Results of the 2010-2011 East-Central Adirondack Stream Survey (ECASS)

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Results of the 2010–2011 East-Central Adirondack Stream Survey (ECASS)

Including Integration with the Western Adirondack Stream Survey (WASS)

Final Report

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Abstract

Streams closely reflect the influences of terrestrial vegetation and soil processes and are more sensitive to acidic deposition than non-flowing waters. Therefore, monitoring of stream chemistry has been conducted in the Adirondack region for several decades to assist in tracking the environmental health of this highly valued region. This monitoring includes the East-Central Adirondack Stream Survey (ECASS), which was designed to (1) assess stream chemistry and biota with respect to acidic deposition effects and (2) establish a baseline for assessing the future impact of drivers on environmental change.

The ECASS survey involved sampling approximately 200 accessible headwater streams, randomly selected from an area that comprised 80% of the Adirondack State Park. Water and diatom samples were collected August 9–11, 2010 during base flow, April 18–20, 2011 during spring snowmelt, and October 31–November 2, 2011 shortly after leaf-fall. Stream water was also collected from 11 streams during summer base flow and 13 streams during snowmelt within the High Peaks region of the Adirondack ecoregion. In addition, six streams that had been sampled five times from early April to early May in either 1980 or 1982 were resampled five times in the same two months in 2011, and macroinvertebrate samples were collected from 36 streams in summer 2011 and an additional 14 streams in 2012.

Assessment of stream acidification indicated that 42% of accessible streams in the study region were prone to episodic acidification to the level at which mobilization of toxic inorganic aluminum (Al) occurred. This percentage of streams equates to approximately 670 miles (mi) of first-order stream reaches within the study region. This analysis also indicated that 11% of streams were chronically acidic, which indicated that the greatest acidification impact occurred on an episodic basis.

All but two high-elevation sites were acidified during snowmelt to the level at which toxic Al mobilization occurred, whereas during summer sampling only three sites were acidified to that level. The acidification during snowmelt occurred through a greater decrease in base-cation concentrations than in strong acid-anion concentrations relative to summer chemistry. Concentrations of dissolved organic carbon (DOC) were also higher during snowmelt than during summer. Resampling of sites previously sampled in the early 1980s indicated small increases in acid-neutralizing capacity (ANC) that were < 0.50 microequivalents per liter per year (μeq L^{-1} y^{-1}) in the three streams that were poorly acid-buffered in that initial sampling. Two of the three streams that were moderately-to-well-buffered showed no change in ANC, but one stream increased at a rate of 1.4 μeq L^{-1} y^{-1}.

Comparing stream chemistry data from the ECASS and the previously conducted Western Adirondack Stream Survey (WASS) indicated that a larger fraction of headwater streams were acidified in the study region of the WASS than the ECASS. In snowmelt samplings, 45% of ECASS streams had ANC values above 50 microequivalents per liter (μeq L^{-1}), the level considered nominally impacted, whereas only 25% of WASS streams had ANC values above this level. Streams determined to be prone to episodic acidification are distributed throughout most of the ECASS region. Base-saturation estimates of the upper B horizon modeled from stream chemistry showed that areas with base-saturation values that provided insufficient acid buffering to prevent Al mobilization (< 17%) were common through the west and central portions of the Adirondack region.

Analysis of macroinvertebrate communities indicated negative effects below a water chemistry threshold that approximated the threshold for mobilization of toxic Al, and diatom species richness was substantially reduced by acidity and Al derived from acidic deposition, but not natural acidity derived organic acids.

Keywords

acid rain, acidic deposition, stream chemistry, aluminum, calcium depletion, stream diatoms, stream macroinvertebrates, Adirondack region

Acknowledgements

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Acronyms and Abbreviations

acidBAP	acid-biological assessment profile
Al	aluminum
Al_i	inorganic monomeric Al
Al_o	organic monomeric Al
Al_t	total unfiltered Al
Al_{tm}	organic monomeric Al
ALSC	Adirondack Lakes Survey Corporation
ANC	acid-neutralizing capacity by Gran titration
ANCOVA	analysis of covariance
BCS	base-cation surplus
C	carbon
Ca	calcium
Ca^{2+}	calcium ion
Cl^-	chloride ion
cp	change point
CV	coefficient of variation
DEC	New York State Department of Environmental Conservation
DOC	dissolved organic carbon
ECASS	East-Central Adirondack Stream Survey
EPA	United States Environmental Protection Agency
ERP	Episodic Response Project
F	fluoride
Fe	iron
H	hydrogen
H^+	hydrogen ion
HES	high elevation survey
H_2SO_4	sulfuric acid
IndVal	indicator value
K^+	potassium ion
kg ha^{-1} y^{-1}	kilograms per hectare per year
kg N ha^{-1} y^{-1}	kilograms of nitrogen per hectare per year
kg S ha^{-1} y^{-1}	kilograms of sulfur per hectare per year
km	kilometers
$KMnO_4$	potassium permanganate
L s^{-1}	liters per second
m	meters
Mg^{2+}	magnesium ion

mi	miles
mm	millimeters
mmol L^{-1}	millimoles per liter
N	nitrogen
Na^+	sodium ion
NADP	National Atmospheric Deposition Program
nCPA	non-parametric change point analysis
NH_4^+	ammonium ion
NO_3^-	nitrate ion
Pt Co	platinum cobalt
QA	quality assurance
Q%	discharge percentile
$RCOO^-$	strongly acidic organic anions
RDA	redundancy analysis
S	sulfur
SBC	sum of base cations
Si	silicon
SO_4^{2-}	sulfate ion
TITAN	threshold indicator taxa analysis
TOC	total organic carbon
µeq L^{-1}	microequivalents per liter
µeq L^{-1} y^{-1}	microequivalents per liter per year
µmol L^{-1}	micromoles per liter
µmol C L^{-1}	micromoles of carbon per liter
µmol H L^{-1}	micromoles of hydrogen per liter
USGS	United States Geological Survey
WASS	Western Adirondack Stream Survey

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Summary

S.1 Background and Purpose

The Adirondack region of New York has an extensive network of flowing waters, of which 14,175 kilometers (km) (8,800 mi) are mapped as first-order headwater streams—60% of all flowing waters within the region. The first large-scale Adirondack stream survey involved sampling of approximately 200 headwater streams in the early 1980s. However, through the 1980s and 1990s, Adirondack surface water monitoring focused on lakes, and data were collected regularly on only a handful of streams. Streams can be acidified more readily than lakes and more closely reflect the influences of terrestrial vegetation and soil processes.

Recognition of the added information that could be provided by streams in evaluating recovery of acidic deposition led to the Western Adirondack Stream Survey (WASS); a pilot project designed to assess the chemistry and biota of headwater streams and the soils in the western 20% of the Adirondack ecoregion. To build on the information gained in the WASS, the East-Central Adirondack Stream Survey (ECASS) was implemented with similar methodological approaches to assess acid rain effects on stream ecosystems and related soil characteristics in the remaining 80% of the Adirondack Park. The ECASS study area, which encompasses nearly 2 million hectares (ha), includes wide variations in geology, topography, surface hydrology, vegetation, soils, and atmospheric deposition, and includes over two thirds of the New York State designated wilderness area within the Adirondack Park.

The two primary objectives of the ECASS were to (1) assess stream chemistry and biota with respect to acidic deposition effects and (2) use chemical and biological measurements of streams to establish a baseline for assessing effects of future changes in atmospheric deposition and other drivers of environmental change such as trending climate. Included in the stream chemistry sampling program were six streams previously sampled in the early 1980s and selected high-elevation streams within an area loosely referred to as the Adirondack High Peaks region. In this report, the High Peaks region refers to the area in the northeastern section of the Adirondack ecoregion that includes all the mountains with summits over 1200 meters (m). To relate information on water chemistry to biological conditions in the survey streams, diatom samples and macroinvertebrate samples were collected. Year-round monitoring of stream chemistry with biweekly and automated high-flow sampling at Buck Creek, near Inlet, NY, was used to place the data obtained from the surveys into the context of variations that occurred throughout the two-year sampling period.

S.1.1 Study Region Characteristics

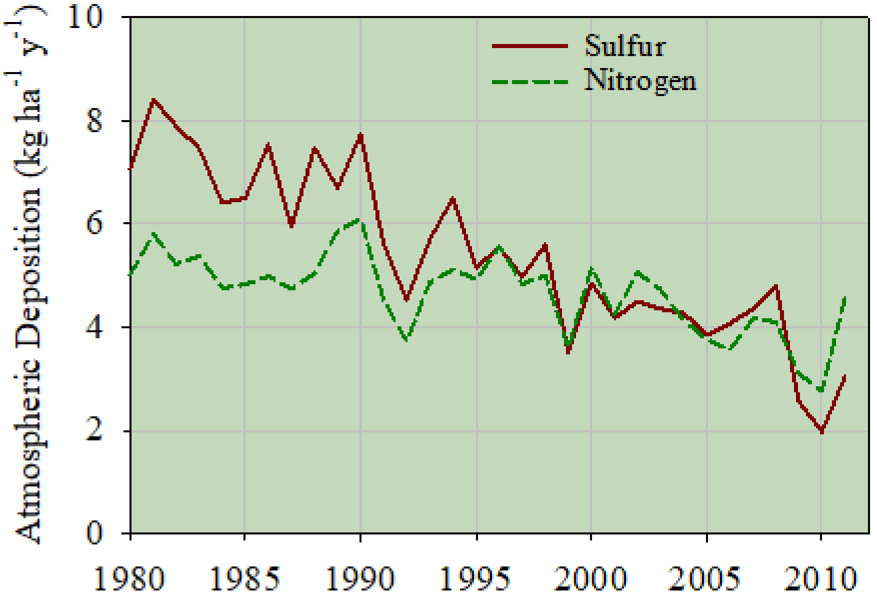
The study region is characterized by rugged, irregular terrain formed by repeated glaciations that last receded approximately 10,000 years ago. Bedrock geology is a complex mixture of granitic and gneissic rocks with a variety of less common metasedimentary formations scattered throughout the region (Baker *et al.*, 1990). Surficial deposits reflect this complexity and include highly-weatherable calcareous minerals in some areas (Baker *et al.*, 1990). Mean annual precipitation ranged from approximately 800 to over 1,600 millimeters (mm) across the region during the 1990s (Ito *et al.*, 2002). Extended periods of below-freezing winter temperatures result in accumulation of snow by the onset of spring, which melts over a few weeks and causes the highest sustained stream flows of the year. Acidic deposition levels have been declining for over two decades in the study region (Figure S-1) but remain among the highest in the Northeast with respect to both sulfate (SO_4^{2-}) and inorganic nitrogen (N) (http://nadp.slh.wisc.edu; accessed August 1, 2018).

S.1.2 Sampling Design and Methods

Streams were identified for possible sampling if they (1) appeared on a U.S. Geological Survey (USGS) topographic map coverage at 1:24,000 scale, (2) were accessible by hiking to and from the sampling location within about 1 hour, and (3) did not contain upstream lakes or ponds that drained more than 25% of the total drainage area defined by the sampling point. Streams were selected for sampling by random selection of cells in a 3 km by 3 km grid that overlaid the ECASS study region. If no appropriate streams occurred within the sampling cell, an alternative cell was randomly selected. If more than one appropriate stream occurred in the sampling cell, then a single stream was randomly selected from the cell.

Figure S-1. Wet Deposition of Sulfur and Inorganic Nitrogen, 1980-2011

Wet (rain and snow) deposition measured at the NADP (National Atmospheric Deposition Program) monitoring station NY20, located at Huntington Wildlife Forest in the central Adirondack region.



Sampling was conducted once during summer base flow (August 9–11, 2010), once during spring snowmelt (April 18–20, 2011), and once during fall (October 31–November 2, 2011) to account for seasonal and flow effects. Samples were also collected from 12 high-elevation streams during snowmelt, and from 11 of those 12 streams in summer. All of these streams were located within the High Peaks region and none met the accessibility criterion. An additional six streams in the southern ECASS study area, previously sampled from early April to early May, in either 1980 or 1982, were resampled five times in early April to early May in 2011.

Continuous monitoring at Buck Creek, near Inlet, NY (USGS Site ID 04253296), was used to relate conditions of flow and chemistry during the samplings to the variations of these measurements during the two-year period that encompassed the study period, and the full record dating back to 2002. Monitoring data from Buck Creek, the North and South Buck Creek tributary watersheds, and Archer Creek were used to determine how stream chemistry at these sites differed between the WASS and ECASS surveys. Flow data were developed using U.S. Geological Survey (USGS) methods and chemical analyses were done using U.S. Environmental Protection Agency (EPA) methods for acidic deposition studies.

Macroinvertebrate communities were sampled from 50 ECASS stream sites to further refine these relationships. Thirty-six sites were sampled in 2011 prior to flooding from Tropical Storm Irene while the remaining 14 sites were sampled in 2012 to allow for biological recovery following the severe flooding. Macroinvertebrates were collected using a standard traveling kick sample (Smith *et al.*, 2014) and a randomly-selected 100-organism subsample was identified to the lowest possible taxonomic resolution (usually genus or species). The resulting data were combined with those of the 2004 WASS.

In each of the randomly selected streams, diatoms were collected from all available habitats in each of the three samplings. The samples were preserved in the field with formaldehyde then processed in the laboratory and mounted onto glass slides. On each slide, 300 diatom frustules were counted and identified to species. Redundancy analysis (RDA) was used to examine how diatom species composition changed along environmental gradients within each of the ECASS sampling periods. To see how diatom flora related to stream chemistry across the entire Adirondack Park, two RDAs were also run on all WASS and ECASS samples combined over all sampling periods.

S.1.3 Variability of Flow and Chemical Concentrations during and among Sampling Periods

Variations in flow over the three-day sampling periods were low to moderate during the August base-flow sampling, moderate during the October–November fall sampling, and high to extremely high during the April snowmelt sampling; based on the percentage of days within the sampling year with flows higher than on the sampling date. These percentages were similar to those determined for the 10-year period from 2002 through 2011, which indicated that the flow ranges in the survey years of 2010 and 2011 were not unusual with regard to ranges in flow.

The large fluctuations in flow during the snowmelt sampling did not result in large changes in stream chemistry. The high-soil water flux that accompanied the high-stream flows during most of the spring snowmelt appeared to maintain acidification of stream water at levels from high to very high. Although the variation in flow during the summer base-flow sampling was low, measurements sensitive to instream biological activity such as concentrations of SO_4^{2-}, nitrate (NO_3^-), and dissolved organic carbon (DOC) exhibited variations that were likely related to the small variations in flow.

Analysis of stream chemistry between the WASS (2003-05) and ECASS (2010-11), based on stream monitoring throughout this period at Buck Creek, North and South Buck Creek tributaries, and Archer Creek, indicated that concentrations of SO_4^{2-} and the sum of base cations (SBC) decreased, while inorganic Al (Al_i) concentrations increased during the period between the two surveys. However, other measured constituents showed varied temporal trend patterns. Overall, the lack of consistent changes in many of the constituents suggested a somewhat weak and complex response to the change in acidic deposition between the WASS and ECASS.

S.1.4 Assessment of Stream Acidification

Buck Creek stream chemistry during 2010–2011 indicated that the level of acidification during the snowmelt sampling did not reflect the most acidic conditions that occurred in the two-year window that encompassed the three samplings. The minimum base-cation surplus (BCS) value measured at Buck Creek with routine monitoring during the overall spring snowmelt period of 2011 was -58 microequivalents per liter (μeq L^{-1}), and similar BCS values also occurred in September 2010, May 2011, and August 2011. These BCS values were lower than the mean at Buck Creek for the full-study period by 19 μeq L^{-1}. However, the most acidic value of BCS at Buck Creek during the two-year study window (-72 μeq L^{-1}) was measured on June 28, 2010. This value was lower than the mean BCS measured at Buck Creek during the snowmelt sampling by 33 μeq L^{-1} and demonstrated that severe acidification episodes occurred throughout the year. On this basis, the maximum acidification of the sampled streams during the two-year study period was estimated to be an average of 33 μeq L^{-1} less than that measured in the April snowmelt sampling, which encompassed the most acidic conditions of the three samplings.

Streams with a BCS value < 0 μeq L^{-1} were considered to be acidified by acidic deposition at the time of sample collection because this BCS value represents the threshold below which toxic Al mobilization occurs (Lawrence *et al.*, 2007). Only 7% of streams sampled during August base flow were acidified based on this criterion, whereas 16 and 11% were acidified during snowmelt and fall samplings, respectively. The 33 μeq L^{-1} adjustment to the April sampling for conditions of maximum acidification indicated that 42% of the streams would likely experience BCS < 0 μeq L^{-1} during conditions of maximum acidity within the two-year study period (Table S-1).

The percentage of streams considered to be acidified at the time of sampling based on the United States Environmental Protection Agency (EPA) criterion of ANC < 0.0 μeq L^{-1} was one-half or less the values based on BCS < 0 μeq L^{-1} (Table S-1). The number of streams with acid-neutralizing capacity (ANC) < 50 μeq L^{-1} 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). However, when this value is applied to the August sampling, only 14% of streams were estimated to be at risk of acidification during high-flow episodes, which is one third of the streams estimated to be prone to acidification based on snowmelt sampling and the BCS threshold.

Concentrations of inorganic Al exceeded 2.0 micromoles per liter (μmol L^{-1}), the level above which biota can be harmed by acidification (Driscoll *et al.*, 2001), in only 3% of streams in the August sampling, 12% in the April sampling, and 4% in the fall sampling (Table S-1). Decreases in pH that reach values near 5.0 can lead to Al_i mobilization, but pH itself has been found to be harmful to aquatic biota when below 6.0 (Driscoll *et al.*, 2001). In the August sampling, 10% of streams had pH values below 6.0, but this more than doubled to 28% in the April sampling. The higher level of acidification during spring snowmelt than summer base flow was in large part due to dilution of base cations, especially Ca^{2+} (calcium ion) that resulted from high-snowmelt runoff. In all three samplings, SO_4^{2-} was the predominant strong acid anion.

Table S-1. Measures of Stream Acidification

BCS is base-cation surplus; ANC is acid-neutralizing capacity by Gran titration; Al_i is inorganic monomeric Al. Percent of streams prone to acidification during the study period is indicated in parentheses.

Survey Date	Aug. 9-11, 2010	Apr. 18-20, 2011	Oct. 31-Nov. 2, 2011
Number of streams sampled	178	195	203
Percent of streams with BCS < 0 μeqL^{-1}	7	16 (42)	11
Percent of streams with ANC < 0 μeqL^{-1}	2	8	4
Percent of streams with Al_i > 2.0 μeqL^{-1}	3	12	4
Percent of streams with pH < 6.0	10	28	16

S.1.5 Chronic versus Episodic Acidification

To evaluate the relative spatial extent of chronic and episodic acidification, results of the April 2011 sampling were chosen to represent high-flow, or episodic conditions, whereas results of the August 2010 sampling were chosen to represent base flow, or non-episodic conditions. A total of 169 streams had data that could be used in this comparison. Streams with a BCS value < 33 μeq L^{-1} in both samplings were considered to be chronically acidified. Streams with a BCS value < 33 μeq L^{-1} in the April 2011 sampling, but > 33 μeq L^{-1} in the August 2010 sampling, were considered episodically acidified. All streams with BCS < 33 μeq L^{-1} in the August 2010 sampling were also acidified in the April 2011 sampling. Streams in the April 2011 sampling with BCS > 33 μeq L^{-1} were considered unacidified. Results of this analysis are summarized in the list below.

Number of streams sampled in August 2010 and April 2011:	**169**
Number of chronically acidified streams:	**19**
Number of episodically acidified streams:	**48**
Number of unacidified streams:	**102**

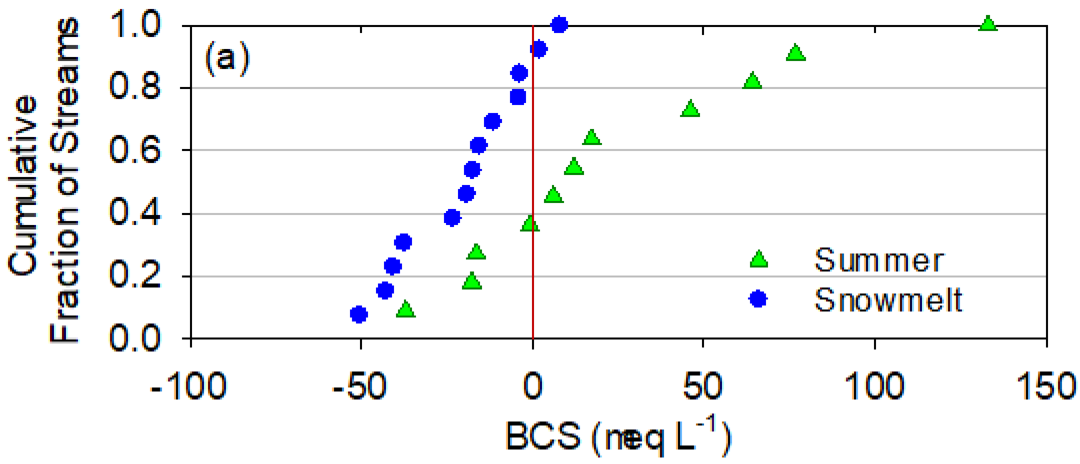
S.1.6 High-Elevation Stream Chemistry

Comparison of stream chemistry between the high-elevation samplings (HES) indicated that conditions were much more acidic during the snowmelt sampling than during the summer sampling. Values of BCS were less than zero in only four streams during the summer sampling, but less than zero in all but two streams during the snowmelt sampling (Figure S-2). Values of pH showed a similar relationship between the two samplings with values ranging from approximately 5.0 to above 7.0 in the summer but shifting downward during snowmelt to a range of approximately 4.6 to 6.0. Concentrations of Al_i were also higher during snowmelt than during the summer although the concentration range was similar between the samplings, with the exception of one stream.

The ionic causes of higher acidification during the snowmelt HES than the summer HES strongly contrasted with the previous findings. Although concentrations of NO_3^- and $RCOO^-_s$ (strongly acidic organic anions) were somewhat higher during snowmelt than summer, SO_4^{2-} concentrations during snowmelt were half those in the summer. During snowmelt, the dilution of base cations overwhelmed the decrease in total acid anions, causing harmful stream acidification despite the low levels of acidic deposition resulting from the steady decrease over the previous two decades. The dilution effect may also have contributed to the higher DOC concentrations during snowmelt than during summer (Monteith *et al.*, 2007). We are not aware of other reports in the literature of increased stream acidification occurring with decreased total strong acid-anion concentration.

Figure S-2. Values of BCS (Base-Cation Surplus) versus the Cumulative Fraction of High-Elevation Streams during Summer and Snowmelt Samplings

Red vertical line indicates the BCS value below which Al_i is mobilized by acidic deposition.



S.1.7 Historical Changes in Stream Chemistry within the ECASS Region

Measurements of ANC in the early 1980s indicated that three of the six sampled streams were poorly buffered at that time (ANC < 5 µeq L^{-1}), whereas two of the streams were moderately well-buffered (65 µeq L^{-1} < ANC < 85 µeq L^{-1}) and one stream was well-buffered (ANC = 165 µeq L^{-1}). Rates of increase in ANC in the two poorly buffered streams that increased significantly from the 1980s to 2011 ($P < 0.10$), were 0.25 µeq L^{-1} y^{-1} and 0.50 µeq L^{-1} y^{-1}. At those rates of recovery, an ANC of 50 µeq L^{-1} would not be achieved in these streams for 65 to 160 years. The most acidic of the resampled streams, did not show a statistical difference between samplings ($P > 0.10$), although ANC was 9.0 µeq L^{-1} higher in the 2011 sampling than the sampling in 1982.

Of the moderately well-buffered streams, one exhibited an increase ($P < 0.10$) in ANC of 40 μeq L^{-1} (1.4 μeq L^{-1} y^{-1}) and the other exhibited a nonsignificant ($P > 0.10$) ANC increase of 30 μeq L^{-1}. The well-buffered stream displayed no change in ANC over the three decades. Measurements of pH showed a more consistent response than ANC, with highest values in 2011 that were statistically significant in three of the streams at the $P < 0.05$ level and one stream at the $P < 0.10$ level. Marked decrease in specific conductance of the three most acidic streams was measured, which reflected the dilution of stream water even as pH increased. The better buffered streams in this comparison did not experience the large decreases in specific conductance.

S.1.8 Stream and Soil Chemistry Comparison for WASS and ECASS Regions

Continuous stream monitoring at Buck Creek, the North and South tributaries of Buck Creek, and Archer Creek during the WASS and ECASS sampling periods showed that changes in the interval between surveys (2003–2005 to 2010–2011) did not preclude comparison of results from the two surveys and development of an Adirondack-wide assessment. The changes observed were consistent with decreasing atmospheric SO_4^{2-} deposition over this period, and included small increases in ANC, but the lack of consistent changes in many chemical constituents suggest a meager and complex response to declines in atmospheric deposition over the seven intervening years between these two stream surveys.

Comparison of WASS and ECASS data for snowmelt periods indicated that more streams sampled in the WASS were acidified than those sampled in the ECASS (Figure S-3). In these snowmelt samplings, fewer than half (approximately 45%) of ECASS streams had values above 50 μeq L^{-1}, whereas only 25% of WASS streams had ANC values above this level. Concentrations of SO_4^{2-} and NO_3^- were higher in WASS streams than ECASS streams, however, concentrations of calcium (Ca^{2+}) were highly similar, which is an indication that acid buffering is, in general, higher in the ECASS watersheds.

The spatial distribution of ECASS streams acidified during the ECASS and WASS snowmelt samplings was largely limited to the western and southern portions of the project region (Figure S-3). The high-elevation streams comprised most of the streams in the northern half of the region that were acidified during the snowmelt sampling. However, streams determined to be prone to episodic acidification were distributed throughout most of the ECASS region.

Soil and stream data from 26 watersheds were used to estimate soil-base saturation of the upper B horizon from BCS values in stream water. Base-saturation estimates of the upper B horizon modeled from stream chemistry showed that areas with base-saturation values that provided insufficient acid buffering to prevent mobilization of toxic forms of Al (< 17 %) were common through the west and central parts of the Adirondack region (Figure S-4). Soils with low-base saturation less than 10% were concentrated in the west, but soils with base saturation less than 25% extended through most of the Adirondack Park, and comprised over 50% of the area mapped within the blue line. Mobilization of Al, which occurs in soil with base saturation below 17% in the upper B horizon, has recently been identified as a control of forest species composition and structure in Adirondack forests (Lawrence *et al.*, 2018).

Figure S-3. Map of Acidification Status of ECASS and WASS Streams during Snowmelt

Circles indicate streams acidified when sampled (red), streams prone to acidification under conditions more acidic than when the stream was sampled (yellow), and streams that are unlikely to acidify to levels that mobilize inorganic Al under worst conditions (teal). Diamonds show high-elevation streams with the same color coding. Green line is the boundary of the Adirondack ecoregion; blue line is the boundary of the Adirondack State Park; and white line separates the WASS and ECASS study areas.

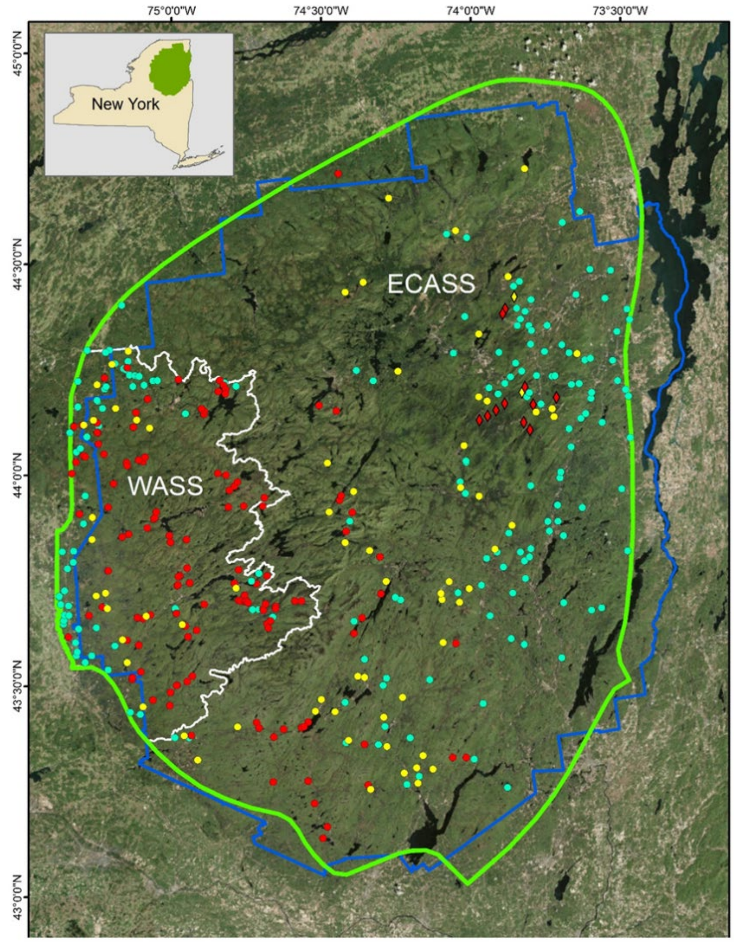
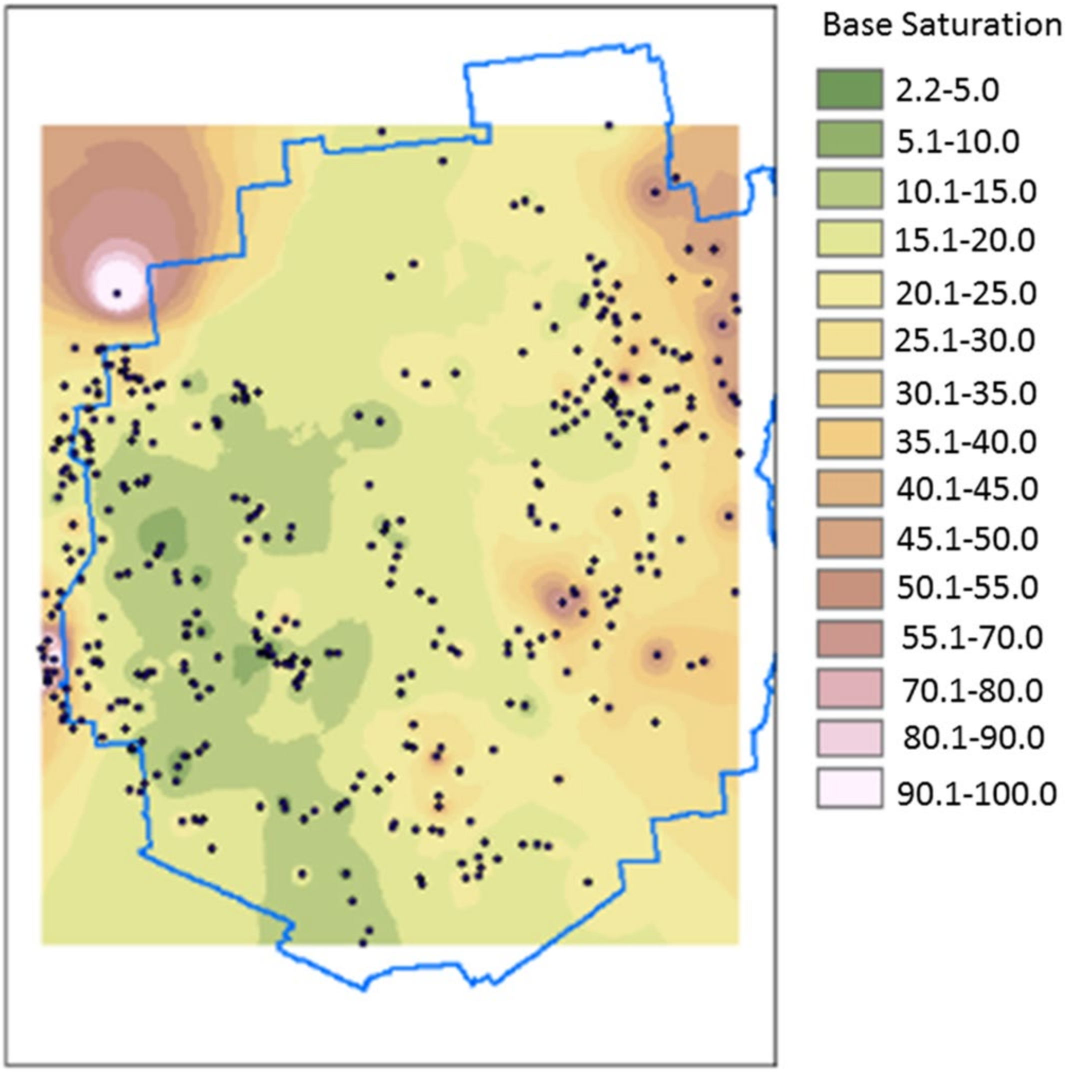


Figure S-4. Variation in Base Saturation (Percent) across the Adirondack Region

Black circles indicate locations of stream sampling used to develop the base-saturation coverage. Blue line indicates the boundary of the Adirondack State Park.



S.1.9 Biological Assessments

Assessments of relationships between stream chemistry and aquatic macroinvertebrate community structure were done with the acid-biological assessment profile (acidBAP) index of acidification effects. This index was developed for the specific purpose of assessing macroinvertebrate taxa of acidic streams in the Adirondack and Catskill regions (Baldigo *et al.*, 2009). Macroinvertebrate data used in a change-point analysis of the relationship between the acidBAP index of acidification effects and the BCS indicated that the most likely threshold for the condition of macroinvertebrate communities occurred at a BCS of 4.9 µeq L^{-1}, which is near the theoretical threshold for Al mobilization of BCS = 0.0 µeq L^{-1}. The weak relationship between acidBAP and BCS at positive BCS values, and the large difference in acidBAP on either side of the BCS change point (cp) may be explained by toxic Al chemistry at lower BCS values. Negative BCS values are often associated with Al_i concentrations greater than 2 µmol L^{-1}, the generally accepted value above which aquatic biota are at risk (Baldigo *et al.*, 2007, Driscoll *et al.*, 2001). The change point for Al_i identified in this analysis was only 0.9 µmol L^{-1}, suggesting that macroinvertebrate communities may be adversely affected by lower Al_i concentrations than previously thought.

Diatom community composition was best explained by gradients of acidity (pH or Ca^{2+} and Al_i) and second best by color, which has been related to iron (Fe) concentrations in previous studies (Maranger *et al.*, 2006). Significant chemical and biological differences were observed among the f our stream classifications identified in regression tree analysis: non-acidified streams with pH > 6.8, moderately acidified streams with 6.09 < pH < 6.8, severely inorganically acidified streams with pH < 6.09 and DOC < 361 micromoles of carbon per liter (µmol C L^{-1}), and severely organically acidified streams with pH < 6.09 and DOC > 361 µmol C L^{-1}. Mean pH differed across all four groups, with severely organically acidified streams having the lowest pH. Mean DOC was highest in severely organically acidified streams and lowest in non-acidified and severely inorganically acidified streams, which did not differ in concentrations of DOC. Species richness was highest in non-acidified streams but did not differ significantly between non-acidified and moderately acidified streams. Species richness was significantly higher in severely organically acidified streams relative to severely inorganically acidified streams, even though severely organically acidified streams had significantly lower pH. The source of acidity (organic versus inorganic), rather than simply pH, was a key factor to diatom community richness and measures of guild composition.

S.1.10 Conclusion

The 42% of accessible streams that were determined to be prone to acidification indicates that episodic acidification caused by acidic deposition was having a substantial effect on stream-water quality on the ECASS region of 19,970 km^2 (7,710 mi^2). When extrapolated to the total length of accessible first-order streams in the study region (3,400 km), approximately 1,400 km (670 mi) of stream reaches were determined to be prone to acidification. Including the WASS region increased the affected length of streams to approximately 6,600 km (4,101 mi) for the Adirondack ecoregion as a whole.

As atmospheric deposition of SO_4^{2-} decreased to levels that approached those of the early 1900s, the leaching of base cations also decreased, which lowered base-cation concentrations in streams. This depletion was evident in (1) the marked decrease in the SBC in Archer Creek and the Buck Creek streams that occurred between the WASS and ECASS, (2) mean Ca^{2+} concentrations in the ECASS snowmelt sampling that were less than half those measured in the summer base-flow sampling, (3) greater acidification during snowmelt than summer base flow in high-elevation streams despite a lower concentration of total strong acid anions, and (4) 58% of ECASS watersheds having base saturation of the upper mineral soil insufficient to prevent Al mobilization under 2010–2011 deposition levels.

The monitoring at Buck Creek showed that not only did spring snowmelt produce sustained high levels of acidification, high flows triggered acidification episodes throughout the year that equaled or surpassed peak acidification during snowmelt. The susceptibility to severe acidification episodes throughout the year is likely to exist in the numerous ECASS streams with high acid-sensitivity, even with low levels of acidic deposition. The frequency of these episodes may increase as a result of increases in the rate extreme weather events that have been identified in the Northeast as a result of trending climate (Hayhoe *et al.*, 2007).

Results from both macroinvertebrate and diatom assessments of the ECASS indicated a strong sensitivity to Al_i. In the macroinvertebrate analysis, the change point determined by relating BCS to the acid sensitivity index, acidBAP, approximated the threshold for Al mobilization. The diatom analyses also showed a marked difference between communities where natural organic acidity reduced concentrations of Al_i and communities exposed to elevated concentrations of Al_i, even under conditions of similarly low pH. The source of acidity, rather than simply pH was strongly related to diatom community richness and measures of guild composition.

Overall results of the ECASS indicated that chronic acidification of streams was not widespread in the study region, but that acid-sensitive watersheds prone to episodic acidification were common through much of the region. The method of linking permanent monitoring streams to periodic surveys to identify variation in stream chemistry under different seasons and flow conditions will need to be continued to further our understanding of how streams and watersheds are responding to changing levels of acidic deposition and trends in climate.

1 Introduction

The Adirondack region of New York has an extensive network of flowing waters, of which 14,175 km (8,800 miles) are mapped as first-order headwater streams—60% of all flowing waters within the region. The first large-scale stream survey to characterize the chemistry of Adirondack streams involved the sampling of approximately 200 Adirondack streams in the early 1980s. Further stream sampling was done from 1988 to 1991 by the United States Environmental Protection Agency (EPA) Episodic Response Project (ERP). The ERP focused on stream acidification and its biological effects during high-flow episodes in three streams during 1988–1990 (Buck Creek, Bald Mountain Brook and Seventh Lake Outlet) and one pond outlet. Sampling of Bald Mountain Brook was extended through 2013 and sampling of Buck Creek is ongoing. Long-term stream monitoring of three additional headwater streams (Archer Creek, North and South tributaries of Buck Creek) was initiated in the late 1990s and is also ongoing. A second large-scale stream survey, named the Western Adirondack Stream Survey (WASS), involved the sampling of 200 streams from 2003–2005 in the western Adirondack region where surface water acidification was most extensive.

Prior to the expansion of Adirondack stream sampling in the late 1990s, an extensive lake chemistry monitoring program was the primary method for evaluating potential recovery of the Adirondack ecosystem (Driscoll *et al.*, 2003). However, despite similarities between lake and stream chemistry that are typical within a region, lake chemistry can be an unreliable indicator of stream chemistry when assessing effects and recovery with regard to acidic deposition (Lawrence *et al.*, 2008b). Streams can be acidified more readily than lakes because they are more influenced by shallow flow paths that are often ineffective at neutralizing acidity. And unlike lakes, streams are not able to attenuate acidic inputs during high flows with acid-buffered water that had been previously stored during base flows. Stream water also reflects the influences of terrestrial vegetation and soil processes more directly than lake water, which is altered by within-lake processes that occur while the water is stored. Lastly, headwater streams provide important habitat for species, some of which share both terrestrial and aquatic ecosystems.

Recognition of the added information that could be provided by streams in evaluating recovery of acidic deposition led to the WASS, which was conducted in 2003–2005 to assess the effects of acidic deposition on stream chemistry, diatoms, macroinvertebrates, and soil chemistry in the Oswegatchie-Black River drainages. The WASS study area, which comprised approximately 20% of the overall Adirondack region, was implemented as a pilot study to evaluate a new, cost efficient sampling method developed to enable regional characterization of both chronic and episodic acidification of headwater streams. The new approach involved flow-synchronized sampling of approximately 200 streams over periods of 3–4 days. A new chemical index of acidification, termed the base-cation surplus (BCS), was also developed through analysis of WASS and Buck Creek data (Lawrence *et al.*, 2007). The BCS enabled the effects of acidic deposition to be distinguished from natural acidity by relating base-cation availability directly to the mobilization of inorganic Al.

The WASS approach was successful in determining the percentage of streams and total stream length prone to episodic and chronic acidification for the 565 streams accessible for sampling within the WASS region (Lawrence *et al.*, 2008a). The WASS also showed that the BCS values related directly to impacts on diatom (Pound *et al.*, 2013) and macroinvertebrate communities (Baldigo *et al.*, 2009), which were moderately to severely impacted by acidic deposition in 66 and 52% of streams, respectively. Furthermore, quantitative relationships were developed between stream chemistry and soil chemistry that enabled a regional assessment of soil acidification from the extensive stream data collected (Lawrence *et al.*, 2008b). The sampling design and methods of the WASS enabled acidic deposition effects to be assessed in terms of the linkages between terrestrial and aquatic ecosystems, which provides a more comprehensive understanding of acidic deposition effects than the conventional approach of assessing aquatic and terrestrial effects separately.

