

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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Abstract. ~~Cationic aluminium species are toxic~~ 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 life. ~~Despite decades of~~ 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 ~~emission reductions~~ deposition, and the aluminum problem was widely considered solved. However, accumulating evidence ~~shows that freshwater~~ indicates that freshwaters still show delays in recovery from acidification ~~recovery is delayed in locations such as Nova Scotia, Canada. Further,~~ with poorly understood implications for aluminum concentrations. Here, we investigate spatial and temporal patterns of labile cationic forms of aluminium (Al_i) ~~remain poorly understood. Here we increase our understanding of Al_i spatial and temporal patterns by measuring Al_i concentrations from 2015-2018 in ten streams in acid-sensitive areas of~~ catchments in Nova Scotia ~~over a four-year time period.~~ Canada – one of the regions hardest hit by acid deposition, yet where aluminum was not considered a problem due to high concentrations of dissolved organic carbon (DOC)

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39 making aluminum less labile to aquatic life. We ~~observe~~find widespread and frequent occurrences of
40 Al_i concentrations that exceed toxic thresholds (~~$>15 \mu\text{g L}^{-1}$~~)in all sampled rivers despite high DOC
41 concentrations. Generalized linear mixed model results reveal that DOC, instead of being inversely
42 related to Al_i , is the strongest predictor (positive) of Al_i concentrations, suggesting that the recruitment
43 properties of DOC in soils outweigh its protective properties in streams. Lastly, we find that, contrary
44 to the common conceptualization that high Al_i ~~patterns appear to be driven by known Al_i drivers—pH,~~
45 ~~dissolved organic carbon, dissolved aluminium, and calcium—but the dominant driver and temporal~~
46 ~~patterns vary by catchment,~~levels are associated with storm flow, high Al_i concentrations are found
47 during base flow. Our results demonstrate that elevated Al_i ~~remains~~concentrations in Nova Scotia pose
48 a threat to aquatic ~~ecosystems. For example, our observed Al_i concentrations are potentially harmful~~
49 ~~to~~organisms, such as the biologically, economically, and culturally significant Atlantic salmon (*Salmo*
50 *salar*).

51

52 1 Introduction

53 ~~Freshwater acidification caused elevated concentrations of cationic aluminium (Al_i) at the end~~
54 ~~of the last century that led to increased freshwater and marine mortality and, ultimately,~~Increased rates
55 of acid deposition, predominantly deriving from upwind fossil fuel burning, resulted in the acidification
56 of soils, rivers, and lakes during the last century (e.g., Kerekes et al., 1986), depleting base cations and
57 increasing toxic aluminum concentrations in soils and drainage waters. Increased aluminum
58 concentrations caused the extirpation of native Atlantic salmon (*Salmo salar*) populations in many
59 rivers (Rosseland et al., 1990), for example in Scandinavia (Henriksen et al., 1984, Hesthagen and

60 Hansen, 1991), the eastern USA (Monette and McCormick, 2008, Parrish et al., 1998), and Nova Scotia,
61 Canada (Watt, 1987). ~~Following~~The acidification problem was widely considered solved following
62 reductions in anthropogenic sulfur emissions in North America and Europe since the 1990s, ~~many~~,
63 Many rivers showed steady improvements in annual average stream chemistry (Evans et al., 2001,
64 Monteith et al., 2014, Skjelkvåle et al., 2005, Stoddard et al., 1999, Warby et al., 2005), including
65 reduced concentrations of ~~Al~~aluminum (Al) in the USA (Baldigo and Lawrence, 2000, Buchanan et
66 al., 2017, Burns et al., 2006) and Europe (Beneš et al., 2017, Davies et al., 2005, Monteith et al., 2014).
67 However, recent evidence highlights delayed recovery from acidification in ~~some areas~~other regions
68 (Houle et al., 2006, Warby et al., 2009, Watmough et al., 2016), including ~~SWNS~~Nova Scotia (Clair et
69 al., 2011), ~~raising concerns~~questions about the possibility of elevated ~~Al~~aluminum concentrations in
70 freshwaters.
71 ~~Aluminium (Al) toxicity in freshwaters can be caused by both precipitated~~exist as inorganic
72 monomers, inorganic polymers, amorphous and dissolvedmicrocrystalline inorganic forms-in, and as
73 fast reactive or unreactive organic forms (Chew et al., 1988, Driscoll et al., 1980, LaZerte, 1984). While
74 a variety of Al species in circumneutral waters are toxic to fish (Gensemer and Playle, 1999), including
75 precipitated forms (Gensemer et al., 2018), ~~however~~, the cationic species of ~~Al~~(Al_i), such as Al³⁺,
76 Al(OH)₂¹⁺, and Al(OH)₂²⁺ are considered to be the most labile and toxic to salmonids ~~as they~~. Al species
77 bind to the negatively charged fish gills causing morbidity and mortality through suffocation (Exley et
78 al., 1991), reducing nutrient intake at gill sites, and altering blood plasma levels (Nilsen et al., 2010).
79 ~~Further, the~~The effects of sub-lethal exposure to freshwater Al elicits osmoregulatory impairment
80 (Monette and McCormick, 2008, Regish et al., 2018) which reduces survival in the hypertonic marine
81 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 °C and below pH 5.7 at 25 °C (Lydersen, 1990), with the most toxic Al species, $\text{Al}(\text{OH})_2^{+1}$ (Helliweli et al., 1983) dominating Al speciation 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 with increased pH up to ~~the formation of~~ approximately 6.0 at 25 °C, or 6.5 at 5 °C, when aqueous aluminum precipitates, forming gibbsite (Lydersen, 1990, Schofield and Trojnar, 1980). ~~Additionally,~~ 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, ~~and dissolved~~. Dissolved organic carbon (DOC), ~~which occludes Al, through~~ also reduces bioavailability of aluminum via the formation of organo-Al complexes (Al_o) ~~that are nontoxic to fish~~ (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 ~~Al solubility and observations confirm that~~ of secondary minerals containing Al; Al_i concentrations ~~are~~ 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 ~~from clay particles,~~ and later into drainage waters

105 (Fernandez et al., 2003) ~~and~~; chronic acidification thus shifts available exchangeable cations in the soil
106 water from Ca and magnesium (Mg) towards Al (Schlesinger and Bernhardt, 2013, Walker et al., 1990).
107 Higher concentrations of DOC in soil water increase the release of Al through two mechanisms: 1) as
108 an organic acid, DOC decreases soil pH, thus increasing Al release (Lawrence et al., 2013), and 2) by
109 forming organic complexes with Al; it maintains a negative Al concentration gradient from the cation
110 exchange sites to the soil water, increasing rates of Al release (Edzwald and Van Benschoten, 1990,
111 Jansen et al., 2003). Field studies confirm Al concentrations to be positively correlated with DOC
112 (Campbell et al., 1992, Kopáček et al., 2006) ~~although at higher concentrations of DOC, Al may be~~
113 ~~organic complexed and less toxic to aquatic organisms (Witters et al., 1990).~~
114 ~~Once mobilized in soil waters, export of Al_i to drainage waters requires anions to maintain~~
115 ~~charge balance. Storm events have been shown to increase Al_i export due to added anions (e.g., Cl⁻,~~
116 ~~SO₄²⁻, F⁻), and from the movement of flow paths to shallower soil horizons where more Al may be~~
117 ~~available for transport.~~ The general consensus in the literature is that elevated Al_i concentrations occur
118 during episodic storm events, due to three possible mechanisms: 1) dilution of base cations during storm
119 events, where flow paths move through shallower, more organic-rich soil layers, 2) added anions in
120 snowmelt or rainfall (e.g., Cl⁻, SO₄²⁻, F⁻) providing mobile anions that increase Al_i export to streams,
121 and 3) low pH associated with storm events, re-dissolving Al accumulated in the soil (Hooper and
122 Shoemaker, 1985) and/or from the streambed (Norton et al., 1987). For example, from 1983 to 1984,
123 Al concentrations for the River Severn in Wales increased ten-fold during the stormflow peak compared
124 to the baseflow (Neal et al., 1986). ~~However, the association of increased Al_i concentrations with storm~~
125 ~~flow is not consistent.~~ The general consensus in the literature ~~(DeWalle et al., 1995, McKnight and~~
126 ~~Bencala, 1988).~~

Annual patterns of Al_i typically show a peak, but the timing of the peak varies. In some areas, Al_i concentrations peak in the is also that Al_i is seasonally elevated during spring snowmelt and autumn rainfall events, and winter, correlated with flow peaks 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). In other areas, Al_i concentrations were found to be higher in Timing of the summer such as in Virginia, USA (Cozzarelli et al., 1987). Al_i peaks is important. If the timing of peak Al_i concentrations coincide with sensitive 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 aquatic organisms) or during the emergence of salmon fry from eggs (e.g., Farmer, 2000), then the potential for large biological impacts is 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 spatial and temporal trends 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). Definitions for both inorganic monomeric Al and cationic Al include all positively charged species of Al.

Acid-sensitive areas of NS Nova Scotia, Canada, here abbreviated as NS_A (see Clair et al., 2007), with once-famous wild Atlantic salmon populations, were heavily impacted by acid 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

150 sensitive to acid deposition due to base cation-poor and slowly weathering bedrock that generates thin
151 soils with low acid neutralizing capacity (ANC), extensive wetlands, and episodic sea salt inputs (Clair
152 et al., 2011, Freedman and Clair, 1987, Watt et al., 2000, Whitfield et al., 2006). Al was not considered
153 to be a threat to Atlantic salmon in Nova Scotia because of the high natural levels of DOC in NS_A rivers
154 following preliminary research by (Lacroix and Townsend, 1997, Lacroix, 1989). A 2006 fall survey,
155 however, (Dennis and Clair, 2012) found that in seven of 42 rivers surveyed Al_i concentrations in NS
156 exceeded the 15 µg L⁻¹ toxic threshold suggested for aquatic health, as determined from an extensive
157 review of toxicological and geochemical literature by the European Inland Fisheries Advisory Council
158 (EIFAC) for aquatic health in seven of 42 rivers surveyed (Dennis and Clair, 2012). However, apart
159 from this study, (Howells et al., 1990). No assessment of Al_i has been done in NS_A since that time, and
160 little is known about the regional current extent and patterns of Al_i in the region. Here, we aim to
161 increase our understanding of current Al_i spatial and temporal patterns in relation to toxic thresholds,
162 and to identify potential drivers by conducting conduct a four-year survey of Al_i concentrations in ten
163 streams across acid sensitive areas of NS, Canada in NS_A, to test the hypothesis that elevated DOC
164 concentrations are sufficient to protect life from Al_i, and to identify the hydrologic conditions associated
165 with elevated Al_i concentrations.

166 2 Materials and methods

167 2.1 Study area

168 We surveyed Al_i concentrations at ten study catchments in NS_A, ranging from headwater to
169 higher-order systems: Mersey River (MR), Moose Pit Brook (MPB), Pine Marten Brook (PMB), Maria
170 Brook (MB), Brandon Lake Brook (BLB), above the West River lime doser (ALD), Upper Killag River

171 (UKR), Little River (LR), Keef Brook (KB), and Colwell Creek (CC) (Table 1, Fig. 1-and-2). Our study
172 catchments are predominantly forested, draining with a mix of coniferous and deciduous species, and
173 drain slow-weathering, base-cation poor bedrock, producing soils with low ANC (Langan and Wilson,
174 1992, Tipping, 1989). The catchments also have relatively high DOC concentrations (Ginn et al., 2007)
175 associated with the abundant wetlands in the region (Clair et al., 2008, Gorham et al., 1986, Kerekes et
176 al., 1986).

177 2.2 Data collection and analysis

178 We measured Al_i concentrations at three of the ten catchments from April 2015 to September
179 2017 (MR, MPB, PMB), on a weekly to monthly frequency during the snow-free season
180 (approximately April to November, Table A2). In 2016-2018, seven sites were added and sampled
181 every two weeks to monthly during the snow-free season.

182 Al_i sampling events comprise grab samples for lab analysis and in situ measurements of pH and
183 water temperature (T_w). We calculate Al_i as the difference between dissolved Al (Al_d) and Al_o following
184 Dennis and Clair (2012) and Poléo (1995) (Eq. 1), separating the species in the field to reduce errors
185 caused by Al species change due to changes in temperature and pH in transport from field to lab.

$$186 \quad Al_i = Al_d - Al_o \quad (1)$$

187 Al_d is measured as the Al concentration of a filtered (45 μm) sample and Al_o is measured as the
188 eluate from passing filtered water through a 3 cm negatively charged cation exchange column (Bond
189 Elut Jr. Strong Cation Exchange Column). Samples were passed through the cation exchange column
190 at a rate of approximately 30 to 60 drops per minute. From this method, Al_o is operationally defined as
191 the non-labile, organically-complexed metals and colloids, and Al_i is defined as the positive ionic
192 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 $\leq 4^\circ C$ 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 $\mu g L^{-1}$, as the majority of our pH observations were greater than or equal to 5.0 (Table A2, Appendix D3).

216 We developed a Generalized Linear Mixed Model (GLMM) to identify the main drivers of Al_i
217 concentration at the study sites. We tested Al_d , DOC, Ca, SO_4^{2-} , F⁻, NO_3^- , season, and T_w as potential
218 drivers. The GLMM analysis was implemented with R version 3.6.2. (R Core Team, 2019) using the
219 lme4 package (Bates et al., 2015). Due to the nonnormality of the Al_i concentration data, the `glmer()`
220 function was employed for model fitting which uses the method of maximum likelihood for parameters
221 estimation through Laplace approximation (Raudenbush et al., 2000). The study sites in the analysis
222 were included as the random effect with fixed effects provided in Table A3; Al_d was not included in
223 the GLMM as it results in an over fit model (singularity). The Wald t Test Statistic and the Akaike
224 Information Criterion (AIC) were used as measures of goodness-of-fit (Akaike, 1974; Bolker et al.,
225 2019). Numerous iterations of fixed effects and interactions were considered in the GLMM
226 development (Table A3). Multiple fixed effects were initially considered; however, several of the
227 effects were not significant, although the overall model fit provides a low AIC. GLMMs were applied
228 to assess season drivers of Al_i concentrations; however, due to the limited amount of seasonal data
229 collected, an analysis of both the site and seasonal random effects could not be carried out due to model
230 singularities.

231 3 Results and discussion

232 3.1 Patterns of Al_i

233 Al_i concentrations exceed toxic levels ($15 \mu g L^{-1}$) at all sites during the study period (Table A2).
234 ~~Sites in the eastern part of the study area have the highest proportion of samples exceeding threshold~~
235 ~~levels, including one site with 100% of samples in exceedance (Fig. 1).~~ despite relatively high DOC
236 concentrations (mean values ranging from 7.2 to 23.1 mg L^{-1} among the catchments, Table 1). Mean

237 Al_i concentrations across all sites range from 13–60 $\mu\text{g L}^{-1}$ (Table 1), with the highest mean
238 concentrations also occurring in the eastern part of the study area (Fig. 21a), where one site had 100%
239 of samples in exceedance (Fig. 1b). Al_i concentrations exceed 100 $\mu\text{g L}^{-1}$ (approximately seven times
240 the threshold) at three sites (Table A2). ~~In the sites with the longest and most frequent data collection~~
241 ~~(MR and MPB), Al_i concentrations exceed the toxic threshold in consecutive samples for months at a~~
242 ~~time, particularly in the late summer (Fig. B1).~~ Our Al_i concentrations are consistent with the 6.9–230
243 $\mu\text{g L}^{-1}$ range of Al_i concentrations measured across ~~NS_A~~ by Dennis and Clair (2012) and are higher
244 than concentrations measured in Norway from 1987–2010 (5–30 $\mu\text{g L}^{-1}$) (Hesthagen et al., 2016).

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

254 The highest concentrations of Al_i (> 100 $\mu\text{g L}^{-1}$) occurred in early summer (late June or early
255 July in 2016-2018) when Al_d , Ca, and DOC concentrations had not yet reached their annual peak (Table
256 A2). The spring/summer extreme events occurred among the first exceptionally warm days (> 21 °C)
257 of the year, in dry conditions, and when the proportion of Al_o/Al_d was low (lowering to approximately
258 60-70% from higher levels of around 80-90%) (Figs. ~~These findings are similar to those found NS by~~
259 ~~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 Laeoroix (1989) (over 90 % Al_i/Al_d). T_w and pH have a significant positive correlation with Al_i/Al_d (Table A3), consistent with an earlier observation that Al toxicity increases with pH (Schofield and Trojnar, 1980). However, even when the percentage of Al_i/Al_d is low, Al_i concentrations remain well above thresholds for toxicity (Fig. B4-B13). Previous studies show Al_i/Al_d is low during baseflow (Bailey et al., 1995; Murdoch and Stoddard, 1992; Schofield et al., 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 $800 \mu g L^{-1}$) 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). 1985), similar to our findings (Figs. B4-B13); more consistent year-round sampling is needed to obtain a better picture of seasonal patterns in Al speciation in NS_A.

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. 32, Table A4), despite the high concentrations of DOC. Al_i is also significantly and positively correlated with DOC in four sites (ALD, KB, MPB, MR) (Fig. 3, Table A4), consistent with other studies (A5). Campbell et al., 1992, Kopáček et al., 2006). The positive correlation between DOC and Al_i concentrations may suggest that the ability of DOC to mobilize Al_d in soils is stronger than its ability to occlude Al_i in streamwaters.

Ca is significantly and positively correlated with Al_i at two sites (MPB, MR) (Fig. 32, Table A4A5). 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. T_w is also significantly positively correlated with Al_i at two sites (MR, MPB) (Fig. 3, Table A4), likely reflective of the temperature-related drivers of Al concentration and speciation. Runoff

Discharge is significantly and negatively correlated with Al_i at one site MPB (Fig. 3, Table A4). 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) and so; more runoff data are needed to improve our understanding of the relation between runoff and Al_i in NS_A .

303 We did not observe the negative association between pH and Al_i observed in previous studies
304 (Campbell et al., 1992, Kopáček et al., 2006). pH is negatively correlated with Al_i in four out of ten
305 sites, but none of these relationships are statistically significant (Fig. 32, Table A4, A5). The lack of
306 significant correlation may be due in part to other mechanisms that may cloud the strength of the inverse
307 relationship between pH and Al_i , such as increased DOC solubility at higher pH, leading to increased
308 Al solubility in soils (Lydersen, 1990), pH buffering by Al in the lower pH range (Tomlinson, 1990),
309 and by the limited pH range in the data set. We did observe a statistically significant positive
310 relationship between pH and Al_i/Al_d (Table A4); thus, it seems that pH may play a more important role
311 in determining the proportion of different Al species rather than the absolute value of Al_i present in
312 streamwaters.

313 stream waters in chronically acidified conditions such as those found Nova Scotia. F^- has also
314 been found to be a complexing agent that affects the speciation of Al at low pH levels and relatively
315 high concentrations of F^- ($>1 \text{ mg L}^{-1}$) (Berger et al., 2015). The concentrations of F^- at the study sites
316 are mostly below this threshold (mean across all sites = 0.045 mg L^{-1}); however, there is still a
317 significant positive effect of F^- on Al_i concentrations across at two sites (KB, MPB) (Fig. 32, Table
318 A4, A5). NO_3^- and SO_4^{2-} are also potential complexing ligands of Al ; however, we did not observe any
319 correlation between Al_i and either of these parameters, except for a significant negative correlation
320 between SO_4^{2-} and Al_i at MB.

