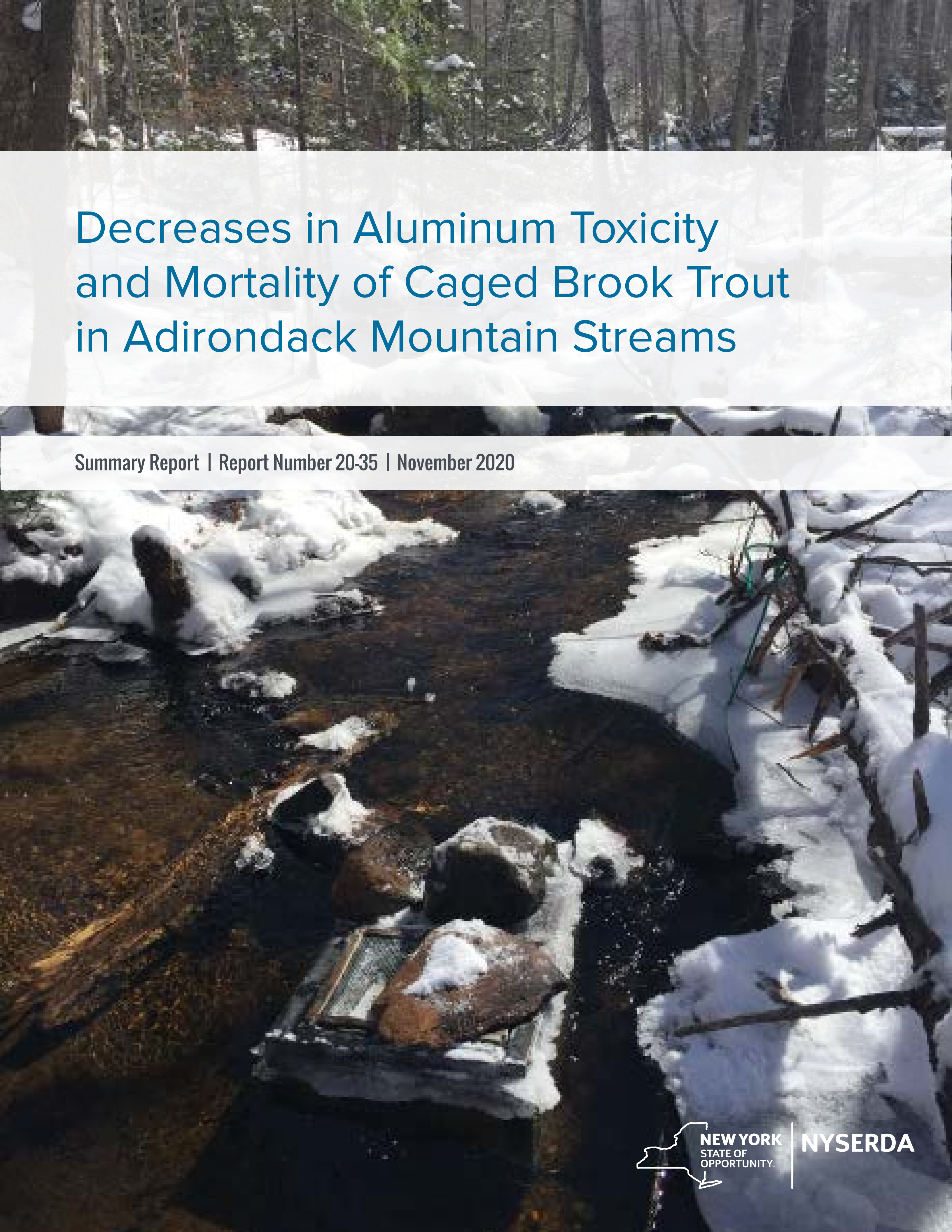

Decreases in Aluminum Toxicity and Mortality of Caged Brook Trout in Adirondack Mountain Streams

Summary Report | Report Number 20-35 | November 2020

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Cover Image:Toxicity test cage at Fly Pond Outlet near Old Forge, NY, April 2015.
Photo credit to Barry Baldigo

Decreases in Aluminum Toxicity and Mortality of Caged Brook Trout in Adirondack Mountain Streams

Summary Report

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Abstract

Mortality of juvenile brook trout and water chemistry were characterized in six western Adirondack streams in northern New York State during spring 2015, 2016, and 2017 and compared with results from comparable tests done between 1980 and 2003 in many of the same streams to assess temporal changes in inorganic monomeric aluminum (Ali) concentrations, Al_i-toxicity, and the role of Al_i-exposure duration on mortality. Al_i concentrations of 2 and 4 micromoles per liter (µmol L^{-1}) corresponded to chronic- and acute-mortality thresholds for brook trout, but prolonged exposure to ≥ 1 µmol Al_i L^{-1} also produced low-to-moderate mortality levels. The variability, mean, and highest Al_i concentrations in Buck Creek (BUC) year-round, and in several other streams during spring, decreased significantly over the past 30 years. Predictive models indicate that Al_i surpassed highly toxic concentrations at BUC for three to four months annually during 2001–2003 but for only two to three weeks annually during 2015–2017. The current lack of extremely high Al_i concentrations indicate toxicity has declined markedly between the 1989–1990, 2001–2003, and 2015–2017 test periods, yet acid- Al_i episodes can still cause moderate-to-high levels of brook trout mortality during high springtime flows. Assembled models show how mortality of brook trout in several Adirondack streams likely declined in response to the 1990 Clean Air Act Amendments and offer a means to predict how changes in United States regulations that limit the atmospheric emissions of nitrogen (N) and sulfur (S) oxides, and the deposition of N and S, could affect brook trout survival and impaired stream ecosystems in the western Adirondack region.

Keywords

Inorganic monomeric aluminum, brook trout, Adirondack streams, acidification, Clean Air Act, recovery

Acknowledgments

This research was supported by funds from the New York State Energy Research and Development Authority under the direction of Diane Bertok and the United States Geological Survey. The authors extend their appreciation to Noel Deyette and Luis Rodriguez of the United States Geological Survey and Howard Simonin (retired), Eric Paul, and Ryan Collins of the New York State Department of Environmental Conservation for field support. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. For more detailed information on the relations between fish assemblages and water chemistry that are summarized in this report, please see Baldigo et al. (2020), published in the *Journal of Environmental Toxicology and Chemistry*.[1]

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Focus

The mortality responses of juvenile brook trout were characterized in six western Adirondack streams each spring during 2015–2017 to better define the effects of inorganic aluminum (Al_i) concentration and duration of exposure on brook trout mortality and to determine if toxicity in stream waters of this region has declined. The 2015–2017 toxicity tests were repeated in many or all of the same streams where toxicity was assessed during four prior periods (1984–1985, 1988–1990, 1997, and 2001–2003) specifically to determine if: (1) Al_i concentrations, water toxicity, and brook trout mortality decreased significantly between the 1980s and present; (2) the relations between stream acidity and Al_i has changed over time, (3) present-day mortality levels reflect previously established Al_i-toxicity thresholds for brook trout mortality, and (4) the effects of Al_i concentration and duration of exposure on brook trout mortality can be defined quantitatively.

1 Context

Forested watersheds in the southwestern Adirondack Mountains of New York State received some of the most acidic deposition in North America from at least the 1960s through the 1990s (NADP 2005), which resulted in the acidification of lakes and streams in the region. During the 1980s and early 1990s, many investigations assessed the effects of acidification on survival of brook trout (*Salvelinus fontinalis*) and found that mortality was generally attributed to elevated concentrations of inorganic monomeric aluminum (Al_i) or more simply inorganic aluminum, which were mobilized by acidic conditions (Baldigo and Murdoch 1997; Gagen et al. 1993; Johnson et al. 1987; Van Sickle et al. 1996). During the 1990s, regional studies waned and were limited to a set of trout species and source/strain tests in 1997 (Simonin et al. 2000), and a survey of fish communities in three dozen streams during fall 1999 (Simonin et al. 2005). During a 2001–2005 study of 200 streams in the western Adirondacks, Lawrence et al. (2008b) determined that roughly half of western Adirondack streams became seasonally toxic to biota from Al_i concentrations surpassing 1 μmol L^{-1}. Baldigo et al. (2007) also assessed brook trout survival in six western Adirondack streams during 2001–2003 and concluded that Al_i toxicity (defined by Al_i concentration and fish mortality) in these streams differed little among prior studies in the 1980s and 1990s, and that the 1990 Clean Air Act Amendments (CAAA) had little or no effect on fish communities in streams of the region. Although Baldigo et al. (2007) identified Al_i exposure thresholds that caused at least low (20%), moderate (50%), and high (90%) levels of brook trout mortality, the effects of exposure duration were not fully incorporated into their models.

The decreases in atmospheric deposition of sulfate (SO_4^{2-}) over the last 20–30 years has generally increased acid-neutralizing capacity (ANC) and decreased Al_i concentrations in a group of Adirondack lakes which have been monitored since at least 1992 (Baldigo et al. 2016; Driscoll et al. 2016; Driscoll et al. 2003). While comparable trends in acid-base chemistry of streams in the Catskill Mountains have been linked to the 1990 CAAA (McHale et al. 2017), little temporal information is available to define such trends in Adirondack Mountain streams. In an analysis of 12 western Adirondack streams, however, Lawrence et al. (2011) reported that on average pH only increased by 0.28 and ANC increased by 13 microequivalents per liter (μeq L^{-1}) between the early 1980s and 2003–2005. Furthermore, flow-driven acidification episodes (hours to weeks long) were found to create or worsen toxic conditions in 124 out of 189 western Adirondack streams that were assessed during 2003–2005 (Lawrence et al. 2008a).

The increases in pH and ANC that have occurred from reduced acidic deposition have been limited by increases in acidity derived from dissolved organic carbon (DOC). Driscoll et al. (2016) reported that DOC concentrations increased in 29 of 48 (60%) Adirondack Long-Term Monitoring lakes between 1992 and 2013, and an increase of 23 millimoles per liter per year (mmol L^{-1} y^{-1}) was reported for the North Tributary of Buck Creek between 1999 and 2009 (Lawrence et al. 2011). Although DOC increases have limited increases in pH and ANC, higher DOC concentrations have also driven a shift in Al speciation from Al_i to organic monomeric Al (Al_o) in Adirondack lakes (Lawrence et al. 2013), which should have reduced Al toxicity to fish. Although notable decreases in toxicity (as indicated by brook trout mortality) were not evident in western Adirondack streams during 2001–2003 (Baldigo et al. 2007), widespread increases in DOC concentrations over the past 10–15 years, along with continued declines in acidic deposition should have reduced Al_i concentrations and toxicity levels in streams across the region, thereby prompting recovery of brook trout and populations of other species. This study assessed the mortality responses of juvenile brook trout in six western Adirondack streams each spring during 2015–2017 to better define the effects of Al_i concentration and duration of exposure on brook trout survival and to determine if toxicity in stream waters in this region has declined.

