Declining Aluminum Toxicity and the Role of Exposure Duration on Brook Trout Mortality in Acidified Streams of the Adirondack Mountains, New York, USA

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Abstract: Mortality of brook trout Salvelinus fontinalis and water chemistry were characterized in 6 headwater streams in the western Adirondacks of New York during spring 2015, 2016, and 2017 and compared with results from analogous tests done between 1980 and 2003 in many of the same streams, to assess temporal changes in toxicity and inorganic monomeric aluminum (Al i) concentrations, and the role of Al i exposure duration on brook trout survival. The Al i concentrations of 2 and 4 µmol L⁻¹ corresponded to low-to-moderate and high mortality thresholds, but prolonged exposure to ≥1 µmol Al i L⁻¹ also produced mortality. The variability, mean, and highest Al i concentrations in Buck Creek year round, and in several other streams during spring, have decreased significantly over the past 3 decades. Logistic models indicate that Al i surpassed highly toxic concentrations in Buck Creek for 3 to 4 mo annually during 2001 to 2003 and for 2 to 3 wk annually during 2015 to 2017. The loss of extremely high Al i episodes indicates that toxicity has declined markedly between the 1989 to 1990, 2001 to 2003, and 2015 to 2017 test periods, yet Al i concentrations can still cause moderate-to-high and complete (100%) mortality. The logistic models illustrate how mortality of brook trout in several Adirondack streams likely decreased in response to the 1990 Amendments to the United States’ Clean Air Act (which decreased acidity, Al i concentrations, and duration of toxic episodes) and offer a means to predict how changes in US regulations that limit emissions of NO x and SO x (and N and S deposition loads) could affect fish survival and stream ecosystems in this region and across the Northeast. Environ Toxicol Chem 2020;39:623–636. © 2019 The Authors. Environmental Toxicology and Chemistry published by Wiley Periodicals, Inc. on behalf of SETAC.

Keywords: Inorganic monomeric aluminum; Brook trout; Adirondack streams; Acidification; Clean Air Act; Recovery

INTRODUCTION

Forested watersheds in the southwestern Adirondack Mountains of New York (USA) received some of the most acidic deposition in North America from at least the 1960s through the 1990s (National Atmospheric Deposition Program 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) mobilized by acidic conditions (Johnson et al. 1987; Gagen et al. 1993; Van Sickle et al. 1996; Baldigo and Murdoch 1997). 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 3 dozen streams during fall 1999 (Simonin et al. 2005). During a 2001 to 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 6 western Adirondack streams during 2001 to 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 United States’ 1990 Amendments to the Clean Air Act had
little or no effect on fish communities in streams of the region. Although Baldigo et al. (2007) identified Al, 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 SO$_4^{2−}$ over the last 20 to 30 yr has generally increased acid-neutralizing capacity (ANC) and decreased Al concentrations in a group of Adirondack lakes that have been monitored since at least 1992 (Driscoll et al. 2003, 2016; Baldigo et al. 2016). Although comparable trends in acid–base chemistry of streams in the Catskill Mountains (NY, USA) have been linked to the 1990 Clean Air Act Amendments (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 µeq L$^{−1}$ between the early 1980s and 2003 to 2005. Furthermore, flow-driven acidification episodes (hours to weeks long) were found to create or worsen toxic conditions in 124 of 189 western Adirondack streams that were assessed during 2003 to 2005 (Lawrence et al. 2008a).

The increases in pH and ANC that have occurred from reduced acid 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 µmol Cl$^{−1}$ 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$_5$ to organic monomeric Al (Al$_6$) 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 to 2003 (Baldigo et al. 2007), widespread increases in DOC concentrations over the past 10 to 15 yr, along with continued declines in acidic deposition should have reduced Al$_5$ concentrations and toxicity levels in streams across the region, thereby prompting recovery of brook trout and other species’ populations.

In the present study, mortality responses of juvenile brook trout were characterized in 6 western Adirondack streams each spring during 2015 to 2017 to better define the effects of Al$_5$, concentration and duration of exposure on brook trout survival and to determine whether toxicity in stream waters in this region has declined. The primary objective of our study was to determine whether the 1990 amendments to the Clean Air Act, related regulations, and changes in other climatic factors have reduced contemporary concentrations of Al$_5$, 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. Our 2015 to 2017 toxicity tests were repeated in many or all of the same streams where toxicity was assessed during 4 prior periods (1984–1985, 1988–1990, 1997, and 2001–2003) specifically to determine whether: 1) Al$_5$, concentrations, water toxicity, and brook trout mortality had decreased significantly between the 1980s and present; 2) the relations between stream acidity and Al$_5$, has changed over time; 3) present-day mortality levels reflect previously established Al$_5$-toxicity thresholds for brook trout mortality; and 4) the effects of Al$_5$, concentration and duration of exposure on brook trout mortality can be quantitatively defined.

**MATERIALS AND METHODS**

Discharge (flow), water chemistry, and brook trout mortality were assessed using 30-d in situ toxicity tests in Buck Creek, Pancake Hall Creek, Moss Lake Inlet, Bald Mountain Brook, Fly Pond Outlet, and Wheeler Creek from 9 April to 8 May 2015; 5 April to 5 May 2016; and 4 April to 4 May 2017 (Figure 1). The US 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 to 2003 assessment (Baldigo et al. 2007), and thus are only summarized in the present study. The 6 streams are in the western Adirondack Mountains of northern New York and are tributaries to the Moose River, which feeds into the Black River, and empties into Lake Ontario (USA/Canada).

**Stream chemistry and discharge**

Stream stage (relative water-surface elevation) at Buck Creek during the 3-yr study was measured continuously (at 15-min intervals) using a submersible pressure transducer and recorded with an electronic data logger. Continuous discharge records for Buck Creek were determined using standard USGS methods (Turnipseed and Sauer 2010). Discharge was not recorded continuously at the other 5 study sites, but discharge was measured 4 to 5 times during the 30-d test periods each year at each site.

