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Ionic aluminium concentrations exceed thresholds for aquatic health in Nova Scotian rivers

Shannon Sterling[1], Sarah MacLeod[2], Lobke Rotteveel[1], Kristin Hart[1], Thomas A. Clair[1], Edmund A. Halfyard[3]

[1] Sterling Hydrology Research Group, Department of Earth Sciences, Dalhousie University, Halifax, Nova Scotia, Canada

[2] Coastal Action, Lunenburg, Nova Scotia, Canada

[3] Nova Scotia Salmon Association, Chester, Nova Scotia, Canada

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

Abstract. Cationic aluminium species are toxic to terrestrial and aquatic life. Despite decades of acid emission reductions, accumulating evidence shows that freshwater acidification recovery is delayed in locations such as Nova Scotia, Canada. Further, 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 in ten streams in acid-sensitive areas of Nova Scotia over a four-year time period. We observe widespread and frequent occurrences of Al_i concentrations that exceed toxic thresholds (>15 µg L^{-1}). Al_i patterns appear to be driven by known Al_i drivers - pH, dissolved organic carbon, dissolved aluminium, and calcium - but the dominant driver and temporal patterns vary by catchment. Our results demonstrate that elevated Al_i remains a threat to aquatic ecosystems. For example, our observed Al_i concentrations are potentially harmful to the biologically, economically, and culturally significant Atlantic salmon (*Salmo salar*).

1 Introduction

Freshwater acidification caused elevated concentrations of cationic aluminium (Al_i) at the end of the last century that led to increased freshwater and marine mortality and, ultimately, the extirpation of native Atlantic salmon (*Salmo salar*) populations in many rivers (Rosseland et al., 1990), for example in Scandinavia (Henriksen et al., 1984, Hesthagen and Hansen, 1991), the eastern USA (Monette and McCormick, 2008, Parrish et al., 1998), and Nova Scotia, Canada (Watt, 1987). Following reductions in anthropogenic sulfur emissions in North America and Europe since the 1990s, many rivers showed steady improvements in annual average stream chemistry (Evans et al., 2001, Monteith et al., 2014, Skjelkvåle et al., 2005, Stoddard et al., 1999, Warby et al., 2005), including reduced concentrations of Al_i in the USA (Baldigo and Lawrence, 2000, Buchanan et al., 2017, Burns et al., 2006) and Europe (Beneš et al., 2017, Davies et al., 2005, Monteith et al., 2014). However, recent evidence highlights delayed recovery from acidification in some areas (Houle et al., 2006, Warby et al., 2009, Watmough et al., 2016), including SWNS (Clair et al., 2011), raising concerns about elevated Al_i concentrations.

Aluminium (Al) toxicity can be caused by both precipitated and dissolved forms in circumneutral waters (Gensemer et al., 2018); however, the cationic species of Al, such as Al^{3+}, $Al(OH)_2^{1+}$, and $Al(OH)^{2+}$ are considered to be the most labile and toxic to salmonids as they bind to the negatively charged fish gills causing morbidity and mortality through suffocation (Exley et al., 1991), reducing nutrient intake at gill sites, and altering blood plasma levels (Nilsen et al., 2010). Further, the effects of sub-lethal exposure to freshwater Al elicits osmoregulatory impairment (Monette and McCormick, 2008, Regish et al., 2018) which reduces survival in the hypertonic marine environment (McCormick et al., 2009, Staurnes et al., 1996). Elevated concentrations of Al_i are also toxic to other freshwater and terrestrial organisms (Boudot et al., 1994, Wauer and Teien, 2010), such as frogs and aquatic birds (Lacoul et al., 2011).

Al speciation varies with pH (Helliweli et al., 1983, Lydersen, 1990), where positive Al species dominate over neutral and negative species below pH 6.3 at 2 °C and below pH 5.7 at 25 °C (Lydersen, 1990), with the most toxic Al species, $Al(OH)_2^{+1}$ (Helliweli et al., 1983) dominating Al speciation between pH 5.0–6.0 at 25 °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 gibbsite (Schofield and Trojnar, 1980). Additionally, 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 organic carbon (DOC), which occludes Al_i through the formation of organo-Al complexes (Al_o) that are nontoxic to fish (Erlandsson et al., 2010).

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 Al_i concentrations are negatively correlated with pH (Campbell et al., 1992, Kopáček et al., 2006). 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 (Fernandez et al., 2003) and chronic acidification thus shifts available exchangeable cations in the soil from Ca and magnesium (Mg) towards Al (Schlesinger and Bernhardt, 2013, Walker et al., 1990). Higher concentrations of DOC in soil water increase the release of Al through two mechanisms: 1) as an organic acid, DOC decreases soil pH, thus increasing Al release (Lawrence et al., 2013), and 2) by forming organic complexes with Al_i it maintains a negative Al concentration gradient from the cation exchange sites to the soil water, increasing rates of Al release (Edzwald and Van Benschoten, 1990, Jansen et al., 2003). Field studies confirm Al concentrations to be positively correlated with DOC (Campbell et al., 1992, Kopáček et al., 2006) although at higher concentrations of DOC, Al may be organic-complexed and less toxic to aquatic organisms (Witters et al., 1990).

Once mobilized in soil waters, export of Al_i to drainage waters requires anions to maintain charge balance. Storm events have been shown to increase Al_i export due to added anions (e.g., Cl^-, SO_4^{2-}, F^-), and from the movement of flow paths to shallower soil horizons where more Al may be available for transport. For example, from 1983 to 1984, Al concentrations for the River Severn in Wales increased ten-fold during the stormflow peak compared to the baseflow (Neal et al., 1986).

However, the association of increased Al_i concentrations with storm flow is not consistent in the literature (DeWalle et al., 1995, McKnight and 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 spring and winter, correlated with flow peaks, 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 concentrations were found to be higher in the summer such as in Virginia, USA (Cozzarelli et al., 1987). If the timing of peak Al_i concentrations coincides with sensitive stages of aquatic organisms, the potential for large biological impacts is high.

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, here abbreviated as NS_A (see Clair et al., 2007), with once-famous wild Atlantic salmon populations, were heavily impacted by acid deposition at the end of the last century, which originated from coal burning in central Canada and Northeastern USA (Hindar, 2001, Summers and Whelpdale, 1976). NS_A catchments are particularly sensitive to acid deposition due to base cation-poor and slowly weathering bedrock that generates thin soils with low acid neutralizing capacity (ANC), extensive wetlands, and episodic sea salt inputs (Clair et al., 2011, Freedman and Clair, 1987, Watt et al., 2000, Whitfield et al., 2006). A 2006 fall survey found that Al_i concentrations in NS exceeded the 15 μg L^{-1} toxic threshold suggested by the European Inland Fisheries Advisory Council (EIFAC) for aquatic health in seven of 42 rivers surveyed (Dennis and Clair, 2012). However, apart from this study, little is known about the regional extent and patterns of Al_i. Here, we aim to increase our understanding of current Al_i spatial and temporal patterns in relation to toxic thresholds, and to identify potential drivers by conducting a four-year survey of Al_i concentrations in ten streams across acid-sensitive areas of NS, Canada.

2 Materials and methods

2.1 Study area

We surveyed Al_i concentrations at ten study catchments in NS_A, ranging from headwater to higher-order systems: Mersey River (MR), Moose Pit Brook (MPB), Pine Marten Brook (PMB), Maria Brook (MB), Brandon Lake Brook (BLB), above the West River lime doser (ALD), Upper Killag River (UKR), Little River (LR), Keef Brook (KB), and Colwell Creek (CC) (Table 1, Fig. 1 and 2). Our study catchments are predominantly forested, draining slow-weathering, base-cation poor bedrock, producing soils with low ANC (Langan and Wilson, 1992, Tipping, 1989). The catchments also have relatively high DOC concentrations (Ginn et al., 2007) associated with the abundant wetlands in the region (Clair et al., 2008, Gorham et al., 1986, Kerekes et al., 1986).

2.2 Data collection and analysis

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

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

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

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

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

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

3 Results and discussion

3.1 Patterns of Al_i

Al_i concentrations exceed toxic levels (15 ug L^{-1}) at all sites during the study period (Table A2). Sites in the eastern part of the study area have the highest proportion of samples exceeding threshold levels, including one site with 100% of samples in exceedance (Fig. 1). Mean Al_i concentrations across all sites range from 13–60 ug L^{-1} (Table 1), with the highest mean concentrations also occurring in the eastern part of the study area (Fig. 2). Al_i concentrations exceed 100 ug L^{-1} (approximately seven times the threshold) at three sites (Table A2). 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). Our Al_i concentrations are consistent with the 6.9–230 ug L^{-1} range of Al_i concentrations measured across NS by Dennis and Clair (2012) and are higher than concentrations measured in Norway from 1987–2010 (5–30 ug L^{-1}) (Hesthagen et al., 2016).

