Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers, even during conditions of high dissolved organic carbon and low flow

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Abstract. Acid deposition released large amounts of aluminum into streams and lakes during the last century in Northern Europe and Eastern North America. Elevated aluminum concentrations caused major environmental concern due to its toxicity to terrestrial and aquatic organisms, and led to the extirpation of wild Atlantic salmon populations. Air pollution reduction legislation that began in the 1990s in North America and Europe successfully reduced acid deposition, and the aluminum problem was widely considered solved. However, accumulating evidence indicates that freshwaters still show delays in recovery from acidification, with poorly understood implications for aluminum concentrations. Here, we investigate spatial and temporal patterns of labile cationic forms of aluminium (Al_i) from 2015-2018 in ten catchments in Nova Scotia, Canada, a region that was one of the hardest hit by acid deposition, but was not considered to have an aluminum problem because its high dissolved organic carbon (DOC) concentrations were expected to reduce Al_i concentrations. Surprisingly, our results show widespread and frequent occurrences of Al_i concentrations that exceed toxic thresholds in all sampled rivers despite high DOC concentrations. Generalized linear mixed model results reveal that DOC, instead of being inversely related to Al_i, is the strongest predictor (positive) of Al_i concentrations, suggesting that the recruitment properties of DOC in soils outweigh its protective properties in streams. Lastly, we find that, contrary to the common conceptualization that high Al_i levels are associated with storm flow, high Al_i concentrations are found during base flow. Our results demonstrate that elevated Al_i concentrations in Nova Scotia continue to pose a threat to aquatic organisms, such as the biologically, economically, and culturally significant Atlantic salmon (*Salmo salar*).

1 Introduction

Increased rates of acid deposition, predominantly deriving from upwind fossil fuel burning, resulted in the acidification of soils, rivers, and lakes during the last century (e.g., Kerekes et al., 1986), depleting base cations and increasing toxic aluminum concentrations in soils and drainage waters. Increased aluminum concentrations caused the extirpation of native Atlantic salmon (*Salmo salar*) populations in many rivers (Rosseland et al., 1990), for example in Scandinavia (Henriksen et al., 1984, Hesthagen and Hansen, 1991), the eastern USA (Monette and McCormick, 2008, Parrish et al., 1998), and Nova Scotia, Canada (Watt, 1987). The acidification problem was widely considered solved following reductions in anthropogenic sulfur emissions in North America and Europe since the 1990s. Many rivers showed steady improvements in annual average stream 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 aluminum (Al) in the USA (Baldigo and 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 other regions (Houle et al., 2006, Warby et al., 2009, Watmough et al., 2016), including Nova Scotia (Clair et al., 2011) raising questions about the possibility of elevated aluminum concentrations in freshwaters.

Al in freshwaters can exist as inorganic monomers, inorganic polymers, amorphous and microcrystalline inorganic forms, and as fast reactive or unreactive organic forms (Chew et al., 1988, Driscoll et al., 1980, LaZerte, 1984). While a variety of Al species in circumneutral waters are toxic to fish (Gensemer and Playle, 1999), including precipitated forms (Gensemer et al., 2018), the cationic species of Al (Al_i), such as Al^{3+}, $Al(OH)_2{}^{1+}$, and $Al(OH)^{2+}$ are considered to be the most labile and toxic to salmonids. Al species bind to the negatively charged fish gills causing morbidity and mortality through suffocation (Exley et al., 1991), reducing nutrient intake at gill sites, and altering blood plasma levels (Nilsen et al., 2010). The effects of sub-lethal exposure to freshwater Al elicits osmoregulatory impairment (Monette and McCormick, 2008, Regish et al., 2018) which reduces survival in the hypertonic marine environment (McCormick et al., 2009, Staurnes et al., 1996). Elevated concentrations of Al_i are also toxic to other freshwater and terrestrial organisms (Boudot et al., 1994, Wauer and Teien, 2010), such as frogs and aquatic birds (Lacoul et al., 2011).

Al speciation varies with pH (Helliweli et al., 1983, Lydersen, 1990), where positive Al species dominate over neutral and negative species below pH 6.3 at 2 ^{o}C and below pH 5.7 at 25 ^{o}C (Lydersen, 1990), with the most toxic Al species, $Al(OH)_2^{+1}$ (Helliweli et al., 1983) dominating Al speciation between pH 5.0–6.0 at 25 ^{o}C, and 5.5–6.5 at 2 ^{o}C (Lydersen, 1990). Thus, the toxicity of Al increases with increased pH up to approximately 6.0 at 25 ^{o}C, or 6.5 at 5 ^{o}C, when aqueous aluminum precipitates, forming gibbsite (Lydersen, 1990, Schofield and Trojnar, 1980), where colder waters will have a higher proportion of toxic species at higher pH values than warmer waters (Driscoll and Schecher, 1990).

The bioavailability of Al is reduced by the presence of calcium (Ca) (Brown, 1983), which can occupy the negatively charged gill sites. Dissolved organic carbon (DOC) also reduces bioavailability of aluminum via the formation of organo-Al complexes (Al_o) (Erlandsson et al., 2010, Neville, 1985). High levels of DOC in rivers have been believed to be sufficient to protect fish gills from adverse Al effects (Lacroix and Kan, 1986, Vogt and Muniz, 1997, Witters et al., 1990).

Despite being the most common metal on Earth’s crust, Al is usually immobilized in clays or hydroxide minerals in soils. Rates of Al release into soil water from soil minerals increase with three drivers: 1) low soil pH, 2) low soil base saturation, and 3) high soil DOC concentrations. Lowered pH increases solubility of secondary minerals containing Al; Al_i concentrations in streamwater are generally negatively correlated with pH (Campbell et al., 1992, Kopáček et al., 2006, Seip et al., 1989).

