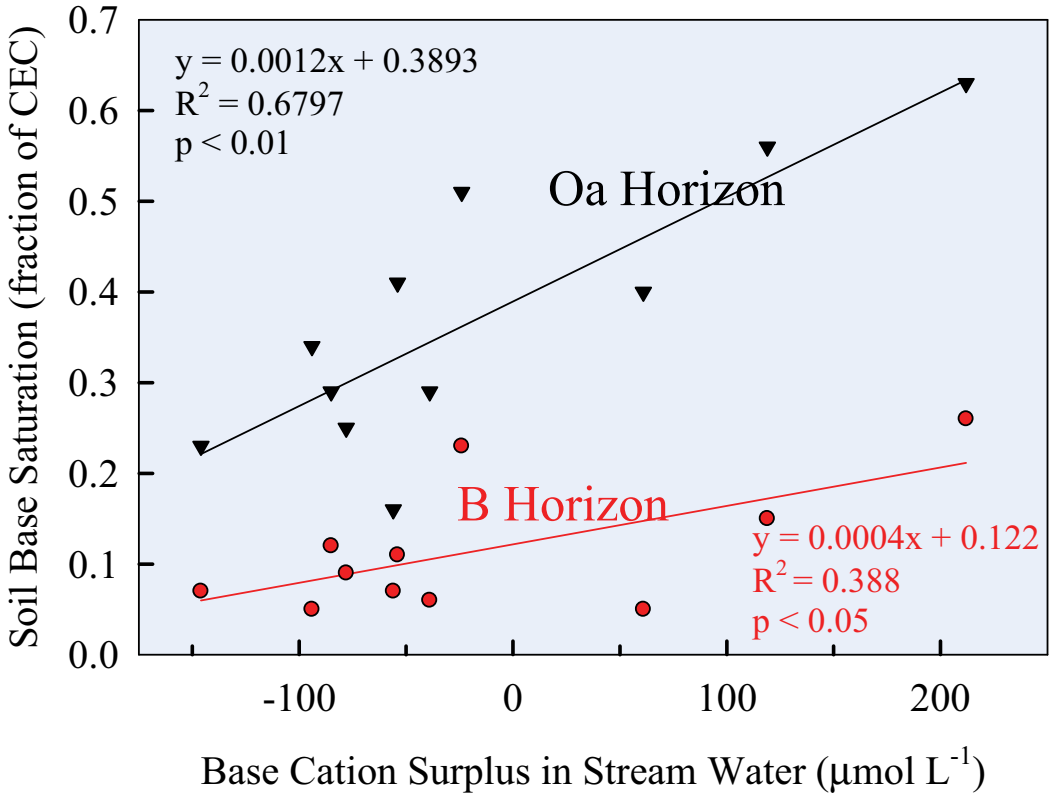


Figure B. Mean soil base saturation of the upper 10 cm of the B horizon in 11 watersheds as a function of base cation surplus values in stream water during the March 2004 survey. The best-fit line for each soil horizon is shown in the same color as the data points for the respective horizon.

have a high degree of uncertainty, the recovery potential of the B horizon in these watersheds is unknown. In addition to impeding recovery of the B horizon, continued inputs of acidic deposition may reduce the effectiveness of the Oa horizon in neutralizing soil water and minimizing the mobilization of inorganic Al. Modeling efforts to predict recovery trajectories for Adirondack surface waters need to incorporate the role of the Oa horizon into models of soil and surface water recovery that are being applied to this region.

Effects of Acidification on Diatoms. Only the most acid-tolerant diatom species were found below a BCS value of 10 μeq L^{-1}, which approaches the geochemical threshold for mobilization of inorganic Al (BCS = 0 μeq L^{-1}). Categories of impact from acidification were defined from regression tree analysis that identified groupings based on the known acid tolerances of diatom species. The percentage of streams in which diatom communities were moderately to severely affected by acidic deposition ranged from 66% to 80% in the four surveys (Figure C). These values are somewhat higher than the percentage of streams estimated to be prone to acidification on the basis of inorganic Al mobilization (a BCS value < 25 μmol L^{-1}) and indicate that diatoms exhibit a high degree of sensitivity to stream acidification.

Limited variation was observed in values of the mean diatom acidification index (ACI) among the four surveys, which reflected the temporal integration provided by the diatoms. Whereas a water sample reflects chemical concentrations at an instantaneous moment in time, the presence or absence of a diatom individual reflects environmental conditions, including water chemistry, over the organism's lifespan. For this reason, the ACI values for the October 2003, March 2004, and August 2004 were almost identical, despite the considerable variation in flow, season, and water chemistry among these surveys. This characteristic makes diatoms highly valuable in the assessment of stream acidification, where water chemistry can vary substantially over a few hours.

Effects of Acidification on Macroinvertebrates. Macroinvertebrate sampling of 36 streams with varying chemistry was used to characterize: (a) the range of acidification impacts on macroinvertebrate communities in the region, (b) the relations between acidification and

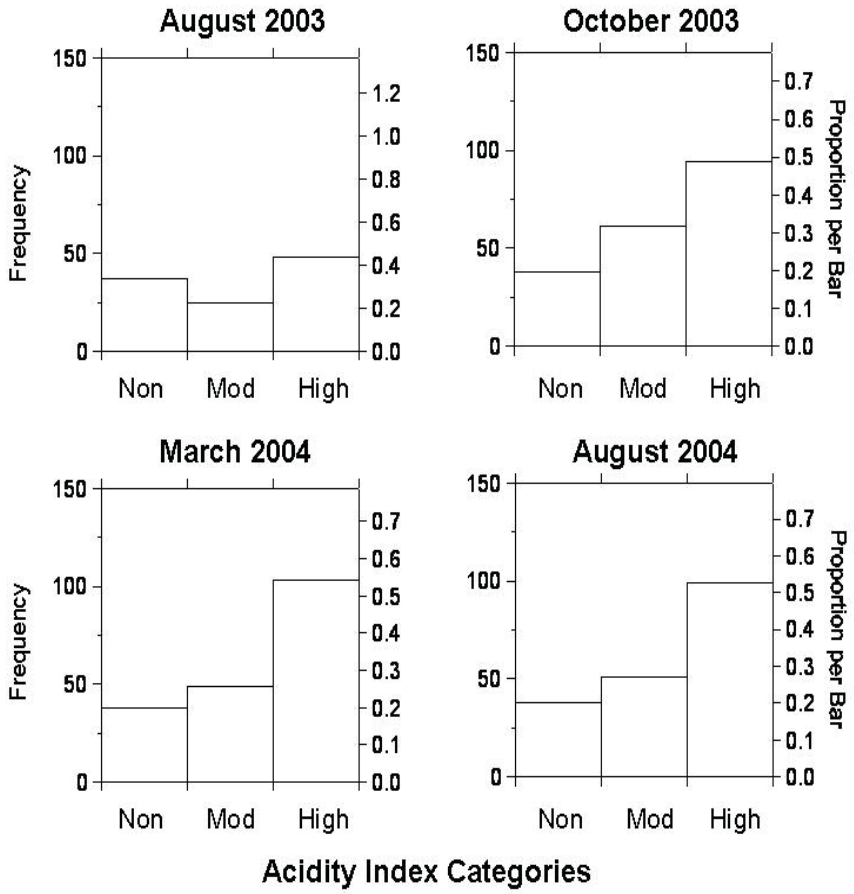


Figure C. The number of streams in each of three categories of acid impact, derived from Acidity Index (ACI) values across the four diatom surveys. ACI represents the proportion of species in a diatom community with preference for acidic conditions. Non = non-impacted (ACI < 0.40), Mod = moderately impacted (0.40 ≤ ACI < 0.85), High = severely impacted sites (ACI ≥ 0.85). In the August 2003 survey, 33 of the 162 sample streams were dry due to extremely dry conditions.

species assemblages, and (c) biologically relevant impact categories based on the relations among BCS, inorganic Al, and a new index that relates the macroinvertebrate community to water chemistry, referred to as the acidBAP. The acidBAP is based on taxa found to be abundant in acidic streams of the Adirondack and Catskill Mountains and uncommon in 20 non-acidic reference streams from across New York State. AcidBAP scores indicated that macroinvertebrates were slightly to severely impacted by

acidification in 34 of the 36 sampled streams. Although these 36 sites were not selected randomly, the macroinvertebrate impact categories could be estimated with the BCS values available for the 200 sample streams, which were representative of the 565 streams in the potential sampling population. Using the March 2005 survey results as the median chemical condition, 52% of the streams in the potential sample population were moderately to severely impacted. Additional results and discussion of results from the macroinvertebrate sampling are presented in Baldigo et al. (2009).

Changes in Stream Chemistry Since the Early 1980s. Comparison with historical data showed statistically higher pH values in 2003-2005 than in the early 1980s in most of the 12 streams and six lake outlets assessed, but less than half of these streams and outlets had a higher ANC_G in 2003-2005 than in the early 1980s. The results were similar for both the streams and the outlets. The amount of change was relatively small, and nearly all of the streams and outlets exhibited episodic acidification during periods of high stream flow in 2003-2005.

These results indicate 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 reached -28 $\mu mol\ L^{-1}$, which is well below the threshold for mobilization of toxic inorganic Al. The overall increase in ANC_G for the 12 streams was 13 $\mu eq\ L^{-1}$ over 23 years. In Bradley Brook, ANC_G increased 14 $\mu eq\ L^{-1}$ over 23 years, but this stream was found to be fishless in 1999 (Simonin et al. 2005).

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.

Major Findings

1. The base cation surplus (BCS) provides an effective measure for assessing acidic deposition effects by relating base cation availability to mobilization of inorganic Al without the complications of pH buffering by organic acids.

2. Of the 565 streams assessed, 66% (718 km of stream reaches) were identified as prone to acidification—likely to be acidified to levels harmful to biota.

3. Of the 66% of streams found to be prone to acidification, approximately half were likely to be episodically acidified, and half were likely to be chronically acidified.

4. The estimated base saturation of the B horizon for the WASS watersheds was less than 20% for 90% of the watersheds, which is a likely result of base depletion by acidic deposition that has rendered this horizon ineffective at buffering inputs of acidity.

5. The percentage of streams determined to be moderately to severely impacted by acidic deposition on the basis of the diatom data ranged from 66% to 80% over four surveys.

6. Macroinvertebrate communities were moderately to severely impacted in 52% of assessed streams.

7. Recovery from acidification in the Adirondack streams and outlets sampled in the early 1980s has been minimal, with the exception of Bald Mountain Brook and Fly Pond Outlet. The overall increase in ANC_G *for the 12 streams was 13* $\mu eq\ L^{-1}$ *over 23 years.*

8. The approach of seasonal sampling surveys conducted within three-day periods throughout the study region was successful for capturing the episodic and seasonal variability of stream chemistry. When indexed to a site with both episodic and long-term monitoring data, this approach was an effective method for the regional assessment of episodic acidification.

1 INTRODUCTION

1.1 Assessments of Adirondack Surface Waters

In a 1980 study of the non-target effects of black fly insecticides on Adirondack stream biota, biologists with the New York State Department of Environmental Conservation (DEC) observed that certain fishless streams were very acidic (Colquhoun et al. 1983). Similar results were found in western Adirondack lakes (Pfeiffer and Festa 1980). The realization that acidic deposition could be causing changes in stream chemistry and losses of fish populations led to additional research. This work included a survey of approximately 200 streams in the early 1980s in which acid-neutralizing capacity (ANC_G, determined by Gran titration) and pH were measured (Colquhoun et al. 1981, Colquhoun et al. 1982, Colquhoun et al. 1984). Concentrations of Ca and total Al also were measured in a subset of these streams. Assessments of stream acidification in the Adirondack region since that time have been limited largely to intermittent data collection on selected streams to support toxicity studies of stream biota (Simpson et al. 1985, Johnson et al. 1987, Simonin et al. 1993, Wigington et al. 1996, Baldigo et al. 2007) and one study that evaluated changes in pH and ANC_G measurements from 1991 to 2001 in three Adirondack streams (Lawrence et al. 2004).

Most of these studies were conducted in the Oswegatchie-Black River drainages because this region of the Adirondack Park was found to have the highest number of acidified streams. The early stream assessments also found that acidification was most prevalent during high flows. Nevertheless, most of the data were collected during base flow conditions—periods between storms or rapid snowmelt when stream flow and chemical concentrations tend to be relatively stable. The transient nature of high flows,

which can last from a few hours to a few weeks, results in episodic acidification that is difficult to characterize both temporally and regionally. Base flow chemistry underestimates the extent of the problem, however, as was shown in a river in the Catskill region of New York, where the linear extent of acidified stream reaches was found to increase from 16% at base flow to 82% at high flow (Lawrence 2002).

The most thorough characterization of episodic stream chemistry in the Adirondack region was conducted through the U.S. Environmental Protection Agency (USEPA) Episodic Response Program (ERP), in which four streams were monitored from 1988 to 1990 (Wigington et al. 1996). Acid episodes involved decreases in ANC_G of up to 200 μeq L^{-1}, decreases in pH of up to one unit, and increases in concentrations of inorganic monomeric Al (Al_i) of up to 15 μmol L^{-1} (Wigington et al. 1996). Results also showed that acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and Al_i concentrations exceeded 3.7 μmol L^{-1}, despite the relatively short duration of episodes (Baker et al. 1996). Largely on the basis of this study, the USEPA concluded that reversal of effects from episodic acidification could be used as a key ecological endpoint for an acid deposition standard that would provide protection for the environment (Baker and Christensen 1991).

Lake chemistry has been much more thoroughly assessed over the past three decades than stream chemistry in the Adirondack region. Chemical analysis of 1,469 lakes was carried out by the Adirondack Lakes Survey Corporation in 1984-1987 (Driscoll et al. 1990), and 43 randomly selected lakes were assessed through the USEPA Time Program in the early 1990s (Stoddard et al. 2003). Ongoing monitoring of water

chemistry also began in 17 lakes in 1982 and in an additional 35 lakes in 1992 (Driscoll et al. 2003). Lake chemistry and stream chemistry are generally similar within a region, but lake chemistry can be an unreliable indicator of stream chemistry when assessing effects of acidic deposition. Streams are more prone to acidification than lakes, particularly during high flows, because they receive a larger fraction of water from shallow flow paths that are often ineffective at neutralizing acidity. Furthermore, streams, unlike lakes, are not able to attenuate acidic inputs during high flows with previously stored water that can be neutralized by in-lake processes. Stream water also reflects the influences of vegetation and soil processes more directly than lake water, which tends to be altered by within-lake processes as water is stored.

1.2 Natural Acidity

Vegetation and soil processes can play an important role in the acid-base status of terrestrial and aquatic ecosystems. Decomposition of plant-derived organic matter within the soil leads to the production of dissolved organic carbon (DOC) and associated organic acidity. This natural source of acidity often complicates assessment of acidic deposition effects on stream chemistry. Limited data are available on DOC concentrations in Adirondack streams, but in Adirondack lakes, DOC concentrations have been shown to vary by a factor greater than 10 (Munson and Gherini 1993). Measurements of pH, ANC_G, and Al can be substantially influenced by DOC. Application of a triprotic model of organic acidity showed that an increase in DOC concentration of 183 μmol L^{-1} could decrease ANC_G by 10 μeq L^{-1} in Adirondack lakes (Driscoll et al. 1994). Organic acidity also was estimated to decrease pH in Adirondack lakes by up to 1.5 units in the ANC_G

range of 0-50 μeq L^{-1} (Munson and Gherini 1993). The influence of organic acidity further complicates assessments of recovery from acidification because concentrations of DOC have increased over the past 10-15 years in Adirondack surface waters, as well as in other regions in the eastern United States (Stoddard et al. 2003), at the same time that S deposition has been decreasing (Driscoll et al. 2003).

1.3 Measures of Acidification

1.3.1 Acid-Neutralizing Capacity

Despite the well-known effects of natural organic acids on ANC_G, this measurement has served as the primary chemical indicator in the United States for assessing past effects of acidic deposition, as well as the recovery expected from decreasing atmospheric deposition (Bulger et al. 2000, Stoddard et al. 2003). European assessments generally use a different approach, in which acidification of surface waters is evaluated by the calculated sum of base cation concentrations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) minus the sum of inorganic strong-acid anion concentrations (SO_4^{2-}, NO_3^{-}, Cl^{-}), which has also been termed ANC (Wright et al. 2005), or calculated ANC (Cosby et al. 2001). The sum of base-cation concentrations reflects the ability of a watershed to neutralize acid inputs through the release of base cations, and the sum of inorganic strong-acid anions largely reflects the input of acidic deposition. The difference in these two quantities provides a relative measure of acidic deposition effects, whereas ANC_G reflects the acid neutralizing capacity of the complete chemical system, including weak acids associated with DOC and inorganic Al (Munson and Gherini 1993).

1.3.2 pH and Aluminum

The measurements most commonly used to determine risk of biological effects from acidic deposition are pH and Al concentrations because they can be directly toxic to biota, whereas ANC_G and ANC do not relate directly to the health of biota. Although most species of plants and animals are sensitive to certain ranges of pH, naturally acidic environments with indigenous species can be diverse and functional (Dangles et al. 2004) and are common in areas affected by acidic deposition, including the Adirondack region. For example, the organic horizons of soils in the Adirondack region typically have pH values (determined by H_2O extraction) less than 3.7 (Sullivan et al. 2006), which is well below the pH of acidic deposition for this region (Lawrence et al. 2004). These types of soils can also acidify surface waters, which makes it difficult to use pH to distinguish the effects of acidic deposition from natural conditions (Lawrence et al. 1995a).

The concentration of Al is a more straightforward indicator than pH, if the Al speciation is known, because only inorganic forms of monomeric Al are generally considered to be toxic (Gensemer and Playle 1999). Acidic deposition can mobilize inorganically-complexed Al in the soil, which can then be hydrologically transported into surface waters. In aquatic ecosystems, inorganic Al has been shown to be toxic to organisms at all levels of the food chain, from phytoplankton (Gensemer and Playle 1999) to top predators such as lake trout (*Salvelinus namaycush*) (Gunn and Noakes 1987). Organically-complexed Al is also mobilized in the soil by organic acids as part of the natural process of podzolization, but it has been shown to have little or no toxic effects in aquatic environments (Gensemer and Playle 1999).

1.4 Project Objectives

There are 9,342 km of streams large enough for sport fishing in the Adirondack region (Pfeiffer, 1979), and there are considerably more small streams that provide habitat for juvenile fish and numerous other forms of aquatic biota. However, insufficient data are available to assess the current acidification status of Adirondack streams. Only limited data have been published on episodic stream chemistry in the Adirondacks since the ERP study (Lawrence 2002, Baldigo et al. 2007), and there has not yet been an assessment to determine the number of Adirondack streams in which episodic acidification occurs. Furthermore, a decrease in acidity has been observed in the monitoring records of Adirondack lakes over the past two decades (Driscoll et al. 2003), but evidence of decreased base saturation of soils also has been documented for this period (Sullivan et al. 2006). Decreasing acidity of lakes suggests that the acidity of streams may also have decreased, but decreased base saturation of soils suggests that streams have become more susceptible to episodic acidification.

To address these information needs we implemented the Western Adirondack Stream Survey (WASS) with the objectives of (1) developing an improved method for distinguishing between chemical effects of acidic deposition and naturally-derived acidity; (2) determining the current extent of acidic deposition effects on streams in this region; (3) investigating the role of soil chemistry as a control of stream chemistry; and (4) determining, to the extent possible, changes in stream chemistry over the past two decades. Through this work, the baseline information needed to monitor the regional response to future changes in acidic deposition was collected. This is the first survey of

Adirondack streams since the early 1980s and the only survey to include the full suite of measurements used to assess acidic deposition effects.

2 METHODS

2.1 Study Region

The stream survey was conducted in the parts of the Black and Oswegatchie River basins that lie within the boundary of the Adirondack Ecological Subregion (McNab and Avers 1994), which roughly corresponds to the boundary of the Adirondack Park of New York State (Figure 2-1). The study region was located in the western portion of the Adirondack region, which is an upland area of 4,585 km^2 that is almost entirely forested with northern hardwood and coniferous tree species (Roy et al. 1997). The study region is characterized by rugged, irregular terrain formed by repeated glaciations that last receded approximately 10,000 years ago. As a result, ridge tops generally are scoured bedrock. Surficial deposits on hillsides are relatively thin, and drift on valley floors can be up to several hundreds of meters thick (Murdoch 1982). Surface elevations of the study region average 504 m and range from 197 to 1159 m. Bedrock geology is a complex mixture of granitic and gneissic rocks with a variety of less common metasedimentary formations scattered throughout the region (Roy et al. 1997). Surficial deposits reflect this complexity and include highly-weatherable calcareous minerals in some areas (Roy et al. 1997).

Mean annual precipitation ranges from approximately 800 to over 1600 mm across the region (Ito et al. 2002). Extended periods of below-freezing winter temperatures usually result in an accumulation of snow by the onset of spring, which melts over a few weeks and causes the highest sustained stream flows of the year

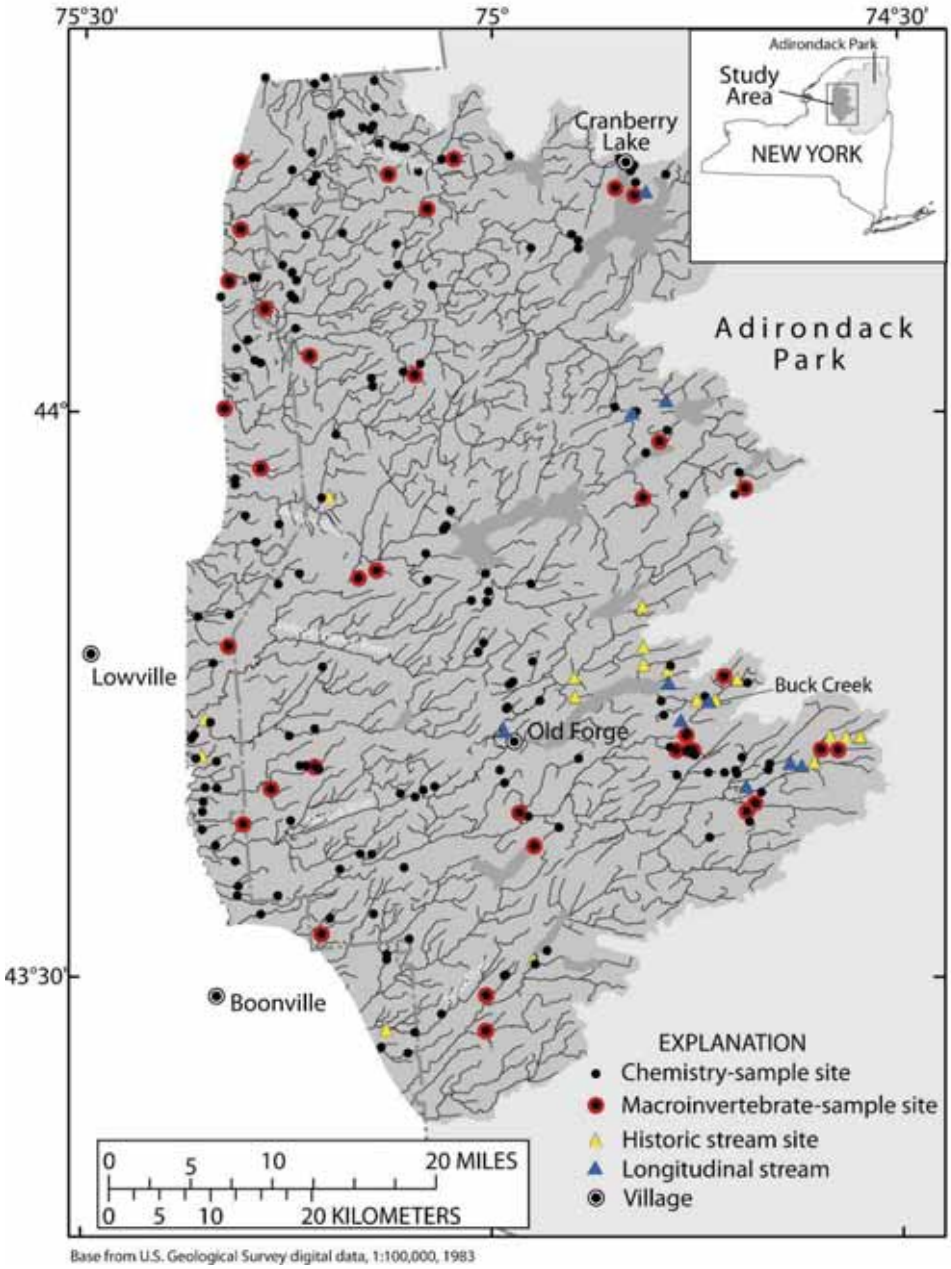


Figure 2-1. Locations of WASS stream sampling sites for collection of water and diatoms (black circles) and macroinvertebrates (red circles with black centers), which are a subset of the stream sampling sites. Sites sampled longitudinally are indicated by blue triangles and those sampled in the early 1980s and resampled in this study are indicated by yellow triangles.

(Lawrence et al. 2004). Acidic deposition levels in the study region remain among the highest in the Northeast with respect to both SO_4^{2-} and N (NADP 2006). From 1994-2004, deposition of SO_4^{2-} decreased at two of the three monitoring stations within or bracketing the study region, but there was no trend in deposition of N (Lawrence et al. 2004). Spatial modeling has shown a decrease in deposition from southwest to northeast across the Adirondack region (Ito et al. 2002). The study region encompasses the area with the highest deposition levels except for the uppermost elevations in the high peaks region (Ito et al. 2002). The combination of high amounts of precipitation and bedrock mineralogy that weathers slowly makes this region particularly susceptible to adverse effects of acidification.

2.2 Study Design, Sampling, and Analysis

This project was implemented through the five following sampling components:

1) Collection of water samples in 200 streams (termed survey streams) randomly chosen from the regional population of accessible streams, plus continuous monitoring of an index stream for stream flow and chemistry
2) Collection of soil samples in nine watersheds of the 200 survey streams
3) Collection of periphytic diatoms in the 200 survey streams
4) Collection of macroinvertebrates in 36 of the 200 survey streams
5) Collection of water samples at specific stream sites that were sampled multiple times in 1980-1985.

2.2.1 Stream Water Sampling Methods

To select streams for sampling, all streams within the study region that fit the following criteria were identified: 1) the stream was mapped on a USGS 1:24,000 quadrangle map as a solid blue line, 2) the stream was accessible by hiking to and from the sampling location within 1 hour, and 3) the stream did not contain upstream lakes or ponds that drained more than 25 % of the total drainage area defined by the sampling point. From the 565 streams that fit these criteria, 200 were randomly selected for sampling (Figure 2-1). The total drainage area of the 200 selected streams was 284 km^2; the total drainage area of the 565 potential streams was 825 km^2. The sampled streams ranged from 1st to 3rd order, but most were first order (Strahler 1952). At least half of these streams contained a sufficient amount of water to support fish during most of the year.

The stream water sampling in this study was designed to account for temporal variations in chemistry that occurred both episodically and seasonally. Flow-driven variations in chemistry that can occur hourly or daily are problematic for regional surveys such as this because flow and stream chemistry can vary over the length of time needed to reach all the sites. To reduce this variability, the sampling periods of each survey were selected when flows were expected to be either elevated or remain low for several days. The goal was to collect all samples within three days. This sampling approach did not measure extreme chemical conditions associated with episodes, but it did enable identification of stream reaches prone to episodic acidification by comparing stream chemistry during high and low flows.

To monitor variations in flow and stream chemistry during the surveys, and place this information within the context of variations throughout the year, Buck Creek (drainage area 3.1 km^2) was used as an index stream (Figure 2-1). The only other unregulated stream monitored for flow in the study region is Independence River, which has a drainage area of 228 km^2— nearly as large as the total drainage area of the 200 sampled streams. Flow at Buck Creek was determined using standard USGS methods (Rantz 1982). Stream water samples were manually collected at Buck Creek every two weeks, year-round, and during selected high-flow events with automated samplers, from April through November. Data are presented in this report for approximately 330 samples collected from May 2001 through April 2006. All samples were analyzed for pH; ANC_G; and concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, Cl^-, DOC, NH_4^+, Si, total Al, total monomeric Al, and organic monomeric Al in the USGS laboratory in Troy, New York following published methods (Lawrence et al. 1995b). Further information on Buck Creek watershed is available (Lawrence 2002).

In addition to episodic variations in stream chemistry, seasonal patterns in the degree of acidification are typical in Adirondack surface waters. During early spring, when flows are elevated from snowmelt and increased precipitation, base flow conditions tend to be more acidic than at other times of the year, and acid episodes are often the most severe (Wigington et al. 1996). Acidic conditions are least common in summer, when evapotranspiration reduces soil moisture, and flows tend to be lowest.

To address seasonal variation, sampling surveys were conducted twice during spring snowmelt (March 29-31, 2004 and March 29-31, 2005), twice during summer base flows (August 25-28, 2003 and August 16-18, 2004), and once during fall storms

(October 27-29, 2003). All samples were collected during the three-day surveys, with the exceptions of one sample that was collected on the fourth day in both the August 2003 and October 2003 surveys and six samples that were collected on the fourth day in the March 2004 survey. To evaluate variations in chemistry that did occur during the surveys, samples were collected at selected sites on each day that the survey was conducted, or in the case of the March 2005 survey, samples were collected twice per day at one site (Buck Creek). At three sites, samples were collected on only two of the three sampling days due to logistical problems.

Regional assessments of stream chemistry can be complicated by spatial variations that commonly occur along stream reaches. A sample collected at a single point along a stream may not be representative of stream chemistry upstream or downstream. However, previous studies in the White Mountains of New Hampshire (Palmer et al. 2005), the Catskill Mountains of New York (Lawrence 2002), and the Blue Ridge Mountains of the southeastern United States (Messer et al. 1988) have shown that headwater streams generally become more acidic in the upstream direction. Therefore, a stream that is acidified at the sampling location could be assumed to be acidified for its entire length upstream from this sampling point. To determine if stream chemistry demonstrates this longitudinal pattern in the western Adirondack region, samples were collected at multiple points along the reaches of 10 selected streams. The blue lines that indicate streams on the USGS quadrangle maps were used to determine stream lengths. The length of each stream was measured as the distance along the main channel from the sampling point upstream to the end of the blue line.

Samples collected in the stream surveys and longitudinal collections were analyzed in the Adirondack Lakes Survey Corporation (ALSC) laboratory for pH; ANC_G; and concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, Cl^-, Si, DOC, NH_4^+, total Al, total monomeric Al, and organic monomeric Al according to USEPA approved methods described elsewhere (Burns et al. 2006). These methods were essentially the same as those used in the USGS laboratory.

2.2.2 Collection of Soil Samples

Ten first-order watersheds were selected for soil sampling to include streams that varied from chronically acidic to non acidic. In each watershed, soil samples were collected in summer 2004 from the Oe, Oa, and upper 10 cm of the B horizon at three locations within each of five plots (15 total sampling locations per watershed). The locations of the five plots were chosen to represent landscape variability within the watershed. Samples of Oe horizon were collected from the surface after removing the litter layer (Oi horizon). Samples were collected from the Oa and upper 10 cm of B horizons from the faces of small pits. Samples from each plot were combined and mixed by horizon before analysis, resulting in five measurements per watershed for each of the three horizons. Data from one watershed were not included in the analysis because sampling revealed that the watershed was located on a deep sand deposit that resulted in minimal expression of surface flow and atypical soils and subsurface flow paths relative to the majority of the study region.

Previously collected soil data from the north and south tributary watersheds of the Buck Creek watershed also were used in this study. Samples were collected from 30

locations on a grid within each watershed in 1997-98. Samples were collected from the Oe, Oa, and upper 10 cm of the B horizon in the same manner as the samples from the nine watersheds sampled in 2004. At upper and lower locations within the north and south tributary watersheds, full profile sampling was done to provide chemical measurements of the mid and lower B horizon, in addition to the measurement of the forest floor and upper B horizon.