321 The highest concentrations of Al_i observed ($>100 \text{ ug L}^{-1}$) often occurred in early summer (late
322 June or early July in 2016–2018) when Al_d , Ca , and DOC concentrations had not yet reached their
323 annual peak (Table A2). The spring/summer extreme events occurred among the first exceptionally
324 warm days ($>21^\circ\text{C}$) of the year, in dry conditions, and when the proportion of Al_i/Al_d was low
325 (lowering to approximately 60–70% from higher levels of around 80–90%) (Figs. B4–B13). pH was not

326 abnormally low during these events (ranging from 4.8 to 6.13), Ca concentrations were low (less than
327 or equal to $800 \mu\text{g L}^{-1}$) and DOC concentrations ranged from 15–21 mg L^{-1} . The observed peak in Al_i
328 concentrations during times of lower discharge contrasts with studies that found higher Al_i
329 concentrations during higher flow (Campbell et al., 1992; Kopacek et al., 2000; Neal et al., 1986;
330 Reduskin et al., 1995). Further research is required to test hypotheses on why high Al_i coincides with
331 high DOC and low flow periods.

332 3.3 Possible seasonal groupings of Al_i in NSA

333 In the two sites with the most samples, MPB and MR, groupings of data are visible that are
334 temporally contiguous, ~~potentially indicating~~suggesting seasonally-dependent Al_i behavior (Fig. 4).
335 This is supported by stronger linear correlations (r^2) among variables when grouped by “season” (Table
336 2); for example, for the correlation between pH and Al_i at MR, r^2 improves from 0.02 for year-round
337 data (Fig. B17B12) to up to 0.78 in season 1 (Fig. 4). The transition dates between the seasons are
338 similar for the two catchments, but not the same (Table A2), and vary by year. Here we propose an
339 initial characterization of ~~the~~ potential “seasons”; more research is needed to test these hypotheses on
340 seasonal divisions and their drivers using larger datasets ~~and Generalized Linear Mixed Model analysis~~
341 to test for statistical significance among the potential seasonal groupings.

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

371 Biological activity further generates DOC which mobilizes Al to drainage waters during summer base
372 flow (Figure 4). Other cases of increased Al_i concentrations occurring during low flow and warming
373 temperatures can be found in the literature in locations such as Ontario and Quebec (Hendershot et al.,
374 1985, Hendershot et al., 1996) and in Virginia, USA (Cozzarelli et al., 1987).
375

376 **3.4 Ecological implications**

377 While the summer peak in Al_i that we observed in NS_A does not coincide with the smoltification
378 period, ~~when salmon transition from parr to smolt and are highly sensitive to Al exposure (Kroglund et~~
379 ~~al., 2007, Monette and McCormick, 2008, Nilsen et al., 2013).~~ continued exposure throughout the year
380 may still negatively affect salmon populations, as accumulation of Al_i on gills reduces salmon marine
381 and freshwater survival (Kroglund et al., 2007). ~~Further, Al_i concentrations as low as 20 µg L⁻¹ may~~
382 ~~impair marine survival without reducing freshwater survival (Kroglund and Staurnes, 1999, Staurnes~~
383 ~~et al., 1996), contributing to the observation that marine threats are driving population declines of~~
384 ~~Atlantic Salmon (e.g. Gibson et al., 2011). In addition, as the higher Al_i concentrations appear to be~~
385 ~~driven—at least in part—by lower flow in the summer months, increases in the length and severity of~~
386 ~~droughts and heat waves due to climate change may further increase Al_i concentrations and exacerbate~~
387 ~~Al_i effects on aquatic life. Increases in Al have already been observed across areas previously affected~~
388 ~~by freshwater acidification (Sterling et al., in prep.). Kroglund and Staurnes, 1999, Staurnes et al.,~~
389 1996, Gibson et al., 2011).

390 ~~For example, because~~ In addition, elevated Al_i concentrations appearing during low flow in the
391 summer months suggest a more chronic delivery of elevated Al_i to rivers, for which increases in the
392 length and severity of droughts and heat waves due to climate change may further exacerbate effects

393 on aquatic life. Because many peak Al_i concentrations occur on the first exceptionally warm day in late
394 spring, ~~the peaks may be exacerbated with~~ springtime warming associated with climate change. ~~As~~
395 ~~warm days begin~~ may cause Al_i peaks to occur earlier ~~in the season, there may be,~~ thus increasing
396 chance of the peak Al_i concentrations overlapping with smoltification season and emergence of salmon
397 fry; ~~both considered,~~ the most vulnerable life stages of Atlantic salmon (e.g., Farmer, 2000), although
398 the phenology of the smolt run is expected to similarly advance earlier in the year.

399 4 Conclusions

400 ~~Our study reveals that~~ Our four-year study of stream chemistry in NS_A has two important
401 findings. First, high DOC concentrations in rivers may not protect aquatic life against Al_i as previously
402 thought – our GLMM analysis suggests rather the opposite – that higher DOC concentrations drive
403 higher levels of Al_i , even possibly on a seasonal basis. Our study thus reveals that despite high DOC
404 levels, widespread and persistent toxic concentrations of Al_i in NS_A freshwaters pose a risk to aquatic,
405 and potentially terrestrial, life. ~~Previously, high DOC concentrations were presumed to protect aquatic~~
406 ~~life against Al_i ; our study shows that this presumption does not hold.~~

407 Second, our study shows a new hydrological pathway that is associated with high Al_i
408 concentrations: base flow, suggesting a chronically acidified/aluminum dynamic, in addition to episodic
409 Al_i peaks associated with storm flow. This new pathway suggests chronically elevated Al_i
410 concentrations during warmer summer months, which may be exacerbated by atmospheric warming.

411 Our results suggest that the recent 88 to 99% population decline of the Southern Uplands Atlantic
412 salmon population in NS_A (Gibson et al., 2011) may be partially attributable to Al_i , in contrast to earlier
413 studies which downplayed the role of Al_i in Atlantic salmon mortality (~~Bowlby et al., 2013,~~ Lacroix

414 and Townsend, 1987). These high Al_i concentrations in NS_A highlight the need to increase our
415 understanding of the influence of Al_i on both terrestrial and aquatic ecosystems, and its implications for
416 biodiversity.

417 The catchments with the highest Al_i levels had particularly low Ca levels, raising concerns as
418 Ca is protective against Al_i toxicity, and highlighting coincident threats of Ca depletion and elevated
419 Al. Recent work has identified globally widespread low levels and declines in Ca (Weyhenmeyer et al.,
420 2019), raising the question of what other regions may also have Al_i levels exceeding toxic thresholds.

421 The serious potential consequences of high Al_i highlight the importance for actions to further
422 reduce acid emissions and deposition, as critical loads are still exceeded across the province (Keys,
423 2015), and to adapt forest management practices to avoid base cation removal and depletion. Addition
424 of base cations through liming and enhanced weathering of soils and freshwaters may accelerate
425 recovery from acidification.

426

427 Data availability

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

430 Author ~~contribution~~contributions

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

438 Competing interests

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

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747 **Tables**

748 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
749 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.

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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 _i (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

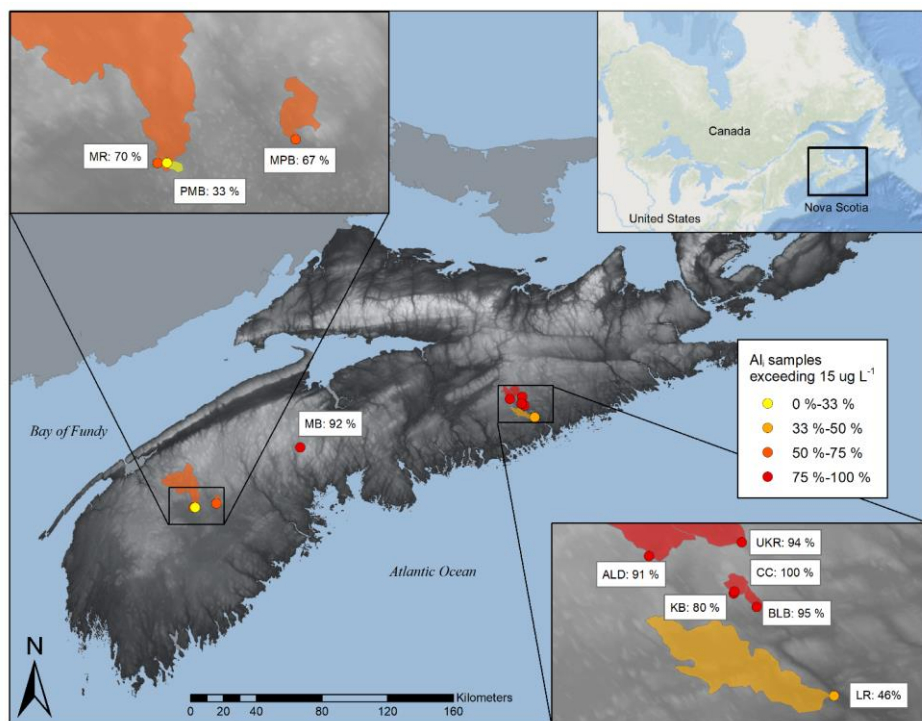
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Table 2. Al_i relations with other stream chemistry parameters separated by possible seasons. Dark shading represents $r^2 > 0.6$. Medium shading represents r^2 0.2-0.6. Light shading represents r^2 0.0-0.2. Green indicates negative relation. Orange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



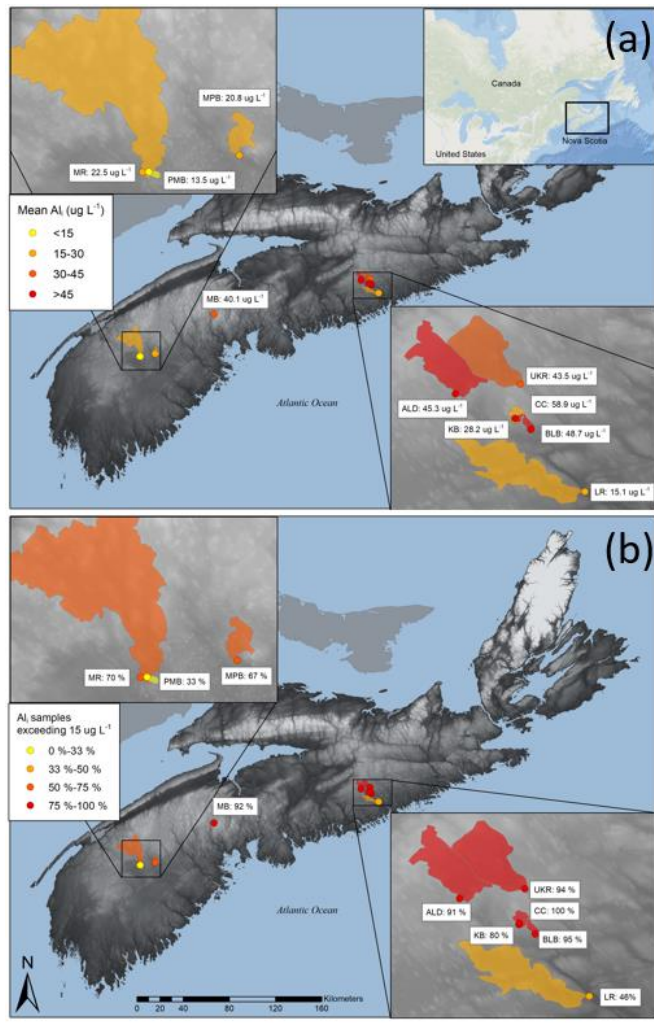


Figure 1. Study site locations showing (a) mean Al_i concentrations and (b) proportion of samples when Al_i concentrations exceeded the $15 \mu g L^{-1}$ toxic threshold: between spring 2015 and fall 2018. Shaded region corresponds to the catchments of monitoring sites. For additional site details, refer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

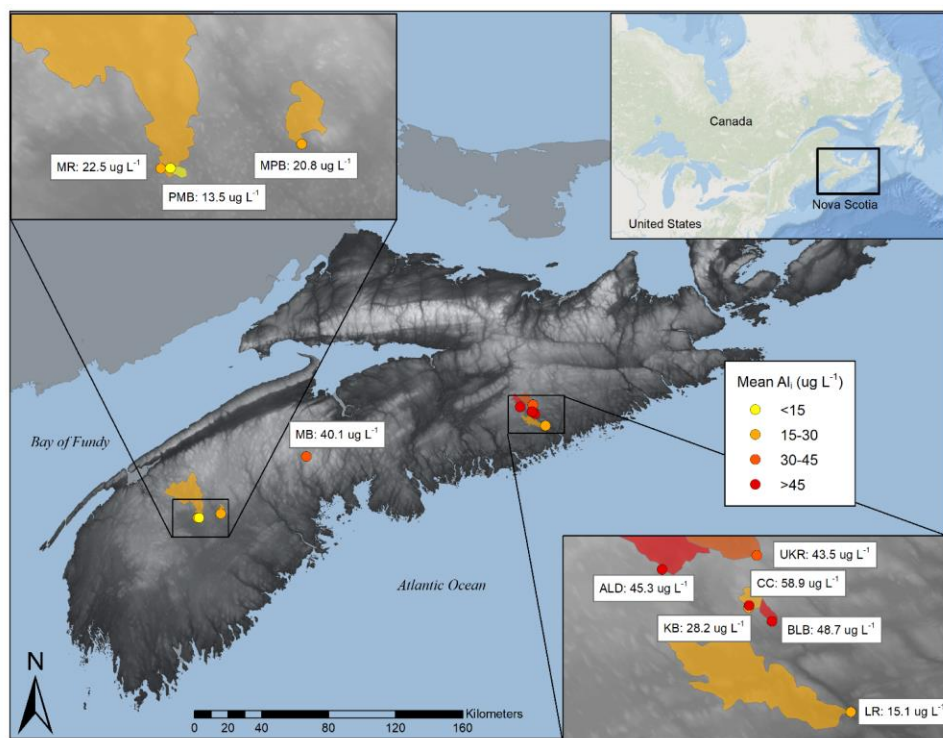


Figure 2. Mean Al_i concentrations between spring 2015 to fall 2018.

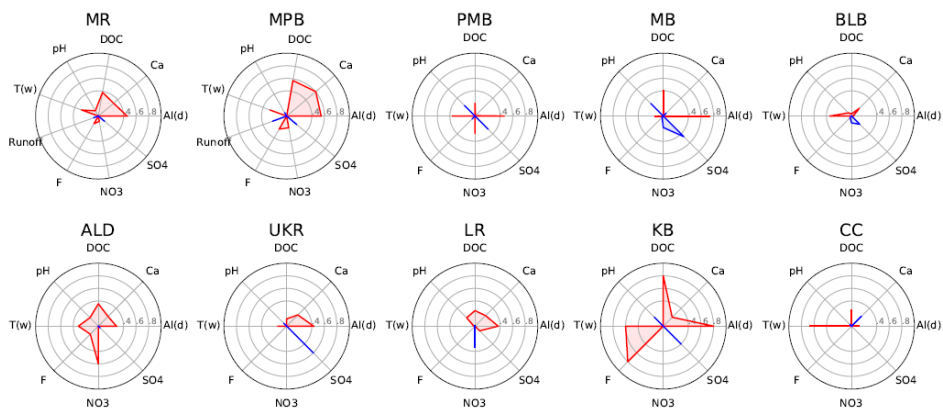


Figure 3.

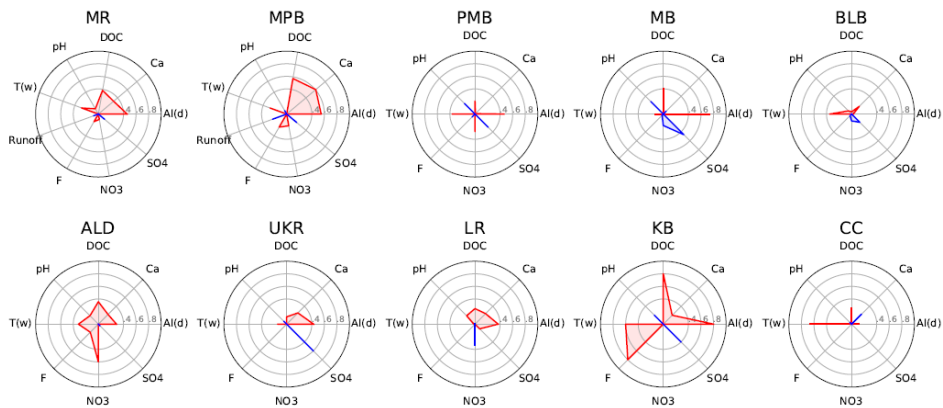


Figure 2. Correlation among water chemistry parameters and Al_i concentration, where red polygons and lines indicate a positive correlation with Al_i, and blue polygons and lines indicate a negative correlation

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

A4-A5.

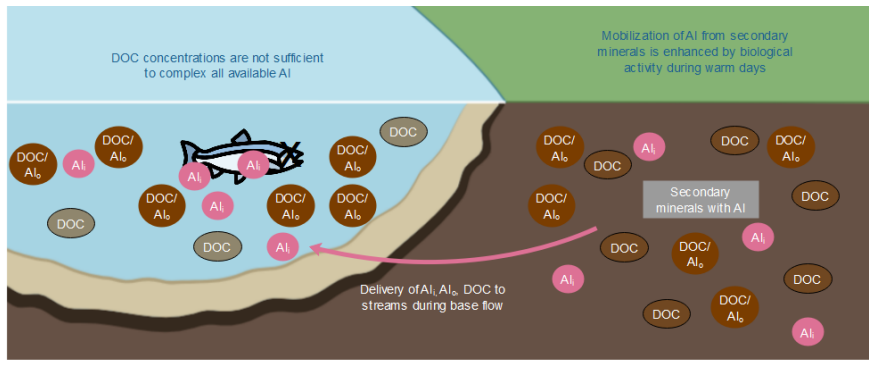


Figure 3. Conceptual model of new mechanism that can produce high concentrations of Al_i in freshwaters. Warm days increase biological activity that helps to mobilize Al from secondary minerals and enhances production of DOC which in turn reduces pH and reduces Al saturation in soil solution by forming 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.

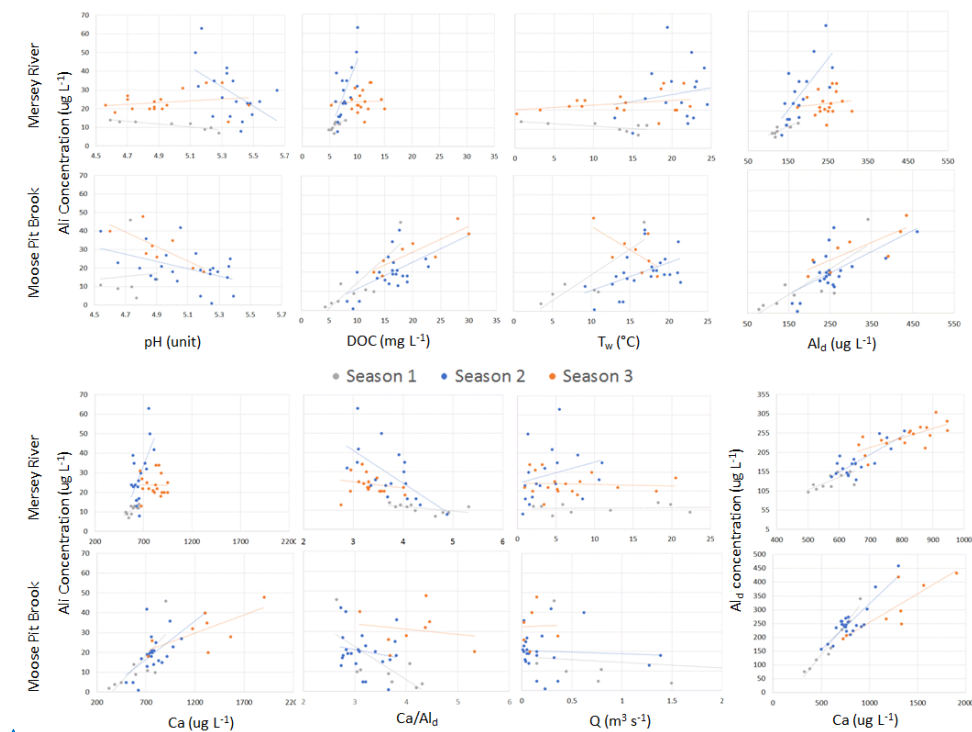


Figure 4. Scatterplot relationships among water chemistry parameters for seasons 1, 2, and 3 at MR and MPB. R² values are listed in Table A5A7. One runoff outlier removed for MR (value: 17.294 m³ s⁻¹, date: 22 April 2015). One runoff outlier removed for MPB (value: 34.994 m³ s⁻¹, date: 22 April 2015).