Stream-water chemistry was determined from grab samples collected at all sites every 1 to 3 d during all toxicity test periods. Chemistry at Buck Creek was supplemented by biweekly grab samples collected year-round and by automated (stage-activated) samples collected during high-runoff events each year from April through November. All stream-water samples collected from 1 October 2013 to 30 September 2017 were used to define the relations between discharge and Al$_5$, concentrations at Buck Creek using nonlinear regression analyses.

All water samples collected from the 6 study streams during test periods in 2001 to 2003 and 2015 to 2017 were analyzed at the USGS New York Water Science Center Soil and Low-Ionic-Strength Water Quality Laboratory (USGS Troy Laboratory, Troy, NY, USA) for pH, ANC, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, SO$_4^{2−}$, NO$_3$$^{−}$, Cl$^{−}$, dissolved organic carbon (DOC), Si, ammonium (NH$_4^+$), total monomeric aluminum (Al$_{5}$), and Al$_{6}$ according to US Environmental Protection Agency (USEPA)-approved methods. Standard operating procedures for these analyses are available from the Lincoln et al. (2019). Concentrations of Al$_5$, in each sample were calculated as the difference between Al$_{5}$ and Al$_{6}$. 

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Negative values were first converted to zeros before subtracting because these values were well below the method operating range of 0.1 mmol L\(^{-1}\) and therefore represented instrument noise. Values obtained from subtracting concentrations of \(\text{Al}_\text{b} \) from \(\text{Al}_\text{i}\) determined on quality control blanks closely approximated zero, and measurements of only 2 of nearly 600 stream samples resulted in a negative value of \(\text{Al}_\text{i}\). Sample handling procedures, quality assurance/quality control (QA/QC) FIGURE 1: Location of study sites in streams of the southwestern Adirondack Mountains where toxicity tests were conducted during spring 2001 to 2003 and spring 2015 to 2017. Modified from Baldigo et al. (2007).

TABLE 1: Exposure dates, stream names, USGS station IDs, mortality levels, and pH and inorganic aluminum (Al) results from various 30-d toxicity tests completed in 6 Adirondack streams using young-of-year brook trout during spring 2015 to 2017

| Test date               | Stream          | USGS station ID | Mortality (%) | Median pH | Median Al, (µmol L\(^{-1}\)) | Min/max Al, (µmol L\(^{-1}\)) | No. of samples |
|-------------------------|-----------------|-----------------|---------------|-----------|------------------------------|-------------------------------|---------------|
| 9 April to 8 May 2015   | Fly Pond Outlet | 04253775        | 0             | 6.71      | 0.68                         | 0.00/1.51                     | 15            |
|                         | Bald Mountain   | 04253770        | 0             | 5.49      | 1.54                         | 0.42/2.79                     | 15            |
|                         | Moss Lake       | 04253715        | 10            | 5.65      | 2.19                         | 0.57/3.43                     | 17            |
|                         | Pancake Hall    | 434945074515901 | 100           | 5.01      | 4.37                         | 0.83/7.15                     | 14            |
|                         | Wheeler Creek   | 434414074445701 | 100           | 4.57      | 7.54                         | 3.00/8.10                     | 9             |
|                         | Buck Creek      | 04253296        | 90            | 5.05      | 5.44                         | 1.84/7.14                     | 15            |
| 5 April to 5 May 2016   | Fly Pond Outlet | 04253775        | 0             | 6.48      | 0.56                         | 0.37/0.85                     | 19            |
|                         | Bald Mountain   | 04253770        | 0             | 5.60      | 0.89                         | 0.54/1.42                     | 17            |
|                         | Moss Lake       | 04253715        | 0             | 5.80      | 1.21                         | 0.52/1.84                     | 19            |
|                         | Pancake Hall    | 434945074515901 | 60            | 5.46      | 1.60                         | 0.78/3.31                     | 19            |
|                         | Wheeler Creek   | 434414074445701 | 25            | 4.94      | 2.93                         | 2.01/4.28                     | 17            |
|                         | Buck Creek      | 04253296        | 18            | 5.26      | 2.13                         | 1.29/3.96                     | 16            |
| 4 April to 4 May 2017   | Fly Pond Outlet | 04253775        | 0             | 6.69      | 0.62                         | 0.32/0.74                     | 18            |
|                         | Bald Mountain   | 04253770        | 0             | 5.57      | 1.24                         | 0.88/2.15                     | 18            |
|                         | Moss Lake       | 04253715        | 0             | 5.71      | 1.23                         | 0.90/2.37                     | 20            |
|                         | Pancake Hall    | 434945074515901 | 100           | 5.03      | 4.28                         | 1.62/5.34                     | 12            |
|                         | Wheeler Creek   | 434414074445701 | 95            | 4.78      | 4.05                         | 2.96/7.51                     | 20            |
|                         | Buck Creek      | 04253296        | 95            | 5.06      | 3.47                         | 2.11/4.93                     | 18            |

USGS = US Geological Survey.
procedures and QA/QC data are summarized in Lincoln et al. (2009). Concentrations of Al, from other water samples collected at Buck Creek, outside of the toxicity-test periods between 1997 and 2017, were derived from measurements of Al, and Al₃, done at either the USGS Troy Laboratory or the Adirondack Lakes Survey Corporation (ALSC) laboratory in Ray Brook, New York (USA) following the same USEPA-approved method. Interlaboratory comparison of 155 sample splits indicated no bias in Al results between laboratories. In addition, concentrations of Al, and Al₃, measured in samples from Buck Creek, Fly Pond Outlet, and Bald Mountain Brook during the period 1989 through 1992 were analyzed at the ALSC laboratory using the method described in Wigington et al. (1996).

