Environmental Chemistry

Detection and Prediction of Toxic Aluminum Concentrations in High-Priority Salmon Rivers in Nova Scotia

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Abstract: Elevated concentrations of toxic cationic aluminum (Al_i) are symptomatic of terrestrial and freshwater acidification and are particularly toxic to salmonid fish species such as Atlantic salmon (*Salmo salar*). Speciated metal samples are rarely included in standard water monitoring protocols, and therefore the processes affecting Al_i dynamics in freshwater remain poorly understood. Previous analysis of Al_i concentrations in Nova Scotia (Canada) rivers found that the majority of study rivers had concentrations exceeding the threshold for aquatic health, but a wide-scale survey of Al_i in Nova Scotia has not taken place since 2006 (Dennis, I. F., & Clair, T. A., 2012, *Canadian Journal of Fisheries and Aquatic Sciences, 69*(7), 1174–1183). The observed levels of dissolved aluminum in Atlantic salmon (*Salmo salar*) rivers of Atlantic Canada have potential serious and harmful effects for aquatic populations. We present the findings of the first large-scale assessment of the Al_i status of Nova Scotia rivers in 17 years; we measured Al_i concentrations and other water chemistry parameters at 150 sites throughout the Southern Uplands region of Nova Scotia from 2015 to 2022. We found that Al_i concentrations exceeded toxic thresholds at least once during the study period at 80% of the study sites and that Al_i concentrations increased during the study period at all four large-sample study sites. Modeling of relationships between Al_i concentrations and other water chemistry parameters showed that the most important predictors of Al_i are concentrations of the dissolved fractions of Al, iron, titanium, and calcium, as well as dissolved organic carbon and fluoride. We developed a fully Bayesian linear mixed model to predict Al_i concentrations from a test data set within 15 µg/L. This model may be a valuable tool to predict Al_i concentrations in rivers and to prioritize areas where Al_i should be monitored. *Environ Toxicol Chem* 2024;00:1–12. © 2024 The Author(s). *Environmental Toxicology and Chemistry* published by Wiley Periodicals LLC on behalf of SETAC.

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INTRODUCTION

Cationic aluminum (Al_i) is toxic to salmonids, and increased concentrations of these aluminum (Al) species are one of the most lethal effects of terrestrial and freshwater acidification. Geology is a major determinant of stream water quality within a drainage basin. The third most common element on the surface of the earth is Al, making it a common constituent of surface water chemistry. It can be toxic to aquatic organisms in circumneutral waters (Gensemer & Playle, 1999), with the Al_i species, such as Al^{3+}, $Al(OH)_2^{1+}$, and $Al(OH)^{2+}$, considered the most labile and therefore the most toxic. These positively charged Al species bind to negatively charged fish gills and cause morbidity and mortality through suffocation (Exley et al., 1991), reduce nutrient intake at gill sites, and alter blood plasma levels (Nilsen et al., 2010). The effects of sublethal exposure to freshwater Al elicit osmoregulatory impairment (Monette & McCormick, 2008; Regish et al., 2018), which reduces survival in the hypertonic marine environment (McCormick et al., 2009; Staurnes et al., 1996).

Burning of fossil fuels has resulted in the acidification of soils and surface waters during the last century through acid deposition (see Kerekes et al., 1986), which has led to increased concentrations of toxic Al_i in soils and drainage waters. Following reductions in anthropogenic sulfur emissions in North America and Europe, the acidification problem was widely considered solved. Many studies observed steady improvements in stream

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chemistry (Evans et al., 2001; Monteith et al., 2014; Skjelkvåle et al., 2005; Stoddard et al., 1999; Warby et al., 2005), including reduced concentrations of Al in the United States (Baldigo & Lawrence, 2000; Buchanan et al., 2017; Burns et al., 2006) and Europe (Beneš et al., 2017; Davies et al., 2005; Monteith et al., 2014). However, recent evidence highlights delayed recovery from acidification in certain regions with slow-weathering geology (Houle et al., 2006; Warby et al., 2009; Watmough et al., 2016), including Nova Scotia, Canada (Clair et al., 2011; Sterling et al., 2020). This raises questions about the possibility of elevated and/or increasing Al concentrations in freshwater systems.

Previous research has shown widespread increases in total Al (Al_t) in Nova Scotia (S. Sterling et al., unpublished data); however, a knowledge gap exists as to which species of Al are driving these trends—Al_i or the less toxic organically complexed Al (Al_o). The concentration at which Al_i becomes toxic to aquatic organisms is dependent on pH, temperature, ionic strength, concentrations of base cations, and the presence of dissolved organic matter (Gensemer & Playle, 1999). Some of this complexity has been recently addressed by advanced modeling, such as biotic ligand models (Santore et al., 2018), but it remains difficult to select a single threshold to guide interpretation of data and the creation of regulatory limits. In the present study we assume a toxic threshold of 15 µg/L, which Kroglund et al. (2007) showed negatively impacts anadromous Atlantic salmon in acidic conditions similar to those of our Nova Scotia study. An earlier study of Al concentrations in Nova Scotia led to the discovery that concentrations of Al_i in Nova Scotia rivers currently exceed this assumed toxic threshold for aquatic health of 15 µg/L (Dennis & Clair, 2012); however, no studies of Al_i concentrations in Nova Scotia have been sufficiently long term to determine speciated temporal trends.

The processes that affect Al_i dynamics remain poorly understood due to limited sampling of speciated Al. Speciated sampling can be time-consuming and expensive, and is not often included in regular water chemistry monitoring programs (Driscoll & Schecher, 1990). Speciation of Al is complex and mostly determined by pH and the presence or absence of organic material (typically measured as dissolved organic carbon [DOC]; Santore et al., 2018). The pH is generally negatively correlated with Al_i concentrations (Campbell et al., 1992; Kopáček et al., 2006; Kroglund et al., 2001; Seip et al., 1989; Teien et al., 2006), because lowered pH increases the solubility of secondary minerals containing Al. Previous studies have also shown that Al concentrations are positively correlated with DOC concentrations (Campbell et al., 1992; Kopáček et al., 2006). Previous modeling has shown that DOC and water temperature (T_w) are the most significant predictors of Al_i concentrations (Sterling et al., 2020), but this model needs to be improved with a larger sample size. The previous model was built from a data set containing 10 sites with 5 to 47 samples collected at each site.

Several programs have been developed to model aqueous Al_i concentrations, such as ALCHEMI, WHAM, and Visual MINTEQ (see Cory et al., 2007; Sjöstedt et al., 2010; Tangen et al., 2002). These models are based on the thermodynamic relationships that control the behavior and speciation of aqueous Al (Gustafsson, 2020; Schecher & Driscoll, 1995; Tipping, 1998). While the thermodynamic constants for inorganic complexes are typically well understood, reactions involving organic complexation are more difficult to quantify and can lead to poor precision and considerable uncertainty in chemical equilibrium modeling (Driscoll & Schecher, 1990; Schecher & Driscoll, 1995; Sjöstedt et al., 2010).

We aimed to complete the first large-scale assessment of Al_i concentrations with repeated measurements in Nova Scotia. We built on a one-sample large-scale survey in 2006 (Dennis & Clair, 2012), to detect temporal trends in speciated Al concentrations as well as to determine potential predictors of Al_i concentrations and use these to build a simple empirical model to increase our understanding of the factors affecting Al_i dynamics in dilute, acidified freshwaters.

MATERIALS AND METHODS

Study area

We surveyed Al_i and other water chemistry parameters at 150 sites in 18 watersheds across the Southern Uplands region of Nova Scotia (Figure 1). Large-sample (2015–2022) water chemistry measurements were conducted at four catchments: Mersey River, Moose Pit Brook, Maria Brook, and Brandon Lake Brook (Table 1). A "snapshot" of the water chemistry conditions was captured at the remaining sites, with 1 to 54 samples being collected at each site between 2020 and 2022. The four major large-sample study catchments and the majority of the "snapshot" sites are predominantly forested and drain slow-weathering, base-cation poor bedrock, producing soils with a low acid-neutralizing capacity (Langan & Wilson, 1992; Tipping, 1989). The catchments also have relatively high aquatic DOC concentrations (Ginn et al., 2007) associated with the abundant wetlands in the region (Clair et al., 2008; Gorham et al., 1986; Kerekes et al., 1986). Due to this combination of characteristics, the study rivers are acidic (mean pH of 4.9), dilute (mean specific conductance (SPC) of 38 µS/cm), and have relatively high levels of organic acidity (mean DOC concentration of 11 mg/L).

