

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

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5 Shannon M. Sterling¹, Sarah MacLeod², Lobke Rotteveel¹, Kristin Hart¹, Thomas A. Clair¹,
6 Edmund A. Halfyard³, Nicole L. O'Brien⁴

7
8 ¹ Sterling Hydrology Research Group, Department of Earth and Environmental Sciences, Dalhousie
9 University, Halifax, Nova Scotia, Canada

10 ² Coastal Action, Lunenburg, Nova Scotia, Canada

11 ³ Nova Scotia Salmon Association, Chester, Nova Scotia, Canada

12 ⁴ Department of Earth and Environmental Sciences, Dalhousie University, Halifax, Nova Scotia,
13 Canada

14
15 *Correspondence to:* Shannon Sterling (shannon.sterling@dal.ca)

16 **Abstract.** Acid deposition released large amounts of aluminum into streams and lakes during the last
17 century in Northern Europe and Eastern North America. Elevated aluminum concentrations caused
18 major environmental concern due to its toxicity to terrestrial and aquatic organisms, and led to the
19 extirpation of wild Atlantic salmon populations. Air pollution reduction legislation that began in the
20 1990s in North America and Europe successfully reduced acid deposition, and the aluminum problem
21 was widely considered solved. However, accumulating evidence indicates that freshwaters still show
22 delays in recovery from acidification, with poorly understood implications for aluminum
23 concentrations. Here, we investigate spatial and temporal patterns of labile cationic forms of aluminium
24 (Al_i) from 2015-2018 in ten catchments in Nova Scotia, Canada – one of the regions hardest hit by acid
25 deposition, yet where aluminum was not considered a problem due to high concentrations of dissolved
26 organic carbon (DOC) making aluminum less labile to aquatic life. We find widespread and frequent
27 occurrences of Al_i concentrations that exceed toxic thresholds in all sampled rivers despite high DOC
28 concentrations. Generalized linear mixed model results reveal that DOC, instead of being inversely
29 related to Al_i , is the strongest predictor (positive) of Al_i concentrations, suggesting that the recruitment
30 properties of DOC in soils outweigh its protective properties in streams. Lastly, we find that, contrary
31 to the common conceptualization that high Al_i levels are associated with storm flow, high Al_i
32 concentrations are found during base flow. Our results demonstrate that elevated Al_i concentrations in
33 Nova Scotia pose a threat to aquatic organisms, such as the biologically, economically, and culturally
34 significant Atlantic salmon (*Salmo salar*).

35 1 Introduction

36 Increased rates of acid deposition, predominantly deriving from upwind fossil fuel burning,
37 resulted in the acidification of soils, rivers, and lakes during the last century (e.g., Kerekes et al., 1986),
38 depleting base cations and increasing toxic aluminum concentrations in soils and drainage waters.
39 Increased aluminum concentrations caused the extirpation of native Atlantic salmon (*Salmo salar*)
40 populations in many rivers (Rosseland et al., 1990), for example in Scandinavia (Henriksen et al., 1984,
41 Hesthagen and Hansen, 1991), the eastern USA (Monette and McCormick, 2008, Parrish et al., 1998),
42 and Nova Scotia, Canada (Watt, 1987). The acidification problem was widely considered solved
43 following reductions in anthropogenic sulfur emissions in North America and Europe since the 1990s.
44 Many rivers showed steady improvements in annual average stream chemistry (Evans et al., 2001,
45 Monteith et al., 2014, Skjelkvåle et al., 2005, Stoddard et al., 1999, Warby et al., 2005), including
46 reduced concentrations of aluminum (Al) in the USA (Baldigo and Lawrence, 2000, Buchanan et al.,
47 2017, Burns et al., 2006) and Europe (Beneš et al., 2017, Davies et al., 2005, Monteith et al., 2014).
48 However, recent evidence highlights delayed recovery from acidification in other regions (Houle et al.,
49 2006, Warby et al., 2009, Watmough et al., 2016), including Nova Scotia (Clair et al., 2011) raising
50 questions about the possibility of elevated aluminum concentrations in freshwaters.