Low levels of base saturation can cause charge imbalances resulting in the release of Al into soil waters and later into drainage waters (Fernandez et al., 2003); chronic acidification thus shifts available exchangeable cations in the soil water from Ca and magnesium (Mg) towards Al (Schlesinger and Bernhardt, 2013, Walker et al., 1990). Higher concentrations of DOC in soil water increase the release of Al through two mechanisms: 1) as an organic acid, DOC decreases soil pH, thus increasing Al release (Lawrence et al., 2013), and 2) by forming organic complexes with Al_i it maintains a negative Al concentration gradient from the cation exchange sites to the soil water, increasing rates of Al release (Edzwald and Van Benschoten, 1990, Jansen et al., 2003). Field studies confirm Al concentrations to be positively correlated with DOC (Campbell et al., 1992, Kopáček et al., 2006).

The general consensus in the literature is that elevated Al_i concentrations occur during episodic storm events, due to three possible mechanisms: 1) dilution of base cations during storm events, where flow paths move through shallower, more organic-rich soil layers, 2) added anions in snowmelt or rainfall (e.g., Cl^-, SO_4^{2-}, F^-) providing mobile anions that increase Al_i export to streams, and 3) low pH associated with storm events, re-dissolving Al accumulated in the soil (Hooper and Shoemaker, 1985) and/or from the streambed (Norton et al., 1987). For example, from 1983 to 1984, Al concentrations for the River Severn in Wales increased ten-fold during the stormflow peak compared to the baseflow (Neal et al., 1986). The general consensus in the literature is also that Al_i is seasonally elevated during spring snowmelt and autumn rainfall events, and seasonally depressed during summer months due to higher levels of DOC, such as in Quebec (Campbell et al., 1992), Russia (Rodushkin et al., 1995), and along the Czech-German border (Kopacek et al., 2000, Kopáček et al., 2006). Timing of the Al_i peaks is important. If peak Al_i concentrations coincide with vulnerable life stages of Atlantic salmon, such as during the spring when salmon transition from parr to smolt (i.e. smoltification) in preparation for life in the ocean (Kroglund et al., 2007, Monette and McCormick, 2008, Nilsen et al., 2013) or during the emergence of salmon fry from eggs (e.g., Farmer, 2000), then the potential for large biological impacts from elevated Al_i is particularly high.

Despite much progress in acidification research, the processes affecting Al_i dynamics are not well understood (e.g., Mulder et al., 1990). Our understanding of Al_i is limited by the relative paucity of samples; Al_i is not measured as part of standard analyses. Our understanding is also limited by the difficulty in comparing the wide variety of methods for estimating Al_i; different definitions, often operational, of toxic Al include inorganic Al, inorganic monomeric Al, labile Al, Al^{3+}, and cationic Al (Table A1).

Acid-sensitive areas of Nova Scotia, Canada, here abbreviated as NS_A (see Clair et al., 2007), with once-famous wild Atlantic salmon populations, were heavily impacted by sulfur deposition at the end of the last century, which originated from coal burning in central Canada and Northeastern USA (Hindar, 2001, Summers and Whelpdale, 1976). NS_A catchments are particularly sensitive to acid deposition due to base cation-poor and slowly weathering bedrock that generates thin soils with low acid neutralizing capacity (ANC), extensive wetlands, and episodic sea salt inputs (Clair et al., 2011, Freedman and Clair, 1987, Watt et al., 2000, Whitfield et al., 2006). Al was not considered to be a threat to Atlantic salmon in Nova Scotia because of the high natural levels of DOC in NS_A rivers following preliminary research by (Lacroix and Townsend, 1997, Lacroix, 1989). A 2006 fall survey, however, (Dennis and Clair, 2012) found that in seven of 42 rivers surveyed Al_i concentrations in NS exceeded the 15 $\mu g\ L^{-1}$ toxic threshold for aquatic health, as determined from an extensive review of toxicological and geochemical literature by the European Inland Fisheries Advisory Council (EIFAC) (Howells et al., 1990). No assessment of Al_i has been done in NS_A since that time, and little is known about the current extent and patterns of Al_i in the region. Here, we conduct a four-year survey of Al_i concentrations in ten streams in NS_A, to test the hypothesis that elevated DOC concentrations are sufficient to protect life from Al_i, and to identify the hydrologic conditions associated with elevated Al_i concentrations.

2 Materials and methods

2.1 Study area

We surveyed Al_i concentrations at ten study catchments in NS_A, ranging from headwater to higher-order systems: Mersey River (MR), Moose Pit Brook (MPB), Pine Marten Brook (PMB), Maria Brook (MB), Brandon Lake Brook (BLB), above the West River lime doser (ALD), Upper Killag River (UKR), Little River (LR), Keef Brook (KB), and Colwell Creek (CC) (Table 1, Fig. 1). Our study catchments are predominantly forested with a mix of coniferous and deciduous species, and drain slow-weathering, base-cation poor bedrock, producing soils with low ANC (Langan and Wilson, 1992, Tipping, 1989). The catchments also have relatively high 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).

2.2 Data collection and analysis

We measured Al_i concentrations at three of the ten catchments from April 2015 to September 2017 (MR, MPB, PMB), on a weekly to monthly frequency during the snow-free season (approximately April to November, Table A2). In 2016-2018, seven sites were added and sampled every two weeks to monthly during the snow-free season.