Data collection and analysis

We measured Al_i concentrations and other water chemistry parameters at the sample locations, including pH, T_w, SPC, and concentrations of constituents such as dissolved metals and DOC. Measurements were taken throughout the year from 2015 to 2021 at Mersey River, Moose Pit Brook, Maria Brook, and Brandon Lake Brook, and measurements were taken from March to December during 2020 to 2022 at all other sample locations. Most study rivers were at least partially ice covered during the winter months.

Sampling events comprised grab samples for laboratory analysis and in situ measurements of pH, T_w, and SPC. We calculated Al_i as the difference between dissolved Al (Al_d) and Al_o, following Dennis and Clair (2012), Tangen et al. (2002), and Sterling et al. (2020; Equation 1). Speciating metals samples in
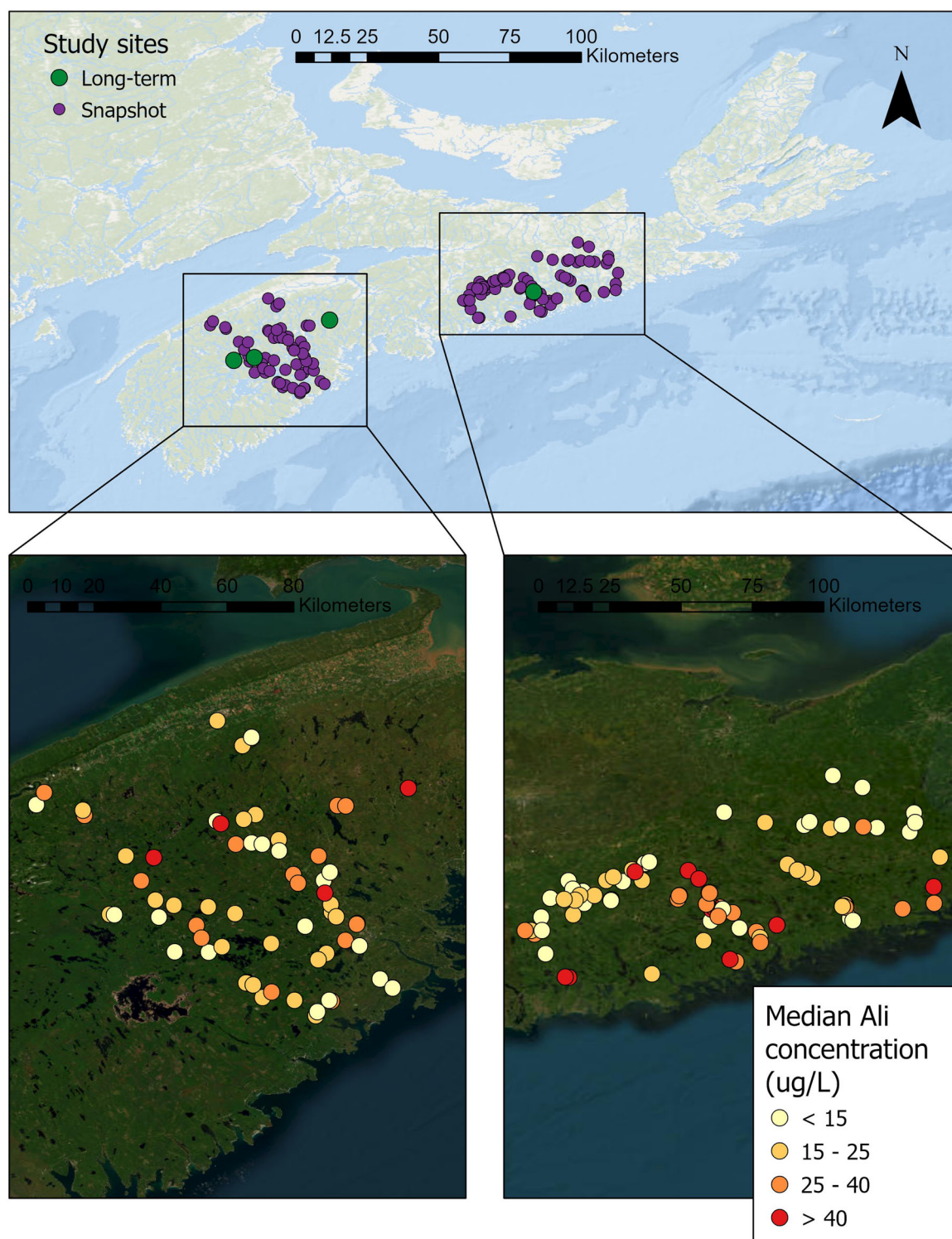
FIGURE 1: Locations of large- and small-sample sites and median Al_i concentration at each site during the study period (2015–2022).

the field reduces errors caused by changes in temperature and pH during transport from field to laboratory.

$$Al_i = Al_d - Al_o \qquad (1)$$

We measured Al_d as the Al concentration of a sample passed through a 0.45-μm polyethersulfone filter. We measured Al_o as

the eluate from passing water through a 3-cm negatively charged cation exchange column (Bond Elut Jr. Strong Cation Exchange Column). The columns were preconditioned with 30 mL of 0.4 mol/L ammonium acetate buffer at pH 5, followed by a rinse with 30 mL of sample water, following previous studies (Dennis & Clair, 2012; Tangen et al., 2002). Water was passed through the cation exchange column at a rate of less than 60 drops/min, to

TABLE 1: Study site characteristics for large-sample study sites

Site	Watershed area (km^2)	Temporal range of samples	No.	Dominant bedrock type
MB	0.47	2016–2021	32	Granite
BLB	1.4	2016–2022	41	Sandstone/slate
MPB	15.8	2015–2021	57	Granite/slate
MR	292.8	2015–2021	61	Granite

BLB = Brandon Lake Brook; MB = Maria Brook; MPB = Moose Pit Brook; MR = Mersey River.

avoid underestimating Al_i (Tangen et al., 2002). From this method, Al_o was operationally defined as the nonlabile, organically complexed species of Al, and Al_i was defined as the cationic species of Al (e.g., Al^{3+}, $Al(OH)_2^{1+}$, $Al(OH)^{2+}$). This speciation process was carried out in the field.

Samples to be analyzed for metal content as just described were collected using sterilized polyethylene syringes into sterilized polyethylene tubes (15 mL). All metal samples were filtered in the field and preserved with nitric acid (HNO_3) within 24 h of arriving at the laboratory. Samples analyzed for DOC, anion content, and physical parameters were not filtered in the field and were collected in sterilized amber glass or polyethylene bottles (1 L). All samples were kept cooled to a temperature of 4 °C during transport to the laboratory and were delivered within 48 h of being collected. Laboratory analytical methods are outlined in the Supporting Information, Appendix A.

Some samples analyzed for organic carbon content were not filtered in the laboratory; however, the suspended loads in rivers with similar characteristics to the study rivers are typically very low, and it has been established that particulate matter typically contributes <5% of total organic carbon (TOC; Clair et al., 2008; Laudon et al., 2001). We therefore used TOC as a proxy for DOC in these cases, as has been done in previous freshwater Al modeling studies (see Cory et al., 2007). All samples analyzed for organic carbon content are grouped here and reported as DOC.

In situ measurements of pH, T_w, and SPC were taken using a portable water chemistry sonde (YSI ProQuatro). The sonde was calibrated at a minimum of once a week, typically the day before samples were collected.

Temporal trends were detected using the Mann–Kendall trend test from the R package "Kendall" (McLeod, 2022), which tests for monotonic trends in time series based on the Kendall rank correlation. Time series plots were smoothed using the locally estimated scatterplot smoother method. Independent linear correlations were detected using the Kendall's tau test. These statistical analyses were carried out in R Ver. 4.1.2.

Bayesian linear mixed modeling

We built a fully Bayesian linear mixed model (BLMM) to predict Al_i concentration. Missing and left-censored values (nondetects) were imputed in one step during model fitting by treating them as parameters; nondetects were constrained with an upper bound equal to the detection limit. That is, each of

the 4000 posterior samples included a different imputed value for each missing and left-censored value.

We split the data into a training set, used to fit the model, and a test set, used to simulate the model's predictive performance on future observations. To avoid issues of non-independence between the training and test sets that might negatively bias the test set error (Kapoor & Narayanan, 2023), we chose a temporal split of the training and test sets. That is, the test set comprised the most recent 20% of observations from sites with at least five observations. The remaining 80% comprised the training set.