Figure 1. Toxicity Test (Exposure) Cage at Buck Creek

Buck Creek gaging station and exposure cage at the beginning of the spring 2015 toxicity tests.

Source photo credit Barry Baldigo.

2 Goals and Objectives

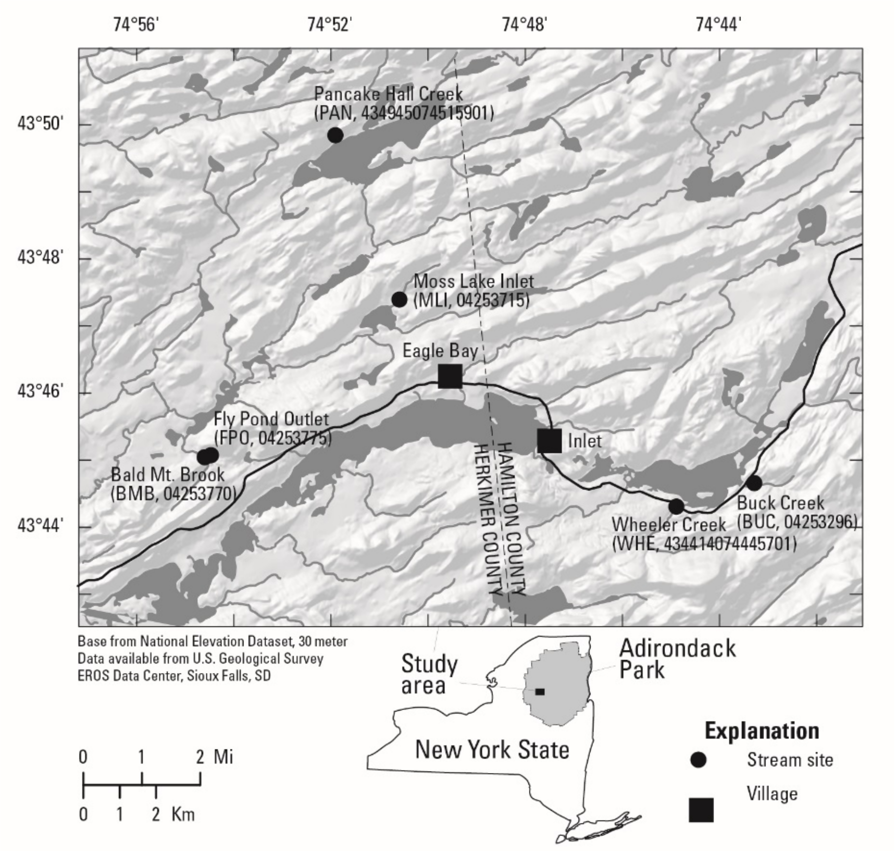
The primary objective of the study was to determine if the 1990 Clean Air Act Amendment (CAAA), related regulations, and changes in other climatic factors have reduced contemporary concentrations of Al_i and toxicity below a threshold that would now permit native brook trout to survive for extended periods in previously acidified streams of the western Adirondacks. During 2015–2017, caged-fish exposures (Figure 1); i.e., toxicity tests, were repeated in many or all of the same streams where toxicity was assessed during four prior periods (1984–1985, 1988–1990, 1997, and 2001–2003) specifically to determine if: (1) Al_i concentrations, water toxicity, and brook trout mortality decreased significantly between the 1980s and present; (2) the relations between stream acidity and Al_i has changed over time, (3) present-day mortality levels reflect previously established Al_i-toxicity thresholds for brook trout mortality, and (4) the effects of Al_i concentration and duration of exposure on brook trout mortality can be quantitatively defined.

3 Study Area and Methods

The six study streams are in the western Adirondack Mountains of northern New York State and are tributaries to the Moose River, which feeds into the Black River, and empties into Lake Ontario. The region is characterized by shallow soils and underlying geology that has low acid-buffering capacity, which make surface waters highly vulnerable to acidification. Discharge (flow), water chemistry, and brook trout mortality were assessed using 30 day (d) in-situ toxicity tests in Buck Creek (BUC), Pancake Hall Creek (PAN), Moss Lake Inlet (MLI), Bald Mountain Brook (BMB), Fly Pond Outlet (FPO), and Wheeler Creek (WHE) from April 9 to May 8, 2015; April 5 to May 5, 2016; and April 4 to May 4, 2017 (Figures 2, 3). Corresponding United States Geological Survey (USGS) station identification numbers are provided in Table 1. Detailed information about the region, study streams, test-site locations, field methods, test fish, and basic analysis of toxicity results for the present study duplicate those used in the 2001–2003 assessment (Baldigo et al. 2007), and thus, are only summarized herein.

Figure 2. Map of Study Streams where Toxicity Tests were Conducted During Spring 2015–2017

Location of study sites in streams of the southwestern Adirondack Mountains where toxicity tests were conducted during spring 2001–2003 and spring 2015–2017; modified from Baldigo et al. (2007).



Base from National Elevation Dataset, 30 meter
Data available from U.S. Geological Survey
EROS Data Center, Sioux Falls, SD

Table 1. Stream Codes, Station ID, Exposure Dates, Mortality, and Number of Water (Chemistry) Samples

Includes pH and inorganic aluminum (Al_i) concentrations from various 30-d toxicity tests completed in six Adirondack streams using young-of-year (YOY) brook trout during spring 2015–2017.

Stream code	USGS Station ID	Mortality (percent)	Median pH	Median Al_i ($\mu mol\ L^{-1}$)	Min/Max Al_i ($\mu mol\ L^{-1}$)	Number of samples
			April 9 to May 8, 2015			
FPO	04253775	0	6.71	0.68	0.00/1.51	15
BMB	04253770	0	5.49	1.87	0.40/2.79	15
MLI	04253715	10	5.65	2.19	0.57/3.43	17
PAN	434945074515901	100	5.01	4.37	0.83/7.15	14
WHE	434414074445701	100	4.57	7.54	3.00/8.10	9
BUC	04253296	90	5.05	5.44	1.84/7.14	15
			April 5 to May 5, 2016			
FPO	04253775	0	6.48	0.56	0.37/0.85	19
BMB	04253770	0	5.60	0.89	0.54/1.42	17
MLI	04253715	0	5.80	1.21	0.52/1.84	19
PAN	434945074515901	60	5.46	1.60	0.78/3.31	19
WHE	434414074445701	25	4.94	2.93	2.01/4.28	17
BUC	04253296	18	5.26	2.13	1.29/3.96	16
			April 4 to May 4, 2017			
FPO	04253775	0	6.69	0.62	0.32/0.74	18
BMB	04253770	0	5.57	1.24	0.88/2.15	18
MLI	04253715	0	5.71	1.23	0.90/2.37	20
PAN	434945074515901	100	5.03	4.28	1.62/5.34	12
WHE	434414074445701	95	4.78	4.05	2.96/7.51	20
BUC	04253296	95	5.06	3.47	2.11/4.93	18

Figure 3. Cages and Plastic Bottles Used for Brook Trout Toxicity Tests

Cages and screen-sided plastic bottles used for 30-d exposures of young-of-year (YOY) Brook Trout *Salvelinus fontinalis* to waters of six Adirondack streams during spring 2015–2017.

Source photo credit Barry Baldigo.

Stream stage at BUC during the three-year study was measured at 15-minute intervals using a submersible pressure transducer and recorded with an electronic data logger. Continuous discharge records for BUC were determined using standard USGS methods (Turnipseed and Sauer 2010). Discharge was not recorded continuously at the other five study sites, but it was measured four to five times during the 30-d test periods each year at each site.

Water chemistry was determined from grab samples collected at each site every one to three days during all toxicity test periods. Chemistry at BUC was supplemented by biweekly grab samples collected year-round and by automated samples collected during high-runoff events from April through November. All stream-water samples collected from October 1, 2013 to September 30, 2017 were used to define the relations between discharge and Al_i concentrations at BUC using nonlinear regression analyses.

All water samples collected from the study streams during test periods in 2001–2003 and 2015–2017 were analyzed at the USGS New York Water Science Center Soil and Low-Ionic-Strength Water Quality Laboratory (USGS Troy Laboratory) for pH, ANC, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), SO_4^{2-}, nitrate (NO_3^{-}), chloride (Cl^{-}), DOC, silicon (Si), ammonium (NH_4^{+}), total monomeric aluminum (Al_t), and Al_o according to U.S. Environmental Protection Agency (EPA) approved methods.[2] Concentrations of Al_i in each sample were calculated as the difference between Al_t and Al_o. Sample-handling procedures, quality assurance/quality control (QA/QC) procedures, and QA/QC data are summarized in Lincoln et al. (2009). Concentrations of Al_i from other water samples collected at BUC, outside of the toxicity-test periods between 1997 and 2017, were derived from measurements of Al_t and Al_o done at either the USGS Troy Laboratory or the Adirondack Lakes Survey Corporation laboratory in Ray Brook, NY (ALSC laboratory) following the same EPA approved method. Additionally, concentrations of Al_t and Al_o measured in samples from BUC, FPO, and BMB during the period 1989 through 1992 were analyzed at the ALSC laboratory using the method described in Wigington et al. (1996).

Young-of-year (YOY) brook trout from the New York State Department of Environmental Conservation (DEC) hatchery in Rome, NY were exposed (in cages) to stream waters for approximately 30 days each spring following the same procedures used by Johnson et al. (1987). Trout were transported to the control stream (FPO) in submerged 4-liter plastic, screen-sided jars (five fish per jar) and placed into larger holding chambers to acclimate for 24 hours prior to the start of tests. The next day, 20 trout (four jars with five fish each) were transported to each study stream and placed into the screen sided holding chamber (Figure 3). Trout mortality was checked and recorded daily for the first four days, then every two to three days during exposures.