51 Al in freshwaters can exist as inorganic monomers, inorganic polymers, amorphous and
52 microcrystalline inorganic forms, and as fast reactive or unreactive organic forms (Chew et al., 1988,
53 Driscoll et al., 1980, LaZerte, 1984). While a variety of Al species in circumneutral waters are toxic to
54 fish (Gensemer and Playle, 1999), including precipitated forms (Gensemer et al., 2018), the cationic
55 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
56 to salmonids. Al species bind to the negatively charged fish gills causing morbidity and mortality

57 through suffocation (Exley et al., 1991), reducing nutrient intake at gill sites, and altering blood plasma
58 levels (Nilsen et al., 2010). The effects of sub-lethal exposure to freshwater Al elicits osmoregulatory
59 impairment (Monette and McCormick, 2008, Regish et al., 2018) which reduces survival in the
60 hypertonic marine environment (McCormick et al., 2009, Staurnes et al., 1996). Elevated
61 concentrations of Al_i are also toxic to other freshwater and terrestrial organisms (Boudot et al., 1994,
62 Wauer and Teien, 2010), such as frogs and aquatic birds (Lacoul et al., 2011).

63 Al speciation varies with pH (Helliweli et al., 1983, Lydersen, 1990), where positive Al species
64 dominate over neutral and negative species below pH 6.3 at 2 °C and below pH 5.7 at 25 °C (Lydersen,
65 1990), with the most toxic Al species, $Al(OH)_2^{+1}$ (Helliweli et al., 1983) dominating Al speciation
66 between pH 5.0–6.0 at 25 °C, and 5.5–6.5 at 2 °C (Lydersen, 1990). Thus, the toxicity of Al increases
67 with increased pH up to approximately 6.0 at 25 °C, or 6.5 at 5 °C, when aqueous aluminum precipitates,
68 forming gibbsite (Lydersen, 1990, Schofield and Trojnar, 1980), where colder waters will have a higher
69 proportion of toxic species at higher pH values than warmer waters (Driscoll and Schecher, 1990).

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

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

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

89 The general consensus in the literature is that elevated Al_i concentrations occur during episodic
90 storm events, due to three possible mechanisms: 1) dilution of base cations during storm events, where
91 flow paths move through shallower, more organic-rich soil layers, 2) added anions in snowmelt or
92 rainfall (e.g., Cl⁻, SO₄²⁻, F⁻) providing mobile anions that increase Al_i export to streams, and 3) low pH
93 associated with storm events, re-dissolving Al accumulated in the soil (Hooper and Shoemaker, 1985)
94 and/or from the streambed (Norton et al., 1987). For example, from 1983 to 1984, Al concentrations
95 for the River Severn in Wales increased ten-fold during the stormflow peak compared to the baseflow
96 (Neal et al., 1986). The general consensus in the literature is also that Al_i is seasonally elevated during
97 spring snowmelt and autumn rainfall events, and seasonally depressed during summer months due to
98 higher levels of DOC, such as in Quebec (Campbell et al., 1992), Russia (Rodushkin et al., 1995), and
99 along the Czech-German border (Kopacek et al., 2000, Kopáček et al., 2006). Timing of the Al_i peaks
100 is important. If peak Al_i concentrations coincide with vulnerable life stages of Atlantic salmon, such as
101 during the spring when salmon transition from parr to smolt (i.e. smoltification) in preparation for life
102 in the ocean (Kroglund et al., 2007, Monette and McCormick, 2008, Nilsen et al., 2013) or during the

103 emergence of salmon fry from eggs (e.g., Farmer, 2000), then the potential for large biological impacts
104 from elevated Al_i is particularly high.

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

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

126 sufficient to protect life from Al_i , and to identify the hydrologic conditions associated with elevated Al_i
127 concentrations.

