Predictive Relations between Acid-Base Chemistry and Fish Assemblages in Streams of the Adirondack Mountains

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Cover Image: Bear Brook near Blue Mountain Lake, NY. Photo credit to Barry Baldigo

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Summary Report

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Abstract

Surface waters across much of New York State's Adirondack Mountains were acidified in the late 20th century but began to recover following the 1990 Title IV Amendments to the Clean Air Act. Previous assessments of acidification recovery in the Adirondacks have generally been based on surface water chemistry data and inferred relationships to fish and other aquatic biota. Little data, however, has been available to characterize biological impacts and predict recovery of fish assemblages in streams of the region. Here, we use quantitative fish surveys combined with chemistry data from 48 headwater streams sampled during summer 2014–2016 to develop logistic (probability) models that characterize the status of contemporary fish assemblages and predict how different N and S deposition loads may affect future fish assemblages. Statistical models for inorganic aluminum (Al_i) and richness ≥1 species; and for acid neutralizing capacity (ANC) and total density >400 fish/0.1 ha, total biomass >1500 g/0.1 ha, brook trout *Salvelinus fontinalis* density >0 or >200 fish/0.1 ha, and brook trout biomass >1000 g/0.1 ha were suitable for evaluating community and population responses to changes in acid-base chemistry. Predictions of fish-assemblage responses using several of these models demonstrated that anticipated changes in national (U.S.) secondary standards for atmospheric emissions of NO_x and SO_x to achieve target N and S deposition loads are likely to alter the acid-base chemistry and the probabilities of observing various levels of brook trout population and fish-community metrics in streams across the region and elsewhere.

Keywords

Fish assemblages; brook trout; stream acidification; oxides of nitrogen and sulfur; Adirondack Mountains; target deposition loads; critical loads

Acknowledgments

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Baldigo, B. P., S. D. George, C. T. Driscoll, S. Shao, T. J. Sullivan, D. A. Burns, and G. B. Lawrence. 2019. 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. 76(11):2013-2026. https://doi.org/10.1139/cjfas-2018-0260.

Additional information on the stream chemistry and fish assemblages, used to develop models summarized in this report and in Baldigo et al. (2019a), are provided in Baldigo et al. (2019b) and published in *Transactions of the American Fisheries Society*. The full citation for that article is as follows:

Baldigo, B. P., S. D. George, G. B. Lawrence, and E. A. Paul. 2019. 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(219):373-392. https://doi.org/10.1002/tafs.10137.

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1 Focus

The primary purpose of this study is to increase our understanding of contemporary relations between indicators of acid-base chemistry and different levels of fish-assemblage metrics, to accurately predict the effects that future changes in the rates of acid deposition may have on the health of fish assemblages in streams of the western Adirondacks.

Fish communities and water chemistry were sampled at study sites in 48 headwater streams across the region during summer months of 2014–2016. Fish communities at six sites were also surveyed annually during the period to measure year-to-year variability. Stream chemistry and fishery data were used to (1) identify thresholds that could be used to gauge biological responses associated with changing pH, acid neutralizing capacity (ANC) and inorganic aluminum (Al_i) concentrations and (2) develop logistic (probability) models that characterize the contemporary status of brook trout *Salvelinus fontinalis* populations and fish communities and predict how different N and S deposition loads might affect these assemblages in the future.

Newly derived predictive models were used to determine how ongoing recovery and potential changes in national (U.S.) secondary standards for atmospheric emissions of NO_x and SO_x (to achieve target N and S deposition loads) are likely to affect acid-base chemistry and the probabilities of observing different levels of fish metrics in streams across the study area and in other parts of the northeast.

2 Context

Acid deposition affected terrestrial and aquatic ecosystems across parts of eastern North America most severely during the 1970s and 1980s (Baldigo et al. 2016; Bedison et al. 2007; Beier et al. 2012; Driscoll et al. 2003). Following the 1990 amendments to the Clean Air Act, emissions of oxides of sulfur (SO_x) and nitrogen (NO_x) declined precipitously (McHale et al. 2017), deposition of sulfate and nitrate decreased, and concentrations of ANC and pH in many Adirondack lakes increased significantly (Driscoll et al. 2016). With only a few exceptions (Josephson et al. 2014; Sutherland et al. 2015), however, anticipated improvements in the chemistry and in the health of species assemblages in acidified streams and lakes of the region did not occur on a broad or regional scale (Baldigo et al. 2016; Simonin et al. 2005). More problematic, extensive chemistry and fishery information were mostly nonexistent and needed to (1) define the current condition of biological assemblages, (2) assess the magnitude and spatial extent of historic impacts, and (3) predict or gauge the potential biological response (recovery) to changing levels of acid deposition and acidification in streams of the Adirondack region (Baldigo et al. 2019b; Baldigo et al. 2007).

Deriving models that accurately predict the responses of stream biological assemblages to changing rates of acid deposition are problematic because the relations between emission rates and deposition loads of nitrogen (N) and/or sulfur (S), acid-base chemistry in surface waters and soils, and the health of species populations (and entire communities) are complicated, regionally variable, and difficult to quantify (Greaver et al. 2012). There is good evidence, however, that certain acid-base constituents, such as inorganic aluminum (Al_i) concentrations, drive toxicity and regulate species populations in acid-sensitive streams of the western Adirondacks (Baldigo et al. 2019b; Baldigo et al. 2007). If specific Al_i thresholds are surpassed for long enough periods, Brook trout mortality and subsequent population losses are likely. Prior studies in streams of the region indicate that Al_i thresholds for survival of juvenile brook trout were in the 1 to 4 µmol L^{-1} range (Baker and Christensen 1991; Baldigo et al. 2007; Simonin et al. 1993; Van Sickle et al. 1996). In addition, Lawrence et al. (2007) showed that Al_i is strongly related to pH, acid neutralizing capacity (ANC), and base-cation surplus (BCS); thus, mortality-thresholds for each can be derived using those relations.

