

Changes in Stream Chemistry in the East-Central Adirondack Region of New York State, 2010–2018

Final Report | Report Number 22-07 | March 2022



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Changes in Stream Chemistry in the East-Central Adirondack Region of New York State, 2010–2018

Final Report

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Preferred Citation

New York State Energy and Research Development Authority (NYSERDA). 2022. “Changes in Stream Chemistry in the East-Central Adirondack Region of New York State, 2010–2018,” NYSERDA Report Number 22-07. Prepared by United States Geological Survey, Troy, NY. nyserda.ny.gov/publications

Abstract

Decreased acidic deposition occurred through the 2010s, extending the long-term decrease begun in the early 1980s. The overall decline has resulted in rates of acidic deposition in the Adirondack region that are similar to those estimated for the early 1900s. This achievement increased attention on the issue of acidic deposition recovery and raised the question of how the low deposition levels of the 2010s were affecting the Adirondack region of New York State, where past acidic deposition effects were among the highest in the United States. This report presents stream resampling results of the East-Central Adirondack Stream Survey (ECASS), the Adirondack high-elevation stream sampling program, and the first five years of stream chemistry measurements in the Boreas River Long-Term Monitoring Watersheds. In addition, a regional comparison of stream chemistry between ECASS and the Western Adirondack Stream Survey (WASS) is presented. The primary objective of these stream resampling programs was to evaluate changes in stream chemistry during the 2010s to evaluate ongoing recovery of acidic deposition within the Adirondack region.

Streams in the ECASS region (19,658 km²) were sampled during spring snowmelt in 2011, 2017, and 2018; summer baseflow in 2010 and 2017; and late autumn in 2011 and 2017. ECASS stream sampling results for snowmelt in 2018 are also compared with WASS stream sampling results during snowmelt of the same year to provide a spatial assessment of stream chemistry for the entire Adirondack region. In addition, high-elevation streams were sampled in 2010-2011 and 2017 during spring snowmelt and summer baseflow, and three streams in the Boreas River watershed were sampled biweekly from 2014 through 2019. Streams were selected for sampling from the approximately 200 streams sampled originally in both the ECASS and WASS. The original ECASS and WASS streams were randomly selected from the populations of accessible streams within their respective regions. For the study reported here, subsets of streams were selected from the two original groups using a random stratified design based on the stream chemistry of the original ECASS and WASS. ECASS data are presented only for streams that were sampled in each of the seasonal surveys, which was 59, 48, and 61 streams for spring snowmelt, summer baseflow, and autumn surveys, respectively. WASS data are presented for 60 streams and high-elevation data are presented for 11 streams sampled during summer baseflow and 12 streams sampled during spring snowmelt.

Overall, mean values of chemical measurements did not indicate large changes between 2010-2011 and 2017-2018 in the ECASS snowmelt, summer baseflow, or autumn surveys. Minimal acidification was observed in mean values measured in any of the surveys. Mean values of acid-neutralizing capacity

(ANC) remained above 80 microequivalents per liter ($\mu\text{eq L}^{-1}$), mean pH remained above 6.37, and inorganic monomeric aluminum (Al_i) remained below 1.0 micromoles per liter ($\mu\text{mol L}^{-1}$), with the exception of the mean value of $1.2 \mu\text{mol L}^{-1}$ in the 2017 autumn survey. However, in the 2017 and 2018 snowmelt samplings 15% and 10% of the streams, respectively, had Al_i concentrations above $1.0 \mu\text{mol L}^{-1}$, the concentration above which is toxic to fish. Based on the estimated total length of headwater streams in the ECASS region of 11,494 km, the 10% of ECASS streams that experienced harmful Al_i concentrations ($\text{Al}_i > 1.0 \mu\text{mol L}^{-1}$) during the 2018 snowmelt survey equated to a total length of 1,091 km of headwater stream length in the region.

During both summer baseflow and snowmelt sampling, high-elevation streams were less acidic in 2017 than in 2010-2011. However, in 2017 the mean Al_i concentration during snowmelt was $2.6 \mu\text{mol L}^{-1}$, a value that reflected low to moderate toxicity to brook trout. Concentrations of Al_i in 9 out of the 12 streams were above $1.5 \mu\text{mol L}^{-1}$, which exceeds the value which impairs fish communities. Greater dilution of calcium (Ca^{2+}) concentrations than sulfate (SO_4^{2-}) concentrations during snowmelt was a contributing factor to the more acidic stream water measured during snowmelt than summer baseflow.

Comparison of 2018 ECASS and WASS snowmelt chemistry under the current low levels of acidic deposition indicated that the spatial pattern of acidification effects on stream chemistry is largely driven by inherent Ca^{2+} availability tied to spatial variations in geologic factors that control acid buffering more effectively in the ECASS region than the WASS region. The higher degree of acidification in the WASS region than the ECASS region is likely to extend into the future as a result of the relatively high dissolved organic carbon (DOC) concentrations in the WASS.

Pronounced increasing trends in DOC and similarly pronounced decreasing trends in Ca^{2+} and nitrate (NO_3^-) were observed in the streams of all three Boreas River watersheds. These strong increasing DOC trends occurred in streams during a period with little or no indication of further chemical recovery from acidic deposition. The strong DOC trends in Durgin Brook and Balsam Brook, which are streams that are unlikely to have ever experienced more than minimal acidification, suggest the need for further investigation to expand our understanding of the mechanisms behind the increasing DOC trends.

Keywords

Acid rain, acidic deposition, stream chemistry, aluminum, dissolved organic carbon, calcium depletion, Adirondack region

Acknowledgments

Financial support for this work was provided by the New York State Energy Research and Development Authority (NYSERDA), the New York State Department of Environmental Conservation (DEC), and the U.S. Geological Survey (USGS). Stream sampling was accomplished through the collaborative efforts of the USGS, the Adirondack Lakes Survey Corporation (ALSC), and the DEC. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the United States Government.

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Acronyms and Abbreviations

Al	aluminum
Al _i	inorganic monomeric aluminum
Al _o	organic monomeric aluminum
Al _{tm}	total monomeric aluminum
ALSC	Adirondack Lakes Survey Corporation
ANC	acid-neutralizing capacity
BCS	base-cation surplus
C	carbon

Ca	calcium
Ca ²⁺	calcium ion
Cl ⁻	chloride ion
DEC	New York State Department of Environmental Conservation
DOC	dissolved organic carbon
ECASS	East-Central Adirondack Stream Survey
F ⁻	fluoride ion
H	hydrogen
H ⁺	hydrogen ion
K ⁺	potassium ion
km	kilometers
Mg ²⁺	magnesium ion
m	meters
m s ⁻¹	meters per second
mi	miles
mm	millimeters
N	nitrogen
Na ⁺	sodium ion
NADP	National Atmospheric Deposition Program
NH ⁴⁺	ammonium ion
NO ₃ ⁻	nitrate ion
NWIS	National Water Information System
NYSERDA	New York State Environmental Research and Development Authority
pH	logarithm ₁₀ of hydrogen concentration in units of moles per liter, multiplied by -1
RCOO ^{-s}	strongly acidic organic ions
S	sulfur
Si	silicon
SO ₄ ²⁻	sulfate ion
µeq L ⁻¹	microequivalents per liter
µmol L ⁻¹	micromoles per liter
µmol C L ⁻¹	micromoles of carbon per liter
µS cm ⁻¹	microsiemens per centimeter
USGS	United States Geological Survey
WASS	Western Adirondack Stream Survey

Executive Summary

Streams in the East-Central Adirondack Stream Survey (ECASS) region (19,658 km²) were sampled during spring snowmelt in 2011, 2017, and 2018; summer baseflow in 2010 and 2017; and late autumn in 2011 and 2017. ECASS stream sampling results for snowmelt in 2018 are also compared with Western Adirondack Stream Survey (WASS) stream sampling results during snowmelt of the same year to provide a spatial assessment of stream chemistry for the entire Adirondack region. In addition, high-elevation streams were sampled in 2010-2011 and 2017 during spring snowmelt and summer baseflow, and three streams in the Boreas River watershed were sampled biweekly from 2014 through 2019. Streams were selected for sampling from the approximately 200 streams sampled originally in both the ECASS and WASS. The original ECASS and WASS streams were randomly selected from the populations of accessible streams within their respective regions. For the study reported here, subsets of streams were selected from the two original groups using a random stratified design based on the stream chemistry of the original ECASS and WASS. ECASS data are presented only for streams that were sampled in each of the seasonal surveys, which was 59, 48, and 61 streams for spring snowmelt, summer baseflow, and autumn surveys, respectively. WASS data are presented for 60 streams and high-elevation data are presented for 11 streams sampled during summer baseflow and 12 streams sampled during spring snowmelt.

Overall, mean values of chemical measurements did not indicate large changes between 2010-2011 and 2017-2018 in the ECASS snowmelt, summer baseflow, or autumn surveys. Minimal acidification was observed in mean values measured in any of the surveys. Mean values of acid-neutralizing capacity (ANC) remained above 80 microequivalents per liter ($\mu\text{eq L}^{-1}$), mean pH remained above 6.37, and inorganic monomeric aluminum (Al_i) remained below 1.0 micromoles per liter ($\mu\text{mol L}^{-1}$), with the exception of the mean value of 1.2 $\mu\text{mol L}^{-1}$ in the 2017 autumn survey. However, in the 2017 and 2018 snowmelt samplings 15% and 10% of the streams, respectively, had Al_i concentrations above 1.0 $\mu\text{mol L}^{-1}$, the concentration above which is toxic to fish. Based on the estimated total length of headwater streams in the ECASS region of 11,494 km, the 10% of ECASS streams that experienced harmful Al_i concentrations ($\text{Al}_i > 1.0 \mu\text{mol L}^{-1}$) during the 2018 snowmelt survey equated to a total length of 1,091 km of headwater stream length in the region.

During both summer baseflow and snowmelt sampling, high-elevation streams were less acidic in 2017 than in 2010-2011. However, in 2017 the mean Al_i concentration during snowmelt was $2.6 \mu\text{mol L}^{-1}$, a value that reflected low to moderate toxicity to brook trout. Concentrations of Al_i in 9 out of the 12 streams were above $1.5 \mu\text{mol L}^{-1}$, which exceeds the value which impairs fish communities. Greater dilution of calcium (Ca^{2+}) concentrations than sulfate (SO_4^{2-}) concentrations during snowmelt was a contributing factor to the more acidic stream water measured during snowmelt than summer baseflow.

Comparison of 2018 ECASS and WASS snowmelt chemistry under the current low levels of acidic deposition indicated that the spatial pattern of acidification effects on stream chemistry is largely driven by inherent Ca^{2+} availability tied to spatial variations in geologic factors that control acid buffering more effectively in the ECASS region than the WASS region. The higher degree of acidification in the WASS region than the ECASS region is likely to extend into the future as a result of the relatively high dissolved organic carbon (DOC) concentrations in the WASS.

Pronounced increasing trends in DOC and similarly pronounced decreasing trends in Ca^{2+} and nitrate (NO_3^-) were observed in the streams of all three Boreas River watersheds. These strong increasing DOC trends occurred in streams during a period with little or no indication of further chemical recovery from acidic deposition. The strong DOC trends in Durgin Brook and Balsam Brook, which are streams that are unlikely to have ever experienced more than minimal acidification, suggest the need for further investigation to expand our understanding of the mechanisms behind the increasing DOC trends.