128 2 Materials and methods

129 2.1 Study area

130 We surveyed Al_i concentrations at ten study catchments in NS_A , ranging from headwater to
131 higher-order systems: Mersey River (MR), Moose Pit Brook (MPB), Pine Marten Brook (PMB), Maria
132 Brook (MB), Brandon Lake Brook (BLB), above the West River lime doser (ALD), Upper Killag River
133 (UKR), Little River (LR), Keef Brook (KB), and Colwell Creek (CC) (Table 1, Fig. 1). Our study
134 catchments are predominantly forested with a mix of coniferous and deciduous species, and drain slow-
135 weathering, base-cation poor bedrock, producing soils with low ANC (Langan and Wilson, 1992,
136 Tipping, 1989). The catchments also have relatively high DOC concentrations (Ginn et al., 2007)
137 associated with the abundant wetlands in the region (Clair et al., 2008, Gorham et al., 1986, Kerekes et
138 al., 1986).

139 2.2 Data collection and analysis

140 We measured Al_i concentrations at three of the ten catchments from April 2015 to September
141 2017 (MR, MPB, PMB), on a weekly to monthly frequency during the snow-free season (approximately
142 April to November, Table A2). In 2016-2018, seven sites were added and sampled every two weeks to
143 monthly during the snow-free season.

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

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

$$148 \quad Al_i = Al_d - Al_o \quad (1)$$

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

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

166 Stream chemistry samples (50 ml) were collected using sterilized polyethylene syringes into
167 sterilized polyethylene bottles. Samples for sulfate (SO_4^{2-}) analysis were not filtered. Trace metal
168 samples were filtered (0.45 μm) and preserved with nitric acid (HNO_3). Samples for DOC analysis were

169 filtered (0.45 μm) and transported in amber glass bottles containing sulfuric acid preservative (H_2SO_4)
170 to prevent denaturation. All samples were cooled to 7 $^\circ\text{C}$ during transport to the laboratories. Samples
171 were delivered to the laboratories within 48 hours of collection, where they were further cooled to \leq
172 4 $^\circ\text{C}$ prior to analysis (Appendix D).

173 We examined correlations between Al_i and water chemistry parameters: Al_d , Ca, DOC, pH,
174 SO_4^{2-} , T_w , fluoride (F^-), nitrate (NO_3^-), and runoff (where data were available). Correlations were
175 analysed within and across sites. For the purposes of this study, we use the toxic threshold of Al_i at 15
176 $\mu\text{g L}^{-1}$, as the majority of our pH observations were greater than or equal to 5.0 (Table A2, Appendix
177 D3).

178 We developed a Generalized Linear Mixed Model (GLMM) to identify the main drivers of Al_i
179 concentration at the study sites. We tested Al_d , DOC, Ca, SO_4^{2-} , F^- , NO_3^- , season, and T_w as potential
180 drivers. The GLMM analysis was implemented with R version 3.6.2. (R Core Team, 2019) using the
181 lme4 package (Bates et al., 2015). Due to the nonnormality of the Al_i concentration data, the glmer()
182 function was employed for model fitting which uses the method of maximum likelihood for parameters
183 estimation through Laplace approximation (Raudenbush et al., 2000). The study sites in the analysis
184 were included as the random effect with fixed effects provided in Table A3; Al_d was not included in
185 the GLMM as it results in an over fit model (singularity). The Wald t Test Statistic and the Akaike
186 Information Criterion (AIC) were used as measures of goodness-of-fit (Akaike, 1974; Bolker et al.,
187 2019). Numerous iterations of fixed effects and interactions were considered in the GLMM
188 development (Table A3). Multiple fixed effects were initially considered; however, several of the
189 effects were not significant, although the overall model fit provides a low AIC. GLMMs were applied
190 to assess season drivers of Al_i concentrations; however, due to the limited amount of seasonal data

191 collected, an analysis of both the site and seasonal random effects could not be carried out due to model
192 singularities.

193 3 Results and discussion

194 3.1 Patterns of Al_i

195 Al_i concentrations exceed toxic levels (15 ug L^{-1}) at all sites during the study period (Table A2)
196 despite relatively high DOC concentrations (mean values ranging from 7.2 to 23.1 mg L^{-1} among the
197 catchments, Table 1). Mean Al_i concentrations across all sites range from 13–60 ug L^{-1} (Table 1), with
198 the highest mean concentrations also occurring in the eastern part of the study area (Fig. 1a), where one
199 site had 100% of samples in exceedance (Fig. 1b). Al_i concentrations exceed 100 ug L^{-1} (approximately
200 seven times the threshold) at three sites (Table A2). Our Al_i concentrations are consistent with the 6.9–
201 230 ug L^{-1} range of Al_i concentrations measured across NS_A by Dennis and Clair (2012) and are higher
202 than concentrations measured in Norway from 1987–2010 (5–30 ug L^{-1}) (Hesthagen et al., 2016).