All samples were analyzed for exchangeable Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, (vacuum extraction followed by inductively-coupled plasma analysis); loss-on-ignition (combustion in muffle oven); moisture analysis (drying oven); organic carbon; total N (Thermo combustion elemental analyzer); and pH (water extraction and $CaCl_2$ extraction) following USEPA methods (Blume et al. 1990). All samples were also analyzed for total acidity and exchangeable Al (KCl extraction with shaker followed by titrimetric analysis), from which exchangeable H could be determined by difference (Thomas 1982). Base saturation was determined by dividing the sum of exchangeable base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) by the cation exchange capacity (the sum of base cations plus exchangeable acidity). All soil analyses were done in the USGS Troy laboratory.

2.2.3 Collection of Periphytic Diatoms

In each of the 200 survey streams, efforts were made to collect diatoms from rock surfaces, moss beds, and fine-grained sediment surfaces. Although these substrates represent the three most common benthic habitats found in the study streams, sampling locations of some streams lacked one or more of the substrate types. Diatoms were collected in four of the five stream surveys (the March 2005 survey was omitted), although collection in the

March 2004 survey was limited by high flows and residual snow and ice along stream banks. The samples were preserved in the field with formaldehyde to a final concentration of 4%. In the laboratory, all samples from each stream were combined, shaken vigorously, and subsampled to include both sample water and substrate. Subsamples were processed either with acids, including concentrated H_2SO_4, $KMnO_4$, and saturated oxalic acid, or bleach (2:1 sample to bleach ratio). The processed samples were washed with distilled water, eight times following the acid digestion and five times following the bleaching. The clean samples were mounted in a synthetic medium with a refractive index of 1.74. At least 300 frustules were counted in each mount with a 1000×1.35 NA oil immersion objective. Identifications were made to the lowest possible taxonomic category. Most cells were identified to the species level, but colonial diatoms that lie on their girdles could only be identified to the genus level.

Chemical measurements were related to diatom data, including the calculated Al ratio (defined as $(Al_{im}+1)/(Al_{om}+1)$) and the base-cation surplus (BCS), defined as the difference between summed concentrations of base cations and strongly acidic anions, which is further discussed in Section 3.1. All variables except pH, Al_{im}:Al_{om} ratio, Al_{im}, and BCS were ln-transformed to normalize them and bring them to a common scale. Al_{im}, which contained zero values, was ln (x+1)-transformed. Negative values of BCS were rescaled to a minimum of zero and then ln (x+1)-transformed.

Diatoms are among the best indicators of surface water acidity (Batterbee et al. 1999) because the pH optima are known for most of the common species, including those that are acidobiontic (can tolerate pH < 5.5) and those that are acidophilous (can tolerate pH < 7), which are useful for assessing acidification effects (Lowe, 1974). The acidity index (ACI), calculated as the relative abundance of acidobiontic and acidophilous species, was shown to

be a reliable measure of acidification impact in the Catskill region of New York (Passy 2000).

Data analysis was done by analysis of variance (ANOVA) and followed up with a Tukey multiple comparison test, which was employed to test for equality of ACI means across sampling periods. The behavior of ACI along the major environmental gradients was non-linear, as revealed by scatter plots fit by DWLS smoother. This result prompted the use of regression trees, which is a technique that does not assume linear response of the dependent variable but estimates the thresholds in the environmental predictors, where the behavior of the dependent variable changes.

Detrended correspondence analysis of species data indicated that diatom datasets from the four collections had comparatively short gradient lengths, which justified the selection of linear methods for further analyses (ter Braak and Smilauer 1998). Redundancy analysis (RDA) with forward selection and 999 Monte Carlo simulations was conducted on diatom and environmental data from each survey separately to select predictors that best explained the variance in diatom data. Only predictors significant at the 0.05 level were retained in the model.

2.2.4 Collection of Macroinvertebrates

Macroinvertebrates were collected in 36 of the 200 survey streams between August 11 and Sept 1, 2004 (Figure 2-1). These 36 streams were selected to represent the full range of acidification identified in the stream surveys. Only streams with flowing water and coarse substrates (stones, gravel, and sand) throughout their reaches were

included. Samples were collected in reaches with a depth of 1 m or less; a current velocity of at least 0.4 m s^{-1}; and a substrate of small stones, gravel, and sand.

The standardized traveling kick method was used to collect macroinvertebrates. In this procedure, an aquatic net is positioned in the water downstream at arms length, and the bottom is disturbed by foot to allow dislodged organisms to flow into the net. Sampling is done for five minutes, over a distance of 5 m. Collection nets had rectangular openings of 23 cm x 46 cm and a mesh size of 0.8 x 0.9 mm. Samples were rinsed in a 500-µm mesh sieve and preserved in 95% ethanol. At the laboratory, a subsample of 100 specimens per sample was randomly sorted from the debris, identified to the lowest possible taxonomic level (generally genus or species), and enumerated. Chironomids and oligochaetes were mounted on slides and viewed with a compound microscope. Most other organisms were identified with a dissecting stereomicroscope. All specimens in the subsamples were preserved and archived.

Standard macroinvertebrate-community indices reflect a variety of water quality impacts, including eutrophication and effects of pollutants such as heavy metals, and they have been applied throughout New York State (Bode et al. 2004, Smith and Bode 2004). Extensive sampling throughout New York has shown that the macroinvertebrate communities tend to be sufficiently stable during late summer to provide consistent index values (Smith and Bode 2004). However, these indices do not reflect the influences of acidification, either natural or from acidic deposition. Therefore, selected taxa were therefore used to develop an acid-sensitive index, termed the Acid Biological Assessment Profile index (acidBAP), which was first applied to acidified streams in the Catskill Mountain region (Burns et al. 2007). The acidBAP is based on taxa found to be abundant

in acidic streams of the Adirondack and Catskill Mountains and uncommon in 20 non-acidic reference streams from across New York State. The acidBAP is calculated from the Percent Mayfly Richness (PMR) and the Acid Tolerant Index (ATI). The PMR is the percentage of alkaliphilous taxa that belong to the order Ephemeroptera (excluding one acidobiontic genus *Epeorus)* and is normalized on a scale of 0 to 10, where 0 denotes 0% mayfly taxa and 10 denotes greater than 20% mayfly taxa. The ATI is the percentage of individuals belonging to the following 10 genera: *Epeoru*s (Ephemeroptera), *Amphinemura, Leuctra, Isoperla* (Plecoptera), *Rhyacophila* (Trichoptera), *Simulium, Conchapelopia, Cricotopus, Eukiefferiella, and Heterotrissocladius* (Diptera) – all of which contain one or more acidophilous species. The ATI is normalized on a scale of 0 to 10, where 0 denotes greater than 40% acidophilous individuals and 10 denotes 0% acidophilous individuals. The acidBAP is the average of the PMR and ATI scores, where a score of 10 indicates no adverse effect from acidification, and a score of 0 indicates a severe effect. The effectiveness of the AcidBAP index in characterizing acidification effects is based on combining the indices derived with both acidophilous species (ATI) and alkaliphilous species (PMR).

2.2.5 Water Sampling in Streams Sampled in 1980-1985

The goal of this component was to replicate stream sampling done in the 1980s to determine if there were differences in water chemistry between the two periods. Historical measurements of ANC_G, pH, and specific conductance were available over several years, so our sampling was scheduled to cover a three-year time period to account for annual variations in precipitation and stream flow. We selected for resurvey the 18

Adirondack streams that had been sampled multiple times over at least two seasons. Most were sampled over two to three years. Data were available in 13 streams from 1980-1982 (Colquhoun et al. 1981, 1982, 1984) and in five streams from 1983-1985 (Simonin, H., report coauthor, unpublished data). The study streams were located in the southern part of the Black River drainage with the exception of a single site that was located in the Oswegatchie River drainage (Figure 2-1). Within the Black River drainage, 13 streams were in the Moose River sub-basin. Collection sites were the same as those used in the 1980s and were always located upstream from bridge or culvert crossings.

The number of samples collected in each stream during the 1980s ranged from 11 to 45. Only pH, ANC, and specific conductance were measured in these samples, which limited our comparisons to these measurements. Because stream water chemistry is strongly influenced by stream flow, variations in flow needed to be accounted for when comparing data from the two time periods. The only flow data available for this region for both sampling periods were from the USGS stream gage on the Independence River site at Donnattsburg, NY (USGS 04256000) (Lawrence et al. 2004). Lawrence et al. (2004) showed a statistically significant positive relation between flow at the Independence River site and flow at Buck Creek (the index site for this project; see Section 2.2.1) for November 1988 to May 1990. Lawrence et al. (2004) also showed strong correlations between both ANC_G and pH and flow in three streams in the study region (including Buck Creek) for water years 1991-2001. Because these streams were not gaged during the study period, flow at the gaged site on the Independence River was used as a surrogate for flow of the sampled streams.

Water samples were collected from April through September of 2003, 2004, and 2005 at nine of the study streams, which is similar to the sampling season in the 1980s for these sites. Three additional sites (Independence River, Otter Creek, and West Branch, Oswegatchie River) were sampled only during the spring snowmelt period (March, April, May) in order to replicate the 1980s sampling. Six other sites were sampled by the Adirondack Long-Term Monitoring Program (ALTM) as part of other monitoring programs, and these data were also used to compare with the 1980s data. These sites included three streams that are monitored on a weekly basis as part of the ALTM (Fly Pond Outlet, Bald Mountain Brook, and Buck Creek). For these three streams we used only the data collected in the first week of each month for comparisons with the 1980s dataset. The other three ALTM sites are monitored as lake outlets on a monthly basis (Cascade Lake Outlet, Constable Creek, and Black River at the North Lake outlet). The number of samples included per stream ranged from 15 to 18 samples from the recent survey period.

The stream samples collected in 2003-05 were analyzed in the Adirondack Lakes Survey laboratory for the same parameters and with the same methods as the samples collected for the stream surveys (see Section 2.2.1). Methods of chemical analysis for samples collected in the early 1980s were the same as those used for the samples collected in 2003-2005. However, quality assurance comparisons between the analyses of the two time periods were not possible. Measurements of ANC_G, pH, and specific conductance were compared between the two time periods using Statistix 8 (Analytical Software 2003). Most comparisons were done with analysis of covariance on individual streams. In order to compare the amount of change in pH, ANC, or specific conductance

in each stream, we used linear regression and calculated the variable at a flow rate of 100 $ft^3\ s^{-1}$ (2.83 m^3/s) in the Independence River. We did this for each of the two time periods and determined the difference in predicted values. Multifactor ANOVA (factors = year, site) also was run for the combined stream sites, with flow as a covariate, to determine an overall value for the difference between time periods. To express this value as a rate of change, the difference was divided by 23, which is the average number of years between samplings.

3 RESULTS AND DISCUSSION

3.1 New Approach for Assessing Acidic Deposition Effects

The natural acidity associated with DOC has long complicated assessments of acidic deposition effects on surface waters. The most commonly used measure of acidification effects, ANC_G, does not distinguish between natural acidity and that derived from acidic deposition. This is a particular problem for Adirondack surface waters because high concentrations of DOC are common, and concentrations have been changing (Driscoll et al. 2007). Therefore, as part of this assessment, a new approach based on Al mobilization was developed to better discriminate between acidic deposition effects and natural acidity derived from natural ecosystem processes.

3.1.1 Contrasting Stream Chemistry Within Buck Creek Watershed

The North and South tributaries of Buck Creek drain subwatersheds with similar geology and levels of acidic deposition, but water chemistry measured during this study differed considerably between the two tributaries. The North Tributary, considered chronically acidic, had pH values that did not vary with changes in flow and remained mostly below 4.5 (Figure 3-1). The South Tributary, considered episodically acidic, had pH values that decreased with increasing flow and varied over two units (Figure 3-1). The general relation of increased inorganic Al concentrations with decreased pH were similar in the two tributaries, but pH values in the North Tributary were approximately one-half unit lower than in the South Tributary at the same concentration of inorganic Al (Figure 3-2).

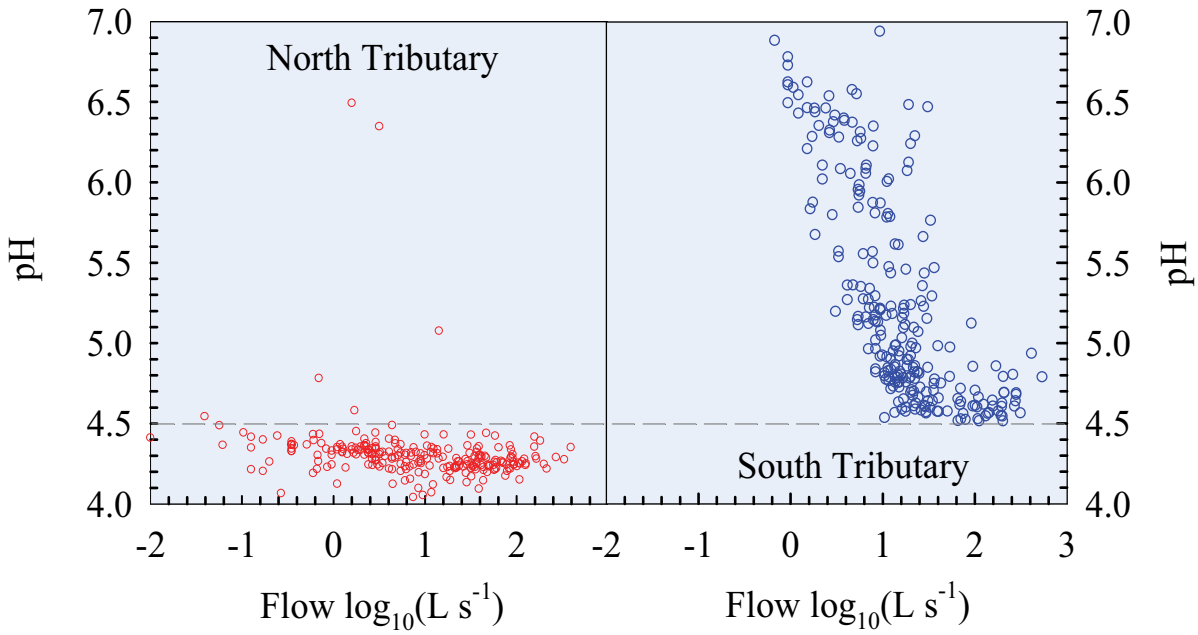


Figure 3-1. Variations in pH as a function of flow in the North and South Tributaries of Buck Creek, Inlet, N.Y.

The differences in the chemical relationships observed in these neighboring watersheds demonstrate the limitation of pH in ascribing acidic deposition effects. These differences are largely the result of differences in concentrations of DOC. In the South Tributary, DOC concentrations in biweekly samples collected from 2001 to 2006 were seldom greater than 400 µmol L^{-1}, whereas concentrations in the North Tributary were seldom less than 900 µmol L^{-1} (Figure 3-3). A headwater wetland and a thick forest floor (average depth 20.7 cm) throughout the North Tributary watershed provided substantial opportunity for the dissolution of soluble organic matter, whereas the relatively shallow forest floor (average depth 7.9 cm) and absence of wetlands in the South Tributary watershed produced relatively low concentrations of DOC throughout the year. High

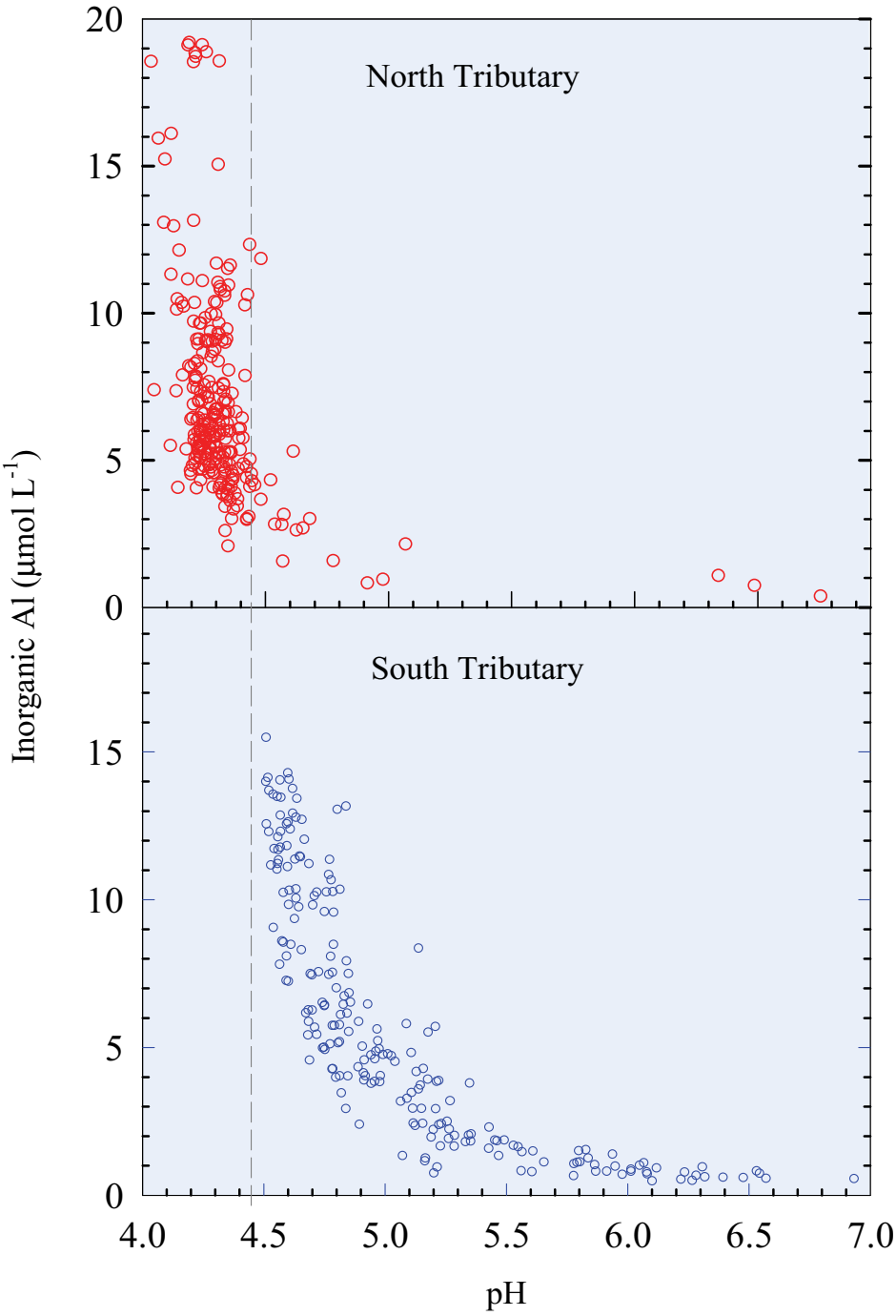


Figure 3-2. Variations of inorganic Al concentrations as a function of pH in the North and South Tributaries of Buck Creek, Inlet, N.Y.

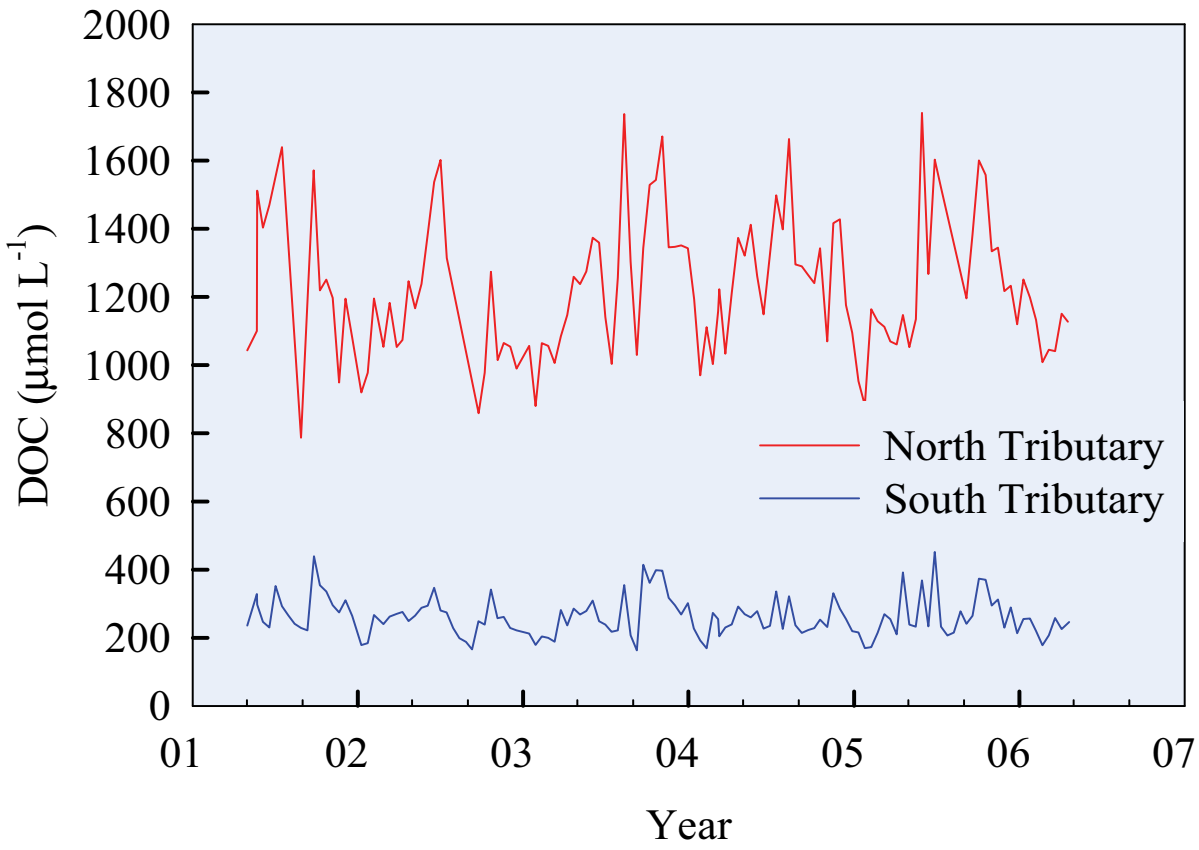


Figure 3-3. Concentrations of dissolved organic carbon (DOC) in the North and South Tributaries of Buck Creek, Inlet, N.Y., May 2001-April 2006.

mobility of soluble organic matter derived from the abundant coniferous vegetation in the North Tributary, in contrast to the less mobile organic matter from the dominant beech vegetation in the South Tributary, also may have contributed to the difference in DOC concentrations between the streams (Dijksta and Fitzhugh 2003). Previous work in the Adirondack region has shown that watersheds with abundant coniferous vegetation tend to have lower pH and higher DOC concentrations in surface waters than predominantly deciduous watersheds (Cronan and Aiken 1985).

3.1.2 The Threshold for Mobilization of Inorganic Aluminum

Despite the complications of DOC, however, a distinct threshold for Al mobilization was observed when ANC ($Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} - SO_4^{2-} - NO_3^{-} - Cl^{-}$) was plotted against inorganic Al concentrations for each tributary (Figure 3-4a, 3-4b). The threshold occurs at a higher ANC value in the North Tributary than in the South Tributary. In contrast, ANC was unrelated to organic Al concentrations in either stream, and the distribution of the values differed markedly between these streams (Figure 3-4c, 3-4d).

An increase in the Al mobilization threshold with increased DOC concentrations suggests a role for organic acidity in the mobilization of inorganic Al. The role of organic acidity in mobilizing organically-complexed Al in soils has long been recognized (DeConinck 1980), but mobilization of inorganic forms of Al has traditionally been attributed to strong inorganic acids from acidic deposition (Cronan and Schofield 1979) or acid mine drainage (Nordstrom and Ball 1986). However, strongly acidic organic acids should be expected to behave similarly to strongly acidic inorganic acids with regard to mobilizing inorganic Al. Although weakly acidic organic acids can mobilize Al by providing H^{+}, they also tend to form dissolved complexes with Al. Strongly acidic organic acids also provide H^{+} to mobilize Al, but they have little tendency to form organic-Al complexes. Previous research has shown that a considerable fraction of organic acidity in Adirondack lakes is attributable to strongly acidic organic acids (Munson and Gherini 1993, Driscoll et al. 1994).

To evaluate the importance of strongly acidic organic acids in Adirondack streams, the anion deficit was vs. against DOC concentrations (Figure 3-5). The anion

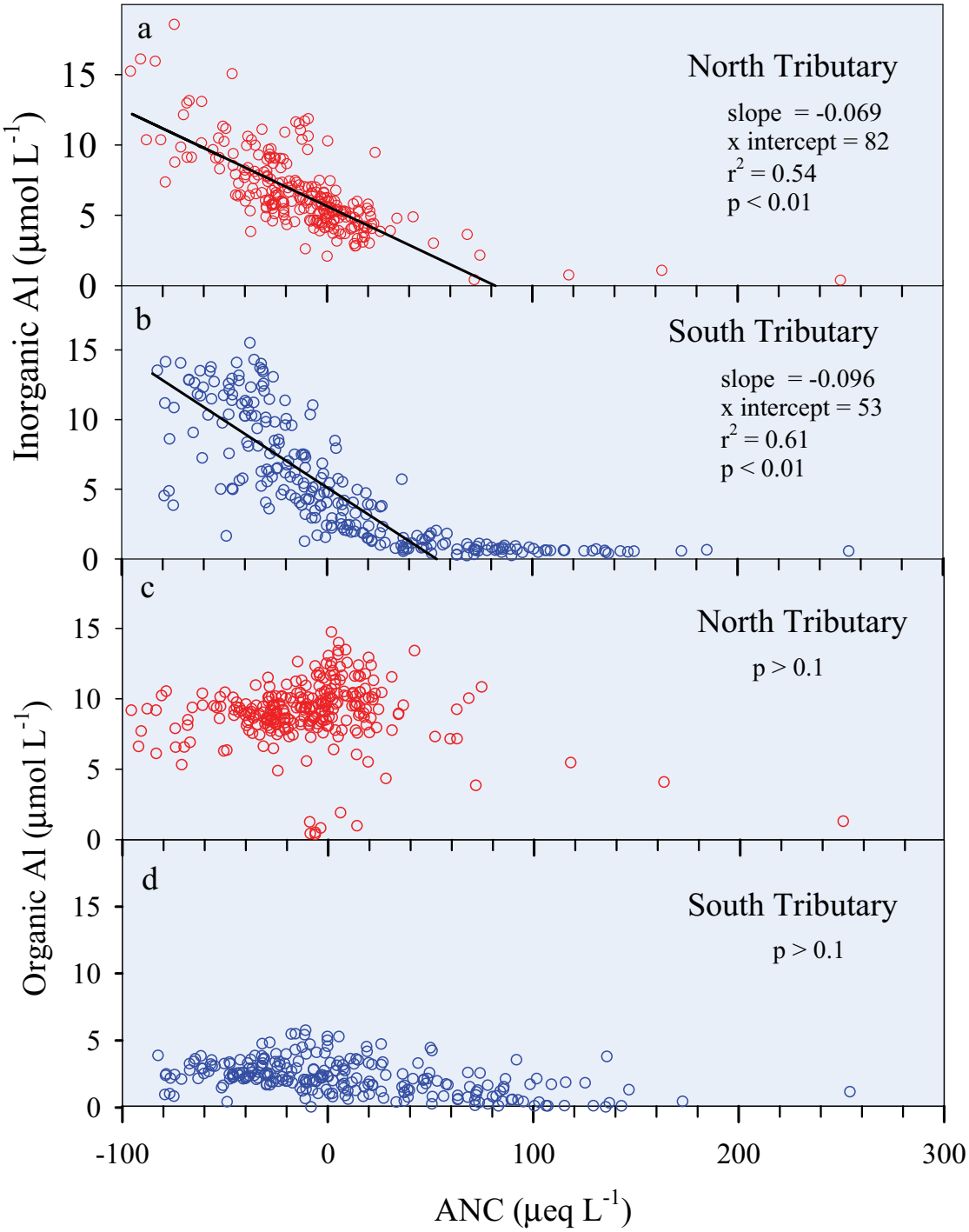


Figure 3-4. Concentrations of inorganic Al in the North (a) and South (b) Tributaries of Buck Creek, and organic Al in the North (c) and South (d) Tributaries of Buck Creek, as a function of ANC (calculated as $Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} - SO_4^{2-} - NO_3^{-} - Cl^{-}$). The x-intercept was determined by iterative comparison between an estimate and the value determined by linear regression, after data to the right of the intercept were removed.

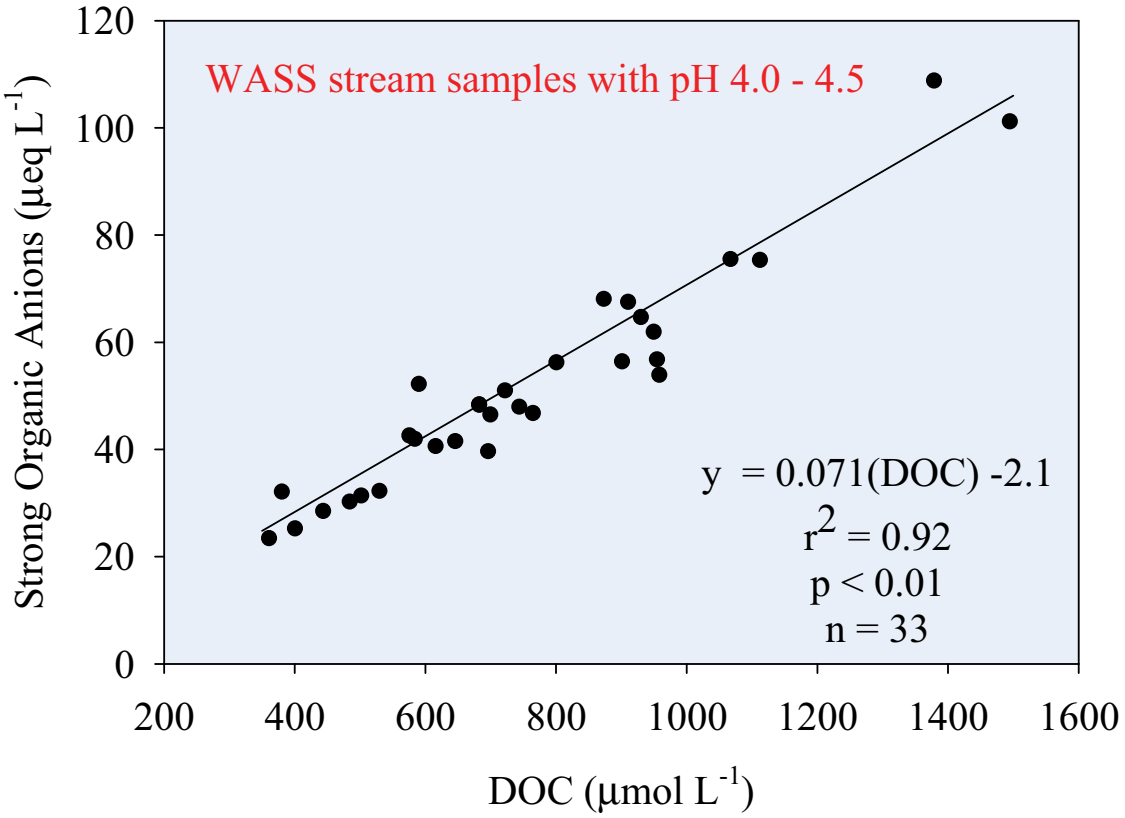


Figure 3-5. Anion deficits of charge balances as a function of dissolved organic carbon (DOC) in WASS stream samples. The best-fit line determined by linear regression is also shown with regression statistics.

deficit is determined by subtracting the sum of all anion concentrations (except organic anion concentrations) from the sum of all cation concentrations. If all anions and cations were included, the sum of positive and negative charges would equal zero. Therefore, the total organic anion concentrations, which cannot be measured directly, are estimated by the anion deficit—the difference between measured cation and anion concentrations.

