

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)

Summary 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 ($\mu\text{eq L}^{-1} \text{y}^{-1}$) 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 $1.4 \mu\text{eq L}^{-1} \text{y}^{-1}$.

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 ($\mu\text{eq L}^{-1}$), 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

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Acronyms and Abbreviations

| | |
|-------------------------------------|---|
| acidBAP | acid-biological assessment profile |
| Al | aluminum |
| Al _i | inorganic monomeric Al |
| ANC | acid-neutralizing capacity by Gran titration |
| BCS | base-cation surplus |
| C | carbon |
| Ca | calcium |
| Ca ²⁺ | calcium ion |
| cp | change point |
| DOC | dissolved organic carbon |
| ECASS | East-Central Adirondack Stream Survey |
| EPA | United States Environmental Protection Agency |
| ha | hectare |
| HES | high elevation survey |
| km | kilometers |
| m | meters |
| mi | miles |
| mm | millimeters |
| N | nitrogen |
| NADP | National Atmospheric Deposition Program |
| NO ₃ ⁻ | nitrate ion |
| RCOO ⁻ | strongly acidic organic anions |
| RDA | redundancy analysis |
| SBC | sum of base cations |
| SO ₄ ²⁻ | sulfate ion |
| 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 |
| USGS | United States Geological Survey |
| WASS | Western Adirondack Stream Survey |

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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 miles [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.

2 Study Region Characteristics

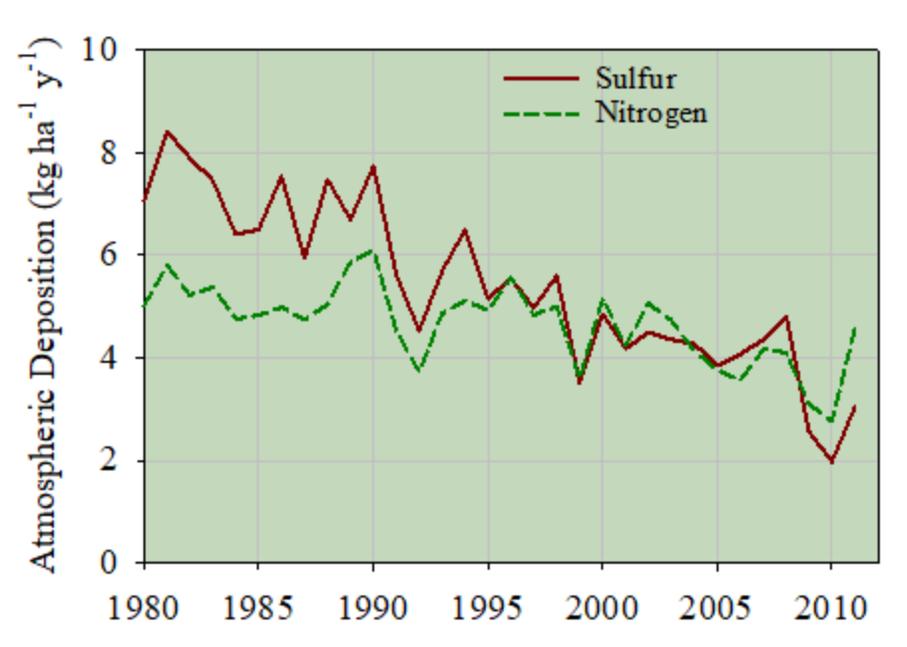
The study region is characterized by rugged, irregular terrain formed by repeated glaciations that last receded approximately 10,000 years ago. Bedrock geology is a complex mixture of granitic and gneissic rocks with a variety of less common metasedimentary formations scattered throughout the region (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 the 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 1) but remain among the highest in the Northeast with respect to both sulfate (SO_4^{2-}) and inorganic nitrogen (N). Visit <http://nadp.slh.wisc.edu> for more information (accessed August 1, 2018).

3 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 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.

4 Project Findings and Implications

4.1 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 (2003–2005) and ECASS (2010–2011), 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.

4.2 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 ($\mu\text{eq L}^{-1}$), 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 $19 \mu\text{eq L}^{-1}$. However, the most acidic value of BCS at Buck Creek during the two-year study window ($-72 \mu\text{eq L}^{-1}$) was measured on June 28, 2010. This value was lower than the mean BCS measured at Buck Creek during the snowmelt sampling by $33 \mu\text{eq L}^{-1}$ 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 $33 \mu\text{eq L}^{-1}$ less than that measured in the April snowmelt sampling, which encompassed the most acidic conditions of the three samplings.