Al_i sampling events comprise grab samples for lab analysis and in situ measurements of pH and water temperature (T_w). We calculate Al_i as the difference between dissolved Al (Al_d) and Al_o following

Dennis and Clair (2012) and Poléo (1995) (Eq. 1), separating the species in the field to reduce errors caused by Al species change due to changes in temperature and pH in transport from field to lab.

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

Al_d is measured as the Al concentration of a filtered (45 μm) sample and Al_o is measured as the eluate from passing filtered water through a 3 cm negatively charged cation exchange column (Bond Elut Jr. Strong Cation Exchange Column). Samples were passed through the cation exchange column at a rate of approximately 30 to 60 drops per minute. From this method, Al_o is operationally defined as the non-labile, organically-complexed metals and colloids, and Al_i is defined as the positive ionic species of Al (e.g., Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^{+}$).

The cation exchange method thus determines concentrations of weak monomeric organic Al complexes (passed through the column), monomeric inorganic Al (retained in the column), and colloidal, polymeric, and strong organic complexes that are measured after acid digestion of the sample (Gensemer and Playle, 1999). An assumption here is that the Al species retained on the exchange column would also be retained on the negatively charged fish gills, and therefore have a potentially toxic effect (see Gensemer and Playle, 1999). The eluate is generally considered to be non-toxic; however, there is some evidence that precipitated polymeric Al and colloidal Al can be toxic to aquatic life (Parent and Campbell, 1994; Gensemer and Playle, 1999, Gensemer et al., 2018) although the nuances of this toxicity is unclear. To this end, the calculated Al_i reported in this study represents a minimum concentration. Ultrafiltration (following Simpson et al., 2014) may improve the accuracy of estimations of recently precipitated colloidal Al concentrations.

Stream chemistry samples (50 ml) were collected using sterilized polyethylene syringes into sterilized polyethylene bottles. Samples for sulfate (SO_4^{2-}) analysis were not filtered. Trace metal samples were filtered (0.45 μm) and preserved with nitric acid (HNO_3). Samples for DOC analysis were filtered (0.45 μm) and transported in amber glass bottles containing sulfuric acid preservative (H_2SO_4) to prevent denaturation. All samples were cooled to 7 °C during transport to the laboratories. Samples were delivered to the laboratories within 48 hours of collection, where they were further cooled to ≤ 4°C prior to analysis (Appendix D).

We examined correlations between Al_i and water chemistry parameters: Al_d, Ca, DOC, pH, SO_4^{2-}, T_w, fluoride (F^-), nitrate (NO_3^-), and runoff (where data were available). Correlations were analysed within and across sites. For the purposes of this study, we use the toxic threshold of Al_i at 15 ug L^{-1}, as the majority of our pH observations were greater than or equal to 5.0 (Table A2, Appendix D3).

We developed a Generalized Linear Mixed Model (GLMM) to identify the main drivers of Al_i concentration at the study sites. We tested Al_d, DOC, Ca, SO_4^{2-}, F^-, NO_3^-, season, and T_w as potential drivers. The GLMM analysis was implemented with R version 3.6.2. (R Core Team, 2019) using the lme4 package (Bates et al., 2015). Due to the nonnormality of the Al_i concentration data, the glmer() function was employed for model fitting which uses the method of maximum likelihood for parameters estimation through Laplace approximation (Raudenbush et al., 2000). The study sites in the analysis were included as the random effect with fixed effects provided in Table A3; Al_d was not included in the GLMM as it results in an over fit model (singularity). The Wald t Test Statistic and the Akaike Information Criterion (AIC) were used as measures of goodness-of-fit (Akaike, 1974; Bolker et al., 2019). Numerous iterations of fixed effects and interactions were considered in the GLMM development (Table A3). Multiple fixed effects were initially considered; however, several of the effects were not significant, although the overall model fit provides a low AIC. GLMMs were applied to assess season drivers of Al_i concentrations; however, due to the limited amount of seasonal data collected, an analysis of both the site and seasonal random effects could not be carried out due to model singularities.

3 Results and discussion

3.1 Prevalence of Al_i

Al_i concentrations exceed toxic levels (15 ug L^{-1}) at all sites during the study period (Table A2) despite relatively high DOC concentrations (mean values ranging from 7.2 to 23.1 mg L^{-1} among the catchments, Table 1). Mean Al_i concentrations across all sites range from 13–60 ug L^{-1} (Table 1), with the highest mean concentrations also occurring in the eastern part of the study area (Fig. 1a), where one site had 100% of samples in exceedance (Fig. 1b). Al_i concentrations exceed 100 ug L^{-1} (approximately seven times the threshold) at three sites (Table A2). Our Al_i concentrations are consistent with the 6.9–230 ug L^{-1} range of Al_i concentrations measured across NS_A by Dennis and Clair (2012) and are higher than concentrations measured in Norway from 1987–2010 (5–30 ug L^{-1}) (Hesthagen et al., 2016).

The percent of Al not complexed by DOC (% Al_i/Al_d) ranges from a minimum of 0.6% to a maximum of 50%, with a median value of 10.7%, across all sites. These findings are similar to those found in NS_A by Dennis and Clair (2012) of the proportion of Al_i in total aluminum (Al_t) (min. = 4%, max. = 70.1%, med. = 12.4%), and less than those found by Lacroix (1989) (over 90 % Al_o/Al_d). These speciation results are also quite similar to other diverse environments such as those for acid sulfate soil environments in Australia (Simpson et al., 2014). However, even when the percentage of Al_i/Al_d is low, Al_i concentrations remain well above thresholds for toxicity (Fig. B2-B11). Similarly to our findings, previous studies show Al_i/Al_d is low during baseflow (Bailey et al., 1995, Murdoch and Stoddard, 1992, Schofield et al., 1985), (Figs. B2-B11).