The percent of Al not complexed by DOC (% Al_i/Al_d) ranges from a minimum of 0.6% to a maximum of 50%, with a median value of 10.7%, across all sites. These findings are similar to those found NS by Dennis and Clair (2012) of the proportion of Al_i in total aluminum (Al_t) (min. = 4%, max. = 70.1%, med. = 12.4%), and less than those found by Lacroix (1989) (over 90 % Al_o/Al_d). 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., 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

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. 3, 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 (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. 3, Table A4). The positive relationship between Ca and Al_i is the opposite of expectations. 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 is significantly and negatively correlated with Al_i at one site MPB (Fig. 3, Table A4). 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.

We did not observe the negative association between pH and Al_i observed in previous studies (Campbell et al., 1992, Kopáček et al., 2006). pH is negatively correlated with Al_i in four out of ten sites, but none of these relationships are statistically significant (Fig. 3, Table A4). We did observe a statistically significant positive relationship between pH and Al_i/Al_d; thus it seems that pH may play a more important role in determining the proportion of different Al species rather than the absolute value of Al_i present in streamwaters.

F^- has also been found to be a complexing agent that affects the speciation of Al at low pH levels and relatively high concentrations of F^- (>1 mg L^{-1}) (Berger et al., 2015). The concentrations of F^- at the study sites are mostly below this threshold (mean across all sites = 0.045 mg L^{-1}); however, there is still a significant positive effect of F^- on Al_i concentrations across at two sites (KB, MPB) (Fig. 3, Table A4). NO_3^- and SO_4^{2-} are also potential complexing ligands of Al; however, we did not observe any correlation between Al_i and either of these parameters, except for a significant negative correlation between SO_4^{2-} and Al_i at MB.

The highest concentrations of Al_i observed (> 100 ug L^{-1}) often occurred in early summer (late June or early July in 2016-2018) when Al_d, Ca, and DOC concentrations had not yet reached their annual peak (Table A2). The spring/summer extreme events occurred among the first exceptionally warm days (> 21 °C) of the year, in dry conditions, and when the proportion of Al_o/Al_d was low (lowering to approximately 60-70% from higher levels of around 80-90%) (Figs. B4-B13). pH was not abnormally low during these events (ranging from 4.8 to 6.13), Ca concentrations were low (less than or equal to 800 µg L^{-1}) and DOC concentrations ranged from 15–21 mg L^{-1}. The observed peak in Al_i concentrations during times of lower discharge contrasts with studies that found higher Al_i concentrations during higher flow (Campbell et al., 1992, Kopacek et al., 2000, Neal et al., 1986, Rodushkin et al., 1995). Further research is required to test hypotheses on why high Al_i coincides with high DOC and low flow periods.

3.3 Possible seasonal groupings of Al_i in NS_A

In the two sites with the most samples, MPB and MR, groupings of data are visible that are temporally contiguous, potentially indicating seasonally-dependent Al_i behavior (Fig. 4). This is supported by stronger linear correlations (r^2) among variables when grouped by “season” (Table 2); for example, for the correlation between pH and Al_i at MR, r^2 improves from 0.02 for year-round data (Fig. B17) to up to 0.78 in season 1 (Fig. 4). The transition dates between the seasons are similar for the two catchments, but not the same (Table A2), and vary by year. Here we propose initial characterization of the potential "seasons"; more research is needed to test these hypotheses on seasonal divisions and their drivers using larger datasets and Generalized Linear Mixed Model analysis to test for statistical significance among the potential seasonal groupings.

Season 1 (approximately April/May) is coincident with snow-melt runoff and is characterized by relatively low concentrations of Al_i (2-46 ug L^{-1}), low pH (4.5-5.3), and lower concentrations of most constituents, including DOC, and cold temperatures (4 ^oC). During this season, Al_i is strongly coupled with pH, DOC, Al_d and Ca in MR, but less so in MPB. A possible explanation is that season 1 is dominated by snowmelt hydrology in which cation exchange between soil and discharge occurs less efficiently, which has been attributed to ice and frozen soil potentially limiting water contact time with soil (Christophersen et al., 1990). 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. 4). 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.

3.4 Ecological implications

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

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

4 Conclusions

Our study reveals that widespread and persistent toxic concentrations of Al_i in NS_A freshwaters pose a risk to aquatic, and potentially terrestrial, life. Previously, high DOC concentrations were presumed to protect aquatic life against Al_i; our study shows that this presumption does not hold.

Our results suggest that the recent 88 to 99% population decline of the Southern Uplands Atlantic salmon population in NS_A (Gibson et al., 2011) may be partially attributable to Al_i, in contrast to earlier studies which downplayed the role of Al_i in Atlantic salmon mortality (Bowlby et al., 2013, Lacroix and Townsend, 1987). These high Al_i concentrations in NS_A highlight the need to increase our understanding of the influence of Al_i on both terrestrial and aquatic ecosystems, and its implications for biodiversity.

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

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

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Data availability

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

Author contribution

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

Competing interests

The authors declare that they have no conflict of interest.

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Tables

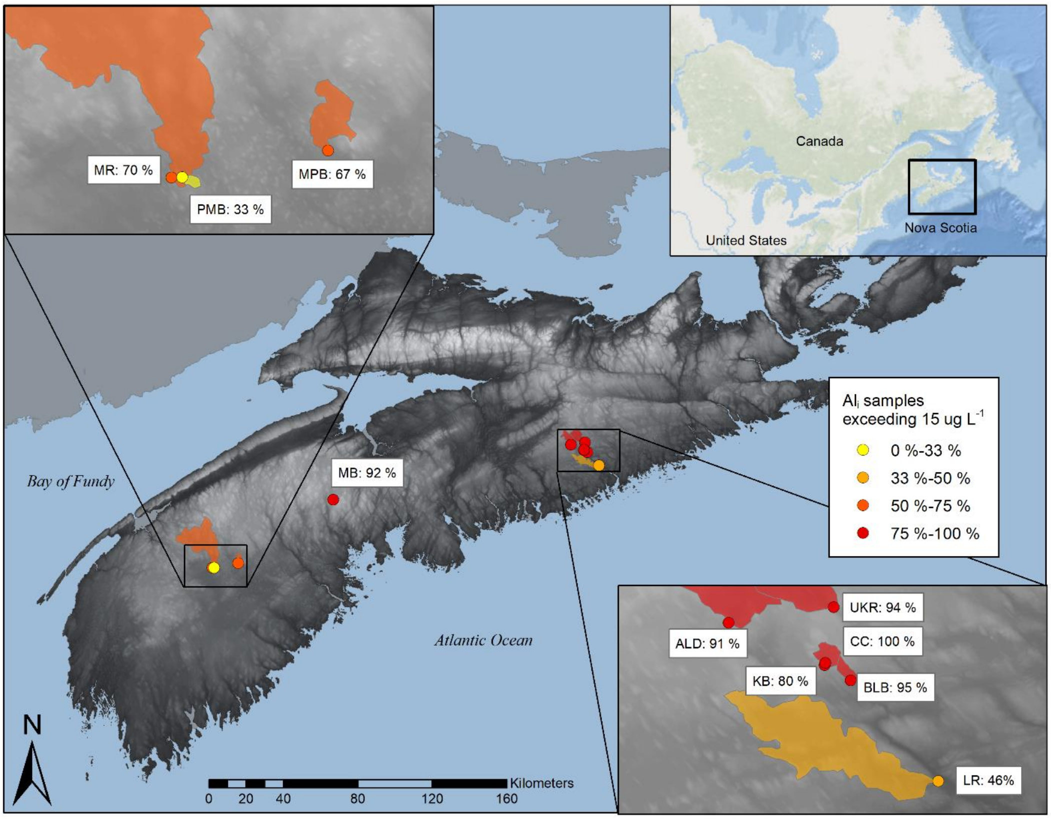
Table 1 Study site characteristics. “n” refers to the number of sampling events. Number in brackets after the mean concentration is the standard deviation. One Al_i outlier removed for MR (value: 2 µg·L^{-1}, date: 30 April 2015). pH is calibrated using the method outlined in Appendix D.4.

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

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

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

542 # Figures



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544 Figure 1. Study site locations showing proportion of samples when Al_i concentrations exceeded the 15 µg
545 L^{-1} toxic threshold. For additional site details, refer to Table 1.