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

212 The highest concentrations of Al_i ($> 100 \mu\text{g L}^{-1}$) occurred in early summer (late June or early
213 July in 2016-2018) when Al_d , Ca, and DOC concentrations had not yet reached their annual peak (Table
214 A2). The spring/summer extreme events occurred among the first exceptionally warm days ($> 21 \text{ }^\circ\text{C}$)
215 of the year, in dry conditions, and when the proportion of Al_o/Al_d was low (lowering to approximately
216 60-70% from higher levels of around 80-90%) (Figs. B2-B11). pH was not abnormally low during these
217 events (ranging from 4.8 to 6.13), Ca concentrations were low (less than or equal to $800 \mu\text{g L}^{-1}$) and
218 DOC concentrations ranged from 15–21 mg L^{-1} .

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

222 **3.2 Potential Al_i drivers**

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

231 Thus, the GLMM results show that DOC is positively correlated with Al_i in the study area, in
232 contrast to the standard conceptualization that DOC is inversely correlated with Al_i , suggesting that the

233 increased recruitment of Al in soils by DOC may outweigh DOC's protective effects in freshwater,
234 consistent with observations in other studies (e.g., Campbell et al., 1992, Kopáček et al., 2006).

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

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

247 We did not observe the negative association between pH and Al_i observed in previous studies
248 (Campbell et al., 1992, Kopáček et al., 2006) - pH is negatively correlated with Al_i in four out of ten
249 sites, but none of these relationships are statistically significant (Fig. 2, Table A5). The lack of
250 significant correlation may be due in part to other mechanisms that may cloud the strength of the inverse
251 relationship between pH and Al, such as increased DOC solubility at higher pH, leading to increased
252 Al solubility in soils (Lydersen, 1990), pH buffering by Al in the lower pH range (Tomlinson, 1990),
253 and by the limited pH range in the data set. We did observe a statistically significant positive
254 relationship between pH and Al_i/Al_d (Table A4); thus, it seems that pH may play a more important role
255 in determining the proportion of different Al species rather than the absolute value of Al_i present in

256 stream waters in chronically acidified conditions such as those found Nova Scotia. F^- has also been
257 found to be a complexing agent that affects the speciation of Al at low pH levels and relatively high
258 concentrations of F^- ($>1 \text{ mg L}^{-1}$) (Berger et al., 2015). The concentrations of F^- at the study sites are
259 mostly below this threshold (mean across all sites = 0.045 mg L^{-1}); however, there is still a significant
260 positive effect of F^- on Al_i concentrations across at two sites (KB, MPB) (Fig. 2, Table A5). NO_3^- and
261 SO_4^{2-} are also potential complexing ligands of Al; however, we did not observe any correlation between
262 Al_i and either of these parameters, except for a significant negative correlation between SO_4^{2-} and Al_i
263 at MB.

264 **3.3 Possible seasonal groupings of Al_i in NS_A**

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

273 Season 1 (approximately April/May) is coincident with snow-melt runoff and is characterized
274 by relatively low concentrations of Al_i ($2\text{-}46 \text{ ug L}^{-1}$), low pH (4.5-5.3), and lower concentrations of
275 most constituents, including DOC, and cold temperatures ($< 4 \text{ }^\circ\text{C}$). During this season, Al_i is strongly
276 coupled with pH, DOC, Al_d and Ca in MR, but less so in MPB. A possible explanation is that season 1
277 is dominated by snowmelt hydrology in which cation exchange between soil and discharge occurs less