The highest concentrations of Al_i (> 100 ug L^{-1}) occurred in early summer (late June or early July in 2016-2018) when Al_d, Ca, and DOC concentrations had not yet reached their annual peak (Table A2). The spring/summer extreme events occurred among the first exceptionally warm days (> 21 °C) of the year, in dry conditions, and when the proportion of Al_o/Al_d was low (lowering to approximately 60-70% from higher levels of around 80-90%) (Figs. B2-B11). pH was not abnormally low during these events (ranging from 4.8 to 6.13), Ca concentrations were low (less than or equal to 800 μg L^{-1}) and DOC concentrations ranged from 15–21 mg L^{-1}.

In the sites with the longest and most frequent data collection (MR and MPB), Al_i concentrations exceed the toxic threshold in consecutive samples for months at a time, particularly in the late summer (Fig. B1).

3.2 Potential Al_i drivers

GLMM results reveal, through multiple fixed effect model combinations, that DOC and T_w are the most significant predictors of Al_i concentrations (Table A3). When both DOC and T_w were included in the GLMM model, the resulting AIC is markedly lower, indicating that the inclusion of both parameters provides better predictive potential than DOC or T_w alone. Furthermore, the interaction between DOC and T_w was not significant in the model, provided a nominally lower AIC, and the correlation between the effects was low (-0.378), indicating that distinct processes are responsible for Al_i concentrations. The strength of the T_w relationship is likely due to the role that increased temperature plays in activating biological drivers that mobilize Al (Hendershot et al., 1986).

Thus, the GLMM results show that DOC is positively correlated with Al_i in the study area, in contrast to the standard conceptualization that DOC is inversely correlated with Al_i, suggesting that the increased recruitment of Al in soils by DOC may outweigh DOC's protective effects in freshwater, consistent with observations in other studies (e.g., Campbell et al., 1992, Kopáček et al., 2006).

Linear regressions show that Al_d is significantly ($\alpha = 0.05$) and positively correlated with Al_i in seven of the ten study sites (ALD, KB, LR, MB, MPB, MR, PMB) (Fig. 2, Table A5). Ca is significantly and positively correlated with Al_i at two sites (MPB, MR) (Fig. 2, Table A5). The positive relationship between Ca and Al_i is the opposite of expectations (following Rotteveel and Sterling, 2019). We hypothesize that this is due to the two study sites having very low Ca concentrations (mean concentrations below 1 mg L^{-1}), below which soil water Ca concentrations are too low to retard Al release.

Discharge is significantly and negatively correlated with Al_i at one site MPB (Fig. 2, Table A5), in contrast with previous observations that Al_i concentrations are positively correlated with discharge (Hooper and Shoemaker, 1985, Neal et al., 1986, Seip et al., 1989, Sullivan et al., 1986). Runoff data are available for only two of the study sites (MR, MPB); more runoff data are needed to improve our understanding of the relation between runoff and Al_i in NS_A.

We did not observe the negative association between pH and Al_i observed in previous studies (Campbell et al., 1992, Kopáček et al., 2006) - pH is negatively correlated with Al_i in four out of ten sites, but none of these relationships are statistically significant (Fig. 2, Table A5). The lack of significant correlation may be due in part to other mechanisms that may cloud the strength of the inverse relationship between pH and Al, such as increased DOC solubility at higher pH, leading to increased Al solubility in soils (Lyderson, 1990), pH buffering by Al in the lower pH range (Tomlinson, 1990), and by the limited pH range in the data set. We did observe a statistically significant positive relationship between pH and Al_i/Al_d (Table A4); thus, it seems that pH may play a more important role in determining the proportion of different Al species rather than the absolute value of Al_i present in stream waters in chronically acidified conditions such as those found Nova Scotia. F^- has also been found to be a complexing agent that affects the speciation of Al at low pH levels and relatively high concentrations of F^- (>1 mg L^{-1}) (Berger et al., 2015). The concentrations of F^- at the study sites are mostly below this threshold (mean across all sites = 0.045 mg L^{-1}); however, there is still a significant positive effect of F^- on Al_i concentrations across at two sites (KB, MPB) (Fig. 2, Table A5). NO_3^- and SO_4^{2-} are also potential complexing ligands of Al; however, we did not observe any correlation between Al_i and either of these parameters, except for a significant negative correlation between SO_4^{2-} and Al_i at MB.

3.3 Possible seasonal groupings of Al_i in NS_A

In the two sites with the most samples, MPB and MR, groupings of data are visible that are temporally contiguous, suggesting seasonally dependent Al_i behavior (Fig. 4). This is supported by stronger linear correlations (r^2) among variables when grouped by “season” (Table 2); for example, for the correlation between pH and Al_i at MR, r^2 improves from 0.02 for year-round data (Fig. B12) to up to 0.78 in season 1 (Fig. 4). The transition dates between the seasons are similar for the two catchments, but not the same (Table A2), and vary by year. Here we propose an initial characterization of potential “seasons”; more research is needed to test these hypotheses on seasonal divisions and their drivers using larger datasets to test for statistical significance among the potential seasonal groupings.