A heightened understanding of the relations between acid-base chemistry and the health of fish assemblages (especially brook trout populations) in streams of the Adirondacks is critically needed to inform a pending assessment of secondary (ecosystem) standards for the emissions of NO_x and SO_x. The United States Environmental Protection Agency (EPA) is considering changes to the secondary national ambient air-quality emission standards for NO_x and SO_x to better protect terrestrial and aquatic ecosystems from acidification impacts, and to promote the recovery of acidified systems to some minimally acceptable condition (EPA 2009). These standards will rely on critical loads research which estimates threshold or target deposition loads of total N and/or S to receiving watersheds, below which significant harmful effects to sensitive elements of terrestrial and (or) aquatic ecosystems should not occur (Fakhraei et al. 2014; Greaver et al. 2012; Porter et al. 2005; Sullivan et al. 2012a). More recent hindcast estimates (~1850) and forecast predictions for years 2015 and 2150 ANC values in 25 Adirondack streams using PnET-BGC models (Driscoll et al. 2019) following methods from Fakhraei et al. (2016) provide a foundation to estimate the pre-industrial (past) and future condition of fish assemblages under different deposition loads of N and/or S across the region. Several acid-base constituents, such as pH, ANC, and Al_i have relatively fixed effect thresholds for some aquatic species, which when exceeded could impair health, cause mortality, reduce population density, shift species distributions, and affect community richness, density, and biomass (Baldigo 2000; Baldigo et al. 2007; Sullivan et al. 2012b; Sullivan et al. 2008). A better understanding of the relations between acid-base chemistry and biological responses will help determine if, and how, specific target deposition loads for N and/or S might better sustain and (or) promote recovery of normal (healthy) brook trout populations, fish communities, and ecosystems in streams of the western Adirondacks.

Figure 1. A Headwater Stream in the Western Adirondacks

Unnamed stream that is a tributary to Lake Lila, near Sabattis, NY.

Source photo credit Barry Baldigo.

3 Goals and Objectives

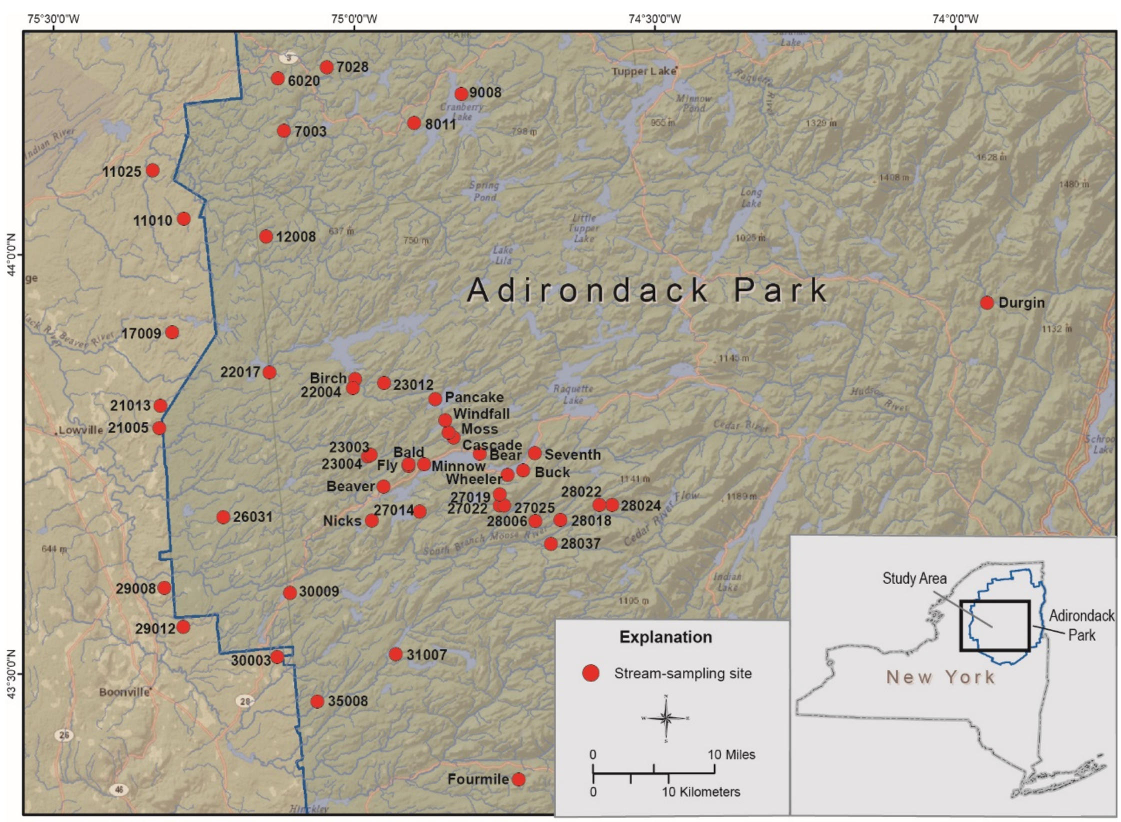
The overall objective of this study is to increase our understanding of the relations between acid-base chemistry and the health or condition of fish populations and fish communities in headwater streams of the western Adirondack Mountain Region. We employ probabilistic models (logistic equations) to quantify the relations between chemical indicators and different levels of key biological indicators (fish metrics) and use them to predict the status of pre-acidified (past) fish assemblages and the probable effects that future changes in target deposition loads of N and S could have on fish assemblages in streams of the region. Specific goals of this report are to (1) examine the relations between chemical indicators of acidification stress, such as inorganic aluminum (Al_i), pH, and acid neutralizing capacity (ANC) and metrics that represent the condition of brook trout populations and fish-communities for likely chemistry and (or) biological (fish mortality or avoidance/emigration) effect thresholds, and (2) quantify the logistic relations between selected chemical indicators and different levels of important fish-assemblage metrics in streams of the region. The logistic models (equations and associated curves) not only illustrate how acidification currently affects local fish assemblages, but they can also forecast and hindcast how different target deposition loads of N and S (which regulate surface water concentrations of Al_i, ANC, and pH) may affect future (and may predict past) fish assemblages and biological recovery in headwater streams of the western Adirondacks.