278 efficiently, which has been attributed to ice and frozen soil potentially limiting water contact time with
279 soil (Christophersen et al., 1990). It is important to note that we did not likely capture the first flush
280 effect of increased Al_i as has been noted in other studies (e.g., Hendershot et al., 1996). The onset of
281 season 2 (approximately late June) is characterized by increasing Al_i concentrations, temperature, and
282 DOC. Al_i and pH values are higher in this season and Al_i becomes strongly negatively correlated with
283 pH as pH increases to the lower threshold for gibbsite. In MR in season 2 Al_i has a strong positive
284 relationship with DOC. The highest observed Al_i concentrations of the year occur in season 2 (Fig. 3).
285 Al_i relations are weak in MR in season 3 (approximately September through March), likely due to the
286 lower frequency of measurements during the winter. Season 3 in MR has the highest concentrations of
287 dissolved constituents (Al_d , Ca, and DOC), whereas in MPB only Ca has the highest concentrations.

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

294 In contrast with the conceptualization that peak Al_i concentrations occur during storm flow (e.g.,
295 Campbell et al., 1992, Kopacek et al., 2000, Neal et al., 1986, Rodushkin et al., 1995), our data show
296 elevated Al_i concentrations during base flow conditions. These results suggest a new pathway for
297 generation of elevated Al_i concentrations that is associated with base flow, warmer summer
298 temperatures, and high DOC concentrations, and thus likely more chronic in nature. Nilsson (1985) had
299 suggested that this flowpath has important consequences for Al concentrations in Swedish catchments.
300 We hypothesize that this pathway is caused by increased temperatures causing higher levels of

301 biological activity that mobilize Al in soils (Figure 3) (following Nilsson and Bergkvist, 1983).
302 Biological activity further generates DOC which mobilizes Al to drainage waters during summer base
303 flow (Figure 4). Other cases of increased Al_i concentrations occurring during low flow and warming
304 temperatures can be found in the literature in locations such as Ontario and Quebec (Hendershot et al.,
305 1985, Hendershot et al., 1996) and in Virginia, USA (Cozzarelli et al., 1987).

306

307 **3.4 Ecological implications**

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

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

320 4 Conclusions

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

341 management practices to avoid base cation removal and depletion. Addition of base cations through
342 liming and enhanced weathering of soils and freshwaters may accelerate recovery from acidification.

343 Data availability

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

346 Author contributions

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

354 Competing interests

355 The authors declare that they have no conflict of interest.

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658 **Tables**

659 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

660 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.