We selected (1) variables having a Pearson correlation with Al_i in the training set greater than 0.1, and (2) supplementary variables used to predict the missing values in the predictors of Al_i (see the equation set following). We excluded variables that were >50% missing or censored. The following variables were selected as predictors: Al_d, DOC, color, pH (sonde), temperature (sonde), sulfate (SO_4), alkalinity, fluoride (F), and dissolved fractions of calcium (Ca_d), titanium (Ti_d), iron (Fe_d), cerium (Ce_d), and lithium (Li_d). All variables were scaled to have zero mean and unit standard deviation.

The i Al_i concentrations, y_i, were predicted using the following equations:

Likelihood:

$$y_i \sim T(\mu_i, \sigma, \nu)$$

Model for μ_i:

$$\mu_i = \alpha_{site_j} + X\beta$$

Model for missing values:

$$p \sim T(\mu_p, \sigma_p, v_p) \text{ for each predictor } p$$

Model for μ_p:

$$Al_d = \beta_{DOC}DOC$$

$$Ti_d = \beta_{Ti_d}Al_d$$

$$DOC = \alpha_{DOC}$$

$$Color = \beta_{color}DOC$$

$$Fe_d = \beta_{Fe_d}DOC$$

$$Ce_d = \beta_{Ce_d}Fe_d$$

$$pH_{sonde} = \beta_{pH}Al_d$$

$$Ca_d = \alpha_{Ca_d}$$

$$\text{Temperature} = \gamma + f(t)$$

$$f(t) = Z_s b_s$$

$$SO_4 = \beta_{SO_4} Ca_d$$

$$\text{Alkalinity} = \beta_{\text{Alkalinity}} Ca_d$$

$$Li_d = \beta_{Li_d} F$$

$$F = \alpha_F$$

Priors:

$$\sigma, \sigma_p, \sigma_\alpha, \sigma_b \sim \text{Half-}T(0, 2.5, 3)$$

$$v, v_p \sim \text{Gamma}(2, 0.1)$$

$$\alpha_{\text{site}_j} \sim N(0, \sigma_\alpha) \text{ for } j \text{ in } 1\ldots150$$

$$\beta \sim N(0, \tau)$$

$$\tau \sim \text{Half-Cauchy}(0, 1)$$

$$\beta_{\mu_p} \sim N(0, 1)$$

$$b_s \sim N(0, \sigma_b)$$

where N represents the Gaussian distribution with mean μ and standard deviation σ, T represents the t-distribution with μ, σ, and v representing the degrees of freedom. The parameter α_{site_j} is a random intercept centered at $\bar{\alpha}$, X is the linear model design matrix, and β is a vector of model coefficients, centered at zero with standard deviation τ. The hierarchical Gaussian prior on β helps to stabilize the estimates of multicollinear predictors (Hastie et al., 2009), and also shrinks coefficient estimates toward zero, which has a similar effect to a multiple comparisons correction (Gelman et al., 2012). Supporting Information, Figure S3, in Appendix B shows the correlations between variables included in the model. In the missing value model for temperature, the function $f(t)$ represents a cyclic cubic regression spline (Wood, 2017) with penalized coefficients b_s and basis function matrix Z_s. The variable t represents ordinal day.

Missing and left-censored values (nondetects) were modeled as parameters and sampled from the joint posterior during model fitting, along with the regression coefficients and the parameters used to predict missing values in new observations (Bürkner, 2017; McElreath, 2020). Left-censored values were constrained to fall below the respective censoring limits.

Model code was written in Stan (Stan Development Team, 2023) using a template generated in brms (Bürkner, 2017, 2018). Several other R packages were used for data cleaning and visualization (Firke et al., 2023; Fischetti, 2022; Grolemund & Wickham, 2011; Kay, 2023; Pedersen, 2022; Ram et al., 2018; Vaughan et al., 2022; Wickham & Bryan, 2023; Wickham et al., 2019; Wilke & Wiernik, 2022).

RESULTS AND DISCUSSION

Status of Al$_i$ concentrations in Nova Scotia

The assumed toxic threshold of 15 µg/L for Al$_i$ concentrations was exceeded at 120 of the 150 study sites (80%) at least once during the study period. Median Al$_i$ concentrations ranged from 1.1 to 76.3 µg/L across all sites (Figure 1), with the median concentration exceeding the toxic threshold at 99 of the 150 sites (66%). For many (~70%) of these sites, sample collection timing was limited to the window of Atlantic salmon (*Salmo salar*) smoltification (typically early April to early June). Exceedances of Al$_i$ during this window would have a large negative impact on salmon smolts because they undergo rapid physiological transformation and experience the osmoregulatory demands associated with anadromy (Monette & McCormick, 2008; Staurnes et al., 1996). The median Al$_i$ concentration at all four large-sample study sites also exceeded the toxic threshold (Table 2).

At the four large-sample study sites, Al$_i$ concentrations exceeded the toxic threshold in 67.2% to 97.4% of samples, depending on the site (Table 2). Over the entire large-sample data set, Al$_i$ concentrations significantly increased from the start to the end of the study period (2015–2022; Table 3). Within individual sites, Al$_i$ concentration increased at all four sites;

TABLE 2: Median and standard deviation values for select water chemistry parameters for large-sample study sites

Site	Variable	Median	SD
MB	Al$_i$ (µg/L)[a]	44.5	28.5
	Al$_o$ (µg/L)	329	110
	Al$_d$ (µg/L)	364	123
	DOC (mg/L)	12.1	5.61
	Ca$_d$ (mg/L)	1.60	0.366
	pH	4.65	0.618
BLB	Al$_i$ (µg/L)[a]	46.4	36.7
	Al$_o$ (µg/L)	362	102
	Al$_d$ (µg/L)	420	111
	DOC (mg/L)	15.1	4.44
	Ca$_d$ (mg/L)	1.12	0.293
	pH	4.43	0.452
MPB	Al$_i$ (µg/L)[a]	21.0	16.2
	Al$_o$ (µg/L)	247	101
	Al$_d$ (µg/L)	260	111
	DOC (mg/L)	17.6	7.70
	Ca$_d$ (mg/L)	0.890	0.388
	pH	4.23	0.394
MR	Al$_i$ (µg/L)[a]	22.0	12.5
	Al$_o$ (µg/L)	170	66.3
	Al$_d$ (µg/L)	204	71.0
	DOC (mg/L)	9.00	3.48
	Ca$_d$ (mg/L)	0.735	0.169
	pH	4.72	0.513

[a]Al$_i$ is a calculated value; all other parameters are directly measured.
BLB = Brandon Lake Brook; DOC = dissolved organic carbon; MB = Maria Brook; MPB = Moose Pit Brook; MR = Mersey River.

TABLE 3: Results of Mann–Kendall test for temporal trends in large-sample study sites

Site	Variable	Tau	p value
All large-sample sites	Al_i	**0.294**	**<0.0001**
	Al_o	**0.545**	**<0.0001**
	Al_d	**0.533**	**<0.0001**
	$\%Al_i$	0.037	0.4522
BLB	Al_i	0.184	0.0920
	Al_o	**0.465**	**<0.0001**
	Al_d	**0.483**	**<0.0001**
	$\%Al_i$	−0.058	0.5976
MB	Al_i	0.103	0.4173
	Al_o	**0.492**	**0.0003**
	Al_d	**0.419**	**0.0008**
	$\%Al_i$	−0.004	0.9871
MPB	Al_i	**0.357**	**<0.0001**
	Al_o	**0.586**	**<0.0001**
	Al_d	**0.574**	**<0.0001**
	$\%Al_i$	0.129	0.1582
MR	Al_i	0.032	0.7226
	Al_o	**0.480**	**<0.0001**
	Al_d	**0.428**	**<0.0001**
	$\%Al_i$	**−0.211**	**0.0166**

Significant trends ($p < 0.05$) are bolded. Visual representations of select temporal trends are shown in Figure 2. All concentrations of aluminum species are reported in units of µg/L.
BLB = Brandon Lake Brook; MB = Maria Brook; MPB = Moose Pit Brook; MR = Mersey River.

however, this increase was statistically significant ($p < 0.05$) only at one site (Moose Pit Brook; Table 3 and Figure 2). Across the entire data set and within each individual site, concentrations of Al_o and Al_d significantly increased in all cases (Table 3 and Figure 2). The only statistically significant change in the proportion of Al_i making up Al_d (% Al_i) occurred at Maria Brook, where there was a decrease in this proportion (Table 3). These trends indicate that the observed trend of increasing Al_d concentrations is likely predominantly driven by increases in Al_o, and visualizing the frequency distribution of the different forms of Al across all sites confirms that most of the Al_d at the study sites is comprised of Al_o (Figure 3). However, concentrations of Al_i are still increasing at all sites, and the majority of samples had Al_i concentrations in exceedance of the toxic threshold for salmon.