ES.1 Primary Findings of ECASS Stream Resampling

Although acidic deposition continued to decrease over the study period, mean chemical concentration values of 59 streams selected to represent the range of stream chemistry of the ECASS region did not indicate clear changes in snowmelt stream acidity over the six-to-seven- year study period.

Mean SO_4^{2-} concentrations measured during summer baseflow decreased substantially between 2010 and 2017, which resulted in diluted stream water expressed by decreased concentrations of base cations and conductivity, and increased DOC concentrations.

Mean values of chemical measurements for the ECASS region during autumn surveys indicated that, in general, large increases in flow during this season triggered only minimal episodic acidification.

ECASS snowmelt sampling indicated that 10% to 15% of streams had ANC and Al_i values harmful to species of fish that occur in the region, which equates to more than 1,091 km (684 miles) of headwater streams in the ECASS region.

In high-elevation streams, snowmelt acidity was appreciably higher than during summer baseflow despite lower concentrations of SO_4^{2-} and NO_3^- during spring snowmelt relative to summer baseflow. Substantially greater acidity in streams during snowmelt than in summer occurred because snowmelt concentrations of Ca^{2+} were only 50% of the values measured during summer baseflow. These results highlight the ongoing effect of soil Ca^{2+} depletion in delaying recovery of stream chemistry.

Stream acidification is currently impacting a larger percentage of headwater streams in the WASS region than the ECASS region primarily due to geologic factors in the ECASS region that provide better acid buffering than in the WASS region.

Stream acidification is likely to continue in some streams of both regions for the foreseeable future due to further increases in DOC, continued release of residual SO_4^{2-} and NO_3^- from soils, and slow recovery of watershed Ca^{2+} availability.

Despite a history of minimal acidic deposition effects, pronounced decreasing trends in NO_3^- and Ca^{2+} and a pronounced increasing trend in DOC were observed in all three streams in the Boreas River monitoring watersheds from 2014 through 2019.

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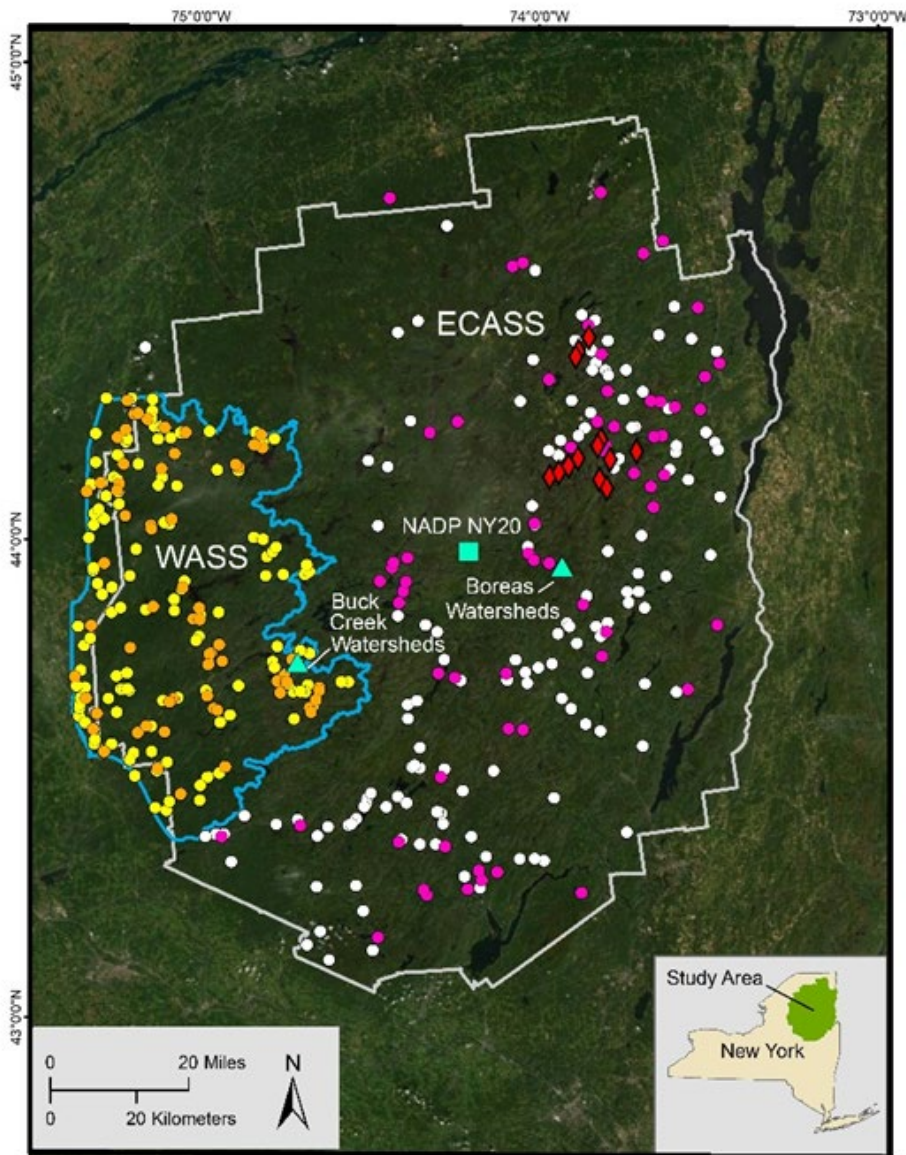
1 Background and Objectives

Reports of fish extinctions in the Adirondack region from acidic deposition in the 1970s (Schofield, 1976) resulted in numerous studies in the region to assess the environmental effects of air pollution. Although passage of the 1990 Clean Air Act Amendments greatly helped to reduce acidic deposition levels, monitoring of Adirondack lakes through the Adirondack Long-Term Monitoring (ALTM) program indicated that acidic deposition continued to chemically impair lake ecosystems into the 2000s (Driscoll et al., 2007). To gain information on surface water effects of acidic deposition beyond the ALTM program, 200 headwater streams were sampled in 2003–2005 in the Western Adirondack Stream Survey (WASS) to characterize stream chemistry throughout the Oswegatchie and Black River drainages—the area considered to be the most impacted within the Adirondack region. Headwater stream sampling provided a more complete picture of surface-water conditions than lake-only monitoring because streams (1) acidify more readily than lakes, (2) provide unique aquatic habitat, and (3) reflect the influences of terrestrial vegetation and soil processes more directly than lakes (Lawrence et al., 2008a). Results of the WASS are detailed in previous publications (Lawrence et al., 2008a; Lawrence et al., 2008b).

The WASS, which comprised approximately 20% of the overall Adirondack region (figure 1), 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 WASS was successful in providing detailed information on spatial, episodic, and seasonal variations in stream chemistry within the study region. To evaluate the remaining 80% of the Adirondack region, which had received less attention in acidic deposition effects studies, the East Central Adirondack Stream Survey (ECASS) was conducted in 2010–2011 with the same sampling approach used in the WASS. The primary objectives of the ECASS was to (1) assess conditions with respect to acidic deposition effects in this less-studied area of the Adirondack region and (2) use the stream measurements 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 sampling program were selected high-elevation streams in the area generally referred to as the High Peaks region of the Adirondack ecoregion. Results of the 2010–2011 ECASS are detailed in Lawrence et al. (2018b).

Figure 1. Study Region Location

The boundary of the Adirondack Park is delineated in gray. Locations of streams sampled only in the original WASS (Western Adirondack Stream Survey) from 2004–2005 are shown in yellow; WASS streams sampled in 2004–2005, 2014–2015, and 2018–2019 are shown in orange. Locations of streams sampled only in the original ECASS (East-Central Adirondack Stream Survey; 2010–2011) are shown in white; ECASS streams sampled in 2010–2011 and 2017–2018 are shown in pink. High-elevation streams are shown as red diamonds. Sampling locations that define the watersheds of Buck Creek, North Buck, and South Buck are located by the green triangle labeled Buck Creek Watersheds. Maple Brook, Balsam Brook, and Durgin Brook are located by the green triangle labeled Boreas Watersheds. The green square locates the NADP (National Atmospheric Deposition Network) wet deposition site, NY20.



Decreased acidic deposition through the 2010s extended the long-term decrease begun in the early 1980s (Lawrence and Roy, 2021). The overall decline has resulted in rates of acidic deposition in the Adirondack region that are similar to those estimated for the early 1900s by hindcast modeling (Shao et al., 2020). Achievement of levels approaching those of early industrialization led to increased attention on the issue of recovery from acidic deposition. This interest included the question of how the relatively low-deposition levels of the 2010s were affecting the chemistry of streams in the ECASS region. To address this question, a subset of ECASS streams, including the high-elevation streams, was resampled in 2017–2018.

To provide intensive stream monitoring records in an area within the ECASS region, sampling of headwater streams in three neighboring watersheds in the Boreas River drainage (hereafter referred to as the Boreas River watersheds) was established in 2014 (Figure 1). Stream sampling and flow monitoring in the Boreas River watersheds matched the design used in the Buck Creek monitoring watersheds previously established within the WASS region (Lawrence et al., 2011). Buck Creek is representative of calcium-depleted systems with streams that have shown limited recovery from acidification (Lawrence et al., 2020), whereas the streams in the Boreas River watersheds reflect relatively minor impacts of acidic deposition.

The specific objectives of the ECASS resampling were to evaluate differences in stream chemistry between the original ECASS conducted in 2010–2011 and ECASS resampling in 2017–2018. Sampling was done during spring snowmelt, summer baseflow, and late autumn. In 2018, ECASS snowmelt sampling coincided with a WASS spring snowmelt sampling. This was the first time that both ECASS and WASS sampling was conducted in the same year and season, providing the opportunity for a direct comparison between the regions. An additional objective of this report was to evaluate the chemical time series generated by the monitoring of the Boreas River watersheds, which began in 2014.

2 Methods

2.1 Study Area and Sampling Design

Data are presented in this report for headwater streams sampled throughout the 24,243 km² Adirondack region, which approximates the area encompassed by the Adirondack Park (Figure 1), the largest state park in the United States. The Adirondack region is almost entirely forested with northern temperate hardwood and coniferous species and includes some areas of high-elevation montane forests. Below-freezing temperatures throughout most of the winter result in accumulation of snow by the onset of spring, which melts over several weeks causing sustained high streamflow. Glaciated terrain and mean annual precipitation levels of 800 to over 1,600 millimeters (mm; Ito et al., 2002) have resulted in a high density of lakes and streams throughout the region. Surficial deposits resulting from glaciation are also spatially variable across the region, with some areas having no till and others having thick deposits (Driscoll et al., 1991). 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). The minerology of surficial deposits reflects this complexity and includes highly weatherable calcareous minerals in a few areas (Roy et al., 1997). The combination of high amounts of precipitation and geological features make much of the Adirondack region susceptible to impacts from acidic deposition, although the severity of effects vary across the region.

In this report, stream sampling results for the ECASS study area (19,658 km²) are presented for spring snowmelt in 2011 (April 18–20), 2017 (April 11) and 2018 (April 16–18), summer baseflow in 2010 (August 9–11) and 2017 (August 10), and late autumn in 2011 (October 31–November 2) and 2017 (November 11). Data are included only for streams that were sampled in each of the seasonal surveys. Some streams were dry during the summer surveys, and a few were not sampled during snowmelt due to accessibility issues. Therefore, data are reported for 59 streams, 48 streams and 62 streams for spring snowmelt, summer baseflow, and autumn surveys, respectively. Sampling during spring snowmelt reflected early spring conditions when soils were saturated, and a large fraction of streamflow was generated through shallow soil flow paths that minimized acid neutralization. Summer baseflow sampling characterized stream water that was largely generated from deep flow paths that maximized acid neutralization. Autumn sampling reflected the effects of the seasonal leaf drop. Data collected from resampling of 60 WASS streams during spring snowmelt in 2018 (April 23–25) are also presented for comparison with the 2018 spring snowmelt ECASS sampling results.