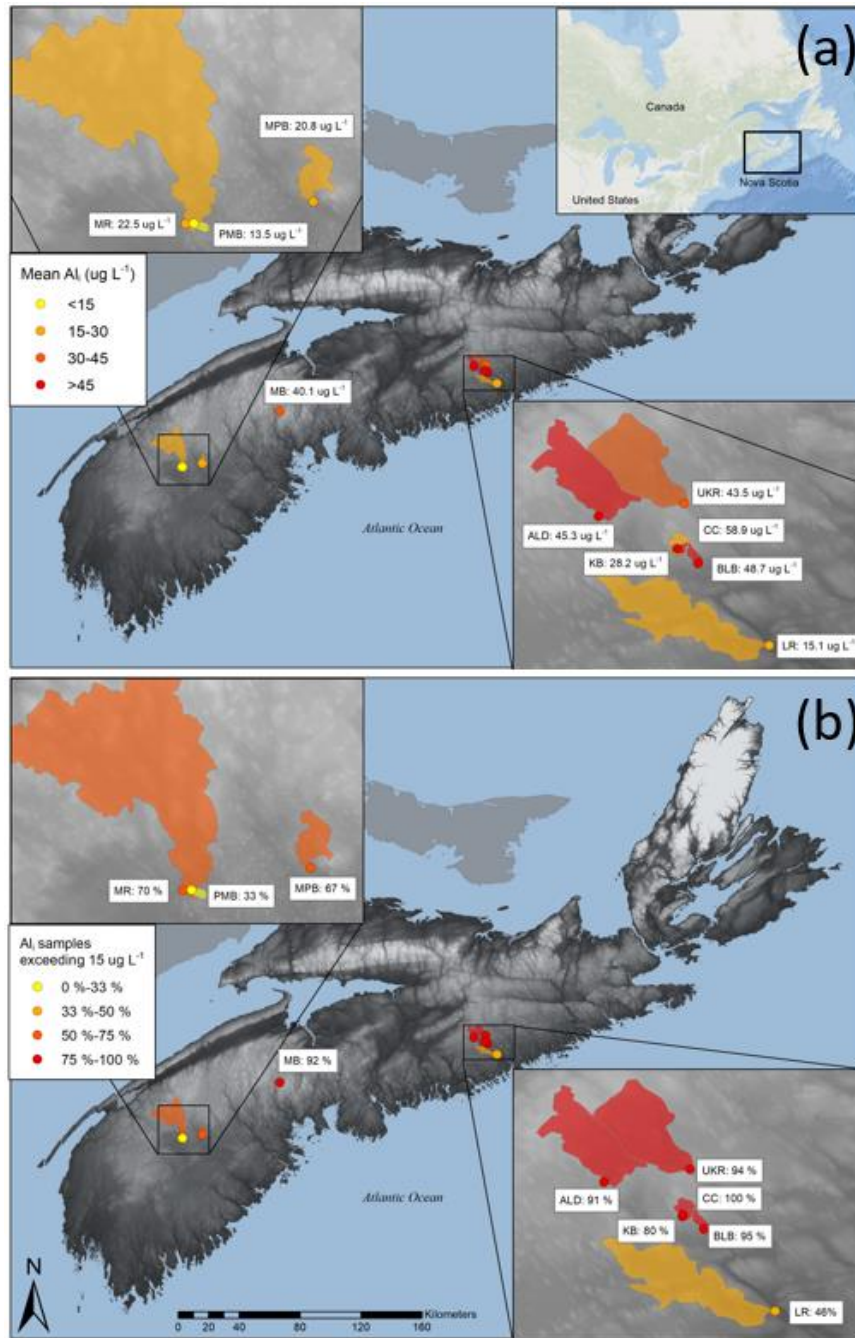
Site	Lat	Long	Area (km ²)	n	Land use	Dominant Bedrock Type	Mean Al _i (ug L ⁻¹)	Mean DOC (mg L ⁻¹)	Mean Al _d (ug L ⁻¹)	Mean Ca (ug L ⁻¹)	Mean pH
Mersey River (MR)	44.437	-65.223	292.8	47	Natural forest	Granite	22.5 (11.7)	8.6 (2.7)	195 (54.9)	699 (120)	5.1
Moose Pit Brook (MPB)	44.462	-65.048	15.8	39	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

662 Table 2. Al_i relations with other stream chemistry parameters separated by possible seasons. Dark shading
 663 represents r² > 0.6. Medium shading represents r² 0.2-0.6. Light shading represents r² 0.0-0.2. Green
 664 indicates negative relation. Orange indicates positive relation.
 665

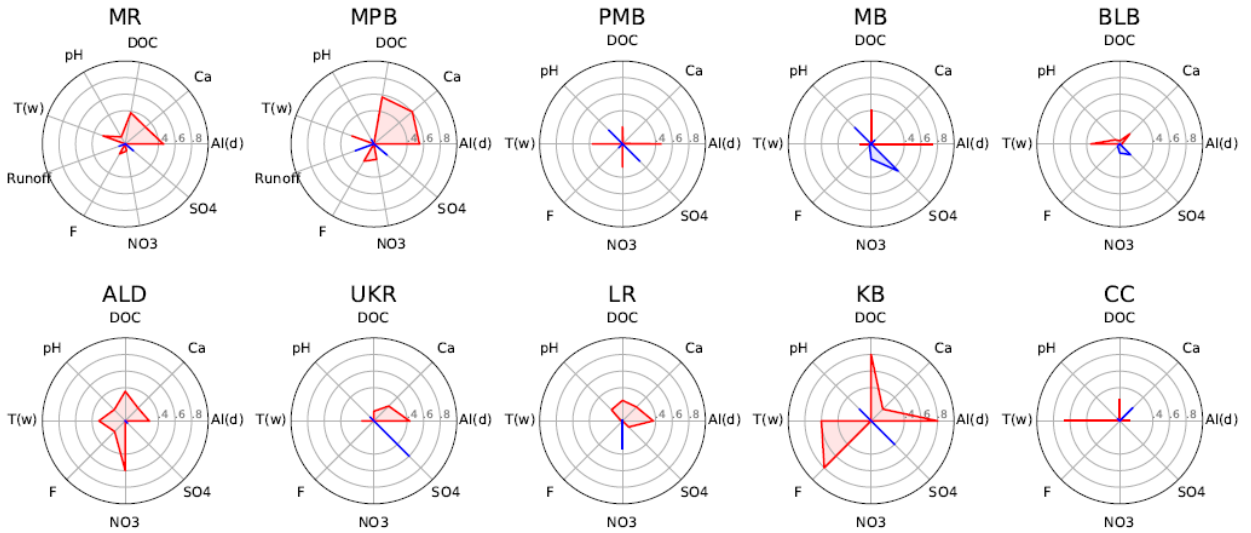
	pH		DOC		Tw		Al _d		Ca	
	slope	r ²	slope	r ²	slope	r ²	slope	r ²	slope	r ²
Season 1										
MR	-7.67	0.78	1.78	0.49	-0.26	0.42	0.084	0.67	0.0329	0.50
MPB	8.44	0.0045	2.62	0.71	2.66	0.72	0.13	0.68	0.053	0.59
Season 2										
MR	-53.2	0.27	7.5	0.51	0.72	0.034	0.23	0.52	0.13	0.37
MPB	-19.6	0.22	1.4	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