Information on the condition of Adirondack streams outside the Oswegatchie-Black drainages has been largely limited to the sampling done in the early 1980s, so recent conditions are unknown. This represents an area of nearly 2 million hectares that contains over two thirds of the New York State designated wilderness area in the Adirondack Park, including the area loosely referred to as the High Peaks region. In this report, the High Peaks region refers to the area in the northeastern section of the Adirondack ecoregion that includes all the mountains with summits over 1,200 m. Wide variations in geology, topography, surface hydrology, vegetation, soils and atmospheric deposition levels exist throughout the Adirondack Park. To build on the success of the WASS, a project was designed with a similar methodological approach to assess acid rain effects on stream ecosystems and related soil characteristics in the remaining 80% of the Adirondack Park. The two primary objectives of this project, referred to hereafter as the East-Central Adirondack Stream Survey (ECASS), were to (1) assess conditions with respect to acidic deposition effects and (2) use chemical and biological measurements of streams to establish a baseline for assessing effects of future changes in atmospheric deposition and other drivers of environmental change such as trending climate. Included in the stream chemistry sampling program were selected high-elevation streams in the High Peaks region of the Adirondack ecoregion, and streams that had been sampled in the early 1980s. To relate information on water chemistry to biological conditions in the survey streams, diatom samples and macroinvertebrate samples were collected. An analysis was also done to determine if temporal changes in stream chemistry occurred between 2003 and 2005 (the WASS study period) and 2010 and 2011 (the ECASS study period), and whether the data from the two projects were sufficiently compatible to assess the condition of headwater streams throughout the Adirondack region.

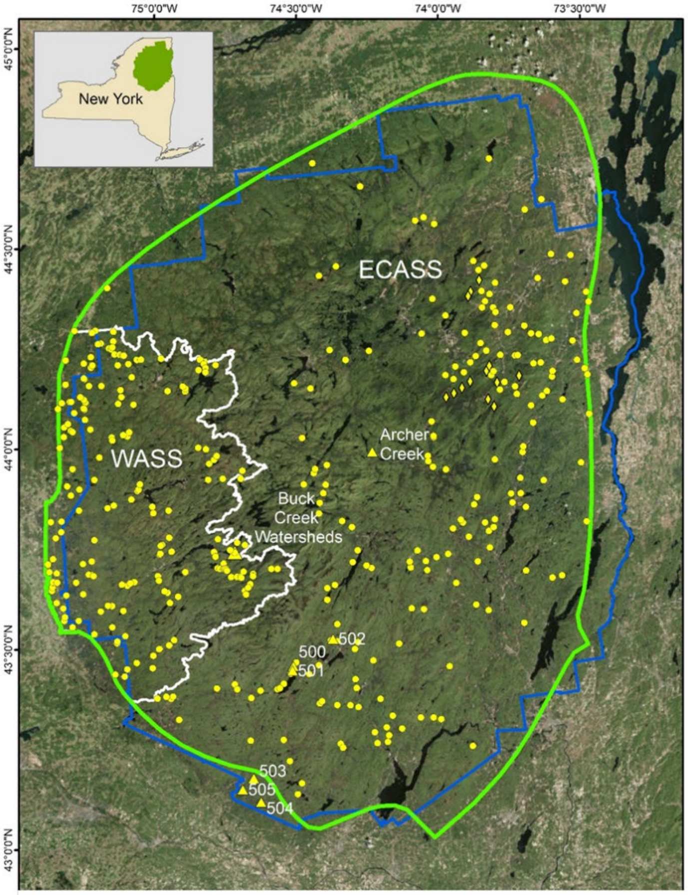
2 Methods

2.1 Study Region

The stream survey was conducted throughout the central and eastern parts of the Adirondack Ecological Region, or ecoregion (McNab & Avers, 1994), which roughly corresponds to the boundary of the Adirondack State Park. The study region comprises approximately 80% of the 24,000 km^2 Adirondack State Park, which 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 receded approximately 10,000 years ago. As a result, ridge tops are generally 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 range from 197 m to 1630 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).

Figure 2-1. Map of Sampling Locations in the Study Region

Yellow circles indicate locations of the streams sampled in the ECASS (East-Central Adirondack Stream Survey) and WASS (Western Adirondack Stream Survey). WASS streams are outlined in white. Historical streams sampled in the 1980s (labeled 500-505) and continuously monitored streams (Buck Creek and Archer Creek) are shown with yellow triangles. Imagery shows forest cover in green and surface waters in black. The green line encompasses the Adirondack ecoregion; the blue line encompasses the Adirondack State Park.



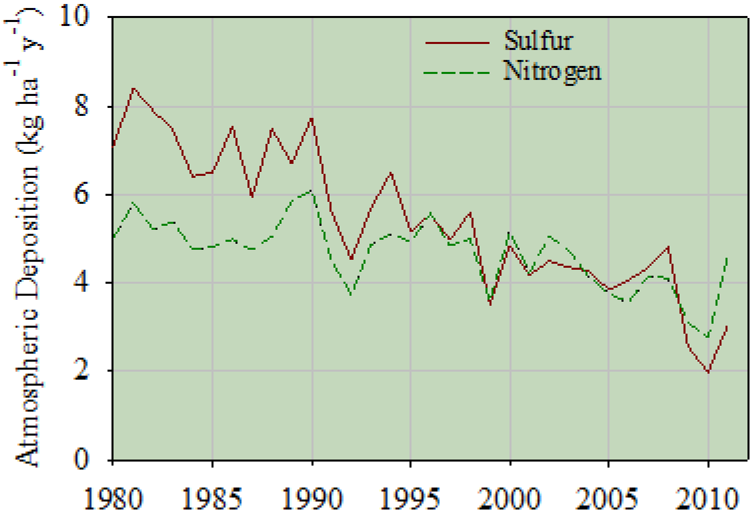
Mean annual precipitation ranges from approximately 800 to over 1,600 mm across the region (Ito *et al.*, 2002). Extended periods of below-freezing winter temperatures result in accumulation of snow by the onset of spring, when the snowpack melts over a few weeks and causes the highest sustained stream flows of the year (Lawrence *et al.*, 2004). Atmospheric deposition of SO_4^{2-} and N in the study region remain among the highest in the Northeast, although levels from Pennsylvania and the Ohio River Valley are considerably higher (http://nadp.slh.wisc.edu/; accessed June 2, 2018). From 1980–2011, deposition of SO_4^{2-} decreased ($P < 0.05$) at the National Atmospheric Deposition Monitoring (NADP) station (NY20) centrally located within the Adirondack region from > 7 to 2 kilograms of sulfur per hectare per year (kg S ha^{-1} y^{-1}), and inorganic N deposition decreased from > 5 to 2.8 kilograms of nitrogen per hectare per year (kg N ha^{-1} y^{-1}) in the same time period (Figure 2-2). Spatial modeling has shown a general decrease in deposition from southwest to northeast across the Adirondack region (Ito *et al.*, 2002). Within the ECASS study region the areas with the highest elevation tend to have the highest atmospheric deposition levels (Ito *et al.*, 2002). The combination of high amounts of precipitation and bedrock mineralogy that weathers slowly make this region particularly susceptible to adverse effects of acidification.

2.2 Stream Water Sampling Design and Chemical Analysis

Streams were identified for possible sampling if they met the following criteria: (1) the stream appeared on a USGS topographic map coverage at 1:24,000 scale, (2) the stream was accessible by hiking to and from the sampling location within about 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. To randomly select streams for sampling, the Adirondack Ecological Region was overlain by a grid of 3 km by 3 km cells. Each cell was given a unique number to enable 200 cells to be selected randomly. If no appropriate streams occurred within the sampling cell, an alternative cell was randomly selected. If more than one appropriate stream occurred in the sampling cell, then a single stream was randomly selected from the cell. Because the southwestern area of the study region was expected to have greater variability with respect to stream chemistry than the rest of the region, an additional 10 sites were randomly selected from this area. The most downstream point within the cell was used as the sampling location.

Figure 2-2. Atmospheric Deposition of Sulfur and Inorganic Nitrogen

Wet (rain and snow) deposition measured at the NADP (National Atmospheric Deposition Program) monitoring station NY20, located at Huntington Wildlife Forest in the central Adirondack region.



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 did enable identification of stream reaches prone to episodic acidification by comparing stream chemistry during high and low flows. All stream samples collected in the surveys were analyzed for pH (without air-equilibration), acid-neutralizing capacity by Gran titration (ANC) and concentrations of Ca^{2+}, Mg^{2+} (magnesium ion), Na^{+} (sodium ion), K^{+} (potassium ion), SO_4^{2-}, NO_3^{-}, Cl^{-} (chloride ion), dissolved organic carbon (DOC), NH_4^{+} (ammonium), Si (silicon), F (fluoride), total unfiltered Al (Al_t), total monomeric Al (Al_{tm}), and organic monomeric Al (Al_o) in the laboratory of the Adirondack Lakes Survey Cooperation (ALSC) with EPA methods (https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=30000TA0.PDF; accessed January 15, 2018). Inorganic monomeric Al (Ali) was determined by subtracting Al_o from Al_{tm}.

A chemical index of stream water termed the base-cation surplus (BCS) was developed to quantify the status of watersheds with respect to the Al mobilization threshold in soils and was calculated from water chemistry measurements as described in Lawrence (et al. 2007). For values of BCS greater than zero, stream water Al concentrations are essentially zero, which indicates that Al mobilization is minimal or not occurring in the watershed. Values of BCS less than zero correlate linearly with stream concentrations of Al_i, the forms of Al that are mobilized by acidic deposition. Therefore the BCS value of zero defines the threshold of Al mobilization (Lawrence *et al.*, 2008a).

In addition to episodic variations in stream chemistry, seasonal patterns in the degree of acidification are also typical in Adirondack surface waters. During early spring, when flows are generally elevated from snowmelt and increased precipitation, 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.*, 1996b). Stream water during summer base flow tends to be the least acidic of the year. Stream flows also tend to be the lowest in summer due to evapotranspiration that reduces soil moisture. To address seasonal variation, sampling was conducted once during summer base flow (August 9–11, 2010), once during spring snowmelt (April 18–20, 2011), and once during fall (October 31–November 2, 2011). All samples were collected over three-day periods, with the exception of a single sample that was collected on the fourth day in the fall 2011 sampling.

To evaluate variations in chemistry that occurred during the sampling periods, samples were collected from selected streams on each day of each of the three sampling periods. Stream water was also collected from 11 high-elevation streams during summer base flow and 13 streams during snowmelt within the High Peaks region of the Adirondack ecoregion. These samples were collected to evaluate stream acidification at elevations that were considerably higher than the other sampled streams. Because of limited accessibility in the mountainous terrain of the High Peaks region, a random selection procedure could not be used to identify streams for sampling. Samples were analyzed in the ALSC laboratory using the same procedures as the survey samples.

To evaluate changes in stream chemistry over the longest period possible, six streams in the southern ECASS region (Figure 2-1) that had been sampled five times from early April to early May in either 1980 or 1982, were resampled five times in 2011, also in early April to early May. Samples collected in 1980 and 1982 were analyzed for ANC by Gran titration, air-equilibrated pH (pH electrode while bubbling with air) and specific conductance (conductivity meter) in the New York State Department of Environmental Conservation Laboratories in either Rome or Ray Brook, NY. Comparisons between these two laboratories were routinely run as a standard quality assurance (QA) procedure during the early sampling (Lawrence *et al.*, 2011). Samples collected in 2011 were analyzed for all constituents in the ALSC laboratory following the same procedures as the survey samples.

To place the water chemistry measurements from the surveys in the context of variations throughout the year, Buck Creek near Inlet, NY (USGS Site ID 04253296, drainage area 3.1 km^2) was used as an index stream (Figure 2-1). During the survey period (2010–2011), Buck Creek was the only Adirondack stream being monitored year-round for water chemistry that exhibited flow-related variations in acidification. Additional samples beyond the routine sampling at the main Buck Creek stream gage (BC01) were collected five times on April 20th to put sampling conditions of the snowmelt sampling in the context of daily variations in stream chemistry that could be encountered during the sampling periods. Flow at Buck Creek was determined using standard USGS methods (Rantz, 1982). Stream water samples were collected manually at Buck Creek every two weeks, year-round, and during selected high-flow events with stage-activated auto samplers, April through November. All samples were analyzed for pH, and ANC by Gran titration, and concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, Cl^-, DOC, NH_4^+, Si, Al_{tm}, and Al_o in the ALSC laboratory using the same procedures as the survey samples. Further information on Buck Creek watershed is available elsewhere (Lawrence *et al.*, 2011).

All stream chemistry data are available at USGS Water Data for the Nation (accessed January 15, 2018, at http://waterdata.usgs.gov/nwis/). Coordinates of sampling locations for all streams are provided with USGS database (NWIS) side identification codes in Appendix Tables A8a through A8k.

2.3 Changes in Stream Chemistry between the WASS and ECASS

2.3.1 Background

Spatial or geographic analysis of surface water chemistry data is often applied to make generalizations at regional to global scales (Hunsaker *et al.*, 1986, Mutema *et al.*, 2015, Pound *et al.*, 2013). Typically, the intent of such an analysis is to make generalizations about water quality or to explore various factors such as climate and land cover that may influence spatial patterns of variation. An important consideration in such spatial analyses is whether the role of temporal trends can be assumed to be negligible when samples were collected over multiple years, which is sometimes not formally addressed (Ito *et al.*, 2005). If the data in a spatial analysis were collected over several years or longer, then temporal trends could present a confounding factor that might partially obscure the spatial patterns that may otherwise be evident.

To assess stream chemistry over the entire Adirondack region, data from the ECASS study, conducted in 2010–2011, were combined with data from the WASS study, conducted in 2003–2005. During the interval between surveys, atmospheric deposition exhibited significant decreases in S and N concentrations and increases in pH across the Adirondack region (Driscoll *et al.*, 2016, Schwab *et al.*, 2016). Similar trends in SO_4^{2-}, NO_3^-, pH, and other chemical constituents were also observed in many Adirondack lakes over this same time interval (Driscoll *et al.*, 2016, Josephson *et al.*, 2014, Waller *et al.*, 2012). These observations suggest a need to evaluate whether trends in water chemistry may also be evident in Adirondack streams from 2003–2005 and 2010–2011, and whether any temporal changes are likely to affect comparisons of spatial patterns in stream chemistry across the WASS and ECASS sites. A previous analysis of trends in Adirondack stream chemistry from the early 1980s to 2008 found some slight trends that were greatest for SO_4^{2-} concentrations, but overall stream chemistry trends were less than those observed in lake chemistry (Lawrence *et al.*, 2011).

2.3.2 Study Approach

Because the WASS and ECASS were conducted five to eight years apart, changes in stream chemistry may have occurred between the surveys as a result of the decreasing trend in acidic deposition that occurred in this interval. These changes could not be readily identified because each stream was sampled only a few times in one of the two periods (2003–2005 or 2010–2011). However, four streams sampled on a regular basis from the 1990s through 2011 provided data that could be used to infer regional stream chemistry trends across the Adirondacks. These streams include Archer Creek (McHale *et al.*, 2002) in the central Adirondacks and Buck Creek along with its two major tributaries, North and South Buck Creek in the western Adirondacks (Lawrence *et al.*, 2007). These streams span a broad ANC range from -40.6 µeq L^{-1} at North Buck Creek to 7.3 µeq L^{-1} at South Buck Creek to 15.3 µeq L^{-1} at Buck Creek, and finally to 122.2 µeq L^{-1} at Archer Creek (water years 2010–2012 median values).

Two three-year periods were selected to represent the WASS (water years 2003–2005) and ECASS (water years 2010–2011) sampling periods. Eight chemical constituents were evaluated in this analysis, pH, ANC, BCS (as defined by Lawrence et al., 2007), the sum of base cations (SBC) expressed as [Ca^{2+} + Mg^{2+} + K^+ + Na^+], SO_4^{2-}, NO_3^-, DOC, and Al_i. Values of ANC by Gran titration were not available at Archer Creek and so a charge balance ANC value was calculated as follows: [Ca^{2+} + Mg^{2+} + K^+ + Na^+) – (SO_4^{2-} + NO_3^- + Cl^-]. Additionally, Al_i was not measured at Archer Creek, and instead total (unfiltered) Al was applied in this analysis. To prepare the data for analysis, chemical constituent values were averaged on days when more than one sample was collected. A discharge percentile (Q%) value was assigned to each sample day by compiling all daily mean discharge values from gaged data at each of the four sites and assigning values based on the combined six-year period.

Two statistical analyses were performed to evaluate differences in chemical constituent values for 2003–2005 and 2010–2011. The first analysis used a non-parametric Wilcoxon grouped rank-sum test to compare the two periods, and a P value < 0.05 was considered to indicate a statistically significant difference. The non-parametric Wilcoxon approach was used because none of the data sets passed ($P > 0.05$) the Shapiro-Wilk test for normality. In this approach, possible effects from differences in flow were not taken into account.

In the second analysis, analysis of covariance (ANCOVA) was applied to explore whether linear regression relations between constituent values and Q% differed across the two time periods. This analysis provided insight to whether any evident changes in constituent values differed at low-flow or high-low conditions or remained consistent across the range of flow conditions. Although most of these data failed tests for normality and equal variance, previous work has indicated that ANCOVA is little affected by violation of assumptions of normality and homoscedasticity when sample sizes are large ($n > 100$) such as in this analysis (Olejnik & Algina, 1984).

2.4 Assessment of Macroinvertebrate Communities

2.4.1 Background

Macroinvertebrates are an important biological component in Adirondack streams. They play an essential role in energy transfer within these ecosystems by accelerating the breakdown of allochthonous detritus (plant material washed into the stream), which is often the primary source of nutrients in headwater streams (Vannote *et al.*, 1980). Macroinvertebrates also serve as an important food source for secondary consumers such as fish (Hynes, 1970). Macroinvertebrates are useful as indicators of water quality because they are relatively immobile, sensitive to environmental impacts, and typically have a life span of a year or more, thereby providing an integrated assessment of antecedent and present water quality. For these reasons, the New York State Department of Environmental Conservation (and many other state and federal agencies) has developed a statewide water quality monitoring program using bioassessment of macroinvertebrate communities (Smith *et al.*, 2014).

Standard bioassessment metrics however, are often ineffective at identifying the effects of acidification on macroinvertebrate communities. Consequently, the effects of acidification and subsequent reductions in acid deposition on macroinvertebrate communities in Adirondack streams are poorly understood. To address this knowledge gap, macroinvertebrates were sampled in 2004 from 36 Adirondack streams in the western Adirondacks. A macroinvertebrate multimetric index of acidification impacts, termed the acid-biological assessment profile (acidBAP), was used to evaluate the relationship between stream acidity and macroinvertebrate community structure in these samples. The acidBAP is composed of two component metrics, percent mayfly richness and the acid tolerance index, and ranges from 0 (severe effects from acidification) to 10 (no effects from acidification) and was developed for the specific purpose of assessing macroinvertebrate taxa in acidic streams that are common in the Adirondack and Catskill regions (Baldigo *et al.*, 2009, Smith *et al.*, 2014). The relations between acidBAP values and acid-base chemistry, however, remain loosely defined, and therefore the chemical thresholds below which macroinvertebrate communities are adversely affected are unknown. This information gap precludes the assessment of future trends in the condition of macroinvertebrate communities that may result from changing rates of acidic deposition or other environmental factors.

2.4.2 Collection and Analysis

Macroinvertebrates were sampled from 50 ECASS stream sites to further refine relations between acidification and macroinvertebrate communities. Thirty-six sites were sampled in 2011 prior to flooding from Tropical Storm Irene while the remaining 14 sites were sampled in 2012 to allow for biological recovery following the severe flooding to better enable spatial comparisons among streams. Sampling by the New York State Department of Environmental Conservation's Stream Biomonitoring Unit before and after the storm in fall 2011 and early summer 2012 in Catskill streams that were similarly impacted suggested that the macroinvertebrate communities had recovered by the following summer based on acidBAP. Macroinvertebrates were collected using a standard traveling kick sample (Smith *et al.*, 2014) and a randomly-selected, 100-organism subsample was identified to the lowest possible taxonomic resolution (usually genus or species). The resulting data were combined with those of the 2004 WASS. Sites were excluded from the final analyses if they were missing chemistry data, less than 80 organisms were collected, mean BCS values > 250 µeqL^{-1}, and sampled in 2012. Sites with less than 80 organisms suggest a representative sample was not obtained or that the stream is ephemeral, while streams with BCS > 250 are not useful for defining chemical thresholds, and streams sampled in 2012 may still have been impacted by unknown residual flood effects.

The final dataset contained 28 ECASS streams and 32 WASS streams (60 total sites). Values for BCS, ANC by Gran titration, pH, and Al_i were averaged for the snowmelt and August base-flow streams samplings preceding the 2004 (WASS) and 2011 (ECASS) macroinvertebrate collections. Data were analyzed to determine (1) if and how communities at ECASS and WASS sites differed and (2) the chemical thresholds at which the greatest changes occurred in macroinvertebrate communities. For the first analysis, the taxa counts at each site were log(x+1) transformed, used to create a resemblance matrix of Bray-Curtis similarities and plotted in a nonmetric multidimensional scaling ordination to visualize differences in community composition between sites (Clarke & Gorley, 2015, Clarke *et al.*, 2014). For the second analysis, non-parametric change-point analysis (nCPA) was applied. This technique determines the level of a predictor variable resulting in a threshold response in a response variable which maximizes differences in the mean and variance of the response variable (King & Richardson, 2003b, Qian *et al.*, 2003). Non-parametric change-point analysis was then used to determine the threshold value for each chemical parameter above and below which the greatest differences in acidBAP were observed.

2.5 Assessment of Diatom Communities

2.5.1 Background

Diatoms are the most speciose group of periphyton, which forms the base of aquatic food chains. Diatoms are sensitive to chemical conditions, especially pH (Battarbee *et al.*, 2010), and the pH tolerances of many common diatom species are known (Van Dam *et al.*, 1994). The origin of low pH can be anthropogenic due to inorganic acid deposition or natural as a result of organic acid enrichment. Diatom communities respond differently to the two forms of acidification in streams (Passy, 2006, Passy *et al.*, 2006), but the indicator values for these forms of acidification are poorly known for individual species.

A number of studies have used diatoms to develop weighted averaging models for DOC or total organic carbon (TOC) for lakes in various regions, with the intent of inferring past organic carbon concentrations (Davis *et al.*, 1985, Dixit *et al.*, 2001, Enache & Prairie, 2002, Kingston & Birks, 1990, Ruhland & Smol, 2002). Considerably less effort has been made to develop diatom indicators for streams, which may have very different species composition from lakes, especially those dominated by phytoplankton rather than periphyton. Battarbee (et al. 1997) developed a weighted averaging model for total organic carbon using diatom samples from 24 sites, including streams. Wunsam (et al. 2002) examined diatom community composition in relation to water color (a surrogate measure of DOC). However, streams in the aforementioned study had pH ≥ 5.8, not nearly as acidic as many of the streams analyzed in this report. In addition, the studies by Battarbee (et al. 1997) and Wunsam (et al. 2002) included a relatively small number of streams (n = 17 and n = 12, respectively). Thus, our knowledge of how diatom community composition responds to inorganic versus organic acidification could benefit from a more thorough larger-scale investigation.

Diatoms have been recently classified into three ecological guilds based on tradeoffs between spatial position in the biofilm and stress tolerance, including low-profile, high-profile, and motile species (Passy, 2007). The low-profile guild comprises species of short-stature that reside in the periphyton understory and are tolerant to nutrient stress and disturbance (Passy & Larson, 2011). The high-profile guild makes up the periphyton overstory and is sensitive to both nutrient stress and disturbance. Motile species can move throughout the biofilm and can also be subject to stress when they travel into the overstory, which is more influenced by the chemistry of water flowing in the stream channel (Passy & Larson, 2011). Guild-based approaches have gained popularity in biological assessment because they have more general application than species-based approaches and reflect community functions (McGill *et al.*, 2006). Diatom ecological guilds are sensitive to a variety of stimuli and stressors, including nutrient enrichment, physical disturbance, acidification, organic pollution, and pesticide contamination (Berthon *et al.*, 2011, Gottschalk & Kahlert, 2012, Rimet & Bouchez, 2011, Stenger-Kovács *et al.*, 2013).

More recently, diatom community diversity and guild composition have also been shown to exhibit distinct responses to source of acidity. Higher diversity and greater abundance of sensitive high-profile and motile species were detected in streams with natural, organic acidity than in streams primarily acidified by inorganic acid deposition, which were dominated by low-profile species (Passy, 2006, Passy *et al.*, 2006, Pound *et al.*, 2013). This finding is important because wetlands, the sources of organic matter to streams (Passy, 2010), compose around 14% of the land cover in the Adirondacks (Roy *et al.*, 1997) and approximately 40% of the streams in the WASS study area belong to watersheds with ≥ 10% wetlands (Pound *et al.*, 2013).

Wetlands and associated organic matter are shown to benefit producer diversity through three potential pathways. The first pathway is through complexation and detoxification of Al_i (Gensemer & Playle, 1999), which lowers the ratio of toxic, Al_i to Al_o (Pound *et al.*, 2013). The second pathway is through stimulation of microbial processing of sulfur and nitrogen, whereby SO_4^{2-} and NO_3^- are removed from watersheds via microbial anaerobic respiration and/or assimilation (Goodale *et al.*, 2009, Whitmire & Hamilton, 2005). The third pathway is through export of organically-bound Fe (Passy, 2010), which is shown to be readily available as a nutrient to algae (Chen & Wang, 2008, Deein *et al.*, 2002, Kuma *et al.*, 1999, Matsunaga *et al.*, 1998).

Understanding the impacts of these two sources of acidity (inorganic versus organic) on biota has become more pressing given the recent increases in surface water organic acids (Driscoll *et al.*, 2003, Evans *et al.*, 2006). This phenomenon is known as “brownification” due to the influence of organic matter on water color. Initial explanations for brownification included climate related mechanisms such as increased decomposition of soil organic matter with higher temperatures, and increased water flux from shallow soil flow paths (Freeman *et al.*, 2001, Freeman *et al.*, 2004), but recent evidence suggests that decreased deposition of SO_4^{2-} and NO_3^- are the main drivers of increased organic matter concentrations in freshwaters (Evans *et al.*, 2006, Evans *et al.*, 2012). In addition to the influence of organic matter, brownification may be attributed in part to increased Fe concentrations in streams (Kritzberg & Ekstrom, 2012, Sarkkola *et al.*, 2013). Indeed, Fe was shown to be highly correlated with both DOC and water color in Adirondack lakes, with color as a better predictor (Maranger *et al.*, 2006).

Due to the prominence of wetlands in the Adirondacks, streams in this region provide an excellent opportunity to examine both the impacts of decreasing acid deposition and increased brownification on biota. Vinebrook and Graham (1997) found that increasing DOC concentrations, associated with lake recovery from acid deposition, was one of the best predictors of periphyton species composition in Canadian Shield lakes. The same is likely true for periphyton communities in streams as diatom communities were shown to differ between an inorganically acidified clear-water stream and organically acidified brown-water stream (Passy, 2006, Passy *et al.*, 2006), but the response of periphyton community composition to different sources of acidity in streams needs to be more thoroughly examined. Thus, the two goals of this report were to examine the impact of both pH and color on diatom species composition, richness, and functional guilds, and to determine which acidophilic and acidobiontic species are potential indicators of organic acidification (color).

2.5.2 Collection of Periphytic Diatoms

In each of the survey streams, diatoms were collected from all available habitats. The samples were preserved in the field with formaldehyde to a final concentration of 4%. In the laboratory, diatom samples were processed with concentrated sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), and saturated oxalic acid. The processed samples were washed with distilled water eight times following the acid digestion. Frustules are allowed to settle to before pouring off of the liquid. The clean samples were mounted onto glass slides with Naphrax® and 300 diatom frustules were counted and identified to species level from each slide. Diatom species were also assigned to one of three ecological guilds, that is, low-profile, high-profile, and motile, based on examination of growth forms in unprocessed samples and classifications of identified diatoms following Passy (2007), Rimet and Bouchez (2011), and Pound (et al. 2013). The low-profile guild comprises species of short stature such as solitary prostrate, adnate, erect or unattached cells, and slow-moving species. The high-profile guild encompasses species of tall stature that reach into the upper layers of the periphyton mat such as erect, filamentous, branched, chain-forming, tube-forming, and stalked species; the motile guild includes fast-moving biraphid species.

2.5.3 Data Analysis

Redundancy analysis (RDA) was used to examine how diatom species composition changed along environmental gradients within each of the ECASS sampling periods: August 9–11, 2010, April 18–20, 2011, and October 31–November 2, 2011. To see how diatom flora related to stream chemistry across the entire Adirondack Park, two RDAs were also run on all WASS and ECASS samples combined over all sampling periods. The first combined RDA related diatom species composition to stream chemistry. The second combined RDA examined how diatom species richness and abundance of the low-profile, high-profile, and motile guilds relate to stream chemistry. The RDAs were run using forward selection and 999 Monte Carlo permutations to select significant predictors in each group ($P < 0.05$). If two predictors were highly correlated, the better of the two predictors was included in the model to keep inflation factors below 10. Species with maximum abundance less than 2.0% were excluded from the analysis. Prior to RDA, all environmental variables except pH were transformed (log normal) to improve normality.

Two different analyses were employed to determine meaningful thresholds in both pH and color for diatom communities and individual diatom species. Threshold Indicator Taxa Analysis (TITAN) was used to identify synchronous changes in diatom community composition and shifts in abundance of individual species along gradients of pH and color (Baker & King, 2010). TITAN estimates uncertainty surrounding taxon-specific responses and maximum aggregate change points by examining the distribution of change-point values across a series of bootstrap replicates of the entire dataset. The approach of TITAN is derived from two existing techniques, namely nCPA (King & Richardson, 2003a) and indicator species analysis (Dufrene & Legendre, 1997). Non-parametric change-point analysis is a technique that orders and partitions observations along an environmental gradient, separating the data into two groups that have the greatest difference in means and/or variances (King & Richardson, 2003a). Whereas nCPA examines community level responses, TITAN extends nCPA by using indicator value (IndVal) scores to identify change points along an environmental gradient for individual taxa (Baker & King, 2010). TITAN splits samples into two groups based on the threshold in the predictor variable that maximizes the association of each taxon with one side of the threshold. The association of each taxon with either side of the threshold is measured as the product of species abundance and occurrence, that is, indicator value (IndVal) scores (Dufrene & Legendre, 1997). Taxa are identified as increasing or decreasing along the gradient depending on the side of the threshold with the highest indicator value. Permutations are used to evaluate the significance of IndVal scores. Unlike indicator species analysis which determines IndVal scores for a priori group classifications, optimal groupings of samples are initially unknown in TITAN and are thus the goal of the analysis. IndVal scores are standardized as z scores by subtracting the mean of randomized permutations from the observed IndVal scores and dividing by its permuted standard deviation. Standardized taxa with increasing responses at a change point are denoted as z+ while taxa with decreasing responses at a change point are labeled as z-. The sum of all z scores of z+ and z- taxa are used to calculate maximum aggregate change points for taxa that increase and decrease along the gradient, respectively.

TITAN provides two diagnostic indices to measure the quality of indicator response for each taxon: purity and reliability. Indicator purity is the proportion of bootstrap replicates resulting in response directions that agree with the observed response (increasing or decreasing), and indicator reliability is the proportion of bootstrap change points whose IndVal scores consistently result in *P*-values below one or more user-defined probability levels, that is, $P < 0.05$ or $P < 0.01$ (Baker & King, 2010). To determine taxa and community thresholds along the gradient of pH, TITAN was first run across all 1246 WASS and ECASS stream samples. TITAN was run a second time to determine taxa and community thresholds along the color gradient. Since our goal was to determine the species that are indicators of brown-water versus clear-water acid streams, only stream samples with pH less than the aggregate community pH threshold for decreasing taxa (taxa affiliated with low pH) were included in the TITAN color analysis. Both TITAN analyses were run with 250 permutations and 500 bootstrap re-samplings. Species that occurred in less than five samples or had maximum abundance less than 2.0% were excluded from the TITAN analyses.

The results of TITAN were validated with a second analysis, indicator species analysis (Dufrene & Legendre, 1997). As mentioned previously, indicator species analysis determines taxon IndVal scores for a priori group classifications. In this analysis, species are assigned as indicators of groups in which they have the highest IndVal score. The significance of IndVal scores is tested with 1000 permutations. Regression tree analysis of Al_o against color and pH was used to determine the a priori groupings of stream samples. Analysis of variance (ANOVA) was also employed to assess differences in mean pH, DOC, diatom species richness, and ratio of relative abundance of tolerant low-profile species sensitive to high-profile and motile species, that is, low:(high +motile) among the groups identified by the regression tree. To improve normality, DOC and the ratio of low:(high +motile) were ln-transformed.

3 Results and Discussion

3.1 Assessment of Stream Chemistry

3.1.1 Variability of Chemical Concentrations during Sampling Periods

Acidity of an individual stream will typically increase with increases in flow; therefore, to compare the chemistry of multiple streams sampled on different dates, the effect of flow variations needs to be incorporated. Increases in acidity with increases of flow can happen throughout the year, but season also plays a role in controlling stream chemistry beyond flow due to the interactions between vegetation and microbes that are closely tied to season. Buck Creek stream flows during the summer base-flow sampling were low and stable from late July through the sampling of August 9–11, 2010, although a slight increase in flow occurred on August 10th (Figure 3-1). The peak flow that occurred in late June was from a high-intensity thunderstorm.

Spring snowmelt caused flows that were high and variable from early April through the stream sampling of April 18–20, 2011 (Figure 3-1). Stream flow at Buck Creek varied from less than 200 liters per second (L s^{-1}) to over 600 L s^{-1} during the three-day sampling period, although the peak flow approached 1000 L s^{-1} one week before the sampling began. Melt events also occurred in March but were followed by resumption of continuous below freezing temperatures. The sampling conducted from October 31 through November 2, 2011 was done on the receding limb of moderate flows that occurred for several days in mid-October (Figure 3-1). When compared to the range during the survey year, flows were low to moderate during the August base-flow sampling, moderate during the October–November fall sampling, and high to extremely high during the April snowmelt sampling (Table 3-1). These percentages were similar to those determined for the 10-year period from 2002 through 2011, which indicated that the flow ranges in the survey years of 2010 and 2011 were not unusual.

Figure 3-1. Average Daily Stream Flow during Stream Sampling Periods

Average daily stream flow at Buck Creek, Inlet, NY for six-weeks prior and one week following the samplings conducted during summer 2010, snowmelt 2011, and fall 2011. Dates of stream samplings are graphed in red.

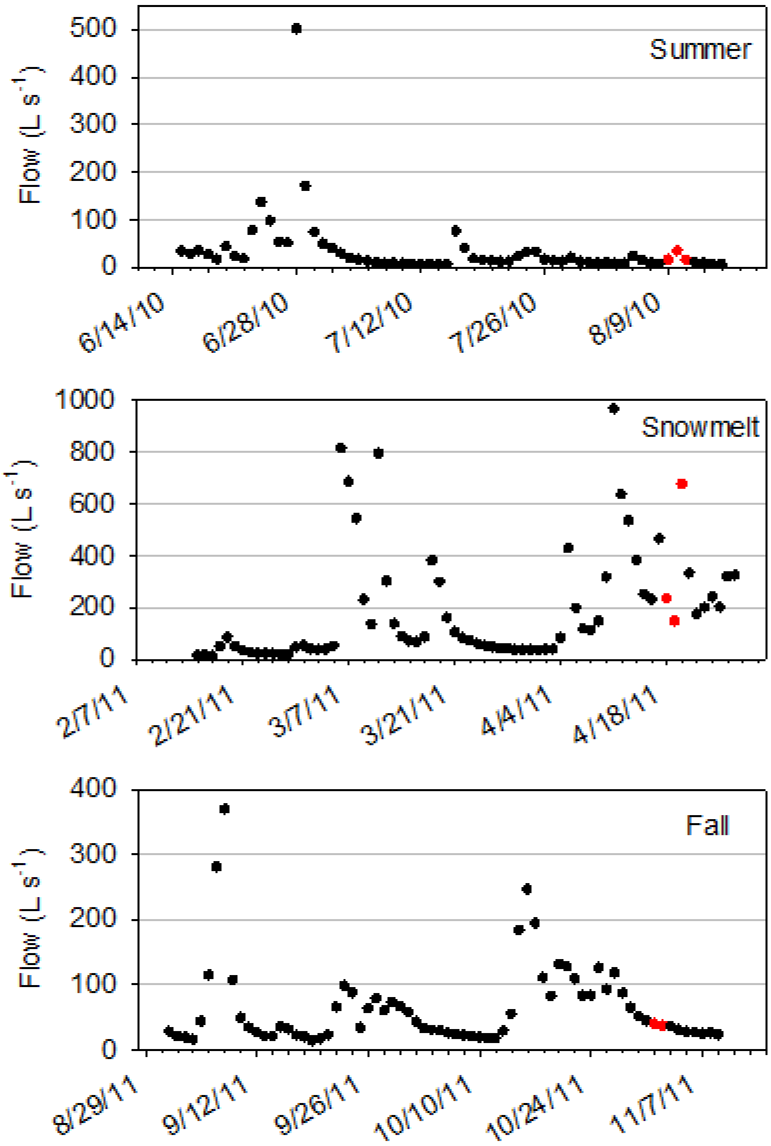


Table 3-1. Summary of Stream Flows for Sampling Periods

Number of sampled streams, range of daily average flow (L s^{-1}) at Buck Creek, percentage of days with flow higher than on the sampling dates within the calendar year of sampling (expressed as the range over the sampling dates), and the percentage of days with flow higher than on the sampling dates (expressed as the range over the sampling dates) over the period January 1, 2002 through December 31, 2011.

Survey Date	Aug. 9-11, 2010	Apr. 18-20, 2011	Oct. 31-Nov. 2, 2011
Number of streams sampled	178	195	203
Range in flow	14 to 34	146 to 676	36 to 44
Percentage of days with higher flow during the sample year	52 to 82	2 to 17	48 to 56
Percentage of days with higher flow over the 10-year record	57 to 81	1 to 14	47 to 54

Sampling of the same stream on each day enabled the effects of flow variations on stream chemistry to be assessed over each three-day sampling period. Daily samples collected during the August sampling showed small variations in SO_4^{2-} concentrations in three of the four repeatedly sampled streams, as shown by coefficient of variation (CV) values from 1 to 13 (Table 3-2). However, the SO_4^{2-} concentration from stream 87 on the first day was substantially higher than the measurement from days two and three. This single exceptionally different value may have been related to transient redox effects that altered S cycling during the low-flow conditions. Values of NO_3^- concentrations exhibited considerable variability among sampling days for several of the samples (Table 3-2), which was likely related to variations in biological utilization of this nutrient within both the soil and stream channel during active growth conditions of the August low flows. Active biological activity also was likely to have contributed to variations in DOC concentrations during the August sampling.

Concentrations of Ca^{2+} showed extremely low variability among sampling days in three of the four repeatedly sampled streams, which indicated minimal effects from variations in biological activity or flow. However, stream 87 was once again the outlier, showing moderate variation in concentrations of Ca^{2+} (CV = 23). Concentrations of Ca^{2+} are much less likely to be affected by biological activity within the stream channel than SO_4^{2-}, NO_3^- and DOC, but can be influenced by varying contributions of water discharging from deep subsurface flow paths. As flow increases, the relative effect of deep flow paths decreases, causing Ca^{2+} concentrations to decrease. Stream 87 was more strongly influenced by deep flow paths than the other streams at low flow, which resulted in higher flow-related variations in chemistry. Variability of ANC and pH measurements was low (all CV values < 4) for all streams, except for ANC in stream 87.

Table 3-2. Results of Repeated Daily Stream Sampling, August 8–11, 2010

Values of the mean, CV (coefficient of variation), and range of values measured in samples collected in the same stream on each day of the August 2010 sampling. Values of pH were converted to micromoles of hydrogen per liter (μmol H L^{-1}) to determine the CV. Units of SO_4^{2-}, NO_3^-, and Ca^{2+} are μmol L^{-1}; units of DOC are micromoles of carbon per liter (μmol C L^{-1}); units of ANC (acid-neutralizing capacity by Gran titration) are μeq L^{-1}.

Stream Code	Statistic	SO_4^{2-} μmol L^{-1}	NO_3^- μmol L^{-1}	DOC μmol C L^{-1}	Ca^{2+} μmol L^{-1}	ANC μeq L^{-1}	pH
87	mean	54	6	284	383	1072	7.46
	CV	35	32	29	23	18	32
	range	42 to 75	4 to 8	198 to 336	321 to 483	918 to 1295	7.32 to 7.56
228	mean	48	0.4	82	102	256	7.00
	CV	1	5	4	0.8	2	8
	range	48 to 49	0.4 to 0.5	79 to 86	101 to 103	249 to 261	6.96 to 7.03
252	mean	23	5	979	95	221	6.46
	CV	13	54	8.0	3	1	8
	range	20 to 26	3 to 9	904 to 1053	90 to 101	200 to 242	6.42 to 6.52
270	mean	46	10	493	45	50	6.31
	CV	9	33	27	1	4	27
	range	42 to 50	8 to 14	372 to 633	44 to 45	48 to 53	6.19 to 6.40

The CV of SO_4^{2-} concentrations among samples collected daily during the 2011 snowmelt sampling varied from 2 to 7, and concentrations varied less than 5 μmol L^{-1} in the four repeatedly sampled streams (Table 3-3). The CV of NO_3^- concentrations was also low; less than 10 in the two streams with mean concentrations above the NO_3^- reporting limit of 2.0 μmol L^{-1} (Lincoln *et al.*, 2009). Values of CV for DOC varied from 8 to 11 whereas CV of Ca^{2+} only varied from 2 to 4 even though mean Ca^{2+} concentrations varied from 31 to 135 among the four streams. Values of CV for ANC and pH were also low in streams, reaching a maximum of 12 for ANC in stream 87.