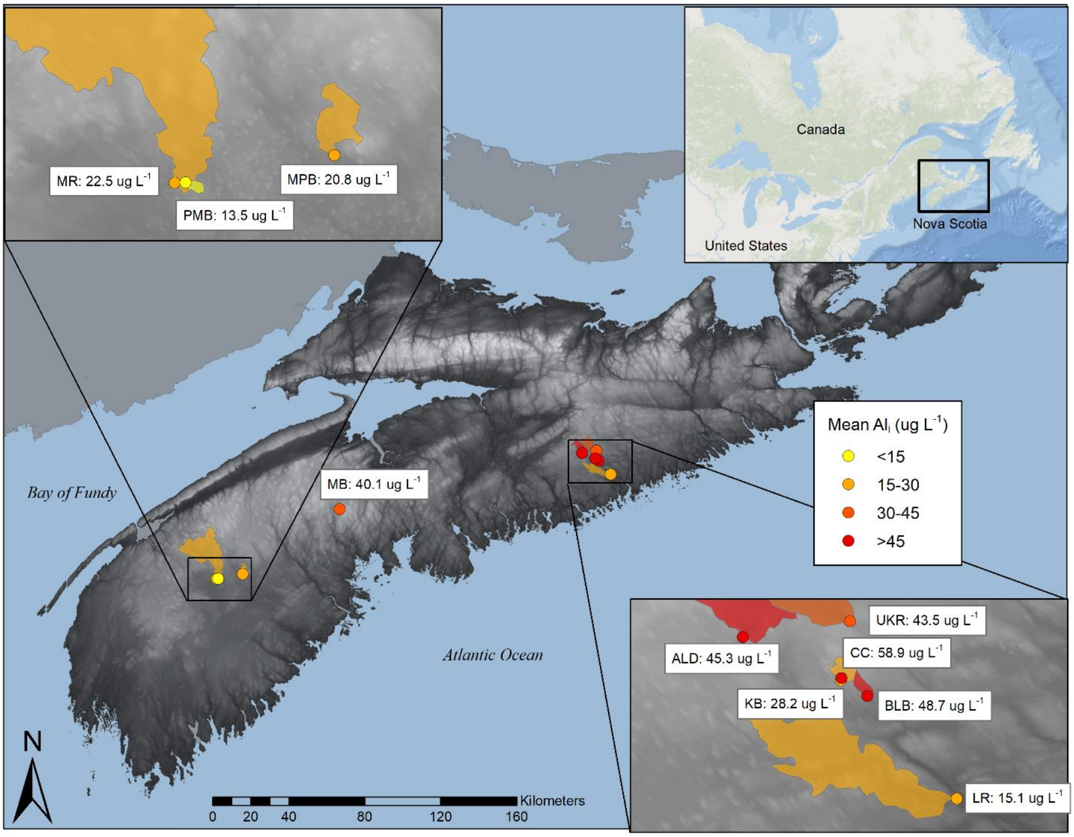

Figure 2. Mean Al$_i$ concentrations between spring 2015 to fall 2018.

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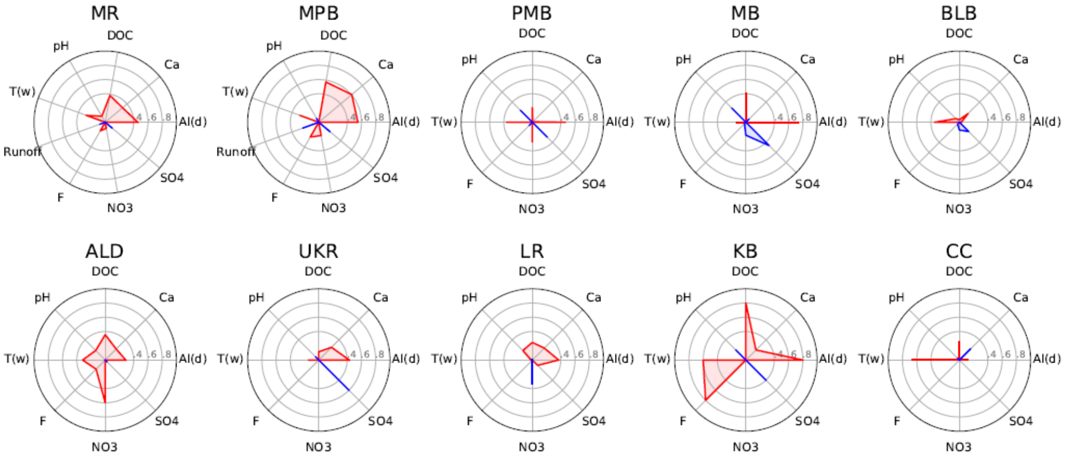

Figure 3. Correlation among water chemistry parameters and Al_i concentration, where red polygons and lines indicate a positive correlation with Al_i, and blue polygons and lines indicate a negative correlation

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.

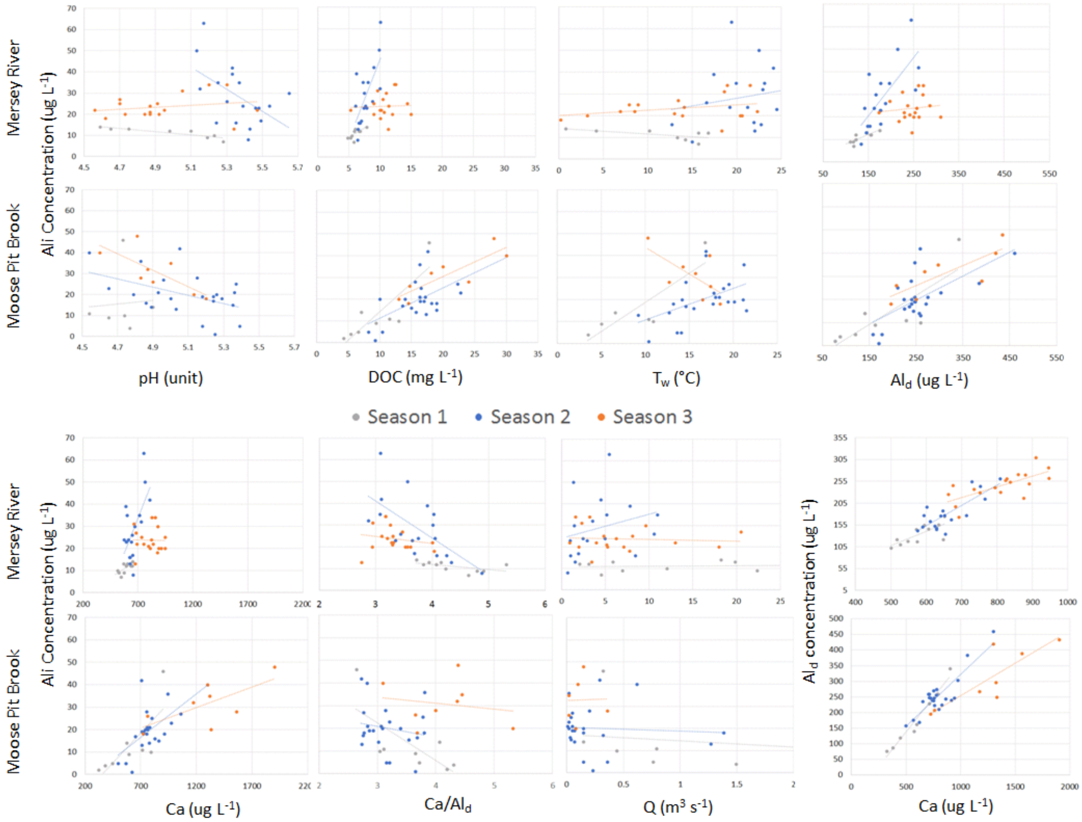

Figure 4. Scatterplot relationships among water chemistry parameters for seasons 1, 2, and 3 at MR and MPB. R^2 values are listed in Table A5. One runoff outlier removed for MR (value: 17.294 m3 s^{-1}, date: 22 April 2015). One runoff outlier removed for MPB (value: 34.994 m3 s^{-1}, date: 22 April 2015).