Strongly acidic organic anions can be estimated by calculating the anion deficit for samples with pH values less than 4.5 (Munson and Gherini 1993). Organic acid functional groups that are generally considered weakly acidic would be protonated (uncharged) in this pH range. The strength and linearity of the relationship between the

anion deficit and DOC over a large range in DOC concentrations indicates that the concentration of titratable (weakly acidic) organic anions in the pH range of 4.0 to 4.5 was low in relation to the concentration of organic anions that would remain unprotonated in this range (Munson and Gherini 1993). On this basis, the anion deficit was considered to be a valid approximation of strongly acidic organic anion concentrations for samples with pH values from 4.0 – 4.5.

In samples with pH above 4.5, the anion deficit could not be used to estimate strongly acidic organic anion concentrations because some of the weakly acidic functional groups would also be unprotonated (charged) and would contribute to the anion deficit. However, the acid-base properties of DOC have been shown to be similar across regions of similar vegetation and environmental conditions (Hruska et al. 2003), so the concentrations of strongly acidic organic anions for samples with a pH value above 4.5 were calculated from DOC concentrations and the equation, below, was developed and in Figure 3-5 and shown below.

$$RCOO^-_s=0.071(DOC)-2.1$$

where $RCOO^-_s$ equals the concentration of strong organic anions. This relationship is similar to that shown by Munson and Gherini (1993) for Adirondack Lakes ($RCOO^-_s=0.058(DOC)-3.7$).

3.1.3 The Base Cation Surplus as an Index of Acidic Deposition Effects

To evaluate the effect of strongly acidic organic anions on the Al mobilization threshold, ANC was adjusted to include the concentration of strong organic anions. This new factor, termed the base-cation surplus (BCS), is defined by the following equation in which concentrations are expressed in μeq L^{-1}.

$$\text{base-cation surplus} = (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) - (SO_4^{2-} + NO_3^{-} + Cl^{-} + RCOO^{-}_{s})$$

The effect of strongly acidic organic anions can be shown by comparing the relation between ANC and inorganic Al to that between the BCS and inorganic Al for 196 streams sampled in October 2003, when DOC concentrations were seasonally high (Figure 3-6). Similar relations occur when both these factors are plotted against inorganic Al concentrations, but the threshold value for Al mobilization is much closer to zero when the BCS is used rather than ANC. The same relationships for samples collected in March 2004, when DOC concentrations were seasonally low, indicated lower threshold values for both ANC and the BCS. However, the threshold obtained with the BCS closely approximated zero (Figure 3-7). Mobilization of inorganic Al would be expected at a BCS value of zero based on the constraint of solution charge balance (Lawrence et al. 2007).

Adjustment of ANC to include $RCOO^{-}_{s}$ lowered the threshold value for both October and March stream samples and reduced the difference between the threshold values for these data sets (Figure 3-6, 3-7). The adjusted threshold value of +20 for the October 2003 samples may reflect an overestimation of inorganic Al concentrations in

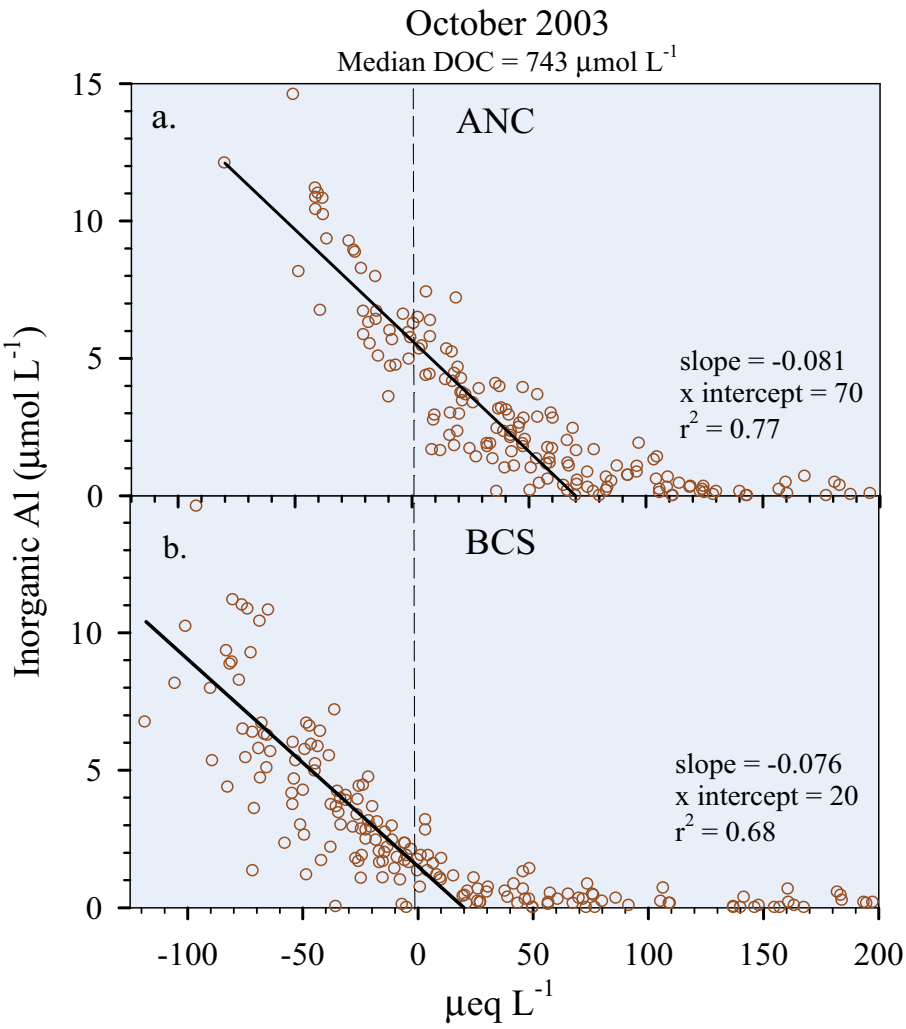


Figure 3-6. Concentrations of inorganic Al measured in the October 2003 survey, when DOC concentrations were high, plotted as a function of (a) ANC (calculated as Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} - SO_4^{2-} - NO_3^{-} - Cl^{-}) and (b) base cation surplus. The x-intercept was determined by iterative comparison between an estimate and the value determined by linear regression after data to the right of the intercept were removed.

samples with high DOC concentrations. The cation-exchange resin used to separate organically complexed Al from inorganically complexed Al disrupts some weak organic complexes in samples with high DOC concentrations (Driscoll 1984), although this widely used Al-speciation method has been shown to be generally reliable (Clarke et al. 1996). Nevertheless, disruption of weak organic-Al complexes in high DOC samples would cause some overestimation of inorganic Al concentrations and shift the position of the threshold to the right (higher base-cation surplus).

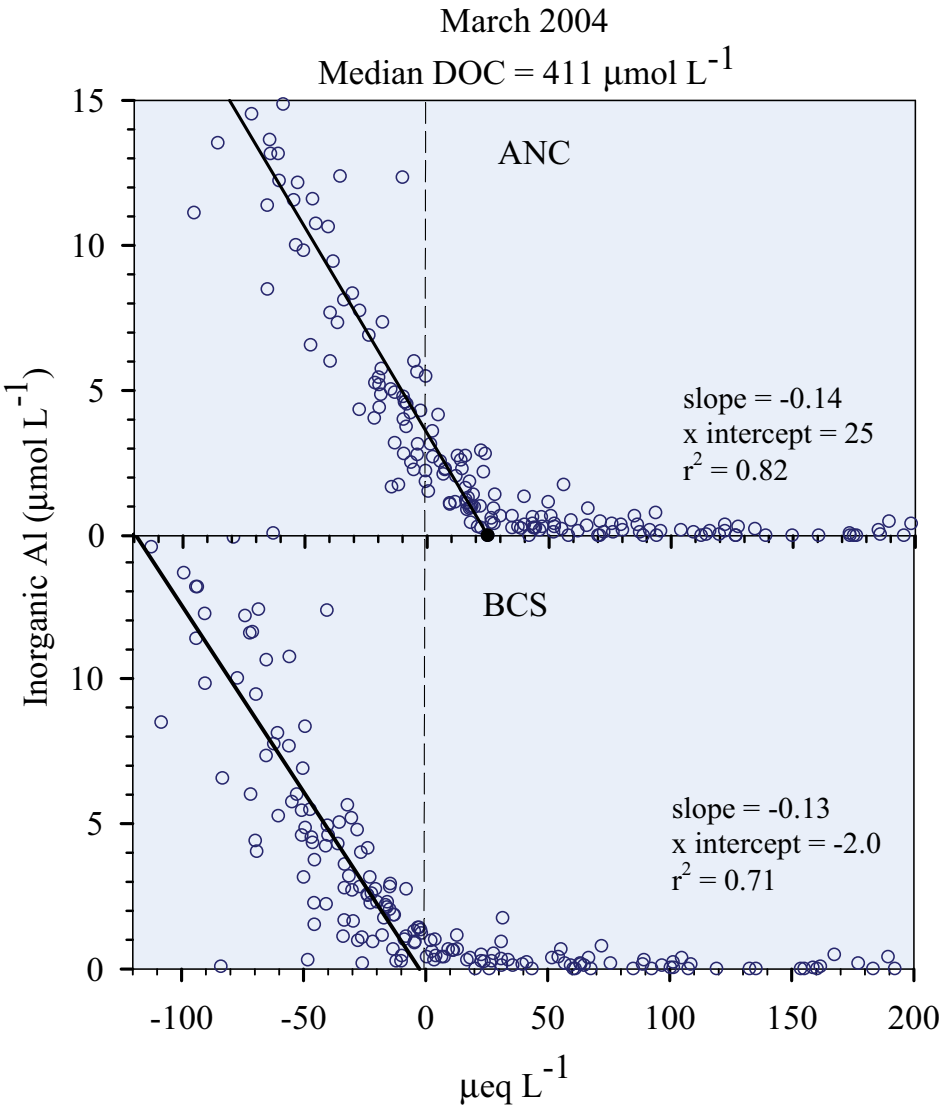


Figure 3-7. Concentrations of inorganic Al measured in the March 2004 survey, when DOC concentrations were low, plotted as a function of (a) ANC (calculated as Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} - SO_4^{2-} - NO_3^{-} - Cl^{-}) and (b) base cation surplus. The x-intercept was determined by iterative comparison between an estimate and the value determined by linear regression after data to the right of the intercept were removed.

The inclusion of naturally occurring, strong organic anions as a negative component in the base-cation surplus does not necessarily imply that mobilization of inorganic Al can occur in the absence of acidic deposition. If the sum of base-cation concentrations exceeds the concentration of strong organic anions, excess H^{+} will not be

available for mobilization of inorganic Al without contributions of SO_4^{2-} and NO_3^- from acidic deposition. We found this to be the case for 388 out of the 389 stream samples collected in the two stream surveys. The sum of base-cation concentrations exceeded the estimate of strong organic anions by an average of 178 μeq L^{-1} for all samples collected in the October 2003 and March 2004 surveys. This finding suggests that strongly acidic organic acids increase the sensitivity of a watershed to acidic deposition in a manner analogous to base-poor bedrock and till.

3.1.4 Comparison Between the BCS and ANC_G

Because the recently developed BCS (Lawrence et al. 2007) had not been previously used to assess acidic deposition effects on surface-water chemistry, a comparison between the BCS and the widely used ANC_G was made for samples collected at Buck Creek. The temporal patterns of the BCS and ANC_G were approximately the same over the five-year record (Figure 3-8). However, below 0 μeq L^{-1}, BCS values were consistently lower than ANC_G values, whereas above 0 μeq L^{-1}, values were similar.

A similar result was obtained when the relation between BCS and ANC_G measurements for the October 2003 survey (when DOC concentrations were relatively high) were compared to those for the March 2004 survey (when DOC concentrations were relatively low). Above a BCS value of about 0 μeq L^{-1}, BCS measurements for the two surveys were somewhat lower than ANC_G values, but the relation in both surveys was linear (Figure 3-9). Slightly lower values for the BCS than ANC_G may have resulted from air equilibration of samples prior to ANC_G titration, which raised pH and deprotonated weak organic acids that would then contribute positively to ANC_G.

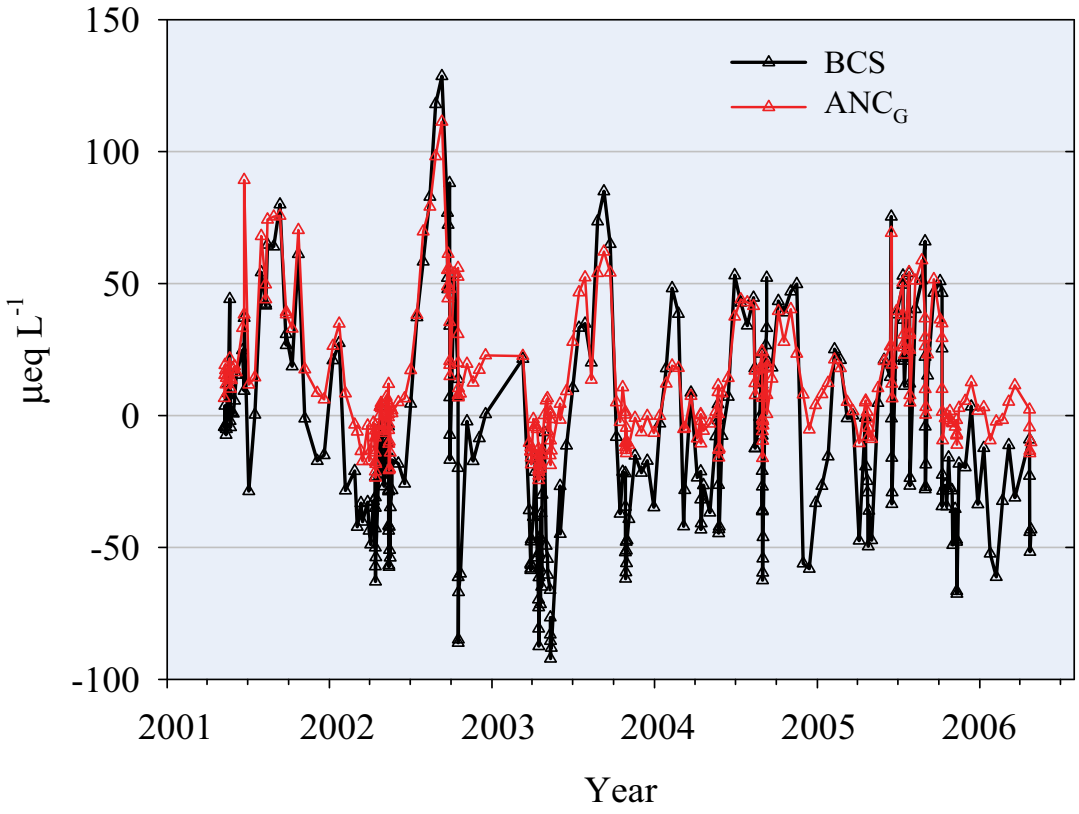


Figure 3-8. Base cation surplus (BCS) and acid-neutralizing capacity determined by Gran titration (ANC_G) in Buck Creek from May 2001 to April 2006.

Below a BCS value of 13 μeq L^{-1}, a significant change in slope ($p < 0.01$, based on piecewise linear regression) occurred in data for the October 2003 survey (Figure 3-9a) but did not occur in data for the March 2004 survey ($p > 0.1$; Figure 3-9b). The break in slope can be attributed to weak organic acids that had a positive effect on ANC_G but did not affect the BCS.

The BCS and ANC_G also differ in that all inorganic Al species are accounted for in the BCS as factors that are indicative of acidification (lower BCS values), whereas measurements of ANC_G are not affected by inorganic forms of Al such as Al^{3+} and AlF^{2+}.

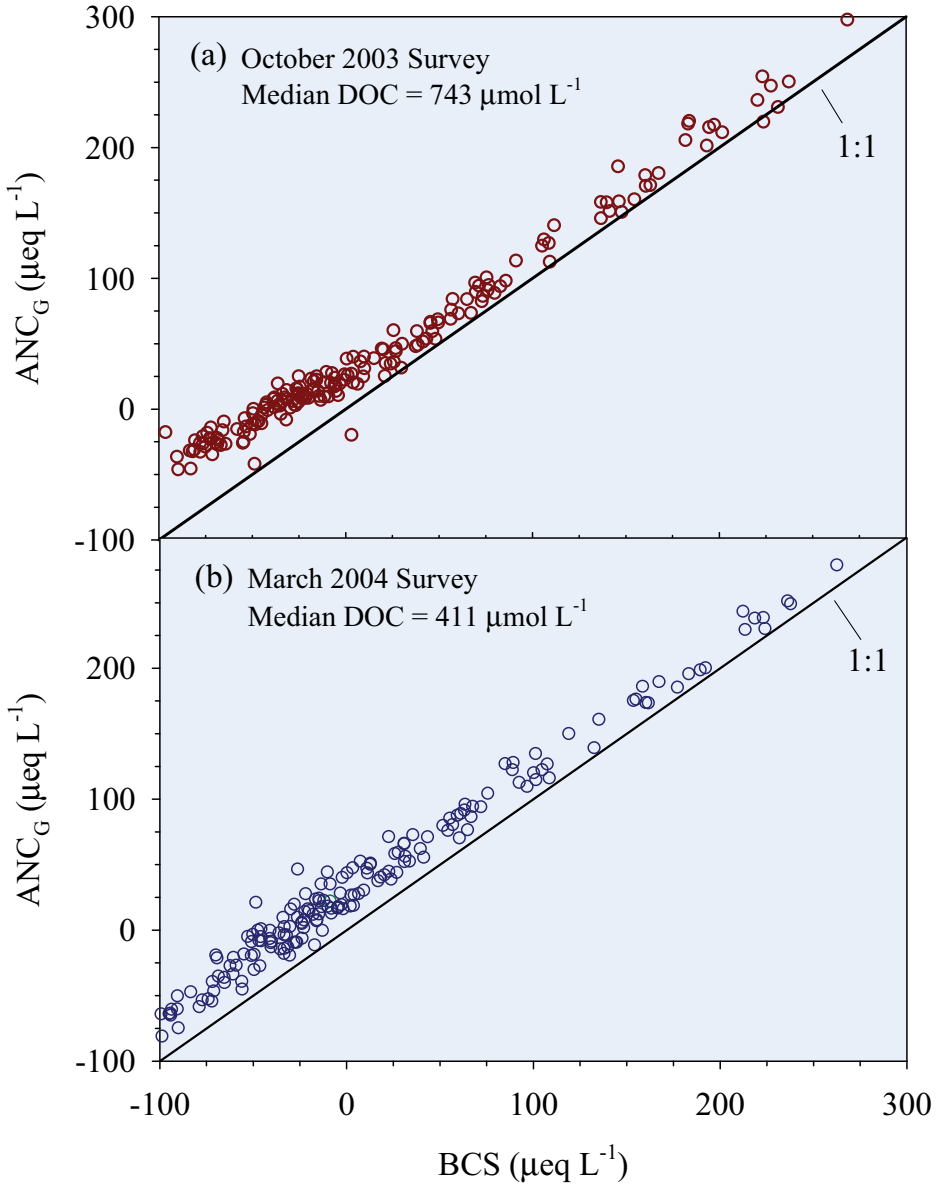


Figure 3-9. Acid-neutralizing capacity by Gran titration (ANC_G) plotted against the base cation surplus (BCS) for samples collected in (a) the October 2003 survey, and (b) the March 2004 survey.

Furthermore, the species $AlOH^{2+}$ and $Al(OH)_2^+$ have a positive affect on ANC_G through their ability to accept protons and buffer pH. In summary, the BCS is a more effective measure of the geochemical effects of acidic deposition than ANC_G because (1)

the variable effects of strong organic acids that increase susceptibility to Al mobilization are accounted for, (2) Al-hydroxide species are included as an effect of acidic deposition rather than a factor that indicates less sensitivity to acidic deposition, and (3) naturally derived weak organic acids do not affect the BCS value.

3.1.5 Conclusions on a New Approach for Acidic Deposition Assessment

The inclusion of strong organic anions as a negative component in the base-cation surplus does not necessarily imply that mobilization of inorganic Al can occur in the absence of acidic deposition. If the sum of base-cation concentrations exceeds the concentration of strong organic anions, excess H^+ will not be available for mobilization of inorganic Al without contributions of SO_4^{2-} and NO_3^-. In 388 out of the 389 stream samples collected in October 2003 and March 2004 stream surveys, the sum of base-cation concentrations exceeded the estimate of strong organic anions by an average of 178 $\mu eq\ L^{-1}$. In combination with inorganic strong acids from acidic deposition, however, strongly acidic organic acids further decreased the value of the base-cation surplus. Production of strongly acidic organic acids through natural processes therefore increases the sensitivity of a watershed to acidic deposition in a manner analogous to base-poor bedrock and till.

Measurements of inorganic Al concentrations do not predate acidic deposition because the necessary analytical methods did not exist at that time. Therefore, it is not possible to directly determine if inorganic Al occurred in surface waters in the absence of acidic deposition. However, the generality of the threshold relationship, its consistency with the theoretical basis for inorganic Al mobilization, and a lack of other known natural

mechanisms to explain regional mobilization of inorganic Al provide strong evidence that the measurable concentrations of inorganic Al in surface waters throughout the western Adirondacks are an unambiguous indication of acidic deposition effects on this region (Lawrence et al. 2007). On the basis of its relationship to inorganic Al concentrations and its ability to quantify the status of base cation availability relative to both inorganic and organic strong acid anions, the base-cation surplus provides a more effective chemical indicator of human-induced acidification than pH, ANC_G, or ANC because it can distinguish between natural organic acidity and acid rain.

3.2 Effects of Acid Rain on Stream Chemistry

Previous studies have established that streams generally become more acidic as flow increases, although factors such as climate (Mitchell et al. 1996), seasonal variability (Stoddard 1994), and antecedent precipitation (Burns et al. 1998a) often complicate this relation. Therefore, our results are presented within the context of both seasonal and episodic flow variations, which are based on stream flow monitoring at Buck Creek. Surveys conducted at both low flows and high flows enabled us to distinguish between chronically acidic and episodically acidic streams. The tendency for streams to become more acidic in the upstream direction enabled us to present our results in terms of the total length of acidified stream reaches.

3.2.1 Relationships Between Flow Variations and Stream Chemistry

Stream flow measured at Buck Creek during the five surveys reflected seasonal variations that were typical for the study region. Flows during the August 2003 and

August 2004 surveys remained stable during the three to four days of sampling (Figure 10). Flow was extremely low during the August 2003 sampling; lower flows occurred only 5-6 % of the time in that year, and 33 streams were dry during the survey. Flows were somewhat higher during the August 2004 survey; lower flows occurred 24 to 38% of the time in that year, and none of the streams were dry during the survey.

Flows during snowmelt sampling in March 2004 and March 2005 were elevated, but they also remained relatively stable during sampling (Figure 3-10). In March 2004, the survey was conducted after the primary snowmelt peak, whereas in March 2005, the survey was conducted in the early stages of the snowmelt period before the primary peak. Lower flows than those measured during the March 2004 survey occurred 90-95% of the time in 2004, and lower flows than those measured during the March 2005 survey occurred 84 to 93% of the time in 2005.

In the October 2003 survey, a major peak approaching the highest flow of the year occurred on the first day of sampling, and a secondary peak occurred on the third day of sampling (Figure 3-10). Although flow varied substantially during the October 2003 survey, the lowest flow at which samples were collected was greater than flows for 90% of the year. The highest flows at which samples were collected were greater than flows for 99.8% of the year. In the month prior to the October 2003 survey, four peaks in flow occurred, including one that approximately equaled the peak on the first day of the survey.

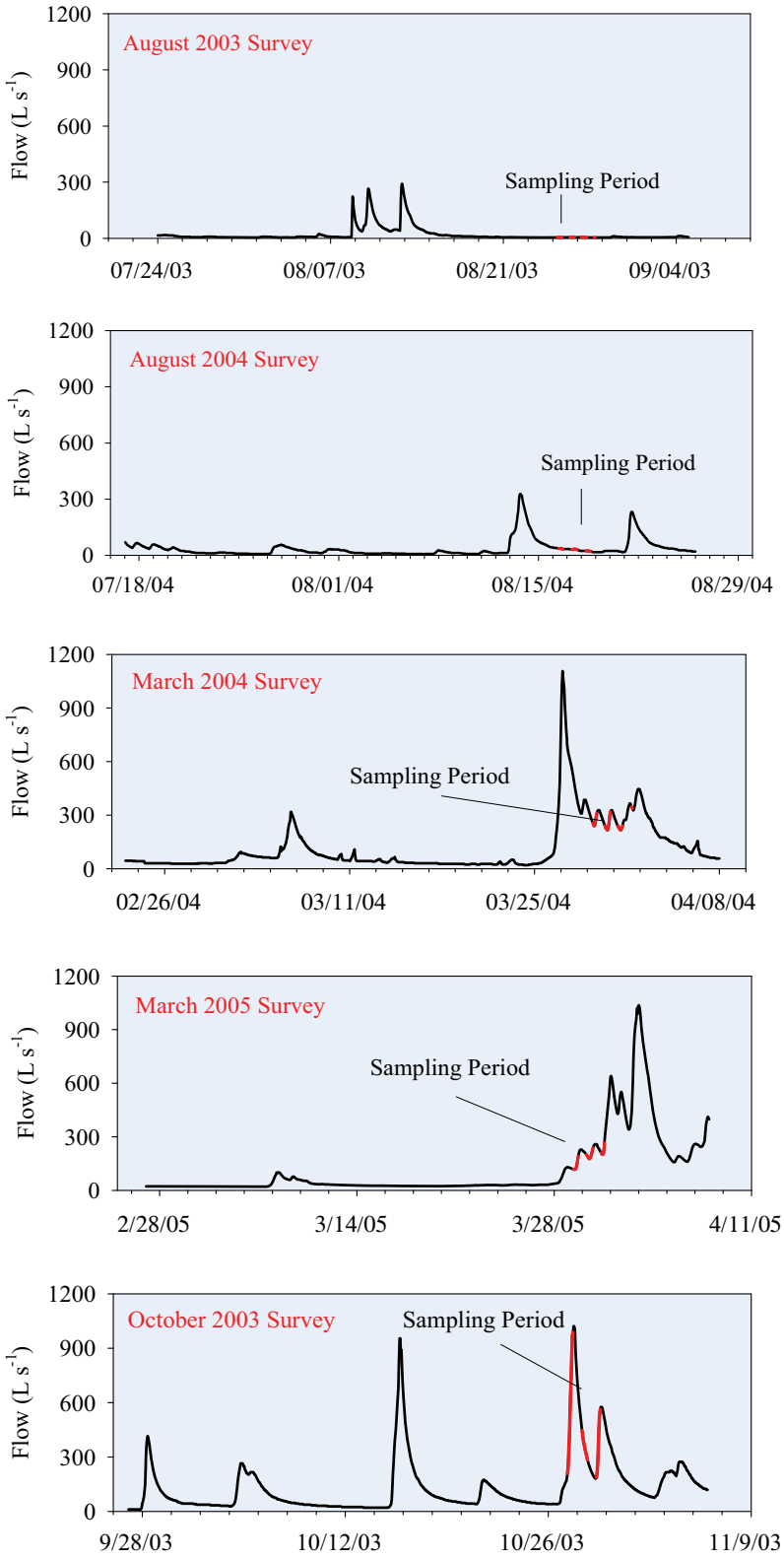


Figure 3-10. Stream flow at Buck Creek, Inlet, N.Y. for six-week periods that encompassed the August 2003 and 2004 surveys, the March 2004 and 2005 surveys, and the October 2003 survey. Sampling periods are shown in red.

Effects of flow variations on stream chemistry were evaluated through stream gaging at Buck Creek. Half the variability in BCS values at Buck Creek during the five-year study period (Figure 3-11) was explained by variations in flow ($p < 0.01$). Variations in the BCS measured at Buck Creek during the five surveys were placed within the context of variations over the five-year record (Figure 3-12). The BCS value measured in the August 2003 survey was similar to the highest values recorded each summer, with the exception of the summer of 2002, in which values were as much as 50 $\mu eq\ L^{-1}$ higher than during the August 2003 survey. Values of BCS during the August 2004 survey were considerably lower than the summer peaks of each year, including 2004. The lowest value for the March 2004 snowmelt was lower than any other measurements during 2001-2006, except for those during the 2003 snowmelt and a storm in October 2002. However, other measurements during the snowmelt of 2002 and storms in August 2004 and November 2005 did approach those of the 2004 March survey. Therefore the values for the March 2004 survey were not exceptional for high flow conditions over this five–year period. Values for the October 2003 survey were similar to minimum values of other fall storms during the five years.

Variations in flow during the surveys resulted in some degree of temporal variability in stream chemistry (Table 3-1). Values of BCS for three sites sampled each day of the August 2004 survey showed the least variation of the five surveys. The difference between minimum and maximum values for each of the three sites did not

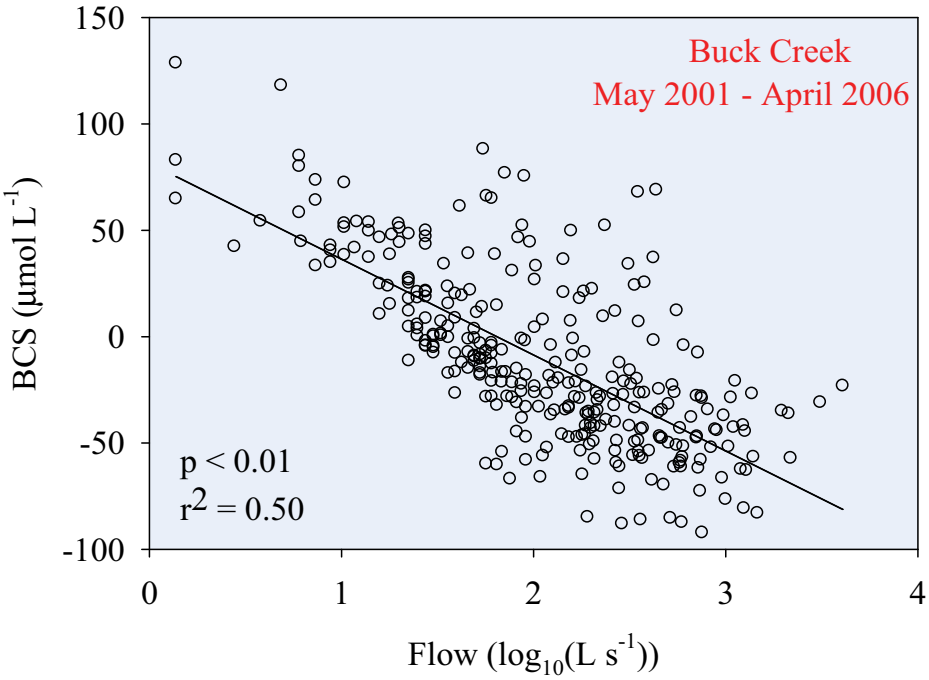


Figure 3-11. Base-cation surplus (BCS) plotted against flow, at Buck Creek, Inlet, N.Y.