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

Appendix A. Tables

Table A1 Al_i terminology, speciation methodology, and trends from published studies. Several methods do not measure Al_i in situ, which can cause error due to changes in temperature, DOC and pH, which vary during transit to the lab. Increased pH and increased temperature in lab conditions can cause the underestimation of Al_i. Al_{nl}=non-labile Al, Al_{tm}=total monomeric Al, Al_{om}=organic monomeric Al, Al_{tr}=total reactive Al, Al_{nlm}=non-labile monomeric Al, Al_m=monomeric Al. CEC= Cation Exchange Column, ICP-AES= Inductively Coupled Plasma-Atomic Emission Spectroscopy. AWMN= Acid Waters Monitoring Network.

Al Species	A	Definition	Analysis Method	Trend	Location	Reference
Al _i	A	Inorganic Al	Colourimetry	Decreasing Al _i from 1988-2008 (Al _{tr} -Al _{nl})	AWM N in UK	Monteith et al. (2014)
	A	Inorganic monomeric Al	Colourimetry	Decreasing Al _i from 2001-2011	New York, USA	Josephson et al. (2014)

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			(Al _{im} - Al _{om})			
	A	Ionic Al	CEC	Mean	Atlanti	Dennis
I _i			(Al _i -Al _o)	NS Al _i =25.3 µg/L	c Canada	and Clair (2012)
				Mean		
				NB Al _i =31.0 µg/L		
	A	Ionic Al	Colouri	Decrea	Norwa	Hesthag
I _i			metry	sing Al _i in lakes	y	en et al. (2011)
	L	Inorganic Al	ICP-	15% of	Norwa	Kristens
Al		(sum of inorganic and monomeric Al species)	AES, Flow injection, Pyrocatechol violet, and CEC (Al _{iq} -Al _{ol})	LA1 samples y were >10 µg/L		en et al. (2009)
	A	Labile/cationic/in	Colouri	Decrea	AWM	Evans
I-l		organic monomeric Al	metry	sing Al-l across	N in UK	& Monteith
			(Al _{im} - Al _{nlm})	the UK		(2001)
	A	Labile Al (free	Van	Mean	China	Wang et
I _{im}		and inorganically complexed Al)	Benschoten method	Al _{im} of 72 µg/L from 2009-2010		al. (2013)

	A	Inorganic	Colouri	Al _i	Czech	Kram et
l _i	monomeric		metry and CEC	fraction	Republic	al. (2009)
			(Al _m -Al _o)	decreased in		
				catchments		
				between 1991 &		
				2007		
	A	Inorganic Al	AAS	Decrea	Adiron	Strock
l _i				sing Al _i from	dack	et al. (2014)
				1990-2010	Mountains,	
				USA		

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Table A2 Raw sample data. RL: rising limb of hydrograph, FL: falling limb of hydrograph, and BF: base flow. Air temperature (T_a) data were collected from the Kejimikujik 1 weather station (Climate ID: 8202592; 44.24°11.020°N, 65.12°11.070°W) for MR, MPB, PMB, and MB, and the Stanfield Airport weather station (Climate ID: 8202251; 44°52'52.000" N, 63°30'31.000" W) for CC, KB, ALD, BLB, UKR, and LR. Missing T_a data were replaced with data from another local meteorological tower located one kilometer to the northwest of the MPB site (44.469549, -65.061295).

ite	ate	A		S	OC		T	D		F	H
		li ($\mu\text{g L}^{-1}$)	lo/Ala (%)		la ($\mu\text{g L}^{-1}$)	a ($\mu\text{g L}^{-1}$)		ischarge ($\text{m}^3 \text{s}^{-1}$)	unoff (mm day $^{-1}$)		ydrograph Stage
LD	016-04-		8								
	29	9	7.7	1	55	91		99	.67		
LD	016-05-		9					1			
	19	2	4.1		02	00	0.7	414	.89	2.0	
LD	016-06-		9							1	
	03	5	0.7	2	68	22	2.5	39	.02	6.6	3.2

LD	016-06-16	2	8	8.3	2	74	74	2.9	5	78	.99	1	3.2	3
LD	016-06-28	8	8	9.4	2	65	20	2.2	5	59	.26	2	2.1	4.2
LD	016-07-15	7	8	7	2	85	92	5	7	61	.11	2	0.7	9.6
LD	016-08-05	8	7	9.9		39	00	9.4	1	414	.98			1.2
LD	016-09-10	8	7	8.2		20	000	4.8	2	000	.03			0.8
LD	016-10-02	3	9	2.3		69	000	4.4	3	000	.27			1.4

LD	016-11-19	4	8 2		45	00	4.6	1 414	.03		.6
LD	017-04-19	7	8 1.1	1	43	00	0.4	1 209	.55	.7 .8	.2
LD	017-05-14	9	6 1	2	77	00	2.1	5 23	.92	1 3.4	
LD	017-05-30	7	8 5.8	2	61	00	1.8	2 536	.77	1 4.3	2.2
LD	017-06-22	00	5 9.8	2	49	00	5.2	1 414	.17	2 2.8	5
LD	017-07-13	2	8 0.3	2	15	00	9.3	1 414	.24	2 0.6	8.5

LD	017-08-01	6	8 9	2	36	00	5.1	1 414	.96	2 5.6	8.4
LD	017-08-23	5	8 4.4	2	24	00	3.2	1 125	.14	2 1.8	1
LD	017-09-16	7	8 2.5	2	39	000	3.5		.73	2 0.7	8.7
LD	018-05-10	6	7 5.7		89	00	.8	1 414	.64		.5
LD	018-06-07	3	8 3.8		66	00	6.1	1 414	.13		1.0
LD	018-07-05	19	6 2.5		17	00	3.6	1 414	.61		3.8

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LB	016-08-		9				1		1.2
	05		8.6	29	000	6.2	414	.29	
LB	016-09-		7				1		0.8
	10	1	7.1	54	00	8.3	414	.87	
LB	016-10-		9				2		1.4
	02	3	0.1	35	000	8.5	000	.1	
LB	016-11-		9				1		.6
	19	8	2.6	79	000	7.2	414	.76	
LB	017-04-		7				1		4
	19	1	9.1	4	96	00	.6	927	.2
LB	017-05-		8				1		7
	14	6	2.6	4	64	00	2.9	550	.7

LB	017-05-		8					1			8	
	30	6	8.3	4	08	00	1.3	795		.4	4.9	
LB	017-06-		7					1			1	
	22	10	0.1	4	68	00	4.9	414	.8	7.3	4.6	
LB	017-07-		8					1			1	
	13	0	8.3	4	27	00	7.6	414	.87	5.8	7	
LB	017-08-		9					1			2	
	01	7	0.7	4	96	00	7.9	414	.7	0.6	9	
LB	017-08-		8					1			1	
	23	4	5.8	3	81	000	7.1	172	.94	8.3	1	
LB	017-09-		9								1	
	16	4	1.9	4	20	000	7.3		.52	6.6	8.9	

LB	018-05-	8					1			.5
	10	7	5.5	56	00	.5	414	.16		
LB	018-06-	7					1			1.0
	07	6	5	44	00	5.7	414	.29		
LB	018-07-	8					1			3.8
	05	3	0.3	21	00	3.8	414	.42		
LB	018-10-	6					1			.7
	02	04	7.4	19	600	2.4	414	.04		
LB	018-11-	9					1			9.1
	23	4	3.5	67	0.7	0.5	414	.8		
C	016-06-	9					2		1	
	03	2	1.9	4	97	01	5.2	85	.66	1.2 3.5

C	016-06-16	6	8.9	4	13	20	7.7	04	.71	0.4	2.8
C	016-06-28	07	8.9	4	07	37	1	01	.82	4.8	4.2
C	016-07-15	3	9.9	4	24	42	6	08	.6	4.6	8.7
C	016-08-05	40	8.6		46	00	9.3	414	.73		1.2
C	016-09-10	2	6.9		44	00	2.2	414	.72		0.8
C	016-10-02	4	5.5		34	00	8.8	414	.95		1.4

C	016-11-19	7	9 4.9		27	100	4.9	1 414	.11		.6
B	016-04-29	4	9 0.6	2	49	110	.7	1 061	.69	.2	8
B	016-06-03	0	9 2.5	2	67	59	.9	€ 11	.89	4.1	1 3.5
B	016-06-16	8	8 7.7	2	10	15	1.3	€ 52	.9	2.3	1 0.8
B	016-06-28	8	9 1.3	2	23	86	1.7	€ 87	.06	7.8	1 4.5
B	016-07-15	1	8 8.5	2	56	35	5.6	€ 21	.03	8.7	1 8.7

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R	017-06-22	4	6 9.9	2	13	00	.2	1 414	.51	1 9.6	9
R	017-07-13	2	8 8.7	2	06	00	.4	1 414	.54	2 1.8	8
R	017-08-01		9 6.9	2	5	00	.6	1 414	.1	1 9.6	4.8
R	017-08-23		8 8.4	2	3	00	.1	1 371	.37	2 1.6	1.3
R	017-09-16		9 4.9	2	9	00	.7	1 414	.01	1 9.4	5.8
R	018-05-10	5	7 4.1		35	00	.7	1 414	.54		.5

R	018-06-07	6	8 4.0		62	00	.2	1 414	.55	1.0
B	016-05-27	0	8 8.9	2	70	200	.8	1 278	.14	9 .8 2
B	016-06-15	5	9 4.2	2	60	590	.4	1 497	.61	1 1.2 4.6
B	016-06-27	7	9 0.5	2	84	610	.6	1 851	.28	1 6.3 6.7
B	016-07-14	0	8 6.9	2	05	780	.4	1 747	.4	1 5.5 8.5
B	017-04-20	5	8 9.8	1	46	48		1 996	.86	2 .3

B	017-05-		8					1		9	
	13	8	4.1	1	02	77	.2	385	.76	.1	7
B	017-05-		8					1		9	
	29	0	7.9	2	30	100		977	.99	.1	4.5
B	017-06-		8					5		1	
	21	6	1.2	2	10	480	5.8	51	.18	3.7	3.3
B	017-07-		8					2		1	
	12	6	7.7	2	75	320	1.5	8968	.13	5.8	5.9
B	017-07-		8					1		1	
	31	3	7.7	2	51	470	2.1	629	.08	5.6	7.4
B	017-08-		8					8		1	
	22	0	5.7	2	60	500	1	28	.91	5.5	7.6

B	017-09-17	0	8 9.3	3	80	600	1	1 258	.14	1 4.7	3						
PB	015-04-22		9 7.1	1	7	23	.3	1 009			.3		6 .41	3 4.992		R L	
PB	015-04-30		9 5.9	1	8	79	.4	1 272	.77	3 .5	.5		1 .49	8 .134		FL	
PB	015-05-06		9 5.8	1	20	46	.6	1 304			4		0 .76	4 .149		B F	
PB	015-05-13		9 6.8	2	58	98	.2	5 58	.18	1 3.6			0 .36	1 .965		R L	
PB	015-05-20		9 9.4	2	70	21	.3	8 15	.25	1 0.4	2		0 .23	1 .256		R L	

PB	015-05-27		9	7.2	2	77	67	0.4	99	.39	4.1	1	.15	.819	R
															L
PB	015-06-03	3	9	5	2	60	10	7.3	39	.03	.2		.27	.933	R
															L
PB	015-06-10	7	9	2.8	2	36	51	3.6	43	.24	4.6	0	.32	.747	R
															L
PB	015-06-17	8	8	8.3	2	39	51	5.6	60	.15	4.6	6	.2	.092	R
															L
PB	015-06-24	8	9	3.4	2	71	51	9	57		3.2	8	.38	.533	R
															L
PB	015-07-02	2	8	3.8	2	59	05	7.6	22	.05	6.9	0	.29	.583	B
															F

PB	015-07-08	9	2.3	2	47	24	6.4	00	.24	9.4	3	.07	.382	B
														F
PB	015-07-15	9	2.3	2	48	10	7	64	.18	0.1	8	.05	.273	B
														F
PB	015-07-22	1	1.5	2	47	56	6.3	52	.36	8.4	7	.05	.273	R
														L
PB	015-07-29	8	2.5	2	40	12	8.2	146	.29	7.7	9	.15	.819	R
														L
PB	015-08-05	5	3.9	2	44	63	9	50	.35	1.5	9	.04	.218	FL
PB	015-08-12	5	8.2	2	11	98	6.5	18	.37	8.9	1	.04	.218	R
														L

PB	015-08-		8					7		2		0	0	B
	19	6	5.4	2	47	41	6.3	21	.83	1.2	4	.02	.109	F
PB	015-08-		9					€		2		0	0	B
	26	0	1.1	2	24	61	0	07	.26	1.1	6	.02	.109	F
PB	015-09-		8					7		1		0	0	B
	02	6	7.5	3	08	60	4.7	11	.9	7.4	1	.02	.109	F
PB	015-09-		9					8		1			0	R
	09	8	0.8	3	96	22	4.5	23	.2	8.5	0			L
PB	015-09-		9					4		1		0	0	B
	16	0	2	3	50	330	3	375	.13	6.5	9	.08	.437	F
PB	015-09-		8					2		1		0	0	B
	23	5	8.2	3	97	320	0	598		4.3	7	.02	.109	F

PB	015-09-30	2	8.1	3	68	170	8.1	902	.87	5.7	9		0	B F
PB	015-10-07	8	8.9	3	34	900	8	576	.81	0.3	3	.15	.819	B F
PB	015-10-14	8	2.8	3	90	560	4	963	.83	2.7	6	.36	.965	R L
PB	016-04-28	4	0.1	1	41	73	.1	00	.9	.6		.15	.819	R L
PB	016-05-27	0	1.7	2	40	40	4	89	.79	4.2	2	.15	.819	R L
PB	016-06-15	4	4.6	2	57	75	5.7	78	.89	2.7	4.1	.07	.382	FL

PB	016-06-27	1	9 2.4	2	75	78	7.2	5 87	.93	1 8	7	0 .01	0 .055	FL
PB	016-07-14	6	9 2.9	2	25	28	5	1 447	.86	1 5.5	0	0 .03	0 .164	FL
PB	017-04-20		9 4.5	1	63	95	.4	1 625	.65	5			0	
PB	017-05-13	1	9 5.2	1	29	12	1.5	1 430	.54	1 0.4	7	0 .79	4 .313	FL
PB	017-05-29	0	9 6.2	1	60	90	3	1 567	.74	1 0.9	2	0 .44	2 .402	FL
PB	017-06-21	6	8 6.5	1	41	01	7.8	2 26	.73	1 6.8	4.2	0 .32	1 .747	FL

PB	017-07-12	7	9 3	2	84	060	2.3	29	.96	1 9.5	5.9	0 .05	0 .273	FL
PB	017-07-31	3	9 2.4	2	03	72	2.8	24	.65	1 7.8	7	0 .02	0 .109	FL
PB	017-08-22	0	9 1.3	2	60	300	0	55	.54	1 6.9	8.4	0 .62	3 .385	FL
PB	017-09-17	0	9 0.5	3	20	300	0	01	.6	1 7.3	0.1	0 .1	0 .546	FL
R	015-04-22	2	9 0.2	1	22	48	.9	321		1 3		5 8.61	1 .837	R L
R	015-04-30		9 8	1	02	00	.6	189		1 .2	4 .5	3 3.03	1 .454	FL

R	015-05-06		9					1			4	2	1	B F
			1.8	1	10	27	.8	112				2.33	.269	
R	015-05-13	0	9					1		1		1	1	FL
			1.8	1	22	17	.5	117	.23	3.3		2.05	.048	
R	015-05-20		9					1		1	2	6	0	FL
			2.3	1	17	74	.3	101	.19	4.2		.95	.912	
R	015-05-27		9					1		1	1	4	0	FL
			4.1	1	18	48	.8	161	.28	5.7		.53	.835	
R	015-06-03	6	8					1		1		8	0	R L
			9.2	2	48	29	.6	069	.35	2.7		.42	.946	
R	015-06-10	9	7					1		1	0	7	0	R L
			4.2	2	51	90	.2	220	.33	7.4		.8	.934	

R	015-06-17	4	8 3.1	42	75	.1	175	.39	1 9.2	4 .98	0 .858	
R	015-06-24	6	8 6.2	88	47	.8	68	.3	1 6.6	1 0.58	1 .028	
R	015-07-02	5	8 2.1	2 96	02	.1	8 97	.25	1 9.9	0 1 0.94	1 .018	B F
R	015-07-08	5	8 0.2	2 77	13	.3	5 72	.37	2 3.1	3 5 .14	0 .864	B F
R	015-07-15	3	8 7	2 77	93	.9	5 59	.46	2 4.5	8 2 .9	0 .76	B F
R	015-07-22	7	9 0.4	2 77	52		1 011	.49	2 1.9	7 1 .9	0 .701	B F

R	015-07-29	4	8	5.3	2	63	11	.7	146	.54	1.2	9	2	0	R L
R	015-08-05	0	8	2	2	67	70	.5	077	.65	5.2	9	1	0	FL
R	015-08-12	3	9	1	2	45	29	.5	094	.43	2	1	1	0	R L
R	015-08-19	3	8	6.9	2	76	41	.4	097	.48	5.3	4	0	0	B F
R	015-08-26	2	8	3.9	2	61	08		179	.33	4.1	6	4	0	B F
R	015-09-02	4	8	7.5	3	71	59	2.3	168	.3	1.5	1	1	0	B F

R	015-09-09	2	9 0.4	3	29	51	0.2	7 76	2 .47	2 2.3	0	0 .93	0 .63	B F
R	015-09-16	4	8 7	3	61	28	2.5	1 108	1 .2	1 8.9	9	3 .2	0 .781	B F
R	015-09-23	3	9 4.7	3	46	75	1.3	5 00	1 .34	1 8.3	7	3 .44	0 .789	B F
R	015-09-30	1	8 6.2	3	25	62	.6	5 11	1 .05	1 8.6	9	2 .3	0 .733	B F
R	015-10-07	1	9 1.3		41	94	0.7	5 89	1 .87	1 3		5 .16	0 .869	
R	015-10-14	4	9 0.7	3	57	24	1.4	1 166	1 .87	1 4.1	6	6 .26	0 .905	R L