Potential drivers of Al_i concentrations

Concentrations of Al_i were significantly correlated with several other water chemistry parameters. When the entire database and also only the large-sample study sites were considered, Al_i concentrations were strongly positively correlated with Al_d, Ti_d, Fe_d, and DOC concentrations (Figure 4 and Table 4) When the entire data set was considered, there were also slight but significant positive correlations between Al_i concentrations and T_w and Ce_d concentrations; however, these correlations became nonsignificant when the data set was filtered to contain only the large-sample study sites. Similarly, when the entire data set was considered, Al_i was significantly
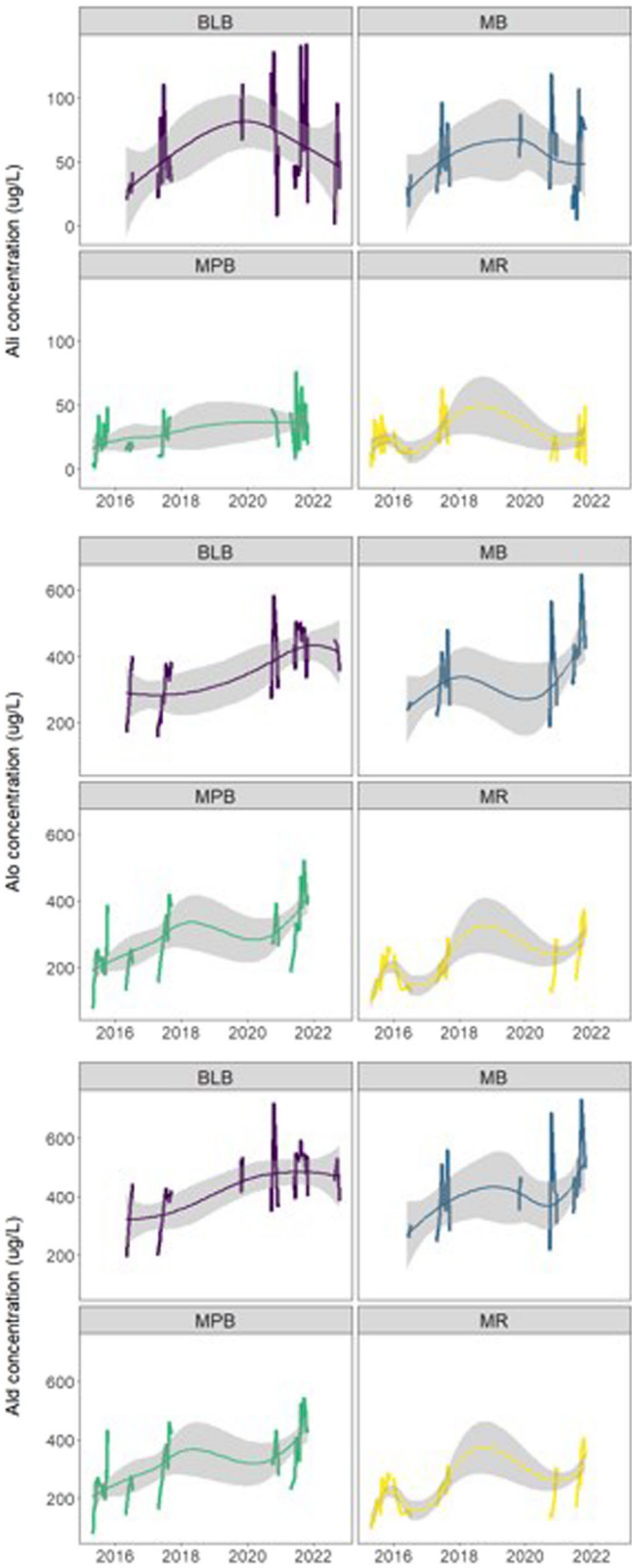

FIGURE 2: Al_i, Al_o, and Al_d concentrations at large-sample study sites during the study period (2015–2022). Trend lines were smoothed using the locally estimated scatterplot smoother (LOESS) method. BLB = Brandon Lake Brook; MB = Maria Brook; MPB = Moose Pit Brook; MR = Mersey River.
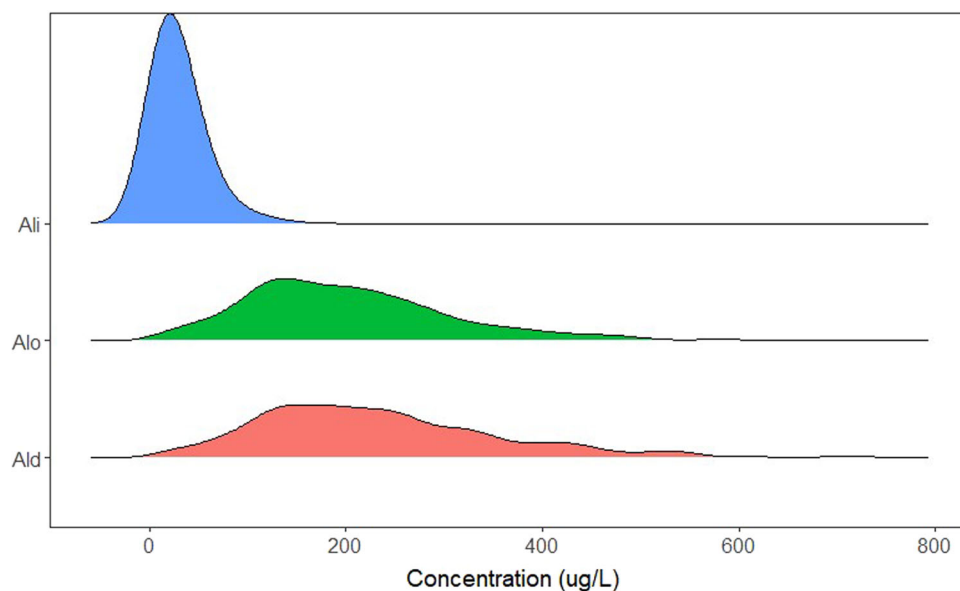
FIGURE 3: Frequency distribution plots of the concentrations of Al_i, Al_o, and Al_d at all study sites.

negatively correlated with SO_4 and Ca_d concentrations as well as with pH; these correlations were nonsignificant when the data set was filtered to contain only the large-sample study sites. Within only the large-sample study sites, the correlation between Al_i and Ca_d concentrations was much stronger but unexpectedly positively correlated.

The positive relationship between Al_i and Al_d was expected because Al_d is the source of Al_i. The positive relationship between Al_i and DOC has also been reported in previous studies (Campbell et al., 1992; Sterling et al., 2020), although it is widely believed that increased DOC levels protect from Al toxicity (Cardwell et al., 2018; Gensemer et al., 2018). Previous studies of metal concentrations in surface freshwaters have

found good correlation between Al and Fe concentrations (Gaillardet et al., 2003; Pokrovsky & Schott, 2002), in agreement with the relationship we observed. Titanium is a tetravalent element that is generally assumed to be immobile during weathering; however, migration of Ti has been observed in organic- and iron-rich rivers, and a strong positive correlation between Ti and Fe has been observed in such rivers (Pokrovsky & Schott, 2002). Cerium is another metal that appears to be associated with Al and Fe concentrations in freshwater, having been observed to be controlled by pH and DOC concentrations and to exhibit strong correlations with Fe and Al (along with the other rare earth metals; Gaillardet et al., 2003; Neal, 2005).
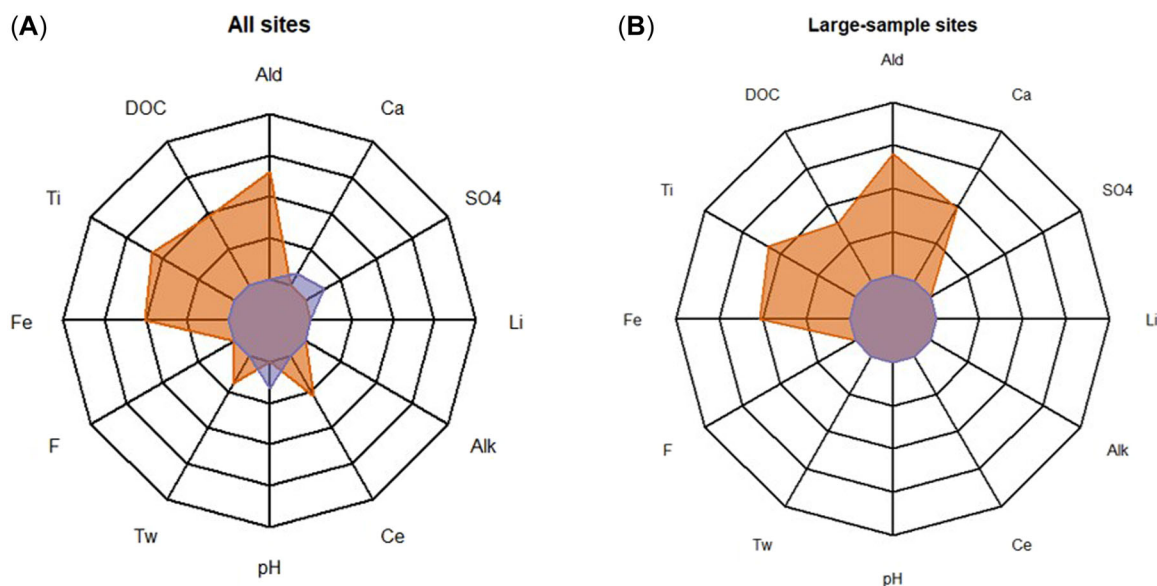