Toxicity tests

Young-of-year (YOY) brook trout from the New York State Department of Environmental Conservation hatchery in Rome (NY, USA) were exposed (in cages) to stream waters for approximately 30 d each spring following the same procedures used by Johnson et al. (1987). Trout were transported to the control stream (Fly Pond Outlet) in submersed 4-L plastic, screen-sided jars (5 fish/jar) and placed into larger holding chambers to acclimate for 24 h prior to the start of tests. The next day, 20 trout (4 jars with 5 fish each) were transported to each study stream and placed into the screen-sided holding chamber. Trout mortality was checked and recorded daily for the first 4 d, and then every 2 to 3 d during in situ exposures. The lengths of brook trout averaged 41 mm (range: 36–48 mm) in 2015, 52 mm (range: 40–59 mm) in 2016, and 42 mm (range: 34–46 mm) in 2017. An analysis of variance (ANOVA) indicated that trout lengths were significantly (p < 0.0001) longer in 2016 than in 2015 and 2017.

Prior studies used brook trout YOY (or fry) to assess water quality and toxicity during the 1980s (Johnson et al. 1987), 1990s (Simonin et al. 1993; Van Sickle et al. 1996; Baldigo and Murdoch 1997), and early 2000s (Baldigo et al. 2007) in some or all of the same streams assessed in the present study. Key objectives, specific study sites, test periods, and brook trout strains (and sizes) used for each set of tests are summarized in Baldigo et al. (2007).

Data analyses

Study objectives and goals were addressed through 4 analyses. First, the 2015 to 2017 trout mortality and water chemistry data from all streams were summarized to characterize present-day toxicity levels (mortality responses) and to determine whether the results reflected previously established Al₃-toxicity thresholds for brook trout survival/mortality. Second, the relations between brook trout mortality and Al₃ concentration were compared across the 5 toxicity-test periods to determine whether the apparent relations differed among periods and/or changed through time. The concentrations of Al₃ measured during the last 2 test periods, and since 1989 at Buck Creek, were also evaluated to determine whether significant temporal declines were evident. Third, results from the 2001 to 2003 and 2015 to 2017 toxicity tests were merged and used in logistic regressions to quantify brook trout mortality responses to differing pH, ANC, and Al₃ concentrations, as well as to various Al₃ concentrations and exposure durations. Lastly, to better understand the significance of elevated Al₃ 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 Al₃, levels at Buck Creek.

The daily cumulative mortality and Al₃ concentration data from the 2015 to 2017 toxicity tests were graphed to illustrate the mortality responses at all streams during the more recent test period. Although brook trout mortality and Al₃, chemistry data were collected every 1 to 3 d at each stream, data for unsampled dates were extrapolated (assuming linearity) from the number of fish alive and the Al₃ concentrations measured on the closest previous and subsequent sample dates. Cumulative mortality levels and the measured and estimated Al₃, concentrations during (and at the end of) each test were examined to identify or confirm low (≤20% mortality) and high (≥90% mortality) Al₃-toxicity thresholds for YOY brook trout. In addition, total mortality and median Al₃ concentrations at the end of all 2015 to 2017 tests were analyzed using linear regression to characterize the present-day toxicity levels and the mortality–Al₃ relation. This equation was compared with those developed for the other 4 test periods (Baldigo et al. 2007) using multiple regression analysis in StatGraphics (StatPoint 2010) to determine whether the slopes of the relations (and Al₃ toxicity) differed among the 5 test periods. Differences among streams and years were obvious, and thus they were not assessed statistically. Changes or differences in trout mortality levels across test periods were evaluated through one-way ANOVA.

The relations between Al₃ concentration and duration of exposure that resulted in brook trout mortality at low (≤20%), moderate (≤50%), high (≥90%), and complete (100%) levels during the 2015 to 2017 and 2001 to 2003 tests were quantified using logistic regression analyses. To perform this analysis, the conditions of fish observed at each site during each day were first translated into binary values (i.e., 0 = alive and 1 = dead) that were organized by test day (1–30), year, and period. In general, there were 20 observations every day at each site; 600 observations for the 30 d at each site each year; 3600 observations at all 6 sites each year; and >10 800 observations at all sites over each 3-yr period. A total of 23 281 observations was generated for all of the 2001 to 2003 and 2015 to 2017 toxicity tests. The daily live/dead observations (0 or 1) for each fish from all sites, years, and both test periods (2001–2003 and 2015–2017) were linked to the median pH, ANC, and Al₃ concentrations; the mean Al₃ concentrations; the cumulative Al₃ concentrations; and the number of days for which Al₃ was >0 and ≥1, 2, 3, 4, 5, 6, 7, and 8 µmol L⁻¹. These data were used to generate logistic equations (and 95% confidence intervals) to estimate the probability of death (100% mortality) for individual brook trout (or groups of brook trout) when Al₃ concentrations exceeded 0 µmol L⁻¹, and were ≥1, 2, 4, and 8 µmol L⁻¹ for durations between 0 and 30 d.
These records were linked to cumulative daily mortality data to generate binary observations for cumulative mortality equal to 0%, and $\geq 0, 20, 30, 40, 50, 60, 70, 80, 90, 100$%; and equal to 100% for tests done at all sites during all years and both test periods. Because only 1 cumulative mortality and 1 chemistry observation was obtained at each site and day, a total of 1178 observations were used to generate logistic equations (and 95% confidence intervals) to predict the probabilities for low ($\geq 20$%), moderate ($\geq 50$%), and high ($\geq 90$%) mortality levels in groups of brook trout (or for individuals) when Al concentrations exceeded 0 and were $\geq 1, 2, 4,$ and 8 $\mu$mol L$^{-1}$ for durations between 0 and 30 d.