R	015-10-21	5	8 9.5	3	37	35		8 90	8 .91	4 .9	0 .83	0 .855	B F
R	015-10-28	2	9 1.3	3	53	37	0	1 153	6 .95	3 .9	0 .98	0 .814	FL
R	015-11-04	5	9 1.3	3	86	45	4.4	5 67	7 .7	8 .9	0 .1	0 .947	R L
R	015-12-02	0	9 2.4	3	62	46	2	1 139	3 .73	1 .2	1 7.96	1 .183	FL
R	016-01-05	0	8 8.9	3	70	80	1	1 245		20	9 .62	0 .998	FL
R	016-02-02	8	9 1.7	3	17	75	0.1	1 290	0 .62	3 .2	7 .75	0 .926	R L

R	016-02-23	4	9 2	1	75	51	.9	1 316	0 .59	6 .8	1 8.21	1 .2	B F
R	016-03-29	3	9 1.1	1	46	06	.1	1 060	4 .65		1 9.81	1 .248	R L
R	016-04-28	3	9 1	1	45	72		5 37	1 .75		5 .85	0 .892	FL
R	016-05-27	2	9 2.3	1	56	35	.8	5 22	1 .98	2 6.8	3 .11	0 .81	FL
R	016-06-15	2	9 2.3	1	55	95	.7	1 217	1 .1	4.4 5.7	2 .05	0 .773	FL
R	016-06-27	6	8 9.5	2	53	24	.8	1 263	2 .24	4 2.7	1 .04	0 .649	FL

R	016-07-14		9					1		1	6	0	0	B F
			4	2	34	54	.4	697	.42	5		.68	.635	
R	017-04-20	2	8					1		8		1		FL
			7.3	3	73	92	.3	625	.56	.5		3		
R	017-05-13	7	8					1		1	3	2	1	FL
			6.3	3	97	83	0.5	437	.7	3.4		0.5	.28	
R	017-05-29	0	9					1		1	0.4	7	0	FL
			1.3	3	30	10		774	.87	3.9		.08	.905	
R	017-06-21	3	7					4		1	0.2	5	0	FL
			4.2	2	44	52	0.1	58	.17	9.4		.42	.881	
R	017-07-12	2	8					5		2	3.9	3	0	FL
			7.4	2	54	29	0	82	.15	2.9		.55	.813	

R	017-07-31	0	7 6.7	2	15	66	.88	1 116	2 .13	2.5	4.9	1 .37	0 .665	FL
R	017-08-22	0	9 3.5	3	10	10	5	8 61	2 .92	0.4	5.5	5 .26	0 .878	FL
R	017-09-17	0	9 2	3	50	90	5	8 17	2 .84	0.6	7.3	1 .98	0 .715	FL
MB	015-05-27		9 8.4	2	28	42	.2	8 45	1 .62	2.6	1			
MB	015-06-03		9 5.7	2	38	86	.8	1 042	1 .28	2.2				
MB	016-04-28		9 3.6	2	3	75	.6	1 244	8 .25	.2				

MB	016-05-27	5	7	2	60	00		€	91	.93	1	2
			8.1								2.7	
MB	016-06-15		9	2	51	150	.1	1	229	.14	1	4.2
			6.7								0.9	
MB	016-06-27		9	2	2	570	.4	3	167	.35	1	4
			4.3								4	
MB	016-07-14	0	8	2	6	770	.9	5	652	.4	1	2
			9.3								5	
MB	017-04-20		9	1	14	1	.3	2	234	.78	8	
			6.5								.5	
MB	017-05-13	1	9	1	39	1	.2	1	328	.69	9	6
			2.1								.8	

MB	017-05-29	0	9 3.8	2	60	30		2 405		1 3.9	0.8
MB	017-06-21	2	8 5.6	2	22	55	1.1	2 89	.98	1 5.5	1.4
MB	017-07-12	5	8 0.3	2	78	580	0.7	1 428	.21	1 6	4.6
MB	017-07-31		9 9.3	2	48	780	3	2 746	.99	1 3.8	5.6
MB	017-08-22	0	9 0.9	3	20	60	3	5 71	.85	1 6.4	6.9
MB	017-09-17	0	9 0	3	00	90	5	6 40	.7	1 6	7.8

KR	016-05-	8								
	19	1	9.7	03	00	0.4	414.2	.83	2.0	
KR	016-08-	8								
	05	8	8.5	57	00	5.1	414.2	.56	1.2	
KR	016-09-	8								
	10	6	9.9	58	00	2.1	414.2	.58	0.8	
KR	016-10-	9								
	02	5	1.8	82	00	3.8	414.2	.77	1.4	
KR	016-11-	8								
	19	1	4.4	62	100	5.1	000	.89	.6	
KR	017-04-	7								
	19	8	2.3	3	37	00	.5	292	.3	.4

KR	017-05-		8					1		1
	14	4	7.2	2	87	00	2.6	049	2.9	
KR	017-05-		8					1		1
	30	7	3.3	2	21	00	.8	115	5.2	2.5
KR	017-06-		6					1		2
	22	6	7.5	2	03	00	2.1	414	.22	3.4 4.2
KR	017-07-		8					1		2
	13	7	5.4	2	22	00	7.6	414	.21	2.3 9
KR	017-08-		8					1		2
	01	6	9.1	2	39	00	5	414	.29	5.6 9.1
KR	017-08-		6					8		2
	23	4	5.6	2	15	00	2.8	89	.31	1.8 1.1

			8						2	
KR	017-09-16	6	2	2	22	000	0.6	.77	0.8	9.2
KR	018-05-10	7	8.1		69	00	.2	414.2	.31	.5
KR	018-06-07	9	3.3		21	00	2.9	414.2	.34	1.0
KR	018-07-05	9	6.3		94	00	2.2	414.2	.46	3.8
KR	018-10-02	7	7.3		07	100	0.5	414.2	.78	.7
KR	018-11-23	3	1.1		27	00	0.8	414.2	.81	9.1

Table A3

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Table A3 Generalized linear mixed model (GLMM) results for complete field data.

<u>Fixed</u>	<u>Parameter</u>	<u>Wald t Test</u>	<u>P-</u>	<u>AIC</u>
<u>Effect</u>	<u>Estimate</u>	<u>Statistic</u>	<u>Value</u>	
<u>Ca</u>	<u>0.281</u>	<u>1.551</u>	<u>0.121</u>	
<u>DOC</u>	<u>0.536</u>	<u>3.285</u>	<u>0.001</u>	
<u>F</u>	<u>-0.04</u>	<u>-0.79</u>	<u>0.429</u>	
<u>NO3</u>	<u>0.068</u>	<u>3.269</u>	<u>0.001</u>	<u>1316.9</u>
<u>pH</u>	<u>-1.123</u>	<u>-0.952</u>	<u>0.341</u>	
<u>SO4</u>	<u>-0.295</u>	<u>-3.038</u>	<u>0.002</u>	
<u>Tw</u>	<u>0.34</u>	<u>1.551</u>	<u>0.046</u>	
<u>DOC</u>	<u>0.321</u>	<u>5.647</u>	<u>0</u>	<u>1946.3</u>
<u>DOC</u>	<u>0.149</u>	<u>4.954</u>	<u>0</u>	
<u>NO3</u>	<u>0.417</u>	<u>2.721</u>	<u>0.007</u>	<u>1816.7</u>
<u>SO4</u>	<u>-0.417</u>	<u>-2.667</u>	<u>0.008</u>	
<u>DOC</u>	<u>0.256</u>	<u>6.908</u>	<u>0</u>	
<u>NO3</u>	<u>0.12</u>	<u>3.335</u>	<u>0</u>	<u>1837.2</u>
<u>DOC*NO3</u>	<u>1.1</u>	<u>4.545</u>	<u>0</u>	
<u>Tw</u>	<u>0.548</u>	<u>4.574</u>	<u>0</u>	<u>1467.8</u>
<u>DOC</u>	<u>1.135</u>	<u>3.445</u>	<u>0</u>	
<u>Tw</u>	<u>0.678</u>	<u>2.215</u>	<u>0.027</u>	<u>1438.2</u>
<u>DOC*Tw</u>	<u>-0.470</u>	<u>0.109</u>	<u>0.109</u>	
<u>DOC</u>	<u>0.623</u>	<u>6.391</u>	<u>0</u>	
<u>Tw</u>	<u>0.24</u>	<u>1.943</u>	<u>0.052</u>	<u>1438.6</u>

-significant parameters at the 5% significance level are bolded

-significant parameters at the 10% significance level are italicized

-Effect connected by "*" represent an interaction term.

Table A4 Linear correlation r^2 values and significance ($\alpha = 0.05$) between Al_i/Al_d and other water chemistry parameters across all sites.

Variable	Unit	Correlation with Al_i/Al_d (R^2)	Significance (p-value)
Al_d	μg	0.007	0.247
	L^{-1}		
Ca	μg	0.001	0.676
	L^{-1}		
DOC	mg	0.007	0.247
	L^{-1}		
pH	unit	0.077	0.000
Water	$^{\circ}C$	0.114	0.000
Temp.			
F^{-}	μg	0.003	0.537
	L^{-1}		
NO_3^{-}	μg	0.002	0.624
	L^{-1}		
SO_4^{2-}	μg	0.000	0.952
	L^{-1}		

Table A4A5 Kendal-tau correlation and significance ($\alpha = 0.05$) between Al_i and other water chemistry parameters

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for each study site. One Al_i outlier removed for MR calculations (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

Site	Variable	Unit	Correlation	
			Slope	Significance (p-value)
ALD	Water Temp.	μg		
		Ald L^{-1}	0.29	0.044
		μg		
		Ca L^{-1}	0.22	0.143
		mg		
		DOC L^{-1}	0.36	0.013
		pH	0.19	0.190
		$^{\circ}\text{C}$	0.32	0.093
		F ⁺ μg	0.182	0.533
BLB	Water Temp.	L^{-1}	0.600	0.142
		NO_3^- μg	0.600	0.142
		L^{-1}		
		SO_4^{2-} μg	-0.037	0.876
		L^{-1}		
		μg		
		Ald L^{-1}	0.03	0.852
		μg		
		Ca L^{-1}	0.17	0.238
CC	Water Temp.	mg		
		DOC L^{-1}	0.08	0.575
		pH	0.07	0.622
		$^{\circ}\text{C}$	0.35	0.099
		F ⁺ μg	-0.036	0.901
		L^{-1}		
		NO_3^- μg	-0.109	0.708
		L^{-1}		
		SO_4^{2-} μg	-0.184	0.468
CC	Ald	μg		
		L^{-1}	0.11	0.708

	Temp.	Ca	L ⁻¹	µg	-0.22	0.451		
				mg				
		DOC	L ⁻¹		0.25	0.383		
		pH		unit	-0.04	0.901		
		Water						
				°C	0.67	0.174		
		F+		µg				
			L ⁻¹					
		NO ₃ ⁻		µg				
			L ⁻¹					
		SO ₄ ²⁻		µg				
			L ⁻¹					
		KB	Temp.	Ald	L ⁻¹	µg	0.800	0.050
						µg		
				Ca	L ⁻¹		0.200	0.624
						mg		
DOC	L ⁻¹				0.800	0.050		
pH				unit	-0.200	0.624		
Water								
				°C	0.600	0.142		
		F+		µg				
			L ⁻¹		0.800	0.050		
		NO ₃ ⁻		µg				
			L ⁻¹					
		SO ₄ ²⁻		µg				
			L ⁻¹		-0.400	0.327		
		LR	Temp.			µg		
				Ald	L ⁻¹		0.37	0.047
				µg				
Ca	L ⁻¹				0.24	0.226		
				mg				
DOC	L ⁻¹				0.25	0.189		
pH				unit	0.19	0.319		
Water								
		°C	0.02	0.937				

	F+		μg		
		L ⁻¹			
	NO ₃ ⁻		μg	-0.333	0.348
		L ⁻¹			
	SO ₄ ²⁻		μg	0.105	0.801
		L ⁻¹			
			μg		
	Ald	L ⁻¹		0.739	0.001
			μg		
	Ca	L ⁻¹		-0.062	0.783
			mg		
	DOC	L ⁻¹		0.400	0.073
	pH		unit	-0.279	0.214
MB	Water				
Temp.			°C	0.125	0.580
	F+		μg	-0.028	0.917
		L ⁻¹			
	NO ₃ ⁻		μg	-0.182	0.533
		L ⁻¹			
	SO ₄ ²⁻		μg	-0.463	0.050
		L ⁻¹			
			μg		
	Ald	L ⁻¹		0.550	0.000
			μg		
	Ca	L ⁻¹		0.580	0.000
			mg		
	DOC	L ⁻¹		0.574	0.000
	pH		unit	-0.169	0.146
MPB	Water				
Temp.			°C	0.280	0.016
			mm		
	Runoff	day ⁻¹		-0.232	0.042
	F+		μg	0.239	0.042
		L ⁻¹			
	NO ₃ ⁻		μg	0.190	0.160
		L ⁻¹			

		SO ₄ ²⁻	μg	-0.206	0.067
		L ⁻¹			
			μg		
		Ald	L ⁻¹	0.459	0.000
			μg		
		Ca	L ⁻¹	0.317	0.002
			mg		
		DOC	L ⁻¹	0.382	0.000
		pH	unit	0.097	0.362
		Water			
MR	Temp.		°C	0.285	0.007
			mm		
		RunOff	day ⁻¹	-0.108	0.291
		F+	μg		
			L ⁻¹	0.139	0.188
		NO ₃ ⁻	μg		
			L ⁻¹	0.086	0.450
		SO ₄ ²⁻	μg		
			L ⁻¹	-0.127	0.215
			μg		
		Ald	L ⁻¹	0.46	0.019
			μg		
		Ca	L ⁻¹	0.01	0.960
			mg		
		DOC	L ⁻¹	0.21	0.295
		pH	unit	-0.23	0.232
		Water			
PMB	Temp.		°C	0.36	0.065
		F+	μg		
			L ⁻¹	-0.063	0.782
		NO ₃ ⁻	μg		
			L ⁻¹	0.276	0.444
		SO ₄ ²⁻	μg		
			L ⁻¹	-0.293	0.135
			μg		
UKR		Ald	L ⁻¹	0.34	0.071

			µg		
	Ca	L ⁻¹		0.38	0.053
			mg		
	DOC	L ⁻¹		0.32	0.086
	pH		unit	0.35	0.063
	Water				
Temp.			°C	0.14	0.621
	F+		µg		
		L ⁻¹			
	NO ₃ ⁻		µg		
		L ⁻¹			
	SO ₄ ²⁻		µg	-0.600	0.142
		L ⁻¹			

|

Table A5A6 Generalized linear mixed model (GLMM) results for seasonal field data.

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<u>Fixed</u> <u>Effect</u>	<u>Parameter</u> <u>Estimate</u>	<u>Wald t Test</u> <u>Statistic</u>	<u>P-</u> <u>Value</u>	<u>AIC</u>
<u>ALd</u>	<u>0.264</u>	<u>6.17</u>	<u>0</u>	
<u>Ca</u>	<u>-0.007</u>	<u>-0.183</u>	<u>0.855</u>	
<u>DOC</u>	<u>0.143</u>	<u>3.727</u>	<u>0</u>	<u>1736.5</u>
<u>F</u>	<u>-0.020</u>	<u>-0.207</u>	<u>0.836</u>	
<u>NO3</u>	<u>0.146</u>	<u>0.991</u>	<u>0.322</u>	
<u>SO4</u>	<u>-0.133</u>	<u>-1.129</u>	<u>0.259</u>	
<u>ALd</u>	<u>0.281</u>	<u>6.921</u>	<u>0</u>	<u>1867.3</u>
<u>DOC</u>	<u>0.078</u>	<u>1.877</u>	<u>0.061</u>	
<u>ALd</u>	<u>0.313</u>	<u>7.393</u>	<u>0</u>	
<u>DOC</u>	<u>0.158</u>	<u>3.152</u>	<u>0.002</u>	<u>1862.8</u>
<u>ALd*DOC</u>	<u>-0.076</u>	<u>-2.490</u>	<u>0.013</u>	
<u>ALd</u>	<u>0.332</u>	<u>11.49</u>	<u>0</u>	<u>1868.3</u>
<u>DOC</u>	<u>0.229</u>	<u>9.445</u>	<u>0</u>	<u>1909.9</u>
<u>DOC</u>	<u>0.247</u>	<u>9.744</u>	<u>0</u>	
<u>NO3</u>	<u>0.329</u>	<u>-2.399</u>	<u>0.016</u>	<u>1768.4</u>
<u>SO4</u>	<u>-0.316</u>	<u>2.515</u>	<u>0.012</u>	
<u>DOC</u>	<u>0.287</u>	<u>9.453</u>	<u>0</u>	
<u>NO3</u>	<u>0.063</u>	<u>1.733</u>	<u>0.083</u>	<u>1797.3</u>
<u>DOC*NO3</u>	<u>0.41</u>	<u>1.709</u>	<u>0.088</u>	

-significant parameters at the 5% significance level are bolded

-significant parameters at the 10% significance level are italicized

-Effect connected by "*" represent an interaction term.