Streams were selected for sampling in both the ECASS and WASS from the accessible population of headwater streams identified throughout the entire Adirondack region. Selection of the ECASS streams was based on 2011 spring snowmelt data. Streams were randomly selected for sampling from four groups stratified by values of the base-cation surplus (BCS). The BCS is an index of acidification similar to acid-neutralizing capacity (ANC) that explicitly includes the effect of strongly acidic organic acids. Details on the derivation and application of the BCS are available elsewhere (Lawrence et al., 2018a; Lawrence et al., 2008a; Lawrence et al., 2007). The BCS categories for ECASS streams were (1) strongly acidified ($BCS \leq 10$ microequivalents per liter; $\mu\text{eq L}^{-1}$), (2) moderately acidic ($10 < BCS \leq 45$), (3) moderately acid buffered ($45 < BCS \leq 100$), and (4) well acid buffered ($BCS > 100$). Selection of the WASS streams was based on 2005 spring snowmelt (March 29-31) data. The BCS categories for WASS streams were (1) strongly acidified ($BCS \leq -30 \mu\text{eq L}^{-1}$), (2) acidified ($-30 < BCS \leq 25$), (3) moderately acid buffered ($25 < BCS \leq 75$), and (4) well acid buffered ($75 < BCS \leq 250$). Ranges of BCS categories for WASS streams were lower than for ECASS streams because streams in the WASS region were, in general, more acidic than those in the ECASS region. Full details of the design and approach, and additional results of the original WASS and ECASS sampling are available elsewhere (Lawrence et al., 2008b; Lawrence et al., 2018b).

Included with the ECASS sampling program in 2011 and resampling in 2017–2018 was the collection of samples from streams at relatively high elevations (Figure 1) in the area generally referred to as the High Peaks Region, which falls within the ECASS study area. Locations of sampling were determined by accessibility, which in all cases required extended hikes on mountain trails. Sampling sites ranged from 866 meters (m) to 1,017 m elevation, and all watersheds were forested to their uppermost elevations except for areas too steep to allow tree growth. Stream chemistry data are reported for 12 high-elevation streams that were sampled in the ECASS program in 2011 and 2017 during spring snowmelt (late April-May) and 11 streams that were sampled during August baseflow in 2010 and 2017 (Figure 1). Further details on high-elevation sampling and stream chemistry are available in Lawrence et al. (2018b).

Results of sampling the streams draining the Boreas River watersheds (Maple Brook, Balsam Brook, and Durgin Brook) from 2014 through 2019 are also included in this report to provide chemical time series for an interim period between the original ECASS sampling in 2010–2011 and resampling in 2017–2018. Boreas River stream chemistry data presented in this report are for samples collected manually every other week.

Because the Boreas River streamflow record also began in 2014, the flow record for Buck Creek, which dates back to 2001, was used in the analysis of the ECASS resampling results to place the effects of flow conditions on stream chemistry during the surveys into context with respect to both seasonal variation and variation over the full length of record. Streamflow data during WASS and ECASS sampling were provided by the Buck Creek stream gaging station (station number 04253296; US Geological Survey, 2020). Stream stage recorded year-round at 15-minute intervals was used with flow measurements to develop a rating curve that enabled a time series of flow to be calculated. Procedures followed standard U.S. Geological Survey (USGS) methods (Rantz, 1982; Sauer and Turnipseed, 2010; Turnipseed and Sauer, 2010).

2.2 Chemical and Statistical Analyses

All stream water samples were analyzed for pH, ANC, BCS, conductivity, and concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), dissolved organic carbon (DOC), silicon (Si), ammonium (NH_4^+), total monomeric Al (Al_{tm}), and organic monomeric Al (Al_{o}). Concentrations of fluoride (F^-) were measured in all samples collected through September 2017. Concentrations of inorganic monomeric Al (Al_{i}) were determined by subtracting Al_{o} from Al_{tm} . The BCS was calculated from measurements of stream chemistry by the following formula: $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{RCOO}^-_{\text{s}}$; where RCOO^-_{s} equals the concentration ($\mu\text{eq L}^{-1}$) of strongly acidic organic anions estimated from DOC and anion deficits of samples with pH less than 4.5. Details on the derivation and application of the BCS are available elsewhere (Lawrence et al., 2018a; Lawrence et al., 2008a; Lawrence et al., 2007).

Chemical analysis of stream samples was done through a collaboration between the USGS New York Water Science Center Soil and Low-Ionic Strength Water Quality Laboratory (<https://www.usgs.gov/centers/ny-water/science/laboratory>; accessed May 3, 2022) and the Adirondack Lake Survey Corporation (ALSC) laboratory. Each of these laboratories followed the same US Environmental Protection Agency approved methods available at: <https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=30000TA0.PDF> (accessed May 3, 2022). Potential bias between laboratory results was evaluated by a comparison of chemical analyses conducted on samples collected biweekly from Buck Creek and North and South Buck streams, near Inlet, New York (Figure 1) from September 2006 through August 2008 (a total of 155 samples). Linear regression was used to adjust values to maintain consistency between laboratory results (Table 1). All stream samples collected before October 1, 2017, were analyzed in the ALSC laboratory. All stream samples collected on or after October 1, 2017, were analyzed in the USGS laboratory and converted to ensure

consistency with ALSC data using the equations in Table 1. Consistency among samples analyzed in the USGS laboratory before September 2006 and after October 2017 are maintained through the USGS Quality Assurance program as described in (Lincoln et al., 2009). There was no conversion between laboratories for F⁻ because it was not measured by the USGS laboratory after October 1, 2017. Values of BCS were determined from individual measurements that had been converted if the measurements had originated from the USGS laboratory.

Table 1. Linear Equations Showing the Adjustment for Bias Between USGS and ALSC Laboratory Results

For each analysis listed under Measurement, the linear equation is provided that adjusts for bias between USGS and ALSC laboratory results. Data in the column labeled USGS are the means of values determined in the USGS laboratory for the 61 samples collected in the November 2017 survey. Data in the column labeled ALSC are the USGS laboratory values after adjustment to ALSC results with the given equation. Where na appears, measurements were not made in both laboratories; $\mu\text{mol L}^{-1}$ is micromoles per liter, $\mu\text{mol C L}^{-1}$ is micromoles of carbon per liter, and $\mu\text{S cm}^{-1}$ is microsiemens per centimeter.

Measurement	Relationship	USGS	ALSC
ANC ($\mu\text{eq L}^{-1}$)	ALSC = 1.391 + (1.132 * USGS)	214.2	243.8
pH	ALSC = -0.381 + (1.090 * USGS)	6.245	6.426
SO ₄ ²⁻ ($\mu\text{mol L}^{-1}$)	ALSC = 7.309 + (0.833 * USGS)	29.4	31.8
NO ₃ ⁻ ($\mu\text{mol L}^{-1}$)	ALSC = 0.744 + (0.943 * USGS)	3.7	4.3
Cl ⁻ ($\mu\text{mol L}^{-1}$)	ALSC = 2.752 + (0.670 * USGS)	23.6	18.6
DOC ($\mu\text{mol C L}^{-1}$)	ALSC = 10.433 + (0.965 * USGS)	458.9	453.3
F ⁻ ($\mu\text{mol L}^{-1}$)	na	na	na
Al _i ($\mu\text{mol L}^{-1}$)	ALSC = 0.0210 + (1.071 * USGS)	1.1	1.2
Al _o ($\mu\text{mol L}^{-1}$)	ALSC = 1.192 + (1.106 * USGS)	1.2	2.4
Ca ²⁺ ($\mu\text{mol L}^{-1}$)	ALSC = 4.759 + (0.762 * USGS)	100.4	81.3
Mg ²⁺ ($\mu\text{mol L}^{-1}$)	ALSC = 0.092 + (0.968 * USGS)	34.5	33.5
Na ⁺ ($\mu\text{mol L}^{-1}$)	ALSC = -2.162 + (1.023 * USGS)	51.4	50.4
K ⁺ ($\mu\text{mol L}^{-1}$)	ALSC = 0.143 + (0.934 * USGS)	5.9	5.6
Si ($\mu\text{mol L}^{-1}$)	ALSC = 0.499 + (1.035 * USGS)	139.6	145.0
NH ₄ ⁺ ($\mu\text{mol L}^{-1}$)	ALSC = 0.0797 + (0.141 * USGS)	0.6	0.1
Conductivity ($\mu\text{S cm}^{-1}$)	ALSC = -2.101 + (1.127 * USGS)	30.8	32.6

All stream chemistry used to produce this report are available in the National Water Information System (NWIS) (US Geological Survey, 2020). Station identification codes, project stream codes, and coordinates for WASS and ECASS stream sampling locations used in this report are listed in appendix A.

Means of chemical concentrations determined in ECASS sampling were analyzed for differences in sampling years by paired t-tests or signed rank tests if the test for normality was not met. Values of pH were not converted to hydrogen (H^+) concentration to determine mean pH values. Time series of chemical concentrations in Maple Brook, Durgin Brook, and Balsam Brook were analyzed by linear regression. All statistical analyses in this study were done with SigmaPlot 14.

3 Changes in ECASS Stream Chemistry Between 2010–2011 and 2017–2018

Changes in the chemistry of spring snowmelt were evaluated in the 59 ECASS streams that were sampled in each of the surveys conducted in 2011, 2017, and 2018 (Table 2). The large number of samples provided high statistical power for discerning differences among means using paired t-tests or signed rank tests. Mean streamflow during each of the spring snowmelt surveys was similar, and when compared to the daily mean flow values over the full Buck Creek record (2001–2019), only 8% or less of daily mean flows were greater than the mean flow of the surveys (Table 2). Because the degree of stream acidification tends to increase as flow increases, the chemistry of these surveys was likely to be among the most acidic of their respective sampling years. The similarly high flow in each survey suggests that the influence of differing flow on stream chemistry was reasonably well controlled among the three surveys, although the lower flow in 2018 than in the other years may have played some role in the comparisons in Table 2.

Values of ANC and BCS were lower in 2017 than in 2011, although values of pH were not statistically different between these two years (Table 2). However, pH was statistically higher in 2018 than 2011. Concentrations of SO_4^{2-} were lower in 2017 and 2018 than in 2011, and NO_3^- concentrations were lower in 2017 than 2011, but not different between 2018 and 2011. Concentrations of Cl^- were lower in 2017 than 2011, but higher in 2018 than 2011, although the mean concentrations of all three surveys were similarly low. Concentrations of DOC were higher in 2017 than 2011, but not different between 2018 and 2011. Concentrations of F^- were lower in 2017 than 2011. There were no differences among surveys in Al_i concentrations. Concentrations of Al_o were higher in 2017 than 2011, but not in 2018. Concentrations of Ca^{2+} were lower in both 2017 and 2018 than in 2011. Concentrations of Mg^{2+} were also lower in 2017 than 2011, but higher in 2018 than 2011. Concentrations of Na^+ were not different between 2017 and 2018, but higher in 2018 than 2011. Concentrations of K^+ were higher in 2017 and 2018 than 2011. Concentrations of Si were lower in 2017 than 2011, but higher in 2018 than 2011. Concentrations of NH_4^+ were below instrument detection for a number of samples in each of the surveys and did not show differences between years. Conductivity was lower in 2017 than 2011, but higher in 2018.