Streams with a BCS value $< 0 \mu\text{eq L}^{-1}$ 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 $33 \mu\text{eq L}^{-1}$ adjustment to the April sampling for conditions of maximum acidification indicated that 42% of the streams would likely experience $\text{BCS} < 0 \mu\text{eq L}^{-1}$ during conditions of maximum acidity within the two-year study period (Table 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 $\text{ANC} < 0.0 \mu\text{eq L}^{-1}$ was one-half or less the values based on $\text{BCS} < 0 \mu\text{eq L}^{-1}$ (Table 1). The number of streams with acid-neutralizing capacity (ANC) $< 50 \mu\text{eq L}^{-1}$ 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 ($\mu\text{mol L}^{-1}$), 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 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 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 |

4.3 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 $\mu\text{eq L}^{-1}$ in both samplings were considered to be chronically acidified. Streams with a BCS value < 33 $\mu\text{eq L}^{-1}$ in the April 2011 sampling, but > 33 $\mu\text{eq L}^{-1}$ in the August 2010 sampling, were considered episodically acidified. All streams with BCS < 33 $\mu\text{eq L}^{-1}$ in the August 2010 sampling were also acidified in the April 2011 sampling. Streams in the April 2011 sampling with BCS > 33 $\mu\text{eq L}^{-1}$ were considered unacidified. Results of this analysis are summarized in the following list.

| | |
|---|------------|
| 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 |

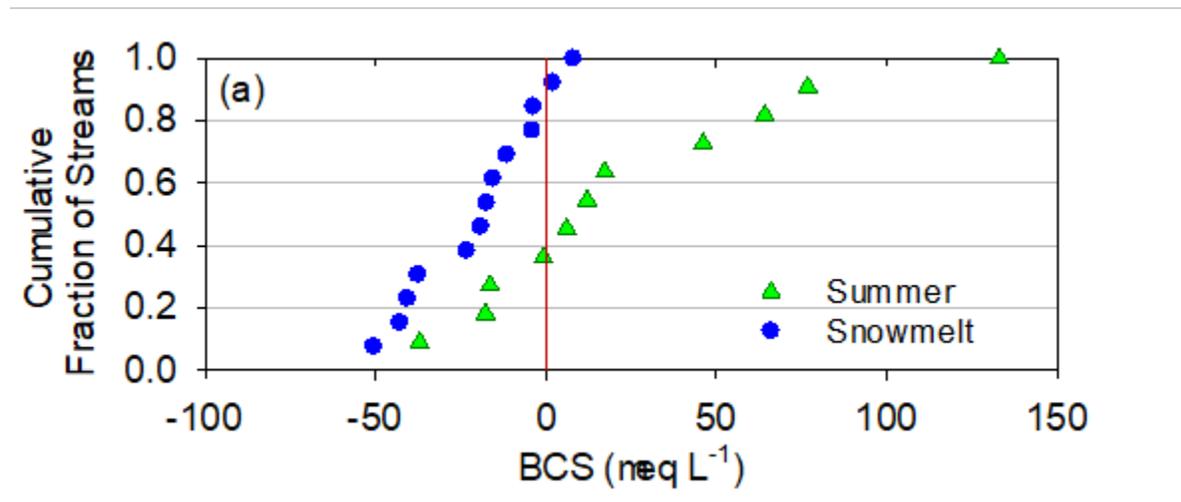
4.4 High-Elevation Stream Chemistry

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 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 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.



4.5 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 ($\text{ANC} < 5 \mu\text{eq L}^{-1}$), whereas two of the streams were moderately well-buffered ($65 \mu\text{eq L}^{-1} < \text{ANC} < 85 \mu\text{eq L}^{-1}$) and one stream was well-buffered ($\text{ANC} = 165 \mu\text{eq L}^{-1}$). Rates of increase in ANC in the two poorly buffered streams that increased significantly from the 1980s to 2011 ($P < 0.10$), were $0.25 \mu\text{eq L}^{-1} \text{ y}^{-1}$ and $0.50 \mu\text{eq L}^{-1} \text{ y}^{-1}$. At those rates of recovery, an ANC of $50 \mu\text{eq L}^{-1}$ 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 $9.0 \mu\text{eq L}^{-1}$ 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 $40 \mu\text{eq L}^{-1}$ ($1.4 \mu\text{eq L}^{-1} \text{ y}^{-1}$) and the other exhibited a nonsignificant ($P > 0.10$) ANC increase of $30 \mu\text{eq L}^{-1}$. 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.