Study objectives and goals were addressed through four analyses. First, the 2015–2017 trout mortality and water chemistry data from all streams were summarized to characterize present-day toxicity levels (mortality responses) and to determine if the results reflect previously established Al_i-toxicity thresholds for brook trout survival/mortality. Second, the relations between brook trout mortality and Al_i concentration were compared across the five toxicity-test periods to determine if the apparent relations differed among periods and (or) changed through time. The concentrations of Al_i that were measured during the last two periods, and since 1989 at BUC, were also evaluated to determine if significant temporal declines were evident. Third, results from the 2001–2003 and 2015–2017 toxicity tests were merged and used in logistic regressions to quantify brook trout mortality responses to differing pH, ANC, and Al_i concentrations, as well as to various Al_i concentrations and exposure durations. Fourth, to better understand the significance of elevated Al_i concentrations to brook trout survival and their populations, the duration of toxic conditions during 2015, 2016, and 2017 was estimated using the daily discharge record, flow-duration curves, and the relations between discharge and Al_i levels at BUC. The specific steps for each of these analyses are described more thoroughly in Baldigo et al. (2020).

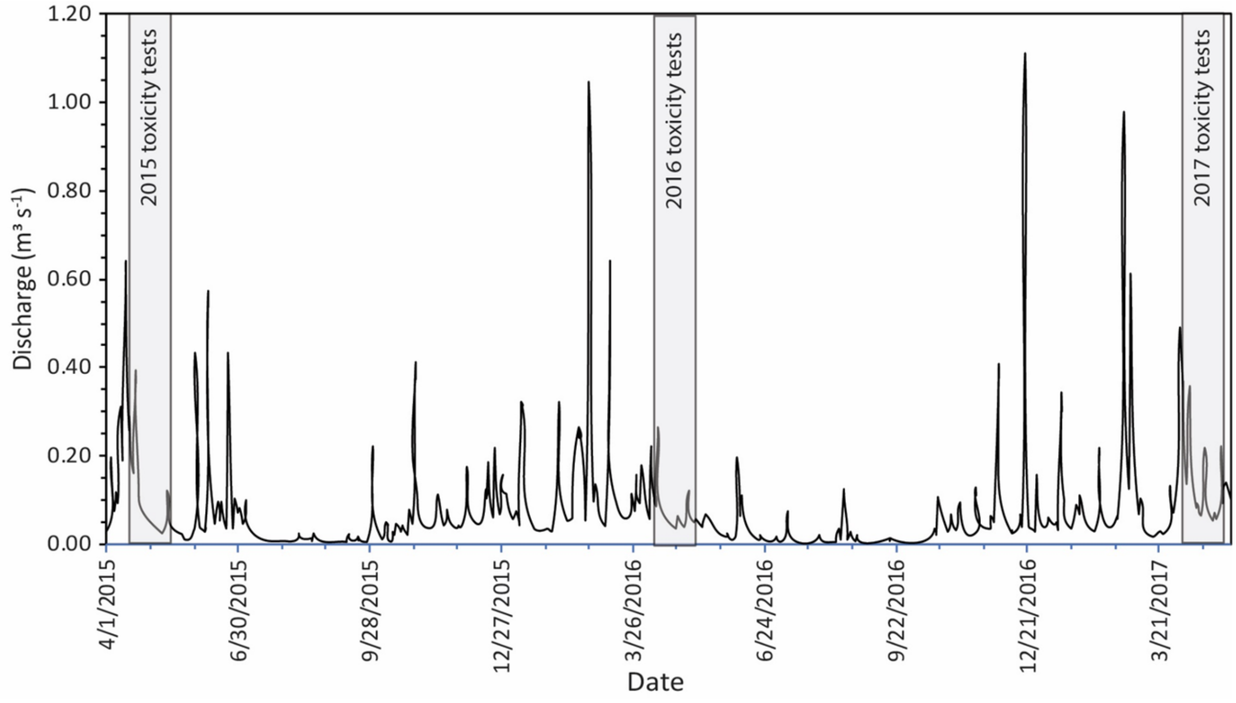
4 Project Findings

4.1 Stream Discharge and Chemistry

Mean daily discharge at BUC during the 2015, 2016, and 2017 toxicity-test periods averaged 0.159, 0.082, and 0.158 cubic meters per second ($m^3\ s^{-1}$; 5.60, 2.88, and 5.57 cubic feet per second [$ft^3\ s^{-1}$]), respectively (Baldigo et al. 2020). All discharge measurements made at each ungauged site (FPO, MLI, BMB, PAN, and WHE) during the spring 2015–2017 tests averaged 32%, 63%, 40%, 31%, and 229%, respectively, of the corresponding average of all discharge values logged at the gaged site (BUC) on the same dates and times. The relations between discharge at BUC and discharge at each of the other five streams were relatively strong (R^2 values ranged from 0.80 to 0.97). The daily discharge record at BUC (Figure 4) suggested that rainfall and (or) snowmelt events frequently elevated flows at all study streams during the 2015 and 2017 toxicity tests, but that only one moderate event occurred during the 2016 test period. Discharge data for BUC (USGS station ID, 04253296) are available through the USGS National Water Information System (NWIS) (USGS 2018).

Figure 4. Daily Discharge at Buck Creek (BUC) During 2015, 2016, and 2017

Daily discharge (in cubic meters per second) measured or estimated at Buck Creek (BUC) during the 30-d toxicity test periods (identified by shaded columns) in calendar years 2015, 2016, and 2017.



Stream chemistry varied considerably among streams and years. Median Al_i concentrations were near or less than 2 µmol L^{-1} at FPO, BMB, and MLI during all three years; whereas, they were ≥ 4 µmol L^{-1} at PAN, BUC, and WHE during 2015; < 3.0 µmol L^{-1} at the same three sites during 2016; and ≥ 4 µmol L^{-1} only at PAN and WHE during 2017 (Table 1). Measured and extrapolated Al_i concentrations did not exceed 2 µmol L^{-1} at FPO during any test year; however, they surpassed 2 µmol L^{-1} at BMB and MLI for one to three days during 2017 and for 16 to 17 days during 2015 (Figures 5A, 6A, and 7A). The Al_i concentrations at PAN, WHE, and BUC surpassed 2 µmol L^{-1} for three to 30 days during each of the 30-d exposure periods in 2015–2017. Concentrations of Al_i at FPO, BMB, and MLI did not exceed 4 µmol L^{-1} anytime during 2015–2017. Although Al_i concentrations at PAN, WHE, and BUC generally did not surpass 4 µmol L^{-1} during 2016, it was exceeded at the other three streams for three to 20 days during 2015 and 2017 (Figures 5A, 6A, and 7A). Original chemistry data from all samples collected during 2015–2017 (and 2001–2003) at each study site are available by USGS station ID (see Table 1) and sample dates through the USGS National Water Information System (NWIS) (USGS 2018).

Figure 5. Daily Al_i Concentrations and Brook Trout Mortality During 2015 Toxicity Tests

Daily measurements or estimates of Al_i concentration (A) and brook trout mortality (B) at each of six western Adirondack streams during toxicity tests done in the spring of 2015.

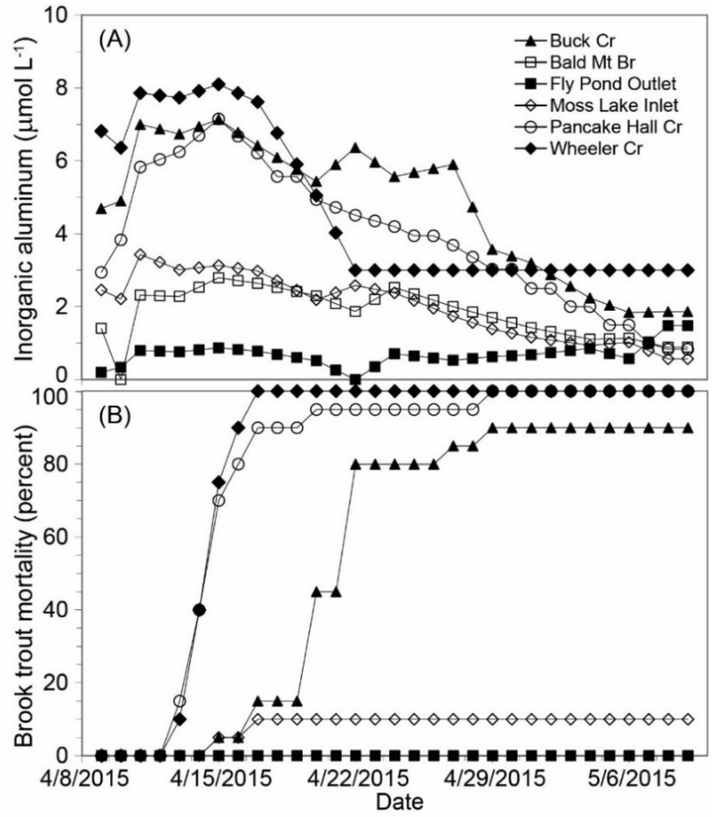


Figure 6. Daily Al_i Concentrations and Brook Trout Mortality During 2016 Toxicity Tests

Daily measurements or estimates of Al_i concentration (A) and brook trout mortality (B) at each of six western Adirondack streams during toxicity tests done in the spring of 2016.