4 Study Area and Methods

The study area is mostly within or near to the western edge of the Adirondack Park in northern New York. The region is characterized by shallow soils and underlying geology that has low acid-buffering capacity, which make surface waters highly vulnerable to acidification. All study sites were low-order streams with drainage areas between 0.43 and 17.3 km^2. Except for Durgin Brook located in the upper Hudson River basin, all sites were in the Black River and Oswegatchie River basins in or near the western Adirondacks (Figure 2). Chemistry and fish-assemblage data from 48 streams, sampled as part of a related study (Baldigo et al. 2019b), were used for all analyses. Methods used to acquire water samples, survey fish assemblages, and analyze water chemistry are fully described in (Baldigo et al. 2019b).

Figure 2. Map of Stream Sites where Fish Surveys Were Conducted

The location of 48 stream sites in the Adirondacks where fish-assemblage and water-chemistry data, used in this investigation, were gathered during 2014–2016. Site information is available in George and Baldigo (2018).

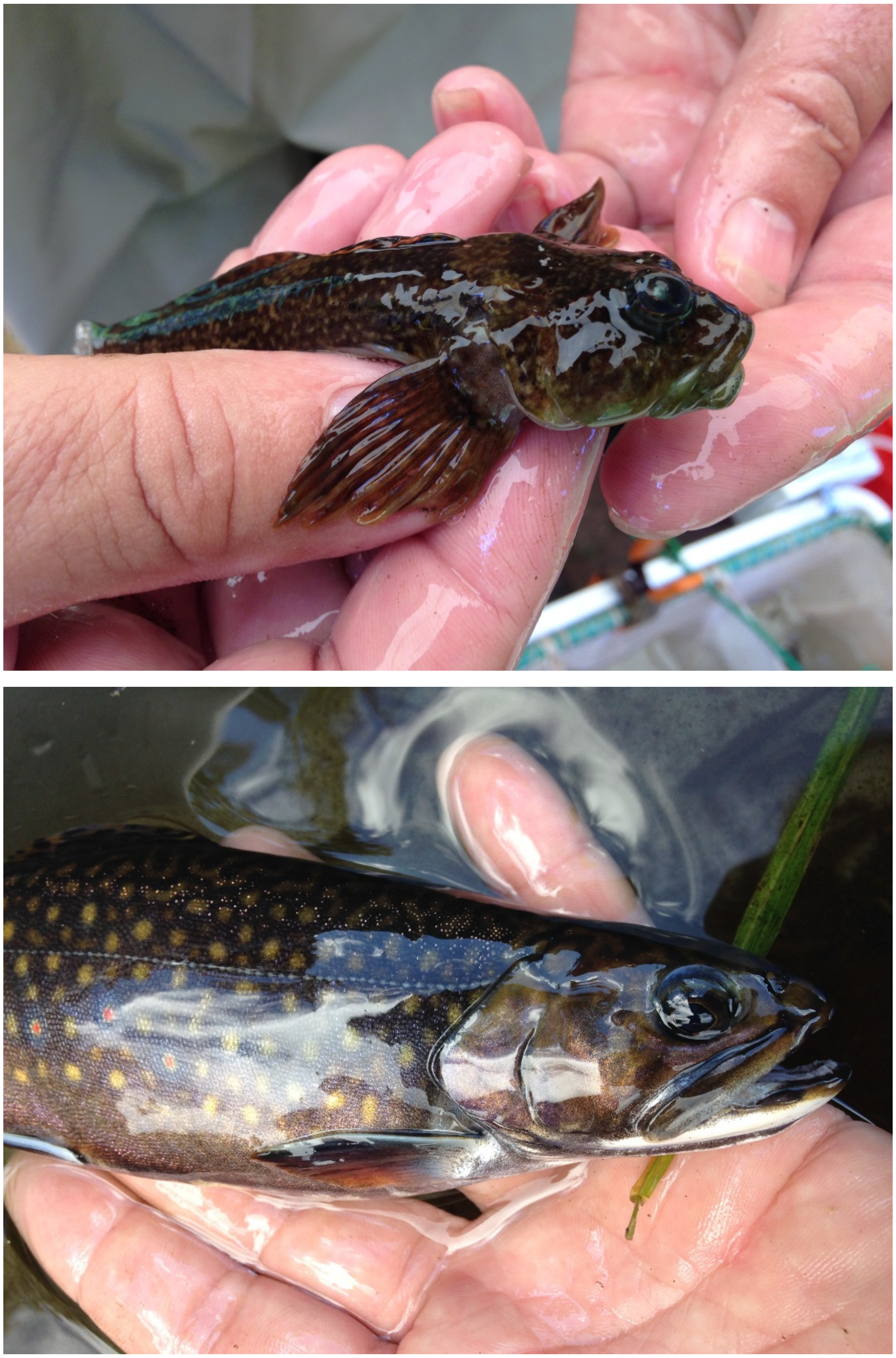


Base from National Geographic / ESRI; NAD 1983 UTM Zone18N 1:700,000

Figure 3. Slimy Sculpin and Brook Trout

Slimy Sculpin C*ottus cognatus* (top panel) was one of the least common species collected, whereas the brook trout *Salvelinus fontinalis* (bottom) was the most common species observed in the Adirondack streams surveyed during 2014–2016.

Source photo credit Barry Baldigo.



All chemistry data from fish-survey sites were sorted by site ID and sample date and can be accessed via the National Water Information System (USGS 2019). Fish-community and species population metrics from the 60 surveys performed at the 48 streams were generated from original data provided in a USGS data release (George and Baldigo 2018). These data include site identification codes, dates, channel dimensions, species names, fish lengths, and fish weights that can be used to estimate species richness, total community density and biomass, as well as population density and biomass for all species observed in each survey. Chemistry data for site 6020 are unavailable, thus, analysis of chemistry and fishery relations were limited to 59 surveys performed at 47 sites.