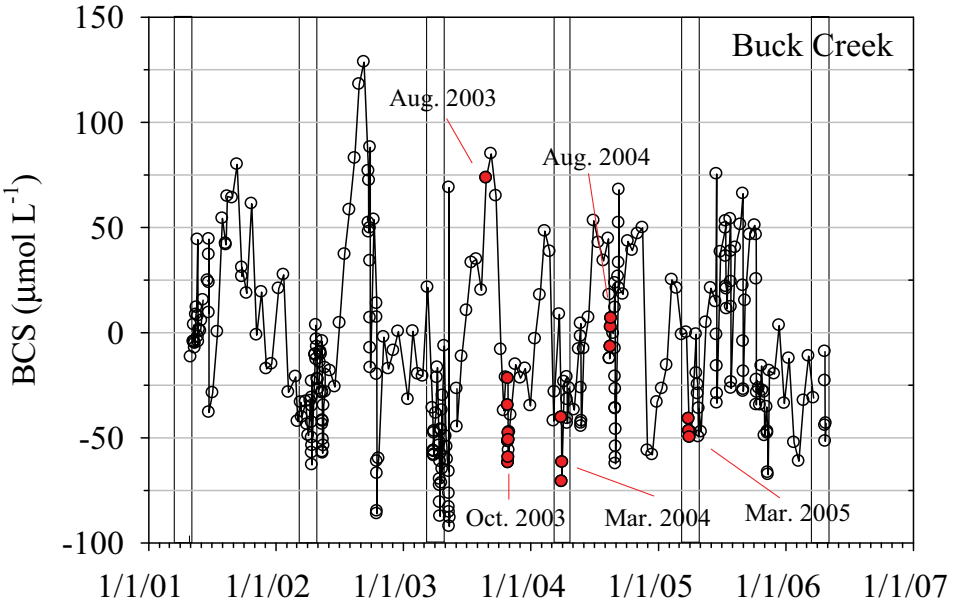


Figure 3-12. Base-cation surplus (BCS) from May 2001 to April 2006 at Buck Creek, Inlet, New York. Measurements of BCS at Buck Creek made during surveys are indicated in red. Blue bars represent the typical snowmelt period for the study region (March 15 to April 30).

exceed 14 μeq L^{-1}, although the coefficient of variation for Buck Creek (site 28630) was excessively large because the mean BCS value for the August 2004 survey was close to 0. Values of BCS at the four sites repeatedly sampled during the March 2005 survey also varied minimally. Coefficients of variation for these sites ranged from 1.4 to 11. Variability of repeated samplings in the October 2003 and March 2004 survey was somewhat higher, but a coefficient of variation of 20% was exceeded at only one site. It should be noted that the variability presented in Table 3-1 also includes data associated with the methods of analysis of the eight measurements used to calculate the BSC. These data indicate that, overall, the effects of flow were reasonably controlled by the sampling approach of this study.

Table 3-1. Summary statistics for the base-cation surplus values of streams that were sampled on multiple days of surveys conducted in October 2003, March 2004, August 2004 and March 2005. Total number of samples is indicated by n; minimum value is indicated by Min.; maximum value is indicated by Max. and coefficient of variation is indicated by C.V. Site 28630* is the Buck Creek index site.

Site Code	Dates Sampled	n	Min.	Max.	C.V.
6020	10/27-10/29/03	3	38	52	8.8
28004	10/27-10/29/03	3	182	497	35
29008	10/27-10/29/03	3	146	205	11
30012	10/27-10/28/03	2	-17	-11	18
28630*	3/29-3/31/04	3	-71	-40	16
29008	3/29-3/31/04	3	183	202	3.3
7024	3/29-4/1/04	4	27	48	14
21013	8/16-8/18/04	3	137	146	2.0
28630*	8/16-8/18/04	3	-7	7	829
29008	8/16-8/17/04	2	215	230	3.0
7019	3/29-3/31/05	3	121	127	1.4
22017	3/29-3/31/05	3	-25	-20	6.4
25013	3/29-3/31/05	2	289	378	11
28630*	3/29-3/31/05	5	-50	-38	5.9

3.2.2 Seasonal Variations of Stream Chemistry

Stream chemistry varied considerably among the five surveys (Table 3-2). Mean pH in the August 2003 survey was 6.58, which is one unit higher than in the October 2003 survey. Values of pH defining the 5th and 95th percentiles differed in the five surveys by about 2.5 to 3 units. Mean values of the BCS ranged from 29 μeq L^{-1} in the March 2004 survey to 279 μeq L^{-1} in the August 2003 survey. The August 2003 survey exhibited the largest range in BCS values among surveys; the 5th percentile was defined by -36 μeq L^{-1}, and the 95th percentile was defined by 1053 μeq L^{-1}. The smallest range in BCS values occurred in the March 2004 survey when -95 μeq L^{-1}defined the 5th percentile and 224 μeq L^{-1} defined the 95th percentile. Values of ANC_G showed similar variations, but in each survey the ranges between the 5th and 95th percentiles were smaller, and values for the 5th percentile were consistently higher than those of the BCS.

In each of the surveys, except August 2003, the mean concentration of inorganic Al (Table 3-2) equaled or exceeded the threshold value of 2 μmol L^{-1}, above which mortality can occur in young-of-the-year brook trout (Baldigo et al. 2007). Concentrations of organic Al were somewhat higher than those of inorganic Al in each of the surveys, except those conducted during spring snowmelt (March 2004 and 2005). Concentrations of inorganic Al at the 95th percentile were 13 and 12 μeq L^{-1} in the March 2004 and March 2005 surveys, respectively. Highest concentrations of total dissolved Al were measured in the October 2003 and March 2004 surveys. Concentrations of total dissolved Al were higher than the sum of inorganic and organic Al (total monomeric Al) in all surveys, which reflected the different species of Al measured by these methods.

Table 3-2. Number of streams sampled, mean flow (L s^{-1}) during sample collection (based on hourly measurements), and the mean and range (5th percentile to 95 percentile) of chemical measurements made in each of the five sampling surveys. The pH units are expressed as the negative log_{10} of H^+ concentration (in moles L^{-1}). The base cation surplus (BCS) and acid-neutralizing capacity by Gran titration (ANC_G) are expressed as μeq L^{-1}. The remaining measurements are expressed as μmol L^{-1}.

Survey Date	**Aug. 25-29 2003**	**Oct. 27-30 2003**	**Mar. 29-31 2004**	**Aug. 16-18 2004**	**Mar. 29 -Apr. 1 2005**
Number of Streams	129	196	188	195	190
Mean flow	5.2	446	255	30.2	182
pH	6.58 4.80 to 7.68	5.58 4.45 to 7.01	5.63 4.43 to 7.16	6.11 4.55 to 7.47	5.85 4.58 to 7.21
BCS	279 -36 to 1053	58 -72 to 241	29 -97 to 224	153 -73 to 604	51 -87 to 284
ANC_G	273 3 to 786	78 -32 to 251	62 -27 to 246	168 -19 to 578	74 -18 to 311
Inorganic Al	0.8 0 to 4	3 0 to 9	3 0 to 13	2 0 to 6	3 0 to 12
Organic Al	2 1 to 5	5 1 to 9	3 1 to 6	4 1 to 9	3 1 to 6
Total Dissolved Al	6 0.6 to 19	14 3 to 26	12 2 to 30	11 1 to 25	10 2 to 26
DOC	410 103 to 929	792 312 to 1350	412 147 to 693	712 142 to 1986	417 163 to 704
SO_4^{2-}	48 18 to 77	53 40 to 71	46 37 to 61	38 14 to 58	45 35 to 57
NO_3^-	17 2 to 37	6 0 to 16	36 5 to 77	6 1 to 16	31 6 to 72
Cl^-	18 4 to 57	26 9 to 77	34 5 to 49	14 4 to 50	21 7 to 56
Ca^{2+}	136 22 to 426	71 19 to 141	62 20 to 134	93 19 to 269	65 22 to 149
Mg^{2+}	45 9 to 121	23 7 to 61	19 7 to 48	31 6 to 99	22 8 to 55
Na^+	67 27 to 120	41 18 to 89	46 18 to 63	44 16 to 83	38 21 to 65
K^+	11 4 to 18	11 4 to 19	9 5 to 13	6 1 to 14	10 5 to 15
Si	204 90 to 330	117 77 to 185	105 75 to 178	158 81 to 247	120 81 to 181
NH_4^+	2 0 to 8	0 0 to 1	1 0 to 2	1 0 to 2	1 0 to 4

Total dissolved Al includes low molecular weight polymeric Al and strongly bound organic monomeric forms of Al that are not measured in the determination for total monomeric Al.

The mean concentration of DOC in the October 2003 survey was 792 μmol L^{-1}, the highest of the five surveys, although the mean value for the August 2004 survey approached this value (Table 3-2). Relatively high values of DOC concentrations in October were a likely result of leaf drop, whereas high values in August 2004 were probably due to growing season dynamics in the upper soil such as root exudation and elevated decomposition, plus relatively high base flows that reflected shallow flow paths through the soil. The low DOC concentrations during the extremely low-flow period of the August 2003 survey were likely the result of deep flow paths that sustained stream flows with ground water that had been recharged in the previous spring (Burns et al. 1998b). Concentrations of DOC during snowmelt, such as those in the two snowmelt surveys of this study, are typically low as a result of high soil water flux and a lack of organic carbon inputs after leaf drop in the previous fall. Deep flow paths also tend to remove DOC from solution more effectively than shallow flow paths through greater contact with mineral surfaces and extended residence times that increase mineralization.

Mean concentrations of SO_4^{2-} showed limited seasonal variation and only ranged from 38 to 53 μmol L^{-1} among the five surveys (Table 3-2). The largest range between the 5th percentile and the 95th percentile occurred in August 2003, and the smallest ranges occurred during the two snowmelt surveys of March 2004 and 2005. In contrast, NO_3^- concentrations showed distinct seasonal variations. Highest concentrations occurred during the March 2004 and March 2005 surveys, and lowest concentrations occurred

during the August 2004 survey and October 2003 survey. Intermediate concentrations were measured during the low flows of the August 2003 survey, which reflected some effect from ground water recharged during the previous spring when NO_3^- concentrations in soil water were high (Burns et al. 1998b). Mean concentrations of Cl^- were lowest in the August 2003 and August 2004 surveys and highest in the March 2004 survey. The range in concentrations between the 5th and 95th percentile were similar among surveys. The cause of low Cl^- concentrations in the summer is unclear.

A clear seasonal pattern in Ca^{2+} and Mg^{2+} concentrations was evident. Highest concentrations occurred during the August 2003 and August 2004 surveys, and lowest concentrations occurred during the March 2004 and March 2005 surveys (Table 3-2). Relatively low stream flows during the summer surveys were indicative of deeper subsurface flow paths than during the high-flow periods of spring snowmelt. Deeper flow paths tend to provide more opportunity for release of Ca^{2+} and Mg^{2+} to solution through the weathering of minerals than shallow flow paths through upper soils that are more heavily leached. Little or no seasonality was apparent in the concentrations of mean Na^+ and K^+ concentrations (Table 3-2). Although maximum Na^+ concentrations occurred in the August 2003 survey, Na^+ concentrations in the other four surveys were similar. Concentrations of K^+ were low in relation to the other three base cations (Ca^{2+}, Mg^{2+} and Na^+) and were similar among the five surveys (Table 3-2).

Mean concentrations of Si were highest during the August 2003 and August 2004 surveys, and they were considerably lower during the snowmelt surveys and the October 2003 survey (Table 3-2). This seasonal pattern also can be explained by the relationship between flow paths and mineral weathering, which provides the primary mechanism for

release of Si into soil solution. Relatively low stream flows in each of the August surveys reflected extended residence time within the subsoil that increases the effectiveness of weathering. Mean concentrations of NH_4^+ were near the analytical reporting limit in each of the surveys, and few streams had concentrations that exceeded 2 μmol L^{-1}.

3.2.3 Assessment of Stream Water Acidification

Streams with a BCS value < 0 μeq L^{-1} were considered to be acidified by acidic deposition because this is the threshold below which inorganic Al appears in stream water (Lawrence et al. 2007). Monitoring at Buck Creek indicated, however, that none of the surveys were conducted during the most acidic conditions of the specific year in which the survey was conducted (Figure 3-12). On several occasions during the five-year study period, BCS measurements at Buck Creek were 25 μeq L^{-1}, or more, below the lowest median value measured at Buck Creek during the sampling periods of the five surveys (Figure 3-12). Therefore, it was assumed that streams with BCS values of up to 25 μeq L^{-1} during the surveys would be likely to have BCS values below 0 μeq L^{-1} during the most acidic conditions of that year. This assumption was supported by data that showed episodic decreases in BCS were greater for samples with BCS values above 0.0 at base flow than those below 0.0 at base flow (see following section 3.2.5. *Chronic versus Episodic Acidification*). Streams with BCS values above 25 μeq L^{-1} during the March 2004 survey, the most acidic of the five surveys, were considered to not be at risk of becoming acidified even under the most acidic conditions. Therefore, the BCS value

of 25 μeq L^{-1} was considered to be the minimum value required for year-round protection from the harmful effects of inorganic Al.

The degree of stream acidification measured in the five surveys varied considerably (Table 3-3). In the March 2004 survey, when conditions were most acidic, 105 of 188 streams (56 %) had BCS values below 0 μeq L^{-1}, and 124 of 188 (66 %) had values less than 25 μeq L^{-1}. In the August 2003 survey, when conditions were least acidic, 15 of 129 streams (12 %) had BCS values less than 0 μeq L^{-1}, and 25 of 129 (19 %) had values less than 25 μeq L^{-1}.

Stream chemistry during the August 2004 and March 2005 surveys was intermediate with respect to the March 2004 and August 2003 surveys. The percentage of acidified streams during the October 2003 survey was similar to the March 2004 survey (54 % and 63 % for 0 and 25 μeq L^{-1}, respectively), although flows were considerably higher than in the March 2004 survey.

Based on the USEPA criterion for acidification of ANC_G < 0 μeq L^{-1} (Stoddard et al. 2003), 55 of 188 streams (29 %) were acidified during the March 2004 survey, and six of 129 streams (5 %) were acidified during the August 2003 survey. For each of the five surveys, approximately half the number of streams with BCS values < 0 μeq L^{-1} were found to have values of ANC_G < 0 μeq L^{-1} (Table 3-3). The number of streams with ANC_G < 50 μeq L^{-1} is also shown in Table 3-3 because this value has been previously suggested as the base flow value below which biota are at risk of being harmed at high flows by episodic acidification (Driscoll et al. 2001). Values of ANC_G fell below this threshold in 133 of 188 streams (71 %) in the March 2004 survey and in 26 of 129 streams (20 %) in the August 2003 survey.

Table 3-3. Summary of chemical conditions for the five stream surveys. Range in flow and percentage of the year with less flow (based on hourly records) are for Buck Creek, Inlet, NY. BCS refers to base-cation surplus, ANC_G refers to acid-neutralizing capacity by Gran titration, Ali refers to inorganic Al, DOC refers to dissolved organic carbon, $RCOO^-_s$ refers to strongly acidic organic anions.

Survey Date	**Aug. 25-29 2003**	**Oct. 27-30 2003**	**Mar. 29-31 2004**	**Aug. 16-18 2004**	**Mar. 29 - Apr. 1 2005**
Number of streams sampled	129	196	188	195	190
Number of streams with BCS < 0 μeq L^{-1}	15	106	105	57	70
Number of streams with BCS < 25 μeq L^{-1}	25	123	124	68	100
Number of streams with ANC_G < 0 μeq L^{-1}	6	49	55	29	36
Number of streams with ANC_G < 50 μeq L^{-1}	26	130	133	74	118
Number of streams with Ali > 2.0 (μmol L^{-1})	14	88	78	49	64
Number of streams with pH < 6.0	26	126	121	79	103
Mean SO_4^{2-} + NO_3^- (percentage of total anions)	77	66	81	62	80
Mean $RCOO^-_s$ (percentage of total anions)	20	29	16	34	17

An inorganic Al concentration of 2.0 μmol L^{-1} also has been suggested as the level above which biota can be harmed by acidification (Driscoll et al. 2001). Exposure to this concentration of inorganic Al for 30 days caused 20% mortality of fingerling brook trout (*Salvelinus fontinalis*; age < 1 year) in Adirondack streams (Baldigo et al. 2007). Concentrations of inorganic Al exceeded 2.0 μmol L^{-1} in 78 of 188 streams (41%) in the March 2004 survey, 88 of 196 streams (45%) in the October 2003 survey, but only 14 of 129 streams (11%) in the August 2003 survey. Although the number of streams with inorganic Al concentrations above the 2.0 μmol L^{-1} threshold were similar in the

October 2003 and March 2004 surveys, the range of concentrations were distributed differently (Figure 3-13). In October 2003, the percentage of streams in each

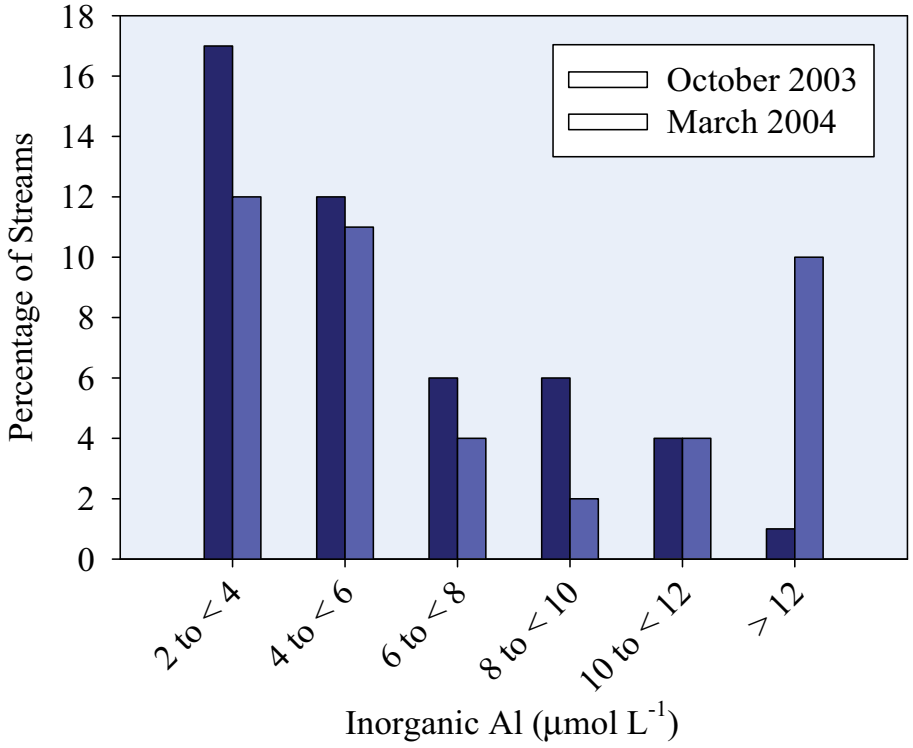


Figure 3-13. Percentage of streams with inorganic Al concentrations in one of six ranges for the October 2003 and March 2004 surveys.

concentration interval decreased as the concentration increased, and only 1% (a single stream) had a concentration that exceeded 12 µmol L^{-1}. In March 2004, the lowest percentage of streams occurred in the mid-concentration intervals, and 10% of the streams had concentrations that exceeded 12 µmol L^{-1} (16 streams). In a recent bioassay experiment at Buck Creek (Baldigo et al. 2007), inorganic Al concentrations that ranged

from 8 to 10 μmol L^{-1} resulted in 100% mortality of young-of-the-year brook trout in three days.

In each of the surveys, the number of streams with a pH value less than 6.0 was similar to the number with an ANC_G less than 50 (Table 3-3). The previous stream survey conducted in the Adirondacks in 1982 (Colquhoun et al. 1984) showed that, of the 59 streams sampled in the Oswegatchie and Black River drainages, 37 (63%) had spring pH values less than 6.0. In our March 2004 survey, 64% of the 188 sites had pH levels less than six (Table 3-3), and in the March 2005 survey, 54% of the 190 sites had a pH less than 6.0. Differences in sampling approaches preclude a direct comparison between the 1982 survey and our study, but pH values were similar.

To compare acidic deposition effects to natural sources of acidity, the concentration of strongly acidic anions resulting from acidic deposition (SO_4^{2-} plus NO_3^-) and natural organic matter (strong organic anions) were expressed as a percentage of the total concentration of strongly acidic anions (Table 3-3). Inputs of H^+ can be neutralized by cation exchange and weathering, (which release base cations or Al to solution), or cause a decrease in pH. Weakly acidic organic anions can also lower pH, but they were not included in this comparison because they also act as pH buffers and do not contribute to the mobilization of inorganic Al (Lawrence et al. 2007).

The percentage attributable to acidic deposition ranged from 62 to 81 for the five surveys. The percentage attributable to natural sources of acidity ranged from 16 to 34 and was positively related to concentrations of DOC ($p < 0.05$). Although the number of streams with a BCS value less than 0 μeq L^{-1} in the October 2003 survey was similar to that of the March 2004 survey, the contribution of natural acidity was 13% greater in the

fall than during spring snowmelt. These results indicate that acidic deposition is the major factor acidifying these streams throughout the year, but that natural sources of acidity could contribute up to approximately 30% of total strong acidity in stream water during periods of elevated DOC.

3.2.4 Chronic versus Episodic Acidification

To evaluate the relative extent of chronic and episodic acidification, results of the March 2004 survey were chosen to represent high-flow, or episodic conditions, whereas results of the August 2004 survey were chosen to represent base flow, or non-episodic conditions. A total of 189 streams were used for this comparison. Streams with a BCS value < 25 $\mu eq\ L^{-1}$ in both surveys were considered to be chronically acidified, whereas, streams with a BCS value < 25 $\mu eq\ L^{-1}$ in the March 2004 survey and > 25 $\mu eq\ L^{-1}$ in the August 2004 survey were considered episodically acidified. All streams that were acidified in the August 2004 survey also were acidified in the March 2004 survey. Results of this analysis are summarized in the list below.

- Number of streams sampled in both surveys: 189
- Number of chronically acidified streams: 67
- Number of episodically acidified streams: 57
- Number of non acidified streams: 65
- Average difference in BCS between March 2004 and August 2004 for chronically acidified sites: 24 $\mu eq\ L^{-1}$
- Average difference in BCS between March 2004 and August 2004 for episodically acidified sites: 104 $\mu eq\ L^{-1}$
- Average difference in BCS between March 2004 and August 2004 for non acidified sites: 209 $\mu eq\ L^{-1}$

Based on this classification, 67 of the 189 streams (35%) were chronically acidified, 57 streams (30%) were episodically acidified, and 65 streams (34%) were not acidified. If August 2003 had been chosen to represent base flow conditions instead of August 2004, a higher number of streams would have been classified as episodically acidic, and a lower number of streams would have been classified as chronically acidic.

In streams classified as chronically acidified, the mean BCS value was 24 μeq L^{-1} lower in March 2004 than in August 2004. In streams classified as episodically acidic, the mean BCS value was 104 μeq L^{-1} less in March 2004 than in August 2004, and in non-acidic streams the mean BCS value was 209 μeq L^{-1} lower in March 2004 than in August 2004. This comparison indicates that episodic decreases in BCS values tend to increase as base flow BCS values increase.

3.2.5 Assessment of Spatial Patterns of Stream Acidification

Results of the March 2004 survey showed a distinct spatial pattern when stream locations were related to BCS values (Figure 3-14). Most of the streams not at risk of acidification (BCS > 25 μeq L^{-1}) were located near the western edge of the study region where deep deposits of lacustrine sand and gravel underlie soil (Roy et al. 1997). Although these deposits are not rich in Ca^{2+}, they do provide extended subsurface residence time for infiltrated water, which provides greater opportunity for acid neutralization through kinetically-limited weathering of minerals. Streams tended to become more acidified in the eastward direction. Some streams not at risk of acidification occurred in the northeastern and southeastern sections of the study region in

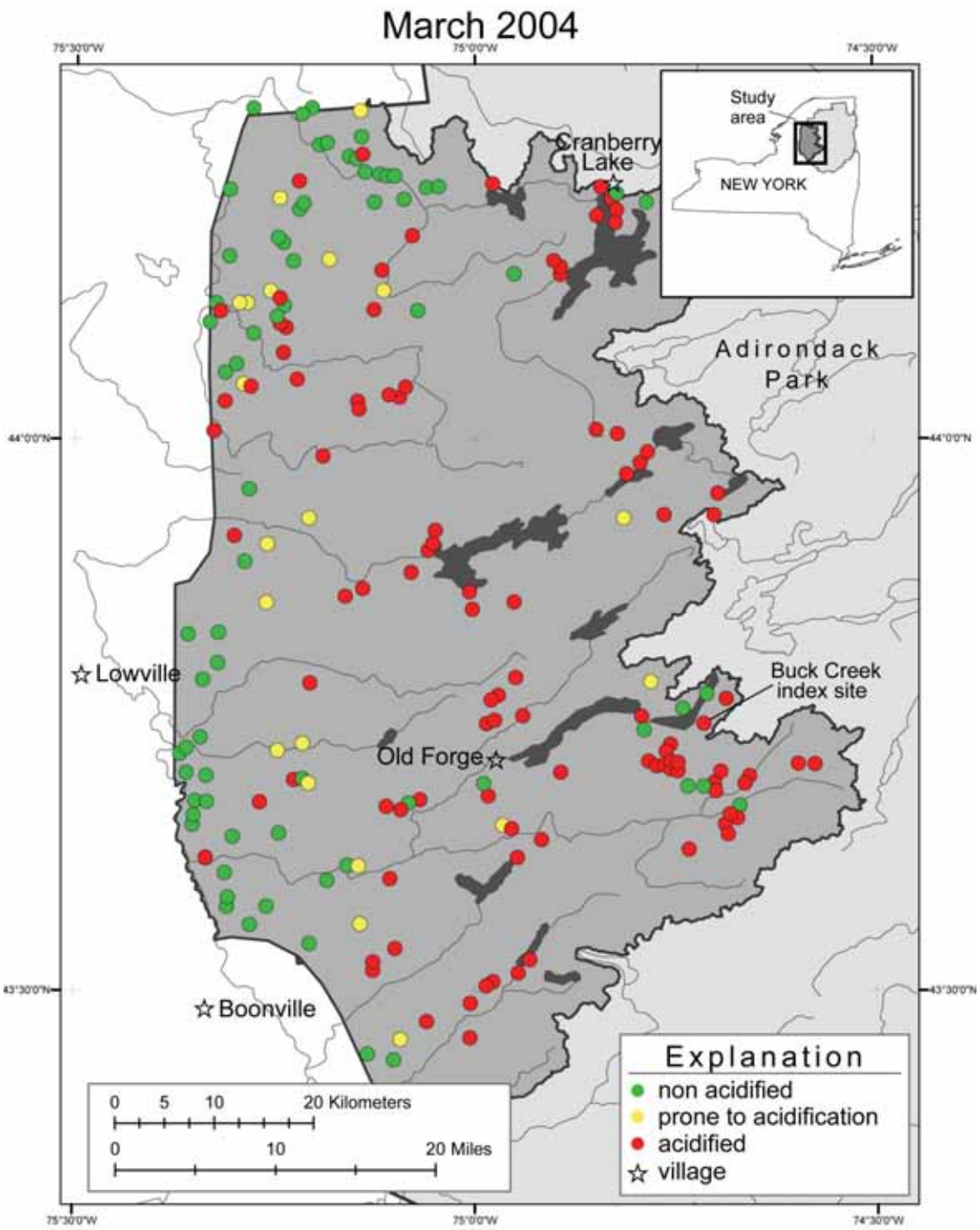


Figure 3-14. Acidification categories of sites sampled in the March 2004 survey. Non-acidified sites had base cation surplus (BCS) values > 25 μeq L^{-1}, sites prone to acidification had BCS values > 0 μeq L^{-1} but < 25 μeq L^{-1}, and acidified sites had BCS values < 0 μeq L^{-1}.

general proximity to acidified streams. This spatial pattern was likely to be a reflection of erratic deposits of calcareous till (Driscoll et al. 1990).

Many streams coded red (BCS < 0 μmol L^{-1}) and all streams coded yellow (BCS 0 – 25 μmol L^{-1}) for the March 2004 survey were coded green in the August 2004 survey (Figure 3-15). These results indicate decreased acidification during summer base flow throughout the region. The spatial pattern of increasing acidification in the easterly direction was also less evident in the August 2004 survey.

Longitudinal sampling along the reaches of 10 streams indicated a general trend of decreasing BCS values in the upstream direction (Figure 3-16). None of the streams showed an increasing trend in BCS values, although two streams showed erratic patterns that were most likely caused by deposits of non-local calcareous till. Based on these results, the assumption was made that stream chemistry did not become less acidic in the upstream direction. Therefore, if a stream sample had a BCS value > 25 μeq L^{-1}, the length of the main channel upstream from the sampling point was assumed not to be at risk of acidification. Similarly, if a stream sample had a BCS value < 25 μeq L^{-1}, the length of the main channel upstream from the sampling point was assumed to be prone to acidification. Results from the March 2004 survey were used to estimate the fraction of total accessible stream length in the study region prone to acidification. The total stream length within the study region not affected by impounded waters (based on criteria given in Section 2.2.1) was 4,322 km, of which 1,237 km were considered to be accessible for sampling. Based on the locations where stream samples were collected, a total stream length of 434 km was sampled, and 251 km (58%) were determined to be prone to acidification (BCS < 25 μeq L^{-1}). Because sampled streams were selected randomly from

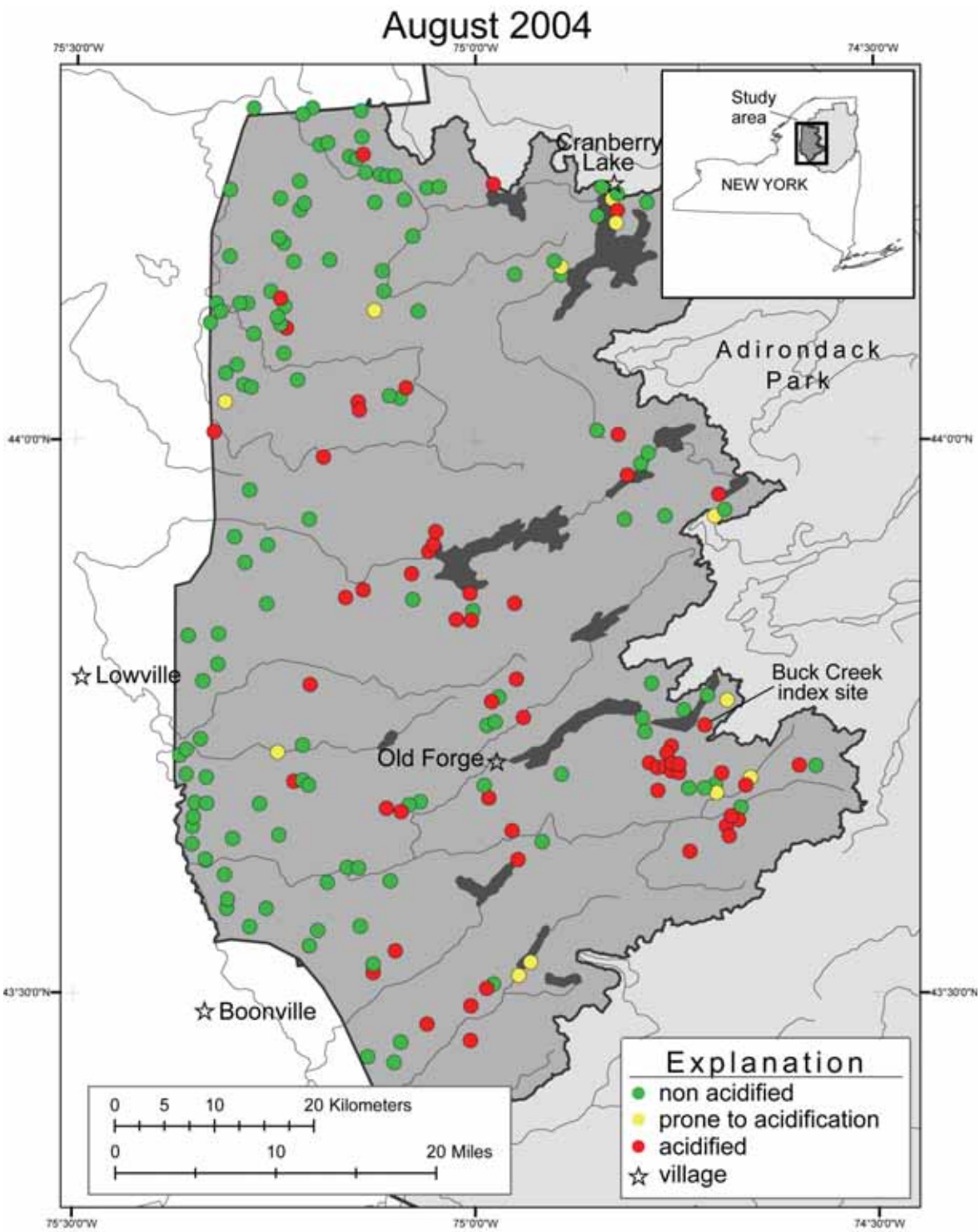


Figure 3-15. Acidification categories of sites sampled in the August 2004 survey. Non-acidified sites had base cation surplus (BCS) values > 25 μeq L^{-1}, sites prone to acidification had BCS values > 0 μeq L^{-1}but < 25 μeq L^{-1}, and acidified sites had BCS values < 0 μeq L^{-1}.