Season 1 (approximately April/May) is coincident with snow-melt runoff and is characterized by relatively low concentrations of Al_i (2-46 ug L^{-1}), low pH (4.5-5.3), and lower concentrations of most constituents, including DOC, and cold temperatures (< 4 ^{o}C). During this season, Al_i is strongly coupled with pH, DOC, Al_d and Ca in MR, but less so in MPB. A possible explanation is that season 1 is dominated by snowmelt hydrology in which cation exchange between soil and discharge occurs less efficiently, which has been attributed to ice and frozen soil potentially limiting water contact time with soil (Christophersen et al., 1990). It is important to note that we did not likely capture the first flush effect of increased Al_i as has been noted in other studies (e.g., Hendershot et al., 1996). The onset of season 2 (approximately late June) is characterized by increasing Al_i concentrations, temperature, and DOC. Al_i and pH values are higher in this season and Al_i becomes strongly negatively correlated with pH as pH increases to the lower threshold for gibbsite. In MR in season 2 Al_i has a strong positive relationship with DOC. The highest observed Al_i concentrations of the year occur in season 2 (Fig. 3). Al_i relations are weak in MR in season 3 (approximately September through March), likely due to the lower frequency of measurements during the winter. Season 3 in MR has the highest concentrations of dissolved constituents (Al_d, Ca, and DOC), whereas in MPB only Ca has the highest concentrations.

With the inclusion of season as the random effect in the GLMM analysis (Table A6) there remains limited data for undertaking a robust comparative analysis but it is included nonetheless to highlight the seasonal impacts that can be garnered from the limited dataset. pH and T_w were omitted due to singularities. The results reinforce that DOC concentrations are associated with Al_i concentrations on a seasonal basis; however, more data are required to ascertain the effects of T_w on seasonal Al_i concentrations.

In contrast with the conceptualization that peak Al_i concentrations occur during storm flow (e.g., Campbell et al., 1992, Kopacek et al., 2000, Neal et al., 1986, Rodushkin et al., 1995), our data show elevated Ali concentrations during base flow conditions. These results suggest a new pathway for generation of elevated Al_i concentrations that is associated with base flow, warmer summer temperatures, and high DOC concentrations, and thus likely more chronic in nature. Nilsson (1985) had suggested that this flowpath has important consequences for Al concentrations in Swedish catchments. We hypothesize that this pathway is caused by increased temperatures causing higher levels of biological activity that mobilize Al in soils (Figure 3) (following Nilsson and Bergkvist, 1983). Biological activity further generates DOC which mobilizes Al to drainage waters during summer base flow (Figure 4). Other cases of increased Al_i concentrations occurring during low flow and warming temperatures can be found in the literature in locations such as Ontario and Quebec (Hendershot et al., 1985, Hendershot et al., 1996) and in Virginia, USA (Cozzarelli et al., 1987).

3.4 Ecological implications

While the summer peak in Al_i that we observed in NS_A does not coincide with the smoltification period, continued exposure throughout the year may still negatively affect salmon populations, as accumulation of Al_i on gills reduces salmon marine and freshwater survival (Kroglund et al., 2007, Kroglund and Staurnes, 1999, Staurnes et al., 1996, Gibson et al., 2011).

In addition, elevated Al_i concentrations appearing during low flow in the summer months suggest a more chronic delivery of elevated Al_i to rivers, for which increases in the length and severity of droughts and heat-waves due to climate change may further exacerbate effects on aquatic life. Because many peak Al_i concentrations occur on the first exceptionally warm day in late spring, springtime warming associated with climate change may cause Al_i peaks to occur earlier, thus increasing chance of the peak Al_i concentrations overlapping with smoltification season and emergence of salmon fry, the most vulnerable life stages of Atlantic salmon (e.g., Farmer, 2000), although the phenology of the smolt run is expected to similarly advance earlier in the year.

4 Conclusions

Our four-year study of stream chemistry in NS_A has two important findings. First, high DOC concentrations in rivers may not protect aquatic life against Al_i as previously thought – our GLMM analysis suggests rather the opposite – that higher DOC concentrations drive higher levels of Al_i, even possibly on a seasonal basis. Our study thus reveals that despite high DOC levels, widespread and persistent toxic concentrations of Al_i in NS_A freshwaters pose a risk to aquatic, and potentially terrestrial, life. Second, our study highlights an overlooked hydrological pathway that is associated with high Al_i concentrations: base flow, suggesting a chronically acidified/aluminum dynamic, in addition to episodic Al_i peaks associated with storm flow. This base flow pathway suggests that Al_i concentrations are chronically elevated during warmer summer months, and thus that this Al pathway may be exacerbated by atmospheric warming. Our results suggest that the recent 88 to 99% population decline of the Southern Uplands Atlantic salmon population in NS_A (Gibson et al., 2011) may be partially attributable to Al_i, in contrast to earlier studies which downplayed the role of Al_i in Atlantic salmon mortality (Lacroix and Townsend, 1987). These high Al_i concentrations in NS_A highlight the need to increase our understanding of the influence of Al_i on both terrestrial and aquatic ecosystems, and its implications for biodiversity. The catchments with the highest Al_i levels had particularly low Ca levels, raising concerns as Ca is protective against Al_i toxicity, and highlighting coincident threats of Ca depletion and elevated Al. Recent work has identified globally widespread low levels and declines in Ca (Weyhenmeyer et al., 2019), raising the question of what other regions may also have Al_i levels exceeding toxic thresholds. The serious potential consequences of high Al_i highlight the importance for actions to further reduce acid emissions and deposition, as critical loads are still exceeded across the province (Keys, 2015), and to adapt forest management practices to avoid base cation removal and depletion. Addition of base cations through liming and enhanced weathering of soils and freshwaters may accelerate recovery from acidification.

Data availability

Readers can access our data from HydroShare supported by CUASHI, a FAIR-aligned data repository (https://www.re3data.org/).