Chemistry data were merged with fishery metrics from all surveys by site and date, then used to generate, summarize, and rank the efficacy of numerous chemical and biological-metric response equations through several steps. First, the relations between key fishery metrics and summer Al_i concentrations, pH, and ANC were examined to assess their form and strength. Second, the raw values for biological metrics from each observation (site/year) were transformed into binary values (0 and 1) within 10-to-16 response levels or classes encompassing the full range of the original data. As an example, community richness for all surveys ranged from 0 to 9 species and was converted to alternating zeros (0s) and ones (1s) representing occurrences of richness 0 or ≥1, <2 or ≥2, <3 or ≥3…<8 or ≥8 species within each of 8 richness classes or responses levels, respectively. Density and biomass data for the fish community and for brook trout populations from all surveys were converted to 0s and 1s in a similar manner [i.e., zeros (0s) represent values of 0 and ≤100, ≤200, ≤300…≤3000, whereas ones (1s) represent values >0, >100, >200, >300…>3000 fish/0.1 ha or g/0.1 ha for as many as 30 different density and biomass responses levels]. Third, the relations between binary data in each of the metric response levels and selected chemical constituents were assessed using logistic regressions. These equations, coefficients, percentages of explained deviance, number of positive (non-zero) observations, and significance of each relation (P-values ≤ 0.05 for each equation), as well as the significance of the Chi-squared goodness-of-fit test were tabularized. Explained deviance is analogous to the sum of squared deviation (R^2) from a linear regression and describes the relative fit of the data to the logistic regression equation. Non-significant Chi-square values (P-values >0.05) indicate little unexplained variance and a good fit to the logistic model. Significant Chi-squares (P-values ≤ 0.05) do not indicate the equation is a poor fit to the logistic function, but that additional non-linearities or interactions may be able to improve the model. The logistic equations (and their associated curves) define probabilities for the occurrences of specific outcomes; thus, they specify the likelihood of observing different levels of fish metrics across gradients of chemical constituents based on the 59 fish surveys completed in streams of the western Adirondacks between 2014 and 2016.

All logistic equations follow the same format, in which the probability of the dependent variable, $F(y)$ (e.g., community biomass >1000 g/0.1 ha) equals or exceeds different levels over a range of an independent variable (x) (e.g., Al_i concentration), is equal to: $e^{(\beta 0+\beta 1*x)}/(1+e^{(\beta 0+\beta 1*x)})$, or more simply: $1/(1+e)^{-(\beta 0+\beta 1*x)}$, where e is the natural logarithm base, β0 is the intercept from a linear regression (i.e., the value when the independent variable is equal to zero), and β1 is the logistic regression coefficient. Finally, representative logistic equations were graphed to demonstrate the array of significant (and some non-significant) relations. The logistic analyses generally produced practical results for fish metrics and chemistry that had some minimum number of observations. Most fish species occurred in far less than a third of all surveys and, thus, did not support derivation of significant logistic models. Brook trout, however, were observed in 47 of 59 surveys, and logistic analysis yielded significant equations at numerous response levels. Thus, logistic analysis of species populations was limited only to brook trout. All response curves show how changes in acid-base chemistry could potentially affect important brook trout population and fish-community metrics. Therefore, these models (equations and curves) provide the context (probable biological consequences) that policy makers and managers need to understand when making decisions that will affect emissions of NO_x and SO_x, deposition of N and S, and acidity of streams across the Adirondack Mountain region.

5 Project Findings

5.1 Fish Community Responses

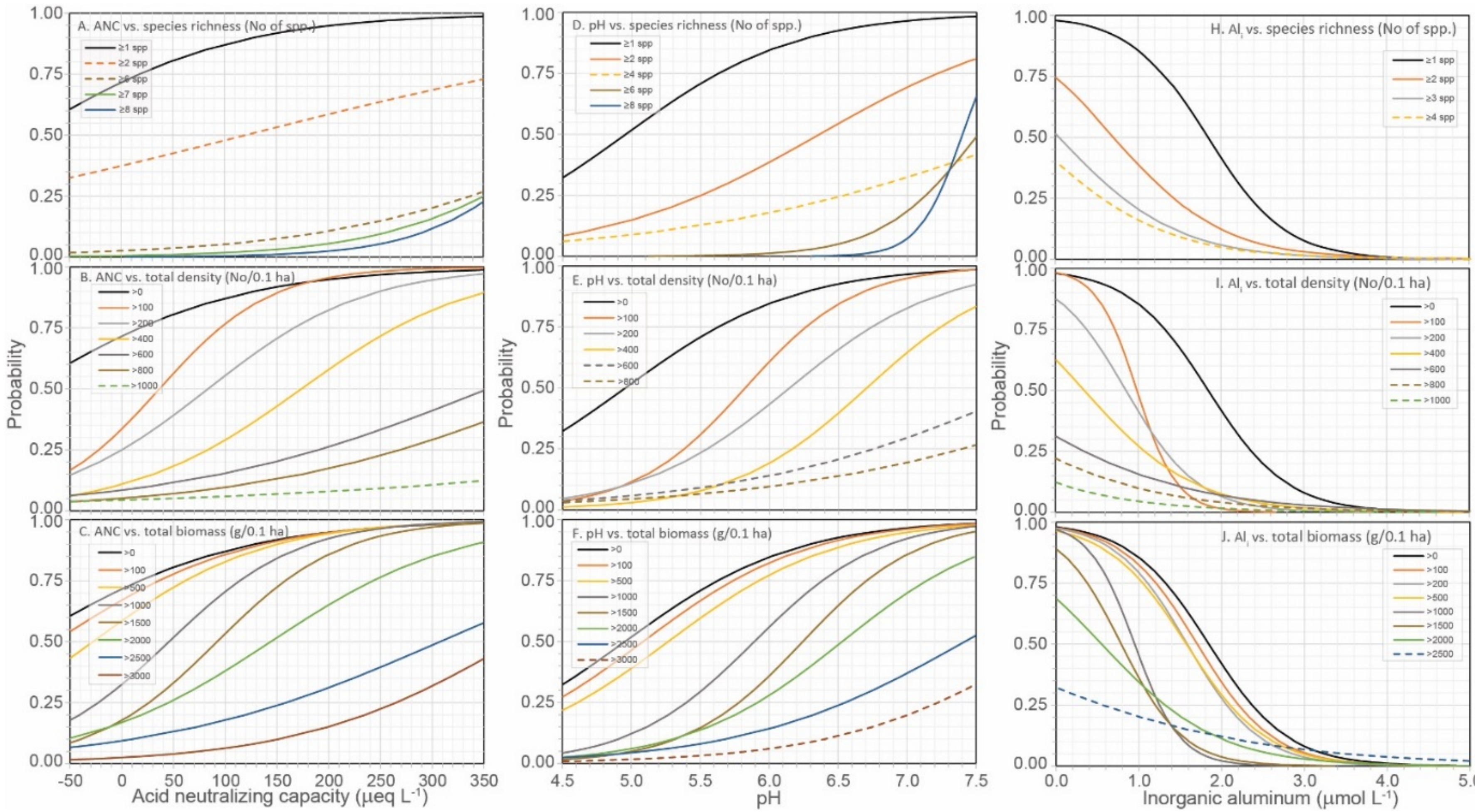
Significant logistic equations (curves) that effectively estimate or model the probability of observing richness of 1, 2, 3…8 or more species in all surveys using ANC, pH, and Al_i could explain from 6.7 to 33.0% of deviance (Baldigo et al. 2019b). The curves for ANC (Figure 4A), pH (Figure 4D), and Al_i (Figure 4H) for richness ≥2 species were suitable for predicting the response of fish communities to changes in acid-base chemistry of streams given that streams with Al_i concentrations <1 and <2 µmol L^{-1} both had an average of 2 or less species (Baldigo et al. 2019b). Because the Al_i equation for ≥1 species accounted for the most deviance (33.0%), this model and a target of 1 or more species (essentially presence versus absence of any fish), would be effective in assessing community responses to changes in acid-base chemistry. The models for both ≥1 and ≥2 species (Figure 4H) also covered the full range of Al_i concentrations (0 to 4 µmol L^{-1}) observed during summer surveys in all study streams. These curves predict that 1 or more species were expected in 42% of streams and 2 or more species were expected in 13% of streams if summer base-flow Al_i concentrations averaged ≤2 µmol L^{-1}, and that 1 or more species were expected in 85% of streams and 2 or more species were expected in 39% of streams if baseflow Al_i concentrations were ≤1 µmol L^{-1} (Figure 4H).