Table A7 R² values for scatterplots of water chemistry relationships shown in Figure 34

Site	Season	Season	Relationship	R ²
		Dates		
MR	S1	April-	Al _i -pH	0.78131
		May		
MR	S2	June-	Al _i -pH	0.27845
		Aug		
MR	S3	Sept-	Al _i -pH	0.04551
		Feb		
MR	S1	April-	Al _i -DOC	0.48879
		May		
MR	S2	June-	Al _i -DOC	0.51343
		Aug		
MR	S3	Sept-	Al _i -DOC	0.0014
		Feb		
MR	S1	April-	Al _i -T _w	0.42004
		May		
MR	S2	June-	Al _i -T _w	0.03442
		Aug		

MR	S3	Sept- Feb	Al _i -T _w	0.08795
MR	S1	April- May	Al _i -Al _d	0.66782
MR	S2	June- Aug	Al _i -Al _d	0.52313
MR	S3	Sept- Feb	Al _i -Al _d	0.0141
MR	S1	April- May	Al _i -Ca	0.50399
MR	S2	June- Aug	Al _i -Ca	0.37339
MR	S3	Sept- Feb	Al _i -Ca	0.00009
MR	S1	April- May	Al _i -Ca/Al _d	0.41377
MR	S2	June- Aug	Al _i -Ca/Al _d	0.32486
MR	S3	Sept- Feb	Al _i -Ca/Al _d	0.0382
MR	S1	April- May	Al _i -Q	0.0374
MR	S2	June- Aug	Al _i -Q	0.0703
MR	S3	Sept- Feb	Al _i -Q	0.0063

MR	S1	April- May	Al _d -Ca	0.55308
MR	S2	June- Aug	Al _d -Ca	0.63892
MR	S3	Sept- Feb	Al _d -Ca	0.5074
MPB	S1	April- June	Al _i -pH	0.00447
MPB	S2	July- Aug	Al _i -pH	0.21629
MPB	S3	Sept- Oct	Al _i -pH	0.56
MPB	S1	April- June	Al _i -DOC	0.70785
MPB	S2	July- Aug	Al _i -DOC	0.43036
MPB	S3	Sept- Oct	Al _i -DOC	0.72722
MPB	S1	April- June	Al _i -T _w	0.72067
MPB	S2	July- Aug	Al _i -T _w	0.2356
MPB	S3	Sept- Oct	Al _i -T _w	0.4353
MPB	S1	April- June	Al _i -Al _d	0.67571

MPB	S2	July-	Al _i -Al _d	0.4225
		Aug		
MPB	S3	Sept-	Al _i -Al _d	0.65683
		Oct		
MPB	S1	April-	Al _i -Ca	0.59175
		June		
MPB	S2	July-	Al _i -Ca	0.4214
		Aug		
MPB	S3	Sept-	Al _i -Ca	0.49111
		Oct		
MPB	S1	April-	Al _i -Ca/Al _d	0.51142
		June		
MPB	S2	July-	Al _i -Ca/Al _d	0.03067
		Aug		
MPB	S3	Sept-	Al _i -Ca/Al _d	0.02961
		Oct		
MPB	S1	April-	Al _i -Q	0.1734
		June		
MPB	S2	July-	Al _i -Q	0.0039
		Aug		
MPB	S3	Sept-	Al _i -Q	0.0004
		Oct		
MPB	S1	April-	Al _d -Ca	0.96289
		June		
MPB	S2	July-	Al _d -Ca	0.7685
		Aug		

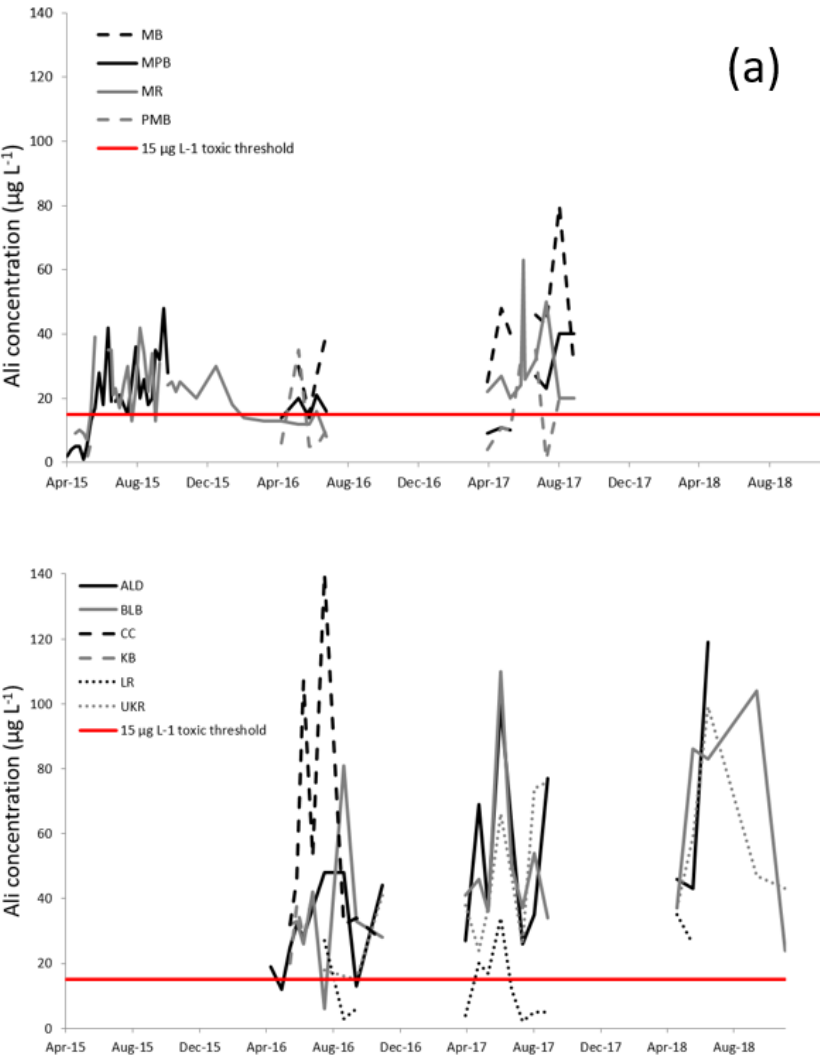
MPB	S3	Sept-	Al _d -Ca	0.72173
	Oct			

Table A6A8 Laboratory detection limit comparison.

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Chemistry		Value		
Parameter	Units	HERC	Maxxam	AGAT
pH	$\mu\text{g L}^{-1}$	n/a	n/a	n/a
DOC	mg L^{-1}	n/a	0.50	n/a
TOC	mg L^{-1}	n/a	n/a	0.5
SO ₄	$\mu\text{g L}^{-1}$	10.00	n/a	2000
Al _d	$\mu\text{g L}^{-1}$	n/a	5.00	5
Al _i	$\mu\text{g L}^{-1}$	n/a	5.00	5
Al _o	$\mu\text{g L}^{-1}$	n/a	5.00	5
Ca _i	$\mu\text{g L}^{-1}$	n/a	100 $\mu\text{g L}^{-1}$	0.1 mg
Ca _d	$\mu\text{g L}^{-1}$	n/a	100	100

Appendix B. Figures



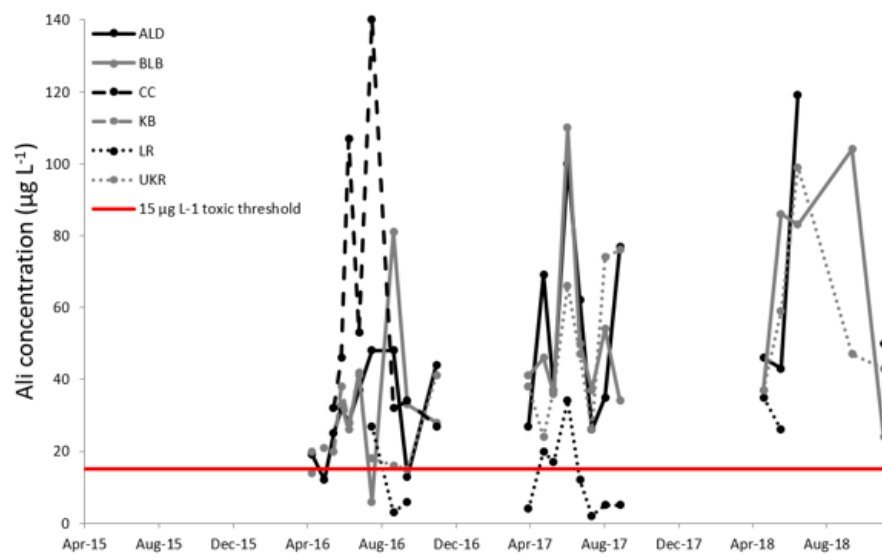
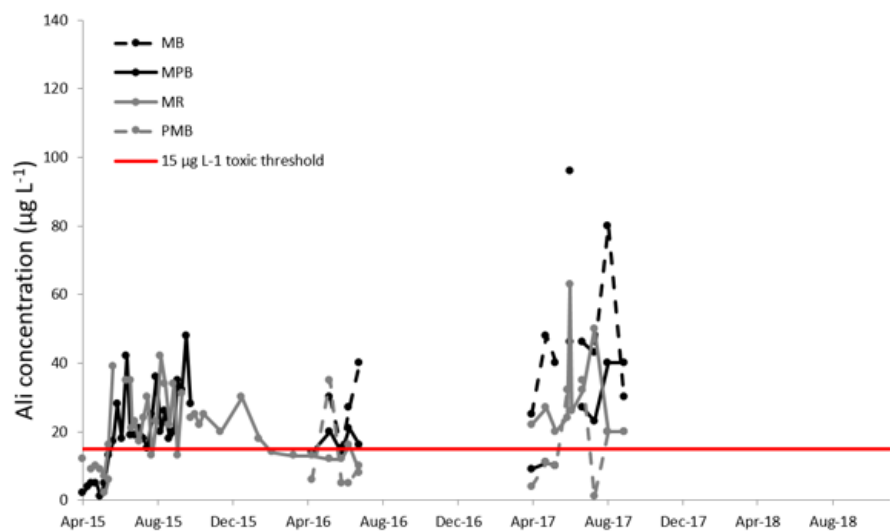


Figure B1 Timeseries of Al_i concentration between 22 April 2015 and 23 November 2018.

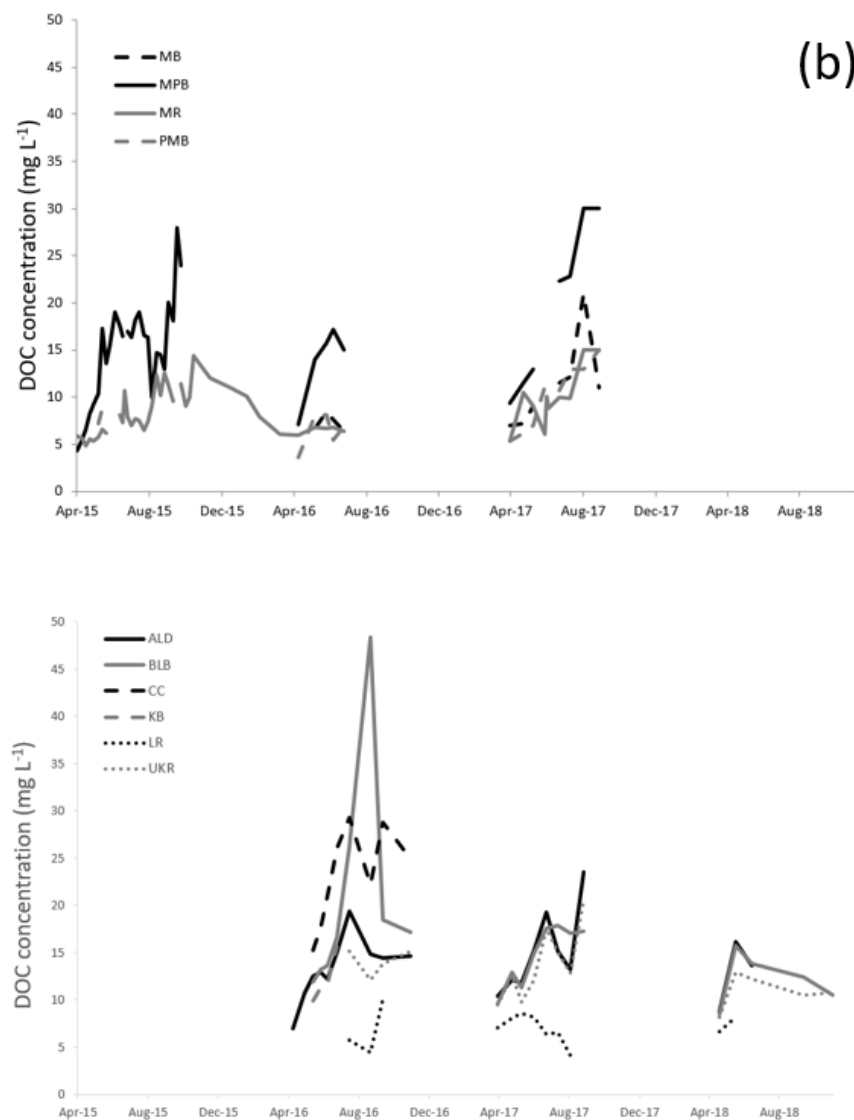


Figure B2 Time series of DOC concentration between 22 April 2015 and 23 November 2018

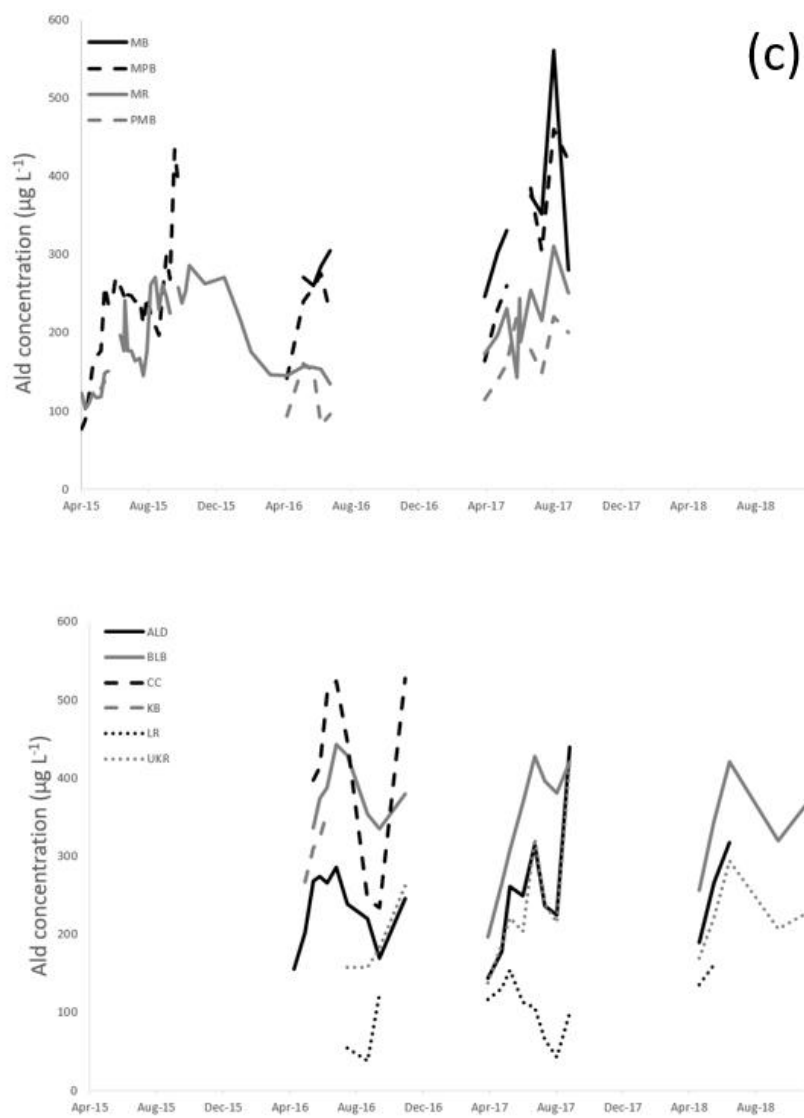


Figure B3 Time series of Al_d concentration between 22 April 2015 and 23 November 2018.

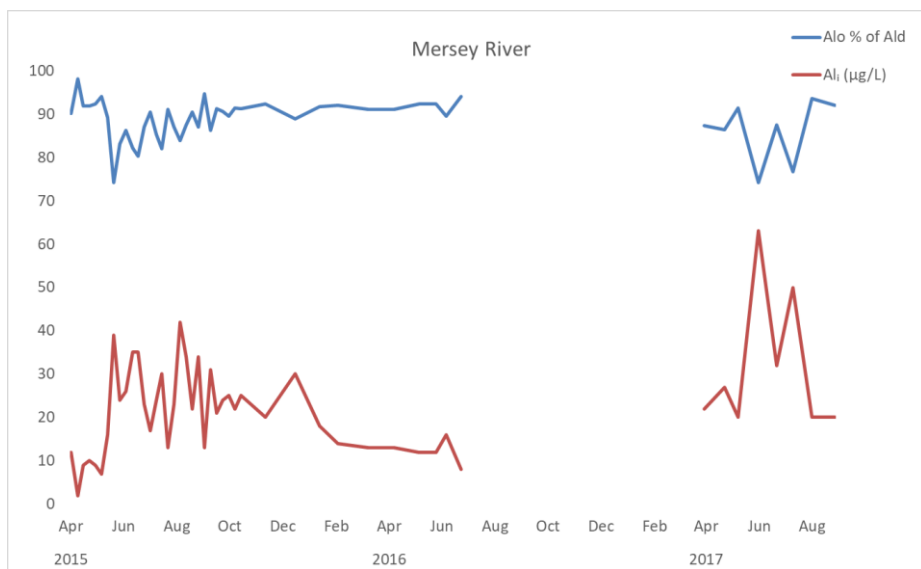


Figure B4

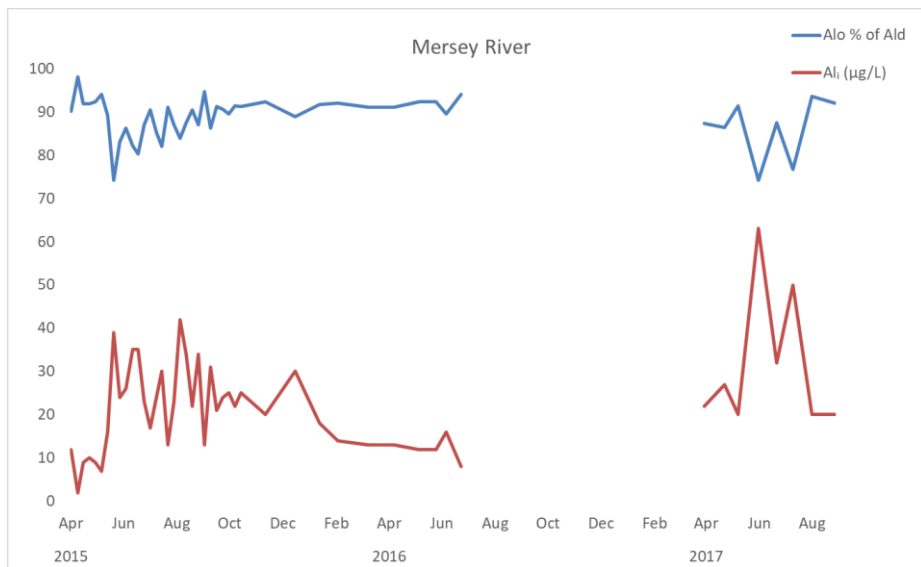


Figure B2 Time series of percentage Al_d comprised of Al_o for MR, compared to absolute value of Al_i in $ug\ L^{-1}$.

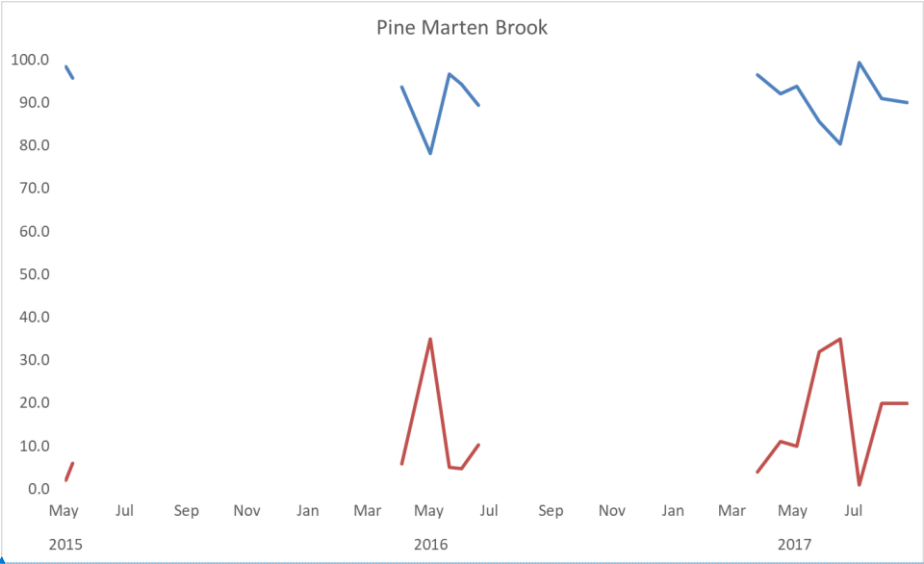


Figure B3 Time series of percentage Al_d comprised of Al_o for PMB, compared to absolute value of Al_i in $ug\ L^{-1}$.