Table 3-3. Results of Repeated Daily Stream Sampling, April 18–20, 2011

Values of the mean, CV (coefficient of variation), and range of values measured in samples collected in the same stream on each day of the 2011 snowmelt sampling. Values of pH were converted to µmol H L^{-1} to determine the CV. Units of SO_4^{2-}, NO_3^-, and Ca^{2+} are µmol L^{-1}; units of DOC are µmol C L^{-1}; units of ANC (acid-neutralizing capacity by Gran titration) are µeq L^{-1}. CV could not be calculated for NO_3^- in stream 228 because the mean equaled zero. Negative concentrations interfered with the CV calculation for ANC in stream 270.

Stream Code	Statistic	SO_4^{2-}	NO_3^-	DOC	Ca^{2+}	ANC	pH
		mmol L^{-1}	mmol L^{-1}	mmol C L^{-1}	mmol L^{-1}	meq L^{-1}	
87	mean	43	0.7	368	135	342	7.37
	CV	7	45	11	2	12	7
	range	40 to 45	0.5 to 1.0	325 to 407	132 to 138	318 to 389	7.34 to 7.40
228	mean	37	0	144	37	36	6.46
	CV	2	*	11	4	2	14
	range	36 to 37	0.1 to 0.3	128 to 160	35 to 38	35 to 36	6.40 to 6.50
252	mean	41	40	522	58	32	6.07
	CV	6	9	20	2	3	6.0
	range	39 to 43	36 to 42	453 to 640	57 to 60	31 to 33	6.05 to 6.10
270	mean	32	51	449	31	-4	4.78
	CV	5	0.6	8	4	*	19
	range	31 to 34	50 to 51	422 to 475	30 to 32	-11 to -2	4.77 to 4.88

In the fall sampling, variations in concentrations over the three sampling days were extremely low for all measurements among all four streams (Table 3-4), with the exception of moderate variability in pH measurements (calculated as H^+ [hydrogen ion]), which had a maximum CV of 19 in stream 228. The highest CV for the remaining data was a value of 9 for NO_3^- in stream 87. The stable stream chemistry was likely related to the stable stream flow during the sampling period that occurred on the lower part of the recession limb of the hydrograph (Figure 3-1).

Table 3-4. Results of Repeated Daily Stream Sampling, October 31–November 2, 2011

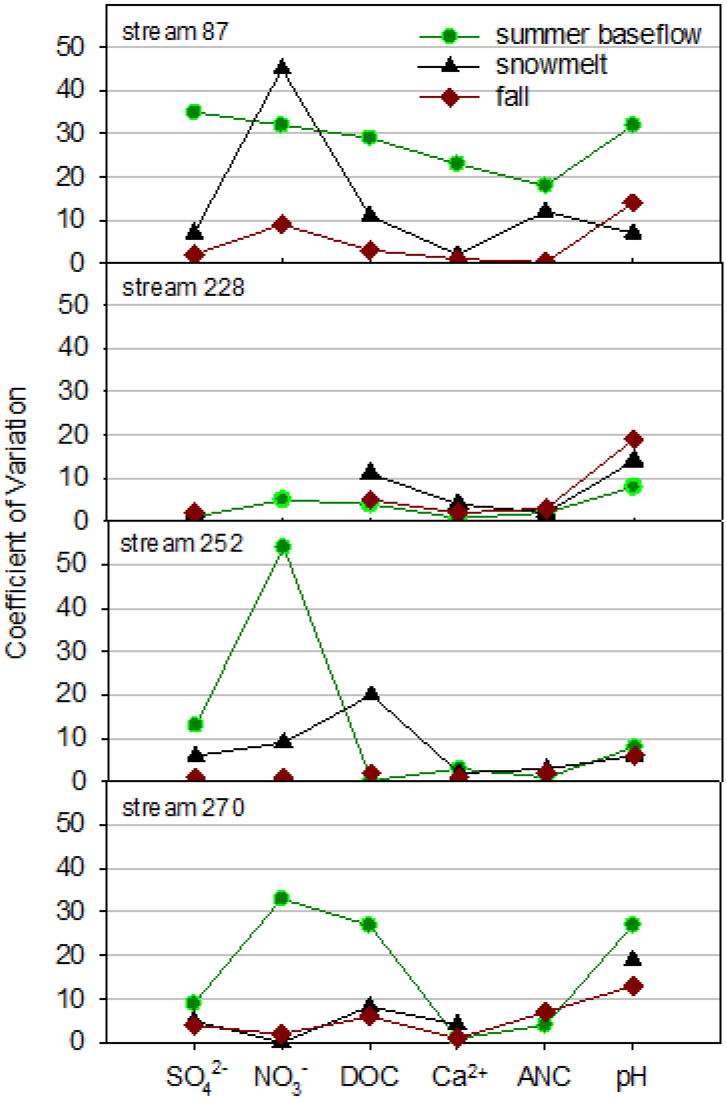
Values of the mean, CV (coefficient of variation), and range of values measured in samples collected in the same stream on each day of the 2011 fall sampling. Values of pH were converted to µmol H L^{-1} to determine the CV. Units of SO_4^{2-}, NO_3^-, and Ca^{2+} are µmol L^{-1}; units of DOC are µmol C L^{-1}; units of ANC (acid-neutralizing capacity by Gran titration) are µeq L^{-1}. CV could not be calculated for NO_3^- in stream 228 because the mean equaled zero.

Stream Code	Statistic	SO_4^{2-}	NO_3^-	DOC	Ca^{2+}	ANC	pH
		mmol L^{-1}	mmol L^{-1}	mmol C L^{-1}	mmol L^{-1}	meq L^{-1}	
87	mean	33	0.4	321	218	568	7.56
	CV	2	9	3	1	0.2	14
	range	32 to 33	0.3 to 0.5	312 to 326	211 to 222	546 to 580	7.50 to 7.61
228	mean	40	0	124	55	108	6.96
	CV	2	*	5	2	3	19
	range	39 to 40	0-0	119 to 131	54 to 56	105 to 112	6.87 to 7.04
252	mean	52	43	246	73	77	6.59
	CV	1	1	2	1	2	7
	range	51 to 53	43 to 45	240 to 252	72 to 73	76 to 78	6.56 to 6.63
270	mean	41	23	455	35	10	5.40
	CV	4	2	6	1	7	13
	range	39 to 42	23 to 24	424 to 472	34 to 35	8.8 to 10	5.35 to 5.47

Overall, the repeated daily sampling suggested some effect of flow on chemical variability, but despite widely varying flows during the snowmelt sampling (Figure 3-1), chemical variability of the snowmelt and fall samplings were highly similar (Figure 3-2). Day-to-day chemical variability was also dependent on the constituent being measured and the stream being sampled. Concentrations of NO_3^- exhibited the highest variability in terms of a CV, but little variability was observed during any of the sampling periods in stream 228 because NO_3^- concentrations were always close to zero. Measurements sensitive to instream biological activity (SO_4^{2-}, NO_3^-, and DOC) exhibited variations that were likely related to the small variations in flow.

Figure 3-2. Coefficients of Variation for All Sampling Periods

Comparison of variability (as coefficient of variation) among stream samplings for measurements of SO_4^{2-}, NO_3^-, DOC (dissolved organic carbon), Ca^{2+}, ANC (acid-neutralizing capacity by Gran titration), and pH in samples collected on each day of the respective samplings.



Concentrations of Ca^{2+} exhibited the least variability among sampling periods for all streams, with all values of CV being less than 4, (except for stream 87 during summer), and other measurements influenced by inputs of deep groundwater flow paths (ANC, pH) showed small variability. Based on these four streams, the constituents shown in Figure 3-2 exhibited an overall limited degree of variability during the sampling periods except for the measurements of low NO_3^- concentrations. Values of CV for additional chemical measurements of repeated daily sampling are available in Tables A-1a and A-1b.

3.1.2 Variability of Chemical Concentrations among Sampling Periods

Stream chemistry varied considerably among the three sampling periods for most, but not all measurements. Values of pH during the August 9–11 base-flow sampling varied from moderately acidic to well neutralized based on the ranges that defined the 5th and 95th percentile that are shown in Table 3-5. The range of pH in the April snowmelt extended from strongly acidic to circumneutral, and the pH range for the October sampling fell between the range of the April and August samplings. Values of BCS and ANC among the three samplings compared similarly to pH, with the most acidic value measured in the April sampling and the most buffered value in the August sampling. Mean concentrations of Al_i were similarly low in all sampling periods, and the low value of the ranges was zero in each sampling. The high end of the ranges followed the seasonal relationship of pH, with the Al_i being lowest in the August sampling and highest in the April sampling. In contrast, the ranges in Al_o among the samplings were quite similar, although the uppermost value in the August sampling was somewhat lower than the other samplings. Concentrations of DOC, which is a strong control of Al_o, were also quite similar among the three samplings, both in terms of means and ranges.

Table 3-5. Summary of ECASS Stream Chemistry

Number of streams sampled, mean stream flow ($L\ s^{-1}$) during the sampling window, and the mean and range (5th percentile and 95th percentile) of chemical measurements made in each of the three samplings. BCS (base-cation surplus) and ANC (acid-neutralizing capacity by Gran titration) are expressed as $\mu eq\ L^{-1}$. Remaining measurements are expressed as micromoles per liter ($\mu mol\ L^{-1}$). Al_i is inorganic monomeric Al; DOC is dissolved organic carbon; Al_o is organic monomeric Al.

Survey Date	Aug. 9-11	Apr. 18-20	Oct. 31-Nov 2
	2010	2011	2011
No. of streams	178	195	203
Mean flow	21	352	40
pH	6.88	6.33	6.67
	5.42 to 7.79	4.87 to 7.33	4.99 to 7.53
BCS	307	83	169
	-6.5 to 985	-46 to 277	-31 to 565
ANC	316	89	181
	9.7 to 1025	-5 to 295	-1.6 to 560
Al_i	0.3	0.8	0.3
	0 to 0.7	0 to 3.4	0 to 1.3
Al_o	1.8	2.3	2.1
	1.3 to 2.7	1.2 to 4.1	1.1 to 4.1
DOC	273	277	253
	102 to 661	124 to 493	107 to 483
SO_4^{2-}	43	34	39
	23 to 60	24 to 47	25 to 51
NO_3^-	9.2	17	9.6
	0.6 to 23.9	0.1 to 52	0 to 29
Cl^-	9.2	7.9	9.4
	5.3 to 16	4.5 to 13	5.7 to 16
Ca^{2+}	133	61	87
	26 to 383	21 to 135	23 to 219
Mg^{2+}	50	21	32
	10 to 139	6.4 to 48	7.5 to 87
Na^+	58	28	40
	29 to 96	18 to 43	21 to 69
K^+	4.8	3.3	3.8
	0.7 to 10	0.7 to 7.1	1.0 to 8.5
Si	203	103	151
	108 to 297	63 to 157	82 to 232
NH_4^+	0.6	0.6	0.3
	0 to 1.2	0 to 1.1	0 to 0.8

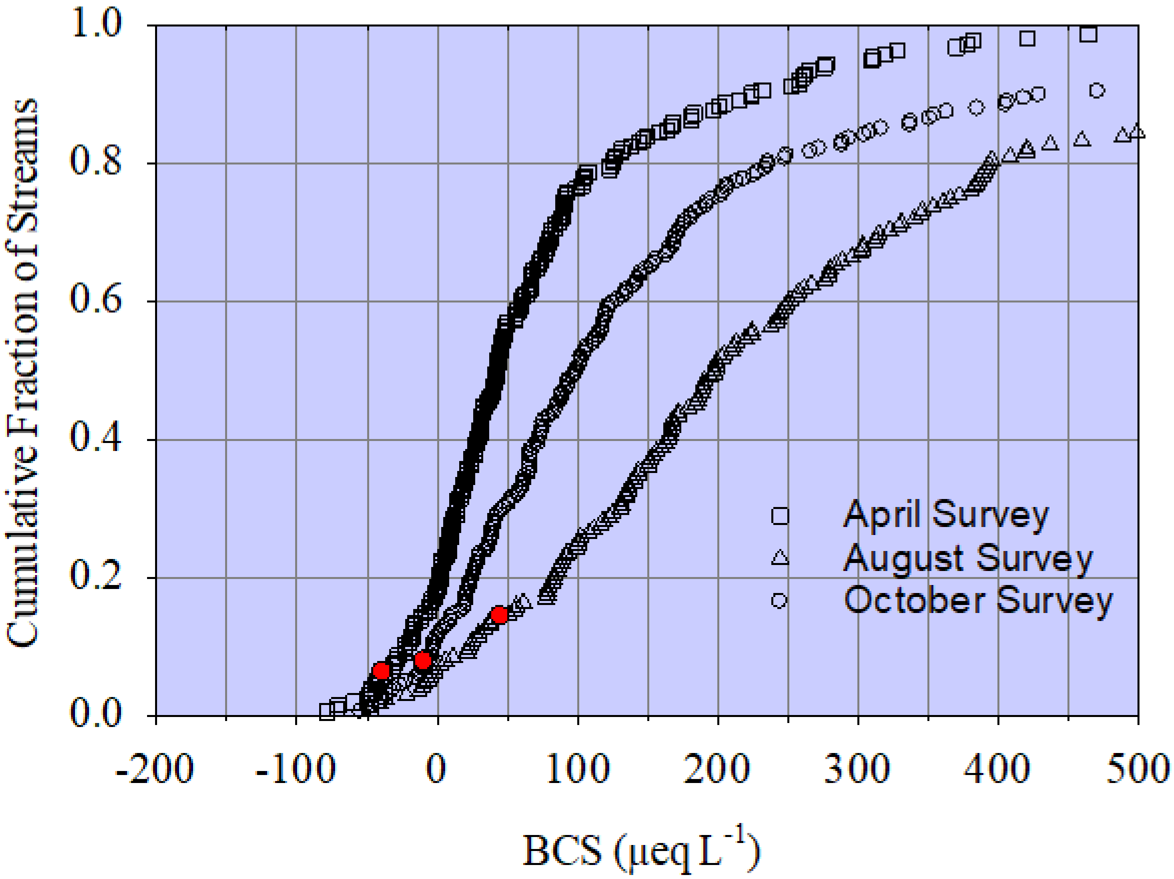
Mean values of the sampling periods for SO_4^{2-} were lowest in the April sampling and highest in the August sampling, whereas NO_3^- exhibited the opposite relationship, with the highest mean concentration in the April sampling and lowest in the August sampling (Table 3-5). Ranges of SO_4^{2-} varied little among the three samplings, and the ranges for NO_3^- in the August and October samplings were similar to each other. However, the upper value for the range in NO_3^- in the April sampling was nearly double that of the other two samplings. The values of Cl^- showed the least variation among samplings of any of the measurements in terms of both means and ranges.

Mean concentration of Ca^{2+} in the August sampling was more than double the mean in the April sampling and approximately 50% higher than the mean in the October sampling (Table 3-5). Concentration ranges of Ca^{2+} were highly similar among samplings, and high values of the ranges followed the same relationship as the mean values. Means and ranges for Mg^{2+} and Na^+ were similar to that of Ca^{2+}. Although K^+ is considered a base cation like Ca^{2+}, Mg^{2+} and Na^+, K^+ concentrations were much lower than those other base cations and showed only small variations in means and ranges among samplings. Mean concentrations of Si showed relationships among the samplings that were similar to Ca^{2+} but differed from Ca^{2+} in that both lower and upper values of the ranges were highest in the August sampling and lowest in the April sampling. The range of NH_4^+ concentrations indicated that this constituent was low in all streams during all samplings (Table 3-5).

To evaluate how the chemistry of Buck Creek compared to the ECASS streams, BCS values for Buck Creek were added to cumulative frequency plots for each sampling. Sampling of Buck Creek was not done during the August and fall samplings, so averages of the manual samples bracketing these samplings were used for the comparison, whereas the average of the five samples collected in Buck Creek during the snowmelt sampling was used in the analysis. The BCS values for Buck Creek, which is located in the eastern portion of the WASS region, fell near the bottom of the distribution of streams in all three samplings. The highest value of the cumulative fraction of the three samplings was 0.15, which indicated that 85% of streams were less acidic than Buck Creek during the August sampling (Figure 3-3). Only 6% of the streams were more acidic than Buck Creek during the April sampling.

Figure 3-3. Cumulative Frequency Distributions for BCS

Distributions of BCS (base-cation surplus) for each stream sampling. Values exceeding BCS values > 500 were not shown because they indicated extremely high-acid buffering. Red circles indicate values at Buck Creek.



3.1.3 Assessment of Stream Acidification during the Three Sampling Periods

Sampling conditions during the snowmelt sampling reflected the typical sustained acidification that occurs in Adirondack streams during the high flows of spring snowmelt. However, variation in acidification occurs throughout snowmelt and can occur for shorter durations throughout the year. Therefore, the degree of acidification that occurred during the snowmelt sampling could have been exceeded at other times during the year. The year-round monitoring at Buck Creek enabled the survey conditions to be related to the most acidic conditions measured with biweekly and high-flow event sampling throughout the years that encompassed the sampling periods.

Buck Creek stream chemistry during 2010–2011 indicated that the degree of acidification during the snowmelt sampling did not reflect the most acidic conditions that occurred in the two-year window that encompassed the three samplings. The BCS value at Buck Creek during the snowmelt sampling reached a minimum of -48 µeq L^{-1} (Figure 3-4), which was also the value measured on the day before the start of the snowmelt sampling (April 17, 2011). The mean BCS value of the five samples collected at Buck Creek during the sampling period equaled -39 µeq L^{-1}.

The minimum BCS value in Buck Creek measured during the overall spring snowmelt period of 2011 was -58 µeq L^{-1} and similar BCS values also occurred in September 2010, May 2011, and August 2011 (Figure 3-5). These BCS values were lower than the mean of the sampling period by 19 µeq L^{-1}. However, the most acidic value of BCS in the two-year window (-72 µeq L^{-1}) was measured on June 28, 2010 (Figure 3-5). This value was lower than the mean BCS measured during the snowmelt sampling by 33 µeq L^{-1}. On this basis, the maximum acidification of the ECASS streams during the two-year survey period was estimated to be an average of 33 µeq L^{-1} less than that measured in the April snowmelt sampling.

Figure 3-4. Values of BCS and Inorganic Al at Buck Creek, April 2011

Stream flow and concentrations of (1) BCS (base-cation surplus) and (2) inorganic monomeric Al determined from manual samples and stage-activated autosamples collected at the main stream gage at Buck Creek between April 4 and 25, 2011. The shaded area indicates the timing of the ECASS snowmelt sampling (April 18-20, 2011).

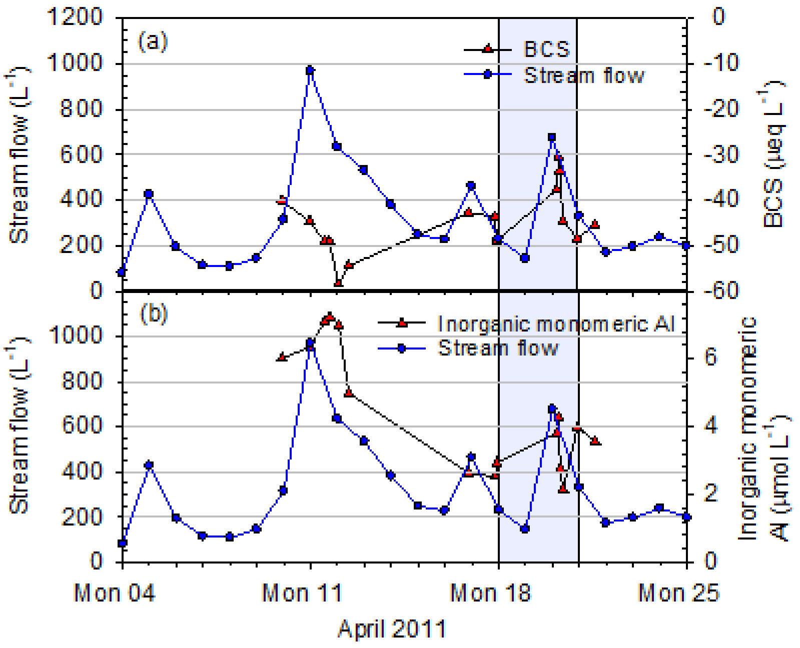
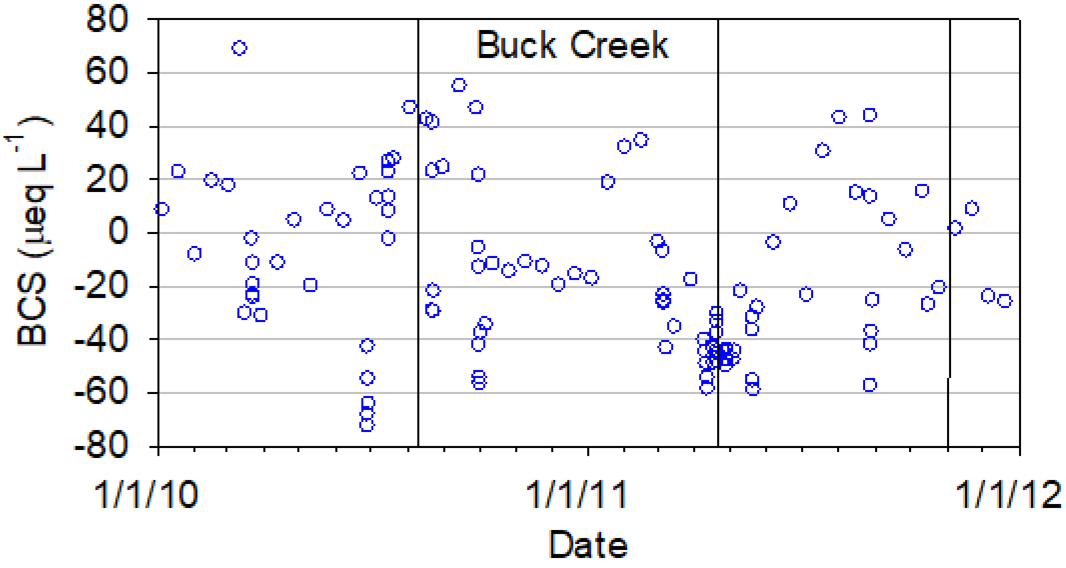


Figure 3-5. Buck Creek BCS from 2010 to 2011

Values of BCS (base-cation surplus) in Buck Creek for the two years encompassing the stream samplings. Vertical lines indicate the sampling dates.



Buck Creek sampling during the WASS suggested that streams with BCS values of up to 25 µeq L^{-1} during the 2004 snowmelt sampling would be prone to have BCS values below 0 µeq L^{-1} during the most acidic conditions of that year (Lawrence *et al.*, 2008a). The smaller adjustment for estimated maximum acidification determined in the WASS reflected more acidic conditions during the snowmelt WASS relative to that study period than during the ECASS. However, the 33 µeq L^{-1} adjustment determined in the ECASS may have underestimated the maximum acidification that was likely to have occurred during the two-year study window in most streams because BCS in Buck Creek was in the 6th percentile of streams (6% of streams were more acidic than Buck Creek) during the April snowmelt. Results of the WASS indicated that episodic depressions in BCS increased as base flow BCS increased (Lawrence *et al.*, 2008a).

Streams with a BCS value < 0 µeq L^{-1} were considered to be acidified by acidic deposition at the time of sample collection because this BCS value represents the threshold below which Al mobilization contributes to acid buffering, thereby resulting in toxic inorganic Al appearing in stream water (Lawrence *et al.*, 2007). Only 7% of streams sampled during August base flow were acidified based on this criterion, whereas 16 and 11% were acidified during snowmelt and fall samplings (Table 3-6).

The 33 μeq L^{-1} adjustment to the April sampling for conditions of maximum acidification indicated that 42% of the streams would likely experience BCS < 0.0 μeq L^{-1} during conditions of maximum acidity within the two-year study period. Because negative BCS values are an unambiguous indication of acidic deposition effects (Lawrence *et al.*, 2007), 42% of the accessible ECASS streams were determined to be prone to acidification during episodic high-flow events.

Based on the EPA criterion for acidification of ANC < 0 μeq L^{-1} (Stoddard *et al.*, 2003), 2% of streams were acidified during the August sampling, 8% were acidified during the April sampling and 4% were acidified during the fall sampling (Table 3-6). This percentage of streams was one-half or less the values based on BCS < 0 μeq L^{-1}. The number of streams with ANC < 50 μeq L^{-1} 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). However, when this value is applied to the August sampling, only 14% of streams were estimated to be at risk of acidification during high-flow episodes, which is one third of the streams estimated to be prone to acidification based on snowmelt sampling and the BCS threshold.

Table 3-6. Measurements of ECASS Stream Acidification

BCS is base-cation surplus; ANC is acid-neutralizing capacity by Gran titration; Al_i is inorganic monomeric Al; $RCOO^-_s$ is strongly acidic organic anions. Percent of streams prone to acidification during the study period is indicated in parentheses.

Survey Date	Aug. 9-11, 2010	Apr. 18-20, 2011	Oct. 31- Nov. 2, 2011
Number of streams sampled	178	195	203
Percent of streams with BCS < 0 μeq L^{-1}	7	16 (42)	11
Percent of streams with ANC < 0 μeq L-1	2	8	4
Percent of streams with Al_i > 2.0 μmol L^{-1}	3	12	4
Percent of streams with pH < 6.0	10	28	16
Mean SO_4^{2-} (percent of strong acid anions)	70	62	69
Mean NO_3^-(percent of strong acid anions)	7	14	8
Mean $RCOO^-_s$ (percent of strong acid anions)	15	16	14

An Al_i concentration of 2.0 mmol 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 Al_i for 30 days caused 20% mortality of fingerling brook trout (*Salvelinus fontinalis*; age < 1 year) in Adirondack streams (Baldigo *et al.*, 2007). Concentrations of Al_i exceeded 2.0 mmol L^{-1} in only 3% of streams in the August sampling, 12% in the April sampling, and 4% in the fall sampling (Table 3-6). Decreases in pH that reach values near 5.0 can lead to Al_i mobilization, but pH itself has been found to be harmful to aquatic biota when below 6.0 (Driscoll *et al.*, 2001). In the August sampling, 10% of streams had values below 6.0, but this more than doubled to 28% in the April sampling and was 16% in the fall sampling.

To compare acidic deposition effects to natural sources of strongly acidic acids, 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 3-6). Of these three anions, SO_4^{2-} was the predominant form in each of the samplings ranging from 62% in the April sampling to 70% in the August sampling. The percentage of NO_3^- was highest during the April sampling, but nevertheless only reached 14%, and was 7 and 8%, respectively, in the August and fall samplings. The percentage attributable to natural sources of acidity was highly similar among the samplings, ranging from 14 to 16%.

3.1.4 Chronic versus Episodic Acidification

Streams in regions affected by acidic deposition are often characterized as being acidified chronically (throughout the year) or episodically (during high-flow events). However, the chemistry within a given stream tends to vary widely over the year due to both seasonal and flow-related factors, and the range of variability tends to differ from stream to stream. For example, because the April sampling occurred during spring snowmelt, the acidification that occurred during this sampling could be viewed as having a seasonal component that elevated base flows over several weeks as well as causing short-term peak flows. Buck Creek data indicated that the second most acidic BCS value in the snowmelt period occurred during the sampling period (Figure 3-4), although this level of acidification was exceeded by 33 µeq L^{-1} during the June 2010 episode (Figure 3-5).

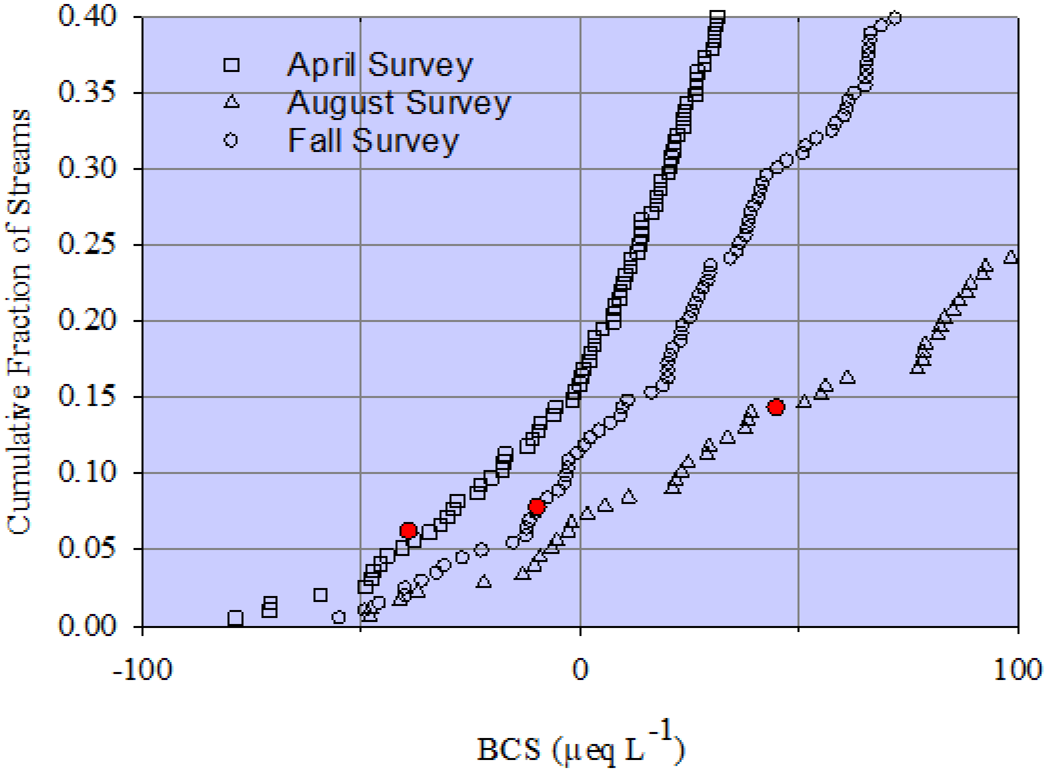
To evaluate the relative spatial extent of chronic and episodic acidification, results of the April 2011 sampling were chosen to represent high-flow, or episodic conditions, whereas results of the August 2010 sampling were chosen to represent base flow, or non-episodic conditions. A total of 169 streams had data that could be used in this comparison. Streams with a BCS value < 33 µeq L^{-1} in both August 2010 and April 2011 samplings were considered to be chronically acidified. Although this criterion included streams not acidified when sampled in August, the August sampling was done under conditions likely to be among the least acidic over the year, based on the season and relatively low flows (Lawrence *et al.*, 2008a). These streams were therefore labeled as chronically acidic because they were likely to be acidified during a substantial portion of the year. All streams with BCS < 33 µeq L^{-1} in the August 2010 sampling were also acidified in the April 2011 sampling. Streams with a BCS value < 33 µeq L^{-1} in the April 2011 sampling, but > 33 µeq L^{-1} in the August 2010 sampling, were considered episodically acidified. Streams in the April 2011 sampling with BCS > 33 µeq L^{-1} were considered unacidified. The streams labeled as "unacidified" also experience decreases in pH and ANC during high flows, but this term was chosen because those streams do not acidify to the level that results in harm to biota through mobilization of Al_i. This classification is the same used in Lawrence et al. (2008a) Results of this analysis are summarized in the list below.

Number of streams sampled in both August 2010 and April 2011:	**169**
Number of chronically acidified streams:	**19**
Number of episodically acidified streams:	**48**
Number of unacidified streams:	**102**
Average difference in BCS between August 2010 and April 2011 for chronically acidified sites:	**29 µeq L^{-1}**
Average difference in BCS between August 2010 and April 2011 for episodically acidified sites:	**131 µeq L^{-1}**
Average difference in BCS between August 2010 and April 2010 for unacidified sites:	**313 µeq L^{-1}**

Approximately 60% of the streams were classified as unacidified, and only 11% were chronically acidified. However, the 28% of streams classified as episodically acidic experienced a wide average difference in BCS of 131 µeq L^{-1} between the August and April samplings. This fluctuation in BCS occurs over a range that can have substantial effects on various components of aquatic ecosystems (Baldigo *et al.*, 2009, Baldigo *et al.*, 2007). Buck Creek was classified as an episodically acidified stream with a BCS difference of 84 µeq L^{-1} between the April sampling and the August sampling (Figure 3-6). Over the two-year study period, the BCS at Buck Creek varied from -72 µeq L^{-1} to 70 µeq L^{-1} (Figure 3-5). As previously observed (Lawrence *et al.*, 2008a), as BCS increased, so did the difference in BCS between the three samplings (Figure 3-3). Divergence of the cumulative fraction curves became more pronounced as BCS values increased above zero.

Figure 3-6. Cumulative Fraction of Streams for Low-BCS Values

Distributions of BCS (base-cation surplus) for each stream sampling from -100 µeq L^{-1} to +100 µeq L^{-1}. Red circles indicate values at Buck Creek.



3.1.5 High-Elevation Stream Chemistry

Because most of the streams at high elevations in the Adirondack High Peaks region are either inaccessible or required extended hiking to access, only a small number of sites were accessible enough to be sampled. Therefore, these sites could not be considered statistically representative of the high-elevation streams in the High Peaks region. Nevertheless, the sampled streams did provide information on stream chemistry that could be used for a general comparison with primary ECASS streams.

Flow conditions during the high-elevation survey (HES) in late summer (Table 3-7) were similar to those during the primary summer ECASS sampling conducted August 9–11, 2010 (Table 3-7). Mean values and ranges of chemical measurements in late summer reflected moderately acidic conditions in the HES with respect to pH, BCS, ANC and Al_i (Table 3-7), and values were considerably more acidic than the values of the primary sampling (Table 3-5).

Table 3-7. Summary of Chemistry in High-Elevation Streams

Number of streams sampled, mean stream flow (L s^{-1}) during the sampling window, and the mean and range of all chemical measurements made in each of the two high-elevation samplings. BCS (base-cation surplus) and ANC (acid-neutralizing capacity by Gran titration) are expressed as μeq L^{-1}. Remaining measurements are expressed as μmol L^{-1}. Al_i refers to inorganic monomeric Al; DOC refers to dissolved organic carbon; Al_o refers to organic monomeric Al; Al_t refers to total unfiltered Al.

Survey Date	Aug. 26-Sep. 1, 2010	Apr. 27-May 5, 2011	Survey Date	Aug. 26-Sep. 1, 2010	Apr. 27-May 5, 2011
No. of streams	11	13	NO_3^-	6.8	14
Mean flow	195	293		0 to 23	4.3 to 31
pH	6.05	5.19	Cl^-	5.2	3.4
	4.95 to 7.01	4.59 to 5.87		2.4 to 11.4	2.8 to 4.1
BCS	26	-20	F^-	1.4	1.1
	-37 to 133	-51 to 8.0		0.6 to 3.6	0.5 to 1.8
ANC	40	1.1	Ca^{2+}	43	20
	-21 to 141	-17 to 15		24 to 102	14 to 42
Al_i	1.1	2.3	Mg^{2+}	11	5.0
	0 to 3.6	0 to 6.1		4.2 to 22	3.4 to 10
DOC	325	437	Na^+	26	11
	160 to 593	206 to 822		17 to 34	9.1 to 15
Al_o	3.4	6	K^+	1.1	2.1
	1.8 to 7.0	3.1 to 13		0 to 2.8	0.1 to 3.8
Al_t	9.3	18	Si	148	46
	3.4 to 19	6.0 to 35		107 to 204	25 to 64
SO_4^{2-}	39	19	NH_4^+	0	0.7
	22 to 50	12 to 25		0 to 0.2	0.3 to 1.8

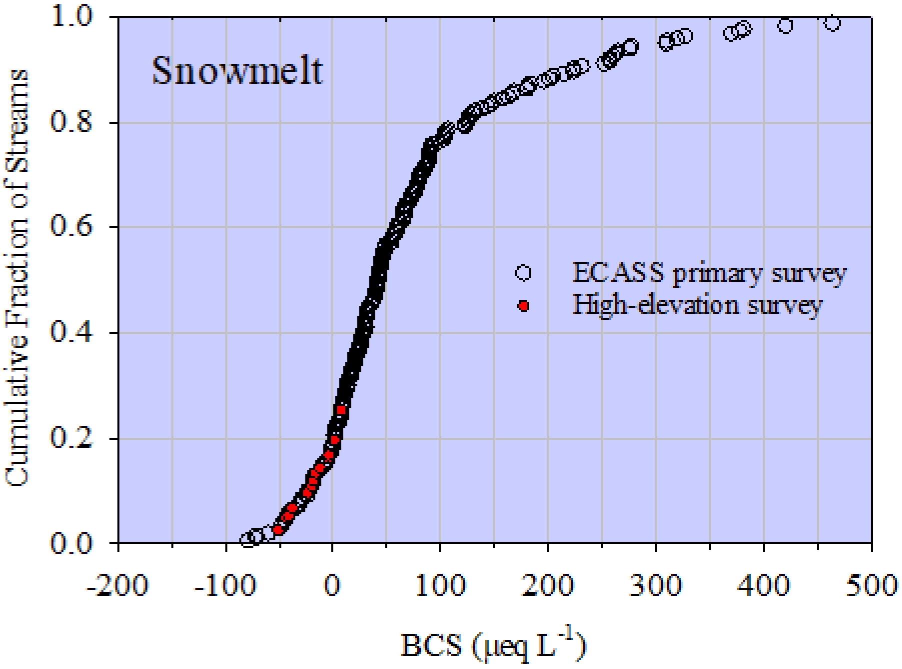
The steep terrain of these watersheds undoubtedly resulted in shallow, well-drained soils and short flow paths that limited contact time with subsurface materials (organic and mineral). However, the mean DOC concentration was approximately 20% higher in the HES (Table 3-7) than the primary summer sampling (Table 3-5), although the range was wider for the primary sampling, which included watersheds with moderate to low slopes with increased opportunity for slow drainage. Increased DOC at upper elevations is consistent with other stream studies in mountainous landscapes that generally show increasing DOC with increasing elevation as a result of increasing forest floor thickness (Lawrence *et al.*, 1986, Lawrence *et al.*, 2000). Higher concentrations of Al_o in the summer HES than in the primary sampling is consistent with the higher DOC concentrations in the summer HES, which have a strong control of Al_o and also Al_t concentrations (Lawrence *et al.*, 2013).

August concentrations of SO_4^{2-}, and NO_3^- were similar between the HES and the primary streams, but concentrations of Cl^- were lower than in the primary sampling (Table 3-7). Mean and maximum concentrations of F suggested low F content in the geologic substrate of the region. Measurements of Ca^{2+}, Na^+ and Si constituents that increase in concentration with increased contribution from deep groundwater flow paths, were also considerably lower in the summer HES than in the primary sampling. Deep flow paths exert a stronger control on stream chemistry during base-flow conditions. The extremely low mean K^+ concentration and range reflect geochemical control of minerals with low K^+ content. All concentrations of NH_4^+ were at or near zero.

Flow conditions during the snowmelt HES were similar to the flow conditions during the primary ECASS snowmelt sampling conducted April 18–20, 2011 (Table 3-7). Stream chemistry measured in the snowmelt HES was extremely acidic, and like the comparison between the primary summer ECASS and the summer HES, mean values and ranges of pH, BCS and ANC during the snowmelt HES were considerably lower and Al_i was considerably higher than those values determined in the primary snowmelt sampling (Table 3-7). The BCS values of the HES streams were all within the lowest 25% of the primary ECASS snowmelt sampling (Figure 3-7).

Figure 3-7. High Elevation—Primary Sampling Comparison

BCS (base-cation surplus) shown as the cumulative fraction of streams during snowmelt for the primary and high-elevation samplings.



Mean DOC concentration in the snowmelt samplings was approximately 60% higher in the HES than the primary sampling, which was a larger difference than seen when comparing summer samplings. The range in DOC concentrations, which was smaller in the HES than in the primary sampling in the summer, was greater in the snowmelt comparison. This difference in DOC concentrations also resulted in a greater difference in mean and concentration range of Al_o. During snowmelt sampling the mean HES concentration was about 1.5 times higher than in the primary sampling, and the maximum Al_o concentration was over three times higher in the HES than the primary sampling.

A large difference in the mean and maximum SO_4^{2-} concentrations between the HES (Table 3-7) and the primary sampling Table 3-5) was observed during snowmelt, which contrasted the similar SO_4^{2-} concentrations observed in the summer samplings. However, mean NO_3^- concentration was similar between the two snowmelt samplings, although the maximum NO_3^- concentration in the primary sampling was considerably higher than in the HES. As in the summer samplings, the mean and range of Cl^- concentrations during the snowmelt samplings were somewhat lower in the HES than in the primary sampling. This value of Cl^- in stream water is extremely low relative to concentrations typically reported (Lawrence *et al.*, 2008b), and is approaching the concentration in rainwater.

Differences in mean concentrations and ranges of all base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) and Si between the HES and primary snowmelt samplings were similar to the differences observed from this comparison during the summer samplings. Mean and maximum concentrations of NH_4^+ in both the HES and primary samplings were similarly low, as seen in the summer measurements.