FIGURE 4: Pearson correlation values among water chemistry parameters and Al_i concentration at (**A**) all study sites and (**B**) only large-sample study sites, where orange polygons indicate a positive correlation with Al_i and purple polygons indicate a negative correlation with Al_i. Only correlations that are statistically significant ($p < 0.05$) are visualized. Correlation data are listed in Table 4. Alk = alkalinity; DOC = dissolved organic carbon; T_w = water temperature.

TABLE 4: Results of Pearson's test for correlation between Al_i concentration and various water chemistry parameters

Site	Variable	Pearson's r	p value
All sites	Al_d	**0.651**	**<0.0001**
	Ca_d	**−0.077**	**0.0458**
	SO_4	**−0.130**	**0.0010**
	Li_d	0.075	0.1048
	Alkalinity	−0.042	0.3623
	Ce_d	**0.283**	**<0.0001**
	pH	**−0.164**	**<0.0001**
	T_w	**0.188**	**<0.0001**
	F	0.041	0.3097
	Fe_d	**0.505**	**<0.0001**
	Ti_d	**0.571**	**<0.0001**
	DOC	**0.480**	**<0.0001**
Large-sample sites	Al_d	**0.702**	**<0.0001**
	Ca_d	**0.484**	**<0.0001**
	SO_4	0.023	0.7597
	Li_d	−0.077	0.5276
	Alkalinity	−0.013	0.9264
	Ce_d	0.314	0.0750
	pH	−0.022	0.7667
	T_w	0.015	0.8454
	F	0.061	0.4349
	Fe_d	**0.520**	**<0.0001**
	Ti_d	**0.580**	**<0.0001**
	DOC	**0.384**	**<0.0001**

Significant relationships ($p < 0.05$) are bolded. A visual representation of these results is shown in Figure 4.
DOC = dissolved organic carbon; T_w = water temperature.

The concentrations of these metals (Al, Fe, Ti, and Ce) in stream water appear to be controlled by similar processes, and thus they are highly inter-related. The dissolved fraction of each of these metals is correlated specifically with the cationic fraction of Al (Al_i; Table 5), meaning we can use the more commonly measured dissolved metal concentrations to predict the rarely measured speciated forms of Al.

Previous modeling research conducted with a smaller subset of the data set we used also found that T_w was one of the most important predictors of Al_i concentrations. Previous studies (Hendershot et al., 1986; Sterling et al., 2020) hypothesized that this positive relationship was caused by the role that increased temperature plays in activating biological drivers that

TABLE 5: Posterior medians of the standardized linear regression coefficients and their 95% credible intervals (2.5th–97.5th percentiles; Q)

Predictor	Median (Q_{50})	$Q_{2.5}$	$Q_{97.5}$
Al_d (µg/L)	0.79	0.65	0.93
DOC (mg/L)	−0.33	−0.49	−0.18
Ti_d (µg/L)	0.20	0.07	0.28
Fe_d (µg/L)	0.16	0.03	0.27
F (µg/L)	−0.11	−0.23	−0.02
T_w (°C)	0.10	0.05	0.16
pH	0.08	0.02	0.14
Ce_d (µg/L)	−0.07	−0.17	0.01
Alkalinity (mg $CaCO_3$/L)	−0.06	−0.12	−0.02
Li_d (µg/L)	0.05	−0.02	0.13
SO_4 (mg/L)	0.04	−0.08	0.15
Ca_d (mg/L)	0.03	−0.09	0.19
Color	−0.01	−0.11	0.10

DOC = dissolved organic carbon; T_w = water temperature.

mobilize Al (Gensemer & Playle, 1999; Santore et al., 2018). In the present study, as in other studies, we observed a statistically significant negative correlation between pH and Al_i concentrations, which agrees with our knowledge of how Al speciation varies with pH, although Sterling et al. (2020) did not find a significant relationship between pH and Al_i concentrations (Campbell et al., 1992; DeForest et al., 2018; Gensemer et al., 2018; Helliweli et al., 1983; Kopáček et al., 2006; Kroglund et al., 2001; Lydersen, 1990; Seip et al., 1989; Teien et al., 2006).

The observed negative relationship between SO_4 and Al_i concentrations was unexpected, because SO_4 is a product of acid deposition and can be considered an indicator of acidification status (see Driscoll & Wang, 2019; Strock et al., 2014). There is also a significant positive relationship between SO_4 and pH across all sites in our data set. Most of the SO_4 concentrations at our study sites are very low (mean concentration of 2.3 mg/L across the entire data set), and the observed relationships indicate that SO_4 is not a major contributor to the acidity at these sites.

Our results are also consistent with previous research on Al dynamics showing a phenomenon of "decoupling" between base cation and Al concentrations when base cations were extremely low (Ca concentrations below 1.4 mg/L; Rotteveel & Sterling, 2020). We hypothesize that the strong positive relationship between Al_i and Ca_d concentrations observed at the large-sample study sites is due to their extremely low Ca_d concentrations (mean = 1.1 mg/L, 75% of observations <1.3 mg/L) leading to this phenomenon of decoupling. Within the larger data set, in which the Ca_d concentrations were slightly higher (mean = 1.8 mg/L), the relationship between Al_i and Ca_d was negative.

Using drivers to create a predictive model for Al_i concentrations

The strongest BLMM predictors of Al_i concentrations were Al_d, DOC, Ti_d, Fe_d, and F concentrations (Figure 5 and Table 5). Dissolved Al has the largest standardized coefficient, but other predictors—particularly DOC and dissolved Ti—are influential. These results are consistent with previous modeling studies using WHAM, which found the most important variables to be Al, pH, DOC, F, Fe, Ca, and Mg; Cory et al., 2007).

The median absolute error of training set predictions was 8 µg/L, with a 95% credible interval of 6.9 to 8.2 µg/L. The median absolute error of test set predictions, used to simulate prediction of future observations, was 13 µg/L, with a 95% credible interval of 11.9 to 15 µg/L. Cumulative distribution functions show that the model slightly overpredicts Al_i at low concentrations and slightly underpredicts Al_i at high concentrations (Figure 6). Pearson correlations among posterior draws representing the Al_i model coefficients are visualized in the Supporting Information, Figure S1, in Appendix B.