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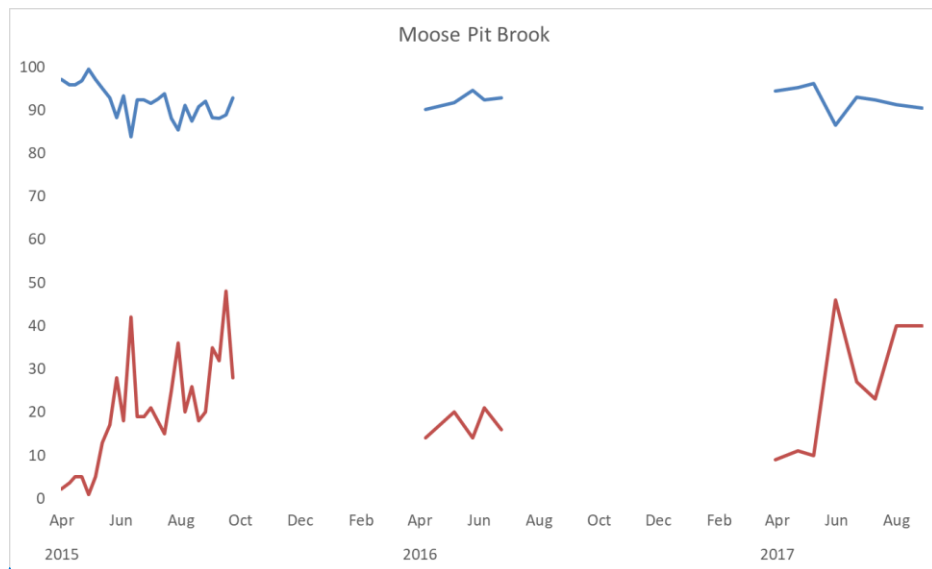


Figure B6B4 Time series of percentage Al_d comprised of Al_o for MPB, compared to absolute value of Al_i in $ug\ L^{-1}$.

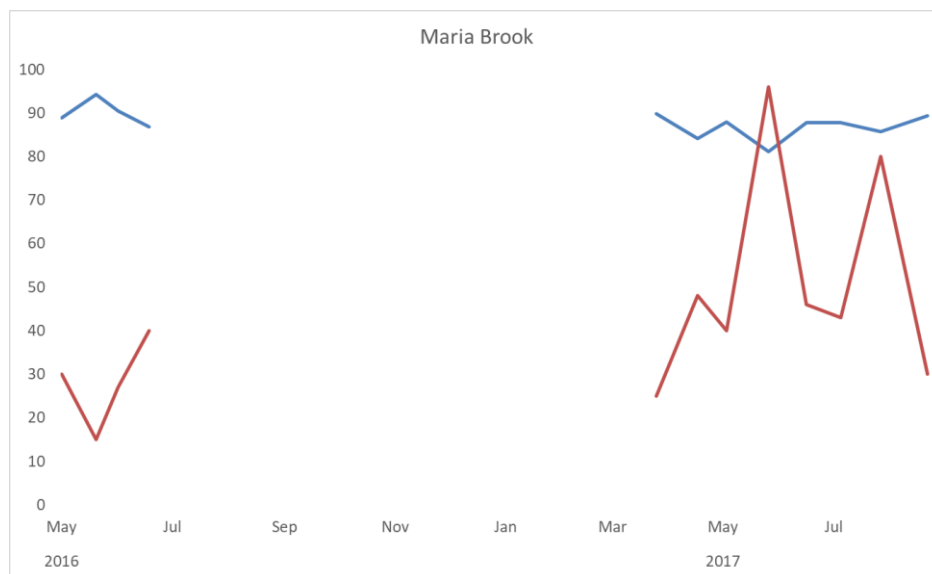
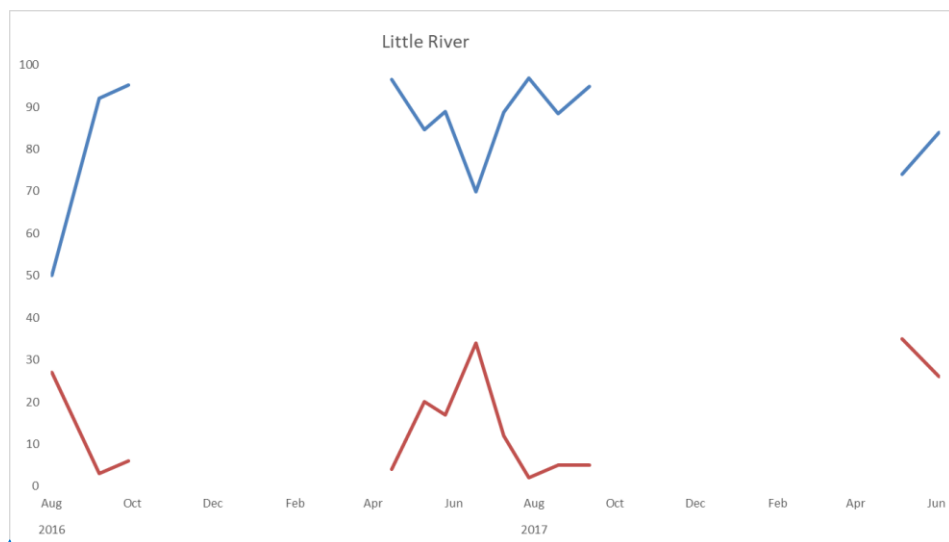
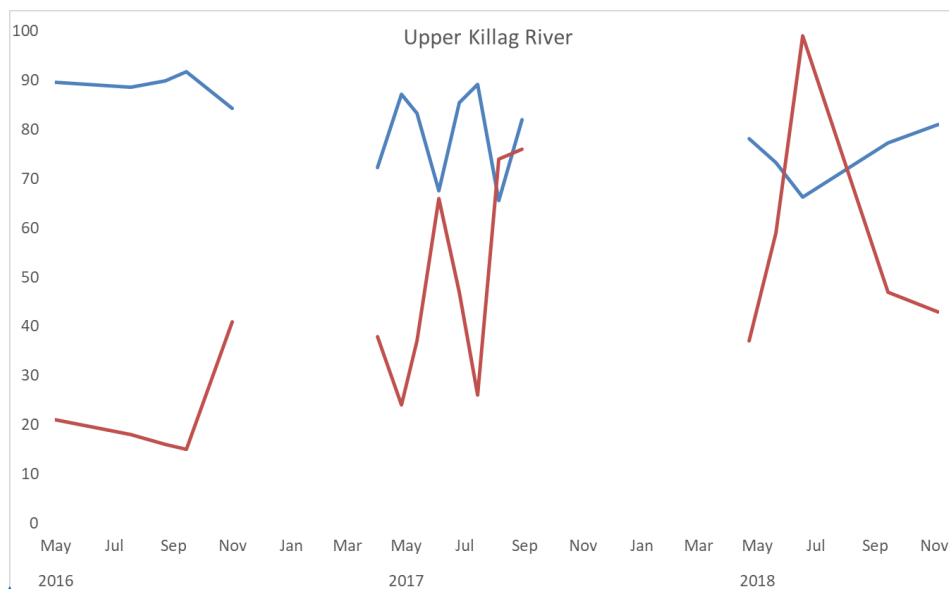


Figure B7B5 Time series of percentage Al_d comprised of Al_o for MB, compared to absolute value of Al_i in $ug\ L^{-1}$.



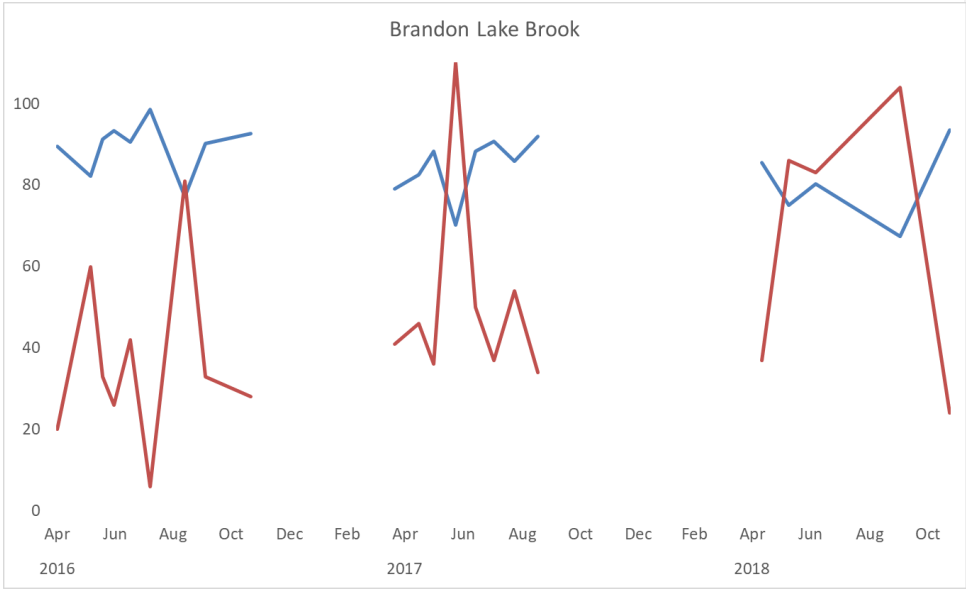
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Figure B8B6 Time series of percentage Al_d comprised of Al_o for LR, compared to absolute value of Al_i in $\mu g L^{-1}$.



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Figure B9B7 Time series of percentage Al_d comprised of Al_o for UKR, compared to absolute value of Al_i in $ug\ L^{-1}$.



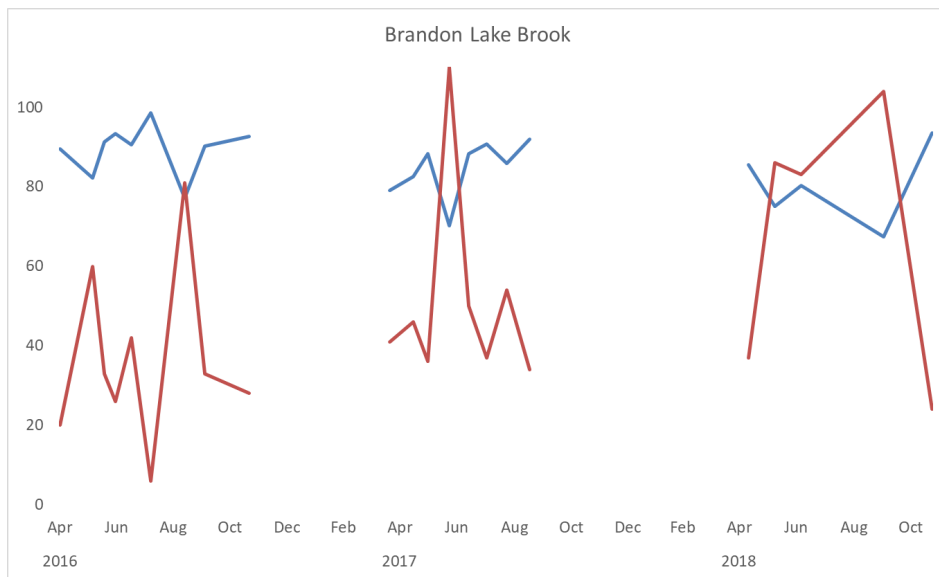
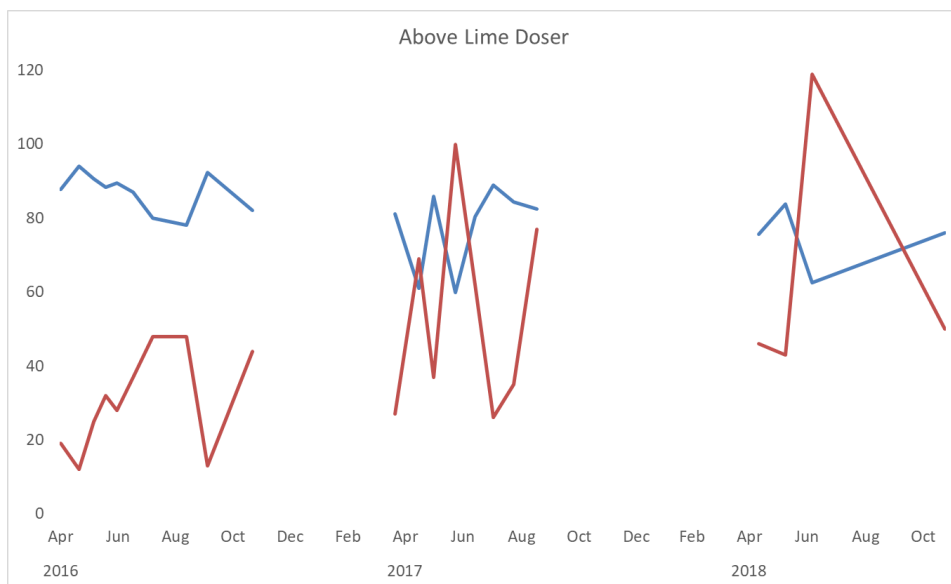


Figure B10B8 Time series of percentage Al_d comprised of Al_o for BLB, compared to absolute value of Al_i in $ug\ L^{-1}$.



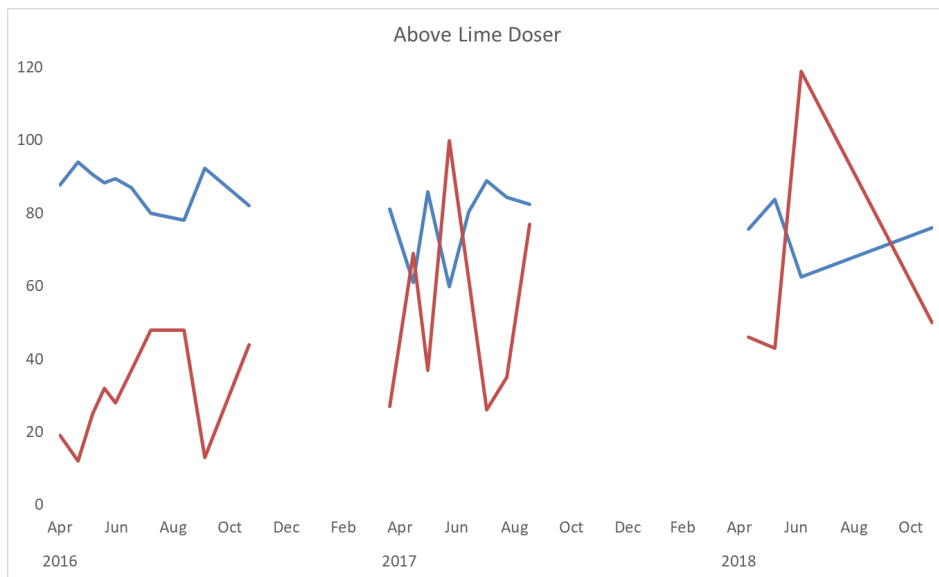
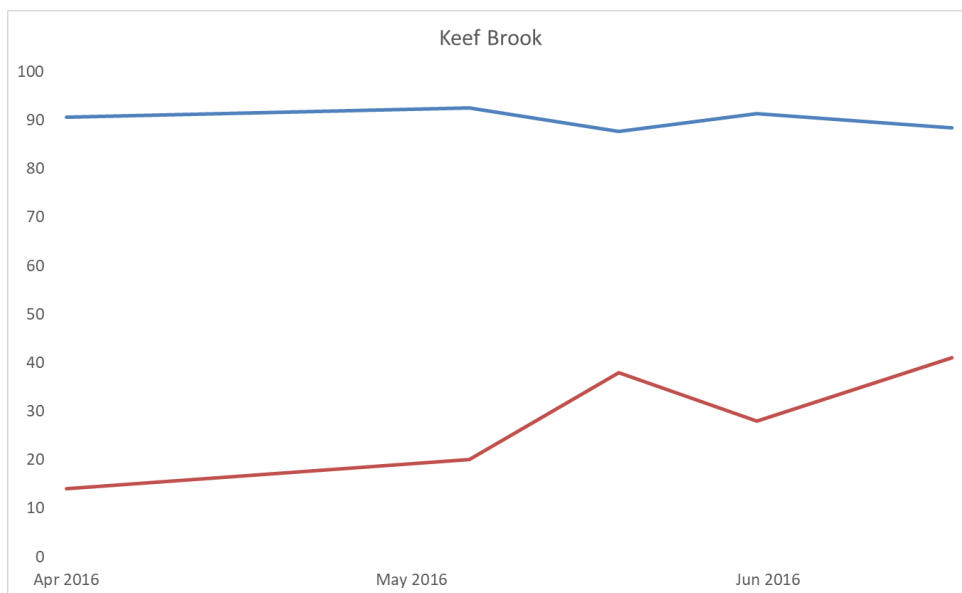


Figure B-1-B9 Time series of percentage Al_d comprised of Al_o for ALD, compared to absolute value of Al_i in $\mu g L^{-1}$.



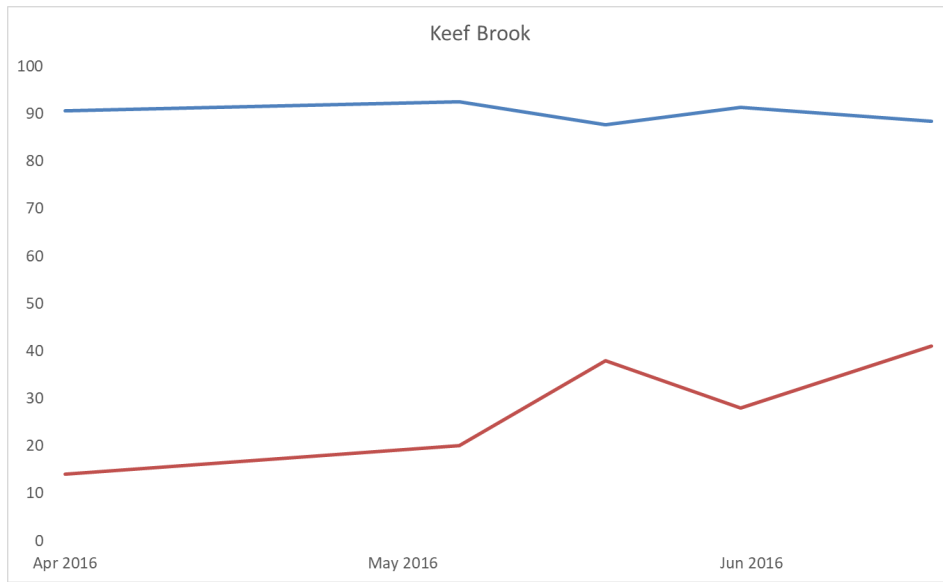
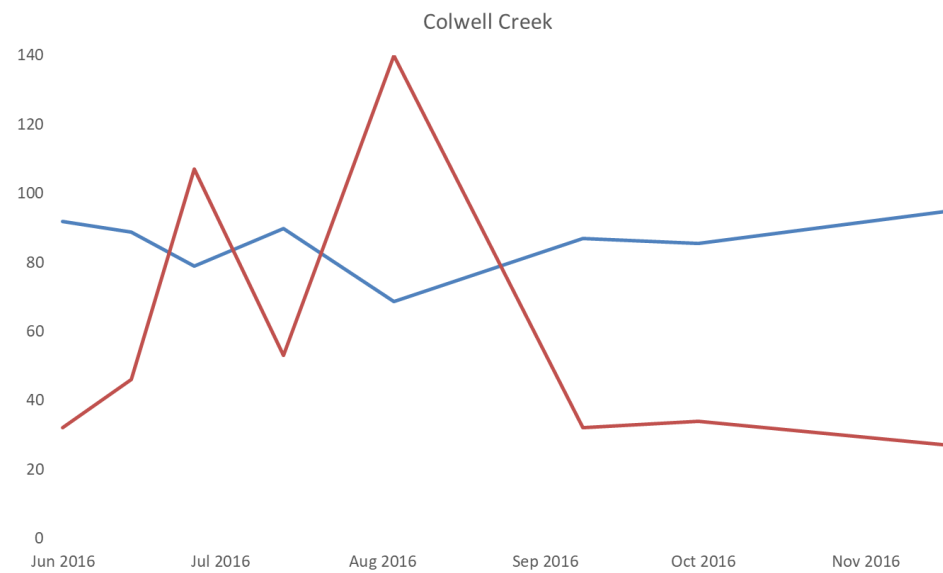


Figure B12B10 Time series of percentage Al_4 comprised of Al_0 for KB, compared to absolute value of Al_1 in $\mu g L^{-1}$.