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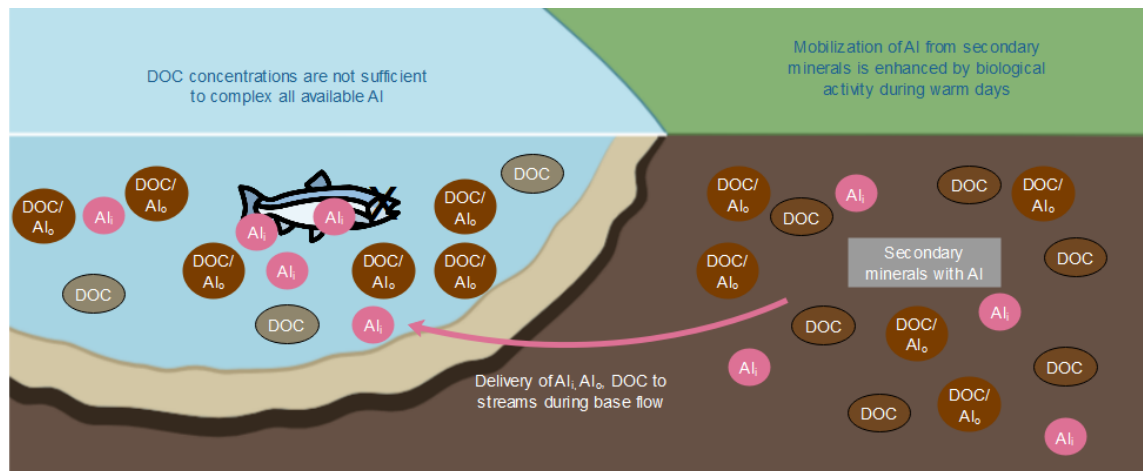
667 Figures



668
 669 Figure 1. Study site locations showing (a) mean Al_i concentrations and (b) proportion of samples when Al_i
 670 concentrations exceeded the $15 \mu g L^{-1}$ toxic threshold between spring 2015 and fall 2018. Shaded region
 671 corresponds to the catchments of monitoring sites. For additional site details, refer to Table 1.



672
 673 Figure 2. Correlation among water chemistry parameters and Al_i concentration, where red polygons and
 674 lines indicate a positive correlation with Al_i , and blue polygons and lines indicate a negative correlation
 675 with Al_i . One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015). Correlation data are listed
 676 in Table A5.