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	**Definition**	**Analysis Method**	**Trend**	**Location**	**Reference**
Al_i	Inorganic Al	Colourimetry (Al_t-Al_{nl})	Decreasing Al_i from 1988-2008	AWMN in UK	Monteith et al. (2014)
Al_{im}	Inorganic monomeric Al	Colourimetry (Al_{tm}-Al_{om})	Decreasing Al_i from 2001-2011	New York, USA	Josephson et al. (2014)
Al_i	Ionic Al	CEC (Al_t-Al_o)	Mean NS Al_i=25.3 µg/L Mean NB Al_i=31.0 µg/L	Atlantic Canada	Dennis and Clair (2012)
Al_i	Ionic Al	Colourimetry	Decreasing Al_i in lakes	Norway	Hesthagen et al. (2011)
LA1	Inorganic Al (sum of inorganic and monomeric Al species)	ICP-AES, Flow injection, Pyrocatechol violet, and CEC (Al_{tr}-Al_{nl})	15% of LA1 samples were >10 µg/L	Norway	Kristensen et al. (2009)
Al-l	Labile/cationic/inorganic monomeric Al	Colourimetry (Al_{tm}-Al_{nlm})	Decreasing Al-l across the UK	AWMN in UK	Evans & Monteith (2001)
Al_{im}	Labile Al (free and inorganically complexed Al)	Van Benschoten method	Mean Al_{im} of 72 µg/L from 2009-2010	China	Wang et al. (2013)

Al_i	Inorganic monomeric	Colourimetry and CEC (Al_m-Al_o)	Al_i fraction decreased in catchments between 1991 & 2007	Czech Republic	Kram et al. (2009)
Al_i	Inorganic Al	AAS	Decreasing Al_i from 1990-2010	Adirondack Mountains, USA	Strock et al. (2014)

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 Kejimkujik 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).

Site	**Date**	**Al_i (µg L^{-1})**	**Al_o/Al_d (%)**	**Season**	**Al_d (µg L^{-1})**	**Ca (µg L^{-1})**	**DOC (mg L^{-1})**	**SO_4 (µg L^{-1})**	**pH (unit)**	**T_w(°C)**	**T_a (°C)**	**Discharge (m^3 s^{-1})**	**Runoff (mm day^{-1})**	**Hydrograph Stage**
ALD	2016-04-29	19	87.7	1	155	591	7	899	4.67	6.8	4			
ALD	2016-05-19	12	94.1		202	800	10.7	1414	5.89		12.0			
ALD	2016-06-03	25	90.7	2	268	722	12.5	639	5.02	16.6	13.2			
ALD	2016-06-16	32	88.3	2	274	674	12.9	578	4.99	13.2	13			
ALD	2016-06-28	28	89.4	2	265	720	12.2	959	5.26	22.1	24.2			
ALD	2016-07-15	37	87	2	285	792	15	761	5.11	20.7	19.6			
ALD	2016-08-05	48	79.9		239	700	19.4	1414	5.98		21.2			
ALD	2016-09-10	48	78.2		220	1000	14.8	2000	5.03		20.8			
ALD	2016-10-02	13	92.3		169	1000	14.4	3000	5.27		11.4			
ALD	2016-11-19	44	82		245	900	14.6	1414	5.03		7.6			
ALD	2017-04-19	27	81.1	1	143	600	10.4	1209	4.55	7.8	3.2			
ALD	2017-05-14	69	61	2	177	600	12.1	923	4.92	13.4	4			
ALD	2017-05-30	37	85.8	2	261	600	11.8	2536	4.77	14.3	12.2			
ALD	2017-06-22	100	59.8	2	249	700	15.2	1414	5.17	22.8	25			

ALD	2017-07-13	62	80.3	2	315	800	19.3	1414	5.24	20.6	18.5
ALD	2017-08-01	26	89	2	236	800	15.1	1414	4.96	25.6	28.4
ALD	2017-08-23	35	84.4	2	224	700	13.2	1125	5.14	21.8	21
ALD	2017-09-16	77	82.5	2	439	1000	23.5		4.73	20.7	18.7
ALD	2018-05-10	46	75.7		189	700	8.8	1414	5.64		7.5
ALD	2018-06-07	43	83.8		266	700	16.1	1414	5.13		11.0
ALD	2018-07-05	119	62.5		317	800	13.6	1414	5.61		23.8
ALD	2018-11-23	50	76		208	800	10.1	1414	5.45		-9.1
BLB	2016-04-29	20	89.5	2	190	476	7.2	936	5.03	5.7	4
BLB	2016-06-03	60	82.1	4	336	770	11.9	669	4.78	10.1	13.5
BLB	2016-06-16	33	91.2	4	373	789	13.2	1158	4.77	9.8	13
BLB	2016-06-28	26	93.3	4	388	894	13.6	1251	4.67	13.1	23.9
BLB	2016-07-15	42	90.5	4	443	887	16.7	723	4.77	14.3	18.7
BLB	2016-08-05	6	98.6		429	1000	26.2	1414	5.29		21.2
BLB	2016-09-10	81	77.1		354	900	48.3	1414	4.87		20.8
BLB	2016-10-02	33	90.1		335	1000	18.5	2000	5.1		11.4
BLB	2016-11-19	28	92.6		379	1000	17.2	1414	4.76		7.6
BLB	2017-04-19	41	79.1	4	196	600	9.6	1927		4.2	4
BLB	2017-05-14	46	82.6	4	264	800	12.9	1550		7.7	6
BLB	2017-05-30	36	88.3	4	308	700	11.3	1795		8.4	14.9
BLB	2017-06-22	110	70.1	4	368	800	14.9	1414	4.8	17.3	24.6

BLB	2017-07-13	50	88.3	4	427	900	17.6	1414	4.87	15.8	17
BLB	2017-08-01	37	90.7	4	396	800	17.9	1414	4.7	20.6	29
BLB	2017-08-23	54	85.8	3	381	1000	17.1	1172	4.94	18.3	21
BLB	2017-09-16	34	91.9	4	420	1000	17.3		4.52	16.6	18.9
BLB	2018-05-10	37	85.5		256	700	8.5	1414	5.16		7.5
BLB	2018-06-07	86	75		344	800	15.7	1414	5.29		11.0
BLB	2018-07-05	83	80.3		421	900	13.8	1414	5.42		23.8
BLB	2018-10-02	104	67.4		319	1600	12.4	1414	5.04		7.7
BLB	2018-11-23	24	93.5		367	70.7	10.5	1414	4.8		-9.1
CC	2016-06-03	32	91.9	4	397	501	15.2	385	4.66	11.2	13.5
CC	2016-06-16	46	88.9	4	413	520	17.7	304	4.71	10.4	12.8
CC	2016-06-28	107	78.9	4	507	537	21	401	4.82	14.8	24.2
CC	2016-07-15	53	89.9	4	524	642	26	208	4.6	14.6	18.7
CC	2016-08-05	140	68.6		446	400	29.3	1414	5.73		21.2
CC	2016-09-10	32	86.9		244	400	22.2	1414	4.72		20.8
CC	2016-10-02	34	85.5		234	900	28.8	1414	4.95		11.4
CC	2016-11-19	27	94.9		527	2100	24.9	1414	6.11		7.6
KB	2016-04-29	14	90.6	2	149	1110	5.7	1061	5.69	8.2	4
KB	2016-06-03	20	92.5	2	267	459	9.9	611	4.89	14.1	13.5
KB	2016-06-16	38	87.7	2	310	515	11.3	852	4.9	12.3	10.8
KB	2016-06-28	28	91.3	2	323	486	11.7	887	5.06	17.8	24.5
KB	2016-07-15	41	88.5	2	356	535	15.6	621	5.03	18.7	18.7

LR	2016-08-05	27	50		54	1100	5.7	1414	6.03		21.2
LR	2016-09-10	3	92.1		38	800	4.4	1414	6.07		20.8
LR	2016-10-02	6	95.2		124	900	10.1	2000	5.76		11.4
LR	2017-04-19	4	96.6	1	116	600	7.1	1416	4.87	6	1.7
LR	2017-05-14	20	84.6	2	130	600	8.1	1213	4.95	12.3	6
LR	2017-05-30	17	89	2	154	600	8.6	1572	5.21	15	12.5
LR	2017-06-22	34	69.9	2	113	700	8.2	1414	5.51	19.6	19
LR	2017-07-13	12	88.7	2	106	600	6.4	1414	5.54	21.8	18
LR	2017-08-01	2	96.9	2	65	600	6.6	1414	5.1	19.6	24.8
LR	2017-08-23	5	88.4	2	43	600	4.1	1371	5.37	21.6	21.3
LR	2017-09-16	5	94.9	2	99	700	6.7	1414	5.01	19.4	15.8
LR	2018-05-10	35	74.1		135	800	6.7	1414	5.54		7.5
LR	2018-06-07	26	84.0		162	900	8.2	1414	5.55		11.0
MB	2016-05-27	30	88.9	2	270	1200	6.8	1278	5.14	9.8	12
MB	2016-06-15	15	94.2	2	260	1590	8.4	1497	5.61	11.2	14.6
MB	2016-06-27	27	90.5	2	284	1610	7.6	1851	5.28	16.3	16.7
MB	2016-07-14	40	86.9	2	305	1780	6.4	1747	5.4	15.5	28.5
MB	2017-04-20	25	89.8	1	246	848	7	1996	4.86	2.3	4
MB	2017-05-13	48	84.1	1	302	977	7.2	1385	4.76	9.1	17
MB	2017-05-29	40	87.9	2	330	1100	9	1977	4.99	9.1	14.5
MB	2017-06-21	96	81.2	2	510	1480	15.8	551	5.18	13.7	23.3
MB	2017-07-12	46	87.7	2	375	1320	11.5	28968	5.13	15.8	25.9