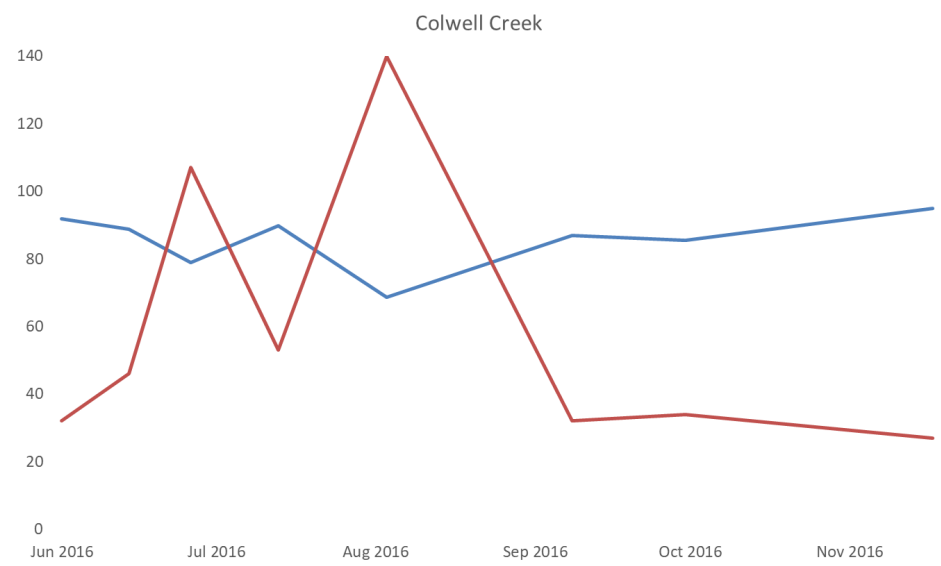
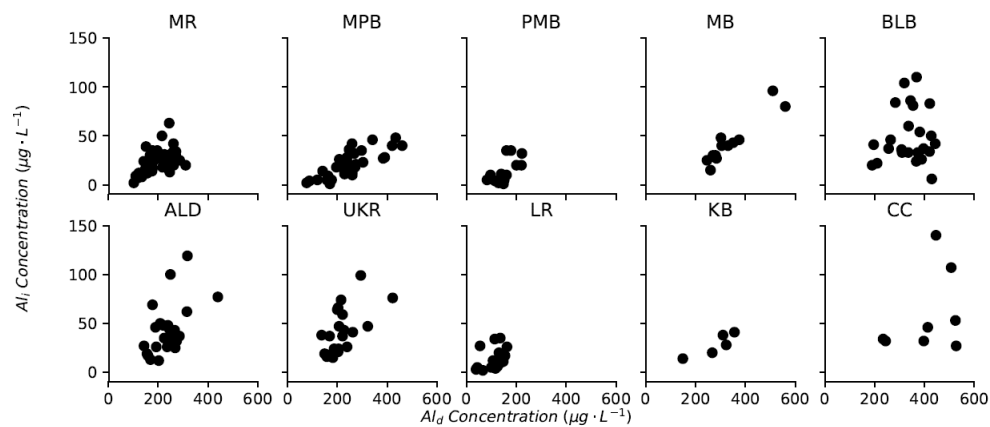


Figure B13B11 Time series of percentage Al_i comprised of Al_o for CC, compared to absolute value of Al_i in $\mu g L^{-1}$

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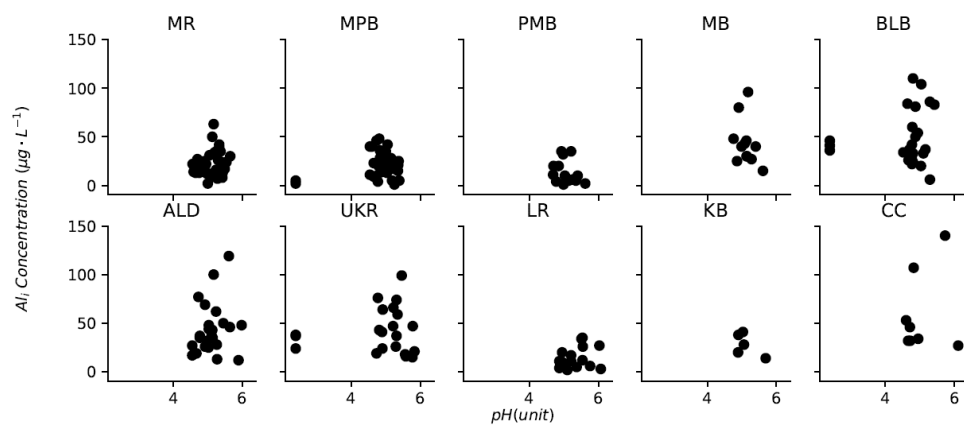


Figure B14B12 Least-squares linear regression of Al_i versus Al_i pH for each study site. One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

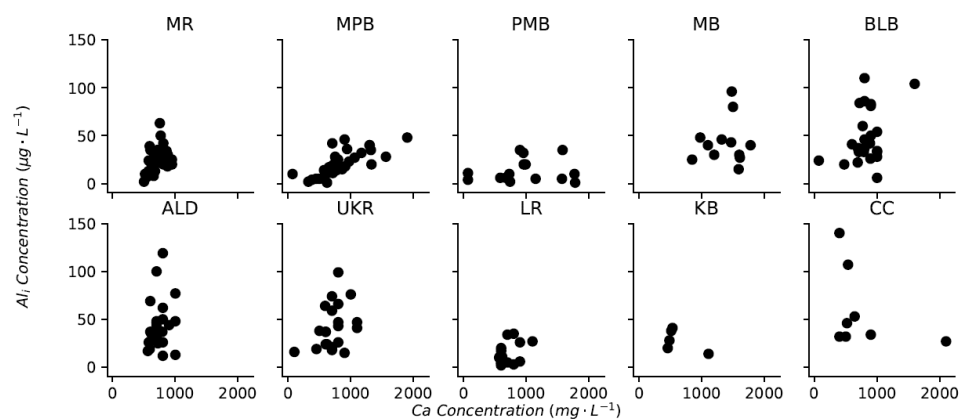


Figure B15

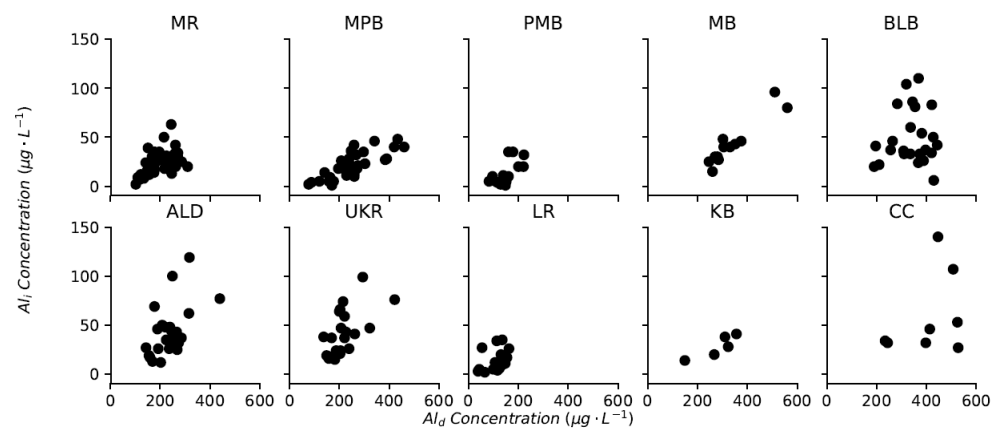


Figure BX Least-squares linear regression of Al_i versus Al_d for each study site. One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

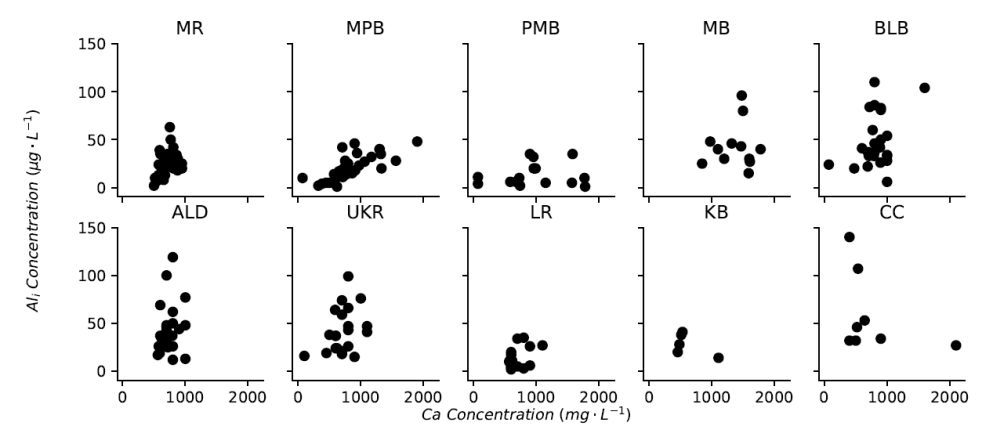


Figure BX Least-squares linear regression of Al_i versus Ca for each study site. One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015). One Ca outlier for KB removed (value: $1110 \mu\text{g L}^{-1}$, date: 29 April 2016).

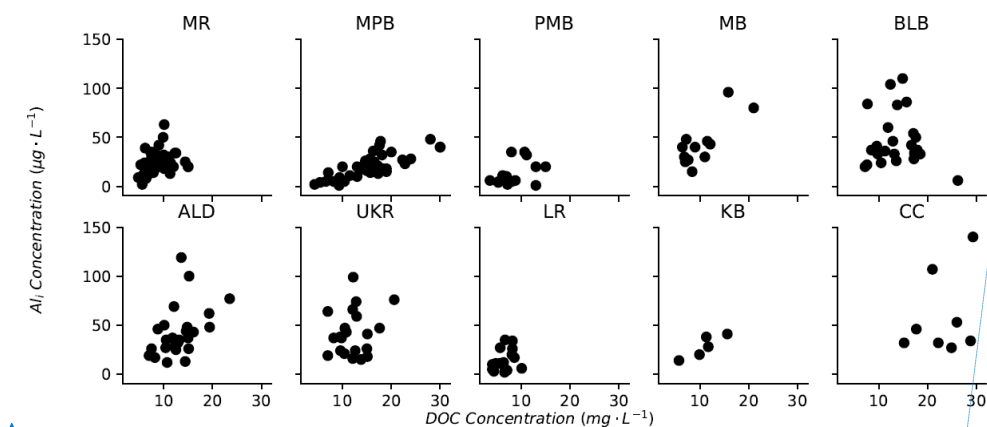


Figure B16BX Least-squares linear regression of Al_i versus DOC for each study site. One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

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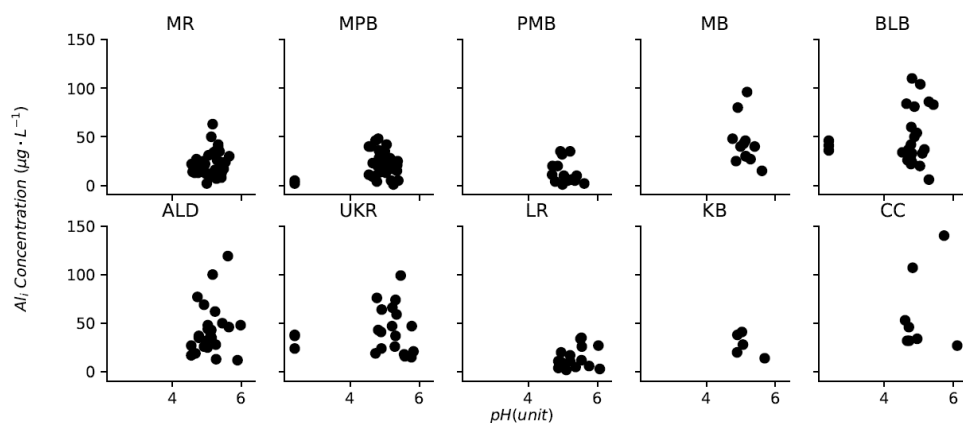


Figure B17 Least-squares linear regression of Al_i versus pH for each study site. One Al_i outlier removed for MR

(value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

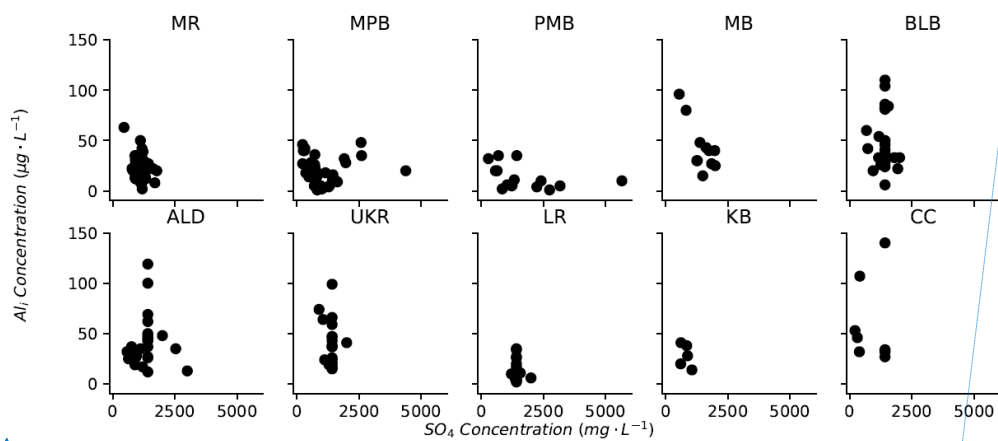


Figure B18BX Least-squares linear regression of Al_i versus SO_4^{2-} for each study site. One Al_i outlier removed for MR

(value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

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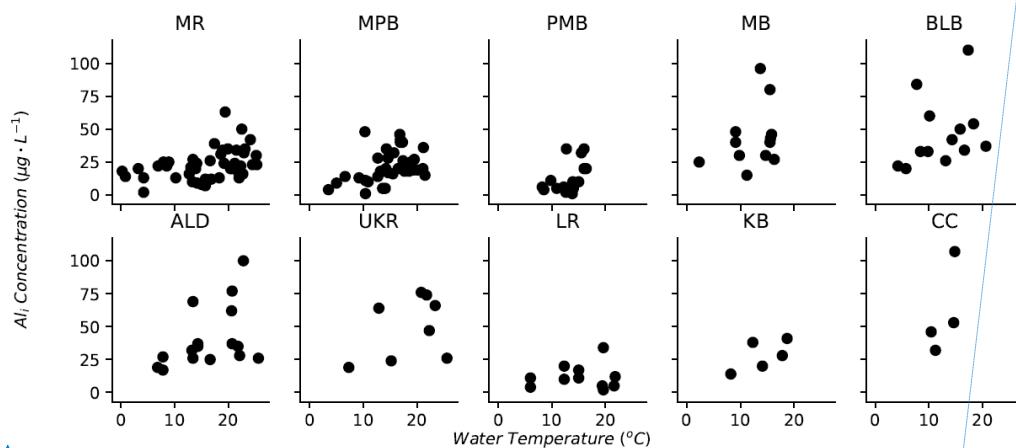


Figure B19BX Least-squares linear regression of Al_i versus T_w for each study site. One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015).

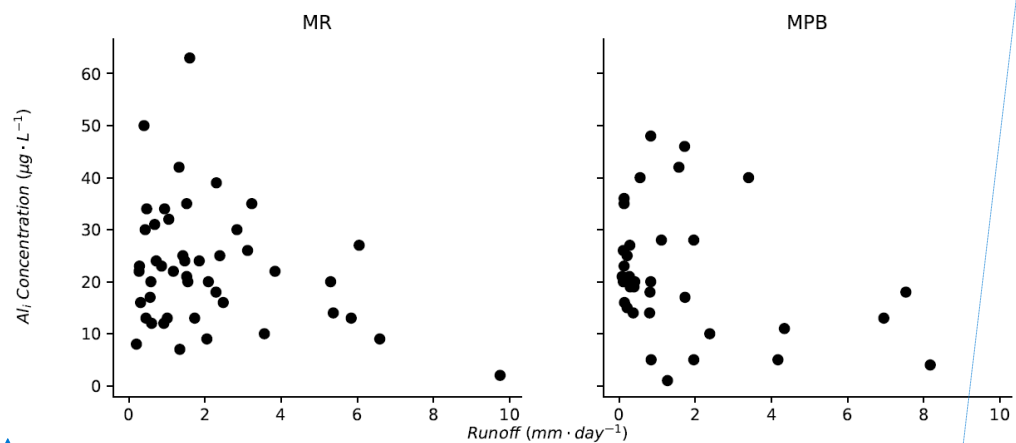


Figure B20BX Least-squares linear regression of Al_i versus runoff for each study site. One Al_i outlier removed for MR (value: $2 \mu\text{g L}^{-1}$, date: 30 April 2015). One runoff outlier for MR removed (value: $17.294 \text{ mm day}^{-1}$, date: 22 April 2015), and one runoff outlier for MPB removed (value: $34.994 \text{ mm day}^{-1}$, date: 22 April 2015).