Of note is that within the BLMM, once all other variables were accounted for, the relationship between DOC and Al_i switched to a negative correlation, as opposed to the positive
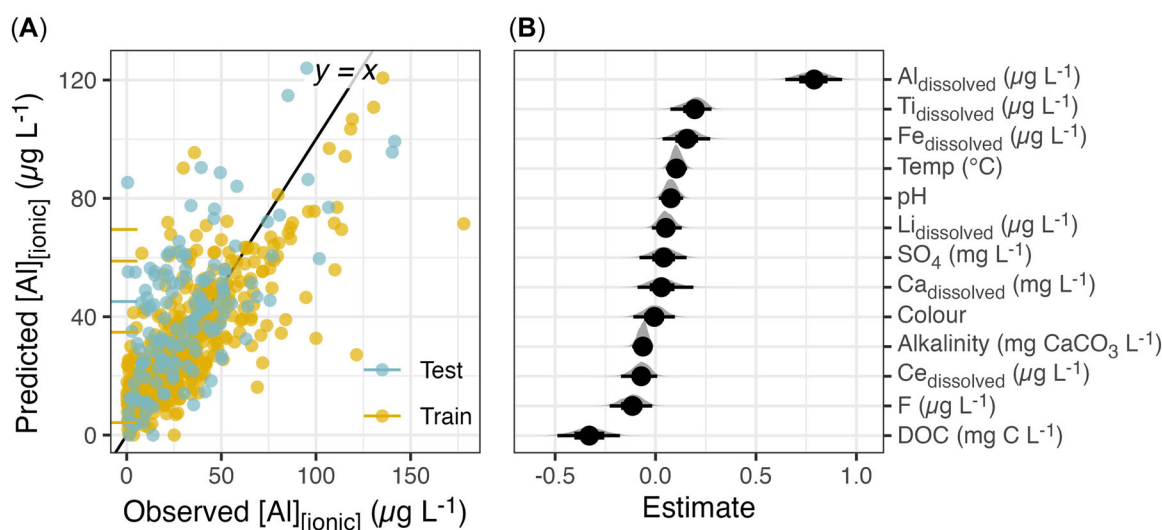
FIGURE 5: (**A**) Observed Al_i concentrations and corresponding model predictions in the training and test sets. Horizontal line segments represent left-censored values; they extend from the left edge of the plot to the censoring limit. (**B**) Posterior probabilities of the regression coefficients; points represent posterior medians, and heavy and light horizontal lines span the middle 66% and 95% of the posterior distributions, respectively.

correlation observed in the independent linear correlations. Dissolved organic carbon can form nonbioavailable complexes with Al, which may be a possible explanation for the negative relationship (Driscoll & Schecher, 1990). The appearance of F as a strong predictor of Al_i concentrations in the model is also of interest, given that there was no significant relationship between F and Al_i concentrations in the independent linear correlations. Previous studies have observed F concentrations to have a significant impact on Al abundance and speciation; however, the negative relationship we observed was unexpected because F typically forms inorganic complexes with Al and has been observed to increase the proportion of Al_i in freshwater (Berger et al., 2015). This positive relationship was observed to occur at high concentrations of F (median ~ 1 mg/L), while the average concentration of F in our data set was only 0.03 mg/L.
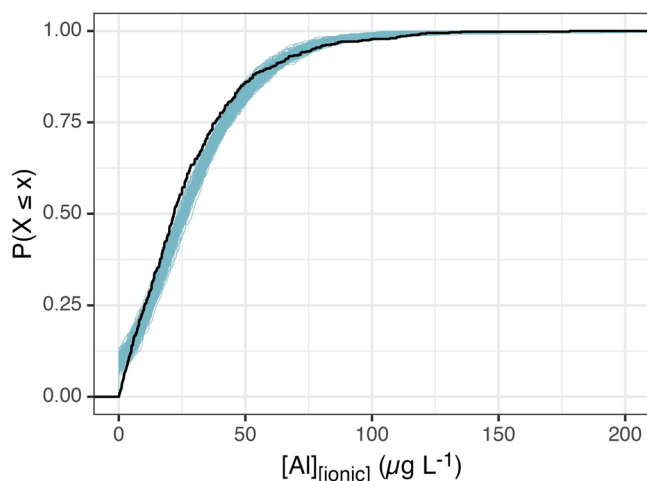

FIGURE 6: Empirical cumulative distribution functions of the observed Al_i concentrations and of a set of 100 posterior predictions. The Al_i concentrations are overpredicted at low concentrations and underpredicted at high concentrations.

The BLMM can be used to predict Al_i concentrations when it is not directly monitored using more commonly measured parameters to within 15 µg/L. As when using any modeled values, caution must be taken when applying predictions from this model, which, furthermore, is not intended for causal inference. Due to the highly variable nature of Al chemistry and its many interactions with other water chemistry parameters, the BLMM will likely perform most effectively when used to make predictions in rivers with similar chemistry to those in our data set, that is, acidic (mean pH of 4.9 across the data set), dilute (mean SPC of 38 µS/cm), and with relatively high levels of organic acidity (mean DOC concentration of 11 mg/L). These conditions are common and widespread in Nova Scotia due to the region's unique combination of historic heavy acid deposition, low-buffering bedrock that is slow-weathering and nutrient-poor, and high organic acidity from wetlands. The model we present is curated specially to handle these conditions, while previous more comprehensive models may lose accuracy in extreme conditions such as low pH or high Al_i concentrations (see Cory et al., 2007; Sjöstedt et al., 2010). To further test the model, we recommend future additional sampling of rivers that do not meet these specific conditions, to test how robust this model to a wider variation in key explanatory variables.

The BLMM may be limited by the distribution of samples collected throughout the year. Sample collection dates are heavily skewed toward the spring months of April and May, with a smaller but even number of samples collected during the summer and fall, and very few samples collected during the winter months (Supporting Information, Figure S2). Previous study of Al chemistry in Nova Scotia has shown that Al dynamics vary seasonally (Rotteveel & Sterling, 2020), so the data set we used may be missing a portion of the Al picture and should likely not be used for making winter predictions.

Discharge (i.e., base flow vs. high flow) plays an important role in water chemistry, but we unfortunately did not have access to consistent discharge measurements for our sites during

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the study period. Because we did not have discharge data, the concentration data are raw (not discharge corrected), meaning we are not able to detect biases related to hydrograph position. We strongly recommend that any future modeling study include the collection of discharge data and the stratification of water chemistry data by flow conditions to improve results.

An additional limitation of our study is the length of the data record. Although we did observe significant trends, they are limited due to the brevity of the data record (6 years). This may also affect the certainty of the correlations that we found. We recommend extended monitoring periods for future research.

Although complex chemical equilibrium models are important tools, the empirical model we present is relatively simple to understand and use with previously collected water chemistry data and could make modeling of Al_i concentrations more widely accessible to groups such as community watershed organizations. It is unrealistic for these groups, as well as government branches and academic researchers, to include speciated Al analysis in their regular sampling programs, but this model could be used to prioritize sites and regions where this type of sampling should be undertaken. This will be especially important in chronically acidified regions such as Nova Scotia, where toxic concentrations of Al_i may be widespread.

Conflict of Interest—The authors declare no conflict of interest.

Author Contributions Statement—**Kristin A. Hart**: Data curation; Formal analysis; Methodology; Project administration; Software; Supervision; Visualization; Writing—original draft; Writing—review & editing. **Benjamin Trueman**: Formal analysis; Methodology; Software; Validation; Visualization, Writing—original draft; Writing—review & editing. **Edmund A. Halfyard**: Conceptualization; Funding acquisition; Methodology. **Shannon M. Sterling**: Conceptualization; Funding acquisition; Methodology; Project administration; Supervision; Writing—review & editing.

Data Availability Statement—The code and data necessary to reproduce the model and its predictions are available at github.com/bentrueman/al-i-prediction.

REFERENCES

Baldigo, B. P., & Lawrence, G. B. (2000). Composition of fish communities in relation to stream acidification and habitat in the Neversink River, New York. *Transactions of the American Fisheries Society*, 129(1), 60–76.

Beneš, F., Horecký, J., Senoo, T., Kamasová, L., Lamačová, A., Tátosová, J., Hardekopf, D. W., & Stuchlík, E. (2017). Evidence for responses in water chemistry and macroinvertebrates in a strongly acidified mountain stream. *Biologia*, 72(9), 1049–1058.

Berger, T., Mathurin, F. A., Gustafsson, J. P., Peltola, P., & Åström, M. E. (2015). The impact of fluoride on Al abundance and speciation in boreal streams. *Chemical Geology*, 409, 118–124.

Buchanan, C., Smith, Z., & Nagel, A. (2017). Long-term water quality trends in USEPA region 3 (Mid-Atlantic). US Environmental Protection Agency.

Bürkner, P.-C. (2017). brms: An R package for Bayesian multilevel models using Stan. *Journal of Statistical Software*, 80, 1–28. https://doi.org/10.18637/jss.v080.i01

Bürkner, P.-C. (2018). Advanced Bayesian multilevel modeling with the R Package brms. *The R Journal*, 10(1), 395–411.

Burns, D. A., McHale, M. R., Driscoll, C. T., & Roy, K. M. (2006). Response of surface water chemistry to reduced levels of acid precipitation: Comparison of trends in two regions of New York, USA. *Hydrological Processes*, 20(7), 1611–1627.