MB	2017-07-31	43	87.7	2	351	1470	12.1	1629	5.08	15.6	27.4			
MB	2017-08-22	80	85.7	2	560	1500	21	828	4.91	15.5	27.6			
MB	2017-09-17	30	89.3	3	280	1600	11	1258	5.14	14.7	23			
MPB	2015-04-22	2	97.1	1	77	323	4.3	1009			7.3	6.41	34.992	RL
MPB	2015-04-30	4	95.9	1	88	379	5.4	1272	4.77	3.5	4.5	1.49	8.134	FL
MPB	2015-05-06	5	95.8	1	120	446	6.6	1304			14	0.76	4.149	BF
MPB	2015-05-13	5	96.8	2	158	498	8.2	958	5.18	13.6	7	0.36	1.965	RL
MPB	2015-05-20	1	99.4	2	170	621	9.3	815	5.25	10.4	12	0.23	1.256	RL
MPB	2015-05-27	5	97.2	2	177	567	10.4	699	5.39	14.1	21	0.15	0.819	RL
MPB	2015-06-03	13	95	2	260	710	17.3	639	5.03	9.2	8	1.27	6.933	RL
MPB	2015-06-10	17	92.8	2	236	651	13.6	443	5.24	14.6	10	0.32	1.747	RL
MPB	2015-06-17	28	88.3	2	239	751	15.6	560	5.15	14.6	16	0.2	1.092	RL
MPB	2015-06-24	18	93.4	2	271	751	19	357	5	13.2	18	1.38	7.533	RL
MPB	2015-07-02	42	83.8	2	259	705	17.6	322	5.05	16.9	20	0.29	1.583	BF
MPB	2015-07-08	19	92.3	2	247	724	16.4	400	5.24	19.4	23	0.07	0.382	BF
MPB	2015-07-15	19	92.3	2	248	710	17	464	5.18	20.1	18	0.05	0.273	BF
MPB	2015-07-22	21	91.5	2	247	756	16.3	552	5.36	18.4	17	0.05	0.273	RL
MPB	2015-07-29	18	92.5	2	240	912	18.2	1146	5.29	17.7	19	0.15	0.819	RL
MPB	2015-08-05	15	93.9	2	244	863	19	650	5.35	21.5	19	0.04	0.218	FL
MPB	2015-08-12	25	88.2	2	211	798	16.5	618	5.37	18.9	21	0.04	0.218	RL
MPB	2015-08-19	36	85.4	2	247	941	16.3	721	4.83	21.2	24	0.02	0.109	BF
MPB	2015-08-26	20	91.1	2	224	761	10	607	5.26	21.1	16	0.02	0.109	BF

MPB	2015-09-02	26	87.5	3	208	760	14.7	711	4.9	17.4	21	0.02	0.109	BF
MPB	2015-09-09	18	90.8	3	196	722	14.5	823	5.2	18.5	20		0	RL
MPB	2015-09-16	20	92	3	250	1330	13	4375	5.13	16.5	19	0.08	0.437	BF
MPB	2015-09-23	35	88.2	3	297	1320	20	2598	5	14.3	17	0.02	0.109	BF
MPB	2015-09-30	32	88.1	3	268	1170	18.1	1902	4.87	15.7	19		0	BF
MPB	2015-10-07	48	88.9	3	434	1900	28	2576	4.81	10.3	13	0.15	0.819	BF
MPB	2015-10-14	28	92.8	3	390	1560	24	1963	4.83	12.7	16	0.36	1.965	RL
MPB	2016-04-28	14	90.1	1	141	573	7.1	800	4.9	6.6	4	0.15	0.819	RL
MPB	2016-05-27	20	91.7	2	240	740	14	489	4.79	14.2	12	0.15	0.819	RL
MPB	2016-06-15	14	94.6	2	257	775	15.7	478	4.89	12.7	14.1	0.07	0.382	FL
MPB	2016-06-27	21	92.4	2	275	778	17.2	587	4.93	18	27	0.01	0.055	FL
MPB	2016-07-14	16	92.9	2	225	828	15	1447	4.86	15.5	20	0.03	0.164	FL
MPB	2017-04-20	9	94.5	1	163	595	9.4	1625	4.65	5	1		0	
MPB	2017-05-13	11	95.2	1	229	712	11.5	1430	4.54	10.4	17	0.79	4.313	FL
MPB	2017-05-29	10	96.2	1	260	790	13	1567	4.74	10.9	12	0.44	2.402	FL
MPB	2017-06-21	46	86.5	1	341	901	17.8	226	4.73	16.8	24.2	0.32	1.747	FL
MPB	2017-07-12	27	93	2	384	1060	22.3	229	4.96	19.5	25.9	0.05	0.273	FL
MPB	2017-07-31	23	92.4	2	303	972	22.8	724	4.65	17.8	27	0.02	0.109	FL
MPB	2017-08-22	40	91.3	2	460	1300	30	255	4.54	16.9	28.4	0.62	3.385	FL
MPB	2017-09-17	40	90.5	3	420	1300	30	301	4.6	17.3	20.1	0.1	0.546	FL
MR	2015-04-22	12	90.2	1	122	648	5.9	1321			7.3	58.61	1.837	RL
MR	2015-04-30	2	98	1	102	500	5.6	1189	5	4.2	4.5	33.03	1.454	FL

MR	2015-05-06	9	91.8	1	110	527	4.8	1112			14	22.33	1.269	BF
MR	2015-05-13	10	91.8	1	122	517	5.5	1117	5.23	13.3	7	12.05	1.048	FL
MR	2015-05-20	9	92.3	1	117	574	5.3	1101	5.19	14.2	12	6.95	0.912	FL
MR	2015-05-27	7	94.1	1	118	548	5.8	1161	5.28	15.7	21	4.53	0.835	FL
MR	2015-06-03	16	89.2	2	148	629	6.6	1069	5.35	12.7	8	8.42	0.946	RL
MR	2015-06-10	39	74.2	2	151	590	6.2	1220	5.33	17.4	10	7.8	0.934	RL
MR	2015-06-17	24	83.1		142	575	6.1	1175	5.39	19.2		4.98	0.858	
MR	2015-06-24	26	86.2		188	647	8.8	968	5.3	16.6		10.58	1.028	
MR	2015-07-02	35	82.1	2	196	602	8.1	897	5.25	19.9	20	10.94	1.018	BF
MR	2015-07-08	35	80.2	2	177	713	7.3	972	5.37	23.1	23	5.14	0.864	BF
MR	2015-07-15	23	87	2	177	593	7.9	959	5.46	24.5	18	2.9	0.76	BF
MR	2015-07-22	17	90.4	2	177	652	7	1011	5.49	21.9	17	1.9	0.701	BF
MR	2015-07-29	24	85.3	2	163	611	7.7	1146	5.54	21.2	19	2.45	0.735	RL
MR	2015-08-05	30	82	2	167	670	7.5	1077	5.65	25.2	19	1.46	0.671	FL
MR	2015-08-12	13	91	2	145	629	6.5	1094	5.43	22	21	1.53	0.686	RL
MR	2015-08-19	23	86.9	2	176	641	7.4	1097	5.48	25.3	24	0.96	0.632	BF
MR	2015-08-26	42	83.9	2	261	808	9	1179	5.33	24.1	16	4.47	0.731	BF
MR	2015-09-02	34	87.5	3	271	859	12.3	1168	5.3	21.5	21	1.59	0.681	BF
MR	2015-09-09	22	90.4	3	229	751	10.2	776	5.47	22.3	20	0.93	0.63	BF
MR	2015-09-16	34	87	3	261	828	12.5	1108	5.2	18.9	19	3.2	0.781	BF
MR	2015-09-23	13	94.7	3	246	675	11.3	900	5.34	18.3	17	3.44	0.789	BF
MR	2015-09-30	31	86.2	3	225	662	9.6	911	5.05	18.6	19	2.3	0.733	BF