Significant logistic curves describing the probability of observing density >0, >100, >200… >1000 fish/0.1 ha in all surveys ANC, pH, and Al_i could explain from 8.1 to 35.7% of deviance (Baldigo et al. 2019b). The curves for ANC (Figure 4B), pH (Figure 4E), and Al_i (Figure 4I) and total density >400 fish/0.1 ha were suitable for predicting the response of fish communities to changes in acid-base chemistry of streams given that streams with Al_i concentrations <1 µmol L^{-1} had an average density of 444.2 fish/0.1 ha and those with Al_i concentrations <2 µmol L^{-1} had an average density of 391.8 fish/0.1 ha (Baldigo et al. 2019b). The ANC curve for >400 fish/0.1 ha accounted for 21.9% of the deviance, whereas, the Al_i curves for >400 fish/0.1 ha only accounted for 8.1% of the deviance (Baldigo et al. 2019b). The Al_i curve for >100 fish/0.1 ha accounted for the most (35.7%) deviance, thus, was more precise than the other two curves. Both density-response models covered the full range in ANC and Al_i concentrations observed during summers in all study streams, thus, would be effective in assessing community responses to changes in acid-base chemistry. The Al_i curves predict about 98%, 48%, and 1% of study streams would have >100 fish/0.1 ha when concentrations of Al_i were undetectable, ≤1 µmol L^{-1}, and ≤2 µmol L^{-1}, respectively (Figure 4I).

Significant logistic curves describing the probability of observing biomass >0, >100, >200… >3000 g/0.1 ha in all surveys indicate that ANC, pH, and Al_i could explain from 8.5 to 33% of the deviance (Baldigo et al. 2019b). The curves for ANC (Figure 4C), pH (Figure 4F), and Al_i (Figure 4J) and total biomass >1500 g/0.1 ha were quite suitable for predicting the response of fish communities to changes in acid-base chemistry of streams given that streams with Al_i concentrations <1 μmol L^{-1} had average biomass of 1924 g/0.1 ha and those with Al_i concentrations <2 μmol L^{-1} had average biomass of 1742 g/0.1 ha (Baldigo et al. 2019b). The ANC curve for >1500 g/0.1 ha accounted for 29.2% of the deviance, whereas, the Al_i curve for >1500 g/0.1 ha accounted for 19.1% of the deviance. Both biomass-response models covered the full range in ANC and Al_i concentrations observed during summers in all study streams, thus, would be effective in assessing community responses to changes in acid-base chemistry. The Al_i curves predict at least 89%, 36%, and 4% of study streams would have biomass >1500 g/0.1 ha if concentrations of Al_i were undetectable, ≤1 μmol L^{-1}, and ≤2 μmol L^{-1}, respectively (Figure 4J). The equations and their coefficients, that define predictive models illustrated by the curves in Figures 4 and 5 are available in Baldigo et al. (2019a).

Figure 4. Logistic Regression Curves for Community Richness, Density, and Biomass

Logistic curves describing the probability of observing community richness from 1 to 8 or more species as a function of (A) acid neutralizing capacity (ANC), (D) pH, and (H) inorganic aluminum (Al_i); density of >0 to >1000 fish/0.1 ha as a function of (B) ANC, (E) pH, and (I) Al_i; and biomass of >0 to >3000 g/0.1 ha as a function of (C) ANC, (F) pH, and (J) Al_i concentrations in 47 headwater streams in the western Adirondack Mountains of New York that were sampled during 2014–2016. [Dashed lines indicate that the relations are not significant ($P > 0.05$).]