Campbell, P. G., Hansen, H. J., Dubreuil, B., & Nelson, W. O. (1992). Geochemistry of Quebec north shore salmon rivers during snowmelt: Organic acid pulse and aluminum mobilization. *Canadian Journal of Fisheries and Aquatic Sciences*, 49(9), 1938–1952.

Cardwell, A. S., Adams, W. J., Gensemer, R. W., Nordheim, E., Santore, R. C., Ryan, A. C., & Stubblefield, W. A. (2018). Chronic toxicity of aluminum, at a pH of 6, to freshwater organisms: Empirical data for the development of international regulatory standards/criteria. *Environmental Toxicology and Chemistry*, 37(1), 36–48. https://doi.org/10.1002/etc.3901

Clair, T. A., Dennis, I. F., & Vet, R. (2011). Water chemistry and dissolved organic carbon trends in lakes from Canada's Atlantic Provinces: No recovery from acidification measured after 25 years of lake monitoring. *Canadian Journal of Fisheries and Aquatic Sciences*, 68(4), 663–674. https://doi.org/10.1139/f2011-013

Clair, T. A., Dennis, I. F., Vet, R., & Laudon, H. (2008). Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. *Biogeochemistry*, 87(1), 83–97.

Cory, N., Andrén, C. M., & Bishop, K. (2007). Modelling inorganic aluminium with WHAM in environmental monitoring. *Applied Geochemistry*, 22(6), 1196–1201. https://doi.org/10.1016/j.apgeochem.2007.03.011

Davies, J., Jenkins, A., Monteith, D. T., Evans, C. D., & Cooper, D. M. (2005). Trends in surface water chemistry of acidified UK freshwaters, 1988–2002. *Environmental Pollution*, 137(1), 27–39.

DeForest, D. K., Brix, K. V., Tear, L. M., & Adams, W. J. (2018). Multiple linear regression models for predicting chronic aluminum toxicity to freshwater aquatic organisms and developing water quality guidelines. *Environmental Toxicology and Chemistry*, 37(1), 80–90. https://doi.org/10.1002/etc.3922

Dennis, I. F., & Clair, T. A. (2012). The distribution of dissolved aluminum in Atlantic salmon (*Salmo salar*) rivers of Atlantic Canada and its potential effect on aquatic populations. *Canadian Journal of Fisheries and Aquatic Sciences*, 69(7), 1174–1183.

Driscoll, C. T., & Schecher, W. D. (1990). The chemistry of aluminum in the environment. *Environmental Geochemistry and Health*, 12(1–2), 28–49.

Driscoll, C. T., & Wang, Z. (2019). Ecosystem effects of acidic deposition. In: P. Maurice (Ed.), *Encyclopedia of water* (pp. 1–12). John Wiley & Sons. [accessed 2023 Jul 10] https://onlinelibrary.wiley.com/doi/abs/10.1002/9781119300762.wsts0043

Evans, C. D., Cullen, J. M., Alewell, C., Kopácek, J., Marchetto, A., Moldan, F., Prechtel, A., Rogora, M., Veselý, J., & Wright, R. (2001). Recovery from acidification in European surface waters. *Hydrology and Earth System Sciences Discussions*, 5(3), 283–298.

Exley, C., Chappell, J. S., & Birchall, J. D. (1991). A mechanism for acute aluminium toxicity in fish. *Journal of Theoretical Biology*, 151(3), 417–428.

Firke, S., Denney, B., Haid, C., Knight, R., Grosser, M., & Zadra, J. (2023). janitor: Simple tools for examining and cleaning dirty data. https://cran.r-project.org/web/packages/janitor/index.html

Fischetti, T. (2022). assertr: Assertive programming for R analysis pipelines. https://cran.r-project.org/web/packages/assertr/index.html

Gaillardet, J., Viers, J., & Dupré, B. (2003). Trace elements in river waters. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on geochemistry* (pp. 225–272). Pergamon. https://www.sciencedirect.com/science/article/pii/B0080437516051653

Gelman, A., Hill, J., & Yajima, M. (2012). Why we (usually) don't have to worry about multiple comparisons. *Journal of Research on Educational Effectiveness*, 5(2), 189–211. https://doi.org/10.1080/19345747.2011.618213

Gensemer, R. W., Gondek, J. C., Rodriguez, P. H., Arbildua, J. J., Stubblefield, W. A., Cardwell, A. S., Santore, R. C., Ryan, A. C., Adams, W. J., & Nordheim, E. (2018). Evaluating the effects of pH, hardness, and dissolved organic carbon on the toxicity of aluminum to freshwater aquatic organisms under circumneutral conditions. *Environmental Toxicology and Chemistry*, 37(1), 49–60. https://doi.org/10.1002/etc.3920

Gensemer, R. W., & Playle, R. C. (1999). The bioavailability and toxicity of aluminum in aquatic environments. *Critical Reviews in Environmental Science and Technology*, 29(4), 315–450.

Ginn, B. K., Cumming, B. F., & Smol, J. P. (2007). Assessing pH changes since pre-industrial times in 51 low-alkalinity lakes in Nova Scotia, Canada. *Canadian Journal of Fisheries and Aquatic Sciences*, 64(8), 1043–1054.

Gorham, E., Underwood, J. K., Martini, F. B., & Ogden III, J. G. (1986). Natural and anthropogenic causes of lake acidification in Nova Scotia. *Nature*, 324(6096), 451.

Grolemund, G., & Wickham, H. (2011). Dates and times made easy with lubridate. *Journal of Statistical Software*, 40, 1–25. https://doi.org/10.18637/jss.v040.i03

Gustafsson, J. P. (2020). Visual MINTEQ—A free equilibrium speciation model. https://vminteq.lwr.kth.se/

Hastie, T., Tibshirani, R., & Friedman, J. (2009). *The elements of statistical learning*. Springer. http://link.springer.com/10.1007/978-0-387-84858-7

Helliweli, S., Batley, G. E., Florence, T. M., & Lumsden, B. C. (1983). Speciation and toxicity of aluminium in a model fresh water. *Environmental Technology Letters*, 4(3), 141–144.

Hendershot, W. H., Dufresne, A., Lalande, H., & Courchesne, F. (1986). Temporal variation in aluminum speciation and concentration during snowmelt. In H. C. Martin (Ed.), *Acidic precipitation* (pp. 1285–1291). Springer.

Houle, D., Ouimet, R., Couture, S., & Gagnon, C. (2006). Base cation reservoirs in soil control the buffering capacity of lakes in forested catchments. *Canadian Journal of Fisheries and Aquatic Sciences*, 63(3), 471–474.

Kapoor, S., & Narayanan, A. (2023). Leakage and the reproducibility crisis in machine-learning-based science. *Patterns*, 4(9), 100804. https://doi.org/10.1016/j.patter.2023.100804

Kay, M. (2023). ggdist: Visualizations of distributions and uncertainty. https://doi.org/10.5281/zenodo.7933524

Kerekes, J., Beauchamp, S., Tordon, R., Tremblay, C., & Pollock, T. (1986). Organic versus anthropogenic acidity in tributaries of the Kejimkujik watersheds in western Nova Scotia. *Water, Air, and Soil Pollution*, 31(1–2), 165–1793.

Kopáček, J., Turek, J., Hejzlar, J., Kaňa, J., & Porcal, P. (2006). Element fluxes in watershed-lake ecosystems recovering from acidification: Čertovo Lake, the Bohemian Forest, 2001–2005. *Biologia*, 61(20), S413–S426.

Kroglund, F., Rosseland, B. O., Teien, H.-C., Salbu, B., Kristensen, T., & Finstad, B. (2007). Water quality limits for Atlantic salmon (*Salmo salar* L.) exposed to short term reductions in pH and increased aluminum simulating episodes. *Hydrology and Earth System Sciences Discussions*, 4(5), 3317–3355.

Kroglund, F., Teien, H. C., Rosseland, B. O., & Salbu, B. (2001). Time and pH-dependent detoxification of aluminum in mixing zones between acid and non-acid rivers. *Water, Air, & Soil Pollution*, 130(1), 905–910. https://doi.org/10.1023/A:1013859602354

Langan, S. J., & Wilson, M. J. (1992). Predicting the regional occurrence of acid surface waters in Scotland using an approach based on geology, soils and land use. *Journal of Hydrology*, 138(3–4), 515–528.