MR	2015-10-07	21	91.3		241	794	10.7	989	4.87	13		5.16	0.869	
MR	2015-10-14	24	90.7	3	257	824	11.4	1166	4.87	14.1	16	6.26	0.905	RL
MR	2015-10-21	25	89.5	3	237	735	9	890	4.91	8.9	5	4.83	0.855	BF
MR	2015-10-28	22	91.3	3	253	837	10	1153	4.95	6.9	3	3.98	0.814	FL
MR	2015-11-04	25	91.3	3	286	945	14.4	967	4.7	7.9	7	8.1	0.947	RL
MR	2015-12-02	20	92.4	3	262	946	12	1139	4.73	3.2	6	17.96	1.183	FL
MR	2016-01-05	30	88.9	3	270	880	11	1245			-20	9.62	0.998	FL
MR	2016-02-02	18	91.7	3	217	875	10.1	1290	4.62	0.2	-3	7.75	0.926	RL
MR	2016-02-23	14	92	1	175	651	7.9	1316	4.59	0.8	-6	18.21	1.2	BF
MR	2016-03-29	13	91.1	1	146	606	6.1	1060	4.65	4.2	2	19.81	1.248	RL
MR	2016-04-28	13	91	1	145	572	6	937	4.75	10.2	4	5.85	0.892	FL
MR	2016-05-27	12	92.3	1	156	635	6.8	922	4.98	16.8	12	3.11	0.81	FL
MR	2016-06-15	12	92.3	1	155	595	6.7	1217	5.1	15.7	14.4	2.05	0.773	FL
MR	2016-06-27	16	89.5	2	153	624	6.8	1263	5.24	22.7	24	1.04	0.649	FL
MR	2016-07-14	8	94	2	134	654	6.4	1697	5.42	15	16	0.68	0.635	BF
MR	2017-04-20	22	87.3	3	173	692	5.3	1625	4.56	8.5	1	13		FL
MR	2017-05-13	27	86.3	3	197	683	10.5	1437	4.7	13.4	13	20.5	1.28	FL
MR	2017-05-29	20	91.3	3	230	810	9	1774	4.87	13.9	10.4	7.08	0.905	FL
MR	2017-06-21	63	74.2	2	244	752	10.1	458	5.17	19.4	20.2	5.42	0.881	FL
MR	2017-07-12	32	87.4	2	254	729	10	982	5.15	22.9	23.9	3.55	0.813	FL
MR	2017-07-31	50	76.7	2	215	766	9.88	1116	5.13	22.5	24.9	1.37	0.665	FL
MR	2017-08-22	20	93.5	3	310	910	15	861	4.92	20.4	25.5	5.26	0.878	FL

MR	2017-09-17	20	92	3	250	890	15	817	4.84	20.6	17.3	1.98	0.715	FL
PMB	2015-05-27	2	98.4	2	128	742	7.2	845	5.62	12.6	21			
PMB	2015-06-03	6	95.7	2	138	586	8.8	1042	5.28	12.2	8			
PMB	2016-04-28	6	93.6	2	93	675	3.6	1244	5.25	8.2	4			
PMB	2016-05-27	35	78.1	2	160	900	8	691	4.93	12.7	12			
PMB	2016-06-15	5	96.7	2	151	1150	8.1	1229	5.14	10.9	14.2			
PMB	2016-06-27	5	94.3	2	82	1570	5.4	3167	5.35	14	24			
PMB	2016-07-14	10	89.3	2	96	1770	6.9	5652	5.4	15	12			
PMB	2017-04-20	4	96.5	1	114	71	5.3	2234	4.78	8.5	2			
PMB	2017-05-13	11	92.1	1	139	71	6.2	1328	4.69	9.8	16			
PMB	2017-05-29	10	93.8	2	160	730	7	2405	5.03	13.9	10.8			
PMB	2017-06-21	32	85.6	2	222	955	11.1	289	4.98	15.5	21.4			
PMB	2017-07-12	35	80.3	2	178	1580	10.7	1428	5.21	16	24.6			
PMB	2017-07-31	1	99.3	2	148	1780	13	2746	4.99	13.8	25.6			
PMB	2017-08-22	20	90.9	3	220	960	13	571	4.85	16.4	26.9			
PMB	2017-09-17	20	90	3	200	990	15	640	4.7	16	17.8			
UKR	2016-05-19	21	89.7		203	700	10.4	1414.2	5.83		12.0			
UKR	2016-08-05	18	88.5		157	700	15.1	1414.2	5.56		21.2			
UKR	2016-09-10	16	89.9		158	100	12.1	1414.2	5.58		20.8			
UKR	2016-10-02	15	91.8		182	900	13.8	1414.2	5.77		11.4			
UKR	2016-11-19	41	84.4		262	1100	15.1	2000	4.89		7.6			
UKR	2017-04-19	38	72.3	3	137	500	9.5	1292		7.3	3.4			

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UKR	2017-05-14	24	87.2	2	187	600	12.6	1049		12.9	6
UKR	2017-05-30	37	83.3	2	221	600	9.8	1115		15.2	12.5
UKR	2017-06-22	66	67.5	2	203	800	12.1	1414	5.22	23.4	24.2
UKR	2017-07-13	47	85.4	2	322	800	17.6	1414	5.21	22.3	19
UKR	2017-08-01	26	89.1	2	239	800	15	1414	5.29	25.6	29.1
UKR	2017-08-23	74	65.6	2	215	700	12.8	889	5.31	21.8	21.1
UKR	2017-09-16	76	82	2	422	1000	20.6		4.77	20.8	19.2
UKR	2018-05-10	37	78.1		169	600	8.2	1414.2	5.31		7.5
UKR	2018-06-07	59	73.3		221	700	12.9	1414.2	5.34		11.0
UKR	2018-07-05	99	66.3		294	800	12.2	1414.2	5.46		23.8
UKR	2018-10-02	47	77.3		207	1100	10.5	1414.2	5.78		7.7
UKR	2018-11-23	43	81.1		227	800	10.8	1414.2	4.81		-9.1

Table A3 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 L^{-1}	0.007	0.247
Ca	µg L^{-1}	0.001	0.676
DOC	mg L^{-1}	0.007	0.247
pH	unit	0.077	0.000
Water Temp.	°C	0.114	0.000
F^+	µg L^{-1}	0.003	0.537
NO_3^-	µg L^{-1}	0.002	0.624
SO_4^{2-}	µg L^{-1}	0.000	0.952

Table A4 Kendal-tau correlation and significance (α = 0.05) between Al_i and other water chemistry parameters for each study site. One Al_i outlier removed for MR calculations (value: 2 µg L^{-1}, date: 30 April 2015).

Site	Variable	Unit	Correlation Slope	Significance (p-value)
ALD	Ald	µg L^{-1}	0.29	0.044
	Ca	µg L^{-1}	0.22	0.143
	DOC	mg L^{-1}	0.36	0.013
	pH	unit	0.19	0.190
	Water Temp.	°C	0.32	0.093
	F^+	µg L^{-1}	0.182	0.533
	NO_3^-	µg L^{-1}	0.600	0.142
	SO_4^{2-}	µg L^{-1}	-0.037	0.876
BLB	Ald	µg L^{-1}	0.03	0.852
	Ca	µg L^{-1}	0.17	0.238
	DOC	mg L^{-1}	0.08	0.575
	pH	unit	0.07	0.622
	Water Temp.	°C	0.35	0.099
	F^+	µg L^{-1}	-0.036	0.901
	NO_3^-	µg L^{-1}	-0.109	0.708
	SO_4^{2-}	µg L^{-1}	-0.184	0.468
CC	Ald	µg L^{-1}	0.11	0.708
	Ca	µg L^{-1}	-0.22	0.451
	DOC	mg L^{-1}	0.25	0.383
	pH	unit	-0.04	0.901
	Water Temp.	°C	0.67	0.174
	F+	µg L^{-1}		
	NO_3^-	µg L^{-1}		
	SO_4^{2-}	µg L^{-1}		
KB	Ald	µg L^{-1}	0.800	0.050
	Ca	µg L^{-1}	0.200	0.624
	DOC	mg L^{-1}	0.800	0.050
	pH	unit	-0.200	0.624
	Water Temp.	°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	Ald	µg L^{-1}	0.37	0.047
	Ca	µg L^{-1}	0.24	0.226
	DOC	mg L^{-1}	0.25	0.189
	pH	unit	0.19	0.319
	Water Temp.	°C	0.02	0.937
	F+	µg L^{-1}		
	NO_3^-	µg L^{-1}	-0.333	0.348
	SO_4^{2-}	µg L^{-1}	0.105	0.801
MB	Ald	µg L^{-1}	0.739	0.001
	Ca	µg L^{-1}	-0.062	0.783
	DOC	mg L^{-1}	0.400	0.073
	pH	unit	-0.279	0.214
	Water Temp.	°C	0.125	0.580
	F+	µg L^{-1}	-0.028	0.917
	NO_3^-	µg L^{-1}	-0.182	0.533
	SO_4^{2-}	µg L^{-1}	-0.463	0.050
MPB	Ald	µg L^{-1}	0.550	0.000
	Ca	µg L^{-1}	0.580	0.000
	DOC	mg L^{-1}	0.574	0.000
	pH	unit	-0.169	0.146
	Water Temp.	°C	0.280	0.016
	Runoff	mm day^{-1}	-0.232	0.042
	F+	µg L^{-1}	0.239	0.042
	NO_3^-	µg L^{-1}	0.190	0.160
	SO_4^{2-}	µg L^{-1}	-0.206	0.067
MR	Ald	µg L^{-1}	0.459	0.000
	Ca	µg L^{-1}	0.317	0.002
	DOC	mg L^{-1}	0.382	0.000
	pH	unit	0.097	0.362
	Water Temp.	°C	0.285	0.007
	RunOff	mm 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
PMB	Ald	µg L^{-1}	0.46	0.019