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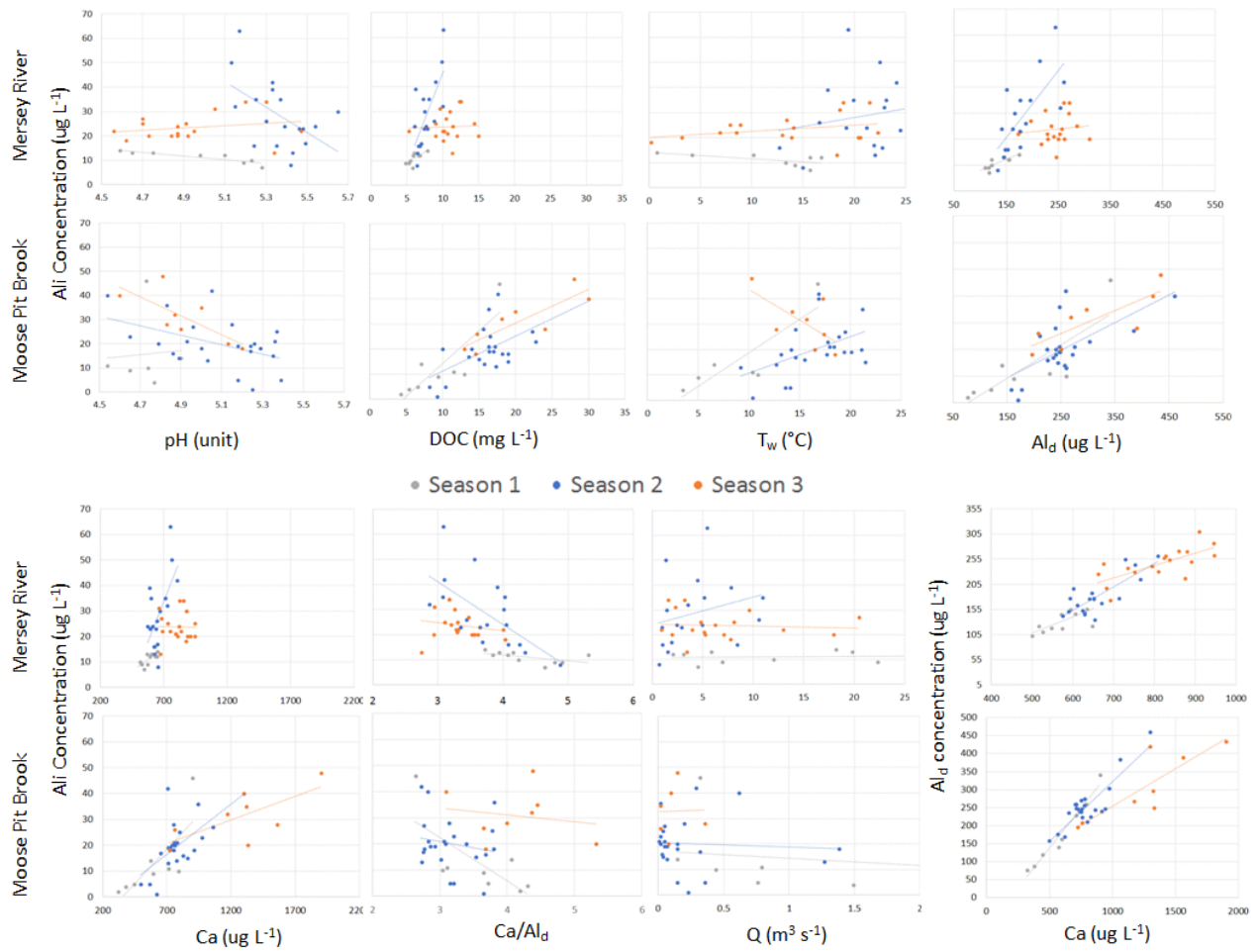
678 Figure 3. Conceptual model of new mechanism that can produce high concentrations of Al_i in freshwaters.

679 Warm days increase biological activity that helps to mobilize Al from secondary minerals and enhances

680 production of DOC which in turn reduces pH and reduces Al saturation in soil solution by forming Al-

681 organic complexes, thus maintaining Al concentration gradient away from secondary minerals. In rivers,

682 the amount of DOC is insufficient to protect the fish from the amount of Al_i mobilized in soils.



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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: $17.294 \text{ m}^3 \text{ s}^{-1}$, date: 22 April 2015). One runoff outlier removed for MPB (value: $34.994 \text{ m}^3 \text{ s}^{-1}$, date: 22 April 2015).