Author contributions

SMS conceived the idea and led the writing of the MS. SM led the field data collection. SM and TAC designed the protocol for Al_i sampling, assisted with data analysis and helped with the writing. LR performed spatial and statistical analysis, produced figures, and assisted with sample collection and draft writing. KH assisted with data analysis, figure production and editing and contributed to the draft. NLO led the GLMM analyses and contributed to the manuscript. TAC provided information on analytical and field sampling methods, and selection of sampling sites. EAH contributed field samples, assisted with data analysis and contributions to the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Tables

Table 1 Study site characteristics. “n” refers to the number of sampling events. Number in brackets after the mean concentration is the standard deviation. One Al_i outlier removed for MR (value: 2 µg·L^{-1}, date: 30 April 2015). pH is calibrated using the method outlined in Appendix D.4.

Site	Lat	Long	Area (km^2)	n	Land use	Dominant Bedrock Type	Mean Al_i (ug L^{-1})	Mean DOC (mg L^{-1})	Mean Al_d (ug L^{-1})	Mean Ca (ug L^{-1})	Mean pH
Mersey River (MR)	44.437	-65.223	292.8	47	Natural forest	Granite	22.5 (11.7)	8.6 (2.7)	195 (54.9)	699 (120)	5.1
Moose Pit Brook (MPB)	44.462	-65.048	15.8	39	Natural forest	Granite/slate	20.8 (12.2)	15.8 (6.1)	249 (85.9)	826 (344)	5.0
Pine Marten Brook (PMB)	44.436	-65.209	1.5	15	Natural forest	Slate	13.5 (12.0)	8.6 (3.3)	149 (43.4)	969 (536)	5.1
Maria Brook (MB)	44.779	-64.414	0.2	12	Natural forest	Granite	40.1 (23.2)	9.8 (4.4)	319 (99.2)	1292 (286)	5.1
Brandon Lake Brook (BLB)	45.021	-62.690	1.3	22	Natural forest	Sandstone/slate	48.7 (27.6)	16.0 (8.3)	350 (71.0)	836 (272)	4.9
Upstream of West River Lime Doser (ALD)	45.054	-62.800	32.3	22	Natural forest	Sandstone/slate	45.3 (26.7)	13.8 (3.7)	243 (64.8)	759 (126)	5.2
Upper Killag River (UKR)	45.064	-62.705	36.8	18	Natural forest	Sandstone/slate	43.5 (23.5)	12.8 (3.0)	224 (68.3)	739 (230)	5.3
Little River (LR)	44.952	-62.611	47.1	13	Natural forest	Sandstone/slate	15.1 (11.7)	7.2 (1.9)	109 (46.1)	746 (166)	5.4
Keef Brook (KB)	45.0284	-62.7153	2.3	5	Natural forest	Sandstone/slate	28.2 (11.5)	10.8 (3.6)	281 (80.4)	621 (275)	5.1
Colwell Creek (CC)	45.0279	-62.7127	1.7	8	Natural forest	Sandstone/slate	58.9 (41.7)	23.1 (5.1)	411 (117)	750 (568)	5.0

Table 2. Al_i relations with other stream chemistry parameters separated by possible seasons. Dark shading represents $r^2 > 0.6$. Medium shading represents r^2 0.2-0.6. Light shading represents r^2 0.0-0.2. Green indicates negative relation. Orange indicates positive relation.

	pH		DOC		Tw		Al_d		Ca	
	slope	r^2	slope	r^2	slope	r^2	slope	r^2	slope	r^2
Season 1										
MR	-7.67	0.78	1.78	0.49	-0.26	0.42	0.084	0.67	0.0329	0.50
MPB	8.44	0.0045	2.62	0.71	2.66	0.72	0.13	0.68	0.053	0.59
Season 2										
MR	-53.2	0.27	7.5	0.51	0.72	0.034	0.23	0.52	0.13	0.37
MPB	-19.6	0.22	1.4	0.43	1.43	0.23	0.1	0.42	0.039	0.42
Season 3										
MR	4.57	0.046	0.089	0.0014	0.25	0.088	0.021	0.014	0.006	0.0001
MPB	-39.6	0.56	1.33	0.73	-2.42	0.44	0.086	0.66	0.018	0.49