	Ca	µg L^{-1}	0.01	0.960
	DOC	mg L^{-1}	0.21	0.295
	pH	unit	-0.23	0.232
	Water 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
UKR	Ald	µg L^{-1}	0.34	0.071
	Ca	µg L^{-1}	0.38	0.053
	DOC	mg 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 L^{-1}	-0.600	0.142

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Table A5 R^2 values for scatterplots of water chemistry relationships shown in Figure 3

Site	Season	Season Dates	Relationship	R^2
MR	S1	April-May	Al_i-pH	0.78131
MR	S2	June-Aug	Al_i-pH	0.27845
MR	S3	Sept-Feb	Al_i-pH	0.04551
MR	S1	April-May	Al_i-DOC	0.48879
MR	S2	June-Aug	Al_i-DOC	0.51343
MR	S3	Sept-Feb	Al_i-DOC	0.0014
MR	S1	April-May	Al_i-T_w	0.42004
MR	S2	June-Aug	Al_i-T_w	0.03442
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-Aug	Al_i-Al_d	0.4225
MPB	S3	Sept-Oct	Al_i-Al_d	0.65683
MPB	S1	April-June	Al_i-Ca	0.59175
MPB	S2	July-Aug	Al_i-Ca	0.4214
MPB	S3	Sept-Oct	Al_i-Ca	0.49111
MPB	S1	April-June	Al_i-Ca/Al_d	0.51142
MPB	S2	July-Aug	Al_i-Ca/Al_d	0.03067
MPB	S3	Sept-Oct	Al_i-Ca/Al_d	0.02961
MPB	S1	April-June	Al_i-Q	0.1734
MPB	S2	July-Aug	Al_i-Q	0.0039
MPB	S3	Sept-Oct	Al_i-Q	0.0004
MPB	S1	April-June	Al_d-Ca	0.96289
MPB	S2	July-Aug	Al_d-Ca	0.7685

MPB	S3	Sept-Oct	Al_d-Ca	0.72173

Table A6 Laboratory detection limit comparison.

Chemistry		Value		
Parameter	Units	HERC	Maxxam	AGAT
pH	µg 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	µg L^{-1}	10.00	n/a	2000
Al_d	µg L^{-1}	n/a	5.00	5
Al_t	µg L^{-1}	n/a	5.00	5
Al_o	µg L^{-1}	n/a	5.00	5
Ca_t	µg L^{-1}	n/a	100 µg L^{-1}	0.1 mg L^{-1}
Ca_d	µg L^{-1}	n/a	100	100

Appendix B. Figures

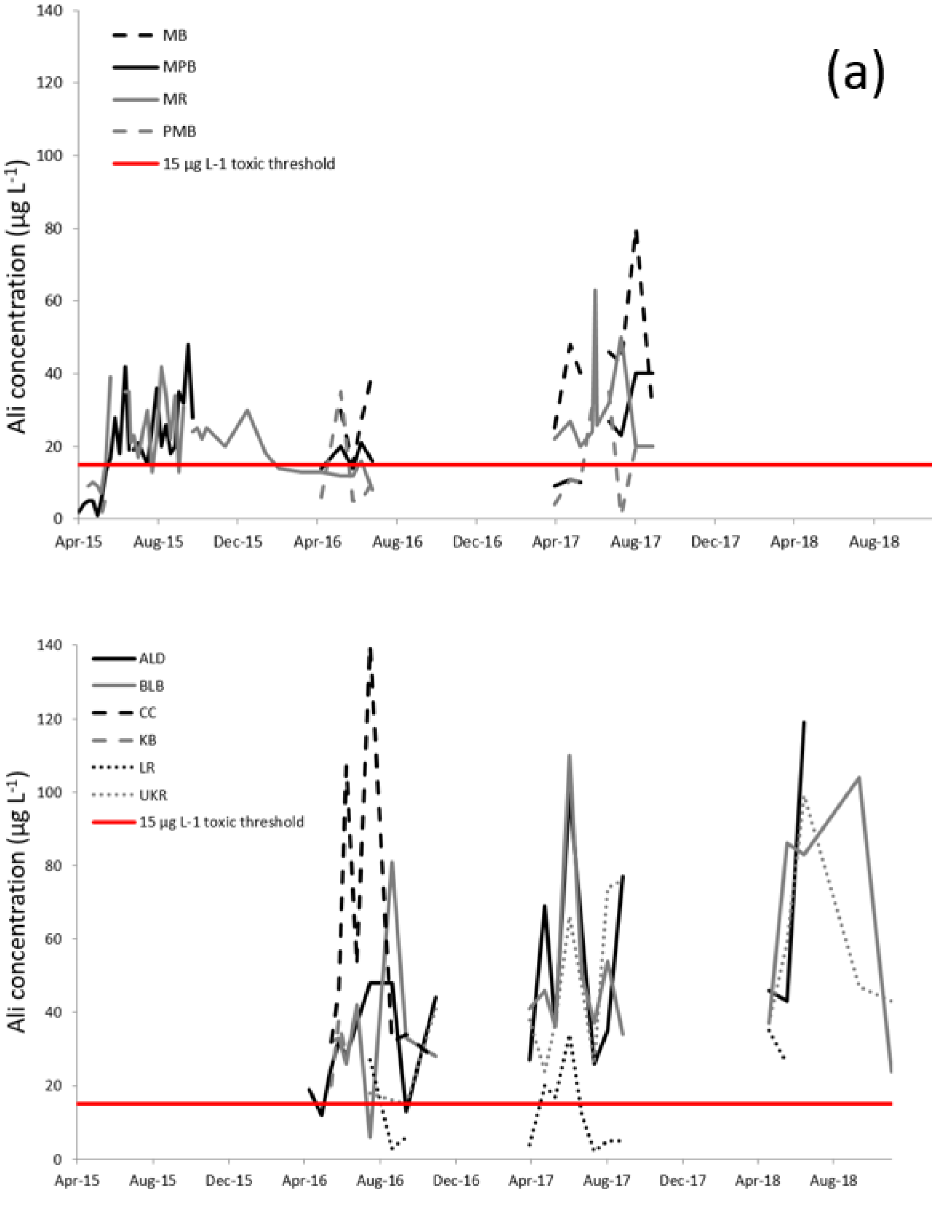

Figure B1 Timeseries of Al_i concentration between 22 April 2015 and 23 November 2018.