Comparison of stream chemistry between the two HES indicated that conditions were much more acidic during the snowmelt sampling than during the summer sampling (Figure 3-8). Values of BCS were less than zero in only four streams during the summer sampling, but less than zero in all but two streams during the snowmelt sampling. Values of pH showed a similar relationship between the two samplings with values ranging from approximately 5.0 to above 7.0 in the summer but shifting downward during snowmelt to a range of approximately 4.6 to 6.0. Concentrations of Al_i were also higher during snowmelt than during the summer although the concentration range was similar between the samplings, with the exception of one stream. A larger difference in Al_i concentrations driven by higher Al_i concentrations at pH values below 5.0 is typically observed (Lawrence *et al.*, 2008b) and may have been limited by the shallow mineral soil depth in the watersheds of these streams, which is typical in steep mountainous terrain (Johnson *et al.*, 2000b).

Past analyses of the chemical factors driving acidification of stream water during snowmelt or high-flow episodes in the Adirondack region has indicated that increases in acidity were due to combined increases in acid-anion concentrations (SO_4^{2-}, NO_3^-, and organic anions) and decreased base-cation concentrations. The relative importance of these factors in causing episodic acidification has been shown to vary among events, but increases in the sum of acid-anion concentrations and decreases in the sum of base-cation concentrations were common to all events (Wigington *et al.*, 1996a). However, this previous work was based on episodic stream chemistry in the Adirondack region in the late 1980s, when S and N deposition levels were three to four times greater than during the ECASS study.

Analysis of the ionic causes of greater acidification during the HES during snowmelt than the HES during summer strongly contrasted with the previous findings. Although concentrations of NO_3^- and $RCOO^-_s$ (strongly acidic organic anion concentration) were somewhat higher during snowmelt than summer, SO_4^{2-} concentrations during snowmelt were half those in the summer, and Cl^- was also lower during snowmelt than summer. The substantial dilution of base cations during snowmelt resulted in much more acidic conditions than during the summer, even though total strong acid-anion concentrations showed a sizable decrease (Figure 3-9). During snowmelt, the dilution of base cations overwhelmed the decrease in acid anions, causing harmful stream acidification despite the effect of large decreases in acidic deposition over the previous two decades (Figure 2-2). The dilution effect may also have contributed to the increase in DOC concentrations during snowmelt than during summer through a decrease in ionic strength (Monteith *et al.*, 2007). This finding demonstrates the highly acid-sensitive condition of the high-elevation watersheds. Without increases in base-cation availability, which are not likely in the near term, the HES streams will continue to experience acid episodes during snowmelt and other high-flow situations.

Figure 3-8. Acidification Measures during Summer and Snowmelt in High-Elevation Streams

Values of BCS (base-cation surplus), pH and Al_i (inorganic monomeric Al) versus the cumulative fraction of streams with the respective chemical measurement. Red vertical line indicates the BCS value below which Al_i is mobilized by acidic deposition.

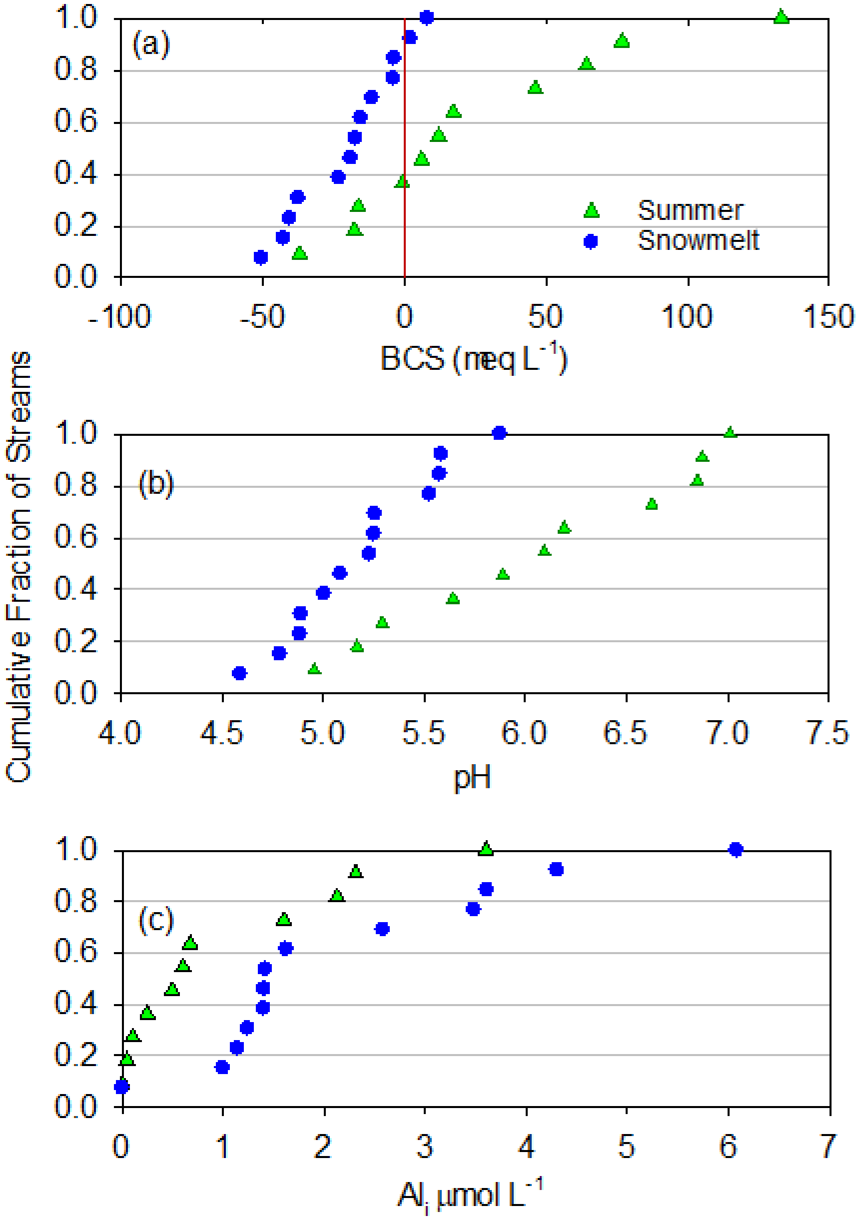
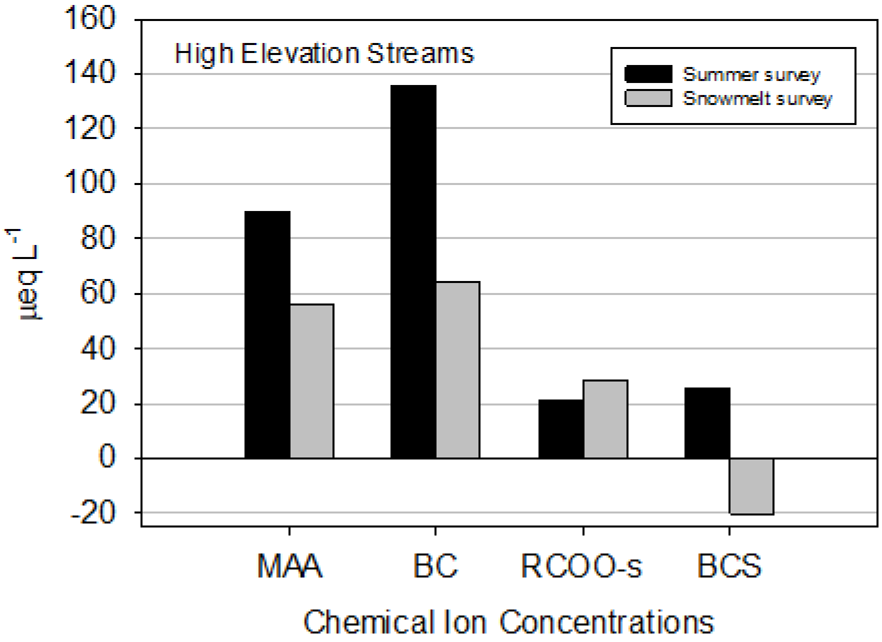


Figure 3-9. Comparison of Ionic Concentrations that Control Acidification

MAA represents the sum of strong acid mineral anions (SO_4^{2-}, NO_3^- and Cl^-); BC represents the sum of base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+); $RCOO^-s$ represents strongly acidic organic anions; BCS represents the base-cation surplus.

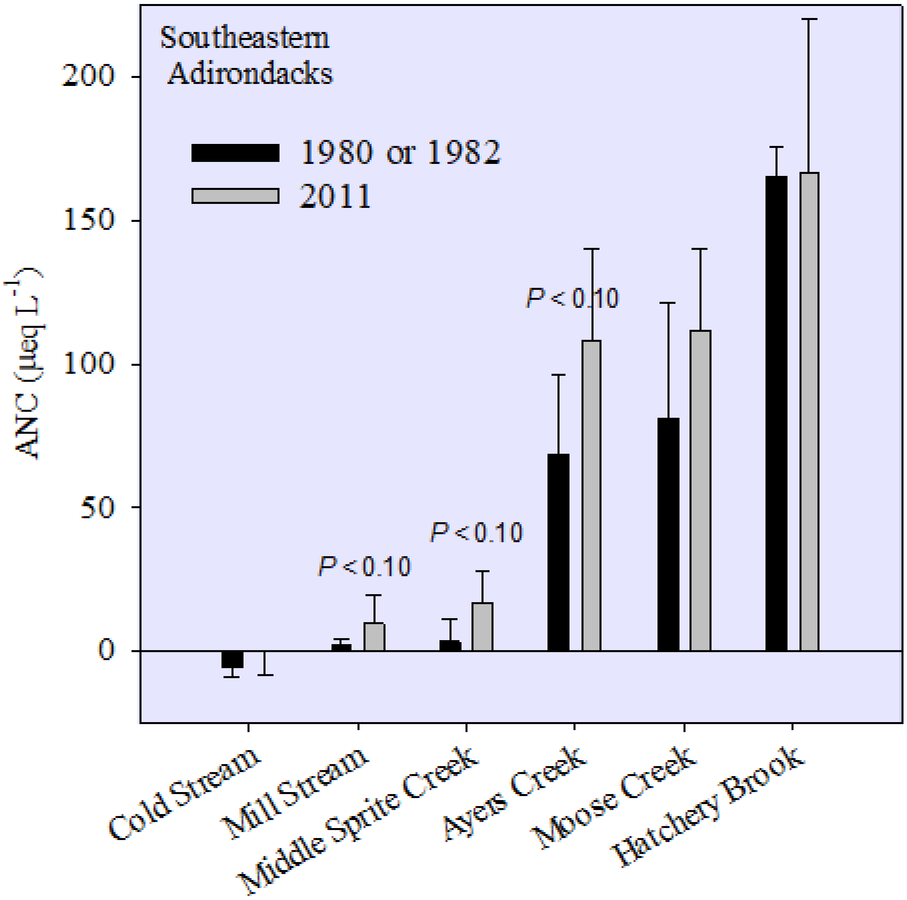


3.1.6 Historical Changes in Stream Chemistry within the ECASS Region

The six streams in the southeastern Adirondack region that were sampled during snowmelt (late March to early May) in either 1980 or 1982 provided an opportunity to evaluate the response of stream chemistry to three decades of decreasing S and N deposition (Figure 2-2). Measurements of ANC in the early 1980s (Figure 3-10) indicated that three of the streams (Cold Stream, Mill Stream and Middle Sprite Creek) were poorly buffered at that time (ANC < 5 $\mu eq\ L^{-1}$), whereas two of the streams were moderately well-buffered (65 $\mu eq\ L^{-1}$ < ANC < 85 $\mu eq\ L^{-1}$) and one stream was well-buffered (ANC = 165 $\mu eq\ L^{-1}$). Values of ANC in two of the poorly buffered streams were higher in 2011 than in the early 1980s, but the differences were small, marginally significant ($P < 0.10$), and equated to annual rates of increase of only 0.25 $\mu eq\ L^{-1}\ y^{-1}$ (Mill Stream) and 0.50 $\mu eq\ L^{-1}\ y^{-1}$ (Middle Sprite Creek). At those rates of recovery, Middle Sprite Creek would not reach an ANC of 50 $\mu eq\ L^{-1}$, the minimum level considered necessary to avoid harmful effects on biota (Driscoll *et al.*, 2001) for 65 years and Mill Stream would not reach this level for 160 years. Cold Stream, the most acidic of the resampled streams, did not show a statistical difference between samplings ($P > 0.10$), although ANC was 9.0 $\mu eq\ L^{-1}$ higher in the 2011 sampling than the sampling in 1982.

Figure 3-10. Snowmelt Values of ANC in the Early 1980s and 2011

Comparison of ANC (acid-neutralizing capacity by Gran titration) values in six streams sampled five times during snowmelt from late March to early May in 1980 or 1982 and again 2011. Whiskers indicate one standard deviation. Differences in values for Cold Stream, Moose Creek and Hatchery Brook were not significant ($P > 0.10$).



Moderately well-buffered Ayers Creek exhibited an increase ($P < 0.10$) in ANC of 40 µeq L^{-1} (1.4 µeq L^{-1} y^{-1}), and Moose Creek exhibited a nonsignificant ($P > 0.10$) ANC increase of 30 µeq L^{-1}, whereas well-buffered Hatchery Brook displayed no change in ANC over the three decades (Figure 3-10). Although this group of streams were located within the same area, they showed widely differing ANC responses to what was likely to be the period of acidification (pre-1980), as well as the period of decreasing deposition (1990–2011).Measurements of pH showed a more consistent response than ANC, with higher values in 2011 than 1980 or 1982, and these pH increases were statistically significant in two of the streams at the $P < 0.05$ level and one stream at the $P < 0.01$ level (Figure 3-11). Both the most acidic stream (Cold Stream) and the most buffered stream (Hatchery Brook) showed significant pH increases. The stronger response in pH than ANC in both of these streams may reflect a direct effect of the large decrease in acidic deposition without much change in the acid buffering capacity of either watershed. Cold Stream is likely to have experienced watershed Ca depletion prior to the initial sampling that has yet to show much recovery (Lawrence *et al.*, 2015), thereby limiting the ANC increase. Well-buffered Hatchery Brook is not likely to have experienced a large degree of watershed Ca depletion but may have shown an increase in pH simply because snowmelt entering the stream channel through shallow flow paths that had become less acidic.

Leaching of Ca and other base cations from the soil decreased the buffering capacity of these watersheds, which resulted in the dilution of stream water that was reflected in lower specific conductance, as reported for other streams in the Adirondack region (Lawrence *et al.*, 2011). Specific conductance of the three most acidic streams decreased from the dilution of stream water even as pH increased (Figure 3-12). The better buffered streams in this comparison did not experience the large decreases in specific conductance, which suggests that base-cation depletion did not occur in the watersheds of Moose Creek or Hatchery Brook (Figure 3-12). The high concentrations of Na^+ and Cl^- in Ayers Creek in 2011 suggested that an increase in specific conductance was due to road salt.

Figure 3-11. Snowmelt pH in the Early 1980s and 2011

Comparison of pH values in six streams sampled five times during snowmelt from late March to early May in 1980 or 1982 and again in 2011. Whiskers indicate one standard deviation. Differences in values for Mill Stream, Middle Sprite Creek and Moose Creek were not significant ($P > 0.10$).

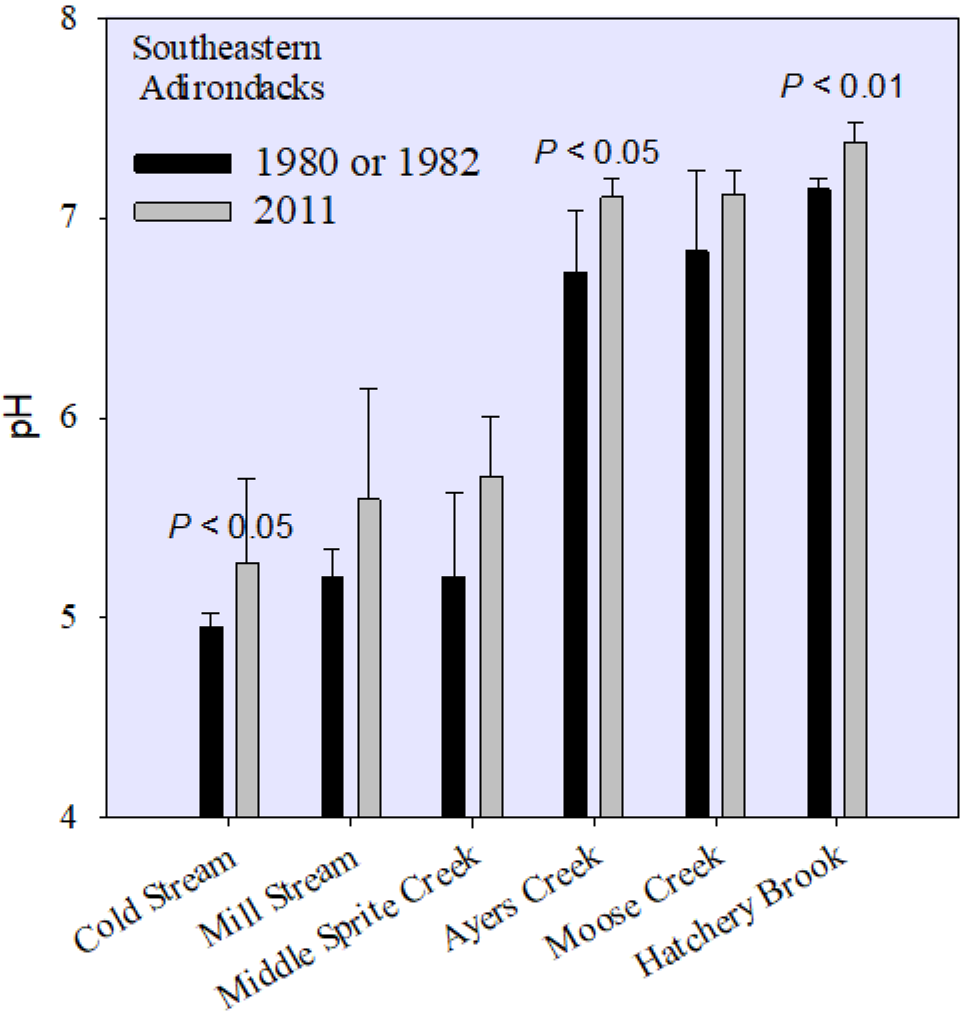
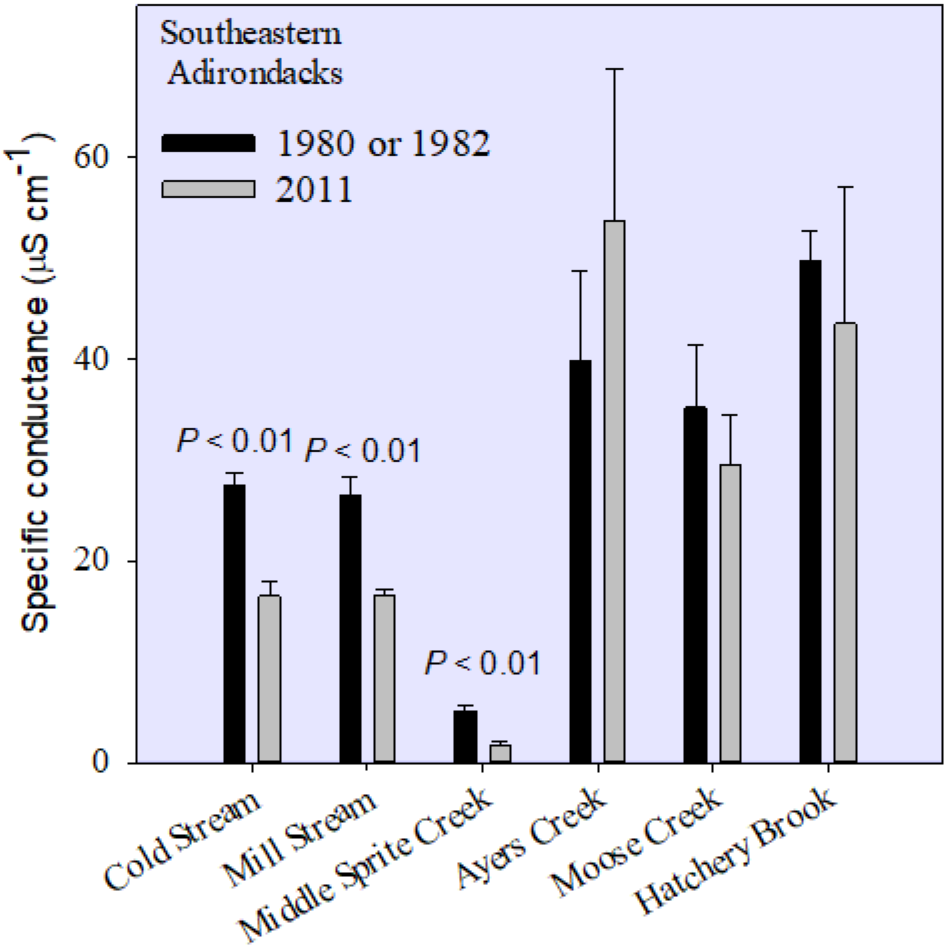


Figure 3-12. Snowmelt Values of Specific Conductance in the Early 1980s and 2011

Comparison of pH values in six streams sampled during five times during snowmelt from late March to early May in 1980 or 1982 and again in 2011. Whiskers indicate one standard deviation. Differences in values for Ayers Creek, Moose Creek and Hatchery Brook were not significant (*P* values > 0.10).



3.1.7 Changes in Stream Chemistry between the WASS and ECASS

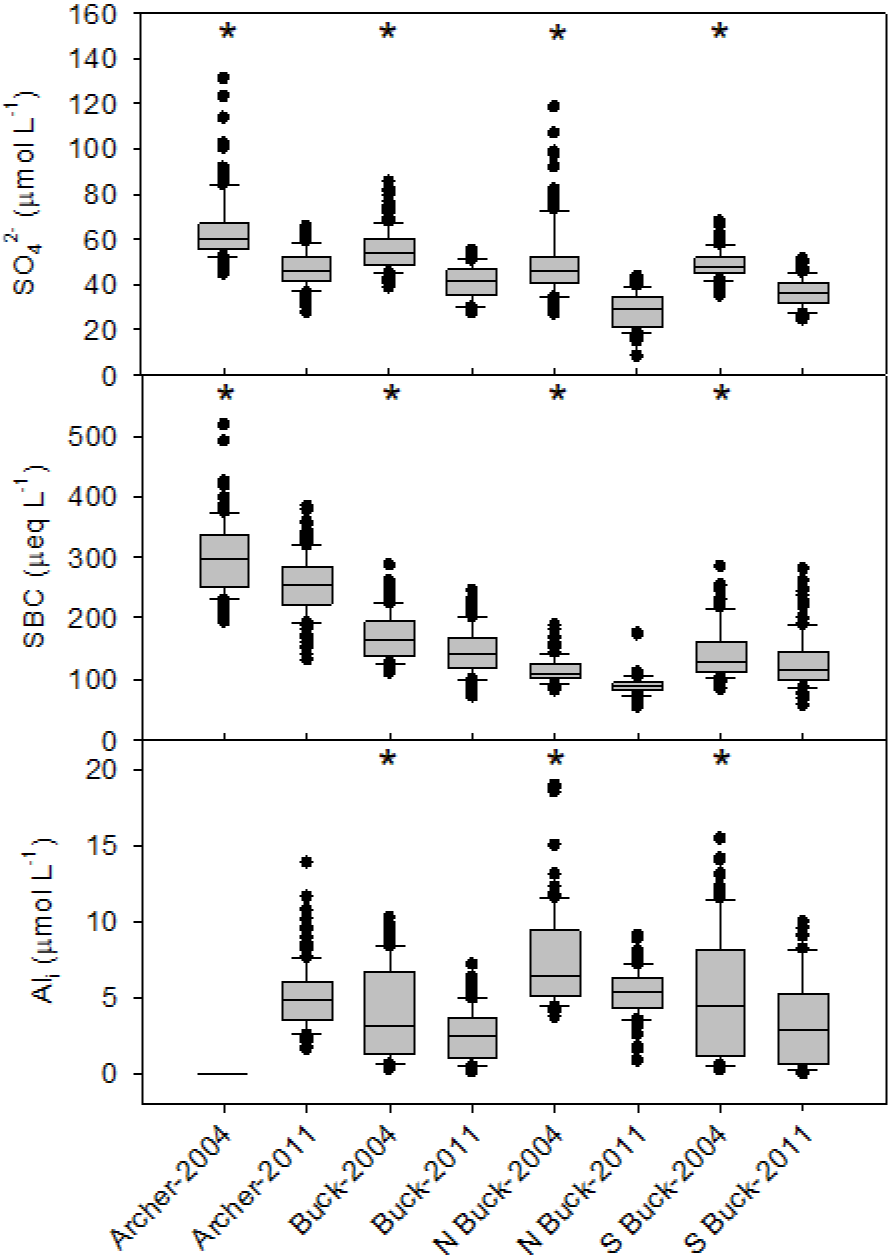
In the five-year interval between the end of the WASS (2005) and the start of the ECASS (2010), acidic deposition of S decreased approximately 2 kilograms per hectare per year (kg ha^{-1} y^{-1}) and N decreased approximately 1.0 kg ha^{-1} y^{-1}. These rates of decreases were similar to the decreasing rates of the previous decade and may have played a role in changing stream chemistry. However, other factors such as release of N and S that had accumulated in soil in the past may also have contributed to changes in stream chemistry between surveys (Lovett & Goodale, 2011, Mitchell *et al.*, 2011). To provide an Adirondack-wide assessment of stream chemistry with these surveys, the possibility of temporal changes needed to be quantified.

Results of Wilcoxon rank-sum analysis indicated that the three measures of acid-base conditions, H^+, ANC, and BCS did not significantly differ ($P > 0.05$) at Archer Creek, Buck Creek, and North Buck Creek between the two survey periods. Only at South Buck Creek were significant differences evident ($P < 0.05$), and both H^+ and ANC (but not BCS) were significantly higher in the more recent 2010–2011 period than during 2003–2005.

Sulfate and the sum of base cations (SBC) were the only constituents that showed significant differences at all four sites in the Wilcoxon rank-sum analysis, and concentrations were lower for each during 2010–2011 than during 2003–2005 (Figure 3-13). Concentrations of Al_i were significantly lower at all three of the Buck sites, but not at Archer Creek (Figure 3-13). Note however that Al_i concentrations were zero or near detection limits in this moderately well-buffered stream. Of the remaining constituents evaluated, NO_3^- concentrations were not significantly different across the two time periods at any of the four sites ($P > 0.05$), and only North Buck Creek showed significant differences in DOC, with higher concentrations during 2010–2011 than during 2003–2005.

Figure 3-13. Comparison of Stream Chemistry between 2003–2005 and 2010–2011

Box plots of SO_4^{2-} concentrations, SBC (sum of base cations), Al_i (inorganic monomeric Al) concentrations for 2003–2005 and 2010–2011 in four Adirondack streams. Gray boxes indicate the 25th and 75th percentiles with a horizontal line indicating the median; whiskers indicate 10th and 90th percentiles; circles show individual values outside the 10th to 90th percentiles. The asterisks indicate the data set with the greatest concentrations or values among the two periods when a significant difference ($P < 0.05$) was indicated by the Wilcoxon rank-sign comparison test.



The ANCOVA analysis indicated that nearly all constituents at all sites were significantly related to Q%, except for SO_4^{2-} and NO_3^- at North Buck Creek. For most constituents, separate regression lines were fit to the two survey periods (Table 3-8). Results of this analysis were generally consistent with the results from the Wilcoxon rank-sum test, and accounting for flow variation did reveal some differences in chemistry between the survey periods, although most were not large. At both low flow and high flow, indices of acidity (H^+, ANC and BCS) suggested small decreases in acidification from the 2003–2005 survey to the 2010–2011 survey in all four streams, except North Buck Creek, which showed small increases in acidification. Note that the negative H^+ values at low flow for Buck Creek and South Buck Creek resulted from the imprecision of the 2010–2011 linear regression model.

In the ANCOVA analysis, the SBC showed the clearest difference between surveys by exhibiting substantially lower concentrations in the 2010–2011 survey than in the 2003–2005 survey at both low and high flows in each of the streams. Lower concentrations of Al_i were also observed in the 2010–2011 survey than the 2003–2005 survey at high flow in Buck Creek, North Buck Creek and South Buck Creek, as well as at low flow in North Buck Creek. Concentrations of DOC increased at both low and high flow in Buck Creek and at low flow in North Buck Creek, but showed little change in the other streams at either flow condition. Concentrations of SO_4^{2-} decreased between surveys in both flow conditions in Archer Creek, Buck Creek and South Buck Creek. South Buck Creek also exhibited increases in NO_3- between surveys under both flow conditions (Table 3-8).

The strongest and most consistent evidence of change was in stream SO_4^{2-} and SBC concentrations, which both declined significantly over this period at all sites. Concentrations of Al_i also decreased significantly in the three streams where this constituent was measured. Other constituents such as pH, ANC, BCS, and DOC showed a mixed response over this period suggesting that varied temporal trend patterns are expected among the WASS and ECASS streams over the two study periods. Concentrations of NO_3^- showed no significant changes during 2003–2005 to 2010–2011 except for a slight increase at high flow at one site. The changes observed were generally consistent with decreasing atmospheric SO_4^{2-} deposition over the period, but changes were not observed in a number of constituents, and the changes that were detected were generally small. Therefore, combining the WASS and ECASS data was considered to be a reasonable approach for assessing stream chemistry over the Adirondack region.

Table 3-8. Covariate Analysis of Chemistry 2003–2005 and 2010–2011

Analysis of covariance to account for flow in determining if differences in stream concentrations occurred between the two survey periods in (a) Archer Creek, (b) Buck Creek, (c) North Buck Creek and (d) South Buck Creek. Flow column lists *P* values for concentration-flow interaction; Slope and Intrcpt (intercept) *P* values are shown where concentration-flow relations differed between survey periods or NS if not significantly different between survey periods. Concentrations are shown for low flow and high flow for each survey period if a significant difference between survey periods was found for either slope or intercept. ANC is based on a Gran titration except for Archer Creek for which ANC was determined by charge balance calculated as (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}) – (SO_4^{2-} + NO_3^{-} + Cl^{-}) in units of µeq L^{-1}. BCS is base-cation surplus; SBC is sum of base cations; DOC is dissolved organic carbon; total Al is total unfiltered Al.

(a) Archer Creek

Chemical Constituent	ANCOVA			Low Flow (Q15)		High Flow (Q85)	
	Flow	Slope	Intrcpt	2003-05	2010-12	2003-05	2010-12
H^+ µmol L^{-1}	<0.001	<0.001	<0.001	0.31	0.36	1.25	0.66
ANC µeq L^{-1}	<0.001	<0.001	NS	181.7	180.2	86	105.5
BCS µeq L^{-1}	<0.001	NS	0.029	148.6	157.3	56.8	65.5
SBC µeq L^{-1}	<0.001	NS	<0.001	338.7	311.5	244.8	217.6
SO_4^{2-} µmol L^{-1}	<0.001	NS	<0.001	135.2	103	119.5	87.4
NO_3^- µmol L^{-1}	<0.001	NS	NS				
DOC µmol C L^{-1}	<0.001	NS	NS				
Total Al µmol L^{-1}	<0.001	NS	NS				

(b) Buck Creek

Chemical Constituent	ANCOVA			Low Flow (Q15)		High Flow (Q85)	
	Flow	Slope	Intrcpt	2003-05	2010-12	2003-05	2010-12
H^+ µmol L^{-1}	<0.001	NS	<0.001	0.59	-1.56	12	9.8
ANC µeq L^{-1}	<0.001	NS	<0.001	39.5	46	0.9	7.4
BCS µeq L^{-1}	<0.001	NS	NS				
SBC µeq L^{-1}	<0.001	NS	<0.001	215.1	188.2	149.4	122.4
SO_4^{2-} µmol L^{-1}	<0.001	NS	<0.001	64.3	49.6	50.8	36.2
NO_3^- µmol L^{-1}	<0.001	NS	NS				
DOC µmol C L^{-1}	<0.001	NS	0.012	304.1	345.3	541.8	583
Total Al µmol L^{-1}	<0.001	<0.001	<0.001	0.7	0.7	5.6	3.5

Table 3-8 continued

(c) North Buck Creek							
Chemical Constituent	**ANCOVA**			**Low Flow (Q15)**		**High Flow (Q85)**	
	Flow	**Slope**	**Intrcpt**	**2003-05**	**2010-12**	**2003-05**	**2010-12**
H^+ μmol L^{-1}	<0.001	<0.001	NS	35.4	41.5	53	46.9
ANC μeq L^{-1}	<0.001	<0.001	NS	-25.1	-37.1	-50.8	-42.2
BCS μeq L^{-1}	<0.001	0.005	<0.001	-83.4	-85.8	-114.6	-91.9
SBC μeq L^{-1}	<0.001	NS	<0.001	125.4	98	109	81.6
SO_4^{2-} μmol L^{-1}	NS						
NO_3^- μmol L^{-1}	NS						
DOC μmol C L^{-1}	0.023	<0.001	0.001	1183.4	1507.4	1403.4	1400.9
Total Al μmol L^{-1}	0.012	NS	<0.001	6.8	4.5	8	5.7

(d) South Buck Creek							
Chemical Constituent	**ANCOVA**			**Low Flow (Q15)**		**High Flow (Q85)**	
	Flow	**Slope**	**Intrcpt**	**2003-05**	**2010-12**	**2003-05**	**2010-12**
H^+ μmol L^{-1}	<0.001	NS	<0.001	2.69	-1.61	17.81	13.51
ANC μeq L^{-1}	<0.001	NS	0.003	37.5	45.5	-11	-3.1
BCS μeq L^{-1}	<0.001	NS	NS				
SBC μeq L^{-1}	<0.001	NS	<0.001	201.6	176.5	116.1	90.9
SO_4^{2-} μmol L^{-1}	<0.001	0.001	<0.001	54.1	43.7	46.1	30.8
NO_3^- μmol L^{-1}	0.003	NS	0.008	27.1	36.1	38.7	47.8
DOC μmol C L^{-1}	<0.001	NS	NS				
Total Al μmol L^{-1}	<0.001	0.024	<0.001	0.4	0.3	7.6	5.7

3.1.8 Adirondack-Wide Representativeness of the WASS and ECASS

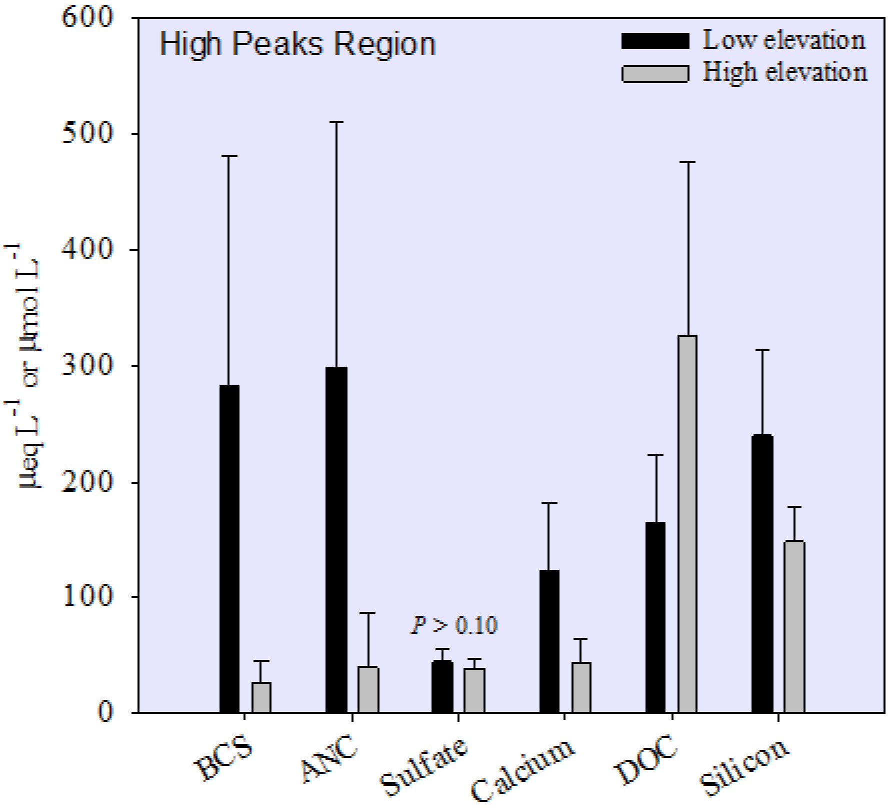
Much of the Adirondack region is accessible only by hiking for a day or more. Furthermore, many streams are remote from trails—reachable only by walking through rugged terrain with thick vegetation and impassible wetlands guided by GPS navigation. These streams were excluded from the random selection process in regional surveys because conducting the sampling within two to three days is not practical. However, the exclusion of these streams raises the question of whether the survey results based on the accessible population of streams can be used to represent the entire population of streams. If accessibility imparts a bias with respect to stream chemistry, the survey results will only apply to the population of accessible streams.

To determine if accessibility imparted a bias in stream chemistry, the high-elevation streams selected non-randomly within the Adirondack High Peaks region were considered to be inaccessible because they all required hiking half a day or more to sample. Thirty primary (accessible) ECASS streams occurred within the area encompassed by the high-elevation streams. From these 30 primary ECASS streams, 12 were randomly selected to represent snowmelt sampling, and 11 of those 12 were randomly selected to represent summer base-flow sampling. In this manner, an equal number of streams during snowmelt and summer base flow could be compared to determine if accessibility introduced a bias into the random selection of the primary ECASS streams. The randomly selected accessible streams within the High Peaks region (hereafter referred to as low-elevation streams) all had portions of their watersheds that extended to at least 900 meters, but sampling elevations ranged from 317 m to 660 m. Sampling locations of the high-elevation streams ranged from 866 m to 1017 m elevation, and all watersheds were forested to their uppermost elevations except for occasional areas too steep to allow tree growth. Although both sets of streams were in the same region, they differed considerably in landscape position. The low-elevation streams were generally in the lower third of the hillslope whereas the high-elevation streams were generally in the top third of the hillslope.

Mean values of the low-elevation streams during summer base flow were significantly different from the high-elevation sites (Figure 3-14) with respect to BCS, ANC, DOC, Ca^{2+} and Si ($P < 0.01$), but not SO_4^{2-} ($P > 0.10$). Measurements of BCS and ANC were much greater in the low-elevation streams than in the high-elevation streams. Concentrations of Ca^{2+} and Si were also highest in the low-elevation streams, but the difference between low- and high-elevations streams was less than for BCS and ANC (Figure 3-14). These results reflected a strong influence of soil and subsoil flow paths on the low-elevation streams that provided greater opportunity for neutralizing chemical reactions with geologic materials. Steeper terrain in the watersheds of the high-elevation streams resulted in shallow soils, fewer areas with underlying till deposits, and shorter subsurface residences times—factors which all limit watershed capacity for acid-neutralization.

Figure 3-14. Elevation Comparison of August Stream Chemistry in the High Peaks Region

Comparison of mean values of a group of 11 streams at low elevation and a second group at high elevation within the Adirondack High Peaks region. Whiskers indicate one standard deviation. BCS is base-cation surplus; ANC is acid-neutralizing capacity by Gran titration; DOC is dissolved organic carbon. Units of BCS and ANC are µeq L^{-1}; units for all other measures are mmol L^{-1}. Significant differences ($P < 0.01$) were found for all histogram pairs except sulfate.



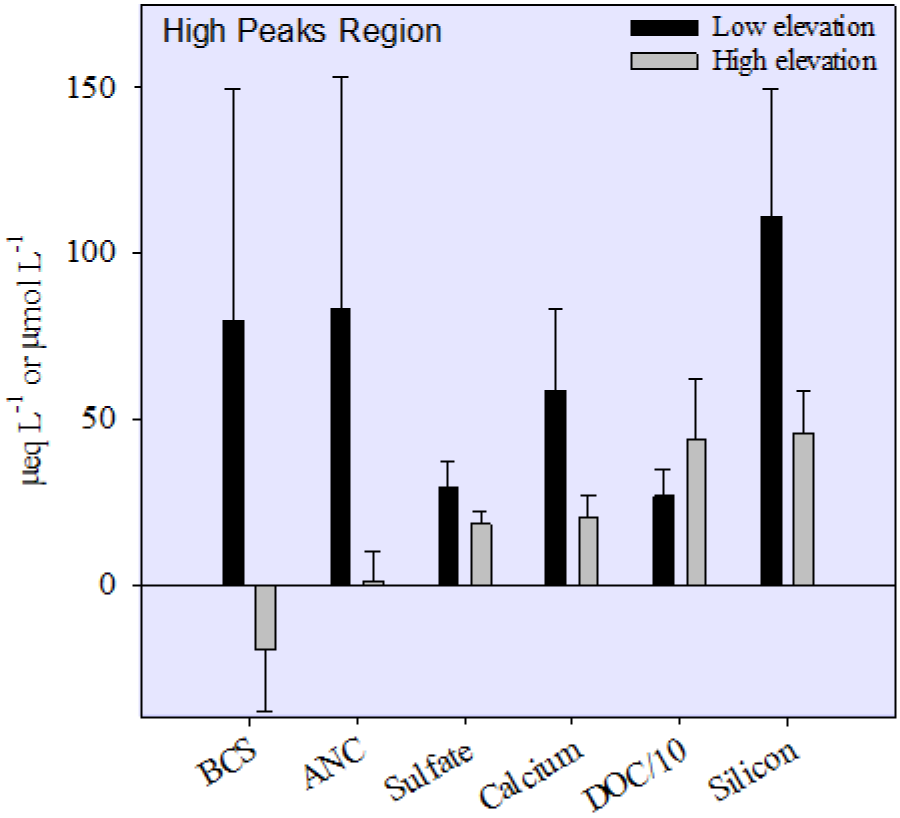
The similarity in SO_4^{2-} concentrations between low- and high-elevation streams suggested that the primary controls of SO_4^{2-} concentrations operated in the upper soil layer, which may involve both organic and mineral influences which can affect mobility of SO_4^{2-}. Previous research in the Adirondack region and elsewhere has suggested that control of SO_4^{2-} release from soils in glaciated regions is largely controlled by labile organic matter (Mitchell *et al.*, 2011), much of which occurs in the organic horizons that comprise the forest floor. Thicker forest floor layers at higher elevations may have increased net SO_4^{2-} retention somewhat through incorporation of S into organic matter. Higher concentrations of DOC in high-elevation streams (Figure 3-14) than low-elevation streams also suggested shallow soil control of this constituent. The steep, forested terrain of the high-elevation sites were likely to have had deep surface organic layers that are a major source of DOC in headwater streams (Lawrence *et al.*, 1986).