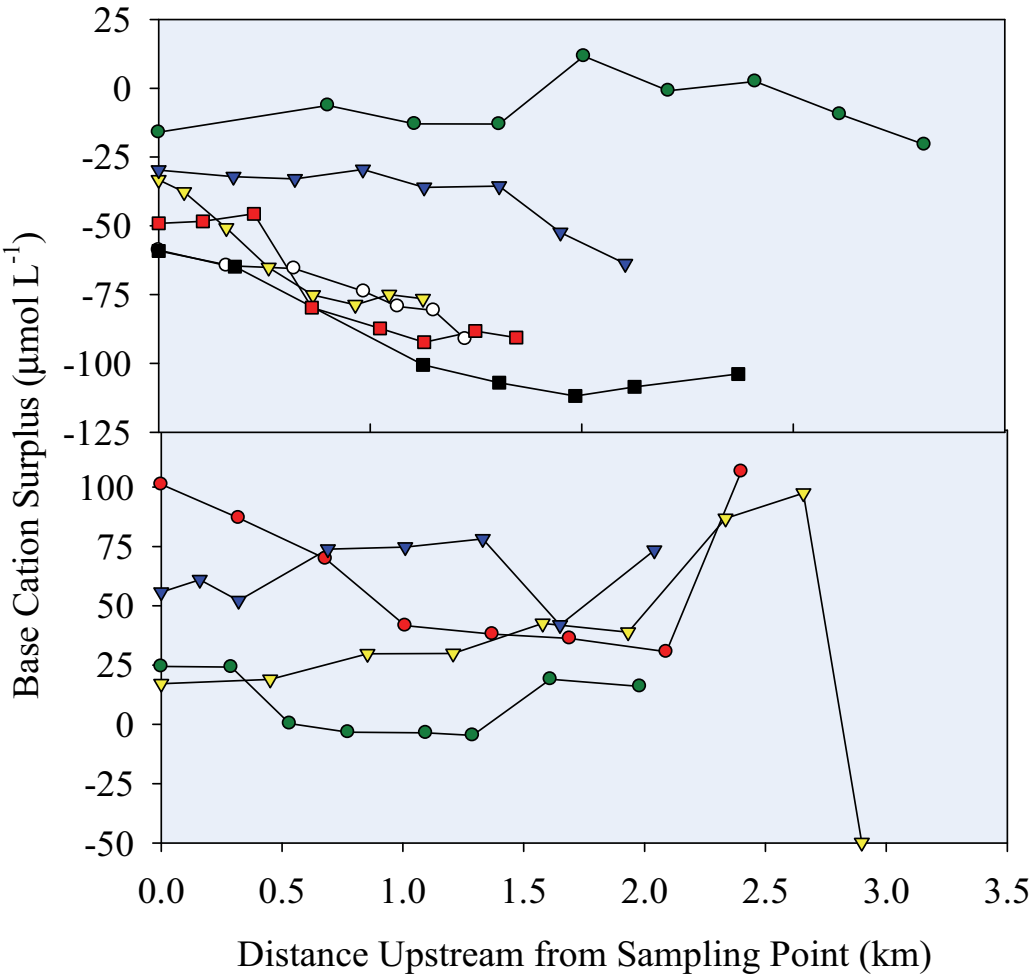


Figure 3-16. Longitudinal measurements of base cation surplus values (BCS) in 10 streams in the study region.

the population of accessible streams, the percentage of sampled stream length prone to acidification was applied to the total length of accessible streams. This resulted in an estimate of 718 km of stream reaches prone to biologically significant acidification within the study region. A remaining 3,085 km (72% of the total stream length) within the study region could not be assessed because of inaccessibility.

3.2.6 Conclusions on Effects of Acidic Deposition on Stream Chemistry

The percentage of streams with a BCS value < 0 μeq L^{-1}, averaged for all five surveys, was 38%, compared to 18% of streams with ANC_G < 0 μeq L^{-1}. The BCS percentage is consistent with the finding that 31% of streams averaged for all surveys had a concentration of inorganic Al > 2.0 μmol L^{-1}, the level above which is toxic to brook trout, a relatively acid tolerant fish species (Baldigo et al. 2007). These results indicate that the USEPA criterion for acidification of ANC_G < 0 is not suitable for protection of aquatic biota.

Assessment of the extent of acidic deposition effects on stream ecosystems requires that the temporal variability of stream chemistry be characterized because episodic acidification has been found to cause harmful effects on biota that can be similar or worse than those from chronic acidification (Baker et al. 1996, Lepori et al. 2003, Passy et al. 2006). Episodic acidification also has been identified as the possible explanation for poor biological recovery in English streams that have exhibited considerable recovery from chronic acidification (Kowalik et al. 2007). The streams sampled in this study showed considerable variability in BCS measurements that were linked to flow and season. If this assessment had been based on samples collected during summer, the extent of acidification would have been substantially underestimated. Our results demonstrated that assessing acidic deposition effects on streams on the basis of chronic acidification is not sufficient for defining the scope of the problem. Even those streams that did not acidify below a BCS value of 25 μeq L^{-1} experienced an average difference in BCS measurements of 209 μeq L^{-1} between surveys in March 2004 and

August 2004. The effects of this type of fluctuation in chemistry on aquatic ecosystems are not known.

3.3 Chemical Linkages Between Soils and Streams

Nearly all of the precipitation that passes through the forest canopy infiltrates into the soil. Some of this water moves downward below the rooting zone into the subsoil and bedrock, where it may reside from weeks to years before discharging into surface waters. During periods without precipitation or melting snow, this type of water sustains stream flow at relatively low levels with minimal variation and is generally defined as base flow. Base flow retains the chemical signature of the subsoil and bedrock that tends to provide effective buffering of acidity. During periods of heavy precipitation or snowmelt, a substantial portion of infiltrated water moves from the soil directly to surface waters. These conditions, referred to as high flow episodes, result in stream water that reflects the chemistry of the soil. Because much of the water that causes high-flow episodes passes through the soil quickly en route to the stream channel, neutralization of acidity is dependant upon rapid cation-exchange reactions that buffer decreases in the pH of soil solution through the release of bases (mostly Ca) adsorbed to particle surfaces (Lawrence 2002). Soil chemistry varies with depth, but generally, it is less effective at neutralizing acidity than subsoil and bedrock. Hourly to seasonal variations in stream chemistry can result from changes in the relative contributions of the flow paths that are producing stream flow.

3.3.1 How the Soil Profile Relates to Stream Chemistry

Soil chemistry can be highly variable in both vertical and horizontal directions, but Spodosols, the predominant soil order in the study region, exhibit distinct horizonation that produces spatial variations in soil chemistry that vary in thickness but generally are consistent downward through the soil profile. The organic layer found at the surface, referred to as the forest floor, includes the Oe and Oa horizons that are formed by decomposing leaves and woody material. Organic acids released in the decomposition process make the forest floor the most acidic layer in the soil profile. Values of pH tend to increase from the forest floor downward into the mineral soil. This

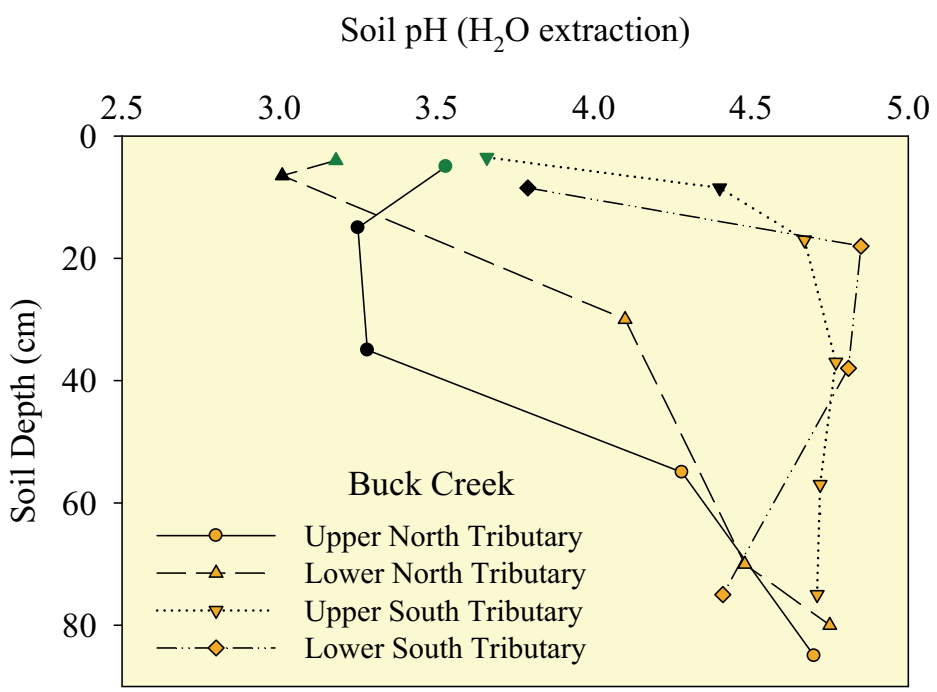


Figure 3-17. Soil pH determined by deionized water extraction at upper and lower elevation sites of the North and South Tributaries of Buck Creek. Green symbols refer to the Oe horizon, black symbols refer to the Oa horizon, and orange symbols refer to the Bs horizon.

general pattern can be seen in soil profiles from the tributary watersheds of Buck Creek. The pH values of the Oe and Oa horizons, which comprise the majority of the forest floor, ranged from 3.0 to 4.4 in the north and south tributaries of Buck Creek (Figure 3-17). Values of pH in the upper B horizon were higher than in the forest floor in each of the profiles, but they varied considerably among the four profiles (Figure 3-17). In the lower B horizon (below 60 cm depth), values for all profiles were similar, and well above pH values of the forest floor, but were nevertheless acidic, with pH values from 4.4 to 4.7.

Base saturation provides a direct measurement of the soil's ability to neutralize inputs of acidic deposition by expressing the total concentration of exchangeable bases (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) as a fraction of total cation exchange capacity (exchangeable bases plus exchangeable H^{+} and Al). Although the Oe and Oa horizons have the lowest pH within the soil profile, these horizons have the highest base saturation (Figure 3-18) because concentrations of exchangeable Ca^{2+} (and Mg^{2+}) are typically an order of magnitude higher than in the mineral horizons deeper in the profile (Figure 3-19). The relatively high concentrations of exchangeable Ca in the forest floor are due to a much higher cation exchange capacity (CEC) than in the mineral soil (a result of high organic matter concentrations) and effective vegetative recycling of Ca^{2+} and Mg^{2+}, which is accomplished by a high density of roots (Lawrence et al. 1997). Values of base saturation in Oe and Oa horizons in the Buck Creek tributaries ranged from 0.1 to 0.7, whereas values in the B horizon ranged from 0.03 to 0.1 (Figure 3-18).

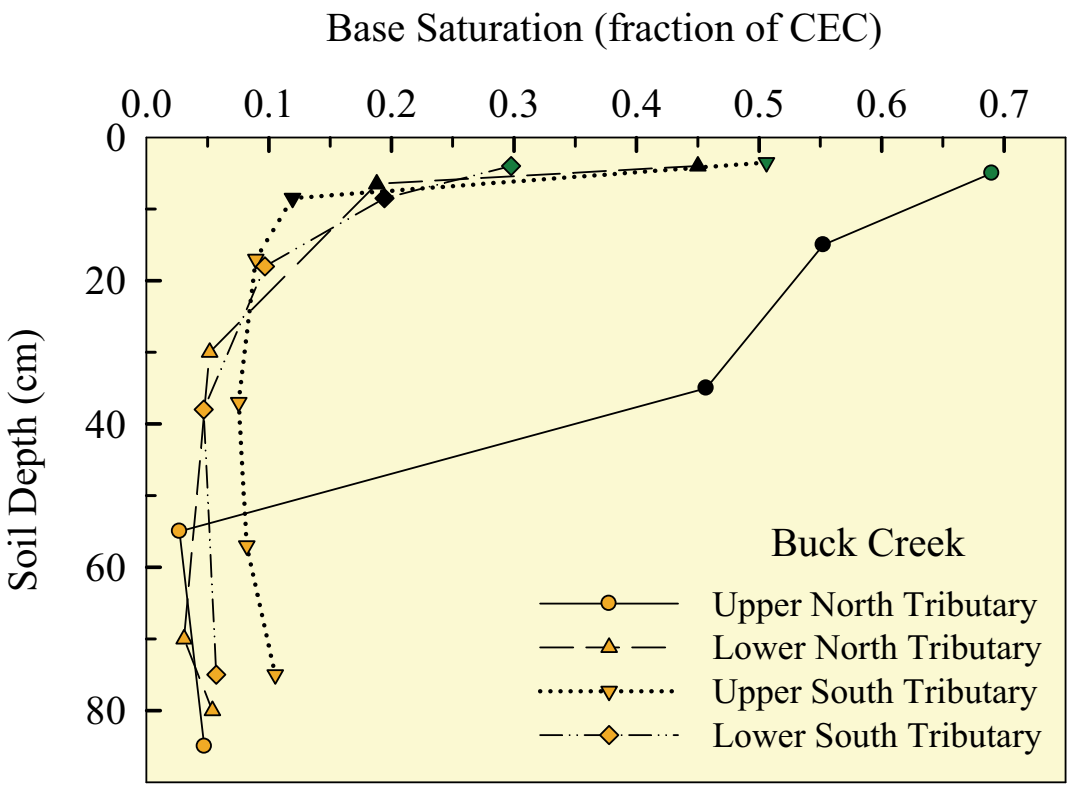


Figure 3-18. Base saturation at upper and lower elevation sites of the North and South Tributaries of Buck Creek. Green symbols refer to the Oe horizon, black symbols refer to the Oa horizon, and orange symbols refer to the Bs horizon.

Chemical variations within the soil profile need to be considered when evaluating the soil as a controlling factor of stream chemistry. When BCS values for the high-flow surveys in October 2003, March 2004, and March 2005 were related to the base saturation of the Oa horizon, statistically significant slopes were observed for each survey (Table 3-4). The linear regression models for these relationships also were similar for the three surveys. These results suggest that the relationship between high-flow BCS and the base saturation of the Oa horizon is relatively consistent during fall and spring.

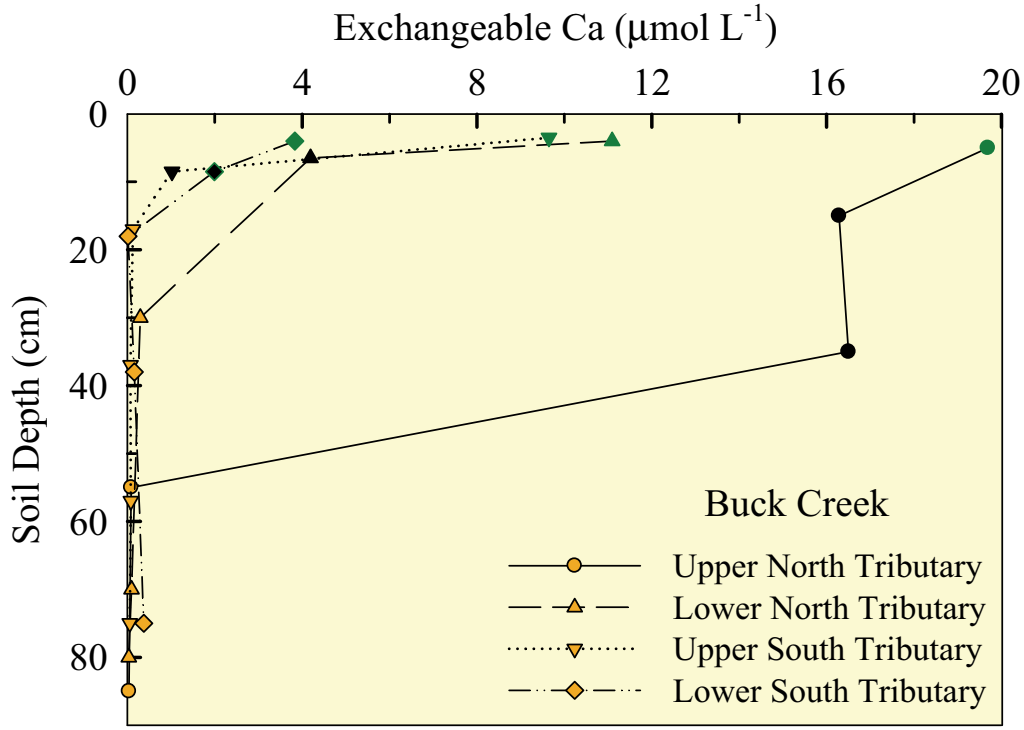


Figure 3-19. Exchangeable Ca concentrations at upper and lower elevation sites of the North and South Tributaries of Buck Creek. Green symbols refer to the Oe horizon, black symbols refer to the Oa horizon, and orange symbols refer to the Bs horizon.

The BCS values for the August 2003 and August 2004 base-flow surveys also were related to base saturation of the Oa horizon. The slopes of the relationships were less than those for the high flow surveys (Table 3-4; Figure 3-20), although the differences in slopes were not statistically significant ($p > 0.1$). In the August 2003 survey, four of the 11 streams were dry during the survey, which reduced the statistical power of the comparison. A lower slope at base flow than at high flow is likely to be a reflection of the increased importance of subsoil and bedrock flow paths during low-flow conditions.

In the upper B horizon, the relations between base saturation and the BCS of stream water were statistically significant for the high-flow surveys ($p < 0.05$) but were not related in the base-flow surveys (Table 3-4). The high-flow relation in the upper B horizon was also weaker than in the Oa horizon on the basis of explained variability (R^2) and statistically smaller ($p < 0.01$) slope values (Table 3-4; Figure 3-21). These results suggest that the Oa horizon plays a greater role than the upper B horizon in controlling the BCS and, therefore, the neutralization of acidity in stream water. Results also indicate that, in general, high-flow stream chemistry relates more strongly to both the Oa and upper B horizon than low-flow stream chemistry.

Table 3-4. Results of linear regression between soil base saturation in 11 watersheds (Oa or upper B horizon) and the base cation surplus measured in the streams of these watersheds during one of 5 stream surveys.

Base Saturation in the Oa Horizon			
Stream Survey	**Model**	**P**	**R^2**
October 2003	0.0010x + 0.34	< 0.01	0.50
March 2004	0.0012x + 0.39	< 0.01	0.68
March 2005	0.0010x + 0.37	< 0.05	0.61
August 2003	0.0005x + 0.29	< 0.10	0.56
August 2004	0.0006x + 0.34	< 0.01	0.62
Base Saturation in the Upper B Horizon			
Stream Survey	**Model**	**P**	**R^2**
October 2003	0.0004x + 0.10	< 0.05	0.40
March 2004	0.0004x + 0.12	< 0.05	0.39
March 2005	0.0004x + 0.11	< 0.10	0.36
August 2003	0.0002x + 0.10	> 0.10	-
August 2004	0.0002x + 0.10	> 0.10	-

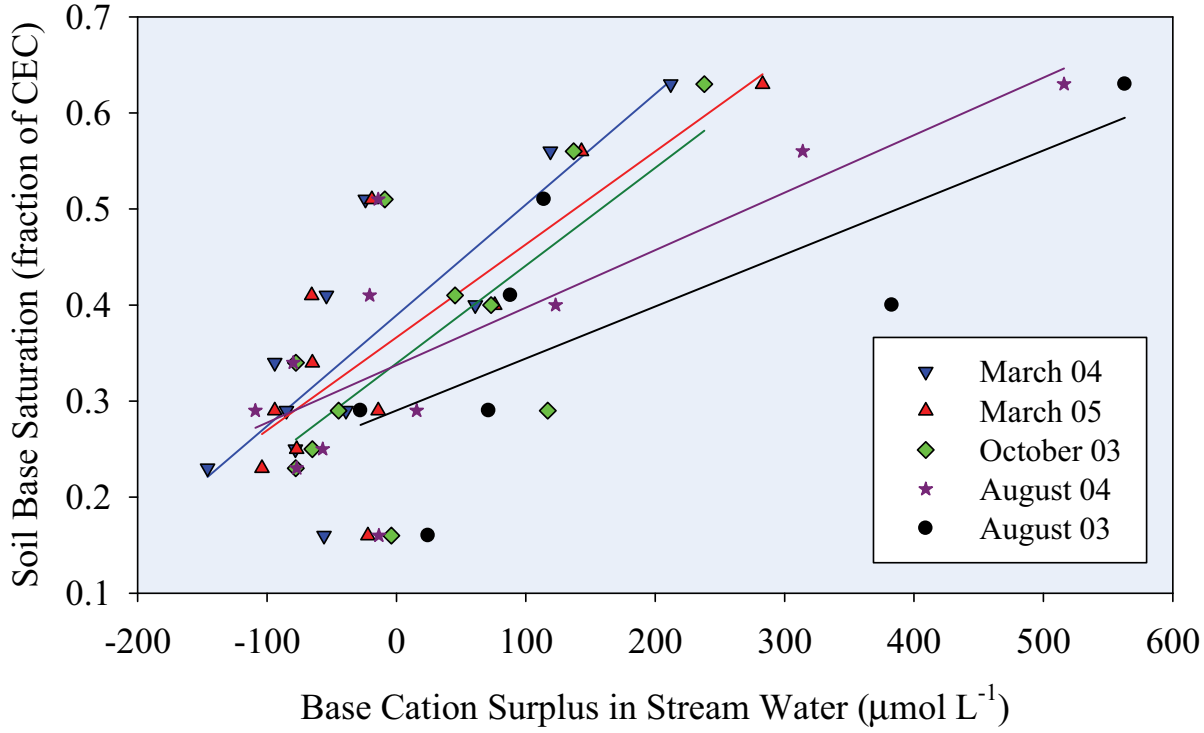


Figure 3-20. Mean soil base saturation of the Oa horizon of the 11 watersheds where soils were sampled, plotted as a function of base cation surplus in the streams of these watersheds during each of the five surveys. The best-fit line for each of the surveys is shown in the same color as the data points for the respective survey.

3.3.2 The Base Status of Western Adirondack Soils

Two previous studies in the Northeast also have investigated relationships between the base status of the upper B horizon and the neutralization of stream chemistry. The calculated ANC of stream chemistry in nine watersheds in PA, ME, NH, and NY (which included Buck Creek) was unrelated ($p > 0.10$) to the exchangeable Ca^{2+} concentration of the upper B horizon, although a strong relationship ($p < 0.01$; $R^2 = 0.84$) was observed between calculated ANC and exchangeable Ca^{2+} concentrations in the Oa horizon (Lawrence 2002). A recent assessment of soil-exchange chemistry in the Adirondack region, which included the WASS study area, also found no statistical

relationship between the ANC_G of lakes and the base saturation of the upper B horizon of the lake watersheds (Sullivan et al. 2006).

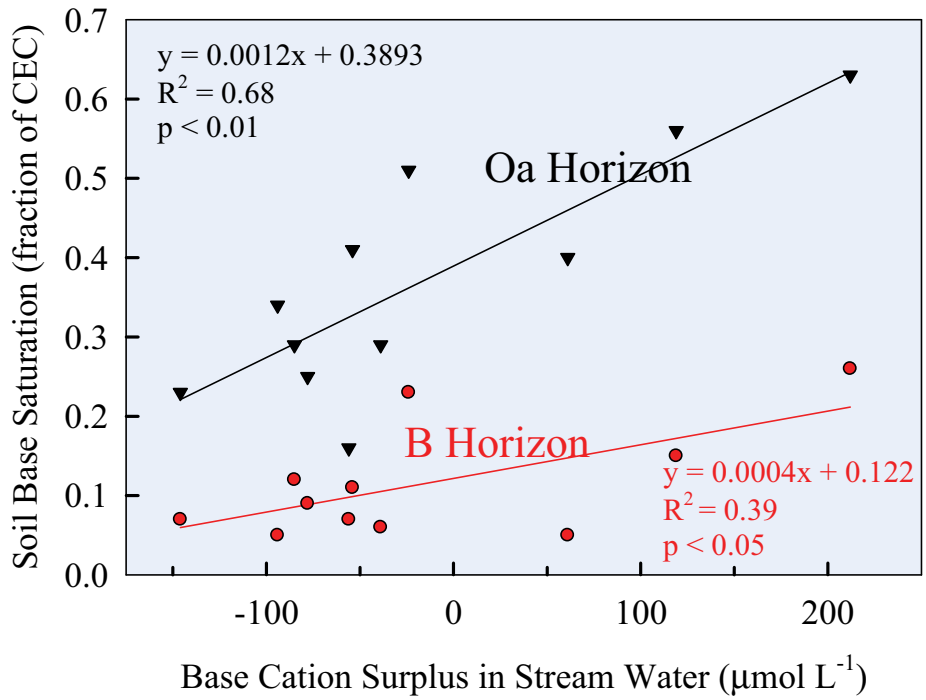


Figure 3-21. Mean soil base saturation of the Oa horizon and upper 10 cm of the Bs horizon in the 11 watersheds where soils were sampled, plotted as a function of base cation surplus in the streams of these watersheds during the March 2004 survey. The best-fit line for each soil horizon is shown in the same color as the data points for the respective horizon.

Results of the WASS study contribute to these earlier studies by showing that the upper B horizon plays a minor role in neutralization of acidic deposition. However, the primary source of Ca^{2+} in forest ecosystems generally is viewed to be weathering of parent material in the B horizon. Therefore, within the B horizon, the concentration of exchangeable Ca^{2+} is expected to reflect the weathering potential of the parent material. Nevertheless, if acidic deposition increases leaching losses to levels that exceed the rate

at which Ca^{2+} is supplied by weathering, then Ca^{2+} concentrations and base saturation will decrease.

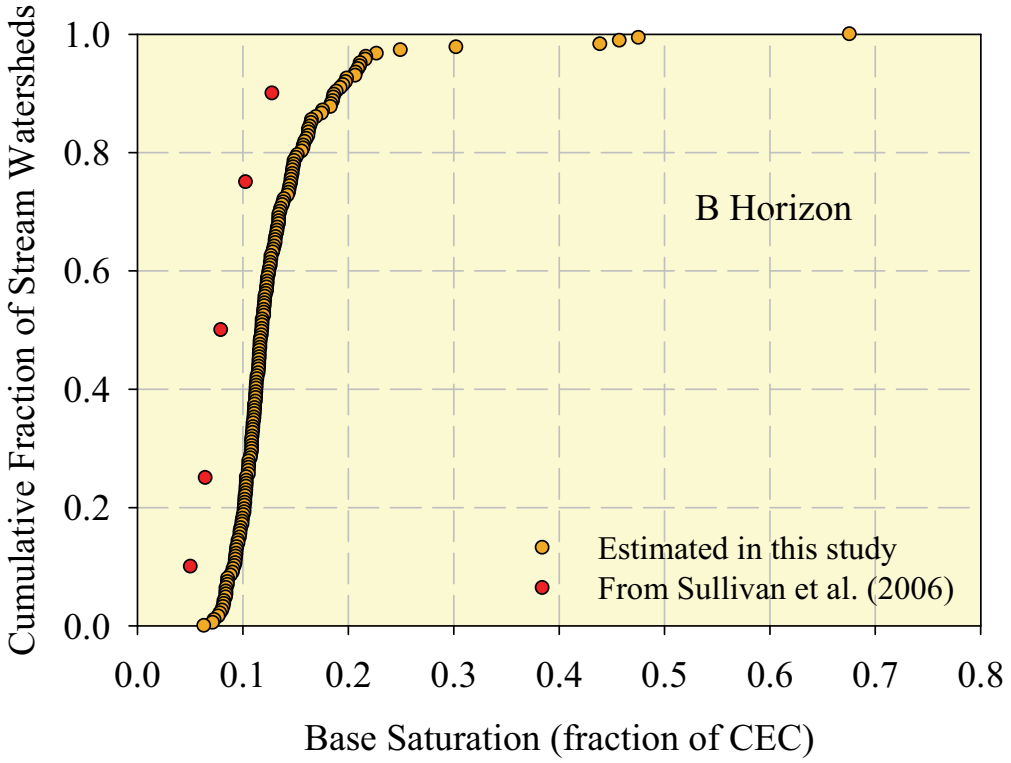
In a study of northeastern spruce forests (Lawrence et al. 1997), exchangeable Ca^{2+} concentrations (expressed as Ca saturation) were found to be only weakly related to relative weathering potential ($p < 0.05$; $R^2 = 0.44$) in the upper B horizon but strongly related to weathering potential in the Oa horizon ($p < 0.01$; $R^2 = 0.92$). In these spruce forests, base saturation of the upper B horizon was less than 14% at all sites, which suggested that high leaching rates had lowered exchangeable Ca^{2+} concentrations to levels that were no longer closely controlled by weathering of parent materials. When base saturation is less than 20%, soil solution is strongly buffered by release of exchangeable Al, and leaching of base cations is minimized (Reuss 1983). In sharp contrast, the base saturation of the Oa horizons in these spruce forests exceeded 20% and strongly reflected the Ca^{2+} weathering potential of the parent material ($p < 0.01$; $R^2 = 0.92$). The high root density of the Oa horizon promoted vegetative recycling of Ca^{2+}, which minimized leaching losses and helped to preserve the Ca^{2+} signature of the parent material.

In the context of this previous research, the weak relationship between the BCS in stream water and the base saturation of the B horizon suggests that acidic deposition has led to base depletion of this horizon in soils of the WASS study area. This conclusion is supported by a recent study in which base saturation values measured in the Adirondack region in 2003 were compared with values from this region measured in the 1980s. Results suggested that base saturation of the B horizon was lower in 2003 than in the 1980s (Sullivan et al. 2006). Other studies have presented evidence of soil Ca depletion

in N.H. (Likens et al. 1996), the Catskill Mountains of N.Y. (Lawrence et al. 1999), and western PA. (Bailey et al. 2005).

To compare WASS results to the study of Sullivan et al. (2006), base saturation was calculated for all the WASS watersheds from the relation listed in Table 3-4 for the March 2004 survey. The estimated base saturation of the B horizon for the WASS watersheds was less than 20% for 90% of the watersheds (Figure 3-22), which indicated that, in most of these watersheds, the B horizon was ineffective at buffering inputs of acidity through the release of exchangeable Ca (Reuss 1983). These data also indicated that the base saturation of the B horizon was lower in the watersheds of the

Figure 3-22. Cumulative distribution of base saturation in the B horizon of the WASS watersheds, based on BSC measurements in stream water in the March 2004 survey.



Sullivan et al. (2006) study than in those measured in the WASS study (Figure 3-22). This difference was likely to be related to methods used for selecting watersheds in the two studies. The Sullivan et al. (2006) study chose only watersheds with summer lake $ANC_G < 200$ μmol L^{-1}, whereas the WASS selection process was random with respect to stream chemistry. In the August 2004 WASS survey, 138 of 195 streams had ANC_G values > 200 μmol L^{-1}, which indicated that the WASS study population was less acidic than that of the Sullivan et al. (2006) study. Had the WASS streams been selected within the lake watersheds of Sullivan et al. (2006), a considerably higher percentage of acidic streams would likely have been the result. A comparison could not be made for the Oa horizon between WASS results and the Sullivan et al. (2006) study, in which the Oe and Oa horizons were combined prior to analysis.