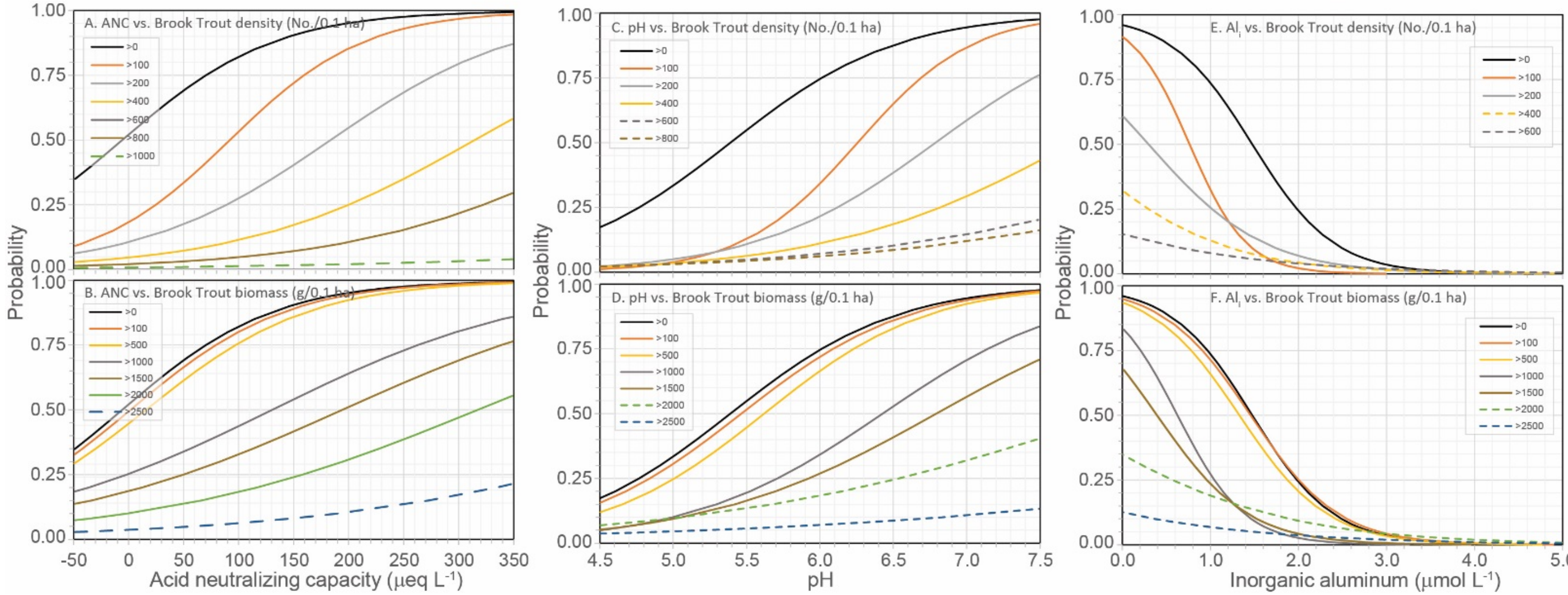
5.2 Brook Trout Population Responses

Significant logistic curves describing the probability of observing density of brook trout populations >0, >100, >200…>1000 fish/0.1 ha in all surveys indicate that ANC, pH, and Al_i could explain from 6.7 to 28.5% of deviance (Baldigo et al. 2019b). The curves for ANC (Figure 5A), pH (Figure 5C), and Al_i (Figure 5E) and brook trout density >200 fish/0.1 ha were suitable for predicting their response to changes in acid-base chemistry given that streams with Al_i concentrations <1 µmol L^{-1} had an average density of 280 fish/0.1 ha and those with Al_i concentrations <2 µmol L^{-1} had an average density of 245 fish/0.1 ha (Baldigo et al. 2019b). The ANC curves for >200 fish/0.1 ha accounted for 20.7% of the deviance, whereas, the Al_i equation for >100 fish/0.1 ha accounted 21.7% of the deviance (Baldigo et al. 2019b). The Al_i curve for >0 fish/0.1 ha accounted for 26.3% of the deviance, and the pH curve for >100 fish/0.1 ha accounted for 28.5% of the deviance, thus, Al_i predicted population responses a little more precisely than ANC. The four brook trout density-response curves covered the full range in ANC, pH, and Al_i concentrations observed during summers in all study streams, thus, were effective in assessing population responses to changes in acidification. The Al_i curve predicts at least 96%, 74%, and 24% of study streams would have small but detectable brook trout populations (>0 fish/0.1 ha) when concentrations of Al_i were undetectable, ≤1 µmol L^{-1}, and ≤2 µmol L^{-1}, respectively (Figure 5E).

Significant logistic curves describing the probability of observing biomass of brook trout populations >0, >100, >200…>2500 g/0.1 ha in all surveys indicate that ANC, pH, and Al_i could explain from 9.0 to 19.7%, 9.3 to 22.5%, and 10.7 to 26.3% of the deviance, respectively (Baldigo et al. 2019a). The curves for ANC (Figure 5B), pH (Figure 5D), and Al_i (Figure 5F) and corresponding curves for brook trout biomass >1000 g/0.1 ha are suitable for predicting population responses to changes in acid-base chemistry given that streams with Al_i concentrations <1 µmol L^{-1} had an average biomass of 1384 g/0.1 ha and those with Al_i concentrations <2 µmol L^{-1} had an average biomass of 1237 g/0.1 ha (Baldigo et al. 2019b). The Al_i curve for >1000 g/0.1 ha accounted for 16.6% of the deviance, whereas, the Al_i curve for >0 g/0.1 ha accounted 26.3% of the deviance (Baldigo et al. 2019a). The ANC and pH curves for >1000 g/0.1 ha accounted for 11.7 and 13.7% of the deviance, respectively, and thus, could predict population responses nearly as well as Al_i. The four brook trout biomass-response models covered the full range in ANC, pH, and Al_i concentrations observed during summers in all study streams and were not highly imbalanced, and thus, would be effective in assessing brook trout population responses to changes in acidification. The Al_i curves predict at least 84%, 27%, and 3% of study streams would have populations of brook trout with biomass >1000 g/0.1 ha when concentrations of Al_i were undetectable, ≤1 µmol L^{-1}, and ≤2 µmol L^{-1}, respectively (Figure 5F).

Figure 5. Logistic Regression Curves for Brook Trout Population Density and Biomass

Logistic curves describing the probability of observing brook trout density of >0 to >1000 fish/ 0.1 ha as a function of (A) acid neutralizing capacity (ANC), (C) pH, and (E) inorganic aluminum (Al_i) and brook trout biomass of >0 to >2500 g/0.1 ha as a function of (B) ANC, (D) pH, and (F) Ali concentrations in 47 headwater streams in the western Adirondack Mountains of New York State that were sampled during 2014–2016. [The dashed lines denote relations that are not significant (*P* > 0.05).]