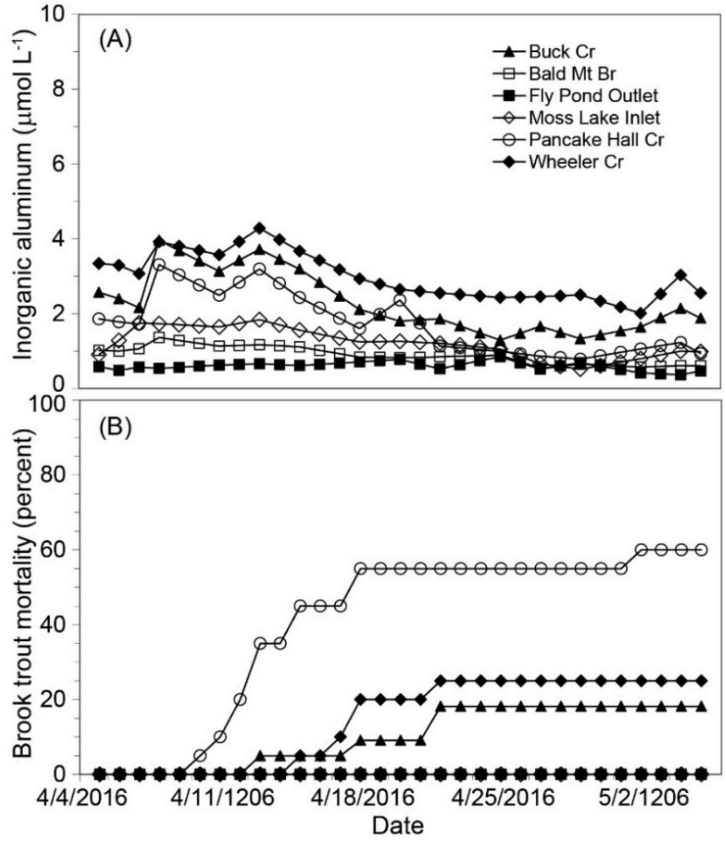
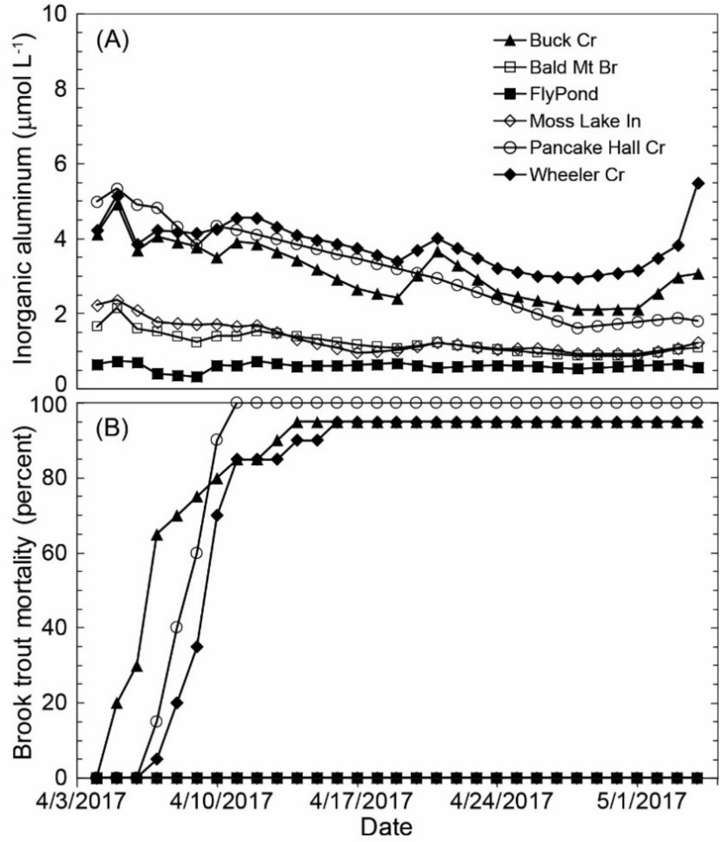


Figure 7. Daily Al_i Concentrations and Brook Trout Mortality During 2017 Toxicity Tests

Daily measurements or estimates of Al_i concentration (A) and brook trout mortality (B) at each of six western Adirondack streams during toxicity tests done in the spring of 2017.



Baldigo et al. (2020) found that discharge was strongly related to Al_i concentration and could account for 55% of the variability in year-round Al_i concentrations at BUC. These authors showed in Supplemental Figure S2 of Baldigo et al. (2020) that discharge levels of 0.02, 0.04, and 0.26 $m^3\ s^{-1}$ corresponded to key Al_i concentration thresholds of 1, 2, and 4 $\mu mol\ L^{-1}$, respectively. Baldigo et al. (2020) also defined the cumulative daily flow-duration curve for calendar years 2015–2017 at BUC in Supplemental Figure S3 of Baldigo et al. (2020) which indicates that the 4 $\mu mol\ Al_i\ L^{-1}$ threshold (0.26 $m^3\ s^{-1}$) was exceeded 4.4% of the time (1.6 months), 2 $\mu mol\ Al_i\ L^{-1}$ (0.04 $m^3\ s^{-1}$) was exceeded 49% of the time (17.9 months), and 1 $\mu mol\ Al_i\ L^{-1}$ (0.02 $m^3\ s^{-1}$) was surpassed 73% of the time (26.7 months) during the 36-month study period. The durations for which Al_i concentrations exceeded these three thresholds were highly variable among years. For example, the flow associated with the 2 $\mu mol\ Al_i\ L^{-1}$ threshold (0.04 $m^3\ s^{-1}$) at BUC was exceeded 37.3% (4.5 months), 48.4% (5.9 months), and 61.9% (7.5 months) of the time during calendar years 2015, 2016, and 2017, respectively.

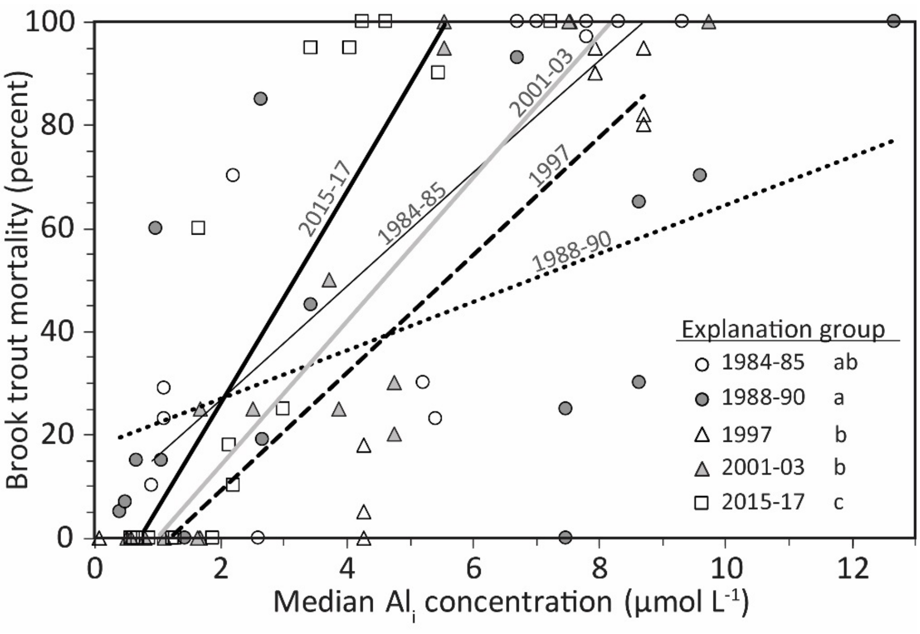
4.2 Brook Trout Mortality and Relation to Al_i Concentration

Like most prior toxicity-test results, mortality of YOY brook trout during the 2015–2017 exposures differed among streams and years (Table 1). During the 2015 tests, no brook trout died at FPO and BMB, 10% died at MLI, and 90 to 100% of trout died at PAN, WHE, and BUC (Figure 5B). During the 2016 tests, no brook trout died at FPO, BMB, and MLI; and only 18 to 60% of trout died at PAN, WHE, and BUC (Figure 6B). During the 2017 tests, no trout died at FPO, BMB, and MLI; and 95 to 100% of trout died at PAN, WHE, and BUC (Figure 7B). Daily observations (and extrapolations) of the numbers of brook trout that were alive and dead during all toxicity tests done during 2001–2003 and 2015–2017 are available in Baldigo and George (2019).

The relation between brook trout mortality and median Al_i concentrations during the 2015–2017 toxicity tests was as strong and significant ($R^2 = 0.76$; $P < 0.0001$) and generally comparable to those from the four earlier test periods; yet several important differences were evident. First, the slope of the 2015–2017 mortality-Al_i relation was greater than, and significantly different from, the slopes of the relations observed during all other test periods (Figure 8). Second, median Al_i concentrations were much lower than those from most earlier test periods as reported in Baldigo et al. (2007); they were frequently in the 1 to 2 µmol L^{-1} range and did not exceed 8 µmol L^{-1} during any 2015–2017 test (Table 1). While extremely high Al_i concentrations were not evident during most 2015–2017 tests, data in Figure 8 and Table 1 show that high and complete (90 to 100%) mortality still occurred at several sites during two of the three years.

Figure 8. Brook Trout Mortality and Alᵢ Concentrations from All Tests Done During Five Periods

Mortality of juvenile brook trout in relation to median Alᵢ concentrations from toxicity tests done in streams of the western Adirondacks during 1984–1985 (open circles), 1988–1990 (shaded circles), 1997 (open triangles), 2001–2003 (shaded triangles), and 2015–2017 (open squares).



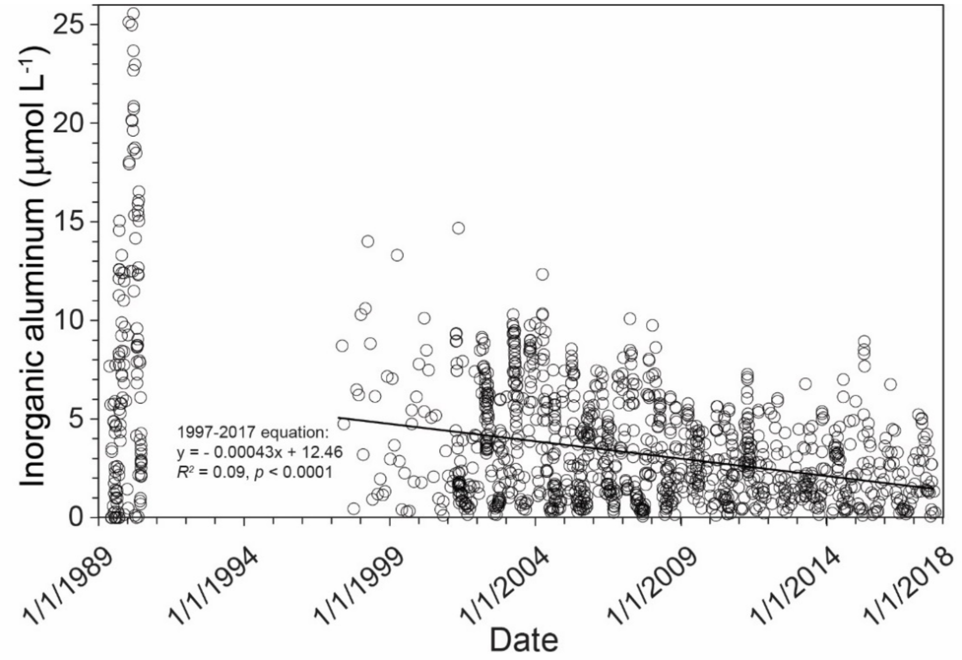
4.3 Temporal Trends in Alᵢ Concentrations and Toxicity

Declining Alᵢ concentrations and reduced brook trout mortality levels indicate that the toxicity of local stream waters decreased markedly over the past 10 or 15 years. Toxicity trends were evaluated by assessing (a) mean mortality responses during the five test periods (1984–1985, 1988–1990, 1997, 2001–2003, and 2015–2017), (b) Alᵢ concentrations from spring toxicity tests during the last three test periods (1989–1990, 2001–2003, and 2015–2017), and (c) temporal trends in Alᵢ concentrations from water samples collected at BUC between 1989 and 2017. One-way ANOVA results indicate that mean mortality levels for all (pooled) sites during each of the five test periods ranged from 30 to 60% and did not differ significantly among periods ($P = 0.328$), but that the mean mortality levels ranged from 0 to 62% at individual sites and differed among years ($P = 0.061$). While year-to-year differences in brook trout mortality levels at several sites were only significant at $\alpha = 0.061$, there was no consistent decreasing trend in pooled mortality results from all study streams over the five test periods.