The same relationships between low- and high-elevation stream chemistry were observed during snowmelt sampling as was observed during summer base flow (Figure 3-15) One minor exception was SO_4^{2-} concentrations, which were not significantly different ($P > 0.10$) between elevations. Concentrations of all constituents shown in Figure 3-15 were more dilute during snowmelt than August base flow (Figure 3-14), except DOC, which increased in concentration relative to summer base flow. Decreased ionic strength of the more dilute soil water during snowmelt appears to have increased DOC mobilization in the soil, leading to the higher DOC concentrations during snowmelt in both low- and high-elevation streams. However, results from the WASS study indicated higher concentrations of DOC during summer base flow than during snowmelt and similar concentrations between snowmelt and extreme summer low-flow conditions (Lawrence *et al.*, 2008a). The cause of the differing relationships between DOC concentrations during summer base flow and snowmelt in the two WASS and ECASS samplings is unclear.

The comparison between high- and low-elevation sites in the High Peaks region indicates that accessibility imparts a strong bias; acidification was substantially higher in streams difficult to access. Clearly the ECASS streams chosen with the standard selection protocol were not fully representative of the High Peaks region, and the information obtained from these streams underestimated the degree of acidification occurring within that region. The topographic variations within the High Peaks region are the most extreme within the Adirondack ecoregion, but information from the WASS survey obtained from longitudinal sampling of streams also indicated that streams tended to become more acidic in the upslope direction (Lawrence *et al.*, 2008a), and this tendency is commonly reported for other upland regions (Johnson *et al.*, 2000a, Lawrence *et al.*, 1999).

Figure 3-15. Elevation Comparison of Snowmelt Chemistry in the High Peaks Region

Comparison of mean values of a group of 11 streams at low elevation and a second group at high elevation within the Adirondack High Peaks region. Whiskers indicate one standard deviation. BCS is base-cation surplus; ANC is acid-neutralizing capacity by Gran titration; DOC/10 is dissolved organic carbon in (μmol L^{-1})10^{-1}. Units of BCS and ANC are μeq L^{-1}; units for all other measures are μmol L^{-1}. Significant differences ($P < 0.01$) were found for all histogram pairs except sulfate, which was not different ($P > 0.10$) between elevations.



Accessible stream length within the WASS study region, as defined by the sampling protocols, was estimated to be approximately 30% of total headwater stream length (Lawrence *et al.*, 2008a). If this percentage is applied to the approximately 14,200 km of first-order streams in the entire ecoregion, the WASS and ECASS results could be considered representative of approximately 4,260 km of stream length. For the remaining 9,940 km of headwater streams, the extent of acidification is underestimated with ECASS and WASS sampling data. However, the degree to which the surveys underestimated acidification for the Adirondack ecoregion as a whole would likely be less than that determined by the analysis of the High Peaks region because topographic variability throughout the ecoregion is, in general, considerably less than that of the High Peaks region.

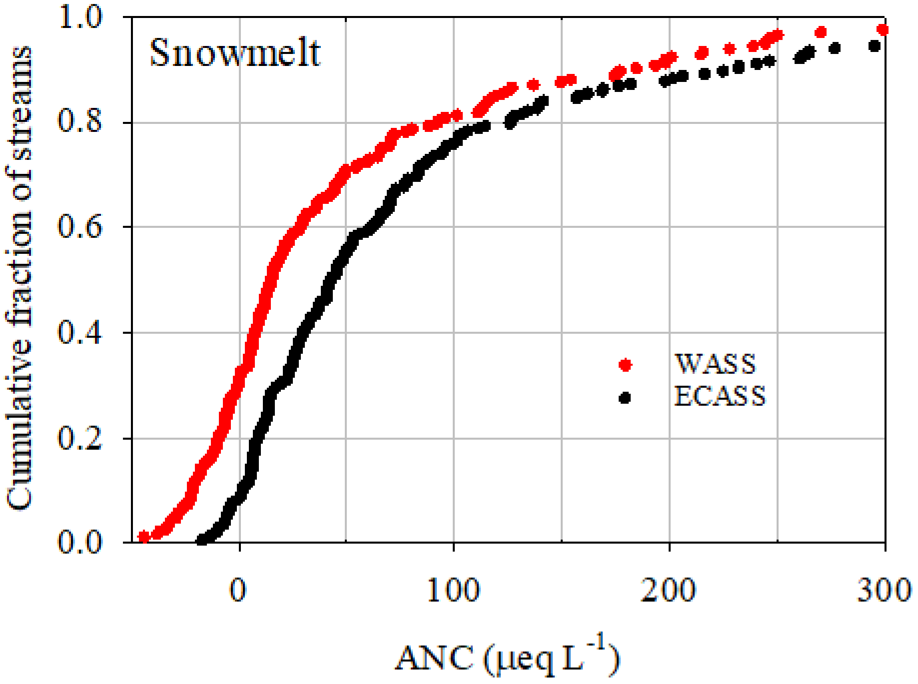
3.1.9 Stream and Soil Chemistry Comparison for WASS and ECASS Regions

Completion of the ECASS enabled results to be compared with WASS results, which focused on the area of the Adirondack ecoregion found to have the highest number of acidified lakes (Baker *et al.*, 1990). Combining results of the two surveys provided an Adirondack-wide assessment of stream chemistry, although the analysis of the continuous monitoring data from Buck Creek, Buck North and South tributaries, and Archer Creek indicated that some recovery had occurred between the two surveys. The temporal change between surveys tended to somewhat bias the ECASS data towards less acidification than would have been measured had the ECASS been done in the same window of time as the WASS.

Values of ANC during the ECASS snowmelt sampling were higher than those measured during the 2004 WASS snowmelt sampling throughout the distribution of values (Figure 3-16), although the difference between surveys was considerably less at ANC values above 100 µeq L^{-1}. In these snowmelt samplings, fewer than half (approximately 45%) of ECASS streams had values above 50 µeq L^{-1}, the level above which aquatic biota are not considered at risk, whereas only 25% of WASS streams had ANC values above this level. Concentrations of SO_4^{2-} were similarly distributed in the ECASS and WASS throughout their respective ranges, with consistently higher values in WASS streams than ECASS streams (Figure 3-17). The difference in concentrations at both the lowest and highest SO_4^{2-} concentrations was approximately 12 µmol L^{-1}. Likewise, concentrations of NO_3^- (Figure 3-18) were higher in WASS streams than ECASS streams with a similar distribution of concentrations.

Figure 3-16. ECASS-WASS ANC Comparison

ANC (acid-neutralizing capacity by Gran titration) as a function of the cumulative frequency of streams during ECASS and WASS snowmelt samplings.



In contrast to SO_4^{2-} and NO_3^-, concentrations of Ca^{2+} during snowmelt followed the same concentration distribution in both the ECASS and WASS (Figure 3-19). Similar Ca concentrations in streams despite lower concentrations of SO_4^{2-} and NO_3^- is an indication that acid buffering is, in general, higher in the ECASS watersheds. With the data available, it’s not possible to quantify how much of the difference in ANC between the surveys is due to spatial differences in ambient buffering and how much is due to recovery from acidification. However, soil monitoring data suggests that soil-Ca availability hasn’t increased (Lawrence *et al.*, 2015), so the similarity in stream water Ca^{2+} concentrations between surveys with lower ECASS SO_4^{2-} and NO_3^- concentrations is an indication of better buffering in the ECASS region than the WASS region rather than strong recovery.

Figure 3-17. ECASS-WASS SO_4^{2-} Comparison

Concentrations of SO_4^{2-} as a function of the cumulative frequency of streams during ECASS and WASS snowmelt samplings.

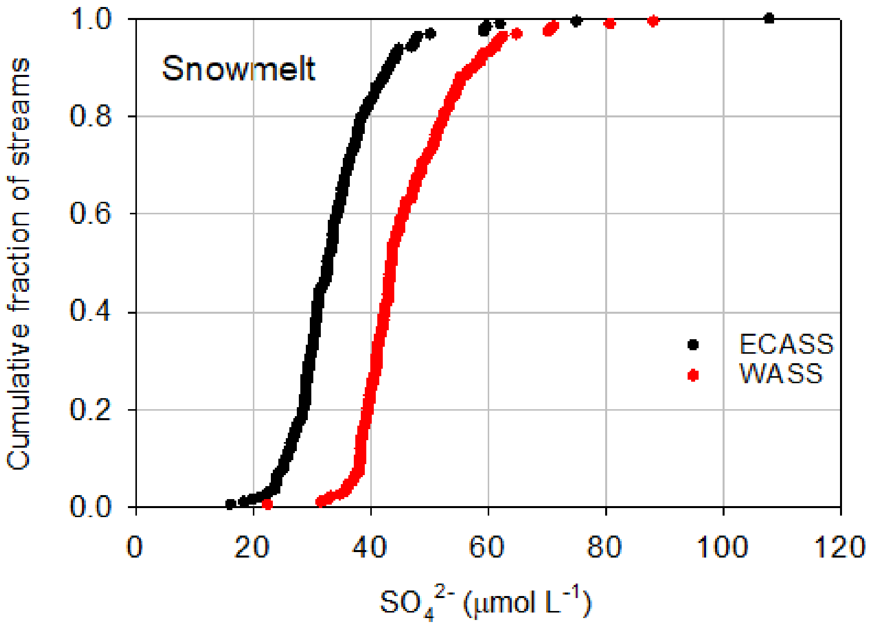


Figure 3-18. ECASS-WASS NO_3- Comparison

Concentrations of NO_3^- as a function of the cumulative frequency of streams during ECASS and WASS snowmelt samplings.

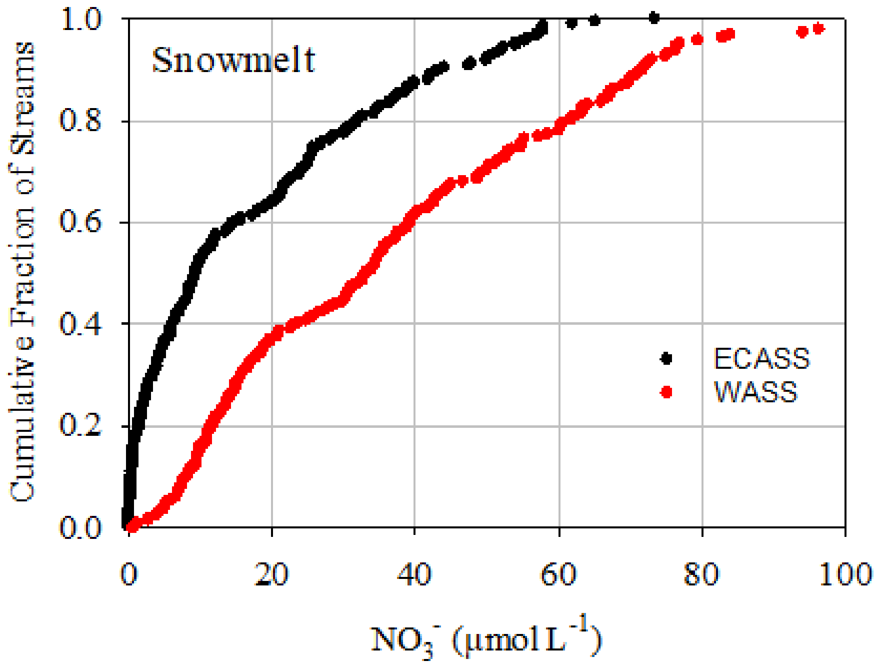
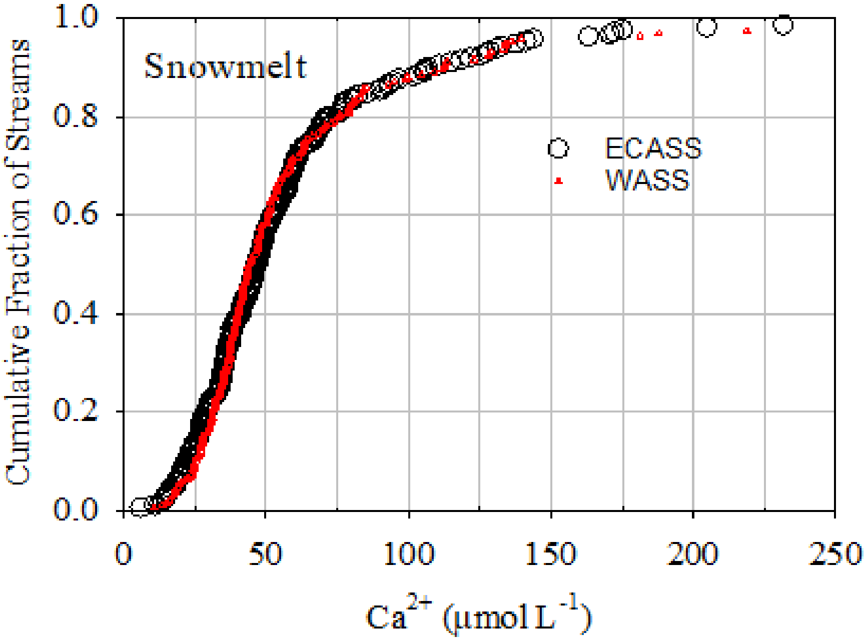


Figure 3-19. ECASS-WASS Ca^{2+} Comparison

Concentrations of Ca^{2+} as a function of the cumulative frequency of streams during ECASS and WASS snowmelt samplings.



The spatial distribution of ECASS streams acidified during the snowmelt sampling was largely limited to the western and southern portions of the ECASS region Figure 3-20). In these areas, the streams that were unacidified during the sampling were the least common. The only streams in the northern half of the region that were acidified during the snowmelt sampling were in the High Peaks region, with the exception of the most northern stream. However, streams determined to be prone to episodic acidification were distributed throughout most of the ECASS region. Within the WASS region streams acidified during snowmelt were common throughout the sampling region with the exception of the westernmost area.

Previous analysis of stream and soil data from 10 watersheds collected during the WASS identified a strong linear relationship between the BCS during snowmelt and base saturation of the Oa soil horizon (Lawrence *et al.*, 2008b). A weaker, but also significant relationship was found between the BCS and the base saturation of the upper B horizon. Additional soil data became available through other project work, increasing the number of watersheds where the BCS could be related to base saturation to a total of 26. These data are all available in Lawrence (et al. 2017). With the additional watersheds, the range in base saturation expanded the area encompassed by the 26 watersheds to include the ECASS region. With the data obtained from the 26 watersheds, a strong statistical relationship based on the upper B horizon was developed (Figure 3-21), as described in Lawrence (et al. 2018). Because the B horizon is the layer within the soil profile where mobilization of toxic Al occurs, the BCS was used to estimate base saturation for this horizon in all watersheds of the WASS and ECASS streams.

Figure 3-20. Map of Acidification Status of ECASS and WASS Streams during Snowmelt

Circles indicate streams acidified when sampled (red), streams prone to acidification under conditions more acidic than when the stream was sampled (yellow), and streams that are unlikely to acidify to levels that mobilize inorganic Al under worst conditions (teal). Diamonds show high-elevation streams with the same color coding. Green line is the boundary of the Adirondack ecoregion; blue line is the boundary of the Adirondack State Park; white line separates the WASS and ECASS study areas.

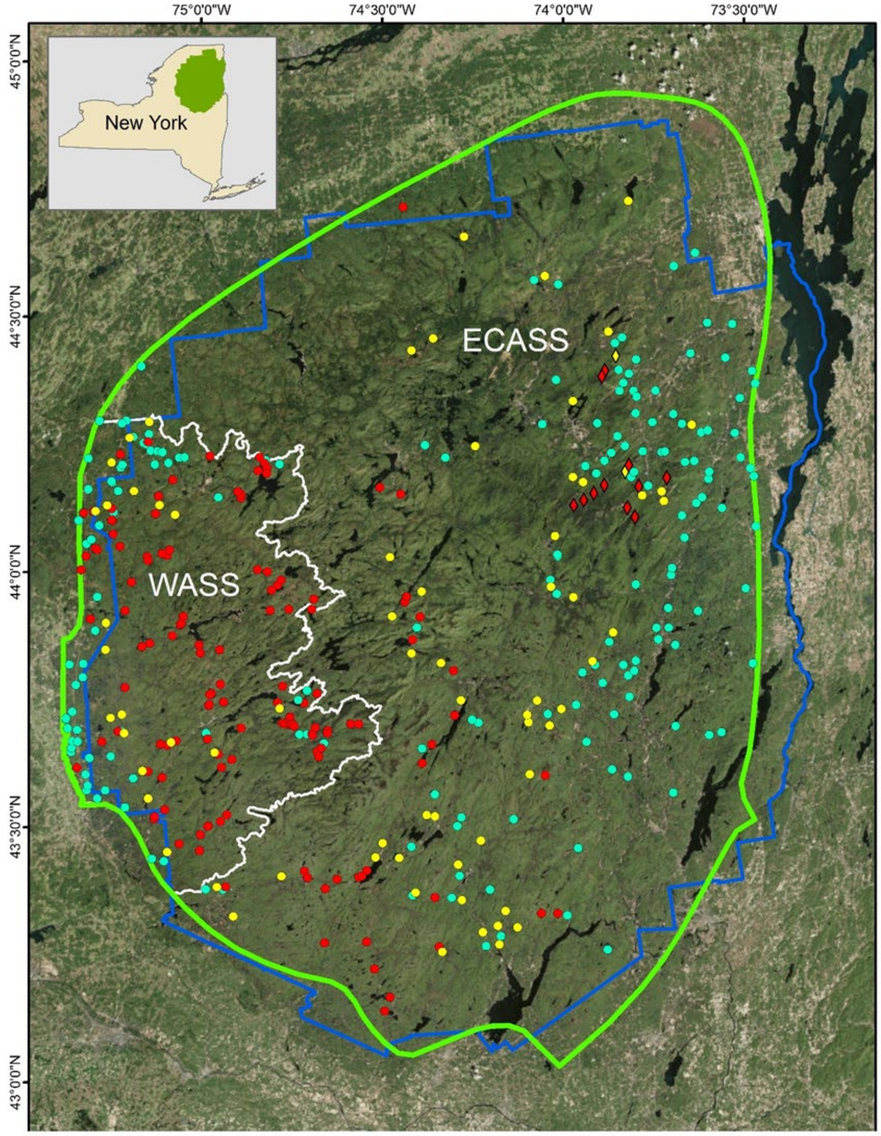
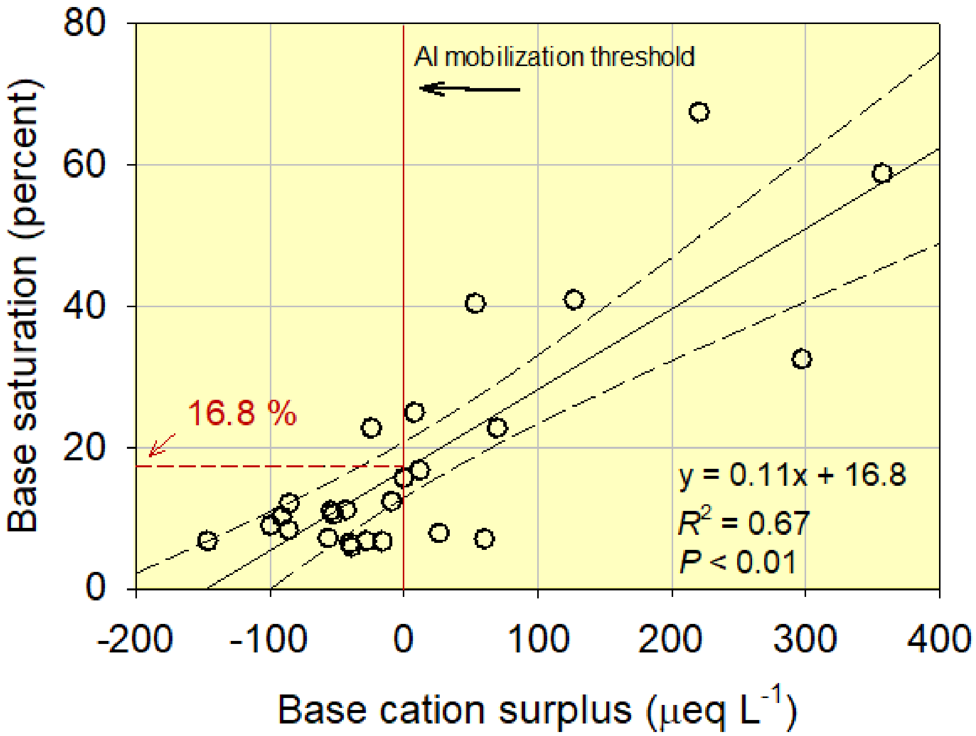


Figure 3-21. Soil-Base Saturation as a Function of Base-Cation Surplus

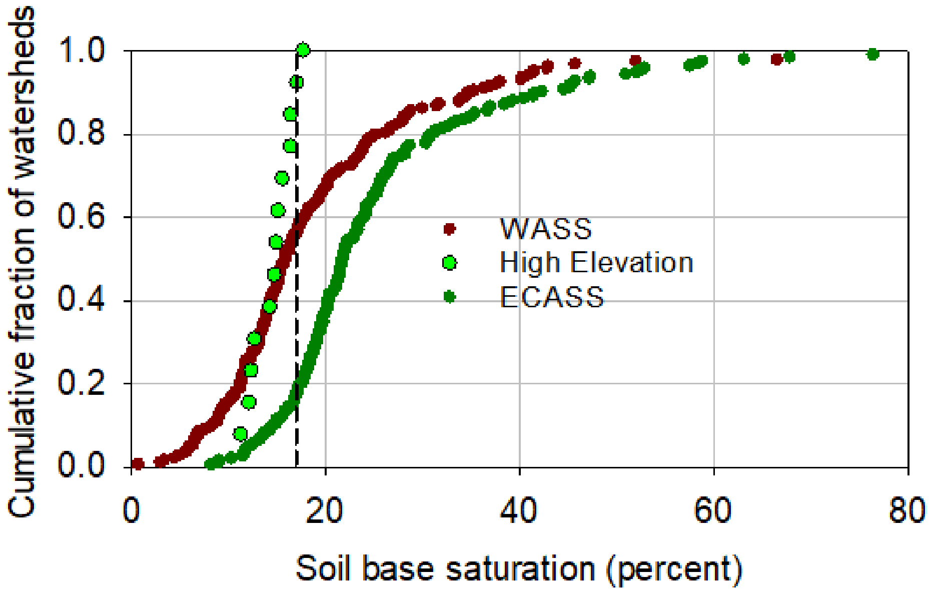
Vertical red line indicates the threshold of Al mobilization (base-cation surplus = 0.0), which corresponds to a base saturation of the upper B horizon of 16.8%. Dashed lines indicate 95 percent confidence intervals around the best fit line.



Plotting base-saturation estimates as cumulative fraction shows a marked difference in base saturation between WASS and ECASS watersheds (Figure 3-22). The vertical dashed line, which delineates the base saturation threshold below which Al mobilization occurs (Lawrence *et al.*, 2018), indicates that 20% of the ECASS watersheds have soils with base saturation of the upper B horizon that provides insufficient acid buffering to prevent mobilization of toxic forms of Al (Lawrence *et al.*, 2018). In 58% of WASS watersheds, estimated base-saturation values fell below this threshold (Figure 3-22). Just one of the high-elevation watersheds had estimated base saturation above the threshold, and only by a small amount.

Figure 3-22. Base Saturation of WASS, High-Elevation, and ECASS Watersheds

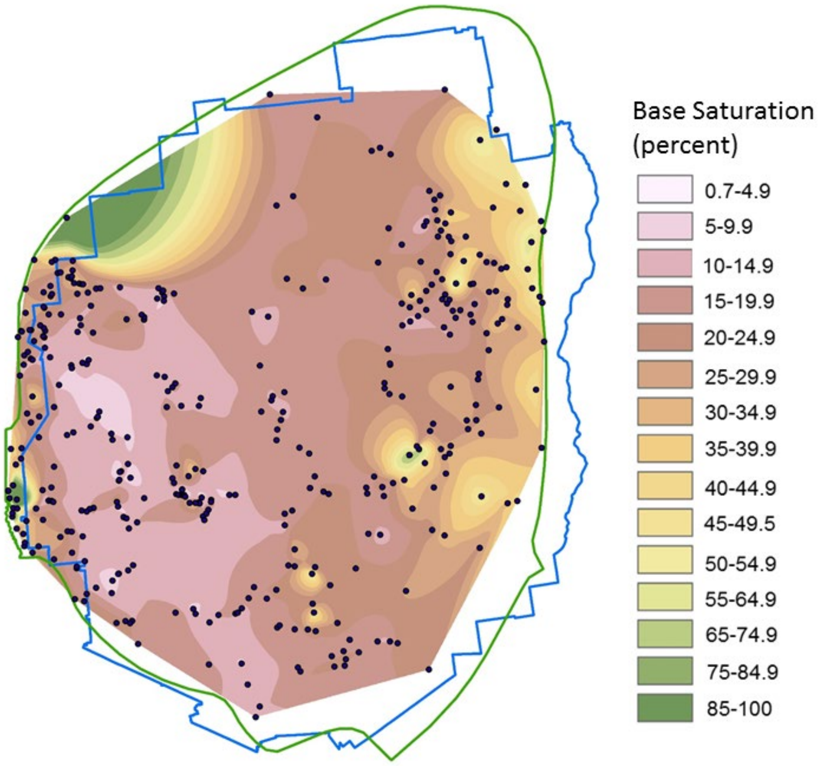
Cumulative fraction of watersheds shown as a function of soil-base saturation in the upper B horizon. Vertical line indicates the base-saturation value below which mobilization of Al occurs.



Spatial representation of base-saturation estimates derived from the BCS-base saturation relationship were developed for the area within the Adirondack Park with ArcGIS software (Figure 3-23). The natural neighbor algorithm (Sibson, 1981)was used for interpretation, as described here: http://desktop.arcgis.com/en/arcmap/10.3/tools/spatial-analyst-toolbox/how-natural-neighbor-works.htm (accessed May 30, 2018). Soils with low-base saturation less than 10% were concentrated in the west, but soils with base saturation less than 25% extended through most of the Adirondack Park, and comprised over 50% of the area mapped within the blue line (Figure 3-23). Areas where base saturation of the B horizon suggested well-buffered soils (base saturation above 30%) occurred largely in the northwest and easternmost areas. The large extent of soils with low acid-buffering capacity has implications for terrestrial as well as aquatic ecosystems throughout much of the Adirondacks. Mobilization of Al, which occurs in soil below base saturation of 17% in the upper B horizon has recently been identified as a control of forest species composition and structure in Adirondack forests (Lawrence *et al.*, 2018).

Figure 3-23. Variation in Base Saturation (Percent) across the Adirondack Region

Base saturation of the upper B horizon estimated from the relationship between BSC in stream water and base saturation in watersheds where soils were sampled. Black circles indicate locations of stream sampling used to develop the base-saturation coverage. Blue line indicates the boundary of the Adirondack State Park; the green line indicates the boundary of the Adirondack ecoregion.



3.2 Macroinvertebrate Assessment Results

Macroinvertebrate communities from the ECASS sites generally differed from those of the WASS sites. The non-metric multidimensional scaling ordination comparing community similarity between all sites showed strong separation of the ECASS and WASS sites (Figure 3-24). Diptera of the genus *Micropsectra* was the most abundant taxon in ECASS samples while *Leuctra*, a genus of acid-tolerant stoneflies, was the most abundant taxon in the WASS samples. The average acidBAP score was 5.5 in the ECASS samples compared to only 4.2 in the WASS samples. A significant linear relations was identified between acidBAP and average BCS (Figure 3-25), suggesting that the acid-base chemistry of the ECASS and WASS streams is at least partly responsible for the differences in macroinvertebrate communities reflected by the acidBAP. Despite this significant relation, a linear regression line fit the data poorly because acidBAP appears largely independent of BCS at higher BCS values.

Change-point analysis was used to estimate the chemical thresholds for BCS, ANC, pH, and Al_i, above and below which the maximum differences in the acidBAP were observed. The strongest observed change point for BCS occurred at 4.9 μeq L^{-1} (Table 3-9). The mean acidBAP score associated with BCS values less than 4.9 μeq L^{-1} was 3.1 compared to 5.9 with BCS values greater than 4.9 μeq L^{-1}. This indicates that the condition of macroinvertebrate communities in streams with BCS below the change point value was markedly poorer than those communities in streams with BCS greater than the change point value. Although the estimated change point in acidBAP occurred at a BCS of 4.9 μeq L^{-1}, the uncertainty expressed in the cumulative probability curve (Figure 3-26) indicates a 95% probability that the true change point occurs at a BCS of ≤ 68.3 μeq L^{-1}. Similarly interpreted change points for ANC, Al_i, and pH are shown in (Table 3-9).

The estimated change point for BCS of 4.9 μeq L^{-1} appears logical and biologically meaningful for a few reasons. First, acidBAP is well-correlated with BCS at values less than 0 μeq L^{-1} but the acidBAP-BCS relationship weakens considerably above 25 μeq L^{-1}, as indicated by nearly horizontal and vertical plot lines (Figure 3-26). A BCS of 0 μeq L^{-1} is the threshold for mobilization of Al_i (Lawrence *et al.*, 2007). Therefore, the weak relationship between acidBAP and BCS at positive BCS values, and the large difference in acidBAP on either side of the BCS change point may be explained by toxic Al chemistry at lower BCS values. Negative BCS values are often associated with Al_i concentrations greater than 2 μmol L^{-1}, the generally accepted value above which aquatic biota are at risk (Baldigo *et al.*, 2007, Driscoll *et al.*, 2001). Interestingly, the change point for Al_i identified in this analysis was only 0.9 μmol L^{-1}, suggesting that macroinvertebrate communities may be adversely affected by lower Al_i concentrations than previously thought.

The ECASS and WASS streams used in the macroinvertebrate assessment were specifically chosen from the group of primary streams to provide a range of chemical conditions. Therefore, these streams are not a representative sample of the full set of streams that were sampled for chemical analysis. However, the percentage of streams falling in each of the macroinvertebrate impact categories can be estimated with the BCS values available for all streams.

Figure 3-24. ECASS-WASS Comparison of Macroinvertebrate Communities

Non-metric multidimensional scaling ordination comparing macroinvertebrate communities from 28 ECASS sites (gray) sampled in 2011 and 32 WASS sites (red) sampled in 2004. Black numbers indicate site identification codes.

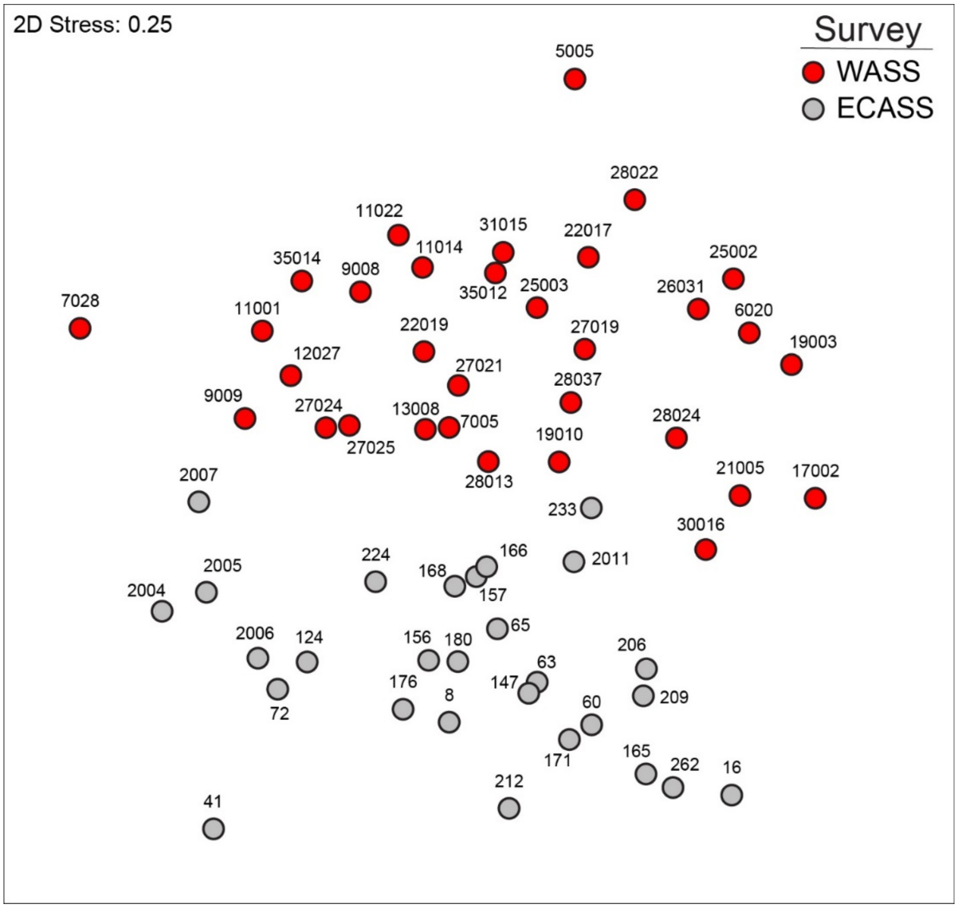


Figure 3-25. Relationship of Macroinvertebrate Communities to the BCS

Acid-biological assessment profile (acidBAP) scores as a function of the base-cation surplus (BCS) at the 28 ECASS streams (gray) sampled in 2011 and the 32 WASS (red) streams sampled in 2004. Best-fit line for all data is shown.

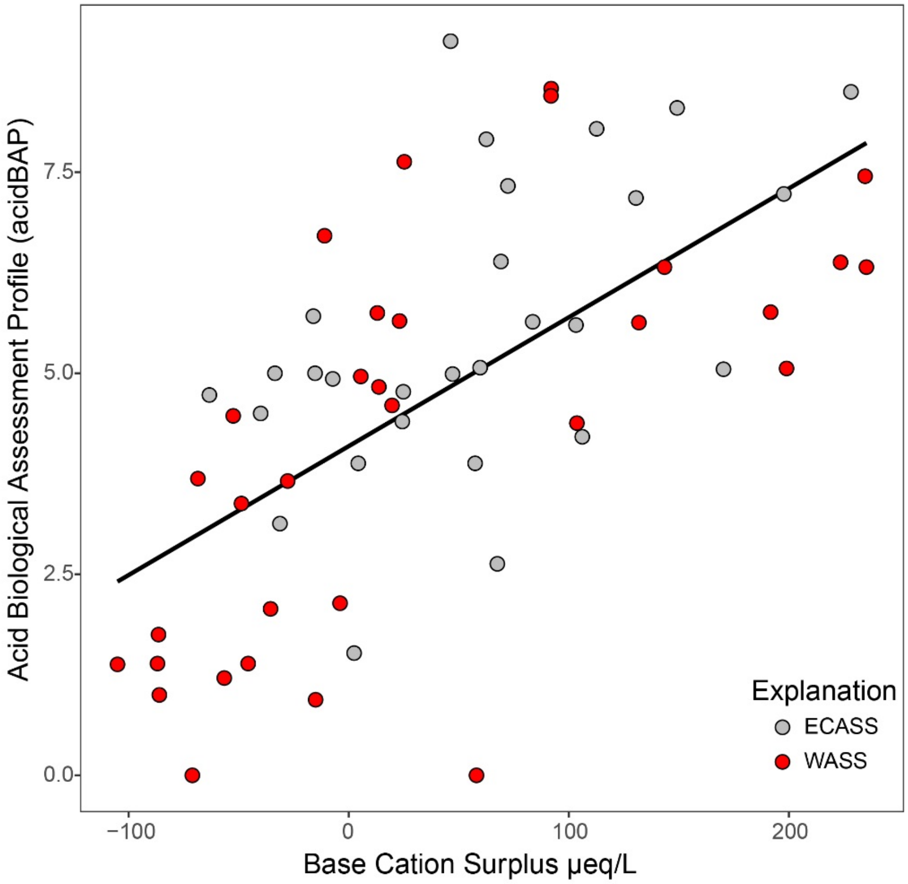


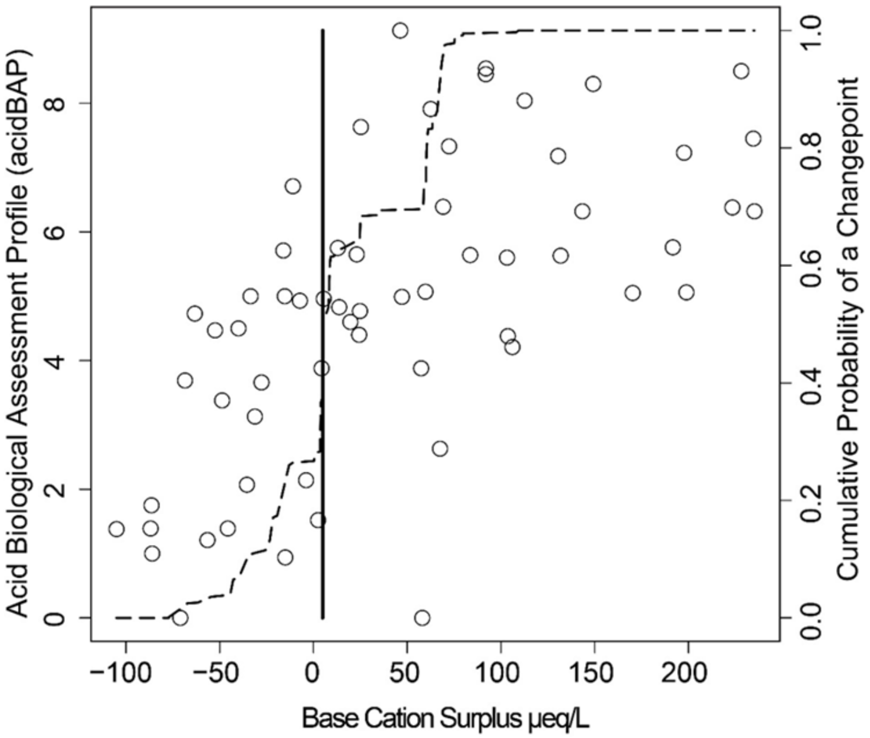
Table 3-9. Macroinvertebrate Change-Point Analysis Results

Results of non-parametric change-point analysis relating the predictor variables BCS (base-cation surplus), ANC (acid-neutralizing capacity by Gran titration), Al_i (inorganic monomeric Al) and pH, to the acidBAP (acid-biological assessment profile). The change point (cp) indicates the best estimate of the change point for a given predictor variable; percentiles show the cumulative probability that a change point occurs equal to or less than a value of a given predictor variable; the acidBAP scores show the mean value left and right of the cp estimate.

		Change point (percentiles of cumulative probability)						Mean acidBAP score	
Parameter	**cp**	**5th**	**25th**	**50th**	**75th**	**95th**	***p***	**Left**	**Right**
BCS	4.9	-42.8	-13	4.9	58.9	68.3	0.001	3.1	5.9
ANC	68.1	-5.7	23.5	68.1	68.9	83.3	0.001	3.6	6.6
Al_i	0.9	0.6	0.9	0.9	0.9	2.8	0.001	6.3	3.1
pH	5.9	4.7	5.8	5.9	6.2	6.4	0.001	3.3	6.3

Figure 3-26. Cumulative Probability of a Change Point (dashed line)

The solid vertical line indicates the strongest observed change point in the acid-biological assessment profile at or below a given base-cation surplus (BCS) concentration.



3.3 Diatoms as Indicators of Acidification

A rich diatom flora of 272 species was observed across the WASS and ECASS streams combined. Tables A-4a through 4e list the species names, acronyms, guild classification, and maximum abundance for diatom species with maximum abundance of ≥2.0%. Redundancy analysis indicated that diatom species were sensitive to stream chemistry, capturing 18.6% to 22.8% of the variance in species composition for the August 2010 sampling (Figure 3-27), the snowmelt 2011 sampling (Figure 3-28), the fall 2011 sampling (Figure 3-29), and 12.0% of the variance in species composition across all 1,245 WASS and ECASS samples combined (Figure 3-30).

Figure 3-27. ECASS Diatom Redundancy Analysis (RDA) for Summer 2010 Sampling

Data represent 197 samples collected during the summer ECASS (August 9–11) and high-elevation sampling (August 26 and September 1). Species acronyms are given in Table A-4(a–e). Al_i represents inorganic monomeric Al.