The logistic equations (and their associated curves) define the probabilities for occurrences of minimum mortality outcomes when YOY brook trout are exposed to a range of Al concentrations over differing lengths of time (durations) in streams of the western Adirondacks. Data from tests done during 2001 to 2003 and 2015 to 2017 were combined to maximize the range of Al, chemistry and mortality responses and to broaden the temporal and spatial applicability of our models. The first set of equations predicts the likelihood for observing death in an individual YOY brook trout (or the proportion of individuals in a group of brook trout) at different mean Al concentrations and exposure durations. The second set of equations estimates probabilities for observing low (>$20$%), moderate (>$50$%), and high (>$90$%) levels of mortality in groups (or populations) of brook trout when Al concentrations exceed 0 $\mu$mol L$^{-1}$ and were $\geq 1, 2, 4,$ and 8 $\mu$mol L$^{-1}$ for durations between 0 to 30 d. All logistic equations follow the same format, where the probability that any dependent variable, $F(y)$ (e.g., mortality) equals or exceeds a given response (e.g., $\geq 90$%) when mean Al concentrations equal or exceed a set criteria (e.g., $\geq 4\mu$mol L$^{-1}$) over the range of exposure durations ($x$; e.g., 0–30 d). All equations take the form of:

$$F(y) = e^{(\beta_0+\beta_1 x)(x)}/(1 + e^{(\beta_0+\beta_1 x)}),$$

or simply

$$1/(1 + e^{(-\beta_0+\beta_1 x)}),$$

where $e$ is the natural logarithm base, $\beta_0$ is the intercept from a linear regression (i.e., the value when the predictor is equal to zero), and $\beta_1$ is the logistic regression coefficient. All logistic equations (and the percentage of the deviance in probabilities explained by each model) were summarized in tables, and representative equations were plotted to illustrate the range of significant relations.

The duration of toxic Al conditions at Buck Creek during 2015, 2016, and 2017 was determined using discharge as a surrogate. The relationship between Al concentration and discharge was developed using 159 chemistry samples and continuous discharge records for the 3-yr period. This equation was then used to estimate specific discharge levels that corresponded to key Al toxicity thresholds. Continuous discharge records for each year and the entire 3-yr period were then ranked from the lowest to highest values, and the percentages of exceedances for the specific discharge values were used as surrogates to estimate the percentage of time that key Al thresholds were surpassed each year and for the entire 3-yr period.

**RESULTS**

**Stream discharge and chemistry**

Mean daily discharge at Buck Creek during the 2015, 2016, and 2017 toxicity-test periods averaged 0.159, 0.082, and 0.158 m$^3$ s$^{-1}$ (5.62, 2.90, and 5.58 ft$^3$ s$^{-1}$), respectively (Supplemental Data, Figure S1). All discharge measurements made at each ungauged site (Fly Pond Outlet, Moss Lake Inlet, Bald Mountain Brook, Pancake Hall Creek, and Wheeler Creek) during the spring 2015 to 2017 tests averaged 32% (16–50%), 63% (21–93%), 40% (27–63%), 31% (25–39%), and 229% (133–319%), respectively, of the corresponding average of all discharge values logged at the gauged site (Buck Creek) on the same dates and at the same times. The relations between discharge at Buck Creek and discharge at each of the other 5 streams were relatively strong ($R^2$ values of 0.80–0.97). The daily discharge record at Buck Creek (Supplemental Data, Figure S1) suggested that rainfall and/or snowmelt events substantially elevated flows during the 2015 and 2017 toxicity tests, but that only one moderate high-flow event occurred during the 2016 test period. Discharge data for Buck Creek (USGS station ID 04253296) are available through the USGS National Water Information System (US Geological Survey 2018).

Stream chemistry varied considerably among tests and streams. Median Al concentrations were near or less than 2 $\mu$mol L$^{-1}$ at Fly Pond Outlet, Bald Mountain Brook, and Moss Lake Inlet during all test periods; whereas they were $\geq 4\mu$mol L$^{-1}$ at Pancake Hall Creek, Buck Creek, and Wheeler Creek during 2015; <3.0 $\mu$mol L$^{-1}$ at the same 3 sites during 2016; and $\geq 4\mu$mol L$^{-1}$ only at Pancake Hall Creek and Wheeler Creek during 2017 (Table 1). Measured and extrapolated Al concentrations did not exceed 2 $\mu$mol L$^{-1}$ at Fly Pond Outlet during any test period; however, they surpassed 2 $\mu$mol L$^{-1}$ at Bald Mountain Brook and Moss Lake Inlet for 1 to 3 d during 2017 and for 16 to 17 d during 2015 (Figures 2A, 3A, and 4A). The Al concentrations at Pancake Hall Creek, Wheeler Creek, and Buck Creek surpassed 2 $\mu$mol L$^{-1}$ for 3 to 30 d during each of the 30-d exposure periods in 2015 to 2017. Concentrations of Al at Fly Pond Outlet, Bald Mountain Brook, and Moss Lake Inlet did not exceed 4 $\mu$mol L$^{-1}$ at any time during the 3 most recent test periods. Although Al concentrations at Pancake Hall Creek, Wheeler Creek, and Buck Creek generally did not surpass 4 $\mu$mol L$^{-1}$ during 2016, this value was exceeded at the 3 streams for 3 to 20 d during 2015 and 2017 (Figures 2A, 3A, and 4A). Original chemistry data from all samples collected during 2015 to 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 (US Geological Survey 2018).