Additional one-way ANOVA results indicate that temporal declines in Al_i concentrations during springtime test periods were significant within individual streams. While Al_i data are only available from several samples collected at study streams during the first and third test periods, extensive chemistry sampling during the second and two most-recent test periods indicate that the maximum, 75th percentile, mean, and median Al_i measurements from all samples collected at five of the six streams were lower during 2015–2017 than during 2001–2003 and 1989–1990 as shown in Supplemental Figure S4 of Baldigo et al. (2020). Data from BUC collected since 1997 also show that mean Al_i concentrations from routine (weekly, biweekly, and monthly) water samples decreased significantly (ANOVA; $P < 0.0001$) by approximately 0.00043 $\mu mol\ L^{-1}$ per day between 1997 and 2017, and by a total of 5.5 $\mu mol\ L^{-1}$ between 1989 and 2017 (Figure 9). Direct comparisons between Al_i concentrations measured during the 1989–1990 tests and the two recent test periods may not be entirely accurate because the method used to analyze Al_i during 1989–1990 (Wigington et al. 1996) differed from that used during 1997 to 2017. The 1989–1990 data suggest, however, that extremely high Al_i concentrations (> 15 $\mu mol\ L^{-1}$) were common during this period, and that Al_i levels above 10 $\mu mol\ L^{-1}$ have not occurred since 2002 (Figure 9). While Al_i concentrations from at least three study streams continued to reach acutely toxic levels during the 2015–2017 tests, the recent absence of extremely high Al_i concentrations in most study streams, and the steady decline in Al_i levels in BUC between at least 1997 and 2017, suggest that Al_i toxicity has declined substantially in these and other acid-sensitive streams throughout the western Adirondacks.

Figure 9. Al_i Concentrations from All Routine Buck Creek Water Samples, 1989–2017

Measured Al_i concentrations from all routine water samples collected at Buck Creek (BUC) between January 1, 1989 and December 31, 2017.



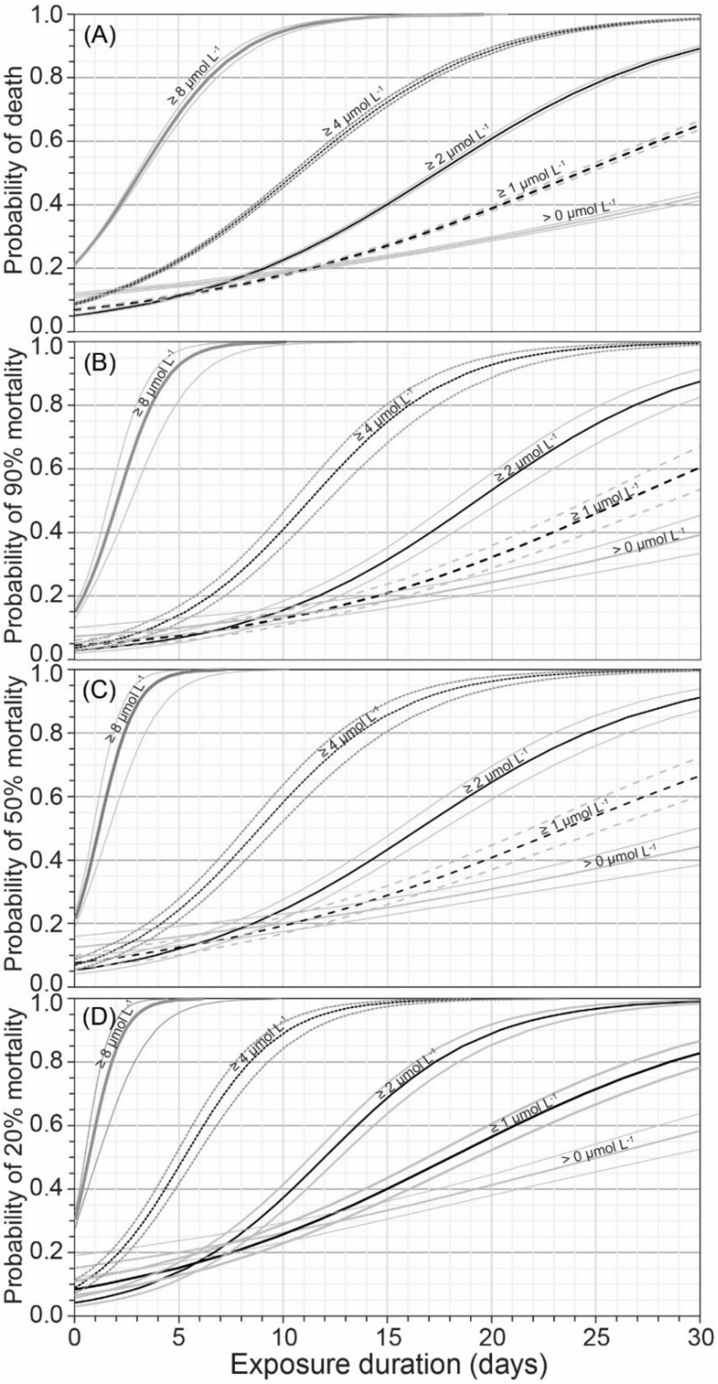
4.4 Probability of Brook Trout Death

All logistic equations describing the probability of brook trout death (essentially 100% mortality) based on median Al_i, pH, and ANC concentrations during the 2001–2003 and 2015–2017 tests were significant, yet only explained from 13.8 to 20.5% of the deviances in probabilities as noted in Table 2 of Baldigo et al. (2020). The two equations using mean and cumulative Al_i concentrations were also significant; mean Al_i explained 26.6% of the deviance, whereas, cumulative Al_i explained 35.4% of the deviances as noted in Table 2 of Baldigo et al. (2020). The simple curve depicting the probability of death versus mean Al_i concentration as noted in Supplemental Figure S5 of Baldigo et al. (2020) is useful in that it predicts low (20%), moderate (50%), and high (90%) mortality levels when mean Al_i concentrations are in the 3–4, 5–6, and 9 µmol L^{-1} ranges, respectively, over 30-d exposure periods. However, no temporal element is factored into this model; that is, it is fixed at the final exposure duration of 30 d.

The effects of exposure duration on survival can be defined by logistic equations that predict the probability of brook trout death based on the total number of days in which Al_i-concentrations exceed 0 µmol L^{-1} and are ≥ 1, 2, 3, 4, 5, 6, 7, and 8 µmol L^{-1} during all 30-d exposures during 2001–2003 and 2015–2017. All such equations were significant and those using the total number of days that Al_i concentrations were ≥ 2, 3, or 4 µmol L^{-1} explained 29.2 to 33.1% of the deviances as noted in Table 2 of Baldigo et al. (2020). The curves in Figure 10A indicate that death is highly probable (≥ 0.90) if Al_i concentrations equal or exceed 8 µmol L^{-1} for 8 d or more, 4 µmol L^{-1} for 21 d or more, or 2 µmol L^{-1} for 30 d or more. Although the predictions are limited to the length of our toxicity tests, extrapolating the curves beyond 30 d suggests that death is also likely if Al_i concentrations surpass 1 µmol L^{-1} for about 40 d or more. These equations predict the probability of death for an individual fish, as well as the percentage of individual fish from a larger group which can be expected to succumb when exposed to the same Al_i concentrations and durations.

Figure 10. Probability of Brook Trout Mortality at Different Al_i Concentrations and Durations

Logistic equations and 95% confidence intervals that define the probabilities for observing (A) death, (B) 90% mortality, (C) 50% mortality, and (D) 20% mortality in YOY brook trout when Al_i concentrations in Adirondack streams exceed 0 μmol L^{-1}, 1 μmol L^{-1}, 2 μmol L^{-1}, 4 μmol L^{-1}, and 8 μmol L^{-1} for exposure durations ranging from 0 to 30 days during spring 2001–2003 and 2015–2017.



4.5 Probabilities for Different Levels of Brook Trout Mortality

A separate set of logistic equations, that predict the probability for low (≥ 20%), moderate (≥ 50%), and high (≥ 90%) levels of brook trout mortality, also quantify the shifting risk of past, present, and future Al_i conditions in the study streams and in other streams across the region. The probabilities for observing at least 90% (Figure 10B), 50% (Figure 10C), and 20% (Figure 10D) mortality in YOY brook trout when exposed to waters of differing median Al_i concentrations are defined by equations in Table 3 of Baldigo et al. (2020). These curves depict archetypical mortality responses to toxic conditions; that is, little or no mortality at low levels (regardless of exposure time) and high mortality at elevated levels (even after short exposure periods) (Breck 1988). For several examples, the equations for at least 90% mortality (Figure 10B) indicate that the probability for high levels of mortality in an individual stream or group of streams could reach (a) 0.44 in 30 d if median Al_i levels were > 0 and < 1 µmol L^{-1}, (b) 0.60 in 30 d if median Al_i levels were ≥ 1 and < 2 µmol L^{-1}, (c) 0.87 in 30 d if median Al_i levels were ≥ 2 and < 4 µmol L^{-1}, (d) 1.00 in 25 to 30 d if median Al_i levels were ≥ 4 and < 8 µmol L^{-1}, and (e) 1.00 in 7 to 8 d if median Al_i levels were ≥ 8 µmol L^{-1}. The equations for at least 50% mortality (Figure 10C) show that the probability for moderate levels of mortality would reach (a) 0.45 in 30 d if median Al_i levels were > 0 and < 1 µmol L^{-1}, (b) 0.65 in 30 d if median Al_i levels were ≥ 1 and < 2 µmol L^{-1}, (c) 0.90 in 30 d if median Al_i levels were ≥ 2 and < 4 µmol L^{-1}, (d) 1.00 in 25 d if median Al_i levels were ≥ 4 and < 8 µmol L^{-1}, and (e) 1.00 in 5-6 d if median Al_i levels were ≥ 8 µmol L^{-1}. The equations for at least 20% mortality (Figure 10D) indicate that the probability for low levels of mortality would reach (a) 0.60 in 30 d if median Al_i levels were > 0 and < 1 µmol L^{-1}, (b) 0.80 in 30 d if median Al_i levels were ≥ 1 and < 2 µmol L^{-1}, (c) 1.00 in 30 d if median Al_i levels were ≥ 2 and < 4 µmol L^{-1}, (d) 1.00 in 14 d if median Al_i levels were ≥ 4 and < 8 µmol L^{-1}, and (e) 1.00 in 4 to 5 d if median Al_i levels were ≥ 8 µmol L^{-1}.