Table 2. Number of Streams and Mean Chemistry Values of Samples Collected During the 2011, 2017, and 2018 ECASS Spring Snowmelt Surveys

The number of streams sampled in each survey; the mean flow at Buck Creek over the survey period based on measurements recorded at 15-minute intervals (meters per second; $m\ s^{-1}$); the percent of daily mean flows greater than the listed value ($\%>$) for the entire Buck Creek record (2001–2018); and mean values of chemical measurements in stream samples collected during spring snowmelt in 2011, 2017 and 2018. Differences in means were evaluated between 2011 and 2017, and between 2011 and 2018. Where $P > 0.10$, means are not considered different. All values of P shown in red indicate differences considered to be statistically significant. Where na appears, P values are not applicable; where nd appears, chemical data were not available.

ECASS Snowmelt	2011	2017	P	2018	P
Number of streams	59	59	na	59	na
Mean Flow ($m\ s^{-1}$)	0.308	0.347	na	0.208	na
$\% >$	4	3	na	8	na
ANC ($\mu eq\ L^{-1}$)	92.9	80.9	<0.01	148	<0.01
BCS ($\mu eq\ L^{-1}$)	98.0	80.5	<0.01	114	<0.01
pH	6.40	6.37	>0.10	6.64	<0.01
SO_4^{2-} ($\mu mol\ L^{-1}$)	35.0	26.1	<0.01	28.3	<0.01
NO_3^- ($\mu mol\ L^{-1}$)	15.9	11.2	<0.01	13.0	>0.10
Cl^- ($\mu mol\ L^{-1}$)	8.2	8.0	<0.10	9.3	<0.01
DOC ($\mu mol\ C\ L^{-1}$)	283	414	<0.01	278	>0.10
F^- ($\mu mol\ L^{-1}$)	1.7	1.3	<0.01	nd	na
Al_i ($\mu mol\ L^{-1}$)	0.7	0.7	>0.10	0.6	>0.10
Al_o ($\mu mol\ L^{-1}$)	2.2	2.6	<0.01	2.1	>0.10
Ca^{2+} ($\mu mol\ L^{-1}$)	63.1	57.3	<0.01	60.1	<0.01
Mg^{2+} ($\mu mol\ L^{-1}$)	20.9	17.5	<0.01	23.6	<0.05
Na^+ ($\mu mol\ L^{-1}$)	28.9	28.8	>0.10	33.7	<0.01
K^+ ($\mu mol\ L^{-1}$)	3.3	4.0	<0.01	4.2	<0.01
Si ($\mu mol\ L^{-1}$)	107	88.1	<0.01	115.6	<0.01
NH_4^+ ($\mu mol\ L^{-1}$)	0.6	0.1	>0.10	0.1	>0.10
Conductivity ($\mu S\ cm^{-1}$)	23.9	20.3	<0.01	26.0	>0.10

In summary, values of most spring snowmelt measurements in 2017 were less than in 2011, but values of most measurements in 2018 were higher than in 2011. If these differences were strongly driven by differences in flow, concentrations of Ca^{2+} would have likely been higher, not lower in 2018 than 2011, and DOC concentrations would have been lower in 2018 than 2011, rather than highly similar. Hydrologic conditions during the surveys may have varied across this large region, which could have contributed to the differences among survey results because flow data during surveys was obtained from a single stream (Buck Creek) located on the boundary of the ECASS and WASS regions. The mean values also did not reveal any indication of reductions of stream acidity over the six- and seven-year periods despite the continued decrease in acidic deposition that occurred through the study period (Lawrence and Roy, 2021). However, mean values of ANC, pH, and Al_i also did not suggest that acidification was impairing a large fraction of stream ecosystems during snowmelt in 2017 or 2018 in the ECASS region. Nevertheless, Ca^{2+} concentrations in streams suggested that Ca limitation in both terrestrial and aquatic ecosystems was likely within the region during the study period (Lawrence and Roy, 2021).

Changes in the chemistry of summer baseflow were evaluated in the 48 ECASS streams that were sampled in each of the surveys of 2010 and 2017 (Table 3). Mean streamflow during the two surveys was similar. When compared to the daily mean flow over the full Buck Creek record (2001–2019), 68% of Buck Creek flows were greater than the mean flow of the ECASS 2010 survey, and 74% of Buck Creek flows were greater than the mean flow during the 2017 survey. These percentages reflected the relatively low flows that are typical in August (Table 3). Nearly all measurements were lower in 2017 than in 2010, including values of ANC, BCS, and pH, and concentrations of SO_4^{2-} , NO_3^- , and Cl⁻. All base cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+) along with Si and conductivity were also lower in 2017 than 2010. Concentrations of NH_4^+ were lower in 2017 than 2010, as well. The only exceptions were Al_i and Al_o , which were not different between years, and DOC, which was higher in 2017 than 2010.

Despite highly similar flows in 2017 and 2010, the differences in chemistry between the surveys suggested that stream chemistry was slightly more acidic in 2017 than 2010. Nevertheless, the summer baseflow stream water acidity in both surveys was well buffered, as indicated by pH values that were approximately circumneutral. Most notably, the ratio of Ca^{2+} to SO_4^{2-} was 4.0 in 2017 and 3.2 in 2011. This increase in the micromoles of Ca^{2+} being leached per micromole of SO_4^{2-} indicates

some improvement in watershed Ca^{2+} availability. The large decrease in conductivity emphasizes that changes in water chemistry between surveys was driven by dilution resulting from the large decrease of SO_4^{2-} concentrations. The dilution was the likely cause of the increased DOC that led to the relatively small decrease in pH. These chemical changes are fully explored in Lawrence and Roy (2021).

Table 3. Number of Streams and Mean Chemistry Values of Samples Collected During the 2010 and 2017 ECASS Summer Baseflow Surveys

The number of streams sampled in each survey; the mean flow at Buck Creek over the survey period based on measurements recorded at 15-minute intervals; the percent of daily mean flows greater than the listed value (%>) for the entire Buck Creek record (2001–2018); and mean values of chemical measurements in stream samples collected during summer surveys in 2010 and 2017. Differences in means were evaluated between 2010 and 2017. Where $P > 0.10$, means are not considered different. All values of P shown in red indicate differences considered to be statistically significant. Where na appears, P values are not applicable.

ECASS Summer Baseflow	2010	2017	<i>P</i>
Number of streams	48	48	na
Mean Flow (m s^{-1})	0.024	0.019	na
% >	68	74	na
ANC ($\mu\text{eq L}^{-1}$)	361.0	281.9	<0.01
BCS ($\mu\text{eq L}^{-1}$)	361.0	307.0	<0.01
pH	6.99	6.92	= 0.01
SO_4^{2-} ($\mu\text{mol L}^{-1}$)	46.4	32.9	<0.01
NO_3^- ($\mu\text{mol L}^{-1}$)	8.8	6.4	<0.01
Cl^- ($\mu\text{mol L}^{-1}$)	10.2	9.4	<0.05
DOC ($\mu\text{mol C L}^{-1}$)	251.0	375.0	<0.01
F^- ($\mu\text{mol L}^{-1}$)	2.2	1.3	<0.01
Al_i ($\mu\text{mol L}^{-1}$)	0.3	0.3	>0.10
Al_o ($\mu\text{mol L}^{-1}$)	1.7	1.9	>0.10
Ca^{2+} ($\mu\text{mol L}^{-1}$)	148.8	131.1	<0.01
Mg^{2+} ($\mu\text{mol L}^{-1}$)	57.2	42.5	<0.01
Na^+ ($\mu\text{mol L}^{-1}$)	63.0	53.7	<0.01
K^+ ($\mu\text{mol L}^{-1}$)	5.0	3.8	<0.01
Si ($\mu\text{mol L}^{-1}$)	214.9	168.7	<0.01
NH_4^+ ($\mu\text{mol L}^{-1}$)	0.7	0.1	<0.01
Conductivity ($\mu\text{S cm}^{-1}$)	51.4	41.1	<0.01

Changes in the chemistry of streams in autumn after leaf drop were evaluated in the 61 ECASS streams that were sampled in each of the autumn surveys of 2011 and 2017 (Table 4). Mean streamflow in 2011 differed substantially from streamflow in 2017 during these surveys. When compared to the daily mean values over the full Buck Creek record (2001–2019), 50% of daily mean flows were greater than the mean flow for the survey in 2011, but only 8% of daily mean flows were greater than the mean flow for the survey in 2017. The mean survey flow of 2017 was nearly the same as that during the 2018 snowmelt survey (Table 2).

Mean ANC and BCS were not different between 2011 and 2017, but mean pH was lower in 2017 than 2011 (Table 4). These results do not fit the typical pattern in which both ANC and BCS increase and decrease together with pH, although the difference in pH between surveys was not large. Concentrations of SO_4^{2-} and NO_3^- were lower in 2017 than in 2011, and concentrations of Cl^- were higher in 2017 than 2011. The concentration of DOC was substantially higher in 2017 than 2011 and can be considered the most pronounced difference between surveys observed in any of the measurements. Concentrations of Al_i increased from 2011 to 2017, exceeding the threshold for negative effects on brook trout in the 2017 survey (Baldigo et al., 2020). However, Al_o concentrations did not differ between surveys. Concentrations of Ca^{2+} were lower in 2017 than 2011, but there was no difference between surveys in Mg^{2+} concentrations. Concentrations of Na^+ and K^+ were higher in 2017 than 2011, whereas concentrations of Si were lower in 2017 than 2011. Concentrations of NH_4^+ did not differ between surveys, and conductivity was lower in 2017 than 2011, although the difference was small.

Differences in the results between autumn surveys were not fully consistent with what would be expected from the large difference in flow conditions. Typically, lower ANC and BCS are generally associated with higher flow, but in this comparison, ANC and BCS were similar under widely differing flow conditions (Lawrence et al., 2008a). The minimal differences in acidity between the two surveys suggests that, overall, episodic acidification was not a major factor in the headwater streams of the region in 2017. The substantially higher DOC concentrations in 2017 than 2011 can be attributed to high flows soon after leaf drop. Under conditions of high streamflow, soluble carbon available from the freshly deposited leaves is more readily transported into stream channels through shallow hydrologic flow paths (Lawrence and Roy, 2021). Because DOC is a source of acidity, the lower pH in 2017 is likely a result of the higher DOC concentrations. However, the higher acidity associated with DOC was not sufficient to result in lower BCS in 2017.

Table 4. Number of Streams and Mean Chemistry Values of Samples Collected During the 2011 and 2017 ECASS Autumn Surveys

The number of streams sampled in each survey; the mean flow at Buck Creek over the survey period based on measurements recorded at 15-minute intervals; the percent of daily mean flows greater than the listed value (%>) for the entire Buck Creek record (2001–2018); and mean values of chemical measurements in stream samples collected during autumn surveys in 2011 and 2017. Differences in means were evaluated between 2011 and 2017. Where $P > 0.10$, means are not considered different. All values of P shown in red indicate differences considered to be statistically significant. Where na appears, P values are not applicable; where nd appears, chemical data were not available.