5.3 Interpretation of Results

The biological-response models (equations and curves) provided herein and in Baldigo et al. (2019a) are empirical models which can be used to approximate the effects that deposition of N and S may have on the health of fish communities and populations in headwater streams across the western Adirondacks and New York State. The models predict the range in probabilities for observing biological (fish assemblage) indicators at certain levels for specific concentrations of a chemical indicator (e.g., summer ANC, pH, and Al_i) in streams of the study area. The probabilities may also be interpreted as the proportion or percentage of a group of streams (with specific levels of a chemical indicator) that should exhibit various responses or levels of the fishery indicator under given summer ANC, pH, and Al_i conditions. For example, the present-day (2015-to-2017) probability for observing at least 1 fish species in a Adirondack stream with a mean summer Al_i concentration of 1 μmol L^{-1} is 0.86 (Figure 4H), which means that about 86% of all streams with these Al_i levels would be expected to have 1 or more fish species, while 14% of such streams should have no resident fish species. The probabilities for observing different levels of the same biological indicators under changing stream ANC, pH, and Al_i levels (predicted to result from alternative target deposition loads of N and S) can be directly estimated using these equations or curves. Accordingly, various ANC, pH, and Al_i thresholds for biological effects provide useful reference points to characterize current biological conditions and to evaluate likely fishery responses if various (target) deposition loads of N and S are achieved in the study region.

Selecting a single "best" chemical and biological indicator and level to characterize stream health is challenging, but essential for evaluating different ecosystem-based secondary standards for limiting the emissions of NO_x, SO_x, and particulate matter (PM) as proposed in EPA (2009). Although good arguments can be made for pH, Al_i, and ANC, the response models based on ANC and (or) Al_i (as predictor variables) appear to be most applicable. Stream ANC is closely linked to deposition chemistry and is usually the indictor most often used as a surrogate for ecosystem response to changes in deposition loads of N and S (Fakhraei et al. 2016; Fakhraei et al. 2014; Sullivan et al. 2012a; Zhou et al. 2015). Specific concentrations of Al_i, however, have been identified as thresholds for brook trout survival (and conversely mortality) in streams of the region (Baldigo et al. 2007; Simonin et al. 1993; Van Sickle et al. 1996). Acid-neutralizing capacity (ANC) thresholds of 20, 50, and 100 μeq L^{-1} have been associated with high, moderate, and low risk, respectively, to brook trout, other species, and entire fish assemblages and have been used as surrogate biological indicators in aquatic systems (Baldigo et al. 2009; USEPA 2009). Several studies that assessed fish assemblages and toxicity in streams of the western Adirondacks (and streams of the Catskills in NY and Poconos in PA) reported Al_i thresholds that significantly reduced survival (caused mortality) of juvenile brook trout were typically in the 1 to 4 µmol L^{-1} range (Baldigo et al. 2007; Simonin et al. 1993; Van Sickle et al. 1996). More important, Baldigo et al. (2019b) found that populations of brook trout (and most other species) were absent from streams with summer Al_i concentrations >2 µmol L^{-1}, and—with one exception—brook trout were usually the only species present (at low densities and biomass) in the six streams with Al_i concentrations between 1 and 2 µmol L^{-1}. Citing results from the 2003–2005 in-situ tests using juvenile brook trout (Baldigo et al. 2007), Baldigo et al. (2019b) indicates that 1 µmol Al_i L^{-1} is a chronic threshold which adversely affects acid-intolerant fish species, entire fish communities, and brook trout populations (to some extent); and 2 µmol Al_i L^{-1} is an acute threshold which, when surpassed under summer low-flow conditions, limits brook trout survival and the occurrence of local populations.

The responses of various fish-community metrics to changes in water quality can be suitable proxies of broader effects in aquatic ecosystems when recovery or protection of biodiversity or trophic structure are primary goals. The response equations for Al_i and community richness ≥1 species, density >0 fish/0.1 ha, or biomass >0 g/0.1 ha generally explained the greatest amount of deviance (33.0%); however, those equations were not well balanced. The equations for Al_i and density >100 fish/0.1 ha or biomass >1000 g/0.1 ha also explained similar amounts of deviance (30.5–35.7%), but were more balanced and better reflected the estimated range of community density and biomass in all study streams (Baldigo et al. 2019a). These results indicate that community richness, density, and biomass were generally low in streams with Al_i concentrations between 1 and 2 µmol L^{-1} and at (or near) zero in most streams with Al_i concentrations >2 µmol L^{-1}. The relations between ANC and total density >400 fish/0.1 ha or total biomass >1500 g/0.1 ha explained 21.9 and 29.2% of deviance, respectively, but best reflect the full range in community density and biomass data that were observed at study streams with nontoxic summer Al_i concentrations (Baldigo et al. 2019a).

The models summarized herein and data from Baldigo et al. (2019b) may be used directly to predict the future condition of fish assemblages from constituents such as ANC because its relations with most fishery metrics are moderately strong and defined by simple regression analyses of untransformed data. If only one response level was selected to assess each metric, the equations for Al_i and richness ≥1 species, ANC and density >400 fish/0.1 ha, and ANC and biomass >1500 g/0.1 ha offer some of the best models to assess and interpret the responses of fish communities to changes in acid-base chemistry that would result from alternative target loads for N and S deposition in streams of the western Adirondacks. The presence of any brook trout (density >0 fish) or density >200 fish/0.1 ha are also good population response targets considering that population density averaged 244.6 and 280.8 fish/0.1 ha in Adirondack streams with Al_i concentrations <2 and <1 µmol L^{-1}, respectively, during summer 2014–2016 (Baldigo et al. 2019b). Likewise, brook trout biomass averaged 1237 and 1384 g/0.1 ha in streams with summer Al_i concentrations <2 and <1 µmol Al_i L^{-1}, respectively, (Baldigo et al. 2019b).