Laudon, H., Westling, O., Löfgren, S., & Bishop, K. (2001). Modeling preindustrial ANC and pH during the spring flood in northern Sweden. *Biogeochemistry*, 54(2), 171–195. https://doi.org/10.1023/A:1010614631588

Lydersen, E. (1990). The solubility and hydrolysis of aqueous aluminium hydroxides in dilute fresh waters at different temperatures. *Hydrology Research*, 21(3), 195–204.

McCormick, S. D., Lerner, D. T., Monette, M. Y., Nieves-Puigdoller, K., Kelly, J. T., & Björnsson, B. T. (2009). Taking it with you when you go: How perturbations to the freshwater environment, including temperature, dams, and contaminants, affect marine survival of salmon. *American Fisheries Society Symposium*, 69, 195–214.

McElreath, R. (2020). *Statistical rethinking: A Bayesian course with examples in R and STAN*. CRC Press.

McLeod, A. I. (2022). Kendall: Kendall rank correlation and Mann–Kendall trend test. https://cran.r-project.org/web/packages/Kendall/index.html

Monette, M. Y., & McCormick, S. D. (2008). Impacts of short-term acid and aluminum exposure on Atlantic salmon (*Salmo salar*) physiology: A direct comparison of parr and smolts. *Aquatic Toxicology*, 86(2), 216–226.

Monteith, D. T., Evans, C. D., Henrys, P. A., Simpson, G. L., & Malcolm, I. A. (2014). Trends in the hydrochemistry of acid-sensitive surface waters in the UK 1988–2008. *Ecological Indicators*, 37, 287–303.

Neal, C. (2005). Lanthanum, cerium, praseodymium and yttrium in waters in an upland acidic and acid sensitive environment, mid-Wales. *Hydrology and Earth System Sciences*, 9(6), 645–656. https://doi.org/10.5194/hess-9-645-2005

Nilsen, T. O., Ebbesson, L. O., Kverneland, O. G., Kroglund, F., Finstad, B., & Stefansson, S. O. (2010). Effects of acidic water and aluminum exposure on gill Na(+), K(+)-ATPase α-subunit isoforms, enzyme activity, physiology and return rates in Atlantic salmon (*Salmo salar* L.). *Aquatic Toxicology*, 97(3), 250–259.

Pedersen, T. L. (2022). patchwork: The composer of plots. https://cran.r-project.org/web/packages/patchwork/index.html

Pokrovsky, O. S., & Schott, J. (2002). Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chemical Geology*, 190(1), 141–179. https://doi.org/10.1016/S0009-2541(02)00115-8

Ram, K., Wickham, H., Richards, C., & Baggett, A. (2018). wesanderson: A Wes Anderson palette generator. https://cran.r-project.org/web/packages/wesanderson/index.html

Regish, A. M., Kelly, J. T., O'Dea, M. F., & McCormick, S. D. (2018). Sensitivity of Na /K -ATPase isoforms to acid and aluminum explains differential effects on Atlantic salmon osmoregulation in fresh water and seawater. *Canadian Journal of Fisheries and Aquatic Sciences*, 75(8), 1319–1328.

Rotteveel, L., & Sterling, S. M. (2020). Five aluminum seasonality regimes identified in chronically acidified rivers of Nova Scotia. *Environmental Science & Technology*, 54(2), 807–817. https://doi.org/10.1021/acs.est.9b04872

Santore, R. C., Ryan, A. C., Kroglund, F., Rodriguez, P. H., Stubblefield, W. A., Cardwell, A. S., Adams, W. J., & Nordheim, E. (2018). Development and application of a biotic ligand model for predicting the chronic toxicity of dissolved and precipitated aluminum to aquatic organisms. *Environmental Toxicology and Chemistry*, 37(1), 70–79. https://doi.org/10.1002/etc.4020

Schecher, W. D., & Driscoll, C. T. (1995). ALCHEMI: A chemical equilibrium model to assess the acid–base chemistry and speciation of aluminum in dilute solutions, In *Chemical Equilibrium and Reaction Models* (pp. 325–356). Wiley. https://onlinelibrary.wiley.com/doi/abs/10.2136/sssaspecpub42.c16

Seip, H. M., Andersen, D. O., Christophersen, N., Sullivan, T. J., & Vogt, R. D. (1989). Variations in concentrations of aqueous aluminium and other chemical species during hydrological episodes at Birkenes, southernmost Norway. *Journal of Hydrology*, 108, 387–405.

Sjöstedt, C. S., Gustafsson, J. P., & Köhler, S. J. (2010). Chemical equilibrium modeling of organic acids, pH, aluminum, and iron in Swedish surface waters. *Environmental Science & Technology*, 44(22), 8587–8593. https://doi.org/10.1021/es102415r

Skjelkvåle, B. L., Stoddard, J. L., Jeffries, D. S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D. T., Mosello, R., & Rogora, M.

(2005). Regional scale evidence for improvements in surface water chemistry 1990–2001. *Environmental Pollution*, *137*(1), 165–176.

Stan Development Team. (2023). R interface to Stan. https://mc-stan.org/rstan/

Staurnes, M., Hansen, L. P., Fugelli, K., & Haraldstad, Ø. (1996). Short-term exposure to acid water impairs osmoregulation, seawater tolerance, and subsequent marine survival of smolts of Altantic salmon (*Salmo salar*). *Canadian Journal of Fisheries and Aquatic Sciences*, *53*(8), 1695–1704.

Sterling, S. M., MacLeod, S., Rotteveel, L., Hart, K., Clair, T. A., Halfyard, E. A., & O'Brien, N. L. (2020). Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers, even during conditions of high dissolved organic carbon and low flow. *Hydrology and Earth System Sciences*, *24*(10), 4763–4775. https://doi.org/10.5194/hess-24-4763-2020

Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D. T., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B. L., Stainton, M. P., Traaen, T., … Wilander, A. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature*, *401*(6753), 575–578. https://doi.org/10.1038/44114

Strock, K. E., Nelson, S. J., Kahl, J. S., Saros, J. E., & McDowell, W. H. (2014). Decadal trends reveal recent acceleration in the rate of recovery from acidification in the northeastern US. *Environmental Science & Technology*, *48*(9), 4681–4689.

Tangen, G., Wickstrøm, T., Lierhagen, S., Vogt, R., & Lund, W. (2002). Fractionation and determination of aluminum and iron in soil water samples using SPE cartridges and ICP-AES. *Environmental Science & Technology*, *36*(24), 5421–5425. https://doi.org/10.1021/es020077i

Teien, H.-C., Standring, W. J. F., & Salbu, B. (2006). Mobilization of river transported colloidal aluminium upon mixing with seawater and subsequent deposition in fish gills. *Science of the Total Environment*, *364*(1), 149–164. https://doi.org/10.1016/j.scitotenv.2006.01.005

Tipping, E. (1989). Acid-sensitive waters of the English Lake District: A steady-state model of streamwater chemistry in the upper Duddon catchment. *Environmental Pollution*, *60*(3–4), 181–208.

Tipping, E. (1998). Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquatic Geochemistry*, *4*(1), 3–47. https://doi.org/10.1023/A:1009627214459

Vaughan, D., Dancho, M., & RStudio. (2022). furrr: Apply mapping functions in parallel using futures. https://cran.r-project.org/web/packages/furrr/index.html

Warby, R. A., Johnson, C. E., & Driscoll, C. T. (2005). Chemical recovery of surface waters across the northeastern United States from reduced inputs of acidic deposition: 1984–2001. *Environmental Science & Technology*, *39*(17), 6548–6554.

Warby, R. A., Johnson, C. E., & Driscoll, C. T. (2009). Continuing acidification of organic soils across the northeastern USA: 1984–2001. *Soil Science Society of American Journal*, *73*(1), 274–284.

Watmough, S. A., Eimers, C., & Baker, S. (2016). Impediments to recovery from acid deposition. *Atmospheric Environment*, *146*, 15–27.

Wickham, H., Averick, M., Bryan, J., Chang, W., McGowan, L., François, R., Grolemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T., Miller, E., Bache, S., Müller, K., Ooms, J., Robinson, D., Seidel, D., Spinu, V., … Yutani, H. (2019). Welcome to the Tidyverse. *Journal of Open Source Software*, *4*(43), 1686. https://doi.org/10.21105/joss.01686

Wickham, H., & Bryan, J. (2023). readxl: Read Excel files. https://CRAN.R-project.org/package=readxl

Wilke, C. O., & Wiernik, B. M. (2022). ggtext: Improved text rendering support for "ggplot2." https://cran.r-project.org/web/packages/ggtext/index.html

Wood, S. N. (2017). *Generalized additive models: An introduction with R* (2nd ed.). CRC Press.