3.3.3 Al Mobilization in the Soil Profile

Possible depletion of Ca^{2+} in the forest floor was not addressed in the study of Sullivan et al. (2006), but an earlier study did provide evidence of a mechanism through which acidic deposition could deplete Ca^{2+} in the Oa horizon through a buildup of exchangeable Al (Lawrence et al. 1995a). Because the Oa horizon develops from the breakdown of plant matter, and Al is not a nutrient, exchangeable Al concentrations in this horizon are expected to be low. However, inorganic Al, mobilized in the upper B horizon by acidic deposition, can move into the Oa horizon through capillary flow, upward saturated flow, and passive vegetative uptake and, in doing so, can displace Ca^{2+} in the Oa horizon (Lawrence et al. 1995a).

Movement of Al into the Oa horizon is suggested by WASS results, which show a statistically significant ($P < 0.05$; $R^2 = 0.44$) relationship between inorganic Al concentrations during the March 2004 survey and the Al saturation (exchangeable Al concentration expressed as a fraction of total CEC) of the Oa horizon (Figure 3-23). In the upper B horizon, Al saturation was high but varied over a narrow range, and it was unrelated ($P > 0.10$) to inorganic Al concentrations in stream water (Figure 3-24). High values of Al saturation in the upper B horizon provide the opportunity for transport of Al

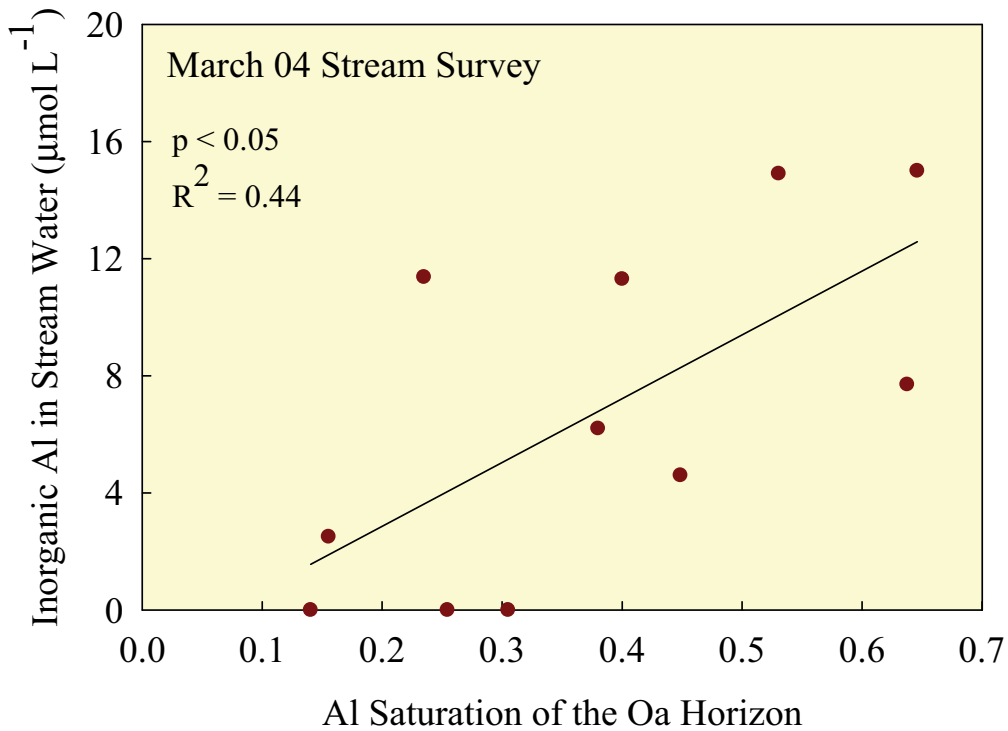


Figure 3-23. Concentrations of inorganic Al during the March 04 survey in streams of the 11 watersheds where soils were sampled, plotted as a function of exchangeable Al concentrations in the Oa horizons (expressed as a fraction of cation-exchange capacity) of these watersheds.

into the Oa horizon in all of the watersheds. Those soils that had the highest Al saturation may receive the greatest upward water flux during saturated conditions. Upward water flux tends to occur in subsurface convergence areas where water can

discharge into surface depressions that connect with ephemeral and perennial stream channels during high-flow conditions. This flow path provides a mechanism for the relationship between Al saturation in the Oa horizon and the concentration of inorganic Al in stream water. The accumulation of exchangeable Al in surface organic horizons from lateral and upward movement of subsurface water has been observed in previous studies in landscapes similar to the WASS study area (Mulder et al. 1991, Pellerin et al. 2002).

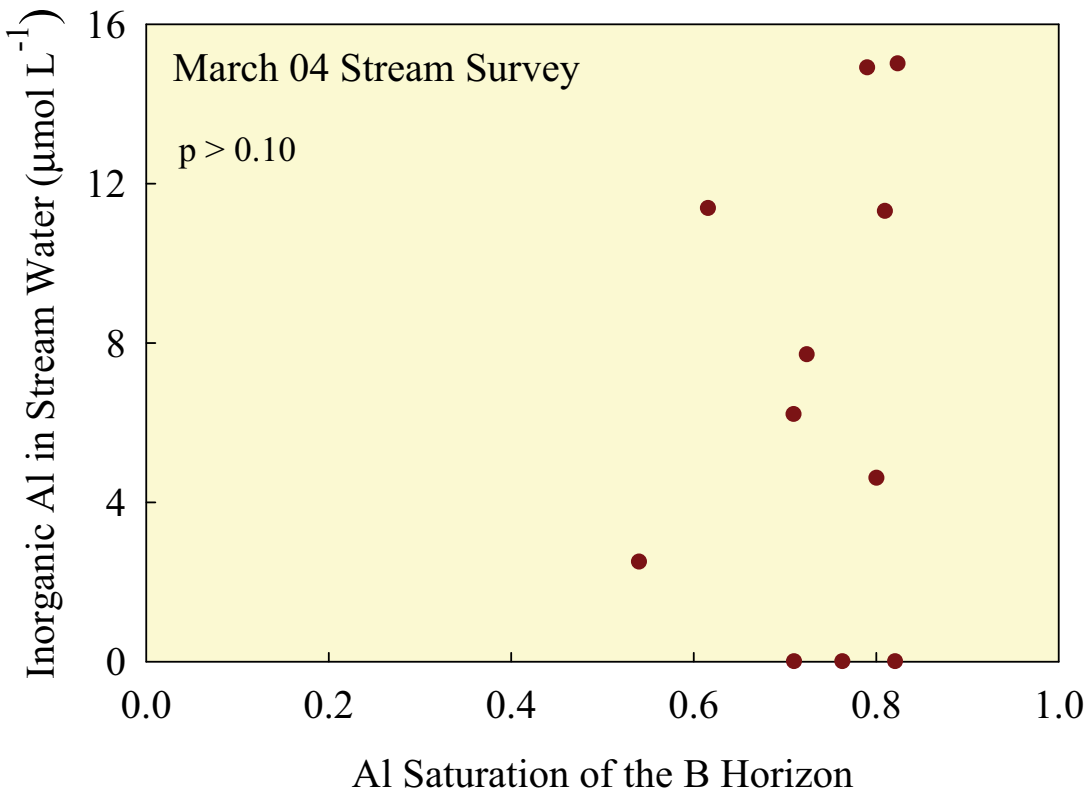


Figure 3-24. Concentrations of inorganic Al during the March 04 survey in streams of the 11 watersheds where soils were sampled, plotted as a function of exchangeable Al concentrations in the B horizons (expressed as a fraction of cation-exchange capacity) of these watersheds.

3.3.4 Conclusions on Chemical Linkages Between Soils and Streams

The low-base saturation values in the B horizon estimated for most of the WASS watersheds is reflected in the ineffectiveness of this horizon in buffering the acidity of soil water. Furthermore, the acidification of the B horizon may be increasing exchangeable Al concentrations in the Oa horizon, which is currently providing most of the buffering of stream water during high flow. Without an increase in base saturation of the B horizon, movement of Al into the Oa horizon is likely to continue. These results have implications for the chemical recovery of both the streams and the soils of these watersheds. Acidic deposition will need to be reduced to levels at which Ca leaching rates become less than the rate at which Ca is released from mineral weathering, if base saturation of the B horizon is to increase. Because estimates of weathering rates have a high degree of uncertainty, the recovery potential of the B horizon in these watersheds is unclear. Without recovery of the base saturation of the B horizon, the degree to which the Oa horizon can continue to neutralize soil water and reduce mobilization of inorganic Al also is unclear. Nevertheless, the interaction between the Oa and B horizons will continue to play a large role in controlling high-flow stream chemistry. Modeling efforts to predict recovery trajectories for Adirondack surface waters are currently based on exchange chemistry for only the B horizon. The role of the Oa horizon needs to be considered for incorporation into models of soil and surface water recovery that are being applied to this region.

3.4 Diatoms as Indicators of Acidification

Diatoms have the largest number of species of any group of benthic algae and are among the best indicators of stream water quality because of their sensitivity to a broad range of environmental impacts (Passy et al. 2004). Their ability to reproduce rapidly also provides greater temporal resolution than higher life forms such as macroinvertebrates or fish. Diatoms are abundant in all aquatic habitats, possess a silica shell that is not easily damaged, and usually can be identified to the species level. The use of diatoms in assessing acid rain effects is well established (Dixit et al. 1992). The optimum pH for most of the common species has been determined (Lowe 1974), and varying sensitivity to Al has been documented for some species (Gensemer and Playle 1999). Recently, data from the tributaries of Buck Creek showed that species richness and diversity were higher in the chronically acidic stream with high DOC concentrations (North Tributary) than in the nearby episodically acidic stream (South Tributary) with low concentrations of DOC but with a high ratio of inorganic to organic Al (Passy et al. 2006).

3.4.1 Diatom Assessment Results

Rich diatom flora encompassing 186 species was observed in the study streams (Table 3-5). The acidity index (ACI) was calculated for all diatom samples collected during the four surveys: August 2003, October 2003, March 2004, and August 2004. Rare species with less than 2% relative abundance were excluded from the analyses. From the remaining species, 24% were identified as acidobiontic or acidophilous, comprising between 0 and 100% of the species across samples (ACI range between 0 and 1). The mean ACI values for

the October 2003, August 2004, and March 2004 surveys only ranged from 0.71 to 0.72 but were significantly higher ($p \leq 0.05$) than the value of 0.62, which was measured in the August 2003 survey (Figure 3-25).

The ACI values combined for the four surveys showed strongly non-linear responses to pH, BCS, and inorganic Al, which were subsequently modeled by regression trees. It was determined that along both pH and BCS gradients, four nearly identical groups of streams could be discriminated in terms of diatom response (Figures 3-26, 3-27). These groups were defined by 1) pH < 5.8 and BCS < 10 with mean ACI of 0.94; 2) 5.8 < pH < 6.3 and 10 < BCS < 75 with mean ACI of 0.73; 3) 6.3 < pH < 7.0 and 75 < BCS < 221 with mean ACI of 0.54; and 4) pH > 7.0 and BCS > 221 with mean ACI of 0.25. There were two ACI groups with respect to inorganic Al—sites with inorganic Al > 0.8 and mean ACI of 0.92 and sites with inorganic Al < 0.8 and mean ACI of 0.51 (Figure 3-28).

Table 3-5. Common diatom species with relative abundance > 2% in at least one sample. Max = maximum and Avg = average percentage relative abundance across all surveys. Diatoms with acid tolerance (AT) are indicated by "+".

No	Species	Acronym	AT	Max%	Avg%
1	*Achnanthes bioretii*	Achbio		4	0
2	*A. exigua et var. constricta*	Achexi		18	0
3	*A. flexella*	Achfle		3	0
4	*A. laevis*	Achlae		6	0
5	*A. lanceolata*	Achlan		26	1
6	*A. lapidosa*	Achlap	+	32	0
7	*A. laterostrata*	Achlat		3	0
8	*A. marginulata*	Achmar	+	39	1
9	*A. minutissima et vars + A. linearis*	Achmin		80	9
10	*A. peragalli*	Achper		19	0
11	*A. subatomoides*	Achsub	+	7	0
12	*A. stewartii*	Achste		2	0
13	*Actinella punctata*	Actpun	+	4	0
14	*Amphora lybica + A. ovalis*	Amplyo		2	0
15	*A. pediculus*	Ampped		6	0

16	*Anomoeoneis brachysira*	Anobra	+	40	0
17	*A. serians var. acuta*	Anoser	+	2	0
18	*A. vitrea*	Anovit		17	0
19	*Asterionella formosa*	Astfor		11	0
20	*Aulacoseira distans*	Auldis	+	48	1
21	*A. valida*	Aulval		3	0
22	*Cavinula cocconeiformis*	Cavcoc		3	0
23	*C. pseudoscutiformis*	Cavpse		6	0
24	*Cocconeis disculus*	Cocdis		8	0
25	*C. placentula*	Cocpla		65	1
26	*Cymbella cuspidata*	Cymcus		6	0
27	*C. aspera*	Cymasp		3	0
28	*C. delicatula*	Cymdel		4	0
29	*C. gracilis*	Cymgra	+	3	0
30	*C. microcephala*	Cymmic		4	0
31	*C. naviculiformis*	Cymnav		5	0
32	*C. subcuspidata*	Cymsub		2	0
33	*Decussata placenta*	Decpla		4	0
34	*Diadesmis contenta*	Dsmcon		31	0
35	*D. gallica*	Diagal		2	0
36	*Diatoma anceps*	Diaanc		25	1
37	*D. mesodon*	Diames		53	1
38	*D. vulgare*	Diavul		5	0
39	*Diploneis elliptica*	Dipell		5	0
40	*Encyonema minuta*	Cymmin		5	0
41	*E. silesiacum*	Cymsil		14	0
42	*Eunotia bilunaris*	Eunbln	+	78	13
43	*E. exigua*	Eunexi	+	76	8
44	*Eunotia spp*	Eunspp	+	72	14
45	*Fragilaria capucina et vars*	Fracap		52	2
46	*F. construens et var. venter + F. pinnata*	Fracon		57	2
47	*F. leptostauron*	Fralep		12	0
48	*Fragilariforma spp (F. virescens + F. constricta et vars)*	Ffospp	+	86	13
49	*Frustulia rhomboides et var. amphipleuroides*	Frurho	+	65	5
50	*F. vulgaris*	Fruvul		6	0
51	*Geissleria decussis*	Geidec		4	0
52	*Gomphonema acuminatum*	Gomacu		2	0
53	*G. angustatum et var. productum*	Gomang		24	2
54	*G. clavatum*	Gomcla		3	0
55	*G. parvulum*	Gompar		19	1
56	*G. pumillum*	Gompum		11	0
57	*G. truncatum*	Gomtru		4	0
58	*Melosira varians*	Melvar		44	0
59	*Meridion circulare et var. constrictum*	Mercir		70	4
60	*Navicula angusta*	Navang	+	3	0

61	*N. capitata*	Navcpt		2	0
62	*N. capitatoradiata*	Navctr		3	0
63	*N. cryptocephala*	Navcry		16	0
64	*N. cryptotenella*	Navten		7	0
65	*N. elginensis*	Navelg		2	0
66	*N. globulifera*	Navglo		2	0
67	*N. gregaria*	Navgre		6	0
68	*N. heimansii*	Navhei	+	3	0
69	*N. lanceolata*	Navlan		16	0
70	*N. mediocris*	Navmed	+	6	0
71	*N. rhynchocephala*	Navrhy		2	0
72	*N. soehrensis et var. hassiaca*	Navsoe	+	13	0
73	*N. subtilissima*	Navsub	+	4	0
74	*N. tripunctata*	Navtri		5	0
75	*Neidium densestriatum*	Neiden	+	4	0
76	*N. iridis*	Neiiri		3	0
77	*Nitzschia acicularis*	Nitaci		24	0
78	*N. dissipata*	Nitdis		19	0
79	*N. linearis*	Nitlin		27	0
80	*N. nana*	Nitnan		26	0
81	*N. palea*	Nitpal		3	0
82	*N. paleacea*	Nitpca		40	0
83	*Pinnularia appendiculata*	Pinapp	+	5	0
84	*P. gibba*	Pingib		4	0
85	*P. microstauron*	Pinmic		3	0
86	*P. schoenfelderii*	Pinsch		2	0
87	*P. subcapitata*	Pinsub	+	15	0
88	*P. viridis*	Pinvir		3	0
89	*Reimeria sinuata*	Reisin		3	0
90	*Rhoicosphenia curvata*	Rhocur		22	0
91	*Sellaphora pupula et var. rectangularis*	Selpup		8	0
92	*Stauroneis anceps*	Stnanc		2	0
93	*S. phoenicenteron*	Stnpho		2	0
94	*S. smithii*	Stnsmi		6	0
95	*Stenopterobia delicatissima*	Stedel	+	7	0
96	*Surirella amphioxys*	Suramp		3	0
97	*Synedra acus et var. angustissima*	Synacu		5	0
98	*S. ulna et var. amphirhynchus*	Synuln		43	1
99	*Tabellaria fenestrata*	Tabfen	+	58	4
100	*T. flocculosa*	Tabflo	+	71	8

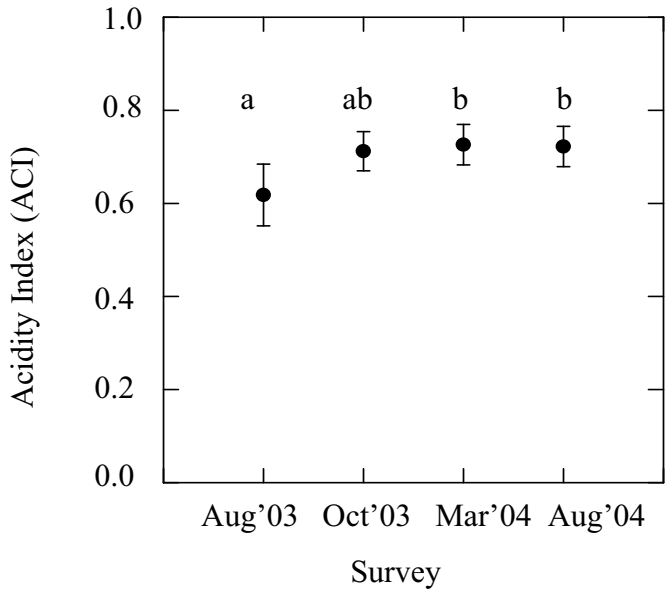


Figure 3-25. Variations of the mean diatom Acidity Index (ACI) for the four surveys in which diatoms were collected. Surveys with significantly different means ($p < 0.05$) were marked with different letters.

The ACI range was divided into groups using the classification provided by the regression trees. Sites with ACI < 0.40 were considered non-impacted because they were found at pH ≥ 7.0, corresponding to the first group in Figure 3-26, with a mean ACI of 0.22 (±0.19 SD). The BCS levels (Figure 3-27) at the non-impacted streams were high, > 221, and the inorganic Al levels were low < 0.8 (Figure 3-28). The next two groups along the pH gradient, with an ACI of 0.54 (±0.25 SD) and 0.73 (±0.19 SD), exhibited highly overlapping confidence intervals and, therefore, were combined. This group, with 0.40 ≤ ACI <0.85, represented the moderately impacted communities, occurring at 7.0 > pH > 5.8, 221 < BCS ≤ 10, and inorganic Al < 0.8. Streams where diatom communities were composed of ≥ 85% acidophilous species were considered severely impacted. The environmental characteristics of these streams included pH < 5.8, BCS < 10 and inorganic Al > 0.8. The diatom communities in this group had a mean ACI value of 0.94, with a standard deviation of 0.08.

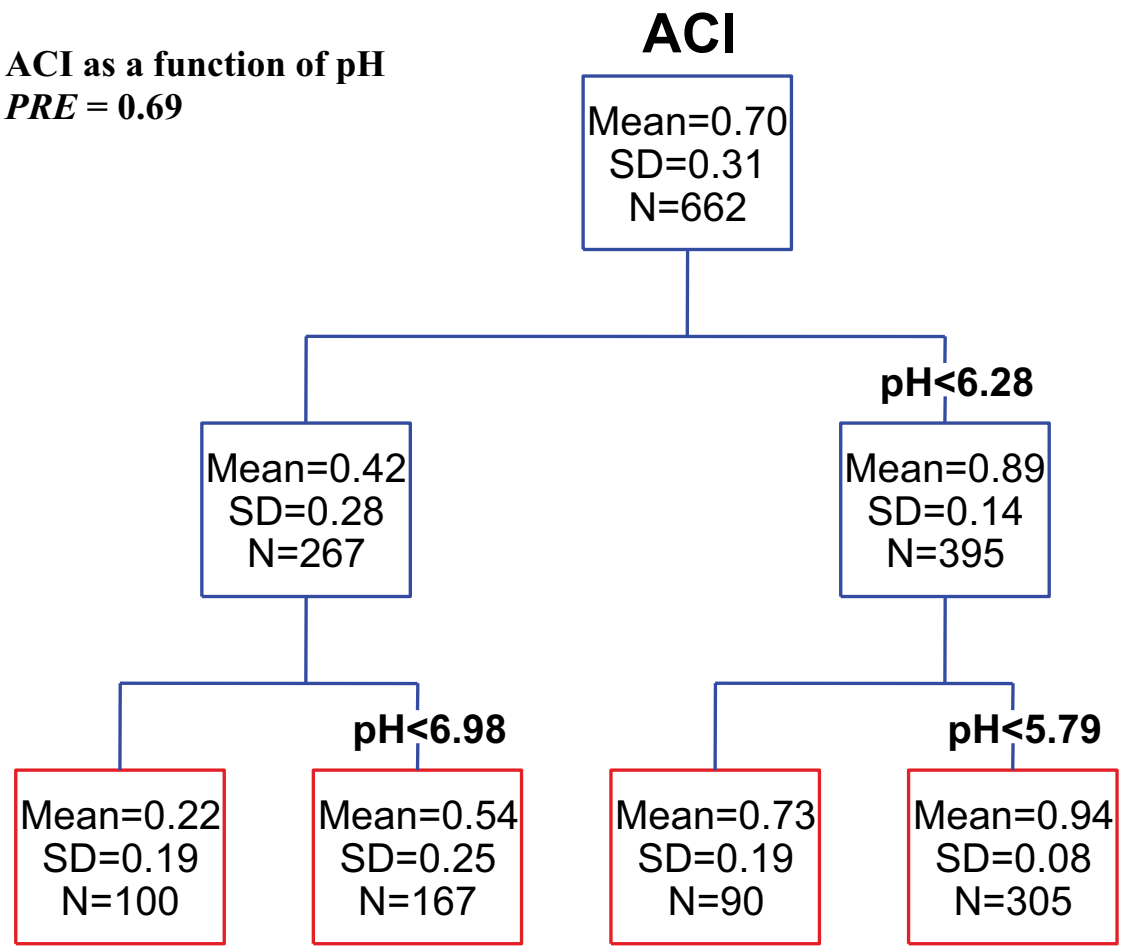


Figure 3-26. Regression trees of the Acidity Index (ACI) as a function of pH, derived from the complete dataset of diatom samples and water chemistry. *PRE* = Proportional reduction in error, SD = standard deviation, N = number of samples.

The three groups of streams were compared across sampling surveys (Figure 3-29). The number of severely impacted streams (between 44 and 54% of all sites) exceeded the number of streams within the other two categories in all four surveys. The number of non-impacted streams was the highest (34%) in the least acidic survey, August 2003, whereas in the other three surveys this percentage was less than 20% of all sites. The number of moderately impacted streams was the lowest in August 2003.

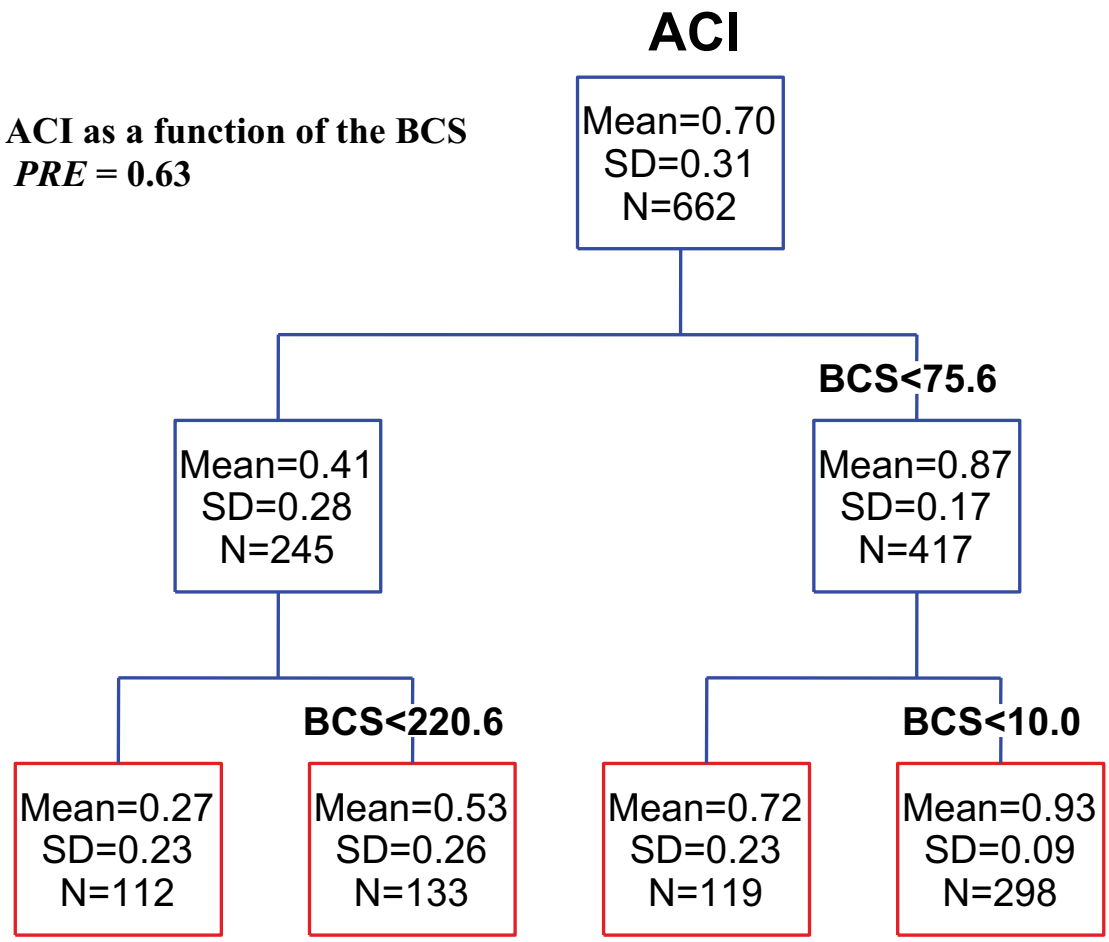
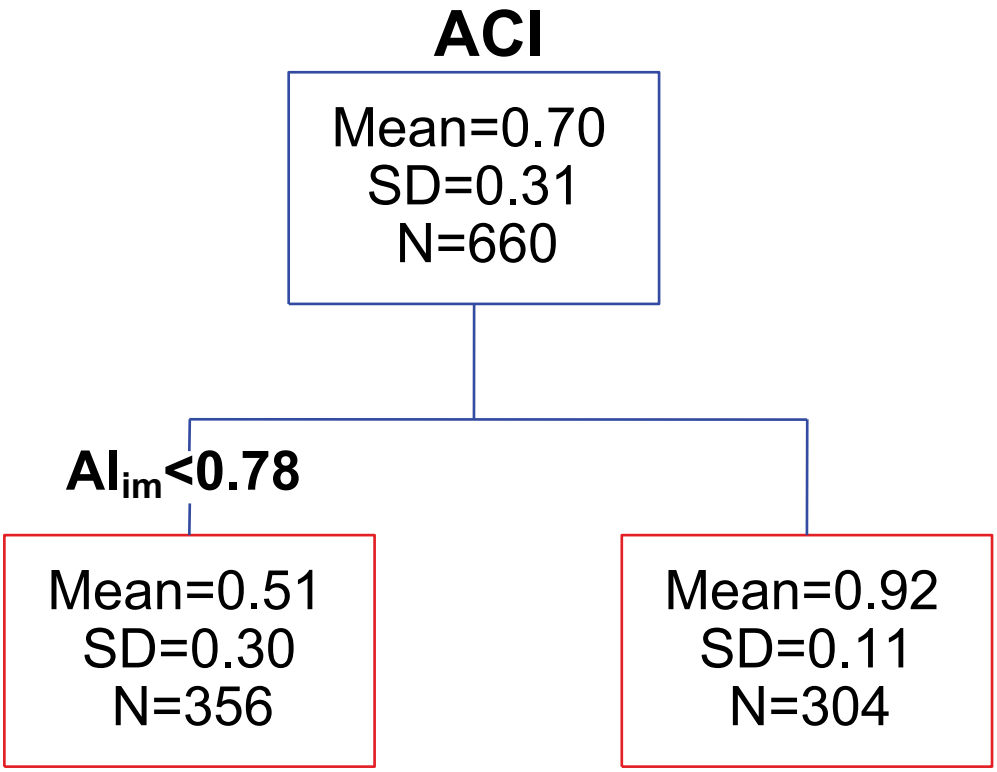


Figure 3-27. Regression trees of the Acidity Index (ACI) as a function of the base cation surplus (BCS), derived from the complete dataset of diatom samples and water chemistry. *PRE* = Proportional reduction in error, SD = standard deviation, N = number of samples.

The RDA values of diatom data and forward selection of the environmental variables including total Al, inorganic Al, organic Al, the ratio of inorganic Al to organic Al, BCS, Ca^{2+}, Cl^{-}, DOC, color, K^{+}, Mg^{2+}, Na^{+}, NH_4^{+}, NO_3^{-}, pH, SiO_2, and SO_4^{2-} produced similar results in the four surveys (Figures 3-30 to 3-33). Only four to five environmental variables captured most of the variance in diatom data and were retained as explanatory variables. Color was the only measurement that was retained as an explanatory variable in all four

surveys. Color is closely related to DOC concentration and, therefore, to organic acidity, but it is unclear why color rather than DOC concentration was selected in the model.



ACI as function of inorganic Al (Al_{im})
***PRE* = 0.44**

Figure 3-28. Regression trees of the Acidity Index (ACI) as a function of inorganic Al (Al_{im}), derived from the complete dataset of diatom samples and water chemistry. *PRE* = Proportional reduction in error, SD = standard deviation, N = number of samples.