The relationship between Al, concentration and discharge (Supplemental Data, Figure S2) indicates that discharge accounted for 55% of the variability in year-round Al concentrations at Buck Creek. The discharge levels that corresponded to key Al concentrations or thresholds of 1, 2, and 4 $\mu$mol L$^{-1}$ were estimated to be 0.02, 0.04, and 0.26 m$^3$ s$^{-1}$, respectively. Linking these values to the cumulative daily flow-duration curve for calendar years 2015 to 2017 at Buck Creek (Supplemental
Data, Figure S3) indicated that the 4 µmol Al L⁻¹ threshold (0.26 m³ s⁻¹) was exceeded 4.4% of the time (1.6 mo), that the 2 µmol Al L⁻¹ (0.04 m³ s⁻¹) threshold was exceeded 49% of the time (17.9 mo), and that the 1 µmol Al L⁻¹ (0.02 m³ s⁻¹) threshold was surpassed 73% of the time (26.7 mo) during the 36‐mo period. The durations for which Al concentrations exceeded these 3 thresholds were highly variable among years. For example, the flow associated with the 2 µmol Al L⁻¹ (0.04 m³ s⁻¹) threshold at Buck Creek was exceeded 37.3% (4.5 mo), 48.4% (5.9 mo), and 61.9% (7.5 mo) of the time during calendar years 2015, 2016, and 2017, respectively.

Brook trout mortality and relation to Al₃ concentration

Like most previous toxicity‐test results, mortality of YOY brook trout during the 2015 to 2017 exposures differed among streams and years (Table 1). During the 2015 toxicity tests, no brook trout died at Fly Pond Outlet and Bald Mountain Brook, 10% succumbed at Moss Lake Inlet, and 90 to 100% of trout died at Pancake Hall Creek, Wheeler Creek, and Buck Creek (Figure 4B). Daily observations (and extrapolations) of the numbers of brook trout that were alive and dead during all toxicity tests done during 2001 to 2003 and 2015 to 2017 are provided in Baldigo and George (2019).

The relation between brook trout mortality and median Al₃ concentrations during the 2015 to 2017 toxicity tests was significant (R² = 0.76; p < 0.0001) and generally comparable to those from the 4 earlier test periods, yet several important differences were evident. First, the slope of the 2015 to 2017 mortality‐Al₃ relation was greater than, and significantly different from, the slopes of the relations observed during all other test periods (Figure 5). Second, median Al₃ 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 to 2017 test (Table 1). Although extremely high Al₃ concentrations were not evident during most of the 2015 to 2017 tests, data in Figure 5 and Table 1 show that high and complete (90‐100%) trout mortality still occurred at several sites during 2 of the 3 yr.

Temporal trends in Al₃ concentrations and toxicity

Declining Al₃ concentrations and reduced brook trout mortality levels indicate that the toxicity of local stream waters decreased markedly over the past 10 or 15 yr. Toxicity trends
were evaluated by assessing 1) mean mortality responses during the 5 test periods (1984–1985, 1988–1990, 1997, 2001–2003, and 2015–2017); 2) Al concentrations from spring toxicity tests during the last 3 test periods (1989–1990, 2001–2003, and 2015–2017); and 3) temporal trends in Al concentrations from water samples collected at Buck Creek between 1989 and 2017. One-way ANOVA results indicated that mean mortality levels for all sites during each of the 5 test periods ranged from 30 to 60% and did not differ significantly among periods ($p = 0.328$, $df = 4$, $F = 1.17$), but that the mean mortality levels for individual sites during each year ranged from 0 to 62% and differed among years ($p = 0.061$, $df = 10$, $F = 1.87$). Although year-to-year differences in brook trout mortality levels were nearly significant statistically, there was no consistent decreasing trend in pooled mortality results from all study streams over the 5 test periods.

Additional one-way ANOVA results indicated that temporal declines in Al concentrations during springtime test periods were significant within individual streams. Although Al data were only available from several samples collected at study streams during the first and third test periods, extensive chemistry sampling during the second and 2 most recent test periods indicated that the maximum, 75th percentile, mean, and median Al concentrations from all samples collected at 5 of the 6 streams were lower during 2015 to 2017 than during 2001 to 2003 and 1989 to 1990 (Supplemental Data, Figure S4). Data from Buck Creek collected since 1997 also showed that mean Al concentrations from routine (weekly, biweekly, and monthly) water samples decreased significantly (ANOVA; $p < 0.0001$, $df = 1042$, and $F = 9.05$) by 0.00043 µmol L$^{-1}$/d between 1997 and 2017, and by approximately 5.5 µmol L$^{-1}$ between 1989 and 2017 (Figure 6). Direct comparisons between Al concentrations measured during the 1989 to 1990 tests and the 2 recent test periods may not be accurate because the method used to analyze Al during 1989 to 1990 (Wigington et al. 1996) differed from that used during 1997 to 2017. The 1989 to 1990 data suggest, however, that extremely high Al concentrations (>15 µmol L$^{-1}$) were common during this period, and that levels >10 µmol L$^{-1}$ have not occurred since 2002 (Figure 6). Although Al concentrations from at least 3 study streams continued to reach acutely toxic levels during the 2015

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**FIGURE 4:** Daily measurements or estimates of inorganic monomeric aluminum (Al) concentration (A) and brook trout mortality (B) at each of 6 western Adirondack streams during toxicity tests done in the spring of 2017. (Data symbols for sites with zero mortality overlap and may not be visible.)

**FIGURE 5:** Mortality of brook trout in relation to median inorganic monomeric aluminum (Al) concentrations from 30-d toxicity tests done in streams of the western Adirondacks during 1984 to 1985 (open circles), 1988 to 1990 (shaded circles), 1997 (open triangles), 2001 to 2003 (shaded triangles), and 2015 to 2017 (open squares). (The test periods with different group letters have equation slopes that differ significantly [$p < 0.05$] from the others.)

**FIGURE 6:** Measured inorganic monomeric aluminum (Al) concentrations from all routine water samples (with automated storm-event samples omitted) collected at Buck Creek between 1 January 1989 and 31 December 2017. (The solid line and equation describe the trend in Al concentrations between 1997 and 2017.)
to 2017 tests, the recent absence of extremely high Al concentrations in most study streams, and the steady decline in Al levels in Buck Creek between at least 1997 and 2017, suggest that Al toxicity has declined substantially in these and other acid-sensitive streams in the western Adirondacks.