|

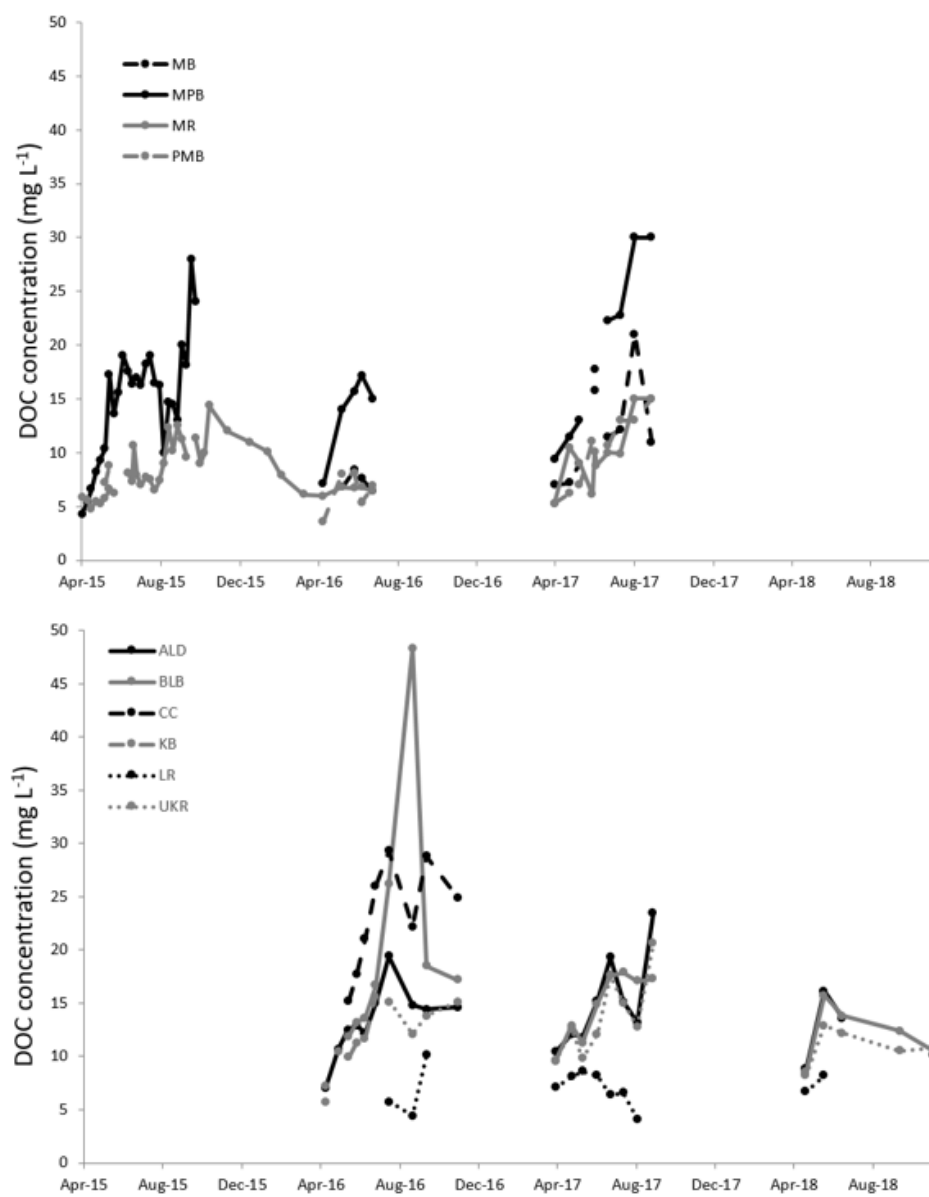


Figure BX Time series of DOC concentration between 22 April 2015 and 23 November 2018

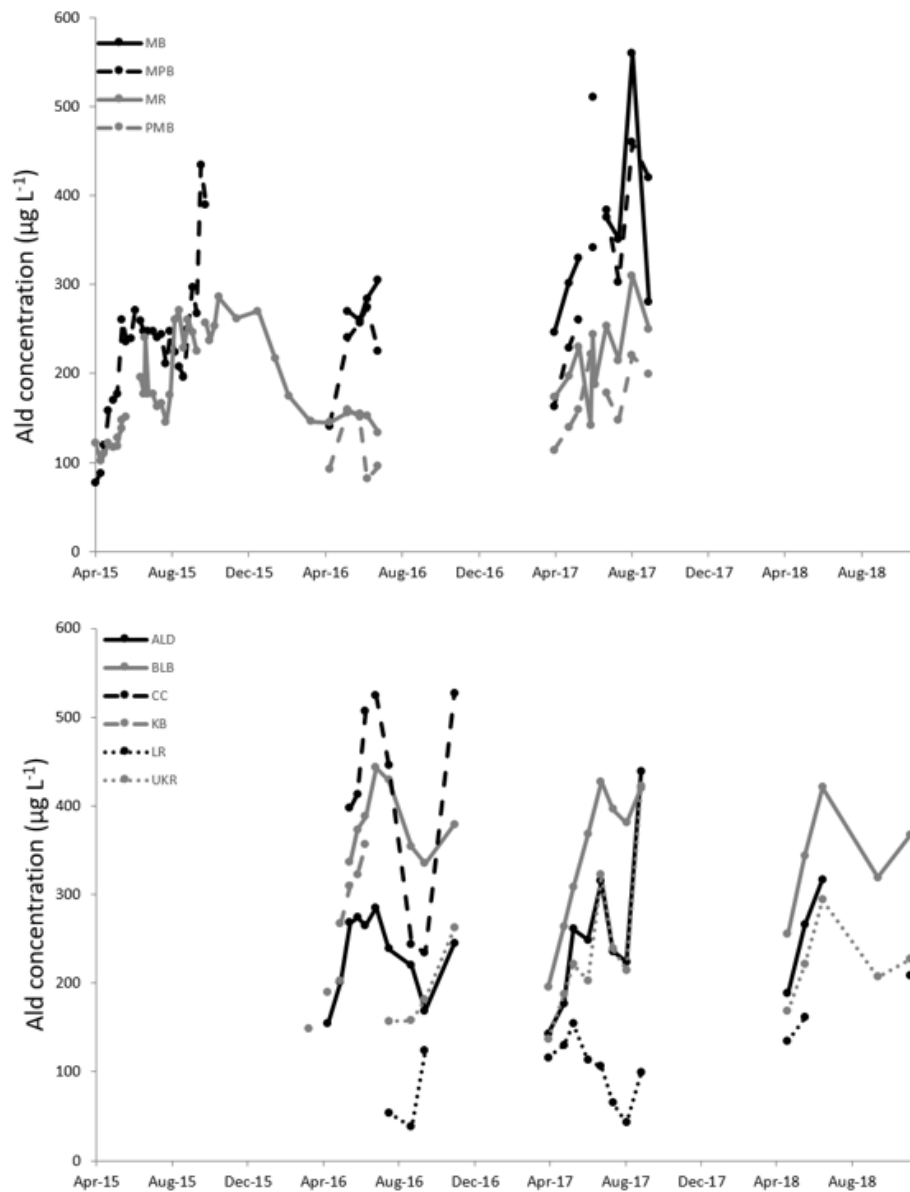


Figure BX Time series of Al_d concentration between 22 April 2015 and 23 November 2018.

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Appendix C. Scripts

C.1. Linear regression

```
"""Linear regression calculation script
```

```
:author: Lobke Rotteveel
```

```
:email: lobke.rotteveel@dal.ca
```

```
"""
```

```
# Import modules
```

```
from scipy import stats
```

```
import pandas as pd
```

```
import csv
```

```
# Import data
```

```
df = pd.read_csv('Input.csv')
```

```
# Run Mann Kendall test on site-variable groups and create table of results
```

```
results = []
```

```
results.append(['site_id', 'variable', 'tau', 'pvalue', 'slope', 'std error of slope'])
```

```
grouped = df.groupby('Site')
```

```
for name, group in grouped:
```

```
chem_groups = [group['Ald'], group['Ca'], group['DOC_TOC'], group['CalibpH'],
group['Tw'], group['RunOff']]
```

```
Ali = group['Ali']
for i in chem_groups:
    pair = {'i':i,'Ali':Ali}
    pair = pd.DataFrame(pair)
    pair = pair.dropna()
    if not pair.empty:
        ken_tau = stats.kendalltau(pair['i'], pair['Ali'])
        slope = stats.linregress(pair['i'], pair['Ali'])
        result_row = [name, i.name, ken_tau.correlation, ken_tau.pvalue, slope.slope,
slope.stderr]
        results.append(result_row)
```

```
with open('LinearRegression_Out.csv', 'w') as f:
    writer = csv.writer(f)
    writer.writerows(results)
```

C.2. Laboratory comparison

```
"""Laboratory result comparison script
:author: Lobke Rotteveel
:email: lobke.rotteveel@dal.ca
```

```

"""

# Import modules

import pandas as pd

import numpy as np

import scipy as sp

from scipy import stats

import warnings

warnings.simplefilter('ignore', np.RankWarning)

# Importing data

df = pd.read_csv('SampDat_CompareInput_LimSur_171105_LR.csv', ',', header=0)

#print (df.head(n=5))

# Run comparisson

with open('SampData_Compare_LimSur.txt', 'w') as f:

    x = df.filter(regex='B_*').columns

    y = df.filter(regex='A_*').columns

    for x_col, y_col in zip(x,y):

        Sig = sp.stats.wilcoxon(df[x_col],df[y_col])

```

```
f.write('x: {}, y: {}, sig:{}'.format(x_col, y_col, Sig))
```

Script for GLMM model

```
#setwd
setwd("C:\\Users\\50nlo\\Documents\\Research\\MS_AliPatterns\\Dat
a")

#load packages
#require(lme4)
require(car)
require(MASS)

#Read in Data
ALiDatDF<-as.data.frame(read.csv("GLMM Input V2.csv",header=T))
ALiDat<-ALiDatDF$Ali ugL

#Exploratory data analysis of ALi data
hist(ALiDat) #data are skewed
```

```

#Test goodness-of-fit of lognormal data

#Normal QQ plot for comparison
qqnorm(ALiDat)
qqline(ALiDat)

qqp(ALiDat, "norm")

#lognormal QQ plot
fit_params <- fitdistr(ALiDat,"lognormal")

quants <-seq(0,1,length=length(ALiDat))[2:138]
fit_quants <- qlnorm(quants,fit_params$estimate['meanlog'],
fit_params$estimate['sdlog'])
data_quants <- quantile(ALiDat,quants)

plot(fit_quants, data_quants, xlab="Theoretical Quantiles",
ylab="Sample Quantiles")
title(main = "Q-Q plot of lognormal fit against data")
abline(0,1)

qqp(ALiDat, "lnorm")

#Gamma QQ plot

```



```

gamma <- fitdistr(ALiDat, "gamma")

qqp(ALiDat, "gamma", shape = gamma$estimate[[1]], rate =
gamma$estimate[[2]])

#Exponential QQ plot
exp <- fitdistr(ALiDat, "exponential")
qqp(ALiDat, "exp", rate = gamma$estimate[[1]])

Site<-ALiDatDF$Site
Season<-ALiDatDF$Season
ALd<-scale(ALiDatDF$ALd ugL)
Ca<-scale(ALiDatDF$Ca ugL)
DOC<-scale(ALiDatDF$DOC mgL)
pH<-scale(ALiDatDF$Calib pH)
SO4<-scale(ALiDatDF$SO4 ugL)
Tw<-scale(ALiDatDF$Tw C)
F<-scale(ALiDatDF$F ugL)
NO3<-scale(ALiDatDF$NO3 ugL)
Dis<-scale(ALiDatDF$Disch m3s)

#ALd and Season cause a singular fit (overfit)
#This means that the effect structure is too complex to be
supported by the data
#ALd is likely due to it being a function of ALi

```

```

#Season is due to limited seasonal data at each site.

Models <- glmer(ALiDat ~ DOC + Tw + Ca+ pH + SO4 + F + NO3 + (1 |
Site), family = gaussian(link = "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ DOC + SO4 + NO3 + (1 | Site), family =
gaussian(link = "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ DOC + NO3 + DOC*NO3+(1 | Site), family =
gaussian(link = "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ DOC +(1 | Site), family = gaussian(link
= "log"),
control=glmerControl(optimizer="bobyqa",optCtrl=list(maxfun=2e5)))
summary(Models)

Models <- glmer(ALiDat ~ Tw +(1 | Site), family = gaussian(link =
"log"))
summary(Models)

```

```

Models <- glmer(ALiDat ~ DOC + Tw +(1 | Site), family =
gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ DOC + Tw + DOC*Tw + (1 | Site), family =
gaussian(link = "log"))
summary(Models)

#pH and Tw causes a singular fit (overfit)
Models <- glmer(ALiDat ~ ALd + DOC + Ca + SO4 + F + NO3 + (1 |
Season), family = gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ ALd + DOC + (1 | Season), family =
gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ ALd + DOC + ALd*DOC + (1 | Season),
family = gaussian(link = "log"))
summary(Models)

Models <- glmer(ALiDat ~ ALd + (1 | Season), family =
gaussian(link = "log"))

```

```

summary(Models)

Models <- glmer(ALiDat ~ DOC + (1 | Season), family =
gaussian(link = "log"))

summary(Models)

Models <- glmer(ALiDat ~ DOC + SO4 + NO3 + (1 | Season), family =
gaussian(link = "log"))

summary(Models)

Models <- glmer(ALiDat ~ DOC + NO3 + DOC*NO3+(1 | Season), family
= gaussian(link = "log"))

summary(Models)

#####For
testing#####
#95% confidence intervals
fm1W <- confint.merMod(Models, method="Wald")

#Check for singularity
tt <- getME(Models,"theta")
ll <- getME(Models,"lower")
min(tt[ll==0])

#Use penalized quazilikelihood to estimate non-normal parameters

```

```

PQL <- glmmPQL(ALiDat ~ ALd + DOC + pH + SO4+ Tw + NO3 + Ca, ~1 |
Site, family = gaussian(link = "log"), verbose = FALSE)

#Fluoride is confounded, remove from model.

summary(PQL)

#At the 5% sig. level, pH, SO4, NO3, and Ca are not significant
effects

#Use penalized quazilikelihood to estimate non-normal parameters
PQL <- glmmPQL(ALiDat ~ ALd + Tw + DOC + ALd*pH + Tw*pH, ~1 |
Site, family = gaussian(link = "log"), verbose = FALSE)

summary(PQL)

resid<-as.matrix(PQL$residuals[,1])

#Explore the model residuals
acf(resid) #good

```

Appendix D. Additional methods

D.1 Laboratory analysis methods

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Samples were analyzed at Maxxam Analytics Laboratory, Health and Environmental Research Centre (HERC), and AGAT Laboratories. Samples from MR, MPB, PMB, MB, KB, and CC were analyzed at Maxxam and HERC labs only. Samples from BLB, ALD, UKR, and LR were analyzed at all three labs.

D1.1 Maxxam Laboratory

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The protocol at Maxxam Laboratory in Bedford, NS, adheres to methods approved by the United States Environmental Protection Agency (US EPA) for identifying trace elements in water (US EPA, 1994) and analyzing samples using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (US EPA, 1998). Cations and anions were analyzed using ICP-MS, while a Continuous Flow Analyzer was used to measure DOC. pH was measured using a standard hydrogen electrode and reference electrode.

D1.2 HERC Laboratory

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SO₄²⁻ samples were analyzed at HERC Laboratory in Halifax, NS, due to lower detection limits at the Maxxam laboratory. Once delivered to the laboratory, samples were filtered using a 0.45 µm glass fiber filter and analyzed using an Ion-Chromatography System (ICS) 5000 Dionex detector.

D1.3 AGAT Laboratory

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Samples collected in the West River, Sheet Harbour area (UKR, ALD, LR, BLB, KB, CC) were analyzed at the AGAT laboratory in Dartmouth, NS. This laboratory holds the

9001:2015 and 17025:2005 International Organization for Standardization accreditations. Cation samples were analyzed using ICP-MS, laboratory pH was measured using a standard hydrogen electrode and reference electrode, and SO_4^{2-} and anions were measured using ICS. Samples analyzed at AGAT were analyzed for total organic carbon (TOC) as opposed to DOC and were analyzed using Infrared Combustion (IR Combustion).

D.2 Data quality assurance and control

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Blanks were used to assess contamination during the Al_0 extraction procedure. Blanks were collected on 10% of samples, taken on arbitrary sampling events. Triple deionized water was collected before passing through filter and column (“Blank Before”), and after (“Blank After”). The triple-deionized water had traces of chemicals below the laboratory detection limits, providing “Not Detectable” results for the Blank Before sample. If chemicals were detected in the Blank After sample, this would have indicated leaching of chemicals from the column.

Duplicates were collected and analyzed for 10% of the samples; on arbitrarily selected sampling events, Al_0 and $\text{Al}_{\text{filtered}}$ or $\text{Al}_{\text{unfiltered}}$, were analyzed twice, independently, by Maxxam laboratory. All laboratories also conducted additional duplicate, blank, reference material, and matrix spike testing, in addition to instrument calibration in adherence to industry standards for quality control and assurance.

Spiked blank samples were conducted using ICP Al standard, 1000 ug/mL, HNO_3 (SCP Science). Three types of measurements were taken. The ‘total’ measurement was an unaltered sample of the diluted solution created above. The ‘dissolved’ measurement was a sample of the above solution passed through a 0.45um PES filter. The ‘organic’ measurement as a sample of the above solution passed through a 0.45um PES filter and a cation exchange column.

The spiked column blanks show that the columns are performing well; the cation exchange column removed virtually all of the Al in the solution (detection limit = 4 ug/L). Additional blanks were conducted in the Dalhousie hydrology lab that was used to prepare the sampling equipment before field collection. The blanks showed no contamination.

To verify that sample analysis results from the Maxxam/HERC laboratory combination were comparable to AGAT, three sets of duplicate samples were collected for ALD, BLB, UKR, and LR (19 April 2017, 14 May 2017, and 30 May 2017) and analyzed by both laboratories. Laboratory results were compared using Wilcoxon Rank Sum statistical test in Python 3.6.5 using the SciPy Stats module (version 0.19) (Appendix C.2). Results indicated a significant difference in pH values between laboratories ($T = 1$, $p = 0.04$), therefore, statistical analysis on pH data was conducted on the calibrated YSI Pro Plus sonde field data. Al_o , $Al_{filtered}$, and $Al_{unfiltered}$ results were found to be comparable between laboratories ($T = 8.5$, $p = 0.674$; $T = 5.0$, $p = 0.249$; and $T = 8.0$, $p = 0.600$, respectively). After adjusting for detection limits (Table A6), Ca results were also found to be comparable between laboratories ($T = 4.0$, $p = 0.173$). However, due to the large difference in SO_4^{2-} detection limits between HERC and AGAT ($10 \mu g L^{-1}$ and $2 mg L^{-1}$, respectively), results for SO_4^{2-} are not comparable between laboratories. Lastly, organic carbon analyzed at Maxxam was analyzed for DOC, while AGAT analyzed for TOC, therefore these results cannot be compared. For dates where duplicate data is present, AGAT data was used to maintain data source consistency, apart from SO_4^{2-} data, for which HERC data was used due to superior detection limits. Analysis for BLB and ALD transitioned from Maxxam to AGAT 19 April 2017 and consequently DOC is approximated as TOC for these two sites after this date.

The YSI Pro Plus sonde was calibrated within 36 hours of in-stream data collection.

D.3 Toxic thresholds of Al_i

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Identified toxic thresholds of Al_i for *Salmo salar* vary in the literature. Based on toxicological and geochemical studies on Al and *Salmo salar*, the EIFAC suggested an Al_i toxic threshold of 15 ug L⁻¹ for Atlantic salmon in freshwaters for pH between 5.0 and 6.0, and 30 ug L⁻¹ in pH <5 (Howells et al., 1990). The lower threshold at higher pH is to account for the increased fraction in the Al(OH)₂⁺ species. At pH > 6, the toxic effects of Al_i to *Salmo salar* are considered negligible, and toxic effects are dominated by other dissolved and precipitated forms (Gensemer et al., 2018), due to the decreased solubility of Al at pH > 6 (Dennis and Clair 2012). However, in colder rivers, the pH-toxicity threshold may be higher, closer to pH 6.5 (Lydersen, 1990). 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).

D.4 Calibration of pH measurements

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In situ pH measurements were taken using a YSI Pro Plus sonde and confirmed with a YSI Ecosense pH Pen. It was found that measurements taken with the YSI Pro Plus sonde deviated from the YSI Ecosense Pen, which is known to measure pH accurately (0.47 ± 0.44 pH units below in-stream pH as measured by YSI Ecosense Pen). Therefore, a calibration curve was created based on simultaneous side-by-side measurements of both instruments (n = 69 pairs) and the in situ pH data were adjusted accordingly (Eq. 1).

$$YSI\ Ecosense\ Pen\ pH = 0.595(Pro\ Plus\ pH) + 2.3868 \quad (1)$$

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