ECASS Autumn	2011	2017	P
Number of streams	61	61	na
Mean Flow (m s^{-1})	0.040	0.210	na
% >	50	8	na
ANC ($\mu\text{eq L}^{-1}$)	197.9	243.8	>0.10
BCS ($\mu\text{eq L}^{-1}$)	187.2	169.1	>0.10
pH	6.72	6.43	<0.01
SO_4^{2-} ($\mu\text{mol L}^{-1}$)	38.9	31.8	<0.01
NO_3^- ($\mu\text{mol L}^{-1}$)	8.1	4.3	<0.01
Cl^- ($\mu\text{mol L}^{-1}$)	9.5	18.6	<0.01
DOC ($\mu\text{mol C L}^{-1}$)	256.4	453.3	<0.01
F ($\mu\text{mol L}^{-1}$)	1.7	nd	na
Al_i ($\mu\text{mol L}^{-1}$)	0.3	1.2	<0.01
Al_o ($\mu\text{mol L}^{-1}$)	2.2	2.4	>0.10
Ca^{2+} ($\mu\text{mol L}^{-1}$)	93.2	81.3	<0.01
Mg^{2+} ($\mu\text{mol L}^{-1}$)	33.7	33.5	>0.10
Na^+ ($\mu\text{mol L}^{-1}$)	41.4	50.4	>0.10
K^+ ($\mu\text{mol L}^{-1}$)	3.6	5.6	<0.01
Si ($\mu\text{mol L}^{-1}$)	153.8	145.0	<0.05
NH_4^+ ($\mu\text{mol L}^{-1}$)	0.2	0.1	>0.10
Conductivity ($\mu\text{S cm}^{-1}$)	33.2	32.6	<0.01

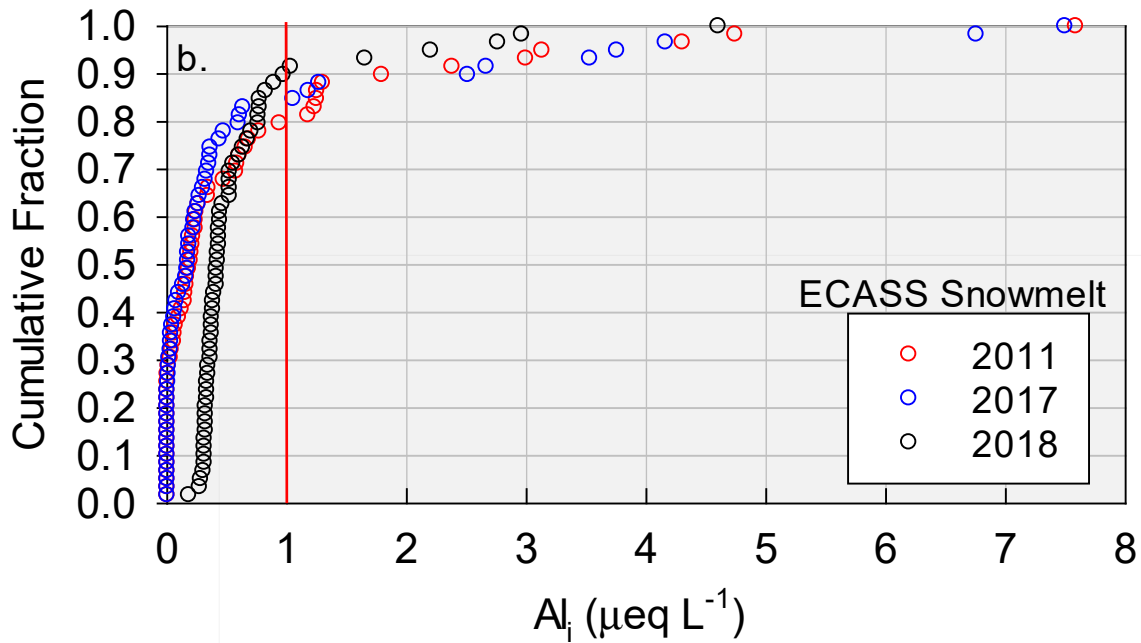
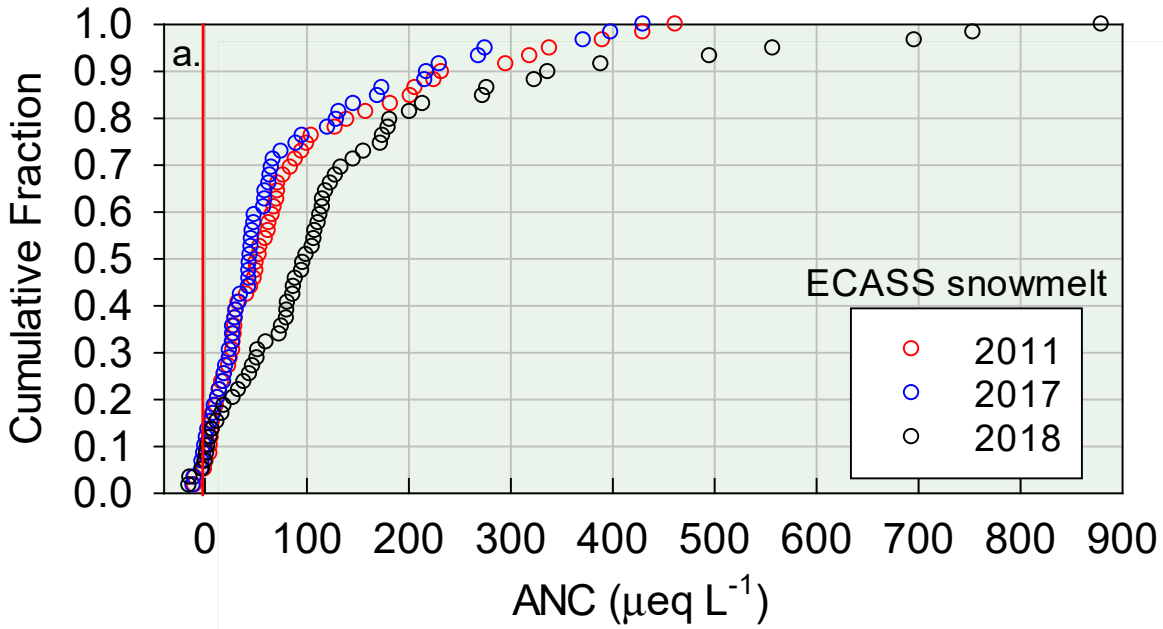
Overall, mean values of chemical measurements did not indicate large changes between 2010–2011 and 2017–2018 in the snowmelt, summer baseflow, or autumn surveys. These results also showed minimal indications of acidification in any of the surveys, with mean values of ANC remaining above $80 \mu\text{eq L}^{-1}$, mean pH remaining above 6.37, and Al_i remaining below $1.0 \mu\text{mol L}^{-1}$, with the exception of the mean of $1.2 \mu\text{mol L}^{-1}$ in the 2017 autumn survey. However, it should be noted that the mean values are based on a range of values among the streams and therefore are influenced by outlier values.

To evaluate the distribution of values across the sampled streams, cumulative fraction diagrams were developed for ANC and Al_i measurements for the 2011, 2017, and 2018 snowmelt surveys. Values of ANC in each of the surveys ranged from less than $0 \mu\text{eq L}^{-1}$ to greater than $400 \mu\text{eq L}^{-1}$ (Figure 2a). Approximately 50% of streams in the 2011 and 2017 surveys had ANC values less than $50 \mu\text{eq L}^{-1}$, which is the minimum value considered to be necessary to avoid ecosystem impairment from acidification (Driscoll et al., 2001). Approximately 15% of the streams in all surveys had ANC values near or below zero. These ANC values have recently shown to be associated with substantial impairment of fish communities (Baldigo et al., 2019).

During the 2011 snowmelt sampling, 20% of streams had Al_i concentrations greater than $1.0 \mu\text{mol L}^{-1}$ (Figure 2b), the concentration above which is toxic to fish (Baldigo et al., 2020). In the 2017 and 2018 snowmelt samplings 15% and 10% of the streams, respectively, had Al_i concentrations above this level. Based on the estimated total length of headwater streams in the ECASS region of 11,494 km (Lawrence et al., 2018b), the 10% of ECASS streams that experienced harmful Al_i concentrations ($\text{Al}_i > 1.0 \mu\text{mol L}^{-1}$) during the 2018 snowmelt survey equated to a total length of 1,091 km of headwater stream length in the region. Because only accessible headwater streams were sampled in the ECASS, the percentages of streams determined to have Al_i concentrations above $1.0 \mu\text{mol L}^{-1}$ were underestimated. With increases in elevation, accessibility of streams tended to decrease, but acidification tended to increase (Lawrence et al., 2008a). Therefore, the sampled streams were somewhat biased towards lower elevations and lower Al_i concentrations.

Figure 2. Cumulative Fractions of ANC Measurements and Al_i Concentrations in ECASS Streams Sampled During Spring Snowmelt Surveys in 2011, 2017, and 2018

The vertical red line in (a) indicates the value of ANC below which fish communities are impaired; the vertical red line in (b) indicates the Al_i concentration above which is harmful to fish species found in these streams.



4 Changes in High-Elevation Stream Chemistry Between 2010–2011 and 2017

High-elevation streams were included in ECASS sampling because these watersheds are generally regarded as those most sensitive to acidic deposition within the Adirondack region and elsewhere (Lawrence et al., 2015). Accessibility limited the number and choice of streams that could be practically sampled so the comparison is based on the mean of 12 streams during spring snowmelt and 11 streams during summer baseflow. There were no stream gages in high-elevation landscapes in the Adirondack region to provide flow data during the high-elevation stream sampling. Results of spring snowmelt sampling showed conditions to be less acidic in 2017 than in 2011, based on higher mean values of ANC, BCS, and pH in the more recent sampling (Table 5). Concentrations of SO_4^{2-} and NO_3^- measured in 2017 did not differ from concentrations measured in 2011. The lack of decrease in SO_4^{2-} concentrations between sample years differed from other ECASS resampling comparisons, which all showed lower SO_4^{2-} concentrations in the more recent samplings. Concentrations of Cl^- were lower in 2017 than 2011, but the difference was less than $0.5 \mu\text{mol L}^{-1}$.

Concentrations of DOC were higher in 2017 than in 2011, concentrations of F^- were lower in 2017 than 2011, and concentrations of Al_i and Al_o did not differ between sampling years (Table 5). Mean concentrations of Al_i , however, were at levels that would cause low to moderate mortality of brook trout in both sampling years (Baldigo et al., 2020). Concentrations of Ca^{2+} in high-elevation streams were higher in 2017 than 2011, which differed from ECASS measurements during spring snowmelt, summer baseflow, and autumn, which all showed lower Ca^{2+} concentrations in 2017 than 2011. Concentrations of Mg^{2+} did not differ between years, but Na^+ concentrations were higher in 2017 than 2011 and K^+ concentrations were lower in 2017 than 2011. Like Ca^{2+} , Si concentrations were higher in 2017 than 2011, which differed from other ECASS comparisons that were lower in 2017 than 2011 in each of the seasons. Concentrations of NH_4^+ were lower in 2017 than 2011, but concentrations were low in both years, and the decrease was less than $0.5 \mu\text{mol L}^{-1}$. Conductivity did not differ between years.

Table 5. Mean Values of Chemical Measurements in High-Elevation Stream Samples Collected During Spring Snowmelt Surveys in 2011 and 2017

Differences in means were evaluated between 2011 and 2017. Where $P > 0.10$, means are not considered different. All values of P shown in red indicate differences considered to be statistically significant. Where na appears, the P value is not applicable.