Although data describing the preindustrial (past) condition of fish assemblages are unavailable, it can now be estimated using our probability-based response curves, present-day ANC data, and predicted ANC levels for individual streams (or groups of streams). Even though chemistry data are also not available for the pre-acidification period, ANC hindcast volume-weighted concentrations for 1850 were calculated for a group of 25 streams using PnET-BGC models as part of a critical loads study in the western Adirondacks (Driscoll et al. 2019). The hindcast estimates of mean annual ANC concentrations for 1850, estimates for 2015 (average of 61st flow percentile or Q_{61}), and forecasts for year 2150 were adjusted to summer low-flow conditions that are directly comparable to mean low-flow and ANC conditions (the 27th flow percentile or Q_{27}) under which the 2014–2016 fish-surveys were completed, and water samples were collected. Estimates of ANC Q_{27} for each of the 25 PnET-BGC model sites were calculated for years 1850, 2015, and 2150 (under seven N and S deposition loading scenarios and site-specific ANC targets) as described in Baldigo et al. (2019a). Estimates of ANC Q_{27} for the PnET-BGC model streams in 1850 averaged 191.0 µeq L^{-1} and had a median of 74.3 µeq L^{-1}. The probabilities for observing 1 or more species, >400 fish/0.1 ha, and >1500 g fish/0.1 ha in a representative stream (with the same median ANC Q_{27}) would have been 0.84, 0.23, and 0.43, respectively, during year 1850 (Figure 4). Though these pre-industrial fish-community metrics, noted levels, and the proportion of streams expected to attain these levels may be appropriate upper targets for biological recovery, they are twice as high as the median ANC Q_{27} for the 25 PnET-BGC model streams (36.3 µeq L^{-1}) in 2015 and probably unattainable for strongly acidified streams in the region. Additionally, the probabilities for the same community richness, density, and biomass metrics that correspond to the 2015 median ANC Q_{27} are 0.78, 0.16, and 0.28, respectively (Figure 4). Although differences between 1850 and 2015 probabilities seem small, the probability for observing more than 1 fish species in a typical stream (summer median ANC of 36.3 µeq L^{-1}) decreased by 7%, and the probabilities for observing moderate fish densities and biomass decreased by 30–35% over the 165-year period. Thus, the present-day probabilities (and percentages of streams) for most fish-community metrics remain substantially lower than the historic values that were determined from hindcast ANC Q_{27} estimates and present-day fish-response curves. These differences quantify the present-day extent and severity of acidification impacts to fish local assemblages, but also provide useful targets for biological recovery in streams of the region.

Our ability to predict how future fish assemblages might react to various target deposition loads of N and S and stream ANC concentrations, under different deposition loading scenarios, is a primary objective of this effort. The logistic response equations (and curves) and ANC Q_{27} projections from PnET-BGC models address this goal but can also be used, inversely, to specify the deposition loads that would be required to meet some best-attainable or suitable biological targets (identified for protection or recovery) in streams of the region. Though quite complicated, examples of both applications can be found in Baldigo et al. (2019a). The first example uses the present-day (2015) median ANC Q_{27} from the 25 PnET-BGC sites (36.3 μeq L^{-1}) to describe community biomass probabilities and the changes predicted to occur in such a representative stream by 2150 if the ANC targets under deposition loading scenario 6 (100% reduction in deposition beyond the EPA Clean Power Plan), or the site-specific ANC targets, were met. The second example uses present-day (2015) and the 1850 ANC Q_{27} estimates for the representative stream (median ANC Q_{27} = 36.6 μeq L^{-1}) and North Buck and the brook trout response equations to identify future ANC Q_{27} concentrations (and indirectly target deposition loads of N and S) that would be required to attain a theoretical brook trout recovery target.

6 Conclusions

Our findings have important implications for assessing the impacts of different deposition loads of N and S, as well as the present-day status and potential recovery of fish assemblages and water quality in streams of the Adirondack Mountains and elsewhere. First, the response curves and equations define the present-day (2014–2016) relations between chemical and biological indicators in headwater streams of one of the most acid-sensitive regions in eastern North America. These equations quantify the contemporary effects of atmospheric regulations on aquatic ecosystems that receive current deposition loads of N and S. Although predictions may have high levels of uncertainty, extrapolation of biological conditions (and acidification impacts) to streams across the Adirondacks is possible given the widespread availability of stream-chemistry data. Second, the response equations and curves represent empirical models which can be used to predict biological changes likely to result from altered target deposition loads of N and S in the Adirondacks. Though proposed secondary ambient air quality standards for the emissions of NO_x, SO_x, and PM rely on ANC (a chemical indicator) as a surrogate for ecological effects (EPA 2009), the response curves and equations presented herein provide a means to directly predict biological responses which would likely occur in local streams under different deposition loads of N and S. Third, the applicability of presented models may be limited by the composition of local species assemblages. The response equations for brook trout density versus ANC in Adirondack streams, for example, differed noticeably from those developed for streams of the Great Smoky Mountains as reported in Baldigo et al. (2018). Such disparities are likely due to different species assemblages and biological interactions occurring in streams of each region. Although fish-chemistry response models from different regions could conceivably be similar, they will likely differ across regions with divergent species assemblages. Thus, the models presented herein may be mainly applicable to streams in the northeastern U.S. and southeastern Canada, but they also serve as examples of the efforts needed to broaden our understanding of the ecological effects of changing deposition loads of N and S across other regions. Thus, their broader applicability needs to be tested and confirmed with additional fishery and chemistry data from across the Adirondacks and elsewhere. Fourth, water chemistry during summer baseflow periods obviously does not reflect the most toxic conditions (and limit acid-sensitive life stages of many species), which typically occur during spring high-flow periods. Thus, our models depict biological responses to baseflow chemistry that do not fully describe or represent highly variable conditions over the long term or during the most toxic spring-time periods. Adjusting the ANC scale to summer low-flow conditions (based on discharge percentiles) indirectly addresses part of the data gap, but additional springtime or year-round chemistry data from fish-survey streams could improve the precision and utility of our response models. Lastly, the small number of streams in our study with very low ANC and very high Al_i concentrations indicate that some fish metrics were not uniformly distributed across the gradient of acid-base chemistry. Previous surveys of Adirondack streams have shown that these conditions are quite common, particularly in the western portion of the Adirondack Region (Lawrence et al. 2008). Therefore, more current fish survey and chemistry data from streams sampled in the 1970s and 1990s (Simonin et al. 2005) are needed to broaden the applicability of chemistry and biology response models in streams of the region. Additional efforts to characterize fish assemblages in more streams and variability in chemistry of fish-study streams throughout the year, including spring runoff periods (when acidity and Al_i concentrations generally peak), are also needed to help decrease uncertainty in predictive response models. In summary, the logistic models, chemical thresholds, and biological targets discussed here and in Baldigo et al. (2019a) are informative, yet additional data is needed to test and confirm results, and prove that the models are capable of predicting biological responses to potential changes in the emissions of NO_x and SO_x, deposition of N and S, and acidity of streams across the Adirondack Region.

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