The first axis (RDA1) explained between 15 and 21% of the variance in the four surveys (Figures 3-30 to 3-33) and represented a strong pH gradient with sensitive species positioned on the high end (right of the plot) and tolerant species on the low end of the axis

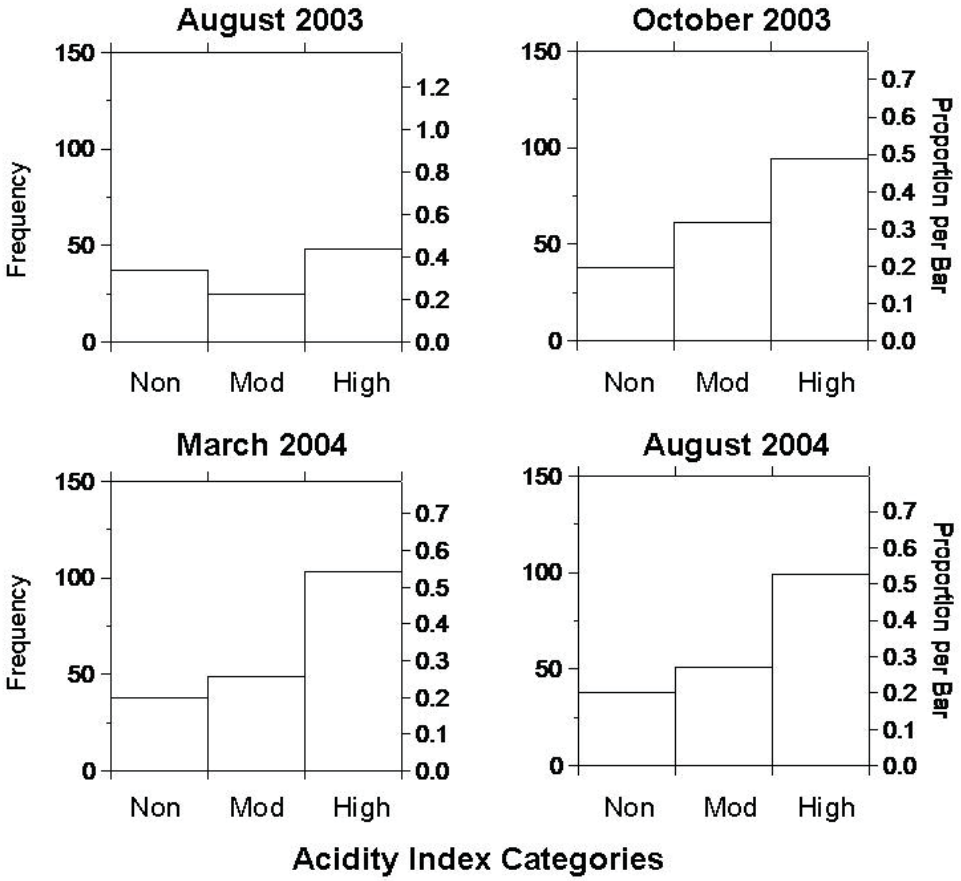


Figure 3-29. Frequency distributions of acid impact, based on Acidity Index values for the four diatom surveys. Non = non-impacted, Mod = moderately impacted, High = severely impacted.

(left of the plot). In all but one survey, pH was the environmental factor with the highest score on RDA1. In August 2003, Ca^{2+} was most closely correlated with RDA1 (Figure 3-30), but since it was strongly related to pH in this survey (Pearson $r = 0.89$, $r < 0.00001$), it constituted the same gradient. In all surveys, one or several forms of Al had the lowest score on RDA1. The species with the highest positive score on RDA1 were the species found at high pH values, including *Achnanthes minutissima*, followed by representatives of *Cocconeis*, *Fragilaria*, *Meridion*, *Navicula*, *Nitzschia*, and *Synedra*, all of which prefered circumneutral or alkaliphilous conditions (Table 3-5). The species with the lowest scores on

RDA1 included the acid-tolerant *Eunotia bilunaris*, followed by *Tabellaria fenestrata*, *Frustulia rhomboides*, and *Pinnularia subcapitata*. The abundance of these species was positively correlated with Al; these diatoms were among the most tolerant to high levels of Al, especially the more toxic inorganic form. Similar results were reported for the chronically acidified North Tributary of Buck Creek, where *E. bilunaris* dominated the diatom flora in periods of high inorganic acidity (Passy 2006).

The second RDA axis (RDA2) explained 5-8% of the variance and was associated with color and inorganic Al (Figures 3-30 to 3-33). Generally, the measurements of color and inorganic Al plotted in different quadrants, which reflected opposing relations.

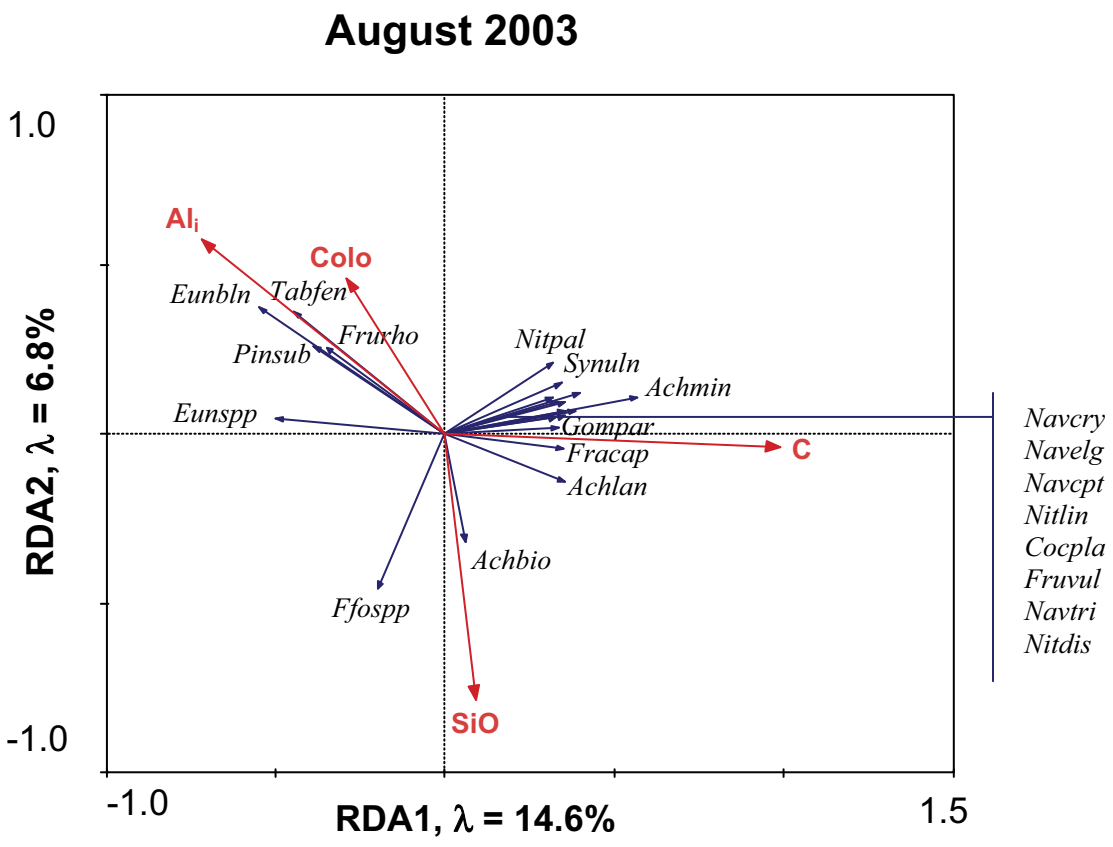


Figure 3-30. Redundancy analysis (RDA) ordination biplots of diatom species and environmental variables in the August 2003 survey. Species acronyms are given in Table 3-5. λ = percentage of explained variance.

This result is expected because color is closely tied to DOC concentrations, which tend to lower inorganic Al concentrations. The August 2003 collection was an exception—inorganic Al and color both had high positive scores on the RDA2 axis and were highly correlated with the acid-tolerant species *E. bilunaris* (Figure 3-30). SiO_2 was correlated with the acid anions (NO_3^-, Cl^-, SO_4^{2-}) and had the most negative score on RDA2.

Members of the genus *Fragilariforma*, which prefer slightly acidic conditions, had the lowest scores on RDA2 and were most strongly correlated with SiO_2 in this survey. These results suggest that the main source of high acidity in August 2003 was organic, and the most

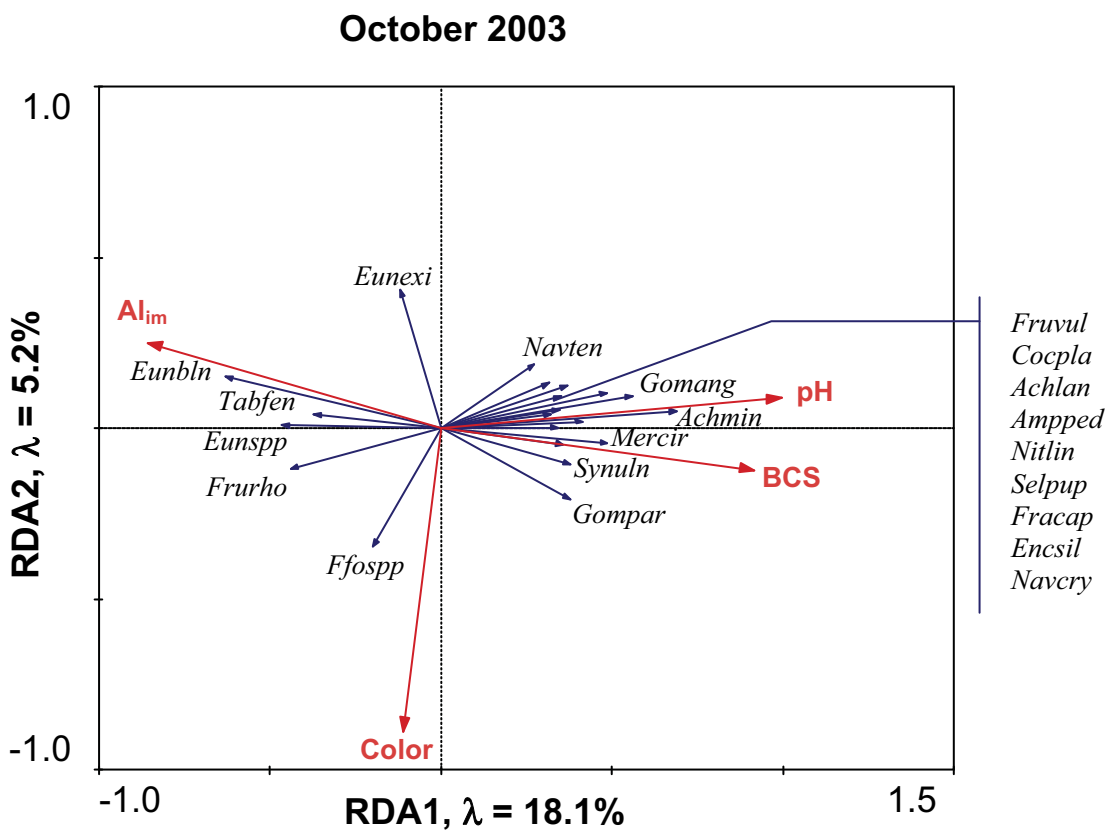


Figure 3-31. Redundancy analysis (RDA) ordination biplots of diatom species and environmental variables in the October 2003 survey. Species acronyms are given in Table 3-5. λ = percentage of explained variance.

acid-tolerant species were found at the highest levels of color. Acidity due to inorganic acid anions was less severe and prompted the proliferation of less acid-tolerant species. These results reflect the deep hydrologic flow paths during this extremely dry period. These types of flow paths generally pass through an inorganic matrix of till and bedrock that effectively neutralize acidity and remove DOC. However, flow in some streams was maintained by water stored in various types of organic-rich matrices that increased concentrations of DOC

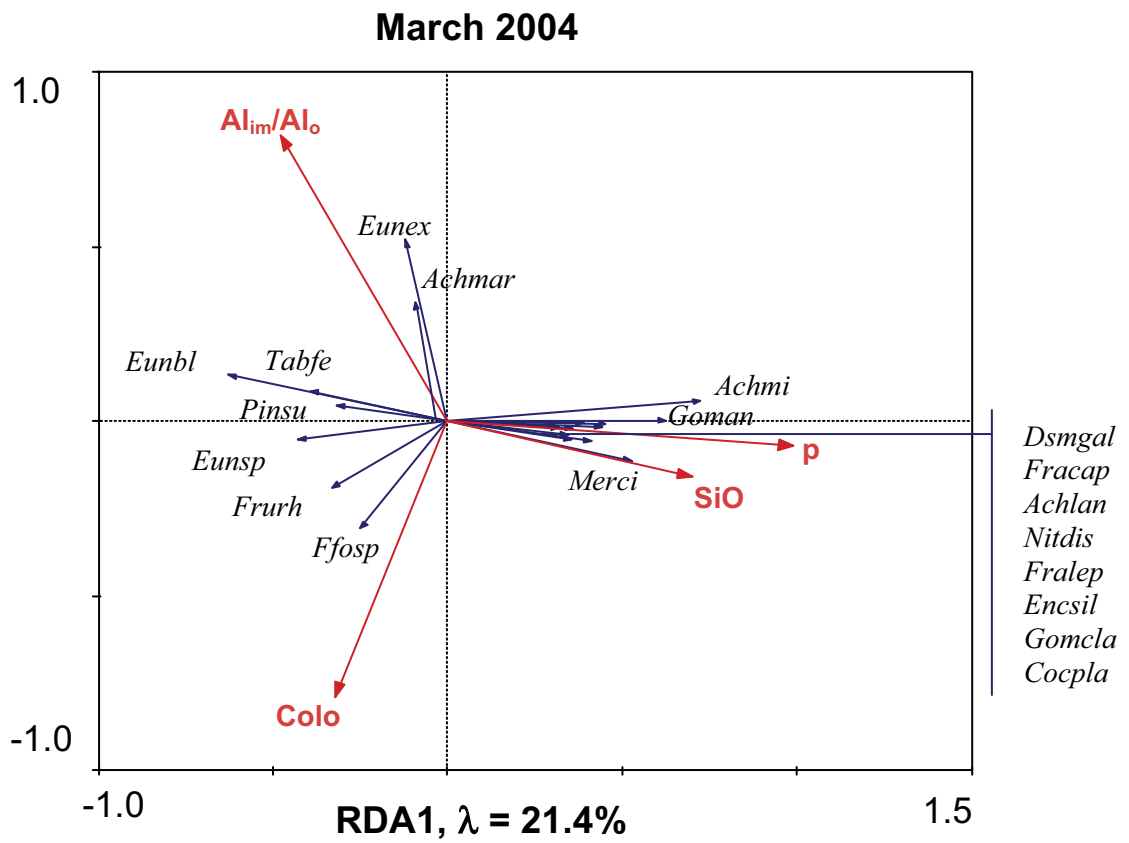
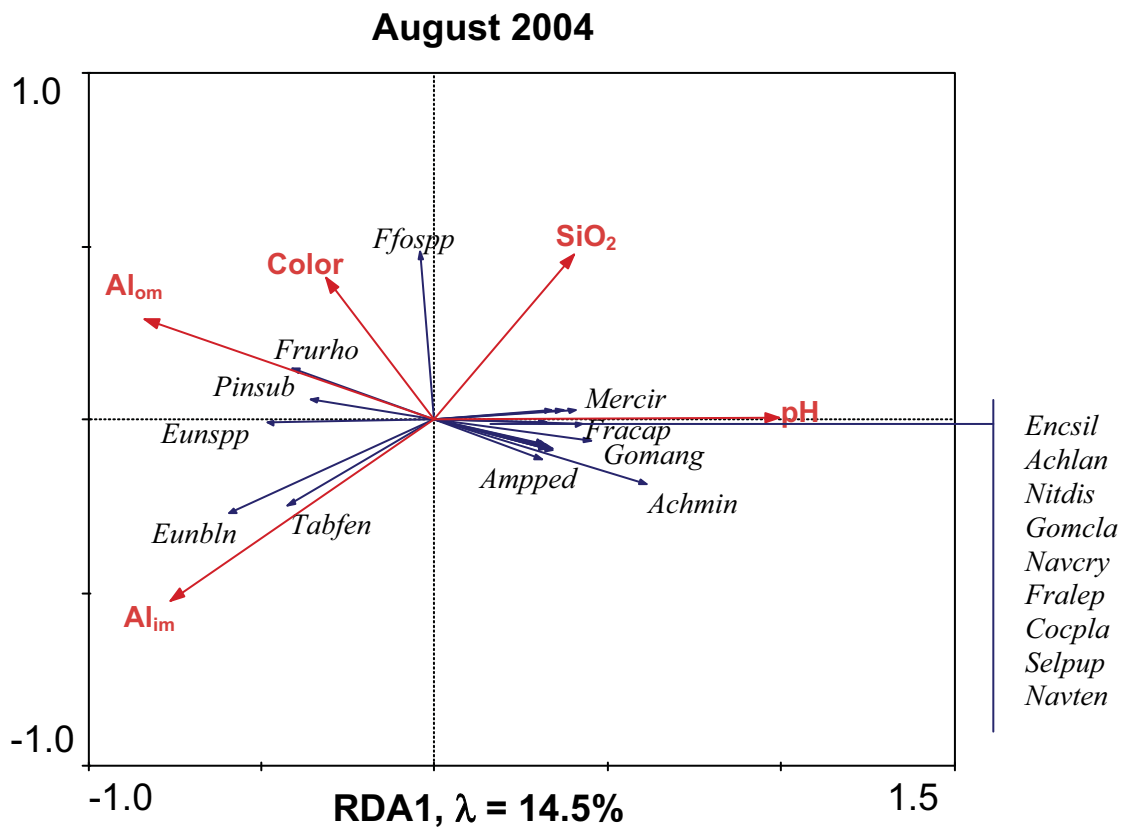


Figure 3-32. Redundancy analysis (RDA) ordination biplots of diatom species and environmental variables in the March 2004 survey. Species acronyms are given in Table 3-5. λ = percentage of explained variance

and associated organic acidity. These types of matrices included wetland riparian areas, organic-rich sediments in the stream bed, and poorly-drained conifer stands with minimal underlying mineral soil.

In the October 2003 survey, DOC concentrations were the highest of the four surveys and color showed a strong negative correlation with RDA2 that was associated with a preponderance of the moderately acid-tolerant *Fragilariforma* species (Figure 3-31). High

Figure 3-33. Redundancy analysis (RDA) ordination biplots of diatom species and environmental variables in the August 2004 survey. Species acronyms are given in Table 3-5. λ = percentage of explained variance.



DOC concentrations tend to increase organic acidity, but they also provide buffering against extremely low pH levels and reduce concentrations of inorganic Al at a given pH through complexation reactions that form non toxic organic Al. These characteristics of DOC may explain why results of the October 2003 survey showed color to be poorly correlated with pH and well correlated with a genus that is only moderately tolerant of acidic conditions. Concentrations of inorganic Al were more strongly related to RDA1 than RDA2 in the October 2003 survey, which indicated a strong relationship with pH.

Results from the March 2004 survey were similar to those of the October 2003 survey in that the ratio of inorganic to organic Al was positively related to RDA2, and color was negatively related to RDA2 (Figure 3-32). However, in contrast to the October 2003 survey, both factors had nearly equal correlations with RDA1 in the March 2004 survey. This difference in results is likely to be associated with lower DOC concentrations in the March 2004 survey than in the October 2004 survey. The mean DOC concentration for the March 2004 survey was approximately half the concentration measured in the October 2003 survey (Table 3-2). Decreased DOC concentrations suggested decreased pH buffering and lower organic acidity. Interpretation of the relationship between color and diatom species is complicated by the fact that organic acidity associated with DOC varies widely in acid strength. A certain fraction is strongly acidic, lowers pH, and contributes to the mobilization of inorganic Al in a manner similar to strongly acidic inorganic acids derived from acid rain. The remaining, weakly acidic fraction, buffers pH and complexes with Al to form non-toxic organic Al.

Weakly acidic organic acids seemed to play a larger role in the October 2003 survey, whereas strongly acidic organic acids seemed to play a larger role in the March 2003 survey.

The influence of strongly acidic inorganic anions, indicated by high NO_3^- concentrations, was also apparent in the March 2004 survey (Table 3-2). *Eunotia exigua*, which is among the most-acid tolerant species, was strongly correlated with the ratio of inorganic to organic Al, whereas the other dominant acid-tolerant species, including *E. bilunaris* and *Eunotia* spp were correlated with both this ratio and color. This pattern persisted in August 2004; the ordination displayed organic and inorganic sources equally affecting the acidic part of the pH gradient with the tolerant species associated with inorganic Al and the less tolerant with color (Figure 3-33).

3.4.2 Conclusions on Diatoms as Indicators of Acidification

These results demonstrated the high degree of sensitivity to acidity shown by diatom species. Only the most acid-tolerant species were found below a BCS value of 10 $\mu eq\ L^{-1}$; a response that adds biological significance to the geochemical threshold for mobilization of inorganic Al at the slightly lower BCS value of 0 $\mu eq\ L^{-1}$. The percentage of streams determined to be moderately to severely affected by acidic deposition, on the basis of the diatom data, ranged from 66% to 80% in the four surveys. These values are somewhat higher than the percentage of streams estimated to be prone to episodic acidification on the basis of BCS values that indicate Al mobilization (19% to 66%) and indicate a high degree of sensitivity to water chemistry.

The limited variation in values of the mean ACI for the four surveys (Figure 3-25) reflected the temporal integration provided by the diatoms. Whereas a water sample reflects chemical concentrations at an instantaneous moment in time, the presence or absence of a diatom individual reflects environmental conditions, including water chemistry, over the

organism's lifetime. For this reason, the ACI values for the October 2003, March 2004, and August 2004 surveys were almost identical, despite considerable variation in flow, season, and water chemistry in these surveys. This characteristic makes diatoms highly valuable in the assessment of stream acidification, where water chemistry can vary substantially over a few hours.

Redundancy analysis segregated the non-impacted from the acid-impacted streams on RDA1 and discriminated on the basis of weak acidity versus strong acidity on RDA2. This large-scale study supports previous investigations, which showed that the source and type of acidity is important in determining diatom community composition (Passy 2006, Passy et al. 2006). Additional research in this area would be useful to better understand how the short-term chemical changes of episodic acidification control diatom populations and communities.

3.5 Macroinvertebrates as an Index of Acidification

Macroinvertebrates are an important biological component in all Adirondack streams. They play an essential role in energy transfer within these ecosystems by accelerating the breakdown of allochthonous detritius (plant material washed into the stream) and serve as important food sources for secondary consumers, including fish (Hynes 1970). Macroinvertebrates are also useful as indicators of water quality because they are sensitive to changes in water chemistry and typically have a life span of a year or more, thereby reflecting the variations in stream chemistry that occur throughout a given year.

Simpson and colleagues assessed the effects of acidification on diversity of macroinvertebrate communities in four headwater Adirondack streams in the 1980s

(Simpson 1983, Simpson et al. 1985), but there have been no other publications that document the effects of acidification on macroinvertebrate assemblages in Adirondack streams. Therefore, the current condition of macroinvertebrate communities, as well as their response to declining acidic deposition levels over the past two decades, is unknown. This information gap also precludes the assessment of future trends in the health of macroinvertebrate communities that may result from changing rates of acidic deposition or other environmental factors. For these reasons, an assessment of macroinvertebrate communities was incorporated into this project.

3.5.1 Macroinvertebrate Assessment Results

About 220 taxa were identified from the 36 study sites surveyed in 2004; more than 190 taxa were identified to the genus or species levels. A linear relation was observed between acidBAP values and pH in the 36 streams, and the distribution of acidBAP scores was approximately even across a pH range from 4.25 to 7.25 (Figure 3-34). Placing these data into four evenly divided (25th percentiles) impact categories showed that communities in 34 of the 36 streams were slightly to severely affected by acidic waters, and 20 of 36 streams were moderately to severely affected (Figure 3-34).

The strong relation between pH and the acidBAP score was illustrated by Figure 3-34, but this relation does not distinguish between the effects of acid rain and the effects of natural acidity. Because measurable concentrations of inorganic Al are an unambiguous indication of acidic deposition in undisturbed watersheds, and macroinvertebrates are sensitive to this form of Al (Gensemer and Playle 1999),

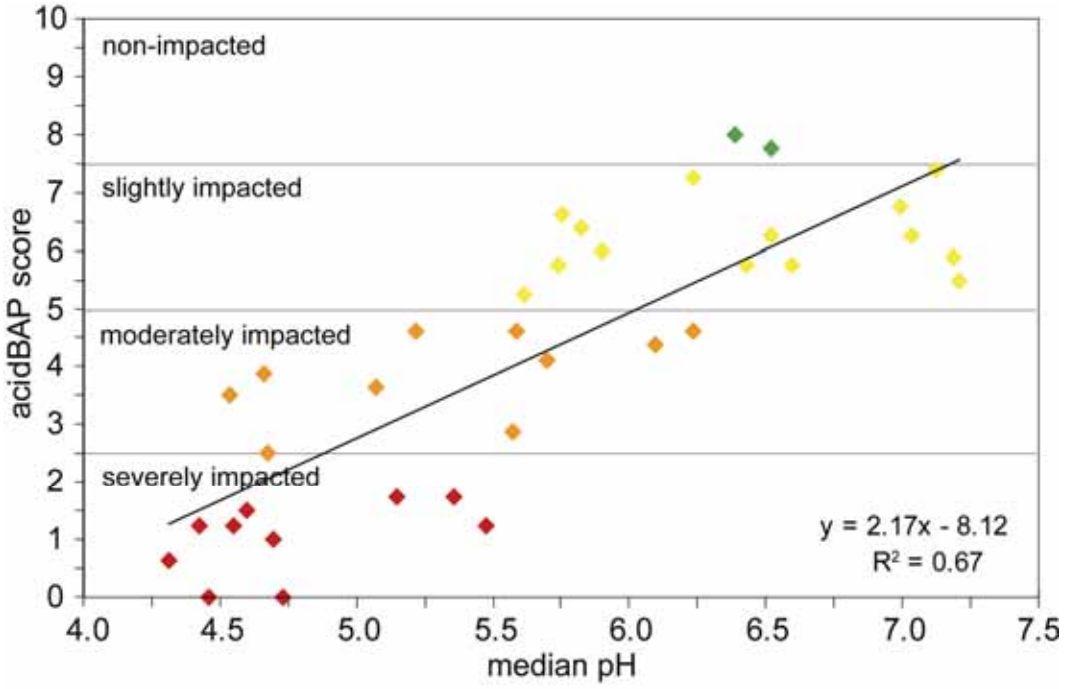


Figure 3-34. Acid Bioassessment Profile (acidBAP) scores as a function of median pH at the 36 streams sampled in the western Adirondack Mountains of New York, 2003-05; four acid-impact categories are defined using 25th percentile divisions.

acidBAP scores were related to inorganic Al concentrations to select acidBAP sensitivity thresholds (Figure 3-35). Although a statistically significant relation was observed, the acidBAP was essentially independent of inorganic Al concentrations below 2.0 µmol L^{-1}. This concentration can, therefore, be considered a threshold above which inorganic Al concentrations have a negative impact on macroinvertebrate communities. Other studies have shown similar results (Gensemer and Playle 1999). However, the precision and accuracy of inorganic Al measurements decrease considerably below approximately 1.5 µmol L^{-1}(Lawrence et al. 1995b), which makes it difficult to identify a statistical relationship in this concentration range.

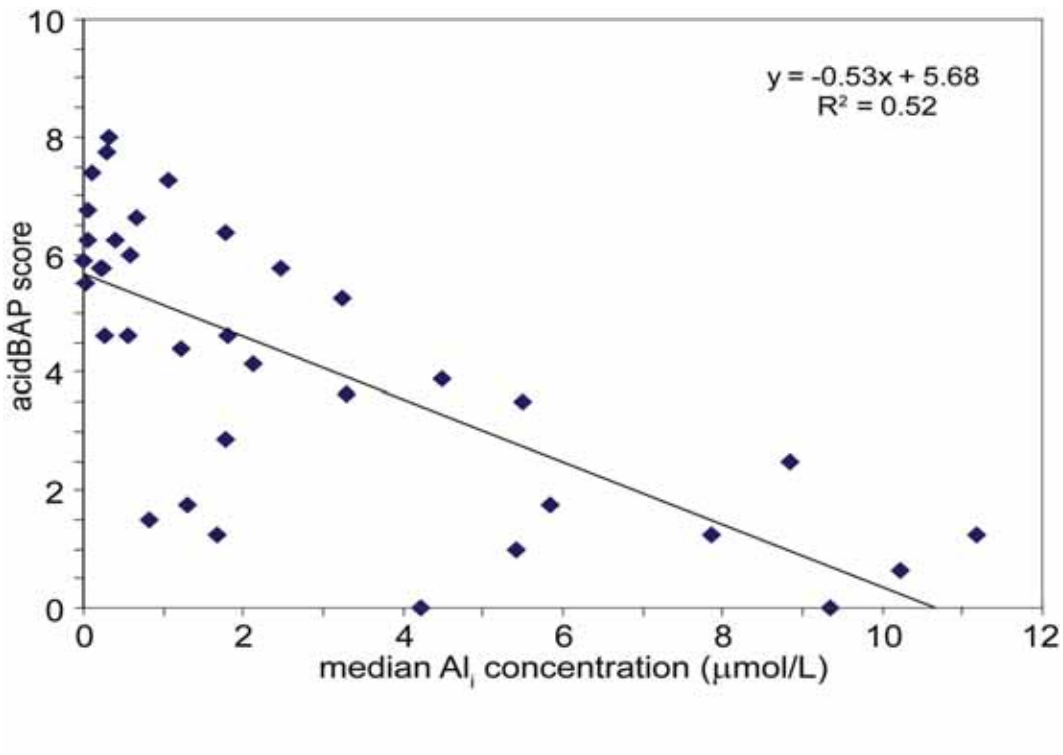


Figure 3-35. Acid Bioassessment Profile (acidBAP) scores as a function of median inorganic Al concentration at the 36 streams sampled in the western Adirondack Mountains of New York, 2003-05.

To define categories of effects for acidBAP data through the full range of acidification, regression tree analysis was used to relate acidBAP to pH and the BCS. Results were divided into three categories: non impacted at an acidBAP value greater than or equal to 5.0, moderately impacted for acidBAP values less than 5.0 but greater than or equal to 2.5, and severely impacted for acidBAP values less than 2.5 (Figure 3-36). The relationship between the acidBAP and BCS is shown with these impact categories in Figure 3-37. At BCS values above approximately 25 µeq L^{-1}, acidBAP scores were not related to BCS values, which suggests that macroinvertebrate populations were unaffected by acidification above this concentration. Below a BCS value of ·ately -50 µeq L^{-1}, macroinvertebrate communities were severely affected. Had

minimum BCS values been related to the acidBAP rather than median BCS values, the value defining the threshold between non-impacted and moderately impacted would have approximated 0.0 μeq L^{-1}, the threshold value for mobilization of inorganic Al. Applying the BCS-based acidBAP thresholds to the median pH-acidBAP relation (Figure 3-38) indicated that macroinvertebrate communities in general, were unaffected above

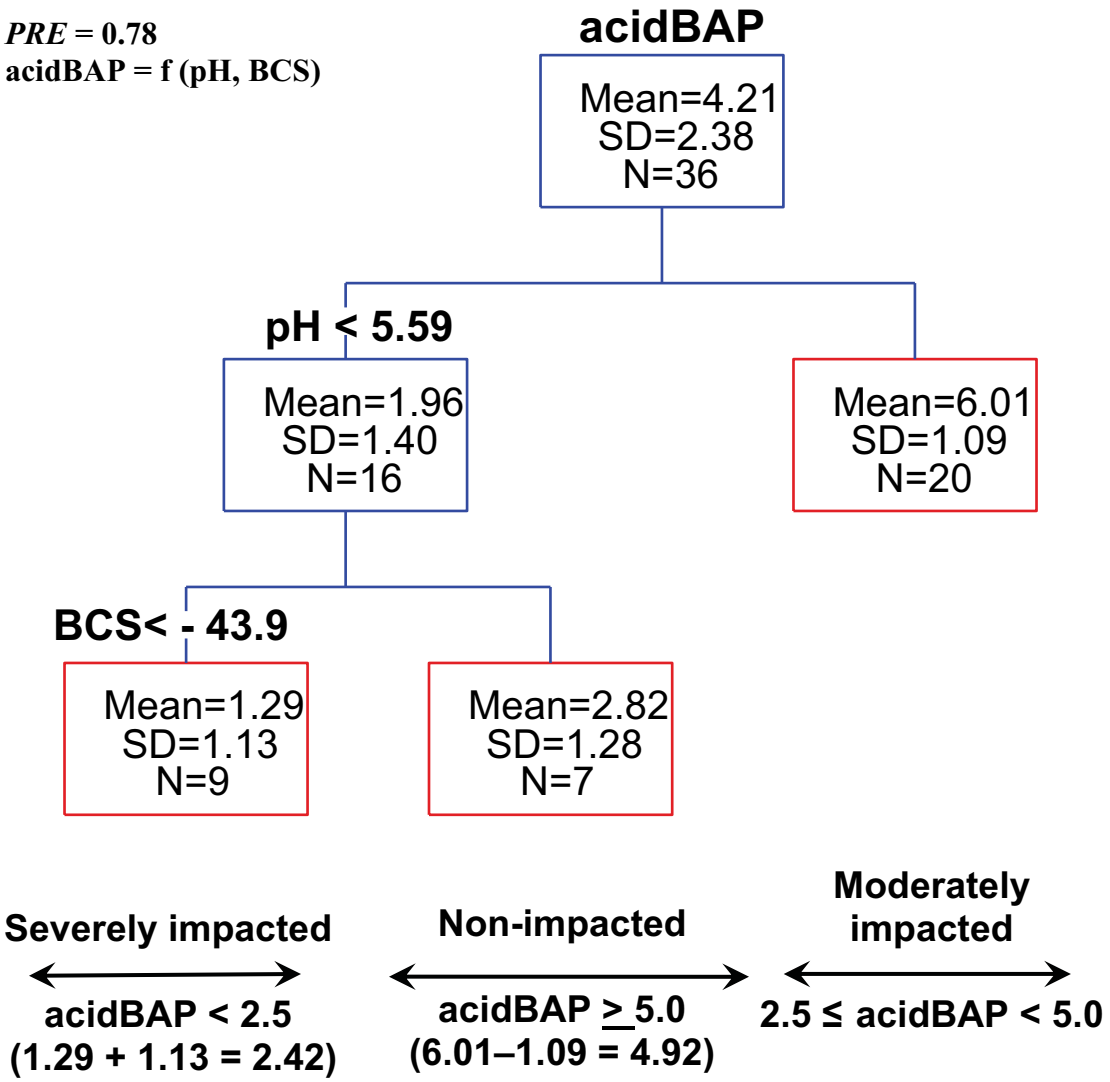


Figure 3-36. Regression tree of the acidBAP as a function pH and base cation surplus (BCS), derived from macroinvertebrate samples and water chemistry. *PRE* = Proportional reduction in error, SD = standard deviation, N = number of samples.