4.6 Implications of Results

Our results generally support the prior findings from Baldigo et al. (2007) but also improve our quantitative understanding of the role of Al_i concentration and exposure duration as a control of brook trout mortality and resident populations. If model probabilities are assumed to correspond directly to percent mortality, then the equations developed in this study indicate that (1) any measurable Al_i in stream waters put YOY brook trout at risk of death and (2) exposure to median Al_i concentrations ≥ 1 µmol L^{-1} could lead to substantial ($\geq 60\%$) mortality if durations approach 30 d. These equations also confirm that a median Al_i concentration of 2 µmol L^{-1} is an appropriate threshold for low-to-moderate mortality levels ($\geq 20\%$ or $\geq 50\%$) and that 4 µmol L^{-1} is an appropriate threshold for high mortality levels ($\geq 90\%$) for YOY brook trout in streams of the region. Our models (Figure 10A) predict that $\geq 20\%$ of brook trout will die if median Al_i concentrations surpasses 2 µmol L^{-1} for 9 d and that $\geq 50\%$ of brook trout will die if median Al_i surpass 2 µmol L^{-1} for 17–18 d. Similarly, $\geq 50\%$ of brook trout will succumb if median Al_i concentrations surpasses 4 µmol L^{-1} for 10–11 d, and $\geq 90\%$ of brook trout will die if median Al_i surpasses 4 µmol L^{-1} for 21 d. Median Al_i concentrations ≥ 8 µmol L^{-1} are severely toxic to YOY brook trout and can produce at least 50% mortality after 3 d and at least 90% mortality levels after 8–9 d of exposure. Furthermore, the probability of moderate ($\geq 50\%$) mortality reaches 0.90 after 29 d at 2 µmol L^{-1} and after 16 d at 4 µmol L^{-1}; whereas, the probability of high ($\geq 90\%$) mortality reaches 0.90 after 19 d at 4 µmol L^{-1} and after four to five days at 8 µmol L^{-1} (Figure 10B, 10C). Although the various Al_i exposure concentrations and durations likely interact to yield more of a continuum in effects (mortality), several Al_i thresholds and mortality levels noted herein appear to reflect gradients in the condition of local brook trout populations.

Results for brook trout mortality in some of the most recent toxicity tests would initially appear to indicate that toxicity of stream waters in the region has not changed markedly since the 2001–2003 tests were done; that is, over the past 14–16 years. While brook trout mortality levels were usually less than 25% at FPO, BMB, and MLI during the 2015–2017 and 2001–2003 tests, mortality levels often reached 100% at PAN, BUC, and WHE during both periods. Since Baldigo et al. (2007) previously determined that brook trout mortality levels did not change significantly from levels observed during comparable tests performed prior to the 2001–2003 tests, it could logically be inferred that toxicity of local stream waters has not changed in a biologically relevant way between 1984 and 2017 despite large decreases in acidic deposition and Al_i concentrations. Although Al_i concentrations have decreased between the two test periods, their low-to-moderate levels still exceed critical survival thresholds for long-enough durations to cause high mortality in several study streams. Thus, changes in the duration that Al_i concentrations surpass important survival thresholds may be the best approach to gaging changes in toxicity (and recovery) of acidified streams across the region. The changes in water chemistry at BUC, and presumably other study streams since the late 1980s and early 1990s, however, suggest that biologically meaningful decreases in Al_i concentrations occurred in response to regional declines in acidic deposition. Figure 9 shows that concentrations of Al_i at BUC decreased steadily from a mean of about 5 µmol L^{-1} in 1997 to a mean of less than 2 µmol L^{-1} in 2017, and that mean and peak concentrations at BUC (and other study sites) were probably much greater in 1989–1990 than in 2001–2003 and 2015–2017 as shown in Supplemental Figure S4 from Baldigo et al. (2020). Data in this figure also show that the interquartile ranges and mean Al_i concentrations were significantly lower during the 2015–2017 tests than during the 2001–2003 tests (at most study streams) and during the 1989–1990 tests (at BUC and BMB).

Despite the large decreases in both mean and peak Al_i concentrations at BUC and other study streams, expected decreases in toxicity levels were not evident during spring 2015–2017 tests. This result may be explained by examining the relations between median Al_i concentrations and brook trout mortality (at the end of 30-d exposures) during the five test periods (Figure 8). Except for 1988–1990, the slopes of all prior relations were not significantly different from each other (Baldigo et al. 2007), but the slope for 2015–2017 was significantly steeper than during all other test periods. This shift implies that either the sensitivity of brook trout to Al_i changed over time, which is unlikely (because the source and strain of most test fish had not changed), or that the underlying range of Al_i concentrations has changed, and brook trout die at high rates above a relatively low Al_i concentration (effect) threshold. The large declines in Al_i concentrations in waters from several study streams support the latter implication. In effect, extremely high Al_i concentrations no longer occur, but they still surpass thresholds of 2, 3, or 4 µmol Al_i L^{-1} for sufficiently long-enough durations to cause high levels of brook trout mortality in some streams of the region.

The effects of concentration and exposure duration on fish mortality (or survival) should be considered together to determine the toxicity of Al_i to brook trout that experience the dynamic chemical regimes of streams in the western Adirondacks. Our probabilistic models (Figure 10) essentially quantify the relations between mortality levels and Al_i-concentration durations. They provide a means to postulate population responses to changing rates of acid deposition and to predict the presence (or absence) and the condition of brook trout populations in streams with well-defined or predicted Al_i concentration and duration regimes. For example, the likelihood of extant brook trout populations in un-surveyed streams within the region may be inferred using models in Figure 10A. If present-day chemistry data show that median Al_i concentrations do not exceed 2 µmol L^{-1} for more than 10 days each year, then the probability of brook trout mortality is ≤ 0.21 and the probability of finding at least some brook trout at such a site would be ≥ 0.79. As another example, the models can predict how potential changes in U.S. secondary standards for target loads of nitrogen (N) and sulfur (S) deposition and stream ANC levels (EPA 2009) would likely affect brook trout mortality and possibly their populations in one or more streams of the region. Given that Al_i concentrations are strongly related to ANC at BUC, as per Supplemental Figure S4 in Baldigo et al. (2020), we can predict that median Al_i concentrations in two hypothetical streams with present-day mean or median ANC levels of 0 and 30 µeq L^{-1} would be about 5 and 1.4 µmol L^{-1}, respectively. Presuming these Al_i concentrations occur for at least 30 d each year, then the probabilities for brook trout mortality in both case streams would be > 0.99 and > 0.65 (Figure 10A), respectively, and the probability for extant brook trout would be low (< 0.01) and moderate (< 0.35), respectively. Emission reduction scenarios that increase ANC of streams in the region by 20 µeq L^{-1} (from 0 to 20 µeq L^{-1} and from 30 to 50 µeq L^{-1}) would decrease median Al_i concentrations in the two case streams to about 2.5 and 0.5 µmol L^{-1}, respectively, and reduce the probabilities for mortality to > 0.90 and > 0.45, respectively. These changes could increase the probabilities for extant brook trout from < 0.01 to < 0.10 and from < 0.35 to < 0.55, respectively, and likely increase the density of resident populations in both case streams.

When combined with continuous Al_i and discharge records, the brook trout response models illustrate how long-term declines in Al_i concentrations may have affected brook trout survival and their wild populations over the past three decades. The continuous (15 minute, hourly, or daily) discharge data at BUC can be used to develop continuous Al_i records because they are moderately related on an annual basis, as per Supplemental Figure S2 in Baldigo et al. (2020), and more strongly related on a seasonal basis (R^2 values as high as 0.73) (Baldigo et al. 2007). This relation indicates that a discharge of 0.04 $m^3 s^{-1}$ corresponds to 2 µmol Al_i L^{-1} and a discharge of 0.26 $m^3 s^{-1}$ corresponds to 4 µmol Al_i L^{-1} at BUC. The 2015–2017 daily discharge-duration curve for BUC, as per Supplemental Figure S2 in Baldigo et al. (2020), shows that Al_i effect thresholds of 2 and 4 µmol L^{-1} were exceeded 50% and 5% of the time, respectively. This means that Al_i concentrations at BUC currently exceed 2 µmol L^{-1} for roughly six months each year and they exceed 4 µmol L^{-1} for two to three weeks each year. The logistic models in Figure 10A indicate that the present-day probabilities for brook trout mortality at BUC, based on exceedance times for 2 and 4 µmol L^{-1}, is 1.00 and 0.67-0.91, respectively. Analogous analyses at BUC during 2001–2003 found that Al_i concentrations exceeded 4 µmol L^{-1} for three to four months each year (Baldigo et al. 2007). Although the probabilities for brook trout mortality at BUC reached 1.00 for part of each year in 2001–2003 and in 2015–2017, the duration that Al_i concentrations were highly toxic (≥ 4 µmol L^{-1}) declined radically between the two test periods.