**Probability of brook trout death**

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

The effects of exposure duration on survival may be defined by logistic equations that predict the probability of brook trout death based on the total number of days in which Al concentrations exceeded 0 µmol L\(^{-1}\), and were ≥1, 2, 3, 4, 5, 6, 7, and 8 µmol L\(^{-1}\) during all 30-d exposures throughout 2001 to 2003 and 2015 to 2017. All such equations were significant, and those using the total number of days that Al concentrations were ≥2, 3, or 4 µmol L\(^{-1}\) explained 29.2 to 33.1% of the deviances (Table 2). The curves in Figure 7A indicate that death is highly probable (≥0.90) if Al 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 concentrations surpass 1 µmol L\(^{-1}\) for approximately 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 may be expected to succumb when exposed to the same Al concentrations and durations.

**Probabilities for low, moderate, and high levels of brook trout mortality**

A third set of logistic equations, which predict the probability for low (≥20%), moderate (≥50%), and high (≥90%) levels of brook trout mortality, were also derived to quantify the shifting risk of past, present, and future Al conditions in our study streams and in others across the region. The probabilities for observing at least 90% (Figure 7B), 50% (Figure 7C), and 20% (Figure 7D) mortality in YOY brook trout exposed to waters of differing median Al concentrations are defined by equations in Table 3. 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 of toxicant exposure.

**Table 2:** Estimates of exponents β0 and β1, percentages of explained deviance, Chi-square statistics, odds ratio, and the number of non-zero observations (of a total of 23 281), and p values for logistic equations describing the probability of brook trout death (mortality) based on median inorganic aluminum (Al\(_{\text{i}}\); µmol L\(^{-1}\)), pH concentrations; cumulative Al concentration; mean Al concentration; and the number of days that Al concentrations were ≥1, 2, 3, 4, 5, 6, 7, and 8 µmol L\(^{-1}\) during 30-d in situ toxicity tests in 6 western Adirondack streams during spring 2001 to 2003 and 2015 to 2017. The estimated coefficients, their standard errors, and Chi-square values are from logistic regressions for all 23 281 observations used to derive the equations. The Chi-square statistics for all logistic equations are <0.0001. The p values for all logistic equations are <0.0001. The no = not applicable.

| Predictor metric | β0       | β1       | Explained deviance (%) | Chi-square statistic | Degrees of freedom | No. of non-zeros | Odds ratio | p value |
|------------------|----------|----------|------------------------|----------------------|--------------------|-----------------|------------|---------|
| Al\(_{\text{i}}\) > 0 µmol L\(^{-1}\) | 1.93690 0.21077 22.9 | 385.2 | 448.5 | 1 | 0.0000 | 7980 | 1.23 |
| Al\(_{\text{i}}\) ≥ 1 µmol L\(^{-1}\) | 1.61727 0.37161 17.8 | 853.3 | 1.68 | 0.0000 | 4900 | 1.45 | 0.0000 |
| Al\(_{\text{i}}\) ≥ 2 µmol L\(^{-1}\) | 1.88204 0.31215 23.8 | 40.5 | 1.37 | 0.0000 | 6000 | 1.49 |
| Al\(_{\text{i}}\) ≥ 3 µmol L\(^{-1}\) | 1.32853 0.42003 8.7 | 78.0 | 1.52 | 0.0000 | 1800 | 1.52 |
| Al\(_{\text{i}}\) ≥ 4 µmol L\(^{-1}\) | 1.93690 0.21077 22.9 | 385.2 | 448.5 | 1 | 0.0000 | 7980 | 1.23 |
| Al\(_{\text{i}}\) ≥ 5 µmol L\(^{-1}\) | 1.61727 0.37161 17.8 | 853.3 | 1.68 | 0.0000 | 4900 | 1.45 |
| Al\(_{\text{i}}\) ≥ 6 µmol L\(^{-1}\) | 1.88204 0.31215 23.8 | 40.5 | 1.37 | 0.0000 | 6000 | 1.49 |
| Al\(_{\text{i}}\) ≥ 7 µmol L\(^{-1}\) | 1.32853 0.42003 8.7 | 78.0 | 1.52 | 0.0000 | 1800 | 1.52 |
| Al\(_{\text{i}}\) ≥ 8 µmol L\(^{-1}\) | 1.93690 0.21077 22.9 | 385.2 | 448.5 | 1 | 0.0000 | 7980 | 1.23 |

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Results for brook trout mortality in some of the most recent toxicity tests would indicate that 1) any measurable Al in stream waters put YOY brook trout at risk of death, and 2) exposure to median Al concentrations ≥1 µmol L⁻¹ could lead to substantial (≥60%) mortality if durations approach 30 d. These equations also confirm that a median Al concentration of 2 µmol L⁻¹ is an appropriate threshold for low-to-moderate mortality levels (≥20% or ≥50%) and that 4 µmol L⁻¹ is an appropriate threshold for high mortality levels (≥90%) for YOY brook trout in streams of the region. Our models (Figure 7A) predict that ≥20% of brook trout will die if median Al concentrations surpass 2 µmol L⁻¹ for 9 d and that ≥50% of brook trout will die if median Al concentrations surpass 2 µmol L⁻¹ for 17 to 18 d. Similarly, ≥50% of brook trout will succumb if median Al concentrations surpass 4 µmol L⁻¹ for 10 to 11 d, and ≥90% of brook trout will die if median Al concentrations surpass 4 µmol L⁻¹ for 21 d. Median Al 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 after 8 to 9 d of exposure. Furthermore, the probability of moderate 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 mortality reaches 0.90 after 19 d at 4 µmol L⁻¹ and after 4 to 5 d at 8 µmol L⁻¹ (Figure 7B and 7C). Although the various Al exposure concentrations and durations likely interact to yield more of a continuum in effects (mortality), several Al thresholds and mortality levels noted in the present study 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 to 2003 tests were done (i.e., over the past 14–16 yr). Whereas brook trout mortality levels were usually <25% at Fly Pond Outlet, Bald Mountain Brook, and Moss Lake Inlet during the 2015 to 2017 and 2001 to 2003 tests, mortality levels often reached 100% at Pancake Hall Creek, Buck Creek, and Wheeler Creek during both test periods. Because 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 to 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 concentrations. Although Al concentrations have decreased between the 2 test periods, their low-to-moderate levels still exceed critical survival thresholds for durations that are long enough to cause high mortality in several study streams. Thus, changes in the duration that Al concentrations surpass important survival thresholds may be the best approach to gauging changes in toxicity (and recovery) of acidified streams across the region.