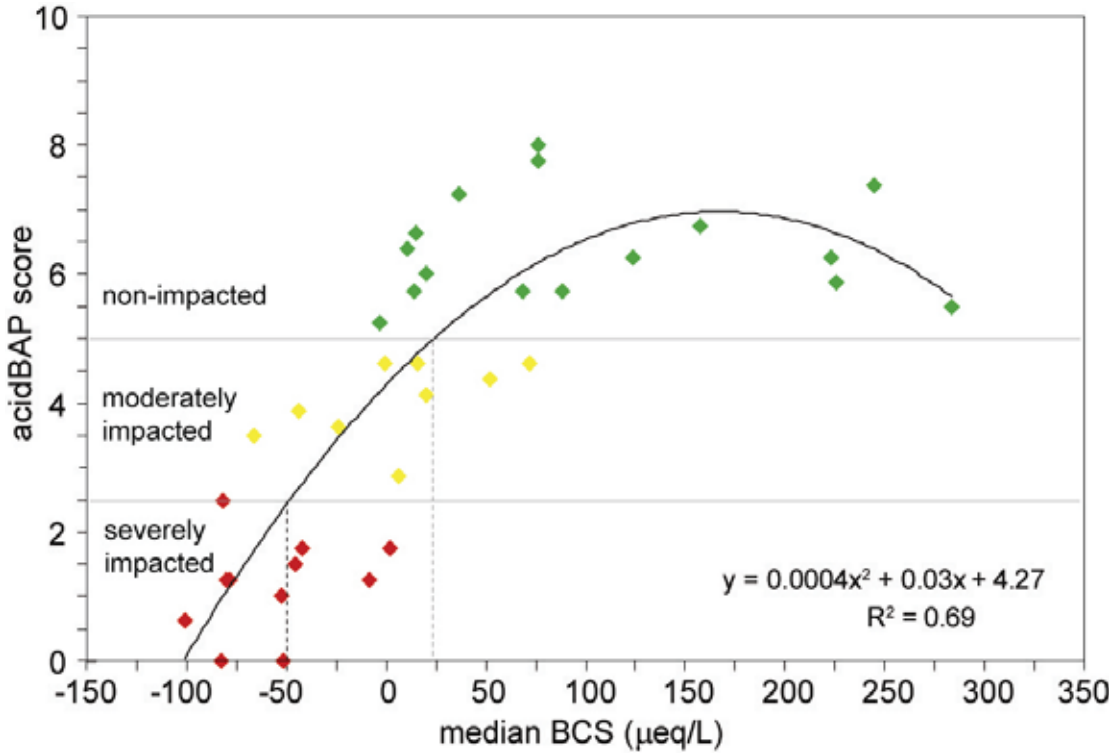


Figure 3-37. Acid Bioassessment Profile (acidBAP) scores as a function of median base cation surplus (BCS) at the 36 streams sampled in the western Adirondack Mountains of New York, 2003-05; acidBAP and BCS levels that potentially impact stream biota are denoted.

pH 6.0, were moderately impacted from pH 4.8 to 6.0, and were severely impacted at pH values less than 4.8. However, because pH is influenced by natural acidity as well as acidic deposition, the pH-acidBAP relation can be used only as an index of overall acidity (combining natural and anthropogenic sources), whereas the BCS-acidBAP relation serves as a specific index of acidic deposition.

3.5.2 Conclusions of the Macroinvertebrate Assessment

The 36 streams used in the macroinvertebrate assessment were specifically chosen to provide a range of chemical conditions. Therefore, these streams are not a representative sample of the 565 streams in the potential sampling population. However, the percentage of streams falling in each of the macroinvertebrate impact categories can be estimated with the BCS values available for the 200 sample streams, which can be considered representative of the population of 565 streams. If the March 2005 survey results are used as the median chemical condition (Table 3-2), 52% of the

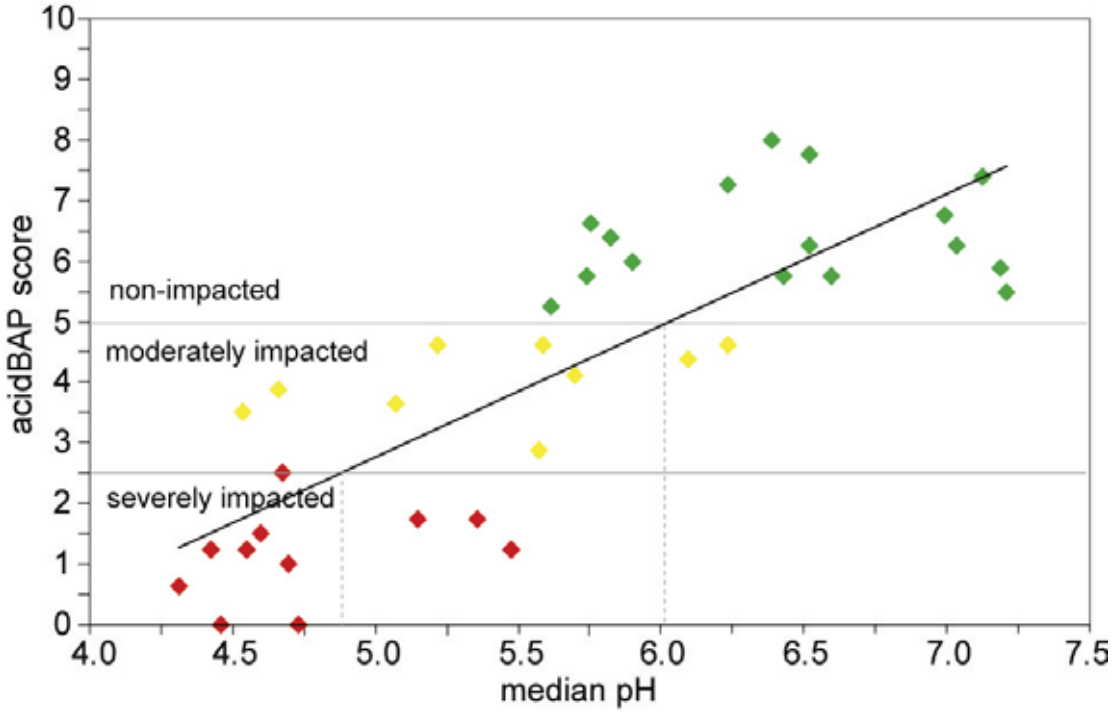


Figure 3-38. Acid Bioassessment Profile (acidBAP) scores as a function of median pH at the 36 streams sampled in the western Adirondack Mountains of New York, 2003-05; Three acid-impact categories are redefined using thresholds based on BCS and inorganic Al concentrations.

streams in the potential sample population were moderately to severely impacted. These percentages are lower than the approximately 80% of the streams in which diatoms were moderately to severely affected, which suggests that macroinvertebrates are less sensitive to acidification than diatoms. Nevertheless, this assessment indicated that macroinvertebrate communities were negatively affected by acidic deposition in about half of the 565 streams in the sampling population.

3.6 Changes in Stream Chemistry Since the Early 1980s

The large-scale stream survey conducted by the New York State DEC in the early 1980s provided documentation of acidic streams throughout the western Adirondack region, but most of this sampling was limited to March and April of 1982. Because differences in climatic factors can lead to substantial variations in stream chemistry over days, seasons, and years (Lawrence et al. 2004), sampling over a two-month period in a single year did not sufficiently characterize natural variations to allow comparisons with recent data. However, sampling of 18 streams was done across seasons and, in most cases, over several years. Therefore, by repeating the sampling of these 18 streams in 2003-2005 in the same seasons, under similar flow conditions, the two time periods to be statistically compared. Of the 18 streams resampled in 2003-2005, six had a large upstream pond or lake. These six streams, hereafter referred to as outlets, were separated from the other 12 streams for statistical analysis because of potential effects from in-lake processes.

3.6.1 Results for pH and ANC

Water chemistry data collected during the 2003-2005 time period were similar to the data collected in the earlier surveys, although median values of pH and ANC were somewhat lower in the early 1980s than in 2003-2005 in most streams and outlets (Table 3-6). Cellar Brook and Bradley Brook were the most acidic streams during both periods. The West Branch of the Oswegatchie River was the most acidic of the outlets. In most streams and outlets, water chemistry was statistically related to stream flow ($p < 0.05$) measured at the Independence River gage. As expected, the most acidic samples were usually collected during the high stream flows in the snow-melt period. The median flows were similar between the two sample periods (Table 3-6), which demonstrated that the 2003-2005 sampling reasonably duplicated the sampling conditions in the early 1980s with regard to flow.

The range in pH measured during both sampling periods was typically greater than two units in most of the streams and outlets (Tables 3-7a, 3-7b). The wide variations within each period emphasized the need to characterize temporal variability related to flow and season when comparing the two periods.

In 2003-2005, pH measurements were higher ($p < 0.05$) than in the early 1980s in eight of the 12 streams, and none of the streams had a lower pH in 2003-2005 than in the early 1980s (Table 3-7a). However, the pH increases in three of the eight streams were less than 0.01 y^{-1}. The difference in mean values between periods for the streams as a group yielded an overall annual rate of increase of 0.012 y^{-1}. The highest rates of increase were measured in Bald Mountain Brook and Independence River, but none of the other streams increased at a rate higher than 0.02 y^{-1}. Statistically higher pH values

Table 3-6. Median pH, acid neutralizing capacity by Gran titration (ANC_G in μeq/L) and specific conductance (Sp. Cond., μS/cm @ 25° C) for 18 Adirondack streams during the two different time periods (early 1980s and 2003-2005). The median flow in the Independence River is also listed for the respective stream sampling dates.

	Early 1980s				2003-2005			
Stream Name	**pH**	**ANC**	**Sp. Cond.**	**Indep. R. flow**	**pH**	**ANC**	**Sp. Cond.**	**Indep. R. flow**
Bald Mt. Bk.	5.30	11.52	20.45	115	6.77	48.97	22.97	88.5
Black Bear Mt. Brook	6.78	84.70	30.45	92	7.02	100.01	27.77	114
Bradley Bk.	4.72	-18.25	32.00	99	4.88	-2.49	25.42	114
Buck Cr.	6.04	29.00	29.75	87	5.87	21.55	24.75	88.5
Cellar Bk.	4.80	-14.70	29.05	98	4.99	2.17	22.11	114
Eagle Cr.	6.89	128.50	36.00	136	7.38	198.77	37.65	114
Independence R.	5.87	15.34	29.00	259	6.24	28.59	20.70	340
Otter Cr.	6.56	59.50	31.90	271	7.04	68.74	23.76	340
Seventh L. Inlet	6.10	34.80	28.65	87	6.00	29.66	23.20	114
Silver Run, downstream	5.58	12.00	27.00	97	5.81	24.27	23.03	114
Silver Run, upstream	6.62	77.00	27.90	98	7.00	76.87	23.80	114
Wheeler Cr.	5.12	3.00	27.10	87	5.01	5.86	22.14	114
Outlet Name								
Black River	4.85	-5.33	28.00	218	5.12	7.17	18.31	92
Cascade L. Outlet	6.93	106.00	32.00	97	6.92	83.97	25.50	132
Constable Cr.	4.88	-10.83	29.60	132.5	5.45	10.89	18.75	112.5
Fly P. Outlet	7.10	174.31	43.00	125	7.65	289.80	46.15	88.5
Little Woodhull Cr.	5.95	41.97	26.00	208	6.55	58.13	22.28	114
Oswegatchie R., West Branch	4.93	-3.75	29.20	296	4.98	1.64	21.28	340

Table 3-7. Ranges and average annual rates of increase for pH and values of acid neutralizing capacity by Gran titration (ANC_G) in water samples collected in streams (a) and lake and pond outlets (b) in the early 1980s and in the WASS 2003-2005 sampling. The annual rate of increase is based on 23 years between the two sampling periods. Rates are not shown for streams in which there were non significant differences between the time periods. No streams or outlets showed significant decreases.

a. Streams Table

	pH (pH units)			ANC_G ($\mu eq\ L^{-1}$)		
Stream Name	**Range 1980-85**	**Range 2003-05**	**Annual Rate of Increase**	**Range 1980-85**	**Range 2003-05**	**Annual Rate of Increase**
Bald Mt. Brook	5.05 to 5.94	5.10 to 7.29	0.050	-1 to 43	3 to 107	1.7
Black Bear Mt. Brook	5.14 to 7.27	5.29 to 7.52	0.015	2 to 191	10 to 177	--
Bradley Brook	4.49 to 5.24	4.47 to 5.60	0.008	-38 to 8	-28 to 17	0.62
Buck Creek	4.62 to 7.10	4.80 to 6.97	--	-19 to 107	-7 to 69	--
Cellar Brook	4.40 to 5.68	4.45 to 5.72	0.007	-42 to 41	-42 to 22	0.52
Eagle Creek	5.72 to 7.43	5.48 to 7.80	0.006	44 to 199	27 to 300	--
Independence River	4.63 to 7.25	5.35 to 7.37	0.031	-29 to 42	10 to 130	--
Otter Creek	5.58 to 7.50	6.40 to 7.52	0.020	15 to 230	38 to 201	--
Seventh Lake Inlet	4.82 to 6.97	4.93 to 7.13	--	-9 to 98	0 to 92	--
Silver Run, downstream	4.67 to 6.74	4.63 to 6.97	0.013	-37 to 76	-12 to 71	0.48
Silver Run, upstream	5.70 to 7.23	5.33 to 7.51	--	20 to 152	12 to 174	--
Wheeler Creek	4.36 to 6.29	4.46 to 6.13	--	-42 to 40	-28 to 34	--
Overall increase for streams as a group	--	--	0.012	--	--	0.57

b. Lake Outlets Table						
	pH (pH units)			ANC_G ($\mu eq\ L^{-1}$)		
Outlet Name	**Range 1980-85**	**Range 2003-05**	**Annual Rate of Increase**	**Range 1980-85**	**Range 2003-05**	**Annual Rate of Increase**
Black River	4.49 to 5.56	4.65 to 6.38	--	-40 to 3	-14 to 30	--
Cascade Lake Outlet	5.56 to 7.39	5.48 to 7.48	--	9 to 183	12 to152	--
Constable Creek	4.54 to 6.02	4.74 to 7.01	0.020	-27 to 23	-8 to77	0.83
Fly Pond Outlet	6.86 to 7.38	7.20 to 7.94	0.015	82 to 322	6 to 453	4.22
Little Woodhull Cr.	5.01 to 7.00	5.16 to 7.27	0.008	-11 to 110	12 to 125	--
Oswegatchie River, W. Br.	4.40 t0 5.50	4.76 to 5.46	0.007	-40 to 8	-7 to14	0.44
Overall increase for outlets as a group	--	--	0.015	--	--	0.85

($p < 0.01$) were also measured in 2003-2005 than in the early 1980s in four of the six outlets, and none of the outlets had lower pH values in 2003-2005 than in the early 1980s (Table 3-7b). The annual rate of increase for the outlets as a group (determined by ANOVA) was 0.015 y^{-1}, which was similar to that of the 12 streams not affected by impounded waters.

Ranges in measurements of ANC_G were similar in both periods and varied from as little as 21 $\mu eq\ L^{-1}$ to as high as 447 $\mu eq\ L^{-1}$ in the streams and outlets (Tables 3-7a and 3-7b). Values of ANC_G were statistically higher ($p < 0.05$) in 2003-2005 than in the early 1980s in only four of 12 streams, although none of the values in 2003-2005 were statistically lower than in the early 1980s (Table 3-7a). The average annual rate of increase for Bald Mountain Brook was 1.7 $\mu eq\ L^{-1}\ y^{-1}$, which was approximately three

times higher than for any of the other streams in which ANC_G increased (Figure 3-39a). The response of the other three streams that showed a significant increase in ANC was typified by that of Bradley Brook (Figure 3-39b). Each of these streams was subject to severe episodic acidification in 2003-2005 despite the increase in ANC values since 1980-1985. The annual rate of increase for the 12 streams as a group (determined by ANOVA) was 0.57 $\mu eq\ L^{-1}\ y^{-1}$. Values of ANC_G were higher ($p < 0.05$) in three of the six outlets in 2003-2005 than in the early 1980s, and none were lower in 2003-2005 than in the early 1980s (Table 3-7). When grouped, the rate of increase determined by ANOVA in the six outlets was 0.85 $\mu eq\ L^{-1}\ y^{-1}$.

3.6.2 Results for Specific Conductance

The range in specific conductance among the streams and outlets in the two periods varied from approximately 10 to 20 $\mu S\ cm^{-1}$ and was smaller in 2003-2005 than in the early 1980s (Tables 3-8a and 3-8b). The difference between the two time periods was also more apparent than for pH or ANC_g (Tables 3-7a and 3-7b). Specific conductance values were lower in 2003-2005 than in the early 1980s ($p < 0.05$) in 14 of the 18 streams and outlets (Tables 3-8a, 3-8b). Annual rates of decrease for individual streams and outlets ranged from 0.14 to 0.35 $\mu S\ cm^{-1}$.

Specific conductance is influenced by the concentrations of both anions and cations. Solutions of inorganic acids, bases, and salts generally are good conductors, and organic compounds generally do not conduct electrical current well (Clesceri et al. 1998). The observed declines in specific conductance were most likely the result of lower

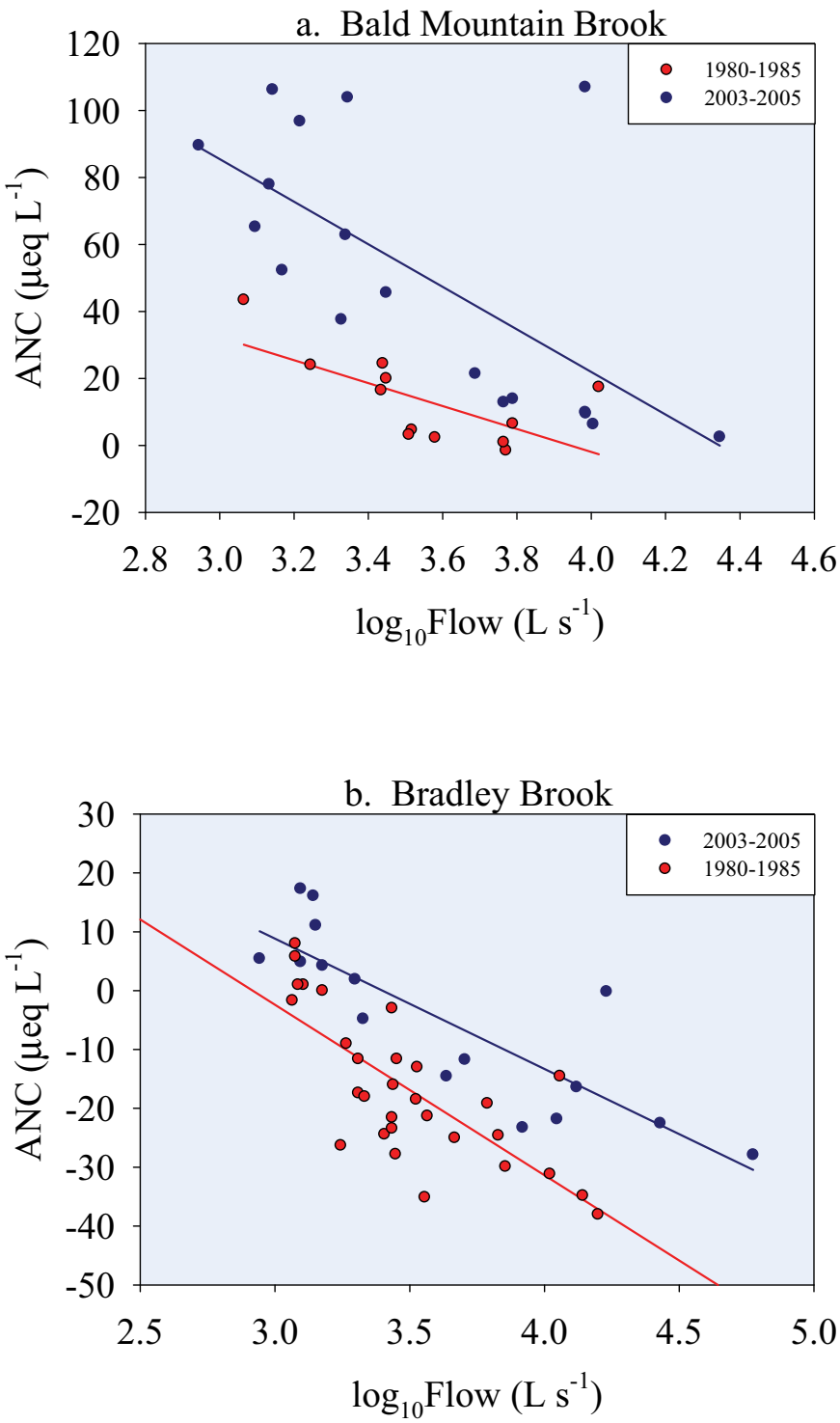


Figure 3-39. Comparisons between ANC measurements in 1980-1985 and 2003-2005 as a function of flow in Bald Mountain Brook (a) and Bradley Brook (b) . Lines represent the regressions of points from each time period ($p < 0.05$).

concentrations of sulfate and calcium, the ions of highest concentrations. Sulfate concentrations have decreased in Adirondack lakes following the reductions in sulfur deposition due to the Clean Air Act Amendments (Driscoll et al. 2003). In Adirondack lakes, a near stoichiometric correspondence was observed between declines in sulfate and nitrate concentrations and declines in base cation concentrations (Driscoll et al. 2003).

Table 3-8. Ranges and average annual rates of decrease for specific conductance of water samples collected in streams (a) and lake outlets (b) in the early 1980's and in the WASS 2003-2005 sampling. The annual rate of decrease is based on 23 years between the two sampling periods. Rates are not shown for streams in which there were non-significant differences between the time periods. No streams or outlets showed increases.

a. Streams table			
	Specific Conductance (µS cm^{-1} @ 25°C)		
Stream Name	**Range 1980-85**	**Range 2003-05**	**Annual Rate of Decrease**
Bald Mt. Brook	16.0 to 29.0	17.9 to 31.0	--
Black Bear Mt. Brook	21.6 to 40.6	21.1 to 36.7	--
Bradley Brook	28.0 to 45.0	21.9 to 33.1	0.35
Buck Creek	26.0 to 36.6	21.4 to 29.2	0.19
Cellar Brook	25.0 to 42.0	20.0 to 33.3	0.30
Eagle Creek	29.0 to 42.0	21.9 to 49.8	--
Independence River	27.0 to 41.5	18.4 to 31.9	0.28
Otter Creek	27.0 to 51.7	19.5 to 38.9	0.25
Seventh Lake Inlet	25.3 to 40.0	19.3 to 29.8	0.27
Silver Run, downstream	23.0 to 34.8	19.8 to 29.7	0.20
Silver Run, upstream	25.0 to 32.0	18.7 to 31.3	0.15
Wheeler Creek	19.7 to 40.0	18.6 to 33.5	0.26
Overall decrease for streams as a group	--	--	0.22

b. Lake Outlets Table			
	Specific Conductance (µS cm^{-1})		
Outlet Name	**Range 1980-85**	**Range 2003-05**	**Annual Rate of Decrease**
Black River	21.0 to 39.0	16.3 to 26.1	0.25
Cascade Lake Outlet	24.5 to 38.0	21.3 to 33.5	0.20
Constable Creek	21.8 to 40.0	15.4 to 26.8	0.34
Fly Pond Outlet	27.6 to 55.0	22.7 to 65.1	--
Little Woodhull Creek	24.0 to 32.0	19.5 to 27.1	0.14
Oswegatchie River, W. Br.	21.0 to 32.0	18.9 to 25.8	0.31
Overall decrease for outlets as a group	--	--	0.24

With these reductions in both anions and cations, the observed declines in specific conductance were to be expected. However, the decrease in specific conductance was inversely related to the median pH in 2003-2005 in the 12 streams (Figure 3-40). Streams with low pH values became more dilute than streams with high pH values as sulfate leaching of soils decreased with lower rates of sulfate deposition. In streams with relatively high pH values, decreased sulfate leaching may have been compensated to some degree by bicarbonate leaching.

3.6.3 Conclusions on Changes in Stream Chemistry Since the Early 1980s

Statistically higher pH values were measured in 2003-2005 than in the early 1980s in most of the streams and outlets, but less than half of the streams and outlets had a higher ANC_G in 2003-2005 than in the early 1980s. The amount of change, however, was relatively small, and nearly all of the streams and outlets exhibited episodic acidification during periods of high stream flow in 2003-2005. A pH value less than 5.0

was measured at least once in 2003-2005 in half of the streams and outlets, and a BCS value less than 25 μeq L^{-1} was measured in all but one of these waters during the study.

Despite some increases in stream pH and ANC_G over the past 20 years, chemical recovery from acidification in these Adirondack streams and outlets has been minimal, with the exception of Bald Mountain Brook and Fly Pond Outlet. The overall increase in ANC_G for the 12 streams was 13 μeq L^{-1} over 23 years. In Bradley Brook, ANC_G increased 14 μeq L^{-1} over 23 years, but no fish were found in a 1999 re-survey (Simonin et al. 2005). The degree of chemical recovery observed in the streams and outlets in this historical comparison probably resulted in little or no biological recovery.

Results from specific conductance measurements showed differences in the recovery capacity between low pH and high pH streams and outlets. The greater decrease in specific conductance in low pH waters than in high pH waters is due to greater decreases in Ca^{2+} (and associated SO_4^{2-}) concentrations than in the more buffered waters. Because Ca^{2+} is an important nutrient for aquatic ecosystems, decreased concentrations of Ca^{2+} may limit the recovery of aquatic life with a high calcium dependency, such as certain species of zooplankton, amphipods, crayfish, and mollusks (Jeziorski and Yan 2008).

4 RELEVANCE OF THIS ASSESSMENT

Assessment of Adirondack stream acidification had previously been limited to a large survey conducted in March and April of 1980 and subsequent studies involving small numbers of streams for limited periods of time. Biological data associated with these previous studies had been largely limited to fish. In contrast, comprehensive monitoring and assessment of Adirondack lakes has been ongoing since the early 1980s. In the absence of sufficient stream data for regional assessments, the lake data have served to represent Adirondack surface waters for the past two decades. Therefore, 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.

The percentage of acidified streams determined in the WASS (66 %) was much higher than the percentage of acidified lakes (8 %) that had been previously reported by the USEPA (Stoddard et al. 2003). The USEPA estimate of acidified lakes was based on summer time, base flow sampling that was designed to provide an estimate of chronic acidification for the overall Adirondack region, whereas our study assessed episodic acidification of streams in the western Adirondack region. Therefore, the percentage of acidified lakes reported by Stoddard et al. (2003) is not applicable to western Adirondack streams.

The tendency of streams to acidify more readily than lakes contributed to the difference in results between the WASS and Stoddard et al. (2003), as did the fact that

our study region included the area with the highest number of acidic streams in the Adirondack Park based on the stream survey in the early 1980s (Colquhoun et al. 1984). Even though WASS assessed only 28% of the streams within the western 20% of the Adirondack Park, we identified 718 km of stream reaches prone to acidification. It is uncertain whether the percentage of inaccessible streams prone to acidification was similar to that of the accessible streams, but we are not aware of any factors that would suggest a different percentage for inaccessible streams. The percentage of acidified streams in the remaining 80% of the Adirondack region is likely to be less, based on the survey from the early 1980s, but the current condition is largely unknown.

Results of WASS included the development of the BCS and provided a robust comparison between this chemical index and standard chemical indices of acidification. Results also showed that the threshold of inorganic Al mobilization (defined by a BCS of 0) approximated the level below which diatom communities were severely impacted and macroinvertebrate communities were moderately to severely impacted. Adirondack studies prior to WASS related chemical indices of acidification primarily to brook trout, a relatively acid-tolerant fish species.

The WASS also provided useful information on current soil conditions and how they related to stream chemistry. These data indicated that the B horizon in most of the WASS watersheds is depleted of Ca and is providing minimal neutralization of acidity. Although a decrease in base saturation of this horizon is likely to have occurred in the past, the current trend is unknown. Without recovery of the base saturation of the B horizon, the degree to which the Oa horizon can continue to neutralize soil water and reduce mobilization of inorganic Al is unknown. Modeling efforts to predict recovery

trajectories for Adirondack surface waters need to consider incorporation of the role of the Oa horizon in soil and surface water recovery.

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 et al. 2007). The recently identified increase in DOC concentrations in surface waters of the Northeast (Driscoll et al. 2007) provides an example of a biogeochemical response that may be related to trends in atmospheric deposition and climate. 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.

5 MAJOR FINDINGS

1. The base cation surplus provides an effective measure for assessing acidic deposition effects by relating base cation availability to mobilization of inorganic Al without the complications of pH buffering by organic acids.

2. Of the 565 streams assessed, 66% (718 km of stream reaches) were identified as prone to acidification—likely to be acidified to levels harmful to biota.

3. Of the 66% of streams found to be prone to acidification, approximately half were likely to be episodically acidified and half were likely to be chronically acidified.

4. The estimated base saturation of the B horizon for the WASS watersheds was less than 20% for 90% of the watersheds; a likely result of base depletion by acidic deposition that has rendered this horizon ineffective at buffering inputs of acidity.

5. The percentage of streams determined to be moderately to severely impacted by acidic deposition on the basis of the diatom data ranged from 66% to 80% over 4 surveys.

6. Macroinvertebrate communities were moderately to severely impacted in 52% of assessed streams.

7. Recovery from acidification in Adirondack streams and outlets sampled previously in the early 1980s has been minimal except for Bald Mountain Brook and Fly Pond Outlet. The overall increase in ANC_G for the 12 streams was 13 $\mu eq\ L^{-1}$ over 23 years.

8. The approach of seasonal sampling surveys conducted within three-day periods throughout the study region was successful for capturing the episodic and seasonal variability of stream chemistry. When indexed to a site with both episodic and long-term monitoring data, this approach was an effective method for the regional assessment of episodic acidification.

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Results from the 2003-2005 Western Adirondack Stream Survey

Final Report 08-22

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