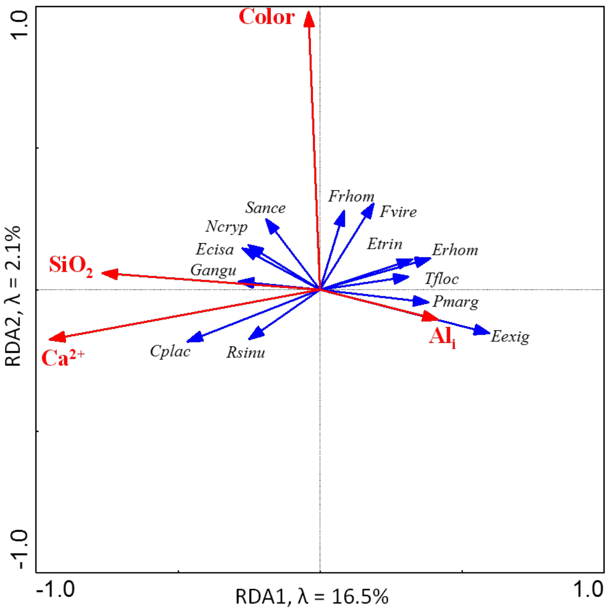


Figure 3-28. ECASS Diatom Redundancy Analysis (RDA) for the Snowmelt 2011 Sampling

Data represent 204 samples collected during the snowmelt ECASS (April 18–20) high-elevation sampling (April 27 and May 5). Species acronyms are given in Table A-4(a–e). Al_i represents inorganic monomeric Al.

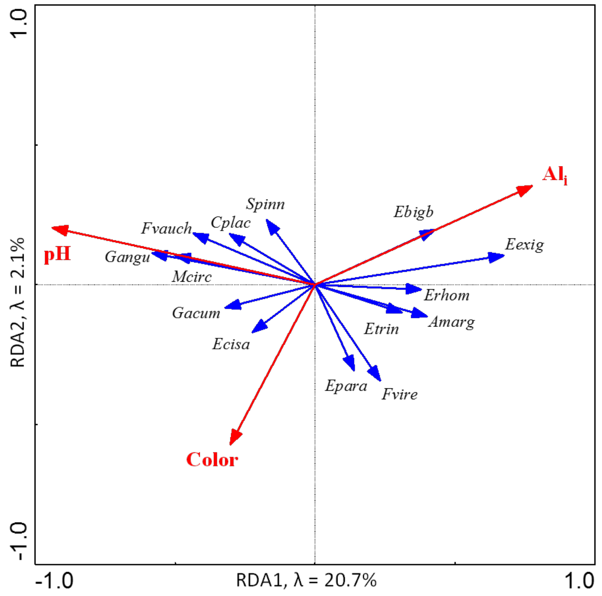


Figure 3-29. ECASS Diatom Redundancy Analysis (RDA) for the Fall 2011 Sampling

Data represent 208 samples collected during the fall ECASS (October 31–November 2). Species acronyms are given in Table A-4(a–e). Alᵢ represents inorganic monomeric Al.

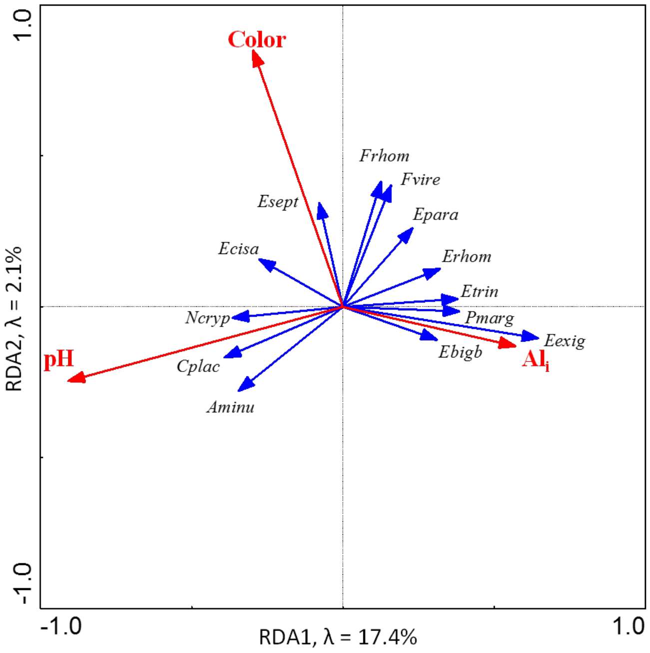
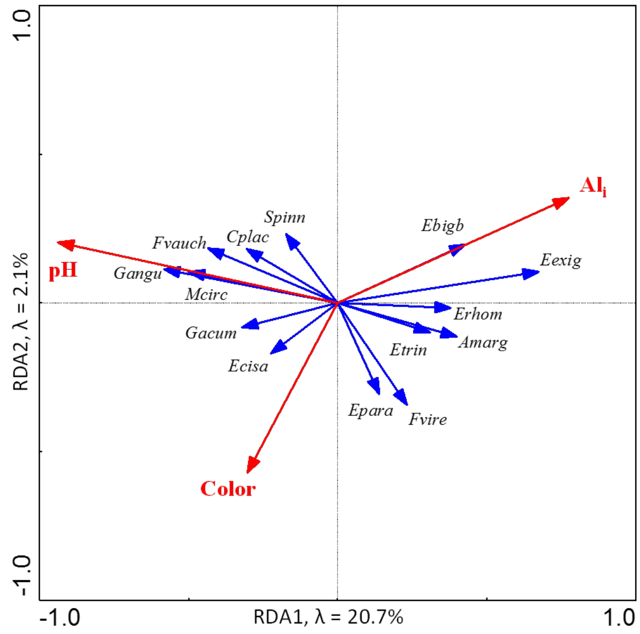


Figure 3-30. Diatom Redundancy Analysis (RDA) of all WASS and ECASS Samples

Data represent all 1,245 WASS and ECASS samples. Species acronyms are given in Table A-4(a–e). Alᵢ represents inorganic monomeric Al.



All RDAs indicated that diatom community composition is explained best by gradients of acidity (pH, Ca^{2+} or Al_i) and second best by color (Figure 3-27, Figure 3-28, Figure 3-29, and Figure 3-30). Across all RDAs, color emerged as a better predictor of diatom community composition than DOC. Although color is a surrogate measure of DOC, water color is also influenced by the quality of organic matter and Fe concentrations, in addition to the amount of organic matter in water (Kritzberg & Ekstrom, 2012, Sarkkola *et al.*, 2013). Furthermore, color was shown to be a better predictor of Fe concentrations than DOC in Adirondack lakes (Maranger *et al.*, 2006). Given the importance of Fe in determining the distribution of diatom diversity in streams at the continental scale (Passy, 2009, Passy, 2010), Fe is likely an important determinant of diatom composition in Adirondack streams. Therefore, color may be a better predictor of diatom community composition than DOC because it better accounts for stream Fe concentrations.

The species Achnanthidium minutissimum, Cocconeis placentula, Eunotia cisalpina, Gomphonema angustatum, Meridion circulare, and Navicula cryptocephala were positively correlated with Ca^{2+} or pH in the RDAs. Although species of the genus Eunotia typically occur in waters with $pH < 5.5$ (Van Dam et al., 1994), E. cisalpina, and a few other Eunotia species were associated with high pH (Tables A-4, A-5, A-6). In addition to being positively correlated with pH, E. cisalpina was also positively correlated with color. The species Fragilariforma virescens and Frustulia rhomboides were associated with low pH and high color.

In the RDAs for each of the ECASS sampling periods (Figure 3-27,Figure 3-28, Figure 3-29), the species *Eunotia biggiba, Eunotia exigua,* and *Psammothidium marginulatum* were highly positively correlated with Al_i, but only moderately correlated with Al_i in the RDA combining the WASS and ECASS streams (Figure 3-30). This difference may be attributed to the significantly higher Al_i concentrations in the WASS streams versus the ECASS streams (Al_i = 2.15 and 0.48 µmol L^{-1}, respectively; t-test, $P < 0.000001$). The species *E. exgiua* in particular may thrive under moderate concentrations of Al_i. MacDougall (et al. 2008) reported a unimodal response of *E. exigua* to Al_i and Passy (2006) found that this species declined under high inorganic to organic Al_i ratios (Al_i:Al_o). Conversely, *Eunotia trinacria* showed the strongest positive correlation with Al_i in the combined RDA of both WASS and ECASS samples, suggesting that this species is the most tolerant of Al_i toxicity.

The second combined RDA of the WASS and ECASS samples showed that diatom richness and relative abundance of functional guilds were sensitive to stream chemistry, with pH, color, and concentrations of SO_4^{2-} and NO_3^-, and Al_i explaining 24.8% of the biotic variance (Figure 3-31). Consistent with the

findings of Pound (et al. 2013), diatom richness increased with both pH and color. Motile guild relative abundance increased with pH whereas high-profile relative abundance was stimulated by stream color. The relative abundance of the tolerant low-profile guild increased with concentrations of acid anions SO_4^{2-} and NO_3^- and decreased with stream color. The RDA also shows that SO_4^{2-} and NO_3^- are negatively correlated with color, which is expected due to the influence of microbial processing and assimilation
of the inorganic acids (Goodale *et al.*, 2009, Whitmire & Hamilton, 2005).

The TITAN results showed that several diatom species are indicators of both pH and color (Tables A-4, A-5, A-6; Figures 3-32, 3-33, 3-34, 3-35). The species *Achnanthidium minutissimum* and *Cocconeis placentula* showed the strongest positive response in relative abundance and occurrence with increasing pH, as indicated by their z-scores (Table A-5 and Figure 3-32). *Eunotia cisalpina, Fragilaria vaucheriae, Gomphonema angustatum, Nupela lapidosa,* and *Planothidium frequentissima* also had strong positive responses to pH. Notably, these species emerged as positive correlates of pH in the RDAs, although not all of them are shown. The species *Eunotia trinacria* had the strongest negative response to high pH. This species was the most highly correlated with Al_i in the combined RDA of both WASS and ECASS samples, suggesting that it is tolerant of stressful conditions and high-metal concentrations. Other species with strong negative responses to pH included *Tabellaria quadrisepta, Fragilariforma virescens, Frustulia rhomboides, Eunotia exigua, Eunotia tautoniensis, Eunotia biggiba,* and *Eunotia bilunaris*. RDA also showed these species to correlate negatively with pH and positively with Al_i. TITAN identified the maximum aggregate change point for taxa that decreased with increasing pH at pH 6.39 and the maximum aggregate change point for taxa that increased with increasing pH at 6.49 (3).

Figure 3-31. Diatom Redundancy Analysis (RDA) for Species Richness and Abundance

Data represent low-profile, high-profile, and motile species and environmental variables across all 1,245 WASS and ECASS samples combined. Species acronyms are given in Table A-4(a–e). Al_i represents inorganic monomeric Al.

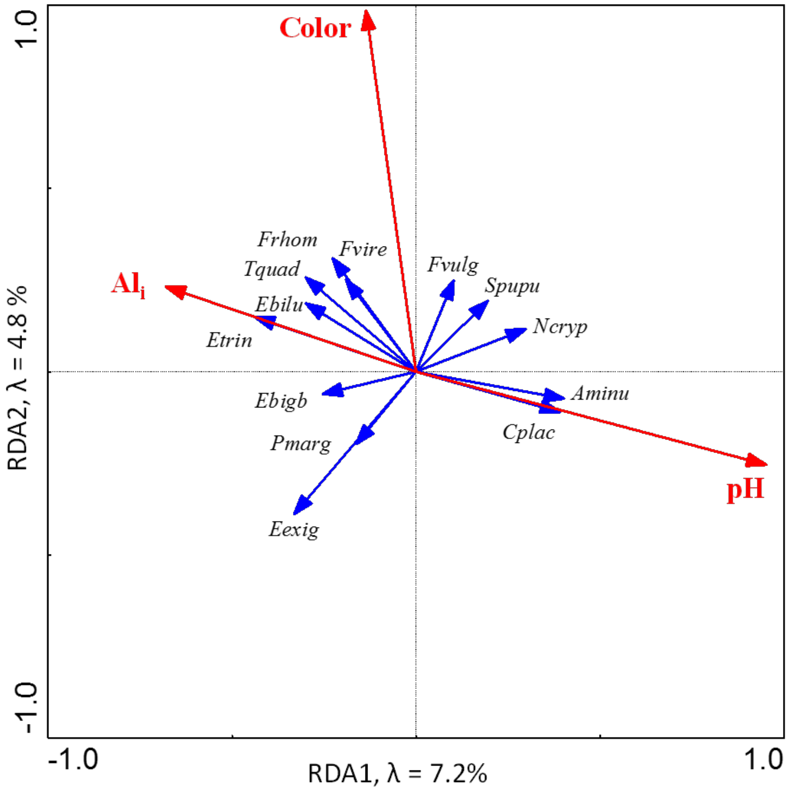


Figure 3-32. Threshold Indicator Species Analysis (TITAN) for pH

Diatom community response to pH. Red and black dots show change points along pH with 95% confidence intervals; z- species declined with increasing pH while z+ species increased with pH. Only species with purity = 1.0 and reliability = 1.0 for *P* value < 0.01 are shown. Full species names are matched with abbreviations in Table A-4.

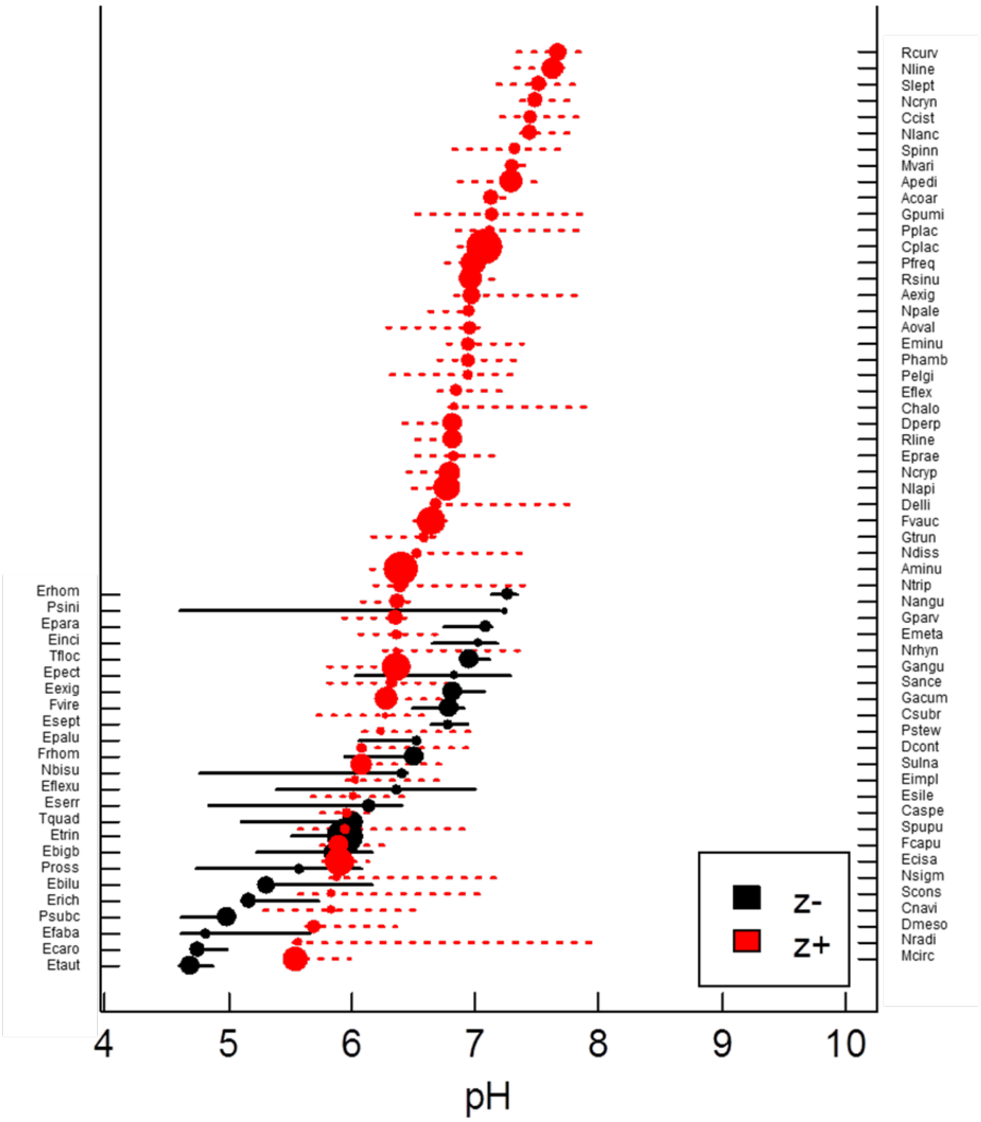


Figure 3-33. TITAN Sum (z) Values of Candidate Change Points over the pH Gradient

Black and red vertical lines represent the cumulative frequency distribution of change points among 500 bootstrap replicates for sum (z-) and sum (z+), respectively. The sum (z) maxima for increasing and decreasing taxa indicate a community-level threshold for decreasing taxa at pH of 6.392 and a community-level threshold for increasing taxa at pH of 6.487, i.e., decreasing taxa decrease in abundance above pH of about 6.4, while increasing taxa increase in abundance above pH of about 6.5.

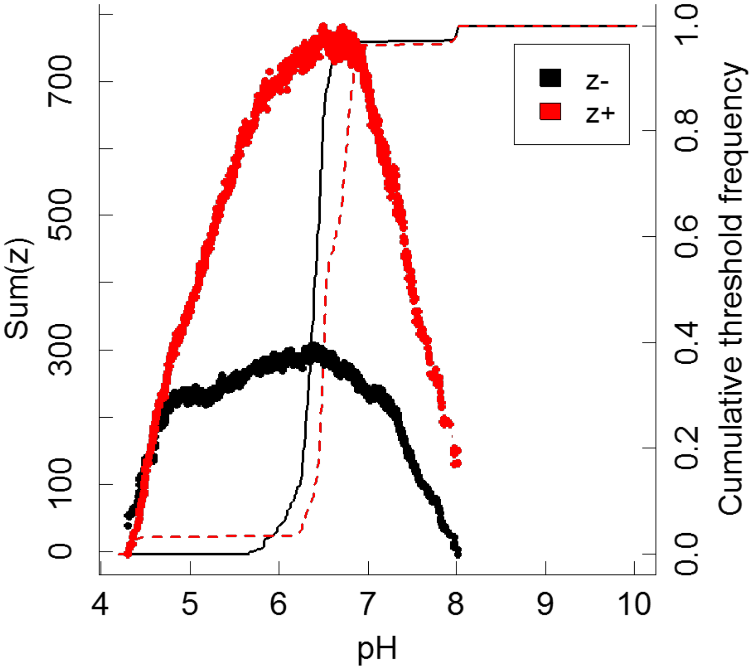


Figure 3-34. Threshold Indicator Species Analysis (TITAN) for Color

Diatom community response to color. Red and black dots show change points along pH with 95% confidence intervals; z- species declined with increasing pH while z+ species increased with pH. Only species with purity = 1.0 and reliability = 1.0 for *P* value < 0.01 are shown. Full species names are matched with abbreviations in Table A-4.

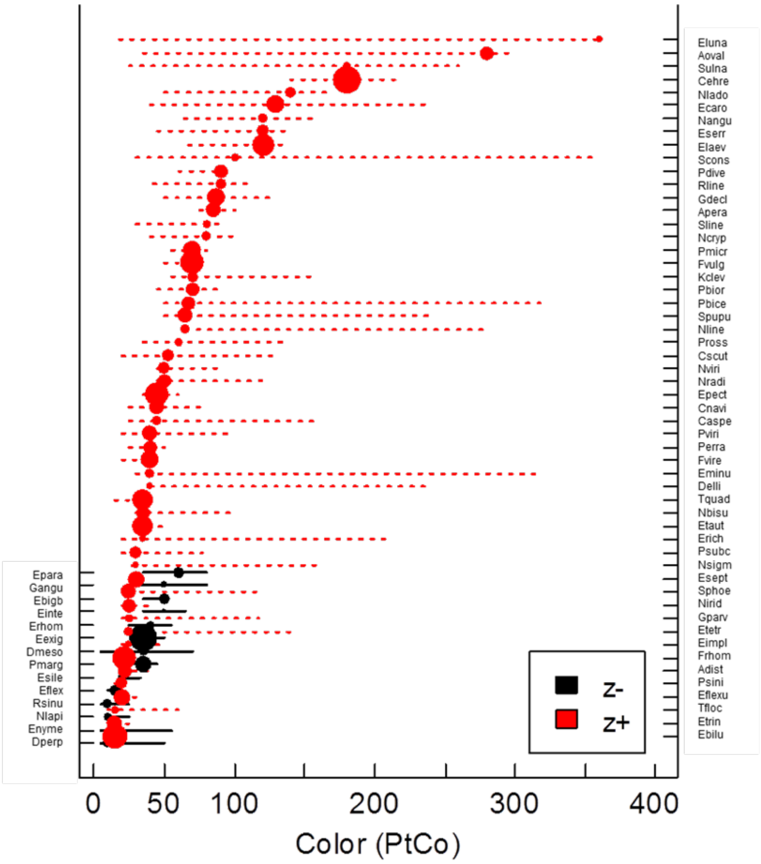
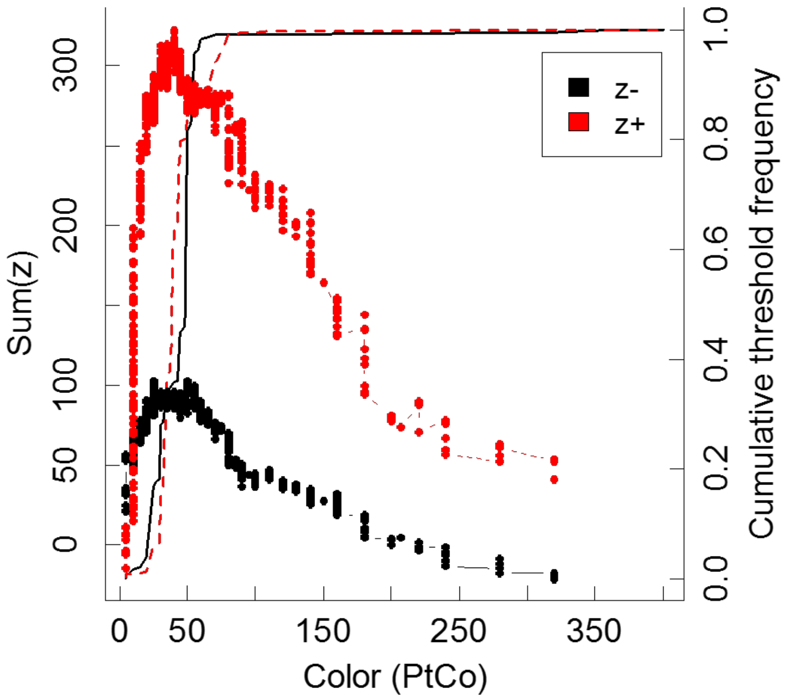


Figure 3-35. TITAN Sum (z) Values of Candidate Change Points over the Color Gradient

The sum (z) maxima for increasing and decreasing taxa indicate a community-level threshold for decreasing taxa at color of 25 Pt Co (platinum cobalt) and a community-level threshold for increasing taxa at color of 40 Pt Co.



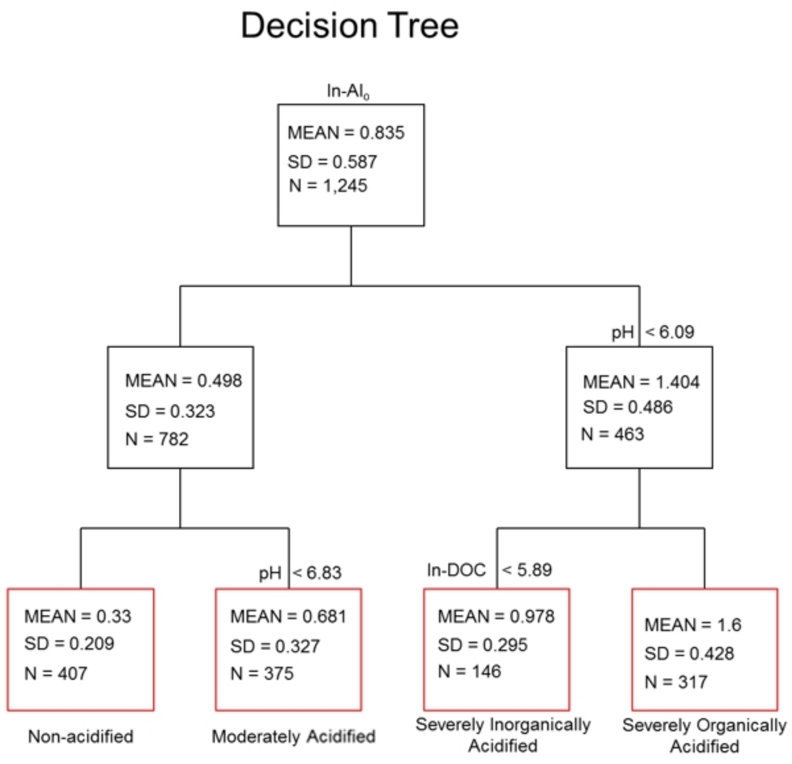
Because our goal was to identify species that are indicators of low pH, brown water streams, the TITAN color analysis was only run on the 590 stream samples with pH ≤ 6.39—the maximum aggregate change point for taxa that decreased with decreasing pH. Taxa with strong positive responses to increasing color included *Eunotia bilunaris, Eunotia pecinalis, Frustulia rhomboides, Tabellaria quadrisepta, Eunotia tautoniensis,* and *Fragilariforma virescens* (Table A-6, Figure 3-34). *Frustulia rhomboides* and *F. virescens* consistently emerged as the best correlates of color in the RDAs. All of these species are tall statured and belong to the high-profile guild. *Eunotia pecinalis, T. quadrisepta,* and *Fragilariforma virescens* form long filamentous chains. *Frustulia rhomboides* is a tube-forming species, and *E. bilunaris* and *E. tautoniensis* are found in tall rosettes. These species are most likely responsible for the shift toward greater abundance of high-profile species with color shown in Figure 3-31. *Eunotia exigua* had the single strongest negative response to color. *Eunotia exigua* is a low-profile species that typically occurs as a solitary cell (as opposed to colonial chains). Dominance of this species is often reported in acid streams, especially those acidified due to anthropogenic causes (Hirst *et al.*, 2004, MacDougall *et al.*, 2008, Passy, 2006, Verb & Vis, 2000).

Results of this study suggest that dominance of *E. exigua* may be one of the best indicators of humic poor, clear-water acid streams. *Psammothidium marginulatum* and *Eunotia biggiba* also had strong negative responses to color. *Psammothidium marginulatum* is also a low-profile species. Thus, *E. exigua and P. marginulatum* are likely responsible for the high-negative correlation between low-profile species and color shown in Figure 3-31. TITAN identified the maximum aggregate change point for taxa that decreased with increasing color at 25 Pt Co (mg L^{-1} of platinum cobalt) and the maximum aggregate change point for taxa that increased with increasing color at 40 Pt Co (Figure 3-35).

Regression tree analysis of ln-Al_o against pH and color was used to identify a priori groups for indicator species analysis. Regression tree analysis separated stream samples into four groups: non-acidified streams with pH > 6.83, moderately acidified streams with 6.09 < pH < 6.8, severely inorganically acidified streams with pH < 6.09 and ln-DOC < 5.89 (or 361 μmol L^{-1}) and severely organically acidified streams with pH < 6.09 and ln-DOC > 5.89 (Figure 3-36). Indicator species analysis demonstrated that these groups were biologically meaningful in terms of differences in species composition (Table A-7). The results were consistent with both TITAN analyses.

Figure 3-36. Regression Tree Analysis of ln-Al_o against pH and ln-DOC

ln is natural logarithm; Al_o is organic monomeric Al; DOC is dissolved organic carbon;
N = number of streams; SD = standard deviation.

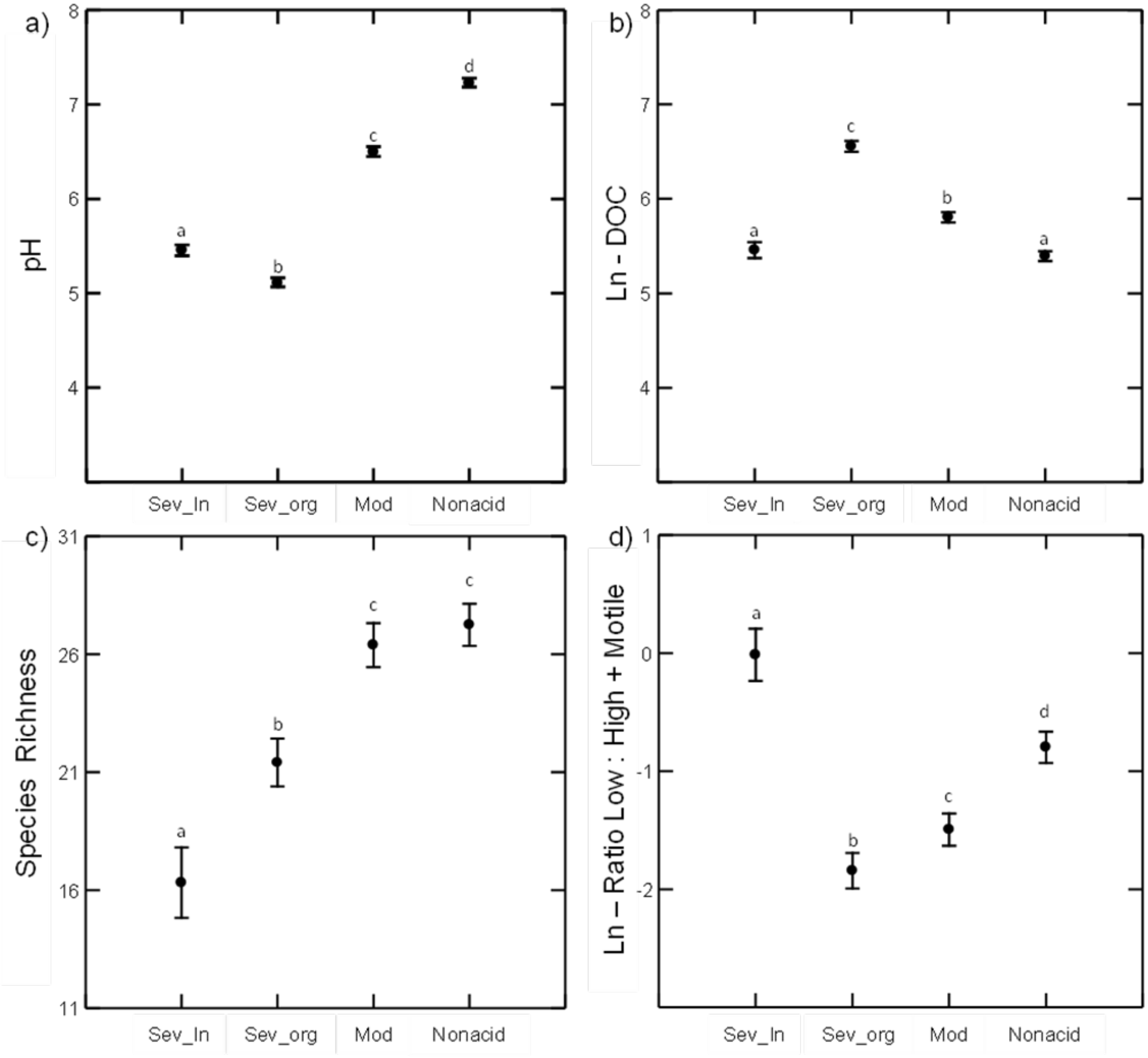


According to indicator species analysis, Cocconeis placentula, Achnanthidium minutissimum, Nupela lapidosa, Gomphonema angustatum, Planothidium frequentissima, and Eunotia cisalpina were the best indicators of non-acidified streams. The species Diatoma mesodon, Fragilaria capucina, and Cavinula scutiformis were characteristic of moderately acidified streams. The two best indicators of severely inorganically acidified streams were Eunotia exigua and Psammotidium marginulatum, which had the strongest negative response to color according to TITAN. Species with the highest indicator values for severely organically acidified streams were Eunotia trinacria, Eunotia bilunaris, Frustulia rhomboides, Tabellaria quadrisepta, Fragilariforma virescens, Eunotia tautoniensis, and Eunotia pectinalis. These species also had strong positive responses to color according to TITAN. While the best indicators of severely inorganically acidified streams are low-profile species (such as E. exigua and P. marginulatum), all the best indicators of severely organically acidified streams, except for E. trinacria, are high-profile.

ANOVA and subsequent Tukey's post-hoc comparison tests revealed significant chemical and biological differences among the four stream classifications (Figure 3-37). Mean pH differed across all four groups, with severely organically acidified streams having the lowest pH. Mean DOC was highest in severely organically acidified streams and lowest in non-acidified and severely inorganically acidified streams, which did not differ in concentrations of DOC. Species richness was highest in non-acidified streams but did not differ significantly between non-acidified and moderately acidified streams. Species richness was significantly higher in severely organically acidified streams relative to severely inorganically acidified streams, even though severely organically acidified streams had significantly lower pH. Severely inorganically acidified streams had the highest ratio of low: high + motile species, followed by non-acidified streams.

Figure 3-37. Chemical and Biological Characteristics of Groups Based on Acidity Type

Average values of (a) pH, (b) DOC, (c) species richness, and (d) ratio of low:high + motile species in the four stream classifications identified by regression tree analysis: Nonacid (non-acidified), Mod (moderately acidified), Sev_Inorg (severely inorganically acidified) and Sev_org (severely organically acidified). Points with differing letters are significantly different (*P* < 0.05).



Low-profile species have been shown to be stress tolerant (Passy & Larson, 2011), and the abundance of low-profile species in both severely inorganically acidified streams and non-acidified streams may be driven by a combination of different stressors. In non-acidified streams, low-profile species may dominate because non-acidophilic high-profile and motile species tend to be eutrophic (Passy & Larson, 2011) and their abundance is limited by the low-nutrient supply in these oligotrophic, headwater streams. In severely inorganically acidified streams, low-profile species may become more abundant due to increased stress of inorganic acidity in addition to the stress of nutrient limitation. The ratio of low: high +motile species decreased in moderately acidified streams and was lowest in severely organically acidified streams. The dominance of acidophilic high-profile and motile species in moderately and severely organically acidified streams may be due to mitigation of toxicity, nutrient (Fe) enrichment, and better light acquisition in the comparatively turbid DOC-rich waters.

Recent increases in surface water organic matter concentrations (i.e., brownification), attributed to climate-related mechanisms (Freeman *et al.*, 2001, Freeman *et al.*, 2004) or stream recovery from acid deposition (Evans *et al.*, 2006, Evans *et al.*, 2012) have been a cause for concern, particularly from the human health perspective (Chow *et al.*, 2003). However, results of this report, including streams throughout the Adirondacks, indicate that stream recovery from acid deposition may result in increased periphyton diversity and shifts toward sensitive high-profile and motile species as streams transition from inorganically acidified clear-water to organically-acidified brown-water.

The spatial complexity of the biofilm increases with abundance of overstory high-profile and motile species (Passy, 2008), and more complex biofilms are associated with higher primary productivity and more opportunities for species coexistence (Passy, 2008, Passy & Legendre, 2006). Thus, the dominance of low-profile, understory species in inorganically acidified streams translates into less complex periphyton communities, shorter internal resource gradients, and fewer opportunities for species coexistence relative to organically acidified streams.

Our results indicate that both diatom species and functional guilds are sensitive to source in addition to extent of acidification. Species and functional groups sensitive to color and organic matter may be used to develop a new diatom index that will distinguish source of acidity. In addition, results from TITAN and indicator species analysis may be used to predict community shifts that will take place as streams recovering from acid deposition undergo brownification.

4 Conclusion

With the completion of the ECASS and WASS, the acidification status of streams with regard to both chronic and episodic stream chemistry has been assessed for accessible streams throughout the Adirondack ecoregion. The randomized stream selection makes the data representative to all Adirondack streams that meet the accessibility criteria for sampling (approximate one-hour maximum hiking time), which created a bias towards lower elevation streams that somewhat underestimated the degree of acidification for the population of headwater streams as a whole. An analysis of all headwater streams in the WASS region indicated that the stream selection procedure resulted in representation of approximately 30% of all the headwater streams in that region. This analysis has not been done for the much larger ECASS region, but the percent of streams represented in the WASS region is assumed to be a reasonable approximation for the ECASS region, the ECASS results represent 3,400 km of headwater streams within the 19,200 km^2 (7,710 mi^2).

The 42% of the streams represented by ECASS that were determined to be prone to acidification indicates that episodic acidification was having a substantial effect on stream water quality in the ECASS study region. When extrapolated to the total length of accessible first-order streams in the study region (3,400 km), approximately 1,400 km (670 mi) of stream reaches were determined to be prone to acidification as a result of acidic deposition. However, because inaccessible streams were likely to be more acidified than accessible streams, the 42% estimate suggests that over 4,700 km (2920 mi) of the total ECASS headwaters (11,340 km) were prone to acidification. Including the WASS region (Lawrence *et al.*, 2008a) increased the length of streams prone to acidification to approximately 7,500 km (4,660 mi) for the Adirondack ecoregion as a whole. However, the small degree of recovery that occurred between surveys would tend to lower the estimate for the WASS region somewhat if normalized to 2010–2011.

As atmospheric deposition of SO_4^{2-} decreased to levels that approached those of the early 1900s, the leaching of base cations also decreased, which lowered base-cation concentrations in streams. The depletion of Ca^{2+} and other bases from acid-leaching of soils in past decades plays an important role in this dilution response, which was evident in (1) the marked decrease in the SBC in Archer Creek and the Buck Creek streams that occurred between the WASS and ECASS, (2) mean Ca^{2+} concentrations in the ECASS snowmelt sampling that were less than half that measured in the summer base-flow sampling, and (3) greater acidification during snowmelt than summer base flow in high-elevation streams despite a lower concentration of total strong acid anions. We are unaware of previous reporting of increased acidification concurrent with a decrease in total strong acid-anion concentrations in recovering surface waters. Dilution of strong acid anions and base cations during spring snowmelt may also have played a role in higher DOC concentrations during snowmelt than during August base flow. The browning of surface waters from higher DOC concentrations has been tied to decreased ionic strength of drainage waters as a result of decreasing acidic deposition (Monteith *et al.*, 2007).

The spatial extent of soil Ca depletion was also evident in the estimate that 58% of ECASS watersheds had base saturation of the upper mineral soil insufficient to prevent Al mobilization. Nevertheless, the strongest recovery response observed in the comparison of monitoring data between the WASS and ECASS was the decrease in concentrations of Al_i, which was strongly linked to the decrease in concentrations of SO_4^{2-}. However, a shift from Al_i to Al_o due to an increase in DOC also played a role in lowering Al_i concentrations. This response was previously documented in Adirondack lakes (Lawrence *et al.*, 2013).

There is yet no reported information suggesting that the overall availability of Ca has increased in ecosystems depleted of Ca in the past, although an increase in Ca concentrations of the forest floor has been reported in the South Buck watershed (Lawrence *et al.*, 2018). The most consequential effect of Ca depletion has been to make these systems more sensitive to acid inputs. This is emphasized by the finding that even with levels of SO_4^{2-} deposition reaching those of the early 20th century, Al mobilization occurred during high-flow episodes in more than a third of the watersheds represented in this study.

Buck Creek monitoring during the study period demonstrated that spring snowmelt produced sustained levels of acidification, as documented over past decades (Baldigo *et al.*, 2007). This monitoring also showed that high flows triggered acidification episodes throughout the year that could equal or exceed peak acidification during snowmelt, a finding not well documented. The susceptibility to severe acidification episodes throughout the year is likely to exist in the numerous ECASS streams with high-acid sensitivity, even with low levels of acidic deposition. The frequency of these episodes may increase as a result of increases in extreme weather events that have been identified in the Northeast as a result of trending climate (Hayhoe *et al.*, 2007).

Results from both biological components of the ECASS indicated a strong sensitivity to Al_i. In the macroinvertebrate analysis, the change point determined by relating BCS to the acid sensitivity index, AcidBAP, approximated the threshold for Al mobilization, which controls the availability of Al_i. The diatom analyses also showed a marked difference between communities where natural organic acidity reduced concentrations of Al_i and communities exposed to elevated concentrations of Al_i, even under conditions of similarly low pH. The source of acidity, rather than simply pH was strongly related to diatom community richness and measures of guild composition, and a number of diatom species were identified as indicators for organic versus inorganic acidification.

Overall results of the ECASS indicated that chronic acidification of streams was not widespread in the study region, but that acid-sensitive watersheds prone to episodic acidification were common throughout much of the region. The method of linking permanent monitoring streams to periodic surveys to identify variation in stream chemistry under different seasons and flow conditions will need to be continued to further our understanding of how streams and watersheds are responding to changing levels of acidic deposition and trends in climate.

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Appendix A. Tables

Table A-1a. Mean, Coefficient of Variation (CV), and Chemical Concentration Range for Samples Collected Daily during Each Survey

Units of all constituents are µmol L^{-1}.