High-Elevation Snowmelt	2011	2017	P
Number of streams	12	12	na
ANC ($\mu\text{eq L}^{-1}$)	0.4	11.6	<0.05
BCS ($\mu\text{eq L}^{-1}$)	-22.0	-8.3	<0.10
pH	5.1	5.54	<0.01
SO_4^{2-} ($\mu\text{mol L}^{-1}$)	18.7	18.9	>0.10
NO_3^- ($\mu\text{mol L}^{-1}$)	14.9	13.6	>0.10
Cl^- ($\mu\text{mol L}^{-1}$)	3.4	3.0	<0.05
DOC ($\mu\text{mol C L}^{-1}$)	455.8	523.2	<0.05
F^- ($\mu\text{mol L}^{-1}$)	1.1	0.9	<0.01
Al_i ($\mu\text{mol L}^{-1}$)	2.4	2.6	>0.10
Al_o ($\mu\text{mol L}^{-1}$)	6.3	6.4	>0.10
Ca^{2+} ($\mu\text{mol L}^{-1}$)	20.2	25.1	<0.05
Mg^{2+} ($\mu\text{mol L}^{-1}$)	5.0	5.6	>0.10
Na^+ ($\mu\text{mol L}^{-1}$)	11.4	17.3	<0.01
K^+ ($\mu\text{mol L}^{-1}$)	2.2	1.0	<0.01
Si ($\mu\text{mol L}^{-1}$)	45.7	66.7	<0.01
NH_4^+ ($\mu\text{mol L}^{-1}$)	0.8	0.4	<0.05
Conductivity ($\mu\text{S cm}^{-1}$)	12.8	12.2	>0.10

Like results obtained during spring snowmelt, the 11 high-elevation streams sampled during summer baseflow were less acidic in the more recent sampling than in the initial sampling. Mean values of ANC, BCS, and pH were higher in 2017 than 2010, although the difference was not significant because of high variability among the streams (Table 6). This variability indicates that some of the watersheds have relatively deep flow paths that provide effective acid buffering during low flow, but some remain chronically acidic despite the differences in flow between snowmelt and summer. Also, in contrast to snowmelt results, SO_4^{2-} concentrations were lower rather than higher in 2017 than in the initial sampling in 2010. Concentrations of NO_3^- , Cl^- , and DOC did not differ between years. Concentrations of F^- were lower in 2017 than 2010. Concentrations of Al_i decreased from slightly above the $1.0 \mu\text{mol L}^{-1}$ threshold

for brook trout harm (Baldigo et al., 2020), to below this value, whereas Al_o did not differ between years. Concentrations of Ca^{2+} , Mg^{2+} , and K^+ did not differ between years, but Na^+ increased. Concentrations of Si and conductivity also did not differ between years, while NH_4^+ concentrations were near zero in both years (although showed an increase).

Table 6. Mean Values of Chemical Measurements in Stream Samples Collected During Summer Baseflow Surveys in 2010 and 2017

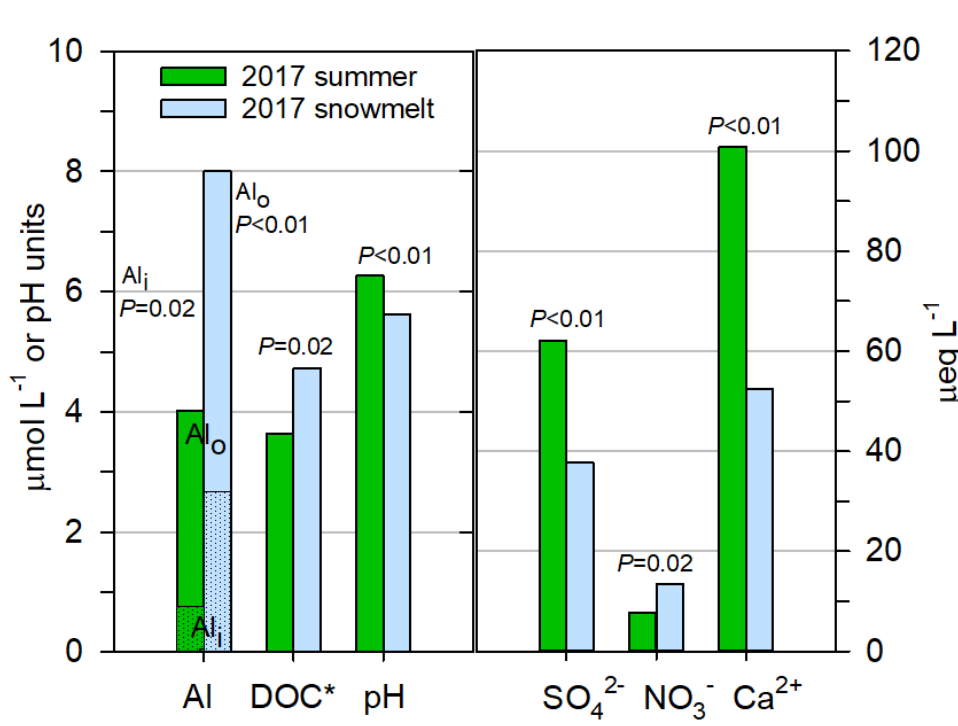
Differences in means were evaluated between 2010 and 2017. Where $P > 0.10$, means are not considered different. All values of P shown in red indicate differences considered to be statistically significant. Where na appears, the P value is not applicable.

High-Elevation Summer Baseflow	2010	2017	P
Number of streams	11	11	na
ANC ($\mu eq L^{-1}$)	39.5	62.6	>0.10
BCS ($\mu eq L^{-1}$)	25.8	57.7	>0.10
pH	6.05	6.27	<0.05
SO_4^{2-} ($\mu mol L^{-1}$)	38.6	31.0	<0.01
NO_3^- ($\mu mol L^{-1}$)	6.8	7.8	>0.10
Cl^- ($\mu mol L^{-1}$)	5.2	5.0	>0.10
DOC ($\mu mol C L^{-1}$)	325.0	363.7	>0.10
F^- ($\mu mol L^{-1}$)	1.4	0.8	<0.01
Al_i ($\mu mol L^{-1}$)	1.1	0.7	<0.10
Al_o ($\mu mol L^{-1}$)	3.4	3.3	>0.10
Ca^{2+} ($\mu mol L^{-1}$)	43.3	50.4	>0.10
Mg^{2+} ($\mu mol L^{-1}$)	11.3	11.9	>0.10
Na^+ ($\mu mol L^{-1}$)	25.6	30.2	<0.10
K^+ ($\mu mol L^{-1}$)	1.1	1.3	>0.10
Si ($\mu mol L^{-1}$)	148.0	134.4	>0.10
NH_4^+ ($\mu mol L^{-1}$)	0.0	0.2	<0.01
Conductivity ($\mu S cm^{-1}$)	17.6	18.4	>0.10

Substantially higher mean concentrations of both Al_i and Al_o were observed during spring snowmelt than during summer baseflow (Figure 3) for the same high-elevation streams sampled in each season. Concentrations of DOC were also higher during snowmelt than summer baseflow and pH was lower during summer baseflow than during snowmelt. The higher DOC concentrations and lower pH may have played a role in higher Al_o and Al_i concentrations, respectively, during snowmelt than summer baseflow. Concentrations of SO_4^{2-} were considerably lower during snowmelt than summer baseflow. Concentrations of NO_3^- were higher during snowmelt than during summer baseflow, but the difference was not large, and NO_3^- concentrations during both surveys were much less than SO_4^{2-} . The mean concentration of Ca^{2+} during snowmelt was approximately half that of the summer baseflow survey.

Figure 3. Mean Values of Chemical Measurements in High-Elevation Stream Samples Collected During Summer Baseflow and Spring Snowmelt in 2017

Mean values of Al_i (inorganic monomeric Al; stippled), Al_o (organic monomeric Al), DOC^* (dissolved organic carbon concentration divided by 100 for graph scaling), pH, SO_4^{2-} , NO_3^- , and Ca^{2+} for summer baseflow and spring snowmelt samples from high-elevation streams sampled in 2017. All comparisons between summer baseflow and snowmelt are considered different based on $P < 0.05$. Note that Al and DOC^* are expressed in $\mu mol L^{-1}$; whereas SO_4^{2-} , NO_3^- , and Ca^{2+} are expressed in $\mu eq L^{-1}$.



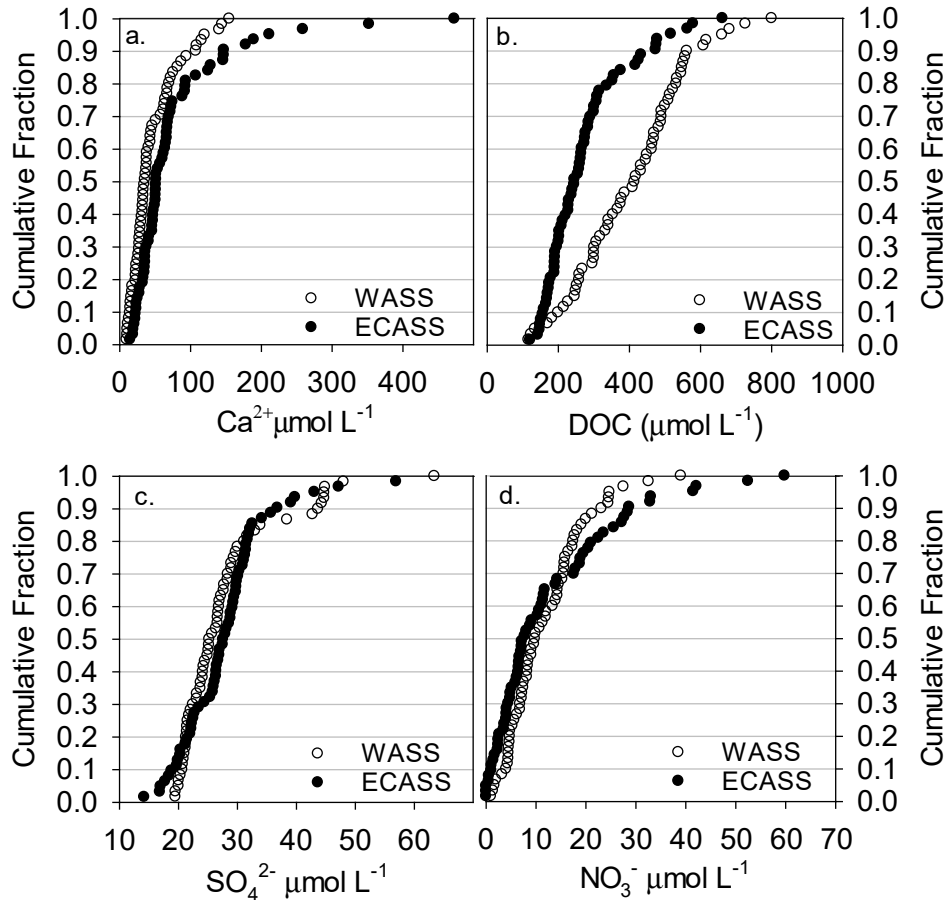
The limited sampling done in the high-elevation streams during snowmelt in 2017 indicated that 9 of 12 streams had Al_i concentrations above $1.5 \mu\text{mol L}^{-1}$, although the mean concentration of Al_i was $2.6 \mu\text{mol L}^{-1}$, which falls in the range causing low to moderate mortality of brook trout (Baldigo et al., 2020). The mean pH for the 12 streams was a moderately acidic 5.62. Nevertheless, stream chemistry during snowmelt was considerably more acidic than during summer baseflow. The higher acidity during snowmelt occurred despite considerably lower combined concentrations of SO_4^{2-} and NO_3^- during snowmelt than during summer baseflow. The higher DOC concentrations during snowmelt were likely to have contributed to greater acidity, but the greatest factor driving higher acidity during snowmelt was the decrease by half of Ca^{2+} concentrations. Because of the low Ca availability in these watersheds, the increased stream flows of spring snowmelt were acidified to levels harmful to biota even though concentrations of SO_4^{2-} and NO_3^- were substantially lower during spring snowmelt

5 Comparison of ECASS and WASS Stream Chemistry in 2018

The overlap in ECASS and WASS sampling during spring snowmelt in 2018 enabled a direct spatial comparison to be made between the regions. The report of Lawrence et al. (2018b) included a spatial comparison of ECASS and WASS regions based on the original samplings, but the WASS data were from 2003–2005, and the ECASS data were from 2010–2011. This 5 to 8-year gap occurred at a time when acidic deposition was steadily decreasing (Lawrence et al., 2020). Analysis of those data showed that some change was likely to have occurred in the chemistry of WASS streams between the two time periods, which complicated the comparison somewhat. In Figure 4, stream chemistry was compared from the same year and season to provide a more recent spatial comparison using temporally compatible data.