Nevertheless, the changes in water chemistry at Buck Creek, and presumably other study streams since the late 1980s and early 1990s, suggest that biologically meaningful decreases in Al concentrations occurred in response to regional declines in acidic deposition. Figure 6 shows that concentrations of Al at Buck Creek decreased steadily from a mean of approximately 5 μmol L⁻¹ in 1997 to a mean of <2.0 μmol L⁻¹ in 2017, and that mean and peak concentrations at Buck Creek (and other study sites) were probably much greater in 1989 to 1990 than in 2001 to 2003 and 2015 to 2017 (Supplemental Data, Figure S4). Also consistent with the Buck Creek record, the interquartile ranges and mean Al concentrations were significantly lower during the 2015 to 2017 tests than during the 2001 to 2003 tests (at most other study streams) and the 1989 to 1990 tests (at Buck Creek and Bald Mountain Brook; Supplemental Data, Figure S4).

Despite these large decreases in both mean and peak Al concentrations at Buck Creek and other study streams, expected decreases in toxicity levels were not evident during spring 2015 to 2017 tests. This result may be explained by examining the relations between median Al concentrations and brook trout mortality (at the end of 30-d exposures) during the 5 test periods (Figure 5). Except for 1988 to 1990, the slopes of all prior relations were not significantly different from each other (Baldigo et al. 2007), but the slope for 2015 to 2017 was significantly steeper than during all other test periods. This shift implies that either the sensitivity of brook trout to Al had changed over time, which is unlikely (because the source and strain of test fish had not changed), or that the underlying range of Al concentrations had changed, and brook trout were dying at high rates above a relatively low Al concentration (effect) threshold. The large declines in Al concentrations in waters from several study streams support the latter implication. In effect, extremely high Al concentrations no longer occur, but they still surpass thresholds of 2, 3, or 4, μmol Al L⁻¹ for durations that are long enough 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, to brook trout that experience the dynamic chemical regimes of streams in the western Adirondacks. Our probabilistic models (Figure 7) essentially quantify the relations between mortality levels and Al-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 concentration and duration regimes. For example, the
likelihood of extant brook trout populations in unsurveyed streams within the region may be inferred using models in Figure 7A. If present-day chemistry data show that median Al concentrations do not exceed 2 µmol L\(^{-1}\) for more than 10 d 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 US secondary standards for target loads of N and S deposition and stream ANC levels (US Environmental Protection Agency 2009) would likely affect brook trout mortality and possibly their populations in one or more streams of the region. Given that Al concentrations are strongly related to ANC at Buck Creek (\(R^2 = 0.69\); Supplemental Data, Figure S6), we can predict that median Al concentrations in 2 hypothetical streams with present-day mean or median ANC levels of 0 and 30 µeq L\(^{-1}\) would be approximately 5.0 and 1.4 µmol L\(^{-1}\), respectively. Presuming these Al 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 7A), respectively, and the probabilities 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 concentrations in our 2 case streams to approximately 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 would likely increase the density of resident populations in both case streams.

When combined with continuous Al and discharge records, our brook trout response models illustrate how long-term declines in Al concentrations may have affected brook trout survival and their wild populations over the past 3 decades. The continuous (15-min, hourly, or daily) discharge data at Buck Creek can be used to develop continuous Al records because they are moderately related on an annual basis (\(R^2 = 0.55\); Supplemental Data, Figure S2) 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 L\(^{-1}\) and a discharge of 0.26 m\(^3\) s\(^{-1}\) corresponds to 4 µmol Al L\(^{-1}\) at Buck Creek. The 2015 to 2017 daily discharge-duration curve for Buck Creek (Supplemental Data, Figure S3) shows that Al effect thresholds of 2 and 4 µmol L\(^{-1}\) were exceeded 50 and 5% of the time, respectively. This means that Al concentrations at Buck Creek currently exceed 2 µmol L\(^{-1}\) for roughly 6 mo each year and that they exceed 4 µmol L\(^{-1}\) for 2 to 3 wk each year. The logistic models in Figure 7A indicate that the present-day probabilities for brook trout mortality at Buck Creek, based on exceedance times for 2 and 4 µmol L\(^{-1}\), are 1.00 and 0.67 to 0.91, respectively. Analogous analyses at Buck Creek during 2001 to 2003 found that Al concentrations exceeded 4 µmol L\(^{-1}\) for 3 to 4 mo each year (Baldigo et al. 2007). Although the probabilities for brook trout mortality at Buck Creek reached 1.00 for part of each year in 2001 to 2003 and in 2015 to 2017, the duration that Al concentrations were highly toxic (≥4 µmol L\(^{-1}\)) declined radically between the 2 test periods.