Site	Dates	Statistic	Si	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-
87	Aug. 9-11, 2010	mean	182.2	178.8	66.0	5.7	0.5	16.4
		range	172-196	152-215	60-76	5.3-6.3	0.4-0.7	14-19
		CV	7.1	18.4	13.6	9.0	30.5	13.7
87	Apr 18-20, 2011	mean	111.7	68.9	36.5	2.7	0.8	11.4
		range	109-115	65-71	35-37	2.0-4.0	0.4-1.0	0.9-11.8
		CV	2.9	5.0	3.4	42.5	43.4	3.8
87	Oct. 31-Nov 2, 2011	mean	147.5	102.0	45.7	3.9	0	20.8
		range	144-149	101-102	45-46	3.6-4.1	0-0.2	20-21
		CV	1.7	0.3	0.5	3.3	na	1.4
228	Aug. 9-11, 2010	mean	192.7	40.8	79.2	3.2	0.4	10.4
		range	187-196	41-41	77-81	3-3.2	0-0.7	10-10
		CV	2.2	0.9	2.2	4.0	116.7	0.2
228	Apr 18-20, 2011	mean	92.1	13.3	27.0	1.5	0.2	7.6
		range	88-95	13-14	26-28	1.3-1.6	0-0.7	7.4-7.7
		CV	4.1	3.8	3.2	9.7	171.2	2.1
228	Oct. 31-Nov 2, 2011	mean	141.1	21.8	40.5	2.7	0.1	10.5
		range	139-143	22-22	40-41	2.4-3.1	0-0.4	10-11
		CV	1.5	0.7	0.5	12.5	500.9	2.1
252	Aug. 9-11, 2010	mean	207.7	31.3	68.6	11.7	4.8	11.7
		range	202-215	29-34	67-70	12-13	3.8-6.2	11-12
		CV	1.4	9.4	4.3	25.1	60.9	25.1
252	Apr 18-20, 2011	mean	116.7	16.3	31.1	5.5	0.8	7.1
		range	113-119	16-17	30-32	5.1-6.2	0.5-1.2	7.0-7.3
		CV	2.5	1.9	2.5	11.2	42.6	2.3
252	Oct. 31-Nov 2, 2011	mean	162.3	18.7	47.4	5.5	0.0	7.8
		range	159-164	18-19	46-49	5.3-5.7	0-0.6	7.5-8.0
		CV	1.6	1.9	2.4	3.7	na	3.3
270	Aug. 9-11, 2010	mean	181.8	17.6	50.0	6.5	0.7	8.3
		range	163-207	18-18	45-57	6.1-7.2	0.5-0.8	7.7-9.0
		CV	12.6	0.5	12.6	10.3	19.3	8.3
270	Apr 18-20, 2011	mean	81.4	9.2	23.1	4.9	1.0	5.9
		range	76-87	8.8-9.5	22-24.2	4.9-4.9	0.9-1.1	5.9-5.9
		CV	9.7	5.3	6.9	0.0	12.2	0.6
270	Oct. 31-Nov 2, 2011	mean	121.6	11.5	33.1	4.6	0.0	7.6
		range	117-124	42686.0	32-34	4.6-4.7	0-0.4	7.5-7.7
		CV	3.3	1.2	3.1	1.4	na	1.5

Table A-1b. Mean, Coefficient of Variation (CV), and Chemical Concentration Range for Samples Collected Daily during Each Survey

Units of all constituents are μmol L^{-1}. Al_t is total unfiltered Al; Al_{tm} is total monomeric Al; Al_o is organic monomeric Al; Al_i is inorganic monomeric Al; F is total fluoride.

Site	Dates	Statistic	Al_t	Al_{tm}	Al_o	Al_i	F
87	Aug. 9-11, 2010	mean	0.9	1.8	1.6	0.2	3.0
		range	0.8-1.0		1.4-1.8	0-0.4	2.8-3.3
		CV	13.6	17.4	12.7	93.5	8.8
87	Apr 18-20, 2011	mean	3.0	1.5	1.4	0.1	2.1
		range	1.6-5.4	1.3-1.8	1.3-1.6	0.0-0.2	2.0-2.1
		CV	71.3	16.8	15.0	48.2	3.6
87	Oct. 31-Nov 2, 2011	mean	1.0	1.4	1.5	0.0	2.5
		range	0.8-1.3	1.3-1.4	1.3-1.6	0-0	2.5-2.6
		CV	24.6	3.4	8.3	212.1	2.6
228	Aug. 9-11, 2010	mean	0.9	1.5	1.3	0.2	5.5
		range	0.7-1.2	1.4-1.7	1.3-1.3	0.1-0.4	5.4-5.6
		CV	31.2	11.3	1.3	78.6	1.4
228	Apr 18-20, 2011	mean	2.7	1.7	1.7	0.1	4.0
		range	2.2-2.3	1.5-2.0	1.4-2.0	0-0.1	3.9-4.0
		CV	20.7	14.3	15.8	117.9	2.3
228	Oct. 31-Nov 2, 2011	mean	1.1	1.4	1.4	0.0	4.0
		range	1.0-1.2	1.3-1.6	1.3-1.6	0-0.1	4.0-4.1
		CV	6.9	11.6	11.3	173.2	1.3
252	Aug. 9-11, 2010	mean	11.1	3.2	2.7	0.4	2.6
		range	10-13	3.0-3.3	2.6-2.8	0.3-0.6	2.3-2.8
		CV	26.4	93.2	108.2	672.1	112.4
252	Apr 18-20, 2011	mean	8.9	3.7	2.9	0.8	1.5
		range	7.6-10.4	3.1-4.1	2.6-3.1	0.5-1.0	1.4-1.5
		CV	15.6	13.2	9.8	26.5	2.2
252	Oct. 31-Nov 2, 2011	mean	3.2	1.9	1.9	0.0	1.5
		range	3.0-3.4	1.7-2.1	1.7-2.0	0.0-0.1	1.4-1.6
		CV	6.8	9.7	9.5	119.3	6.7
270	Aug. 9-11, 2010	mean	9.8	3.6	3.0	0.6	3.5
		range	7.7-11.8	2.9-4.5	2.7-3.5	0.2-1.0	3.3-3.8
		CV	20.8	22.5	14.2	66.4	6.7
270	Apr 18-20, 2011	mean	19.2	10.1	5.0	5.2	3.1
		range	19.1-19.3	9.5-11	4.3-5.7	5.1-5.2	3.0-3.2
		CV	0.8	8.7	20.2	2.4	2.9
270	Oct. 31-Nov 2, 2011	mean	13.2	6.9	5.5	1.3	2.9
		range	42719.0	6.1-7.3	4.9-5.9	1.2-1.5	2.8-3
		CV	13.9	9.7	10.4	9.4	3.8

Table A-2a. Values of Coefficient of Variation (CV) for Chemical Analysis of Triplicate Samples Collected within Five Minutes from the Same Stream

Calculation of CV for all constituents was done in μmol L^{-1}. Asterisks indicate where ANC concentrations included negative values, which interfered with calculation of CV.

Sample Date	Stream Code	SO_4^{2-}	NO_3^-	Cl^-	F	ANC	DOC	Ca^{2+}	Si
8/9/2010	126	1	0	1	4	1	4	0	1
8/9/2010	220	0	1	0	10	3	2	0	3
8/10/2010	22	1	1	2	8	1	1	1	3
8/10/2010	72	0	1	1	5	*	0	1	1
8/10/2010	81	1	7	0	2	1	2	2	3
8/10/2010	217	1	1	27	11	1	0	0	2
8/11/2010	131	1	1	1	2	2	1	0	2
8/11/2010	166	0	2	5	1	1	1	0	2
8/11/2010	180	0	0	1	2	2	3	1	3
4/18/2011	41	1	1	1	0	22	1	0	0
4/18/2011	65	0	0	2	2	10	1	0	1
4/18/2011	98	0	7	0	1	0	0	1	1
4/18/2011	117	0	1	1	2	0	2	2	1
4/18/2011	212	0	1	0	2	25	2	0	1
4/19/2011	123	0	0	1	0	8	2	0	3
4/19/2011	253	1	0	1	0	1	1	1	2
4/20/2011	150	0	1	1	1	11	2	1	6
10/31/2011	35	0	8	2	10	1	2	1	2
10/31/2011	127	0	*	8	0	*	2	3	3
10/31/2011	132	0	1	3	1	1	3	1	3
10/31/2011	164	2	1	3	2	1	1	0	1
10/31/2011	222	0	3	1	1	3	2	1	0
10/31/2011	276	0	2	4	12	1	3	3	3
11/1/2011	119	0	10	2	2	1	1	1	3
11/2/2011	138	0	1	2	1	*	1	1	1

Table A-2b. Values of Coefficient of Variation (CV) for Triplicate Samples Collected within Five Minutes from the Same Stream

Calculation of CV for all constituents was done in μmol L^{-1}, except pH (mmol L^{-1}). Al_t is total unfiltered Al; Al_{tm} is total monomeric Al; Al_{om} is organic monomeric Al; BCS is base-cation surplus. Asterisks indicate where individual measurements needed to calculate the BCS were missing.

Sample Date	Stream Code	Mg^{2+}	Na^{+}	K^{+}	pH	AL_t	AL_{tm}	AL_{om}	BCS
8/9/2010	126	1	1	1	4	3	2	10	0
8/9/2010	220	0	0	0	4	8	0	1	1
8/10/2010	22	1	1	2	2	8	2	6	1
8/10/2010	72	1	0	2	2	2	2	2	*
8/10/2010	81	0	3	1	9	4	2	3	2
8/10/2010	217	1	3	1	7	25	6	0	5
8/11/2010	131	0	0	0	2	7	8	1	1
8/11/2010	166	0	0	1	5	23	3	5	0
8/11/2010	180	1	2	5	1	41	4	5	1
4/18/2011	41	1	0	1	3	1	5	6	*
4/18/2011	65	0	0	1	2	1	6	3	11
4/18/2011	98	1	1	1	7	7	4	5	1
4/18/2011	117	0	1	0	9	19	4	7	2
4/18/2011	212	1	0	1	6	1	0	3	16
4/19/2011	123	0	0	0	1	4	3	4	1
4/19/2011	253	0	1	1	4	7	4	2	1
4/20/2011	150	0	1	1	6	5	6	13	2
10/31/2011	35	1	2	7	4	74	1	5	0
10/31/2011	127	1	3	1	0	3	6	2	*
10/31/2011	132	1	0	0	3	3	3	5	2
10/31/2011	164	0	0	3	3	2	1	7	1
10/31/2011	222	0	1	1	14	2	1	2	2
10/31/2011	276	1	0	2	3	6	2	1	3
11/1/2011	119	1	1	1	3	9	10	2	0
11/2/2011	138	1	1	1	2	2	0	3	*

Table A-3a. Chemical Concentrations of High-Elevation Streams during Base Flow (August–September) and Spring Snowmelt (April–May)

Stream code	Date	SO_4^{2-}	NO_3^-	Cl^-	F^-	ANC	DOC	Si	Ca^{2+}
	mm/dd/yy	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}	µeq L^{-1}	µmol L^{-1}	µmol L^{-1}	µmol L^{-1}
2000	8/26/2010	36.8	1.0	4.5	1.6	29.5	410	159	38.7
2000	4/27/2011	20.8	6.0	4.1	1.5	6.8	585	61.0	22.3
2001	8/26/2010	36.5	0.0	3.5	1.5	49.6	160	149	41.3
2001	4/27/2011	19.3	4.4	3.8	1.5	1.7	292	36.6	15.8
2002	8/26/2010	31.4	5.6	3.4	0.8	10.7	413	108	33.2
2002	4/27/2011	13.6	17.2	3.3	0.7	3.4	417	25.6	16.0
2003	8/26/2010	22.3	0.0	2.4	0.9	13.0	249	107	24.4
2003	4/27/2011	16.0	4.3	2.8	0.8	0.8	299	48.9	17.0
2004	8/26/2010	48.7	22.8	4.5	1.4	-21.1	203	120	32.7
2004	4/27/2011	22.9	22.2	3.9	1.2	-3.9	315	39.4	15.0
2005	8/26/2010	49.8	8.2	5.7	2.0	141.4	439	165	102
2005	4/27/2011	25.4	30.5	3.4	1.8	15.1	505	63.8	41.6
2006	8/26/2010	39.5	1.8	6.4	1.1	6.1	501	124	32.8
2006	4/27/2011	20.1	22.9	2.8	0.8	-16.8	514	39.2	14.1
2008	9/1/2010	43.8	13.0	6.1	1.0	19.0	593	204	38.8
2008	5/3/2011	17.5	8.6	3.4	1.0	-6.0	822	50.7	21.7
2009	9/1/2010	37.6	14.5	4.5	0.6	20.2	246	148	32.2
2009	5/3/2011	19.9	21.5	3.5	0.7	5.7	345	62.0	22.2
2010	5/3/2011	11.7	22.6	3.5	0.5	-12.9	733	25.1	18.9
2011	9/1/2010	39.0	7.2	5.0	1.0	75.4	171	168	50.9
2011	5/3/2011	17.3	13.5	3.5	0.9	4.7	358	46.3	18.8
2012	9/1/2010	38.9	0.9	11.4	3.6	91.3	188	179	49.6
2012	5/5/2011	20.2	4.6	3.3	1.4	6.3	285	50.1	18.8
2007b	5/3/2011	16.0	5.8	2.8	1.3	9.3	206	46.2	20.6

Table A-3b. Chemical Concentrations of High-Elevation Streams during Base Flow (August–September) and Spring Snowmelt (April–May)

Stream code	Date	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	Al_t	Al_o	Al_i	pH
	mm/dd/yy	μmol L^{-1}	μmol L^{-1}	μmol L^{-1}	μmol L^{-1}	μmol L^{-1}	μmol L^{-1}	μmol L^{-1}	pH units
2000	8/26/2010	9.4	26.7	0.6	0.0	10.2	3.6	0.7	6.2
2000	4/27/2011	5.3	15.2	1.7	0.9	19.1	6.4	3.6	5.1
2001	8/26/2010	13.0	22.8	0.4	0.0	3.4	1.9	0.0	6.6
2001	4/27/2011	5.1	10.0	2.2	0.6	10.6	3.6	1.6	5.3
2002	8/26/2010	5.4	20.6	0.7	0.0	13.3	5.0	1.6	5.6
2002	4/27/2011	3.4	9.7	3.3	0.9	16.8	5.5	3.5	5.0
2003	8/26/2010	4.3	17.5	-0.1	0.0	6.8	2.6	0.5	5.9
2003	4/27/2011	3.6	13.0	0.1	0.5	11.6	3.9	1.4	5.5
2004	8/26/2010	5.6	20.8	2.8	0.0	12.7	2.8	3.6	5.0
2004	4/27/2011	3.4	9.7	2.8	0.8	22.4	4.3	6.1	4.9
2005	8/26/2010	22.2	24.7	2.4	0.0	8.0	3.0	0.2	7.0
2005	4/27/2011	10.5	13.5	2.8	0.7	15.5	5.9	2.6	5.6
2006	8/26/2010	7.8	22.1	1.2	0.0	14.8	5.1	2.1	5.2
2006	4/27/2011	3.8	11.1	2.7	0.7	20.3	6.1	4.3	4.6
2008	9/1/2010	9.4	31.3	1.2	0.2	18.7	7.0	2.3	5.3
2008	5/3/2011	4.8	11.5	1.2	0.3	30.4	13.0	1.1	4.9
2009	9/1/2010	9.5	30.6	1.4	0.0	6.9	2.5	0.6	6.1
2009	5/3/2011	5.2	13.2	1.9	0.3	15.0	5.9	1.4	5.2
2010	5/3/2011	4.0	9.1	3.8	1.8	34.8	11.1	1.4	4.8
2011	9/1/2010	14.0	33.5	1.3	0.0	3.4	1.8	0.1	6.9
2011	5/3/2011	4.3	11.0	2.2	0.6	27.1	6.1	1.0	5.2
2012	9/1/2010	23.8	30.7	0.5	0.0	3.4	1.9	0.0	6.9
2012	5/5/2011	6.9	10.0	1.3	0.7	9.8	3.5	1.2	5.6
2007b	5/3/2011	4.2	10.7	0.9	0.4	6.0	3.1	0.0	5.9

Table A-4a. Species Names, Acronyms, and Maximum Abundance (Max) of Diatom Species with Maximum Abundance ≥ 2.0%

Species Name	**Acronym**	**Guild**	**Max %**
Achnanthes biasolettiana Grunow	Abias	low profile	3
Achnanthes coarctata (Brébisson) Grunow	Acoar	low profile	2
Achnanthes exigua Grunow	Aexig	low profile	8
Achnanthes peragalli Brun & Héribaud-Joseph in Héribaud	Apera	low profile	4
Achnanthes subatomoides (Hustedt) Lange-Bertalot & Archibald	Asuba	low profile	17
Ac*hnanthidium minutissimum* (Kützing) Czarnecki	Aminu	low profile	96
Actinella punctata F.W.Lewis	Apunc	high profile	19
Amphora ovalis (Kützing) Kützing	Aoval	low profile	11
Amphora pediculus (Kützing) Grunow ex A.Schmidt	Apedi	low profile	19
Aulacodiscus affinis Grunow in Schmidt	Aaffi	high profile	4
Aulacoseira distans (Ehrenberg) Simonsen	Adist	high profile	66
Brachysira serians (Brébisson) Round & D.G.Mann	Bseri	motile	28
Brachysira vitrea (Grunow) R.Ross	Bvitr	motile	11
Caloneis bacillum (Grunow) Cleve	Cbaci	motile	3
Cavinula pseudoscutiformis	Cpseu	motile	5
(Hustedt) Mann and Stickle in Round, Crawford and Mann			
Cavinula scutiformis (Grunow ex A.Schmidt) D.G.Mann & A.J.Stickle	Cscut	motile	10
Cocconeis placentula Ehrenberg	Cplac	low profile	83
Craticula cuspidata (Kutzing) D.G.Mann	Ccusp	motile	5
Craticula halophila (Grunow) D.G.Mann	Chalo	motile	5
Cymbella affinis Kützing	Caffi	low profile	6
Cymbella aspera (Ehrenberg) Cleve	Caspe	high profile	4
Cymbella caespitosa (Kützing) Brun	Ccaes	high profile	4
Cymbella cistula (Ehrenberg) O.Kirchner	Ccist	high profile	5
Cymbella ehrenbergii Kützing	Cehre	high profile	10
Cymbella laevis Nägeli	Claev	low profile	5
Cymbella naviculiformis Auerswald ex Heiberg	Cnavi	low profile	8
Cymbella parva (W.Smith) Cleve	Cparv	low profile	2
Cymbella tumida (Brébisson) van Heurck	Ctumd	high profile	6
Cymbopleura subrostrata (Cleve) Krammer	Csubr	high profile	8
Delicata delicatula (Kützing) Krammer	Ddeli	high profile	7
Diadesmis contenta (Grunow ex Van Heurck) D.G.Mann	Dcont	motile	34
Diadesmis perpusilla (Grunow) D.G.Mann	Dperp	motile	70
Diatoma anceps (Ehrenberg) Kirchner	Dance	high profile	41
Diatoma mesodon (Ehrenberg) Kützing	Dmeso	high profile	61
Diatoma vulgaris Bory de Saint-Vincent	Dvulg	high profile	15
Diploneis elliptica (Kützing) Cleve	Delli	motile	8
Encyonema lunatum (W.Smith) Van Heurck	Eluna	high profile	3
Encyonema minutum (Hilse) D.G.Mann	Eminu	high profile	4

Table A-4b. Species Names, Acronyms, and Maximum Abundance (Max) of Diatom Species with maximum Abundance ≥ 2.0%

Species Name	**Acronym**	**Guild**	**Max %**
Encyonema silesiacum (Bleisch) D.G.Mann	Esile	high profile	81
Encyonopsis cesatii (Rabenhorst) Krammer	Ecesa	low profile	19
Eucocconeis flexella (Kützing) Meister	Eflex	high profile	3
Eucocconeis laevis (Østrup) Lange-Bertalot	Elaev	low profile	12
Eunotia arcus Ehrenberg	Earcu	high profile	4
Eunotia bidens Ehrenberg	Ebidn	high profile	26
Eunotia bidentula W. Smith	Ebide	high profile	2
Eunotia biggiba Krasske	Ebigb	high profile	55
Eunotia bilunaris (Ehrenberg) Schaarschmidt	Ebilu	high profile	70
Eunotia carolina R.M.Patrick	Ecaro	high profile	36
Eunotia cisalpina Lange-Bertalot & Cantonati	Ecisa	high profile	67
Eunotia exigua (Brébisson in Kutzing) Rabenhorst	Eexig	low profile	99
Eunotia exsecta (Cleve-Euler) Nörpel-Schempp & Lange-Bertalot	Eexse	high profile	23
Eunotia faba (Ehrenberg) Grunow	Efaba	high profile	12
Eunotia fallax A.Cleve	Efall	high profile	4
Eunotia flexuosa (Brébisson ex Kützing) Kützing	Eflexu	high profile	57
Eunotia glacialis Meister	Eglac	high profile	3
Eunotia hexaglyphis Ehrenberg	Ehexa	high profile	45
Eunotia implicata Nörpel, Lange-Bertalot & Alles in E.Alles	Eimpl	high profile	26
Eunotia incisa W.Smith ex W.Gregory	Einci	high profile	78
Eunotia intermedia (Krasske) Nörpel & Lange-Bertalot	Einte	high profile	36
Eunotia meisteri Hustedt	Emeis	high profile	30
Eunotia metamonodon Lange-Bertalot	Emeta	high profile	9
Eunotia microcephala Krasske	Emicr	high profile	2
Eunotia minor (Kützing) Grunow	Emino	high profile	51
Eunotia naegelii Migula	Enaeg	high profile	5
Eunotia neofallax M.Nörpel-Schempp & Lange-Bertalot	Eneof	high profile	39
Eunotia nymaniana Grunow	Enyma	high profile	24
Eunotia paludosa Grunow	Epalu	high profile	18
Eunotia parallela Ehrenberg	Eparal	high profile	3
Eunotia paratridentula Lange-Bertalot & Kulikovskiy	Epara	low profile	38
Eunotia pectinalis (Kützing) Rabenhorst	Epect	high profile	67
Eunotia praerupta Ehrenberg	Eprae	high profile	26
Eunotia rhomboidea Hustedt	Erhom	high profile	87
Eunotia richbuttensis Furey, low profilee and Johansen	Erich	high profile	46
Eunotia septentrionalis Østrup	Esept	high profile	13
Eunotia serra Ehrenberg	Eserr	high profile	41
Eunotia soleirolii (Kützing) Rabenhorst	Esole	high profile	50
Eunotia steineckei Petersen	Estei	high profile	8

Table A-4c. Species Names, Acronyms, and Maximum Abundance (Max) of Diatom Species with Maximum Abundance ≥ 2.0%

Species Name	**Acronym**	**Guild**	**Max %**
Eunotia tautoniensis Hustedt	Etaut	high profile	43
Eunotia tetraodon Ehrenberg	Etetra	high profile	6
Eunotia trinacria Krasske	Etrin	low profile	87
Fragilaria capucina Desmazières	Fcapu	high profile	17
Fragilaria construens (Ehrenberg) Grunow	Fcons	high profile	73
Fragilaria vaucheriae (Kützing) J.B.Petersen	Fvauc	high profile	78
Fragilariforma virescens (Ralfs) D.M.Williams & Round	Fvire	high profile	98
Frustrulia rhomboides (Ehrenberg) De Toni	Frhom	high profile	70
Frustulia vulgaris (Thwaites) De Toni	Fvulg	high profile	25
Geissleria declivis (Hustedt) Lange-Bertalot	Gdecl	motile	3
Geissleria ignota (Krasske) Lange-Bertalot & Metzeltin	Gigno	motile	3
Gomphonema acuminatum Ehrenberg	Gacum	high profile	41
Gomphonema angustatum (Kützing) Rabenhorst	Gangu	high profile	54
Gomphonema augur Ehrenberg	Gaugu	high profile	15
Gomphonema gracile Ehrenberg	Ggrac	high profile	6
Gomphonema parvalum Kützing	Gparv	high profile	73
Gomphonema pumillum (Grunow) Reichardt & Lange-Bertalot	Gpumi	high profile	11
Gomphonema truncatum Ehrenberg	Gtrun	high profile	11
Karayevia clevei (Grunow) Bukhtiyarova	Kclev	low profile	4
Melosira varians C.Agardh	Mvari	high profile	43
Meridion circulare (Greville) C.Agardh	Mcirc	high profile	78
Navicula angusta Grunow	Nangu	motile	6
Navicula cryptocephela Kützing	Ncryp	motile	9
Navicula cryptotenella Lange-Bertalot in Krammer & Lange-Bertalot	Ncryn	motile	20
Navicula lanceolata (Agardh) Ehrenberg	NLanc	motile	11
Navicula mediocris Krasske	Nmedi	motile	3
Navicula meniscus J.Schumann	Nmeni	motile	5
Navicula molestiformis Hustedt	Nmole	motile	2
Navicula radiosa Kützing	Nradi	motile	11
Navicula rhynchocephela Kützing	Nrhyn	motile	5
Navicula saxophila W.Bock ex Hustedt	Nsaxo	motile	3
Navicula tripunctata (O.F.Müller) Bory de Saint-Vincent	NTrip	motile	18
Navicula veneta Kützing	NVene	motile	3
Navicula viridula (Kützing) Ehrenberg	NViri	motile	3
Neidium bisulcatum (Lagerstedt) Cleve	Nbisu	motile	7
Neidium iridis (Ehrenberg) Cleve	NIrid	motile	4
Neidium ladogensis (Cleve) Foged	Nlado	motile	5
Nitzschia dissipata (Kützing) Grunow	Ndiss	motile	9
Nitzschia linearis (C.Agardh) W.Smith	NLine	motile	26

Table A-4d. Species Names, Acronyms, and Maximum Abundance (Max) of Diatom Species with Maximum Abundance ≥ 2.0%

Species Name	**Acronym**	**Guild**	**Max %**
Nitzschia palea (Kützing) W.Smith	Npale	motile	49
Nitzschia sigma (Kützing) W.Smith	NSigm	motile	4
Nupela lapidosa (Krasske) Lange-Bertalot	NLapi	low profile	78
Orthoseira roeseana (Rabenhorst) O'Meara	Oroes	high profile	45
Pinnularia biceps W.Gregory	PBice	motile	3
Pinnularia borealis Ehrenberg	PBore	motile	4
Pinnularia brebissonii (Kützing) Rabenhorst	Pbreb	motile	9
Pinnularia divergens W.Smith	Pdive	motile	4
Pinnularia erratica Krammer	PErra	motile	35
Pinnularia lange-bertalotii K.Krammer	Plang	motile	2
Pinnularia mesolepta (Ehrenberg) W.Smith	Pmesp	motile	7
Pinnularia microstauron (Ehrenberg) Cleve	PMicr	motile	4
Pinnularia obscura Krasske	Pobsc	motile	4
Pinnularia polyonca (Brébisson) O.Müller	Ppoly	motile	2
Pinnularia sinistra Krammer	PSini	motile	25
Pinnularia subcapita W.Gregory	Psubc	motile	9
Pinnularia viridis (Nitzsch) Ehrenberg	Pviri	motile	7
Placoneis elginensis (W. Gregory) Ralfs	Pelgi	motile	4
Placoneis hambergii (Hustedt) K.Bruder	Phamb	motile	4
Placoneis placentula (Ehrenberg) Mereschkowsky	Pplac	motile	4
Planothidium conspicuum (A.Mayer) M.Aboal	Pcons	low profile	4
Planothidium frequentissima (Lange-Bertalot in Krammer and Lange-Bertalot) Lange-Bertalot	PFreq	low profile	79
Planothidium stewartii (Patrick) Lange-Bertalo	Pstew	low profile	6
Psammothidium marginulatum (Grunow) Bukhtiyarova & Round	Pmarg	low profile	80
Psammothidium rossii (Hustedt) L.Bukhtiyarova & Round	Pross	low profile	3
Psammotidium bioretti (Germain) Bukhtiyarova and Round	Pbior	low profile	9
Reimeria sinuata (Gregory) Kociolek & Stoermer	Rsinu	low profile	36
Rhocoisphenia curvata (Kützing) Grunow	Rcurv	high profile	44
Rossithidium linearis (W.Smith) Round & Bukhtiyarova	Rline	low profile	21
Rossithidium petersenii (Hustedt) Round & Bukhtiyarova	Rpete	low profile	3
Sellaphora pupula (Kützing) Mereschkovsky	SPupu	motile	3
Stauroneis anceps Ehrenberg	SAnce	motile	2
Stauroneis phoenocenteron (Nitzsch) Ehrenberg	SPhoe	motile	5
Staurosirella leptostauron Ehrenberg	Slept	high profile	8
Staurosirella pinnata (Ehrenberg) Williams and Round	Spinn	high profile	7
Stenopterobia curvula (W.Smith) Krammer in Lange-Bertalot & Krammer	Scurv	motile	2
Surirella delicatissima F.W.Lewis	Sdeli	motile	5

Table A-4e. Species Names, Acronyms, and Maximum Abundance (Max) of Diatom Species with Maximum Abundance ≥ 2.0%

Species Name	Acronym	Guild	Max %
Surirella linearis (Ehrenberg) Cleve	Sline	motile	11
Synedra ulna (Nitzsch) Ehrenberg	Sulna	high profile	60
Tabellaria flocculosa (Roth) Kützing	TFloc	high profile	94
Tabellaria quadrisepta Knudson	Tquad	high profile	77
Ulnaria delicatissima (W.Smith) M.Aboal & P.C.Silva	Udeli	high profile	9

Table A-5a. Threshold Indicator Taxa Analysis (TITAN) Individual Diatom Taxa Results for pH

The table shows the response direction (±), z-score, environmental change point (Obs.), purity, and reliability for *P* < 0.05 and 0.01. Only taxa with purity >0.95 and reliability >0.95 for *P* < 0.05 are shown.

Species Name	**Acronym**	**±**	**Obs.**	**z**	**Purity**	**p ≤ 0.05**	**p ≤ 0.01**
Achnanthes coarctata (Brébisson) Grunow	Acoar	+	7.1	17.6	1	1	1
Achnanthes exigua Grunow	Aexig	+	7.0	19.4	1	1	1
Achnanthes peragalli Brun & Héribaud-Joseph in Héribaud	Apera	+	6.2	5.0	1	0.99	0.94
Achnanthes subatomoides *(Hustedt) Lange-Bertalot & Archibald*	Asuba	+	7.1	5.7	1	1	0.94
Achnanthidium minutissimum (Kützing) Czarnecki	Aminu	+	6.4	39.4	1	1	1
Actinella punctata F.W.Lewis	Apunc	−	4.4	15.5	1	1	1
Amphora ovalis (Kützing) Kützing	Aoval	+	7.0	15.2	1	1	1
Amphora pediculus (Kützing) Grunow ex A.Schmidt	Apedi	+	7.3	26.6	1	1	1
Aulacoseira distans (Ehrenberg) Simonsen	Adist	−	4.8	9.0	0.99	0.99	0.99
Brachysira vitrea (Grunow) R.Ross	Bvitr	+	5.6	4.0	0.98	0.97	0.88
Caloneis bacillum (Grunow) Cleve	Cbaci	+	5.8	7.3	1	1	1
Cavinula pseudoscutiformis *(Hustedt) Mann and Stickle in Round, Crawford and Mann*	Cpseu	+	7.5	10.7	1	1	0.99
Chamaepinnularia mediocris *(Kraskke) Lange-Bertalot & Krammer*	Cmedi	+	7.2	11.6	1	0.98	0.96
Cocconeis placentula Ehrenberg	Cplac	+	7.1	41.6	1	1	1
Craticula halophila (Grunow) D.G.Mann	Chalo	+	6.8	8.5	1	1	1
Cymbella affinis Kützing	Caffi	+	7.4	11.0	1	1	1
Cymbella aspera (Ehrenberg) Cleve	Caspe	+	6.0	11.0	1	1	1
Cymbella cistula (Ehrenberg) O.Kirchner	Ccist	+	7.4	14.9	1	1	1
Cymbella naviculiformis Auerswald ex Heiberg	Cnavi	+	5.8	8.2	1	1	1
Achnanthes coarctata (Brébisson) Grunow	Acoar	+	6.6	13.2	1	1	1
Achnanthes exigua Grunow	Aexig	+	6.7	13.0	1	1	1
Achnanthes peragalli Brun & Héribaud-Joseph in Héribaud	Apera	+	6.7	12.9	1	1	1
Achnanthes subatomoides	Asuba	+	6.7	12.7	1	1	1
Diatoma mesodon (Ehrenberg) Kützing	Dmeso	+	5.7	15.7	1	1	1

Table A-5b. Threshold Indicator Taxa Analysis (TITAN) Individual Diatom Taxa Results for pH

The table shows the response direction (±), z-score, environmental change point (Obs.), purity, and reliability for *P* < 0.05 and 0.01. Only taxa with purity >0.95 and reliability >0.95 for *P* < 0.05 are shown.

Species Name	**Acronym**	**±**	**Obs.**	**z**	**Purity**	**p ≤ 0.05**	**p ≤ 0.01**
Diploneis elliptica (Kützing) Cleve	Delli	+	6.7	12.7	1	1	1
Encyonema lunatum (W.Smith) Van Heurck	Eluna	+	5.8	6.8	1	1	1
Encyonema minutum (Hilse) D.G.Mann	Eminu	+	6.9	15.2	1	1	1
Encyonema silesiacum (Bleisch) D.G.Mann	Esile	+	6.0	8.5	1	1	1
Eucocconeis flexella (Kützing) Meister	Eflex	+	6.9	12.3	1	1	1
Eucocconeis laevis (Østrup) Lange-Bertalot	Elaev	−	4.7	9.9	0.99	0.99	0.96
Eunotia bidens Ehrenberg	Ebidn	+	6.0	6.3	1	1	1
Eunotia biggiba Krasske	Ebigb	−	5.8	21.2	1	1	1
Eunotia bilunaris (Ehrenberg) Schaarschmidt	Ebilu	−	5.3	20.7	1	1	1
Eunotia carolina R.M.Patrick	Ecaro	−	4.8	17.8	1	1	1
Eunotia cisalpina	Ecisa	+	5.9	33.2	1	1	1
Eunotia exigua (Brébisson in Kutzing) Rabenhorst	Eexig	−	6.8	22.9	1	1	1
Eunotia faba (Ehrenberg) Grunow	Efaba	−	4.8	11.9	1	1	1
Eunotia flexuosa (Brébisson ex Kützing) Kützing	Eflexu	−	6.4	10.8	1	1	1
Eunotia implicata Nörpel, Lange-Bertalot & Alles in E.Alles	Eimpl	+	6.0	8.9	1	1	1
Eunotia incisa W.Smith ex W.Gregory	Einci	−	7.0	9.4	1	1	1
Eunotia intermedia (Krasske) Nörpel & Lange-Bertalot	Einte	−	6.1	5.9	1	1	0.98
Eunotia meisteri Hustedt	Emeis	−	6.7	2.8	0.98	0.96	0.76
Eunotia metamonodon	Emeta	+	6.4	9.8	1	1	1
Eunotia microcephala Krasske	Emicr	−	6.6	3.8	0.98	0.95	0.79
Eunotia minor (Kützing) Grunow	Emino	+	6.4	9.5	1	1	1
Eunotia nymaniana Grunow	Enyma	+	5.5	4.9	0.97	0.97	0.96
Eunotia paludosa Grunow	Epalu	−	6.5	12.1	1	1	1
Eunotia parallela Ehrenberg	Eparal	+	7.8	6.9	0.97	0.95	0.83
Eunotia paratridentula Lange-Bertalot & Kulikovskiy	Epara	−	7.1	13.7	1	1	1
Eunotia pectinalis (Kützing) Rabenhorst	Epect	−	6.8	9.2	1	1	1
Eunotia praerupta Ehrenberg	Eprae	+	6.8	9.8	1	1	1
Eunotia rhomboidea Hustedt	Erhom	−	7.3	15.1	1	1	1
Eunotia richbuttensis Furey, Lowe and Johansen	Erich	−	5.2	17.6	1	1	1
Eunotia septentrionalis Østrup	Esept	−	6.8	10.9	1	1	1
Eunotia serra Ehrenberg	Eserr	−	6.1	16.1	1	1	1
Eunotia soleirolii (Kützing) Rabenhorst	Esole	+	5.8	5.7	0.99	0.99	0.99
Eunotia tautoniensis Hustedt	Etaut	−	4.7	22.8	1	1	1
Eunotia trinacria Krasske	Etrin	−	5.9	44.8	1	1	1
Fragilaria capucina Desmazières	Fcapu	+	5.9	22.1	1	1	1
Fragilaria construens (Ehrenberg) Grunow	Fcons	+	5.8	7.7	1	1	1
Fragilaria vaucheriae (Kützing) J.B.Petersen	Fvauc	+	6.6	33.2	1	1	1
Fragilariforma virescens (Ralfs) D.M.Williams & Round	Fvire	−	6.8	23.3	1	1	1
Frustrulia rhomboides (Ehrenberg) De Toni	Frhom	−	6.5	23.0	1	1	1

Table A-5c. Threshold Indicator Taxa ANalysis (TITAN) Individual Diatom Taxa Results for pH

The table shows the response direction (±), z-score, environmental change point (Obs.), purity, and reliability for *P* < 0.05 and 0.01. Only taxa with purity >0.95 and reliability >0.95 for *P* < 0.05 are shown.

Species Name	Acronym	±	Obs.	z	Purity	p ≤ 0.05	p ≤ 0.01
Gomphonema acuminatum Ehrenberg	Gacum	+	6.3	25.1	1	1	1
Gomphonema angustatum (Kützing) Rabenhorst	Gangu	+	6.4	33.2	1	1	1
Gomphonema augur Ehrenberg	Gaugur	+	6.9	5.8	1	0.99	0.94
Gomphonema parvalum Kützing	Gparv	+	6.4	18.4	1	1	1
Gomphonema pumillum	Gpumi	+	7.1	15.0	1	1	1
(Grunow) Reichardt & Lange-Bertalot							
Gomphonema truncatum Ehrenberg	Gtrun	+	6.6	9.9	1	1	1
Karayevia clevei (Grunow) Bukhtiyarova	Kclev	+	6.7	8.8	1	1	1
Melosira varians C.Agardh	Mvari	+	7.3	14.2	1	1	1
Meridion circulare (Greville) C.Agardh	Mcirc	+	5.5	27.8	1	1	1
Navicula angusta Grunow	Nangu	+	6.4	16.7	1	1	1
Navicula cryptocephela Kützing	Ncryp	+	6.8	24.7	1	1	1
Navicula cryptotenella	NCryn	+	7.5	17.9	1	1	1
Lange-Bertalot in Krammer & Lange-Bertalot							
Navicula lanceolata (Agardh) Ehrenberg	Nlanc	+	7.4	16.9	1	1	1
Navicula meniscus J.Schumann	Nmeni	+	7.9	16.8	1	0.98	0.95
Navicula radiosa Kützing	Nradi	+	5.6	8.6	1	1	1
Navicula rhynchocephela Kützing	Nrhyn	+	6.4	7.5	1	1	1
Navicula tripunctata (O.F.Müller) Bory de Saint-Vincent	Ntrip	+	6.4	14.8	1	1	1
Navicula veneta Kützing	Nvene	+	7.3	7.3	0.99	0.98	0.9
Navicula viridula (Kützing) Ehrenberg	Nviri	+	7.3	10.5	1	1	1
Neidium bisulcatum (Lagerstedt) Cleve	Nbisu	−	6.4	10.7	1	1	1
Neidium iridis (Ehrenberg) Cleve	NIrid	−	4.5	4.2	0.99	0.97	0.84
Nitzschia dissipata (Kützing) Grunow	Ndiss	+	6.5	11.6	1	1	1
Nitzschia linearis (C.Agardh) W.Smith	Nline	+	7.6	23.2	1	1	1
Nitzschia palea (Kützing) W.Smith	Npale	+	7.0	13.3	1	1	1
Nitzschia sigma (Kützing) W.Smith	Nsigm	+	5.9	8.6	1	1	1
Nupela lapidosa (Krasske) Lange-Bertalot	Nlapi	+	6.8	29.7	1	1	1
Pinnularia biceps W.Gregory	Pbice	−	7.1	3.4	0.97	0.97	0.67
Pinnularia borealis Ehrenberg	Pbore	+	7.0	6.3	0.98	0.96	0.82
Pinnularia erratica Krammer	Perra	+	6.8	6.0	1	1	0.99
Pinnularia microstauron (Ehrenberg) Cleve	Pmicr	−	4.6	6.2	1	0.99	0.93
Pinnularia sinistra Krammer	Psini	−	7.2	6.2	1	1	1
Pinnularia subcapita W.Gregory	Psubc	−	5.0	23.5	1	1	1
Pinnularia viridis (Nitzsch) Ehrenberg	Pviri	−	4.5	7.3	0.96	0.96	0.93
Placoneis elginensis (W. Gregory) Ralfs	Pelgi	+	6.9	11.1	1	1	1
Placoneis hambergii (Hustedt) K.Bruder	Phamb	+	6.9	14.3	1	1	1
Placoneis ignorata (Schimanski) Lange-Bertalot	Pigno	+	7.4	9.4	1	1	1
Placoneis placentula (Ehrenberg) Mereschkowsky	Pplac	+	7.1	10.1	1	1	1

Table A-5d. Threshold Indicator Taxa Analysis (TITAN) Individual Diatom Taxa Results for pH

The table shows the response direction (±), z-score, environmental change point (Obs.), purity, and reliability for *P* < 0.05 and 0.01. Only taxa with purity >0.95 and reliability >0.95 for *P* < 0.05 are shown.