The results from recent fish surveys done in 48 western Adirondack streams help demonstrate how various Al_i concentration thresholds and associated probabilities for brook trout mortality correspond to the condition of resident populations in local streams, and in other streams across the region. Although many physical, chemical, and biological factors act in concert to regulate density and biomass of natural populations, these models can predict the potential or probable effects on their populations—due to acid-base chemistry alone—if it is assumed that population-level responses correspond roughly to predicted mortality levels. Baldigo et al. (2019b) showed that brook trout were entirely absent from sites with summer Al_i concentrations greater than 2 µmol L^{-1}, present generally in low densities and biomass at sites with Al_i concentrations between 1 and 2 µmol L^{-1}, and present in moderate to high densities and biomass at sites with concentrations < 1 µmol L^{-1}. Thus, it is not surprising that the probabilities for existing brook trout populations decreased from 0.96 at streams with summer Al_i concentrations of 0 µmol L^{-1}, to 0.75 at 1 µmol L^{-1}, to 0.25 at 2 µmol L^{-1}, and to 0.04 at 3 µmol L^{-1}; and that the probabilities for > 100 brook trout/0.1 hectare (ha) decreased from about 0.33 at 1 µmol L^{-1} to 0.02 at 2 µmol L^{-1} in these same streams (Baldigo et al. 2019a). Because streams are normally at baseflow and water chemistry is typically least acidic (and have their lowest Al_i concentrations) during summer, these apparent Al_i thresholds for local brook trout populations may not always represent the most toxic acid-Al_i periods or even annual mean or median Al_i levels, but simply the least toxic/stressful conditions which occur each year in each stream. Except for BUC, annual mean or median Al_i values for the fish-survey sites considered in this study are unavailable. Yet, data from 55 nearby western Adirondack streams, sampled as part of a long-term chemistry monitoring program (G. Lawrence personal communication), provide a way to formulate an adjustment factor that can make Al_i thresholds for brook trout populations more broadly relevant. The mean summer 2014 Al_i concentration (0.57 µmol L^{-1}) was 0.45 µmol L^{-1} lower than the mean of spring, summer, and fall 2014 samples (1.02 µmol L^{-1}) at the same 55 sites. Thus, the Al_i-effect thresholds for brook trout population density and biomass identified by Baldigo et al. (2019b) could justifiably increase by roughly 0.5 µmol L^{-1} to make natural population and Al_i relations (and effect thresholds) representative of year-round (mean or median) Al_i conditions in streams of the region. Consequently, Al_i concentrations of 2.0 to 2.5 µmol L^{-1} are suitable upper thresholds for the occurrence of any brook trout, and 1.0 to 1.5 µmol L^{-1} are appropriate thresholds for the occurrence of healthy (normal) brook trout populations depending if concentrations represented summer (baseflow) or annual mean or median conditions. While (Baker et al. 1996) indicates that an upper Al_i threshold for brook trout populations in streams of the Northeast may be closer to 100 to 200 µg L^{-1} (3.7–7.5 µmol L^{-1}), Simonin et al. (2005) found that densities of brook trout populations were low and YOY were absent from Adirondack streams with springtime (high flow) pH < 5.0. Current (2014–2015) chemistry relations from Baldigo et al. (2019b) show that a pH of 5.0 corresponds to an Al_i concentration of 2.2 µmol L^{-1}, which supports our thesis that springtime concentrations of 2 µmol L^{-1}, or mean (representative year-round) concentrations of 2.5 µmol L^{-1} are upper limits or thresholds for the occurrence of any resident brook trout. Consequently, the probability model for brook trout mortality and duration of Al_i concentrations ≥ 2 µmol L^{-1} is most appropriate for predicting the occurrence of brook trout at low densities, whereas, the model for duration of Al_i concentrations ≥ 1 µmol L^{-1} is most appropriate for predicting the occurrence of YOY brook trout and healthy populations in streams of the western Adirondacks.

The presence or absence of resident brook trout have some important implications concerning the health of local fish communities. Identifying an upper Al_i threshold that impairs entire fish communities is challenging because different species have variable tolerances to acid-Al_i conditions. The task is not too complicated in the western Adirondacks, however, because brook trout are one of the most (if not the most) acid-tolerant fish species in surface waters of New York State (Baker and Christensen 1991; Baker et al. 1996; Baldigo and Lawrence 2001). This means that most other fish species (and community richness) may be limited by the same threshold for the presence of healthy brook trout populations (summer Al_i concentrations < 1 µmol L^{-1}). In fact, Baldigo et al. (2019b) found that community richness rarely surpassed one species in Adirondack streams where summer Al_i concentrations were > 1 µmol L^{-1}. More important, the probabilities for one or more fish species are similar to those for brook trout presence; the probabilities for ≥ 2 fish species decreases from 0.75 at 0 µmol Al_i L^{-1}, to 0.34 at 1 µmol Al_i L^{-1}, and to 0.12 at 2 µmol Al_i L^{-1} in the same streams (Baldigo et al. 2019a). Thus, some variation of the probability model for brook trout mortality and duration ≥ 1 µmol Al_i L^{-1} may be appropriate for predicting total community richness in local streams. Additionally, because total community density and biomass only reach moderate and high levels in streams with summer Al_i concentrations < 1 µmol L^{-1}, such a model may also be appropriate for predicting community density and biomass. Although probabilities for low-to-moderate levels of community biomass approximate those for brook trout presence, the decrease in probability for community density > 100 fish/0.1 ha from 0.96 at 0 µmol Al_i L^{-1} to 0.50 at 1 µmol Al_i L^{-1}, and the loss of all other fish species at Al_i concentrations > 1 µmol L^{-1} (Baldigo et al. 2019a), supports 1 µmol Al_i L^{-1} as an upper limit or threshold for evading community impacts.

5 Conclusions

Our probabilistic models quantify the interconnected effects of Al_i concentration and duration of exposure on mortality of YOY brook trout and help to define or confirm important thresholds for biological impacts. Depending on exposure duration, the models indicate that Al_i concentrations, well below previously established thresholds, can lessen the survival of YOY brook trout. An Al_i concentration of 1 $\mu mol\ L^{-1}$ serves as a chronic-toxicity threshold; 2 $\mu mol\ Al_i\ L^{-1}$ can be considered an acute-toxicity threshold; and 4 $\mu mol\ Al_i\ L^{-1}$ represents a threshold for high or complete toxicity. The first two Al_i-effect thresholds correspond to limits for specific brook trout population and community characteristics. Thus, several toxicity models explicitly categorize the present-day spatial extent and magnitude of ecosystem impairment and provide a yardstick to quantify the potential for biological recovery in local streams where acidity and Al_i concentrations are declining. Accordingly, the models combined with water chemistry measurements can help resource managers and policy makers better understand the present-day status of fish assemblages in acid-sensitive streams across the region.

At a national level, these mortality models and refined Al_i-effect thresholds can help U.S. policymakers to base decisions on more accurate predictions of the ecological responses to future changes in federal air-quality standards. The current process projected to revise U.S. secondary standards that limit atmospheric emissions of nitrous (NO_x) and sulfur oxides (SO_x) to achieve target N and S deposition loads is based mainly on surrogate indicators such as ANC to protect aquatic and terrestrial ecosystems within receiving watersheds (EPA 2009). Though a number of studies model how various N and S deposition loads affect ANC levels in streams and lakes across the eastern U.S. (Fakhraei et al. 2016; Fakhraei et al. 2014; Sullivan et al. 2012a; Sullivan et al. 2012b; Zhou et al. 2015a; Zhou et al. 2015b), these mortality models, fish-assemblage models from Baldigo et al. (2019a), and various Al_i-effect thresholds provide useful predictions of the biological responses that may be expected from altered national emission standards and regional N and S deposition loads.

The mortality models can also help demonstrate how regulations imposed by the Clean Air Act of 1970 and 1990 CAAA reduced Al_i concentrations and toxicity in streams of the western Adirondacks over the past three decades. The variability, mean, and highest Al_i concentrations observed in BUC year-round, and in other study streams during spring tests have decreased significantly between the late 1980s or early 1990s and present (2015–2017). The length of time or duration that estimated concentrations of Al_i surpass highly toxic thresholds (4 $\mu mol\ L^{-1}$) at BUC decreased from about three to four months each year during 2001–2003 to about two to three weeks each year during 2015–2017. Although Al_i

concentrations in waters still surpass toxic thresholds for periods sufficiently long to cause high levels of mortality in YOY brook trout at BUC and several other study sites during 2015–2017, the absence of extremely high Ali levels confirm that toxicity levels have declined substantially since the 1989–1990 and 2001–2003 test periods. Whether declines in acidity and Ali concentrations in western Adirondack streams are caused directly or indirectly by the 1990 CAAA is arguable. The decreasing trend in Ali concentrations, however, suggests that tangible changes in the acid-base chemistry of the system can be expected to continue for acid-sensitive watersheds across the region. Based on the results of this study, brook trout populations in previously acidified streams should experience significant recovery as Ali concentrations continue to decline below critical survival thresholds and sustain those levels for longer and longer durations.

Although decreases in acidity, Al_i concentrations, and the duration that Al_i levels are elevated suggest toxicity levels have recently declined noticeably, high mortality levels at several streams during the 2015–2017 tests indicate that acid-Al_i episodes remain a serious threat to brook trout survival, and to the sustainability of their populations and native fish communities in streams of the western Adirondacks. This means that the 1990 CAAA may have had only negligible effects on the biological recovery in streams across the region. At a minimum, the timing and degree of biological recovery may simply be lagging chemical recovery in local streams for various reasons. Though quantitative fish surveys in 2014–2016 (Baldigo et al. 2019b) recently provided limited evidence for shifting fish assemblages at a few sites, more current chemistry and fisheries information is needed from a broader range (and more) of previously surveyed streams to fully ascertain how much biological recovery has actually taken place, what factors drive biological recovery (or the lack of recovery), and what acid-mitigation or resource-management strategies might be employed to accelerate biological recovery in streams of the western Adirondacks.

6 References

Baker, J. P., and S. W. Christensen. 1991. Effects of acidification on biological communities in aquatic ecosystems. Pages 83-106 in D. F. Charles, editor. Acidic deposition and aquatic ecosystems. Springer-Verlag New York Inc., New York, NY. https://doi.org/10.1007/978-1-4613-9038-1_5

Baker, J. P., J. Van Sickle, C. J. Gagen, D. R. DeWalle, W. E. Sharpe, R. F. Carline, B. P. Baldigo, P. S. Murdoch, D. W. Bath, W. A. Kretser, H. A. Simonin, and P. J. Wigington, Jr. 1996. Episodic acidification of small streams in the northeastern United States: Effects on fish populations. Ecological Applications 6(2):422-437. DOI: https://doi.org/10.2307/2269380

Baldigo, B. P., and S. D. George. 2019. Brook trout toxicity data from bioassays conducted in Western Adirondack Streams, 2001-03 and 2015-17. U.S. Geological Survey, Troy, NY. 10.5066/P9IBY7W6.