The results from recent fish surveys done in 48 western Adirondack streams help to demonstrate how various Al concentration thresholds and associated probabilities for brook trout mortality correspond to the condition of wild 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 wild populations, our models can predict the potential or probable effects on their populations—due to acid–base chemistry alone—if we assume 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 concentrations >2 µmol L\(^{-1}\), were present generally in low densities and biomass at sites with Al concentrations between 1 and 2 µmol L\(^{-1}\), and were 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 extant brook trout populations decreased from 0.96 at streams with summer Al 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 3.0 µmol L\(^{-1}\), and that the probabilities for >100 brook trout/0.1 ha decreased from approximately 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 base flow and water chemistry is typically least acidic (and have their lowest Al concentrations) during summer, these apparent “wild-population” Al thresholds may not always represent the most toxic acid-Al periods or even annual mean or median Al levels, but simply the least toxic/stressful conditions that occur each year in each stream. Except for Buck Creek, annual mean or median Al values for our fish-survey sites are unavailable. However, data from 55 nearby western Adirondack streams, sampled as part a long-term chemistry monitoring program (G. Lawrence, personal communication), provide a way to formulate an adjustment factor that can make wild-population Al thresholds more broadly relevant. The mean summer 2014 Al 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 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 wild-population and Al relations (and effect thresholds) representative of year-round (mean or median) Al conditions in streams of the region. Consequently, Al 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 on whether concentrations represented summer (base flow) or annual mean or median conditions. Whereas (Baker et al. 1996) indicates that an upper Al 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 pH 5.0 corresponds to an Al concentration of 2.2 µmol L⁻¹, which supports our thesis that springtime concentrations of 2.0 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 wild brook trout. Consequently, our probability model for brook trout mortality and duration of Al concentrations of ≥2 µmol L⁻¹ is most appropriate for predicting the occurrence of brook trout at low densities, whereas the model for duration of Al concentrations of ≥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 wild brook trout has some important implications concerning the health of local fish communities. Identifying an upper Al threshold that impairs entire fish communities is challenging because different species have variable tolerances to acid-Al 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 (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 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 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 L⁻¹, to 0.34 at 1 µmol Al L⁻¹, and to 0.12 at 2 µmol Al L⁻¹ in the same streams (Baldigo et al. 2019a). Thus, some variation of our probability model for brook trout mortality and duration of ≥1 µmol Al L⁻¹ may be appropriate for predicting total community richness in local streams. In addition, because total community density and biomass only reach moderate and high levels in streams with summer Al 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 L⁻¹ to 0.50 at 1 µmol Al L⁻¹, and the loss of all other fish species at Al concentrations >1 µmol L⁻¹ (Baldigo et al. 2019a), supports 1 µmol Al L⁻¹ as an upper limit or threshold for avoiding community impacts.

**Study implications**

Our probabilistic models quantify the interconnected effects of Al 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 concentrations well below previously established thresholds can lessen the survival of YOY brook trout. An Al concentration of 1 µmol L⁻¹ may serve as a chronic-toxicity threshold; 2 µmol L⁻¹ can be considered an acute-toxicity threshold; and 4 µmol L⁻¹ represents a threshold for high or complete toxicity. The first 2 Al 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 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, our mortality models and refined Al effect thresholds can help US 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 US secondary standards that limit atmospheric emissions of NOₓ and SO₂ 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 (US Environmental Protection Agency 2009). Although a number of studies have modeled how various N and S deposition loads affect ANC levels in streams and lakes across the eastern United States (Sullivan et al. 2012a, 2012b; Fakhraei et al. 2014, 2016; Zhou et al. 2015a, 2015b), our mortality models, fish-assemblage models from Baldigo et al. (2019a), and various Al 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.

Our models can also help demonstrate how regulations imposed by the Clean Air Act of 1970 and the 1990 Amendments to the Clean Air Act reduced Al concentrations and toxicity in streams of the western Adirondacks over the past 3 decades. The variability, mean, and highest Al concentrations observed in Buck Creek 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 surpass highly toxic thresholds (4 µmol L⁻¹) at Buck Creek decreased from approximately 3 to 4 mo each year during 2001 to 2003 to approximately 2 to 3 wk each year during 2015 to 2017. Although Al concentrations in waters still surpass toxic thresholds for periods sufficiently long to cause high levels of mortality in YOY brook trout at Buck Creek and several other study sites during 2015 to 2017, the absence of extremely high Al levels confirms that toxicity levels have declined substantially since the 1989 to 1990 and 2001 to 2003 test periods. Whether declines in acidity and Al concentrations in western Adirondack streams are caused directly or indirectly by the 1990 amendments to the Clean Air Act is arguable. The decreasing trend in Al 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 our study, brook trout populations in previously acidified streams should experience significant recovery as Al concentrations continue to decline below critical survival thresholds and should sustain those levels for longer and longer durations.
Although decreases in acidity, Al, concentrations, and the duration that Al levels are elevated suggest that toxicity levels have recently declined noticeably, high mortality levels at several streams during the 2015 to 2017 tests indicate that acid-Al 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 Amendments to the Clean Air Act may have had only negligible effects on biological recovery in streams across the region. At a minimum, the timing and degree of biological recovery may simply be lagging behind chemical recovery in local streams for various reasons. Although quantitative fish surveys in 2014 to 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.

Supplemental Data—Supplemental figures are available on the Wiley Online Library at DOI: 10.1002/etc.4645.

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Data Availability Statement—Discharge data pertinent to Buck Creek (US Geological Survey [USGS] station ID 04253296) in this manuscript are available through the USGS National Water Information System (NWIS) at https://nwis.waterdata.usgs.gov/nwis/sw. Chemistry data pertinent to all water samples collected during 2001 to 2003 and 2015 to 2017 at each of the study sites described in this manuscript are available by USGS station ID (see Table 1) and dates through NWIS at https://nwis.waterdata.usgs.gov/usa/nwis/quant. Daily observations (and extrapolations) of the numbers of brook trout that were alive and dead during all toxicity tests done during 2001 to 2003 and 2015 to 2017 are provided in Baldigo and George (2019).

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