Figures

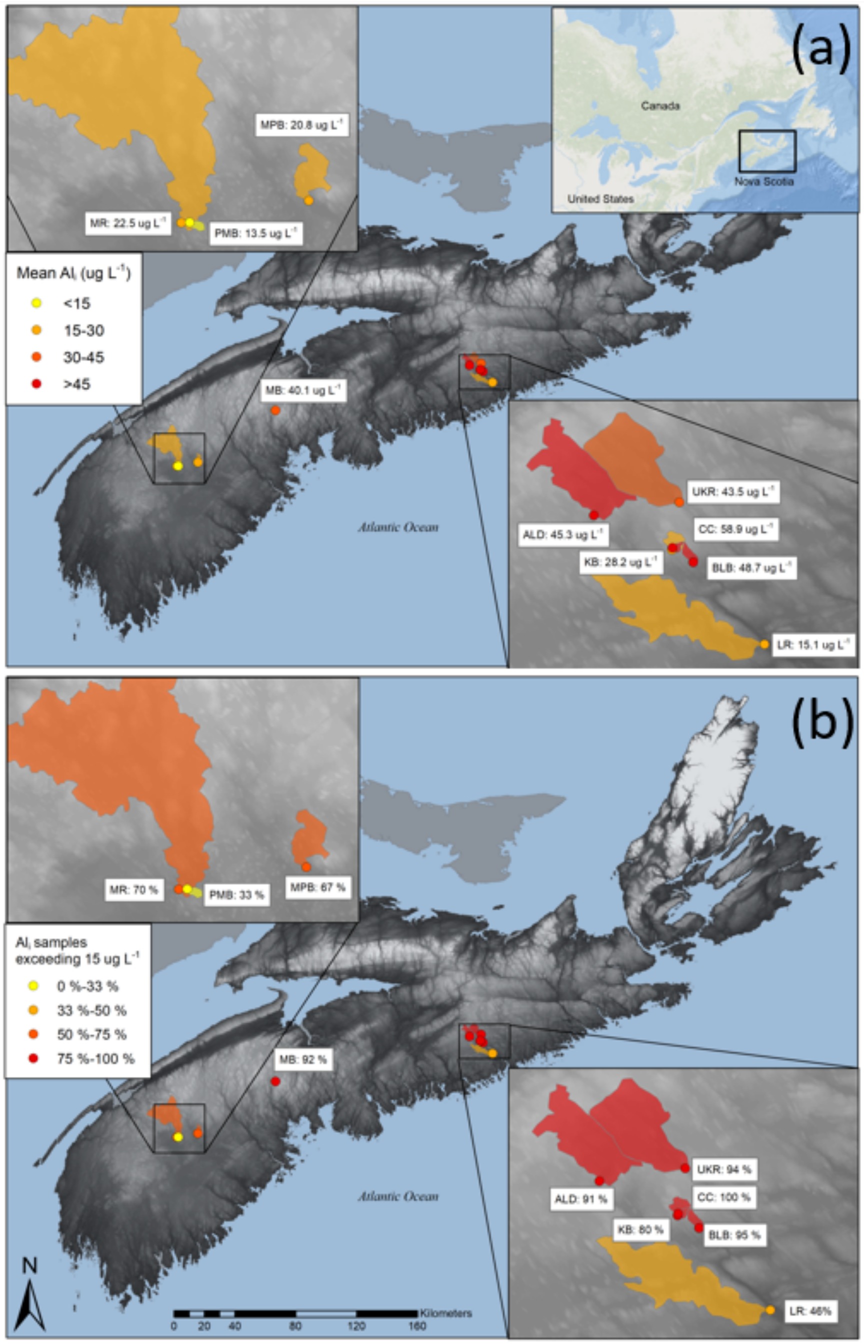

Figure 1. Study site locations showing (a) mean Al_i concentrations and (b) proportion of samples when Al_i concentrations exceeded the 15 µg L^{-1} toxic threshold between spring 2015 and fall 2018. Shaded region corresponds to the catchments of monitoring sites. For additional site details, refer to Table 1.

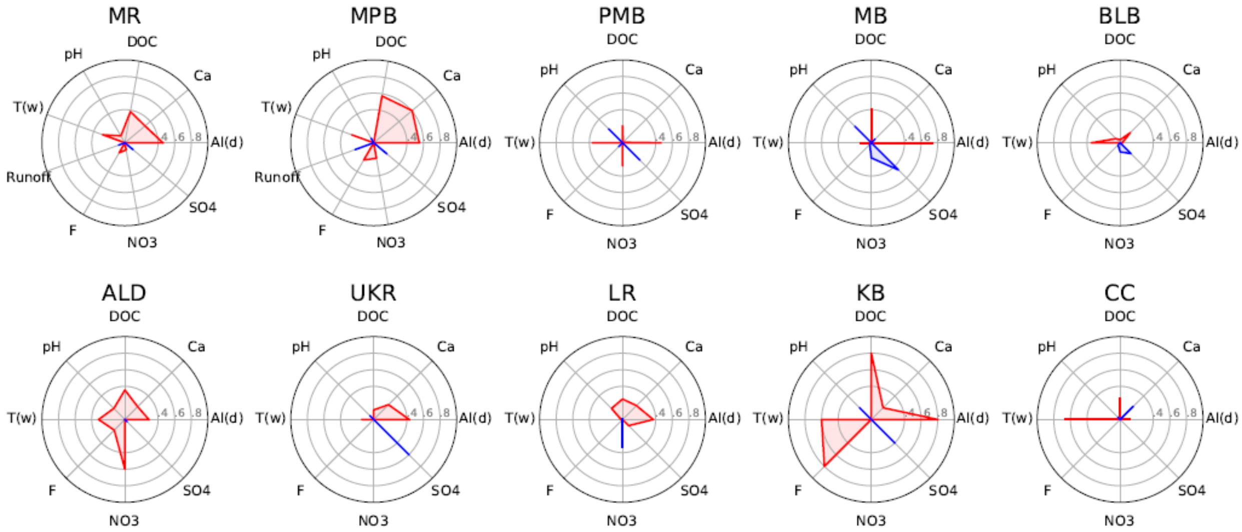

Figure 2. Correlation among water chemistry parameters and Al_i concentration, where red polygons and lines indicate a positive correlation with Al_i, and blue polygons and lines indicate a negative correlation with Al_i. One Al_i outlier removed for MR (value: 2 µg L^{-1}, date: 30 April 2015). Correlation data are listed in Table A5.