The distribution of Ca^{2+} concentrations indicated higher values in ECASS than WASS streams throughout the full concentration range, with a widening difference at the highest concentrations (Figure 4a). Concentrations of DOC were substantially higher in WASS streams than ECASS streams throughout the full range except for the lowest 5% of values (figure 4b). In the mid-concentration range, DOC concentrations in WASS streams were approximately double those of the ECASS streams. Concentrations of SO_4^{2-} in WASS and ECASS streams were similar, overlapping at two points in the distributions (Figure 4c). At the lowest concentrations, values in ECASS streams were somewhat lower than in WASS streams. Concentrations of NO_3^- tended to be lower in ECASS streams than WASS streams in the lowest 70% of the concentration range but were higher in the highest 30% of the range (Figure 4d).

Figure 4. Cumulative Fractions of Ca^{2+} (a), DOC (dissolved organic carbon) (b), SO_4^{2-} (c), and NO_3^- (d) Concentrations in WASS (Western Adirondack Stream Survey) and ECASS (East-Central Adirondack Stream Survey) Streams Sampled During 2018 Snowmelt Surveys



These data provided the first surface water assessment of the full Adirondack region using the same statistical sampling design while avoiding temporal effects of season and year. Lower Ca^{2+} concentrations and minimal difference in SO_4^{2-} concentrations in WASS streams than ECASS streams throughout the concentration ranges support the findings of the prior analyses (Lawrence et al., 2018b), which suggested a greater sensitivity to acidic deposition in the WASS region than the ECASS region. Prior studies also suggested that lower levels of acidic deposition in the ECASS region than the WASS region contributed to a lower degree of ecosystem acidification in the ECASS region (Sullivan et al., 2013). Under previous high levels of acidic deposition, the general decrease in acidic deposition moving from the southwest to the northeast (Ito et al., 2002) is likely to have been a causal factor in the general west to east decrease

in acidification. However, under the current low levels of acidic deposition, the stream chemistry results indicate that the spatial pattern of acidification effects is largely driven by inherent Ca^{2+} availability tied to spatial variations in geologic factors that control acid buffering. The higher degree of acidification in the WASS region than the ECASS region is likely to extend into the future as a result of the relatively high DOC concentrations in the WASS. The organic acidity associated with DOC combined with (1) the release of residual SO_4^{2-} and NO_3^- from soils and (2) low Ca levels available to buffer acidity will continue to suppress pH and ANC increases, and mobilize harmful levels of Al_i in the WASS region (Lawrence and Roy, 2021; Lawrence et al., 2020). These affects will also continue in some ECASS watersheds, but to a lesser degree in a lower percentage of watersheds across the region.

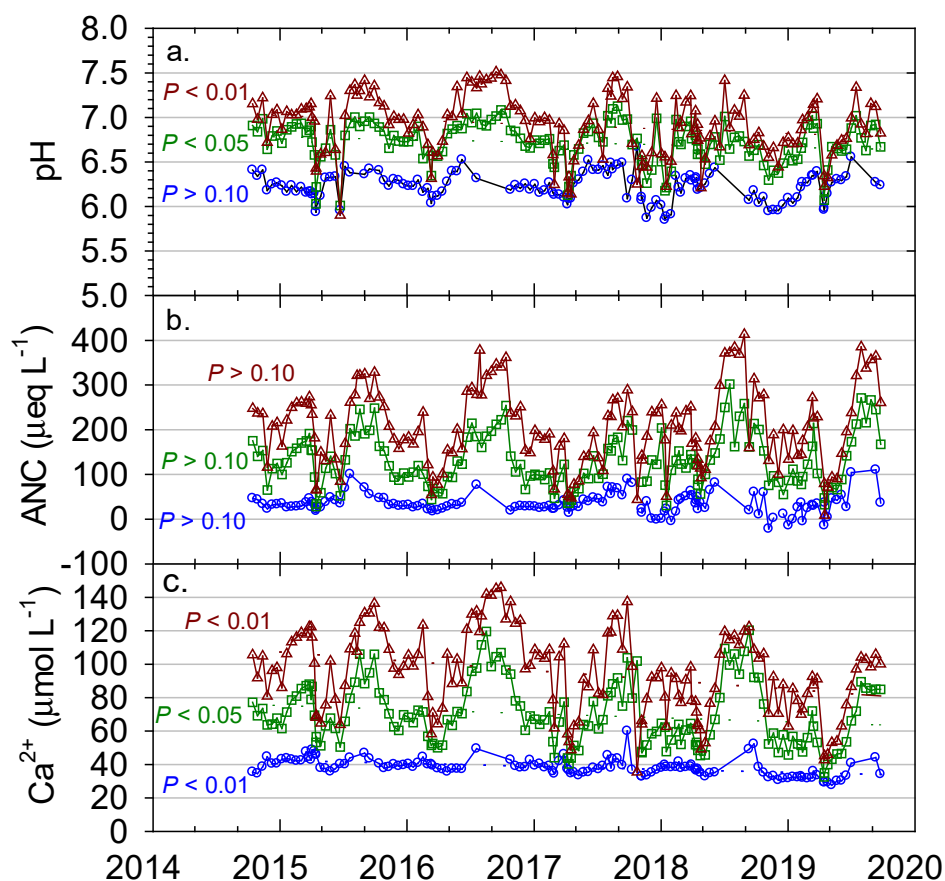
6 Temporal Trends in Stream Chemistry in the Boreas River Watersheds 2014–2019

The 2010–2011 ECASS did not show a high degree of acidification in most streams (Lawrence et al., 2018b), therefore acidic deposition decreases would, in general, not be expected to cause strong trends in stream chemistry during the 2010s, particularly since levels of acidic deposition were relatively low at the start of the decade in 2010 (Lawrence and Roy, 2021). However, stream chemistry might reflect factors related to long-term acidic deposition effects on soils, possible trending climate factors, or other influences not yet identified. Long-term monitoring of stream chemistry in the Boreas River watersheds is therefore warranted although there is no evidence of a strong degree of past ecosystem acidification. Nevertheless, the number of statistically significant trends in stream chemistry observed for the period 2014–2019 in the Boreas River watersheds is somewhat remarkable given the relatively short five-year record.

Values of pH did not exhibit a trend in Maple Brook, which had the lowest pH (occasionally dropping below 6.0) but did decrease in Balsam Brook and Durgin Brook (Figure 5a). Although pH decreased in two streams, none of the streams exhibited trends in ANC. Most ANC values in Balsam Brook and Durgin Brook were above $100 \mu\text{eq L}^{-1}$, but in Maple Brook most values were below $100 \mu\text{eq L}^{-1}$, and less than $0.0 \mu\text{eq L}^{-1}$ on a few occasions (Figure 5b). Concentrations of Ca^{2+} exhibited clear decreases over the five years in all three streams, which is similar to measurements throughout the Adirondack region (Lawrence and Roy, 2021). Durgin Brook had the highest concentrations of Ca^{2+} and also exhibited the largest decrease in concentrations of the three streams (Figure 5c). Concentrations of Ca^{2+} in Maple Brook were below levels that are considered to be growth limiting in aquatic and terrestrial ecosystems (Lawrence et al., 2020; Weyhenmeyer et al., 2019).

Figure 5. Chemical Measurements Based on Biweekly Sampling of Durgin Brook, Balsam Brook, and Maple Brook

Durgin Brook shown as red triangles, Balsam Brook shown as green squares, and Maple Brook shown as blue circles. Best-fit lines (where $P < 0.05$ or 0.01) are shown as dashes color-matched by stream. Values of P are also color-matched by stream and are positioned near their respective stream. ANC represents acid-neutralizing capacity.

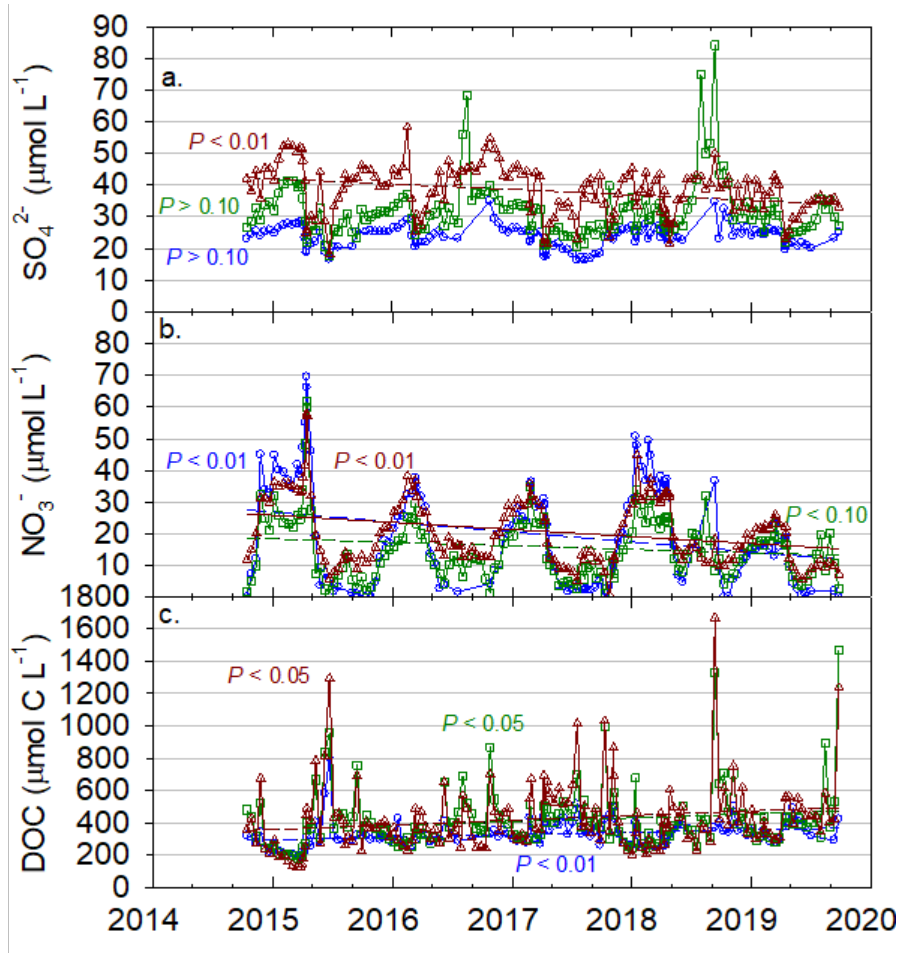


Balsam Brook and Maple Brook did not exhibit a decrease in SO_4^{2-} concentrations from 2014 through 2019, although Durgin Brook did exhibit a decrease over this period (Figure 6a). Concentrations of NO_3^- showed distinct synchronous seasonal variability in each of the streams (Figure 6b). Concentrations in Durgin Brook and Maple Brook were highly similar, but somewhat lower in Balsam Brook. Most notable was the pronounced downward trends in Durgin Brook and Maple Brook. Values of the best fit lines at the end of 2019 were approximately half that of the values in 2014. The similarity in concentrations and trends occurred despite differences in watershed vegetation and drainage. Maple Brook watershed is forested primarily by hardwoods and is well drained throughout,

whereas Durgin Brook watershed has extensive wetlands and conifer vegetation. A more modest but also distinct decrease in NO_3^- concentrations was measured in Balsam Brook. Measurements of DOC concentrations showed the same increasing trends in each stream (Figure 6c) that have been seen in many Adirondack surface waters (Driscoll et al., 2016; Lawrence and Roy, 2021). These strong increasing trends in DOC occurring in streams during a period with little or no indication of further chemical recovery from acidic deposition indicates that the primary driver of the trends is not a simple decrease in the acidity of atmospheric deposition. The strong DOC trends in Durgin Brook and Balsam Brook, which are streams that are unlikely to have ever experienced more than minimal acidification, suggest the need for further investigation to expand our understanding of (1) the mechanisms behind the increasing DOC trends and (2) the processes through which the increasing DOC trends are related to other trends exhibited by these streams.