Baldigo, B. P., S. D. George, C. T. Driscoll, S. Shao, T. J. Sullivan, D. A. Burns, and G. B. Lawrence. 2019a. Probabilistic relationships between indicators of acid-base chemistry and fish assemblages in streams of the western Adirondack Mountains, New York, USA. Canadian Journal of Fisheries and Aquatic Sciences NA(NA):NA. DOI: 10.1139/cjfas-2018-0260

Baldigo, B. P., S. D. George, G. B. Lawrence, and E. A. Paul. 2019b. Acidification impacts and goals for gauging recovery of Brook Trout populations and fish communities in streams of the western Adirondack Mountains, New York, USA. Transactions of the American Fisheries Society 148(2019):373-392. DOI: https://doi.org/10.1002/tafs.10137

Baldigo, B. P., S. D. George, G. B. Lawrence, and E. A. Paul. 2020. Declining aluminum toxicity and the role of exposure duration on brook trout mortality in acidified streams of the Adirondack Mountains, New York, USA. Environmental Toxicology and Chemistry 39(3):623-636. DOI: https://doi.org/10.1002/etc.4645

Baldigo, B. P., G. Lawrence, and H. A. Simonin. 2007. Persistent mortality of Brook Trout in episodically acidified streams of the southwestern Adirondack Mountains, New York. Transactions of the American Fisheries Society 136:121-134. DOI: https://doi.org/10.1577/T06-043.1

Baldigo, B. P., and G. B. Lawrence. 2001. Effects of stream acidification and habitat on fish populations of a North American river. Aquatic Sciences 63(2):196-222. DOI: https://doi.org/10.1007/PL00001352

Baldigo, B. P., and P. S. Murdoch. 1997. Effect of stream acidification and inorganic aluminum on mortality of brook trout (Salvelinus fontinalis) in the Catskill Mountains, New York. Canadian Journal of Fisheries and Aquatic Sciences 54(3):603-615. DOI: https://doi.org/10.1139/f96-314.

Baldigo, B. P., K. M. Roy, and C. T. Driscoll. 2016. Response of fish assemblages to declining acidic deposition in Adirondack Mountain lakes, 1984–2012. Atmospheric Environment 146:223–235. DOI: https://doi.org/10.1016/j.atmosenv.2016.06.049

Breck, J. E. 1988. Relationships among models for acute toxic effects: applications to fluctuating concentrations. Environmental Toxicology and Chemistry 7:775-778. DOI: 10.1002/etc.5620070911.

Driscoll, C. T., K. M. Driscoll, H. Fakhraei, and K. Civerolo. 2016. Long-term temporal trends and spatial patterns in the acid-base chemistry of lakes in the Adirondack region of New York in response to decreases in acidic deposition. Atmospheric Environment 146:5-14. DOI: https://doi.org/10.1016/j.atmosenv.2016.08.034

Driscoll, C. T., K. M. Driscoll, M. J. Mitchell, and D. J. Raynal. 2003. Effects of acidic deposition on forest and aquatic ecosystems in New York State. Environmental Pollution 123(3):327-336. DOI: 10.1016/S0269-7491(03)00019-8.

Fakhraei, H., C. T. Driscoll, J. R. Renfro, M. A. Kulp, T. F. Blett, P. F. Brewer, and J. S. Schwartz. 2016. Critical loads and exceedances for nitrogen and sulfur atmospheric deposition in Great Smoky Mountains National Park, United States. Ecosphere 7(10):e01466-n/a. DOI: 10.1002/ecs2.1466.

Fakhraei, H., C. T. Driscoll, P. Selvendiran, J. V. DePinto, J. Bloomfield, S. Quinn, and H. C. Rowell. 2014. Development of a total maximum daily load (TMDL) for acid-impaired lakes in the Adirondack region of New York. Atmospheric Environment 95:277-287. DOI: 10.1016/j.atmosenv.2014.06.039.

Gagen, C. J., W. E. Sharpe, and R. F. Carline. 1993. Mortality of brook trout, mottled sculpins, and slimy sculpins during acidic episodes. Transactions of the American Fisheries Society 122(4):616-628. DOI: 10.1577/1548-8659(1993)122<0616:MOBTMS>2.3.CO;2.

Johnson, D. W., H. A. Simonin, J. R. Colquhoun, and F. M. Flack. 1987. In situ toxicity tests of fishes in acid waters. Biogeochemistry 3:181-208. DOI: 10.1007/BF02185192.

Lawrence, G. B., B. P. Baldigo, K. M. Roy, H. A. Simonin, R. W. Bode, S. Passy, and S. B. Capone. 2008a. Results from the 2003-2005 western Adirondack stream survey, Albany, NY.

Lawrence, G. B., J. E. Dukett, N. Houck, P. Snyder, and S. Capone. 2013. Increases in dissolved organic carbon accelerate loss of toxic Al in Adirondack lakes recovering from acidification. Environmental Science & Technology 47(13):7095-7100. DOI: 10.1021/es4004763.

Lawrence, G. B., K. M. Roy, B. P. Baldigo, H. A. Simonin, S. B. Capone, J. W. Sutherland, S. A. Nierzwicki-Bauer, and C. W. Boylen. 2008b. Chronic and episodic acidification of Adirondack streams from acid rain in 2003-2005. Journal of Environmental Quality 37:2264-2274. DOI: https://doi.org/10.2134/jeq2008.0061

Lawrence, G. B., H. A. Simonin, B. P. Baldigo, K. M. Roy, and S. B. Capone. 2011. Changes in the chemistry of acidified Adirondack streams from the early 1980s to 2008. Environmental Pollution 159(10):2750-2758. DOI: https://doi.org/10.1016/j.envpol.2011.05.016

Lincoln, T. A., D. A. Horan-Ross, M. R. McHale, and G. B. Lawrence. 2009. Quality-assurance data for routine water analyses by the U.S. Geological Survey Laboratory in Troy, New York--July 2005 through June 2007. U.S. Geological Survey, Open-File Report 05-3121, Troy, New York. http://pubs.usgs.gov/of/2009/1234/

McHale, M. R., D. A. Burns, J. Siemion, and M. R. Antidormi. 2017. The response of soil and stream chemistry to decreases in acid deposition in the Catskill Mountains, New York, USA. Environmental Pollution 229:607-620. DOI: https://doi.org/10.1016/j.envpol.2017.06.001

NADP. 2005. National atmospheric deposition program 2004 annual summary. Illinois State Water Survey, NADP Data Report 2005-01, Champaign, IL.

Simonin, H. A., J. R. Colquhoun, E. A. Paul, J. Symula, and H. J. Dean. 2005. Have Adirondack stream fish populations changed in response to decreases in sulfate deposition? Transactions of the American Fisheries Society 134:338-345. DOI: https://doi.org/10.1577/T03-138.1

Simonin, H. A., E. A. Paul, and J. Symula. 2000. Survival of caged hybrid brook trout in Adirondack headwater streams. New York State Department of Environmental Conservation, Data Report, Rome, New York.

Sullivan, T. J., B. J. Cosby, C. T. Driscoll, T. C. McDonnell, A. T. Herlihy, and D. A. Burns. 2012a. Target loads of atmospheric sulfur and nitrogen deposition for protection of acid sensitive aquatic resources in the Adirondack Mountains, New York. Water Resources Research 48:1547-1547. DOI: 10.1029/2011WR011171.

Sullivan, T. J., B. J. Cosby, T. C. McDonnell, E. M. Porter, T. Blett, R. Haeuber, C. M. Huber, and J. Lynch. 2012b. Critical loads of acidity to protect and restore acid-sensitive streams in Virginia and West Virginia. Water Air and Soil Pollution 223(9):5759-5771. DOI: https://doi.org/10.1007/s11270-012-1312-4

Turnipseed, D. P., and V. B. Sauer. 2010. Discharge Measurements at Gaging Stations. U.S. Geological Survey, Reston, VA. https://doi.org/10.3133/tm3A8

EPA. 2009. Risk and exposure assessment for review of the secondary national ambient air quality standards for oxides of nitrogen and oxides of sulfur. U.S. Environmental Protection Agency Final Report EPA/452/R-09/008A, Research Triangle Park, NC. https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/191774

USGS. 2018. National Water Information System—Web interface. Troy, NY: U.S. Geological Survey. [2018, October 23]. dx.doi.org/10.5066/F7P55KJN.

Van Sickle, J., J. P. Baker, H. A. Simonin, B. P. Baldigo, W. A. Kretser, and W. E. Sharpe. 1996. Episodic acidification of small streams in the northeastern United States: Fish mortality in field bioassays. Ecological Applications 6(2):408-421. DOI: https://doi.org/10.2307/2269379

Wigington, P., Jr.; DeWalle, DR, P. K. Murdoch, WA, H. V. S. Simonin, J, and J. Baker. 1996. Episodic acidification of small streams in the northeastern United States: Ionic controls of episodes. Ecological Applications 6(2):389-407. DOI: 10.2307/2269378.

Zhou, Q., C. T. Driscoll, S. E. Moore, M. A. Kulp, J. R. Renfro, J. S. Schwartz, M. Cai, and J. A. Lynch. 2015a. Developing critical loads of nitrate and sulfate deposition to watersheds of the Great Smoky Mountains National Park, USA. Water Air and Soil Pollution 226(8):1-16. DOI: https://doi.org/10.1007/s11270-015-2502-7

Zhou, Q. T., C. T. Driscoll, T. J. Sullivan, and A. Pourmokhtarian. 2015b. Factors influencing critical and target loads for the acidification of lake-watersheds in the Adirondack region of New York. Biogeochemistry 124(1-3):353-369. DOI: 10.1007/s10533-015-0102-7.

Endnotes

[1] Baldigo, B.P., George, S.D., Lawrence, G.B., Paul, E.A., 2020. Declining aluminum toxicity and the role of exposure duration on brook trout mortality in acidified streams of the Adirondack Mountains, New York, USA. Environmental Toxicology and Chemistry 39, 623-636, https://doi.org/10.1002/etc.4645

[2] Standard operating procedures for these analyses are available at the USGS New York Water Science Center - Soil and Low-Ionic-Strength Water Quality Laboratory web site: https://www.sciencebase.gov/catalog/item/55ca2fd6e4b08400b1fdb88f

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