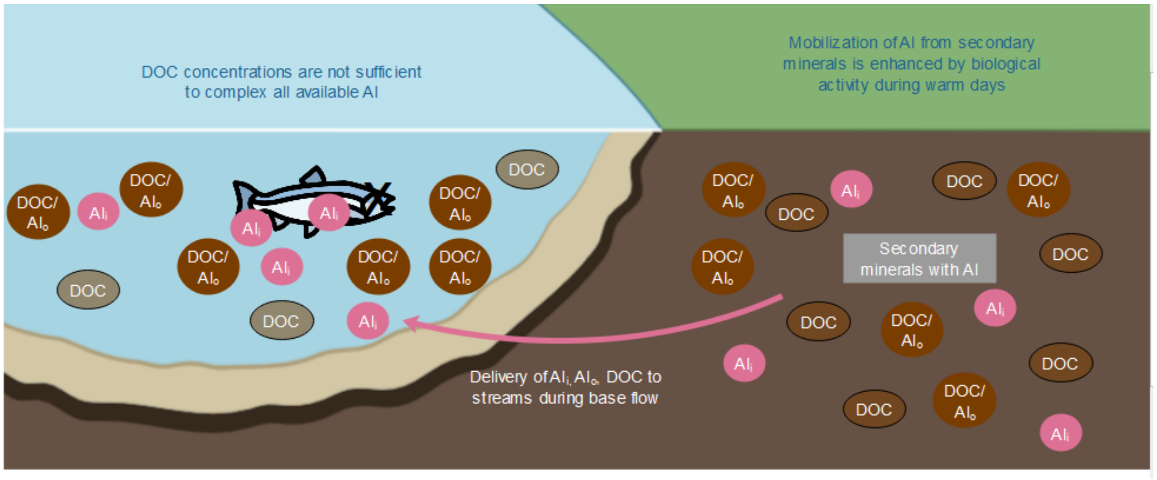

Figure 3. Conceptual model of new mechanism that can produce high concentrations of Al_i in freshwaters. Warm days increase biological activity that helps to mobilize Al from secondary minerals and enhances production of DOC which in turn reduces pH and reduces Al saturation in soil solution by forming Al-organic complexes, thus maintaining Al concentration gradient away from secondary minerals. In rivers, the amount of DOC is insufficient to protect the fish from the amount of Al_i mobilized in soils.

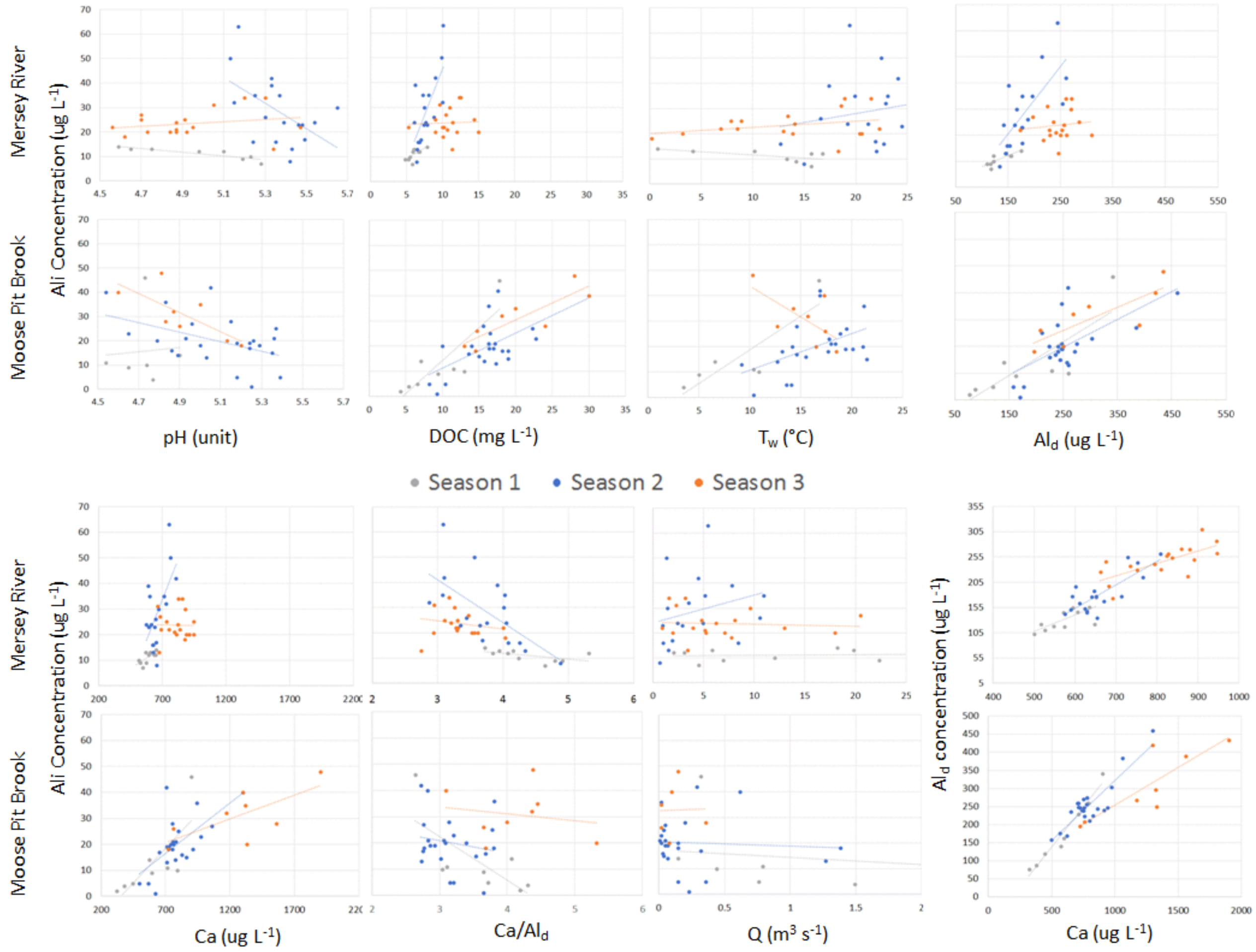

Figure 4. Scatterplot relationships among water chemistry parameters for seasons 1, 2, and 3 at MR and MPB. R^2 values are listed in Table A7. One runoff outlier removed for MR (value: 17.294 m3 s^{-1}, date: 22 April 2015). One runoff outlier removed for MPB (value: 34.994 m3 s^{-1}, date: 22 April 2015).