Figure 6. Chemical Measurements Based on Biweekly Sampling of Durgin Brook, Balsam Brook, and Maple Brook

Durgin Brook shown as red triangles, Balsam Brook shown as green squares, and Maple Brook shown as blue circles. Best-fit lines are shown as dashes color-matched by stream. Values of P are also color-matched by stream and are positioned near their respective stream.



7 Primary Findings of ECASS Stream Resampling

- Although acidic deposition continued to decrease over the study period, mean chemical concentration values of 59 streams selected to represent the range of stream chemistry of the ECASS region did not indicate clear changes in snowmelt stream acidity over the six-to-seven- year study period.
- Mean SO_4^{2-} concentrations measured during summer baseflow decreased substantially between 2010 and 2017, which resulted in diluted stream water expressed by decreased concentrations of base cations and conductivity, and increased DOC concentrations.
- Mean values of chemical measurements for the ECASS region during autumn surveys indicated that, in general, large increases in flow during this season triggered only minimal episodic acidification.
- ECASS snowmelt sampling indicated that 10% to 15% of streams had ANC and Al_i values harmful to species of fish that occur in the region, which equates to more than 1,091 km (684 miles) of headwater streams in the ECASS region.
- In high-elevation streams, snowmelt acidity was appreciably higher than during summer baseflow despite lower concentrations of SO_4^{2-} and NO_3^- during spring snowmelt relative to summer baseflow. Substantially greater acidity in streams during snowmelt than in summer occurred because snowmelt concentrations of Ca^{2+} were only 50% of the values measured during summer baseflow. These results highlight the ongoing effect of soil Ca^{2+} depletion in delaying recovery of stream chemistry.
- Stream acidification is currently impacting a larger percentage of headwater streams in the WASS region than the ECASS region primarily due to geologic factors in the ECASS region that provide better acid buffering than in the WASS region.
- Stream acidification is likely to continue in some streams of both regions for the foreseeable future due to further increases in DOC, continued release of residual SO_4^{2-} and NO_3^- from soils, and slow recovery of watershed Ca^{2+} availability.
- Despite a history of minimal acidic deposition effects, pronounced decreasing trends in NO_3^- and Ca^{2+} and a pronounced increasing trend in DOC were observed in all three streams in the Boreas River monitoring watersheds from 2014 through 2019.

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Appendix A

National Water Information System (NWIS) station IDs, project codes and sampling coordinates for all study streams. Note: Maple Brook and Balsam Brook have NWIS names of Vanderwhacker Brook, Trib 1 and Vanderwhacker Brook, Trib 2, respectively.

Table A-1. NWIS Station IDs, Project Codes and Coordinates for all Streams

NWIS Station ID	Project Stream Code	Latitude	Longitude
04253296	Buck Creek	43.743889	-74.722222
04253295	North Buck	43.745	-74.714444
04253294	South Buck	43.743056	-74.714722
01315226	Maple Brook	43.945444	-73.988361
01315227	Balsam Brook	43.533806	-74.861833
01315170	Durgin Brook	43.939833	73.953611
441353073474701	4	44.231442	-73.796611
441613073370701	9	44.270403	-73.618889
440759073442801	10	44.133181	-73.741208
435626074265101	15	43.940711	-74.447661
441324074200401	22	44.223344	-74.334661
444319073493501	26	44.721972	-73.826444
442300073495101	32	44.383539	-73.831019
435132073534001	35	43.859083	-73.894603
434307074185401	36	43.718650	-74.315033
440151074015501	45	44.031033	-74.032117
432407074425401	52	43.401953	-74.715142
441432073504301	57	44.242339	-73.845519
435446074285901	65	43.912778	-74.483158
435704074263401	68	43.951383	-74.442997
431522073543501	75	43.256150	-73.909983
433555074042001	76	43.598808	-74.072475
441127073491501	77	44.190850	-73.821111
442137073291101	79	44.360419	-73.486561
432242074563101	80	43.378578	-74.942011
431705074114501	81	43.284828	-74.195978
441237073392501	82	44.210511	-73.656947
442839073324801	87	44.477578	-73.546708
441820073485301	105	44.305750	-73.814861
443535073421401	112	44.593069	-73.703986

441957073314601	114	44.332678	-73.529664
441452074232501	119	44.247892	-74.390544
433005074183801	120	43.501447	-74.310594
441654073394201	125	44.281742	-73.661894
440742073391001	128	44.128356	-73.652889

Table A-2. NWIS Station IDs, Project Codes and Coordinates for all Streams

NWIS Database Code	Project Stream Code	Latitude	Longitude
431517074211201	129	43.254925	-74.353489
441702073411801	130	44.283992	-73.688378
435740074240801	139	43.961272	-74.402339
435441074242501	140	43.911467	-74.407125
434233074160501	150	43.709178	-74.268211
435806074030401	156	43.968428	-74.051339
435201074254001	157	43.866956	-74.427978
434304074070901	159	43.717839	-74.119197
441051073494401	171	44.181078	-73.828894
435650073592601	175	43.947319	-73.990739
431818074121301	176	43.305000	-74.203700
431557074140901	188	43.266042	-74.235844
444252074264401	214	44.714703	-74.445789
435714074020701	215	43.953969	-74.035350
432532074183401	216	43.425811	-74.309566
434503073503001	218	43.751028	-73.841919
431000074294001	224	43.166922	-74.494692
434043073354101	227	43.678867	-73.594811
443706073384301	231	44.618558	-73.645411
434805073494101	234	43.801617	-73.828147
441120073552501	237	44.188994	-73.923878
441551073324101	242	44.264353	-73.544850
431805074090401	246	43.301594	-74.151356
441446074151301	252	44.245303	-74.252979
440340073411001	258	44.061264	-73.686189
443337074011601	259	44.560336	-74.021306
441715073551001	261	44.287506	-73.919706
442638073520601	265	44.444136	-73.868411
443409074051501	271	44.569361	-74.087750
441232073405301	272	44.208931	-73.681511
433605074065001	274	43.601578	-74.114061
440615073413201	275	44.104169	-73.692358

434845073302501	277	43.812603	-73.507017
431555074214301	281	43.265283	-74.362019
441549075114301	1001	44.263831	-75.195383
441512075092701	1006	44.253353	-75.157519
441556075110701	1007	44.265556	-75.185489
441731075125901	1009	44.291972	-75.216408
432157074255501	1010	43.366078	-74.432200
441042073435701	2000	44.178392	-73.732522
440714073502701	2001	44.120819	-73.841067

Table A-3. NWIS Station IDs, Project Codes and Coordinates for all Streams

NWIS Database Code	Project Stream Code	Latitude	Longitude
440609073491401	2002	44.102536	-73.820603
441214073500601	2003	44.204033	-73.835208
442322073535101	2004	44.389589	-73.897578
442243073542001	2006	44.378683	-73.905822
440945073483301	2008	44.162633	-73.809400
440738073591201	2009	44.127264	-73.986858
440813073573301	2010	44.137039	-73.959369
440900073555301	2011	44.150056	-73.931472
440956073540901	2012	44.165758	-73.902622
440932075133301	6007	44.159156	-75.226053
441255075143901	6014	44.215389	-75.244419
441352075131401	6015	44.231372	-75.220569
440859075065901	7003	44.149778	-75.116478
441053075044101	7005	44.181411	-75.078131
441408075062001	7019	44.235767	-75.105628
441332075024401	7028	44.225814	-75.045636
440910074533001	8003	44.153025	-74.891894
440931074540101	8011	44.158617	-74.900389
441311074493001	9006	44.219928	-74.825044
441137074492001	9008	44.193814	-74.822369
441158074504501	9009	44.199611	-74.845881
440710075173501	11020	44.119569	-75.293139
440606075200201	11025	44.101719	-75.333908
440151075084801	12003	44.030897	-75.146819
440125075084201	12008	44.023786	-75.145056
440705075141901	12017	44.118075	-75.238642
440613075144301	12024	44.103836	-75.245458
440303075131601	12027	44.050856	-75.221144

435705075165501	17002	43.951592	-75.281969
435403075031401	18002	43.900878	-75.053981
434915075190901	21013	43.820942	-75.319406
435004075012401	22003	43.834619	-75.023569
435001075001701	22005	43.833722	-75.004914
435128075002301	22007	43.858033	-75.006533
435139075082201	22017	43.860919	-75.139558
435115075093901	22019	43.854408	-75.161067
434628075122101	22024	43.774472	-75.206083
434547074582101	23003	43.763128	-74.972606
434539074583801	23004	43.760969	-74.977328

Table A-4. NWIS Station IDs, Project Codes and Coordinates for all Streams

NWIS Database Code	Project Stream Code	Latitude	Longitude
434652074565401	23014	43.781128	-74.948489
433811075180601	25003	43.636589	-75.301817
434006075200101	25013	43.668375	-75.333728
434249075215601	25022	43.713747	-75.365633
434001075045401	26008	43.667211	-75.081928
433940075053201	26009	43.661169	-75.092336
434025074585901	27002	43.673811	-74.983317
433849074575101	27005	43.647067	-74.964350
433837074571401	27006	43.643731	-74.954061
434256074453801	27019	43.715700	-74.760600
434217074465001	27020	43.704756	-74.780628
434211074452401	27024	43.703089	-74.756928
434208074450901	27025	43.702269	-74.752711
434049074462001	27027	43.680339	-74.772281
434421074584901	27036	43.739269	-74.980442
434446074562301	27039	43.746369	-74.939950
433953074400801	28010	43.664869	-74.669144
433854074411501	28013	43.648444	-74.687708
433820074410001	28014	43.639069	-74.683419
434124074393301	28017	43.690053	-74.659328
434105074393501	28018	43.684742	-74.659978
434500074441601	28030	43.750047	-74.737983
433613075184301	29008	43.603875	-75.312183
433324075165001	29012	43.556864	-75.280742
433117075073501	30003	43.521664	-75.126400
433553075062101	30009	43.598219	-75.105869

433548075110101	30019	43.596681	-75.183794
433639075093101	30023	43.610944	-75.158681
433130074555201	31007	43.525133	-74.931383
432806075033501	35008	43.468411	-75.059775
441130073504301	2007b	44.191794	-73.845464

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