4.6 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 3). In these snowmelt samplings, fewer than half (approximately 45%) of ECASS streams had values above $50 \mu\text{eq L}^{-1}$, 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 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 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 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.

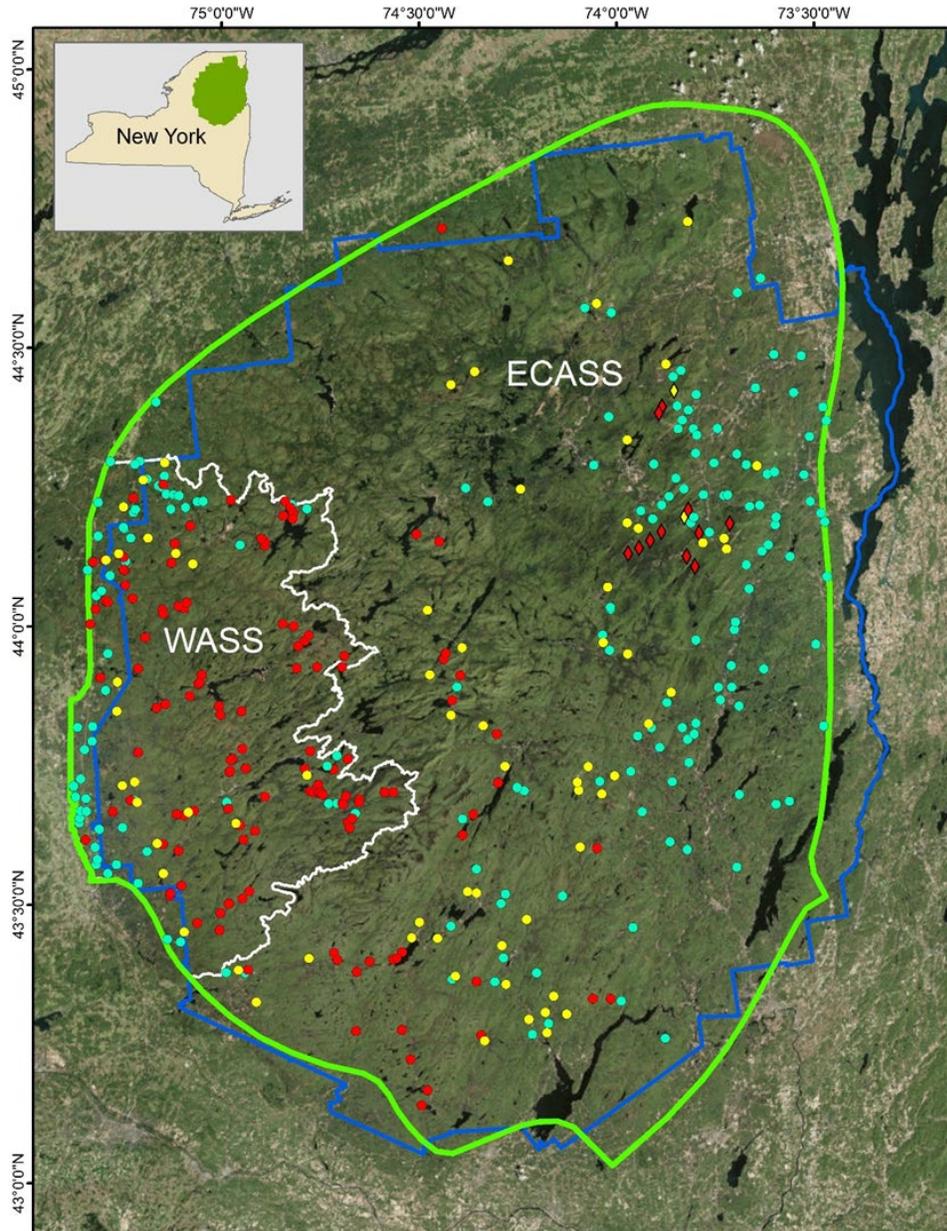
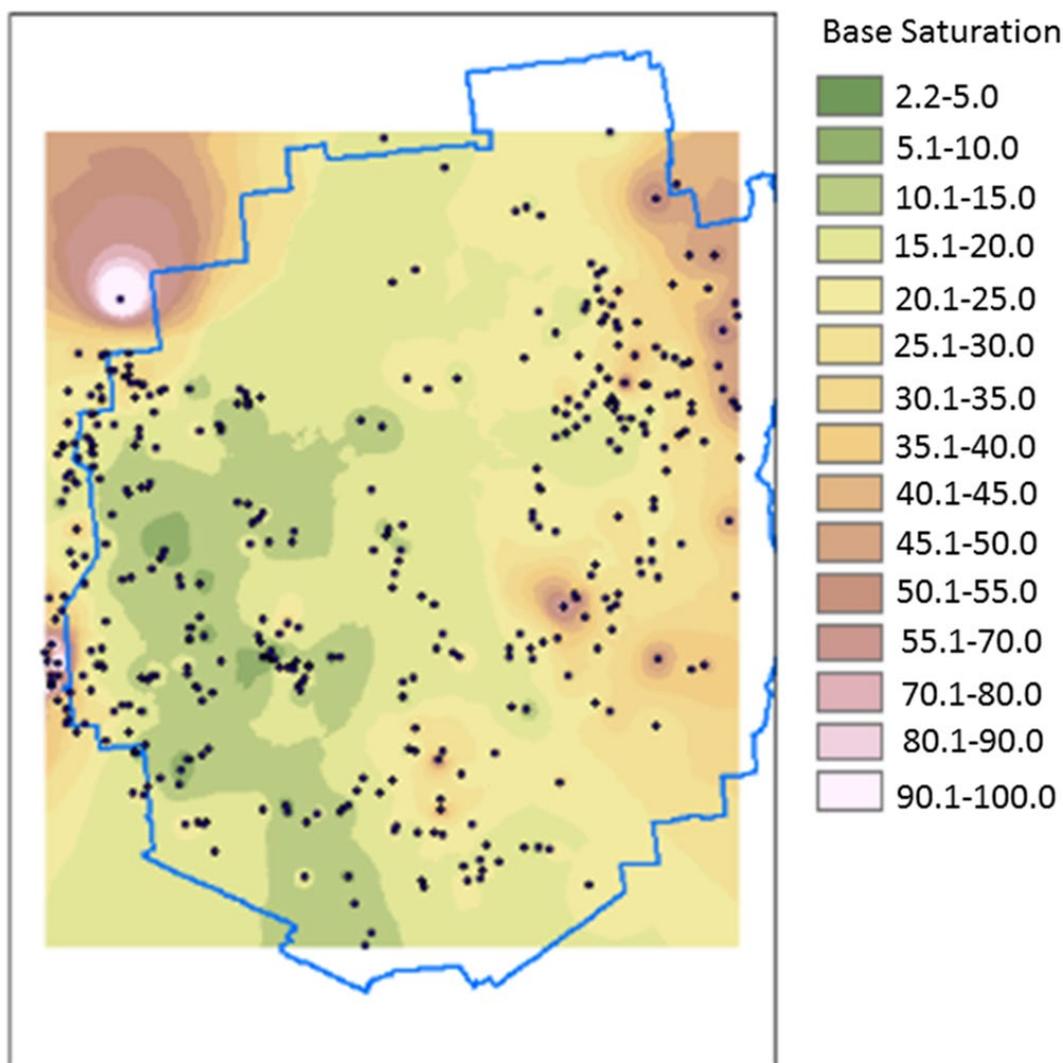


Figure 4. Variation in Base Saturation (Percent) across the Adirondack Region

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



4.7 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 $4.9 \mu\text{eq L}^{-1}$, which is near the theoretical threshold for Al mobilization of $\text{BCS} = 0.0 \mu\text{eq L}^{-1}$. 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 $2 \mu\text{mol L}^{-1}$, 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 $0.9 \mu\text{mol L}^{-1}$, 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 four stream classifications identified in regression tree analysis: non-acidified streams with $\text{pH} > 6.8$, moderately acidified streams with $6.09 < \text{pH} < 6.8$, severely inorganically acidified streams with $\text{pH} < 6.09$ and $\text{DOC} < 361$ micromoles of carbon per liter ($\mu\text{mol C L}^{-1}$), and severely organically acidified streams with $\text{pH} < 6.09$ and $\text{DOC} > 361 \mu\text{mol C L}^{-1}$. 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.

5 Conclusions

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 km² (7,710 mi²). 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 SO₄²⁻ 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 Ca²⁺ 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.

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