Species Name	**Acronym**	**±**	**Obs.**	**z**	**Purity**	**p ≤ 0.05**	**p ≤ 0.01**
Planothidium conspicuum (A.Mayer) M.Aboal	Pcons	+	7.0	6.2	0.99	0.97	0.87
Planothidium frequentissima (Lange-Bertalot in Krammer *and Lange-Bertalot) Lange-Bertalot*	Pfreq	+	7.0	28.2	1	1	1
Planothidium stewartii (Patrick) Lange-Bertalo	Pstew	+	6.2	9.0	1	1	1
Psammothidium rossii (Hustedt) L.Bukhtiyarova & Round	Pross	−	5.6	11.5	1	1	1
Psammotidium bioretti (Germain) Bukhtiyarova and Round	Pbior	+	6.4	7.2	1	1	1
Reimeria sinuata (Gregory) Kociolek & Stoermer	Rsinu	+	7.0	25.7	1	1	1
Rhocoisphenia curvata (Kützing) Grunow	Rcurv	+	7.7	19.3	1	1	1
Rossithidium linearis (W.Smith) Round & Bukhtiyarova	Rline	+	6.8	20.9	1	1	1
Sellaphora pupula (Kützing) Mereschkovsky	Spupu	+	5.9	10.1	1	1	1
Stauroneis anceps Ehrenberg	Sance	+	6.3	12.3	1	1	1
Stauroneis phoenocenteron (Nitzsch) Ehrenberg	Sphoe	+	5.6	6.4	0.97	0.97	0.97
Staurosirella leptostauron Ehrenberg	Slept	+	7.5	16.6	1	1	1
Staurosirella pinnata (Ehrenberg) Williams and Round	Spinn	+	7.3	12.8	1	1	1
Surirella linearis (Ehrenberg) Cleve	Sline	+	5.6	6.8	1	1	1
Synedra ulna (Nitzsch) Ehrenberg	Sulna	+	6.1	24.9	1	1	1
Tabellaria flocculosa (Roth) Kützing	Tfloc	−	7.0	23.4	1	1	1
Tabellaria quadrisepta Knudson	Tquad	−	6.0	26.0	1	1	1

Table A-6a. Threshold Indicator Taxa Analysis (TITAN) Individual Diatom Taxa Results for Color

The table shows the response direction (±), z-score, environmental change point for color (Obs.), the approximate DOC (dissolved organic carbon, in µmol C L^{-1}) concentration for the observed color value, purity, and reliability for *P* < 0.05 and 0.01. Only taxa with purity > 0.95 and reliability > 0.95 for *P* < 0.05 are shown.

Species Name	**Acronym**	**±**	**z**	**Obs.**	**~ DOC**	**Purity**	***P* ≤ 0.05**	***P* ≤ 0.01**
Achnanthes peragalli Brun & *Héribaud-Joseph in Héribaud*	Apera	+	10.4	85	646.1	1	1	0.99
Amphora ovalis (Kützing) Kützing	Aoval	+	8.6	280	1741.1	0.99	0.99	0.97
Aulacoseira distans (Ehrenberg) Simonsen	Adist	+	8.8	21.7	290.5	1	1	1
Cavinula scutiformis (Grunow ex Schmidt) *Mann et Stickle*	Cscut	+	8	52.5	463.6	1	1	1
Cymbella aspera (Ehrenberg) Cleve	Caspe	+	6.2	45	421.5	1	1	0.99
Cymbella ehrenbergii Kützing	Cehre	+	19.4	180	1179.5	0.99	0.99	0.97
Cymbella naviculiformis Auerswald ex Heiberg	Cnavi	+	9.8	45	421.5	1	1	1
Diadesmis perpusilla (Grunow) D.G.Mann	Dperp	−	8.5	10	225	1	1	1
Diatoma mesodon (Ehrenberg) Kützing	Dmeso	−	6.5	35	365.4	1	1	1
Diploneis elliptica (Kützing) Cleve	Delli	+	3.9	40	393.4	1	1	0.89
Encyonema lunatum (W.Smith) Van Heurck	Eluna	+	3.8	360	2190.3	0.98	0.97	0.79
Encyonema minutum (Hilse) D.G.Mann	Eminu	+	5.8	40	393.4	1	1	0.98
Encyonema silesiacum (Bleisch) D.G.Mann	Esile	−	5.3	20	281.1	1	1	0.95
Eucocconeis flexella (Kützing) Meister	Eflex	−	9.8	15	253.1	1	1	0.97
Eucocconeis laevis (Østrup) Lange-Bertalot	Elaev	+	15.2	120	842.6	1	1	1
Eunotia biggiba Krasske	Ebigb	−	10	50	449.6	1	1	1
Eunotia bilunaris (Ehrenberg) Schaarschmidt	Ebilu	+	16.6	15	253.1	1	1	1
Eunotia carolina R.M.Patrick	Ecaro	+	11.9	130	898.8	1	1	1
Eunotia exigua (Brébisson in Kutzing) Rabenhorst	Eexig	−	25.9	35	365.4	1	1	1
Eunotia flexuosa (Brébisson ex Kützing) Kützing	Eflexu	+	11	20	281.1	1	1	1
Eunotia implicata Nörpel, Lange-Bertalot & *Alles in E.Alles*	Eimpl	+	4	25	309.2	1	1	0.89
Eunotia intermedia (Krasske) Nörpel & *Lange-Bertalot*	Einte	−	3.1	50	449.6	0.98	0.97	0.83
Eunotia nymaniana Grunow	Enyma	−	4.1	10	225	0.99	0.98	0.81
Eunotia paratridentula Lange-Bertalot & *Kulikovskiy*	Epara	−	8.9	60	505.7	1	1	1
Eunotia pectinalis (Kützing) Rabenhorst	Epect	+	16.5	45	421.5	1	1	1
Eunotia rhomboidea Hustedt	Erhom	−	7	40	393.4	1	1	1
Eunotia richbuttensis Furey, Lowe and Johansen	Erich	+	3.8	35	365.4	1	0.98	0.85
Eunotia septentrionalis Østrup	Esept	+	10.7	30	337.3	1	1	1
Eunotia serra Ehrenberg	Eserr	+	7.7	120	842.6	1	1	1
Eunotia tautoniensis Hustedt	Etaut	+	13.7	35	365.4	1	1	1
Eunotia tetraodon Ehrenberg	Etetra	+	5.9	25	309.2	1	1	0.99
Eunotia trinacria Krasske	Etrin	+	9.7	15	253.1	1	1	1
Fragilaria construens (Ehrenberg) Grunow	Fcons	+	5.3	100	730.3	1	1	0.98
Fragilariforma virescens (Ralfs) D.M.Williams & *Round*	Fvire	+	12.1	40	393.4	1	1	1
Frustulia rhomboides (Ehrenberg) De Toni	Frhom	+	15.9	21.7	290.5	1	1	1
Frustulia vulagaris (Thwaites) De Toni	Fvulg	+	16.6	70	561.9	1	1	1

Table A-6b. Threshold Indicator Taxa Analysis (TITAN) Individual Diatom Taxa Results for Color

The table shows the response direction (±), z-score, environmental change point for color (Obs.), the approximate DOC (dissolved organic carbon, in µmol C L^{-1}) concentration for the observed color value, purity, and reliability for $P < 0.05$ and 0.01. Only taxa with purity > 0.95 and reliability > 0.95 for $P < 0.05$ are shown.

Species Name	**Acronym**	**±**	**z**	**Obs.**	**~ DOC**	**Purity**	**$P \leq 0.05$**	**$P \leq 0.01$**
Geissleria declivis (Hustedt) Lange-Bertalot	Gdecl	+	12.4	87.5	660.2	1	1	1
Gomphonema angustatum (Kützing) Rabenhorst	Gangu	−	4.9	50	449.6	0.99	0.99	0.93
Gomphonema parvalum Kützing	Gparv	+	4.8	25	309.2	1	1	0.96
Karayevia clevei (Grunow) Bukhtiyarova	Kclev	+	7.4	70	561.9	1	0.99	0.94
Navicula angusta Grunow	Nangu	+	6.4	120	842.6	0.97	0.96	0.84
Navicula cryptocephela Kützing	Ncryp	+	6.5	80	618	1	1	0.99
Navicula radiosa Kützing	Nradi	+	9	50	449.6	1	1	1
Navicula viridula (Kützing) Ehrenberg	Nviri	+	7.6	50	449.6	1	1	0.99
Neidium bisulcatum (Lagerstedt) Cleve	Nbisu	+	8.9	35	365.4	1	1	1
Neidium iridis (Ehrenberg) Cleve	NIrid	+	9.5	25	309.2	1	1	1
Neidium ladogensis (Cleve) Foged	Nlado	+	7.3	140	954.9	1	1	0.97
Nitzschia linearis (C.Agardh) W.Smith	Nline	+	5.9	65	533.8	1	0.97	0.88
Nitzschia sigma (Kützing) W.Smith	Nsigm	+	4.4	30	337.3	1	0.99	0.89
Nupela lapidosa (Krasske) Lange-Bertalot	Nlapi	−	7.3	10	225	1	1	0.99
Pinnularia biceps W.Gregory	Pbice	+	9.5	67.5	547.8	1	1	1
Pinnularia divergens Smith	Pdive	+	8.7	90	674.2	1	1	0.99
Pinnularia erratica Krammer	Perra	+	8.6	40	393.4	1	1	1
Pinnularia microstauron (Ehrenberg) Cleve	Pmicr	+	11.9	70	561.9	1	1	1
Pinnularia sinistra Krammer	Psini	+	7.6	20	281.1	1	1	1
Pinnularia subcapita W.Gregory	Psubc	+	8	30	337.3	1	1	1
Pinnularia viridis (Nitzsch) Ehrenberg	Pviri	+	10	40	393.4	1	1	1
Psammothidium marginulatum (Grunow) Bukhtiyarova & Round	Pmarg	−	14.6	35	365.4	1	1	1
Psammothidium rossii (Hustedt) L.Bukhtiyarova & Round	Pross	+	5.2	60	505.7	0.99	0.99	0.93
Psammotidium bioretti (Germain) Bukhtiyarova and Round	Pbior	+	8.8	70	561.9	0.98	0.98	0.98
Reimeria sinuata (Gregory) Kociolek & *Stoermer*	Rsinu	−	8.1	10	225	1	0.97	0.83
Rossithidium linearis (W.Smith) Round & *Bukhtiyarova*	Rline	+	6.6	90	674.2	0.99	0.98	0.92
Sellaphora pupula (Kützing) Mereschkovsky	Spupu	+	10.2	65	533.8	1	1	1
Stauroneis phoenocenteron (Nitzsch) Ehrenberg	Sphoe	+	10.4	25	309.2	1	1	1
Surirella linearis (Ehrenberg) Cleve	Sline	+	5.3	80	618	1	1	0.96
Synedra ulna (Nitzsch) Ehrenberg	Sulna	+	5.3	180	1179.5	1	1	0.99
Tabellaria flocculosa (Roth) Kützing	Tfloc	+	5.3	15	253.1	1	1	0.98
Tabellaria quadrisepta Knudson	Tquad	+	14.3	35	365.4	1	1	1

Table A-7a. Results from Indicator Diatom Species Analysis

The table shows the stream classification for which each species is an indicator (Class), the indicator value (IndVal), and the *P*-value of the indicator value based on 1000 permutations. Only species with significant indicator values ($P < 0.05$) are shown. Non-acidified streams are denoted as nonacid, moderately acidified as mod, severely organically acidified streams as sev_org, and severely inorganically acidified streams as sev_inorg.

Species Names	Acronym	Class	IndVal	*P* value
Achnanthes coarctata (Brébisson) Grunow	Acoar	Nonacid	4.1	0.001
Achnanthes exigua Grunow	Aexig	Nonacid	12.7	0.001
Achnanthidium minutissimum (Kützing) Czarnecki	Aminu	Nonacid	56.8	0.001
Amphora ovalis (Kützing) Kützing	Aoval	Nonacid	14.4	0.001
Amphora pediculus (Kützing) Grunow ex A.Schmidt	Apedi	Nonacid	19.5	0.001
Aulacoseira distans (Ehrenberg) Simonsen	Adist	Sev_org	16.7	0.001
Cavinula pseudoscutiformis (Hustedt) *Mann and Stickle in Round, Crawford and Mann*	Cpseu	Nonacid	2.4	0.014
Cavinula scutiformis (Grunow ex Schmidt) Mann et Stickle	Cscut	Mod	10.7	0.005
Chamaepinnularia mediocris (Kraskke) Lange-Bertalot & Krammer	Cmedi	Nonacid	1.6	0.016
Cocconeis placentula Ehrenberg	Cplac	Nonacid	57.9	0.001
Craticula halophila (Grunow) D.G.Mann	Chalo	Nonacid	4.6	0.002
Cymbella aspera (Ehrenberg) Cleve	Caspe	Mod	7.7	0.001
Cymbella cistula (Ehrenberg) O.Kirchner	Ccist	Nonacid	4.1	0.002
Cymbella naviculiformis Auerswald ex Heiberg	Cnavi	Nonacid	9.2	0.003
Cymbella parva (W.Smith) Cleve	Cparv	Nonacid	3.6	0.003
Cymbella tumida (Brébisson) van Heurck	Ctimd	Nonacid	2.4	0.008
Diadesmis contenta (Grunow ex Van Heurck) D.G.Mann	Dcont	Nonacid	10.3	0.002
Diadesmis perpusilla (Grunow) D.G.Mann	Dperp	Nonacid	34	0.001
Diatoma mesodon (Ehrenberg) Kützing	Dmeso	Mod	19.8	0.001
Diploneis elliptica (Kützing) Cleve	Delli	Nonacid	7.5	0.001
Encyonema minutum (Hilse) D.G.Mann	Eminu	Nonacid	13.1	0.001
Eucocconeis flexella (Kützing) Meister	Eflex	Nonacid	4.9	0.003
Eucocconeis laevis (Østrup) Lange-Bertalot	Elaev	Sev_org	5.4	0.01
Eunotia bidens Ehrenberg	Ebidn	Mod	7	0.001
Eunotia biggiba Krasske	Ebigb	Sev_inorg	27.5	0.001
Eunotia bilunaris (Ehrenberg) Schaarschmidt	Ebilu	Sev_org	48.9	0.001
Eunotia carolina R.M.Patrick	Ecaro	Sev_org	16.6	0.001
Eunotia cisalpina	Ecisa	Nonacid	40.1	0.001
Eunotia exigua (Brébisson in Kutzing) Rabenhorst	Eexig	Sev_inorg	64.2	0.001
Eunotia faba (Ehrenberg) Grunow	Efaba	Sev_inorg	8.4	0.009
Eunotia flexuosa (Brébisson ex Kützing) Kützing	Eflex	Sev_org	25.2	0.001
Eunotia hexaglyphis Ehrenberg	Ehexa	Mod	3.1	0.028
Eunotia implicata Nörpel, Lange-Bertalot & Alles in E.Alles	Eimpl	Nonacid	9.5	0.003
Eunotia metamonodon	Emeta	Nonacid	6.3	0.002

Table A-7b. Results from Indicator Diatom Species Analysis

The table shows the stream classification for which each species is an indicator (Class), the indicator value (IndVal), and the *P*-value of the indicator value based on 1000 permutations. Only species with significant indicator values ($P < 0.05$) are shown. Non-acidified streams are denoted as nonacid, moderately acidified as mod, severely organically acidified streams as sev_org, and severely inorganically acidified streams as sev_inorg.

Species Names	**Acronym**	**Class**	**IndVal**	***P* value**
Eunotia microcephala Krasske	Emicr	Sev_org	1.7	0.039
Eunotia minor (Kützing) Grunow	Emino	Nonacid	13	0.02
Eunotia nymaniana Grunow	Enyma	Mod	6.6	0.003
Eunotia paludosa Grunow	Epalu	Sev_inorg	8.4	0.013
Eunotia paratridentula Lange-Bertalot & Kulikovskiy	Epara	Sev_inorg	20.2	0.001
Eunotia pectinalis (Kützing) Rabenhorst	Epect	Sev_org	31.7	0.001
Eunotia praerupta Ehrenberg	Eprae	Nonacid	5.6	0.001
Eunotia rhomboidea Hustedt	Erhom	Sev_inorg	26.5	0.001
Eunotia richbuttensis Furey, Lowe and Johansen	Erich	Sev_org	15.8	0.001
Eunotia septentrionalis Østrup	Esept	Sev_org	16.9	0.001
Eunotia serra Ehrenberg	Eserr	Sev_org	21.2	0.001
Eunotia soleirolii (Kützing) Rabenhorst	Esole	Nonacid	10.9	0.019
Eunotia tautoniensis Hustedt	Etaut	Sev_org	36	0.001
Eunotia tetraodon Ehrenberg	Etetra	Mod	7.9	0.001
Eunotia trinacria Krasske	Etrin	Sev_org	56.7	0.001
Fragilaria capucina Desmazières	Fcapu	Mod	17.5	0.001
Fragilaria construens (Ehrenberg) Grunow	Fcons	Nonacid	7.2	0.019
Fragilaria vaucheriae (Kützing) J.B.Petersen	Fvauc	Nonacid	39	0.001
Fragilariforma virescens (Ralfs) D.M.Williams & Round	Fvire	Sev_org	37.9	0.001
Frustrulia rhomboides (Ehrenberg) De Toni	Frhom	Sev_org	48.2	0.001
Geissleria declivis (Hustedt) Lange-Bertalot	Gdecl	Sev_org	3.6	0.014
Gomphonema acuminatum Ehrenberg	Gacum	Nonacid	34.1	0.001
Gomphonema angustatum (Kützing) Rabenhorst	Gangu	Nonacid	45.4	0.001
Gomphonema augur Ehrenberg	Gaugu	Nonacid	1.9	0.017
Gomphonema parvalum Kützing	Gparv	Nonacid	27.2	0.001
Gomphonema pumillum (Grunow) Reichardt & Lange-Bertalot	Gpumi	Nonacid	11.2	0.001
Gomphonema truncatum Ehrenberg	Gtrun	Nonacid	5.2	0.019
Karayevia clevei (Grunow) Bukhtiyarova	Kclev	Nonacid	3.7	0.004
Melosira varians C.Agardh	Mvari	Nonacid	4	0.011
Meridion circulare (Greville) C.Agardh	Mcirc	Nonacid	36.2	0.001
Navicula angusta Grunow	Nangu	Nonacid	11.1	0.001
Navicula cryptocephela Kützing	Ncryp	Nonacid	28.1	0.001
Navicula cryptotenella Lange-Bertalot in Krammer & Lange-Be	Ncryn	Nonacid	4.8	0.006
Navicula lanceolata (Agardh) Ehrenberg	Nlanc	Nonacid	6.5	0.001
Navicula meniscus J.Schumann	Emeni	Nonacid	1.2	0.041
Navicula radiosa Kützing	Nradi	Nonacid	9.2	0.003

Table A-7c. Results from Indicator Diatom Species Analysis

The table shows the stream classification for which each species is an indicator (Class), the indicator value (IndVal), and the *P*-value of the indicator value based on 1000 permutations. Only species with significant indicator values ($P < 0.05$) are shown. Non-acidified streams are denoted as nonacid, moderately acidified as mod, severely organically acidified streams as sev_org, and severely inorganically acidified streams as sev_inorg.

Species Names	Acronym	Class	IndVal	*P* value
Navicula tripunctata (O.F.Müller) Bory de Saint-Vincent	Ntrip	Nonacid	11.4	0.001
Navicula viridula (Kützing) Ehrenberg	Nviri	Nonacid	5.1	0.006
Neidium bisulcatum (Lagerstedt) Cleve	Nbisu	Sev_org	7.8	0.002
Neidium iridis (Ehrenberg) Cleve	NIrid	Sev_org	9.1	0.002
Nitzschia dissipata (Kützing) Grunow	Ndiss	Nonacid	7.9	0.001
Nitzschia linearis (C.Agardh) W.Smith	Nline	Nonacid	8.7	0.001
Nitzschia palea (Kützing) W.Smith	Npale	Nonacid	19.3	0.001
Nitzschia sigma (Kützing) W.Smith	Nsigm	Nonacid	3.6	0.014
Nupela lapidosa (Krasske) Lange-Bertalot	Nlapi	Nonacid	48.8	0.001
Pinnularia divergens Smith	Pdive	Mod	7.1	0.017
Pinnularia erratica Krammer	Perra	Nonacid	9.8	0.012
Pinnularia microstauron (Ehrenberg) Cleve	Pmicr	Sev_org	6.9	0.001
Pinnularia subcapita W.Gregory	Psubc	Sev_org	15.6	0.001
Pinnularia viridis (Nitzsch) Ehrenberg	Pviri	Sev_org	10.4	0.003
Placoneis elginensis (W. Gregory) Ralfs	Pelgi	Nonacid	8.5	0.001
Placoneis hambergii (Hustedt) K.Bruder	Phamb	Nonacid	7.7	0.001
Placoneis ignorata (Schimanski) Lange-Bertalot	Pigno	Nonacid	3.1	0.007
Placoneis placentula (Ehrenberg) Mereschkowsky	Pplac	Nonacid	5.5	0.002
Planothidium frequentissima (Lange-Bertalot in Krammer *and Lange-Bertalot) Lange-Bertalot*	Pfreq	Nonacid	44.4	0.001
Planothidium stewartii (Patrick) Lange-Bertalo	Pstew	Nonacid	3.5	0.021
Psammothidium marginulatum (Grunow) Bukhtiyarova & Rou	Pmarg	Sev_inorg	51.4	0.001
Psammothidium rossii (Hustedt) L.Bukhtiyarova & Round	Pross	Sev_org	5.8	0.002
Psammotidium bioretti (Germain) Bukhtiyarova and Round	Pbior	Nonacid	6.1	0.023
Reimeria sinuata (Gregory) Kociolek & Stoermer	Rsinu	Nonacid	23.2	0.001
Rhocoisphenia curvata (Kützing) Grunow	Rcurv	Nonacid	10.5	0.001
Rossithidium linearis (W.Smith) Round & Bukhtiyarova	Rline	Nonacid	21.9	0.001
Sellaphora pupula (Kützing) Mereschkovsky	Spupu	Nonacid	6.8	0.003
Stauroneis anceps Ehrenberg	Sance	Nonacid	8.8	0.001
Stauroneis phoenocenteron (Nitzsch) Ehrenberg	Sphoe	Mod	8.2	0.011
Staurosirella leptostauron Ehrenberg	Slept	Nonacid	4.4	0.001
Staurosirella pinnata (Ehrenberg) Williams and Round	Spinn	Nonacid	4.8	0.001
Synedra ulna (Nitzsch) Ehrenberg	Sulna	Nonacid	37.7	0.001
Tabellaria flocculosa (Roth) Kützing	Tfloc	Sev_org	28.8	0.001
Tabellaria quadrisepta Knudson	Tquad	Sev_org	46.6	0.001

Table A-8a. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes, and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
04253295	AB07	43.743563	-74.712255
04253294	BB07	43.741597	-74.710971
441953073590801	0	44.331639	-73.985561
441353073474701	4	44.231442	-73.796611
442851073365401	5	44.480939	-73.615194
435238073530101	8	43.877425	-73.883811
441613073370701	9	44.270403	-73.618889
440759073442801	10	44.133181	-73.741208
442518073394401	11	44.421897	-73.662481
441812073424301	14	44.303358	-73.712008
435626074265101	15	43.940711	-74.447661
432413074181801	16	43.403728	-74.305164
440703073345901	17	44.117733	-73.583089
434444074052901	21	43.745572	-74.091658
441324074200401	22	44.223344	-74.334661
432741074260501	24	43.461639	-74.434764
444319073493501	26	44.721972	-73.826444
431606074120201	28	43.268611	-74.200561
442300073495101	32	44.383539	-73.831019
434916073562801	34	43.821144	-73.941156
435132073534001	35	43.859083	-73.894603
434307074185401	36	43.718650	-74.315033
435306073455901	39	43.885031	-73.766514
435813073491301	40	43.970508	-73.820472
431320074321001	41	43.222492	-74.536125
440403074021901	42	44.067614	-74.038814
435917073432801	44	43.988278	-73.724667
440151074015501	45	44.031033	-74.032117
434758073580401	46	43.799456	-73.968003
431632074332401	49	43.275692	-74.556819
433113074221401	51	43.520542	-74.370647
432407074425401	52	43.401953	-74.715142
442307073294101	53	44.385344	-73.494800
441248073540501	56	44.213575	-73.901508
441432073504301	57	44.242339	-73.845519
434131073430801	59	43.692139	-73.718939
432355074380801	60	43.398686	-74.635636

Table A-8b. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes, and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
432122074175901	62	43.356267	-74.299742
434820074190201	63	43.805825	-74.317369
432002074105701	64	43.333928	-74.182711
435446074285901	65	43.912778	-74.483158
441021073573601	67	44.172594	-73.960275
435704074263401	68	43.951383	-74.442997
434305074185601	70	43.718206	-74.315633
433729074241401	72	43.624750	-74.404139
440908073444901	73	44.152222	-73.747139
431522073543501	75	43.256150	-73.909983
433555074042001	76	43.598808	-74.072475
441127073491501	77	44.190850	-73.821111
441349073441001	78	44.230281	-73.736294
442137073291101	79	44.360419	-73.486561
432242074563101	80	43.378578	-74.942011
431705074114501	81	43.284828	-74.195978
441237073392501	82	44.210511	-73.656947
442443073340101	83	44.412175	-73.567075
435306073435801	84	43.885103	-73.733011
440908074272601	86	44.152497	-74.457333
442839073324801	87	44.477578	-73.546708
431926074005901	97	43.324000	-74.016539
441716073460801	98	44.287908	-73.768947
434451074175301	99	43.747556	-74.298206
432417074470401	102	43.404814	-74.784533
434024073374201	103	43.673594	-73.628503
432217074252801	104	43.371600	-74.424619
441820073485301	105	44.305750	-73.814861
441031073370601	107	44.175403	-73.618506
441140073301401	108	44.194689	-73.504069
441258073314701	109	44.216358	-73.529919
442758073531101	110	44.466378	-73.886436
443535073421401	112	44.593069	-73.703986
440007073431901	113	44.002086	-73.722033
441957073314601	114	44.332678	-73.529664
442156073504901	115	44.365678	-73.847058
433914074241401	116	43.653906	-74.404092

Table A-8c. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
434850073560401	117	43.814022	-73.934539
441452074232501	119	44.247892	-74.390544
433005074183801	120	43.501447	-74.310594
441712074041001	123	44.286700	-74.069472
432452074432101	124	43.414447	-74.722775
441654073394201	125	44.281742	-73.661894
431942074023401	127	43.328561	-74.042900
440742073391001	128	44.128356	-73.652889
431517074211201	129	43.254925	-74.353489
441702073411801	130	44.283992	-73.688378
434211074150201	131	43.703181	-74.250808
435327074245401	132	43.890944	-74.415028
434343074013501	134	43.728764	-74.026492
430823074303201	138	43.139769	-74.509031
435740074240801	139	43.961272	-74.402339
435441074242501	140	43.911467	-74.407125
442059073491001	142	44.349889	-73.819697
440141074015301	143	44.028253	-74.031456
434211074065801	145	43.703233	-74.116308
435024074255001	147	43.840117	-74.430697
434848073512801	148	43.813356	-73.857831
434233074160501	150	43.709178	-74.268211
440821073381401	151	44.139267	-73.637222
431943074051001	153	43.328650	-74.086275
440841073475901	154	44.144828	-73.799761
435806074030401	156	43.968428	-74.051339
435201074254001	157	43.866956	-74.427978
434304074070901	159	43.717839	-74.119197
441214073571301	162	44.204036	-73.953844
434916073492501	163	43.821167	-73.823764
434733073504201	164	43.792528	-73.845008
434308074034901	165	43.719114	-74.063664
434147074033101	166	43.696575	-74.058786
433942074223901	167	43.661714	-74.377725
433049074093101	168	43.513750	-74.158631
441051073494401	171	44.181078	-73.828894
432141074222001	172	43.361611	-74.372228

Table A-8d. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes, and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
435650073592601	175	43.947319	-73.990739
431818074121301	176	43.305000	-74.203700
435851074030701	177	43.981945	-74.052308
435145073454301	180	43.862525	-73.762181
441344073444201	183	44.229069	-73.745083
442440073484001	184	44.411247	-73.811139
431557074140901	188	43.266042	-74.235844
442600074253001	189	44.433347	-74.425122
442101073512801	192	44.350450	-73.857839
440144074291301	194	44.028956	-74.487058
432234074132601	197	43.376319	-74.224122
433105074175801	199	43.518256	-74.299658
442018073484101	200	44.338533	-73.811489
431934074545101	201	43.326239	-74.914350
433348074221201	204	43.563394	-74.370211
440949073470101	206	44.163878	-73.783692
432139074193601	209	43.360928	-74.326942
433123074233301	211	43.523211	-74.392756
434916074210101	212	43.820631	-74.350747
443437074032801	213	44.577078	-74.057794
444252074264401	214	44.714703	-74.445789
435714074020701	215	43.953969	-74.035350
432532074183401	216	43.425811	-74.309567
443920074164401	217	44.655794	-74.278892
434503073503001	218	43.751028	-73.841919
432820074145201	220	43.472350	-74.247969
440955074305001	222	44.165453	-74.513914
431000074294001	224	43.166922	-74.494692
442058073453501	225	44.349692	-73.759772
435524073440001	226	43.923422	-73.733461
434043073354101	227	43.678867	-73.594811
433632073533001	228	43.609128	-73.891842
441600073381201	229	44.266667	-73.636922
432720073590701	230	43.455681	-73.985494
443706073384301	231	44.618558	-73.645411
434300073530301	232	43.716728	-73.884397
432303074560401	233	43.384275	-74.934672

Table A-8e. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes, and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
434805073494101	234	43.801617	-73.828147
435733073312201	236	43.959439	-73.522789
441120073552501	237	44.188994	-73.923878
441058073591701	238	44.182814	-73.988267
432302074572801	239	43.384072	-74.957936
440451073293001	240	44.080853	-73.491772
441551073324101	242	44.264353	-73.544850
441540073515201	243	44.261331	-73.864689
435459073391001	244	43.916594	-73.652894
434643073545001	245	43.778686	-73.914094
431805074090401	246	43.301594	-74.151356
433948073573401	248	43.663611	-73.959594
441044073294101	249	44.179008	-73.494917
435103073425801	250	43.851094	-73.716203
442716073505501	251	44.454533	-73.848611
441446074151301	252	44.245303	-74.252979
442414075095001	253	44.404033	-75.163953
433830073555601	254	43.641942	-73.932406
441121073365701	256	44.189172	-73.616042
442445073542301	257	44.412700	-73.906614
440340073411001	258	44.061264	-73.686189
443337074011601	259	44.560336	-74.021306
442223074015001	260	44.373289	-74.030803
441715073551001	261	44.287506	-73.919706
432623074280401	262	43.439817	-74.467944
442724074215601	264	44.456917	-74.365781
442638073520601	265	44.444136	-73.868411
443409074051501	271	44.569361	-74.087750
441232073405301	272	44.208931	-73.681511
434410073591101	273	43.736281	-73.986531
433605074065001	274	43.601578	-74.114061
440615073413201	275	44.104169	-73.692358
442328073513201	276	44.391361	-73.859114
434845073302501	277	43.812603	-73.507017
433540073505701	278	43.594469	-73.849386
432248074400001	279	43.380242	-74.666669
431733074144101	280	43.292661	-74.244733

Table A-8f. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
431555074214301	281	43.265283	-74.362019
433342073434001	282	43.561811	-73.727889
432730074312101	500	43.458611	-74.522572
432654074313101	501	43.448353	-74.525358
433136074231001	502	43.526772	-74.386150
431048074393401	503	43.180056	-74.659711
430712074380501	504	43.120178	-74.634967
430905074414901	505	43.151614	-74.697217
441549075114301	1001	44.263831	-75.195383
432652074243301	1003	43.447992	-74.409178
432455074331601	1004	43.415297	-74.554675
441750075121501	1005	44.297306	-75.204269
441512075092701	1006	44.253353	-75.157519
441556075110701	1007	44.265556	-75.185489
441731075125901	1009	44.291972	-75.216408
432157074255501	1010	43.366078	-74.432200
432626074315201	1011	43.440756	-74.531242
432416074340801	1013	43.404519	-74.568894
432245074591901	1014	43.379192	-74.988681
441615075083301	1016	44.270839	-75.142653
441741075083101	1017	44.294789	-75.142086
441503075085501	1019	44.250844	-75.148619
441520075084301	1020	44.255800	-75.145375
440752075152001	5001	44.131364	-75.255822
440946075182701	5002	44.162928	-75.307614
441323075182701	5005	44.223247	-75.307678
440933075105901	6004	44.159322	-75.183156
440932075133301	6007	44.159156	-75.226053
441034075143101	6009	44.176228	-75.242131
441041075144001	6010	44.178114	-75.244514
441218075131001	6012	44.205175	-75.219594
441240075125301	6013	44.211125	-75.214986
441255075143901	6014	44.215389	-75.244419
441352075131401	6015	44.231372	-75.220569
441418075081501	6019	44.238436	-75.137567
441242075073401	6020	44.211708	-75.126239
440859075065901	7003	44.149778	-75.116478

Table A-8g. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
441053075044101	7005	44.181411	-75.078131
441415075070901	7017	44.237556	-75.119281
441408075063501	7018	44.235583	-75.109761
441408075062001	7019	44.235767	-75.105628
441252075052101	7024	44.214533	-75.089317
441329075033701	7027	44.224906	-75.060536
441332075024401	7028	44.225814	-75.045636
440846074533101	8002	44.146183	-74.892156
440910074533001	8003	44.153025	-74.891894
440931074540101	8011	44.158617	-74.900389
441340074583501	8015	44.227981	-74.976522
441331074502801	9002	44.225533	-74.841178
441252074494001	9005	44.214531	-74.827814
441311074493001	9006	44.219928	-74.825044
441216074491701	9007	44.204617	-74.821586
441137074492001	9008	44.193814	-74.822369
441158074504501	9009	44.199611	-74.845881
441242074471201	9013	44.211850	-74.786764
440016075193501	11001	44.004506	-75.326628
440250075171901	11008	44.047372	-75.288664
440239075165601	11010	44.044328	-75.282408
440320075184201	11011	44.055775	-75.311803
440351075175501	11012	44.064272	-75.298736
440530075163801	11014	44.091789	-75.277264
440711075171501	11019	44.119942	-75.287767
440710075173501	11020	44.119569	-75.293139
440701075192101	11022	44.117147	-75.322747
440657075191301	11023	44.115983	-75.320492
440606075200201	11025	44.101719	-75.333908
440154075184701	11027	44.031914	-75.313175
440151075084801	12003	44.030897	-75.146819
440125075084201	12008	44.023786	-75.145056
440654075073001	12012	44.115014	-75.125158
440705075141901	12017	44.118075	-75.238642
440729075143701	12019	44.124908	-75.243669
440430075142201	12020	44.075128	-75.239719
440603075143001	12022	44.100961	-75.241822

Table A-8h. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
440610075143701	12023	44.102939	-75.243831
440613075144301	12024	44.103836	-75.245458
440303075131601	12027	44.050856	-75.221144
440201075053401	13008	44.033656	-75.092789
440213075062701	13009	44.036972	-75.107519
440239075051001	13012	44.044194	-75.086314
440647075041601	13019	44.113261	-75.071169
440019074505101	15001	44.005500	-74.847756
440005074491401	15002	44.001408	-74.820700
435705075165501	17002	43.951592	-75.281969
435431075180201	17009	43.908686	-75.300822
435308075171401	17016	43.885764	-75.287261
435405075153301	17018	43.901137	-75.258819
435352075032701	18001	43.897814	-75.057589
435403075031401	18002	43.900878	-75.053981
435450075025601	18003	43.913936	-75.049011
435233075044401	18004	43.876103	-75.078975
435529075122601	18007	43.925012	-75.206976
435852075112301	18010	43.981225	-75.189839
435540074454401	19002	43.927925	-74.762492
435531074484701	19003	43.925317	-74.813328
435755074483401	19006	43.965286	-74.809464
435830074473601	19010	43.975072	-74.793350
435905074465901	19011	43.984958	-74.783089
435540074420101	20001	43.927869	-74.700328
435651074414101	20003	43.947572	-74.694747
434644075202101	21003	43.779106	-75.339192
434739075191601	21005	43.794375	-75.321131
434908075212501	21009	43.818939	-75.357075
434915075190901	21013	43.820942	-75.319406
435054075153501	21016	43.848372	-75.259958
435032075000901	22004	43.842275	-75.002550
435128075002301	22007	43.858033	-75.006533
435139075082201	22017	43.860919	-75.139558
435115075093901	22019	43.854408	-75.161067
434628075122101	22024	43.774472	-75.206083
434637074464701	23001	43.777147	-74.779989

Table A-8i. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
434547074582101	23003	43.763128	-74.972606
434539074583801	23004	43.760969	-74.977328
434652074565401	23014	43.781128	-74.948489
434606074424901	24001	43.768447	-74.713675
434544074411101	24002	43.762253	-74.686622
434005075160601	25002	43.668275	-75.268608
433811075180601	25003	43.636589	-75.301817
433753075211101	25006	43.631400	-75.353111
433851075210501	25007	43.647522	-75.351469
433922075210201	25009	43.656167	-75.350650
434008075205301	25011	43.669142	-75.348122
434006075200101	25013	43.668375	-75.333728
434127075200801	25015	43.691058	-75.335592
434139075213801	25018	43.694314	-75.360800
434242075215601	25021	43.711675	-75.365622
434249075215601	25022	43.713747	-75.365633
434336075205601	25023	43.726853	-75.348953
434012075040501	26006	43.670100	-75.068286
434001075045401	26008	43.667211	-75.081928
433940075053201	26009	43.661169	-75.092336
433949075063801	26011	43.663764	-75.110572
433822075143901	26021	43.639517	-75.244303
434118075133101	26030	43.688358	-75.225517
434116075125501	26031	43.687899	-75.214433
434106075123101	26032	43.685239	-75.208756
434317075125401	26044	43.721603	-75.215214
434254075144401	26046	43.715058	-75.245603
434025074585901	27002	43.673811	-74.983317
434107074591301	27003	43.685336	-74.987158
433849074575101	27005	43.647067	-74.964350
433837074571401	27006	43.643731	-74.954061
433800074550101	27010	43.633536	-74.917128
434142074533201	27014	43.695103	-74.892347
434442074473801	27015	43.745028	-74.793894
434301074453701	27018	43.717050	-74.760347
434256074453801	27019	43.715700	-74.760600
434217074465001	27020	43.704756	-74.780628

Table A-8j. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
434211074462301	27021	43.703122	-74.773064
434207074453801	27022	43.702194	-74.760781
434204074452401	27023	43.701378	-74.756811
434211074452401	27024	43.703089	-74.756928
434208074450901	27025	43.702269	-74.752711
434154074445701	27026	43.698481	-74.749378
434427074584401	27037	43.741069	-74.978950
434446074562301	27039	43.746369	-74.939950
434056074440401	28004	43.682419	-74.734556
434101074420301	28006	43.683867	-74.700925
434051074415901	28007	43.680892	-74.699947
433953074400801	28010	43.664869	-74.669144
433918074403501	28011	43.655078	-74.676514
433854074411501	28013	43.648444	-74.687708
433820074410001	28014	43.639069	-74.683419
434124074393301	28017	43.690053	-74.659328
434105074393501	28018	43.684742	-74.659978
434208074354501	28022	43.702361	-74.596086
434208074343001	28024	43.702286	-74.575236
434500074441601	28030	43.750047	-74.737983
433920074403401	28037	43.655708	-74.676386
434057074425001	28039	43.682731	-74.713958
434145074413201	28041	43.696000	-74.692303
433423075183301	29002	43.573089	-75.309300
433422075153301	29003	43.572853	-75.259392
433453075182501	29005	43.581650	-75.306992
433613075184301	29008	43.603875	-75.312183
433702075200701	29009	43.617317	-75.335553
433324075165001	29012	43.556864	-75.280742
433102075073801	30002	43.517250	-75.127381
433117075073501	30003	43.521664	-75.126400
433206075055601	30004	43.535197	-75.098953
433553075062101	30009	43.598219	-75.105869
433325075083601	30012	43.557119	-75.143436
433223075122001	30016	43.539828	-75.205653
433548075110101	30019	43.596681	-75.183794
433639075093101	30023	43.610944	-75.158681

Table A-8k. NWIS (USGS Water Data for the Nation) Site Identification Codes, Project Codes and Coordinates for All Streams Sampled in the Study

NWIS Database Code	Project Stream Code	Latitude	Longitude
433636075084101	30026	43.610061	-75.144800
433130074555201	31007	43.525133	-74.931383
433014074585101	31009	43.503903	-74.980889
433010074585901	31010	43.502914	-74.983114
433044074565301	31011	43.512267	-74.948222
433706074564501	31015	43.618425	-74.945903
432622075075801	34006	43.439447	-75.133025
432602075060201	35004	43.434167	-75.100639
432708075053101	35005	43.452453	-75.092142
432806075033501	35008	43.468411	-75.059775
432718075001801	35012	43.455100	-75.005006
432910075001001	35014	43.486256	-75.002906
441345073525501	2E	44.229272	-73.882056
441749075163901	2W	44.296969	-75.277600

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