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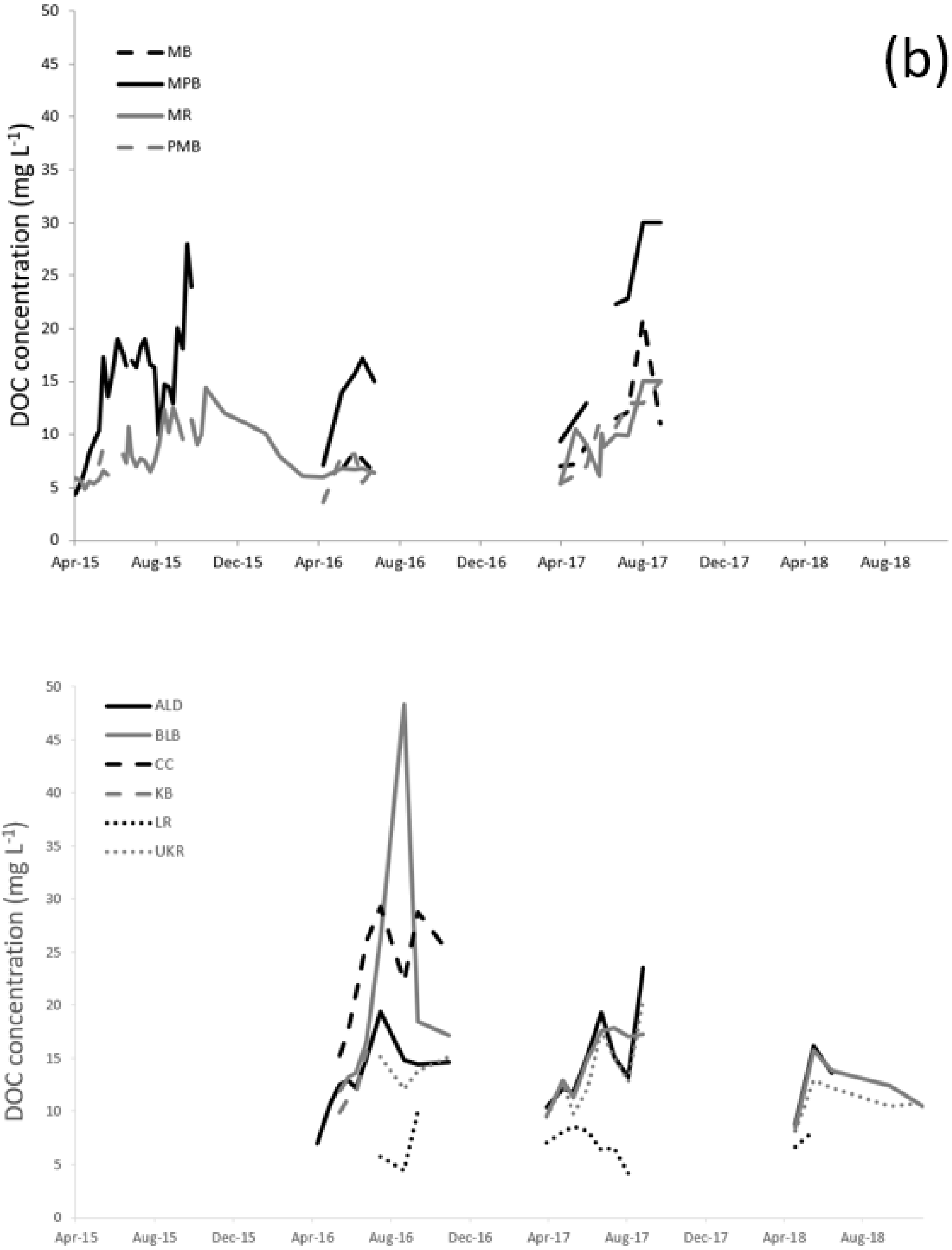

Figure B2 Time series of DOC concentration between 22 April 2015 and 23 November 2018

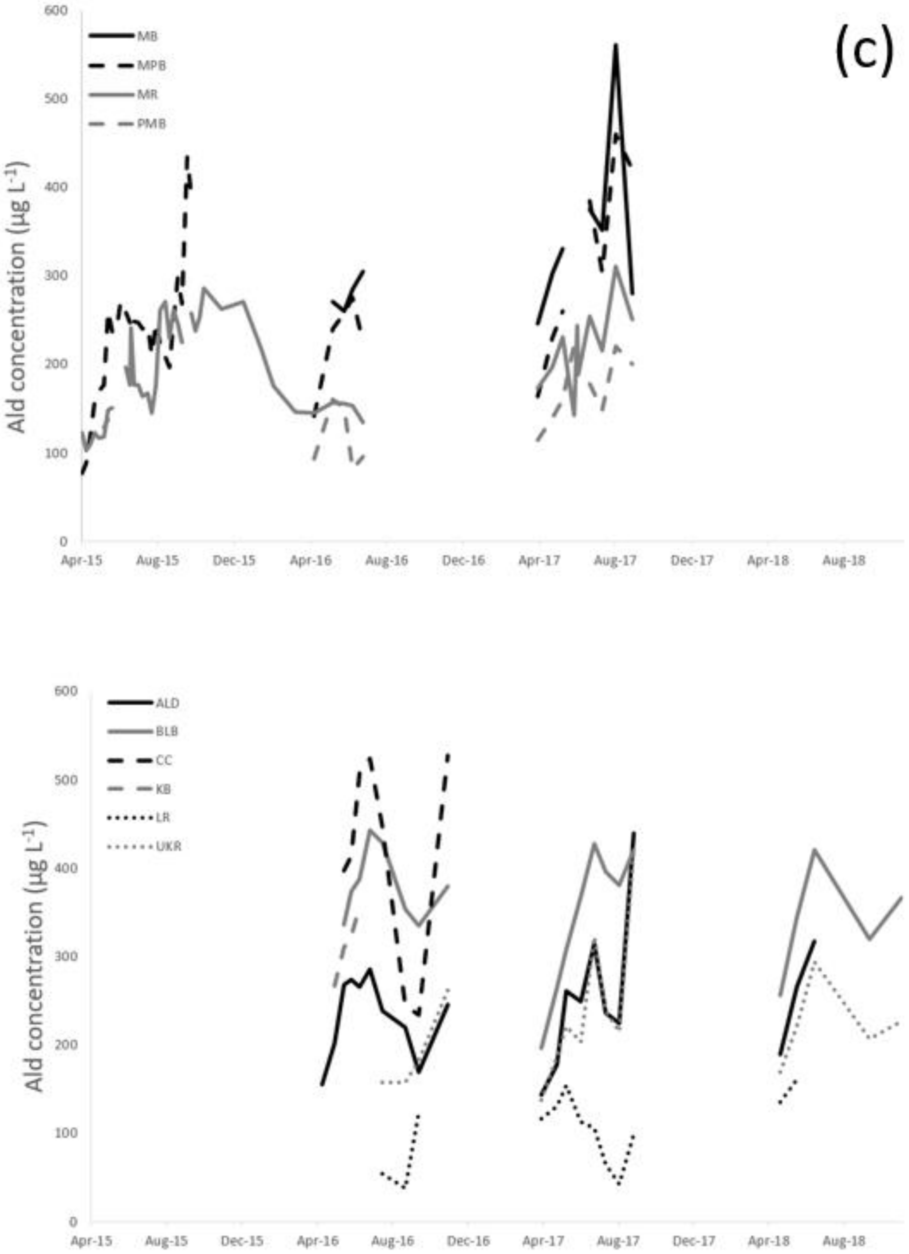

Figure B3 Time series of Al_d concentration between 22 April 2015 and 23 November 2018.

https://doi.org/10.5194/hess-2019-438
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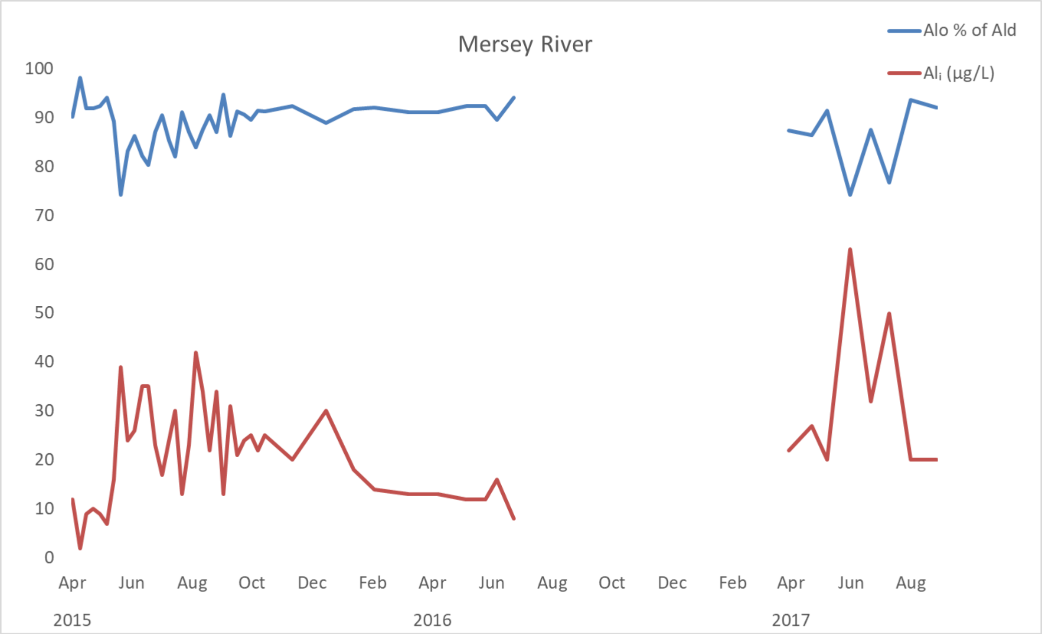

Figure B4 Time series of percentage Al_d comprised of Al_o for MR, compared to absolute value of Al_i in ug L^{-1}.

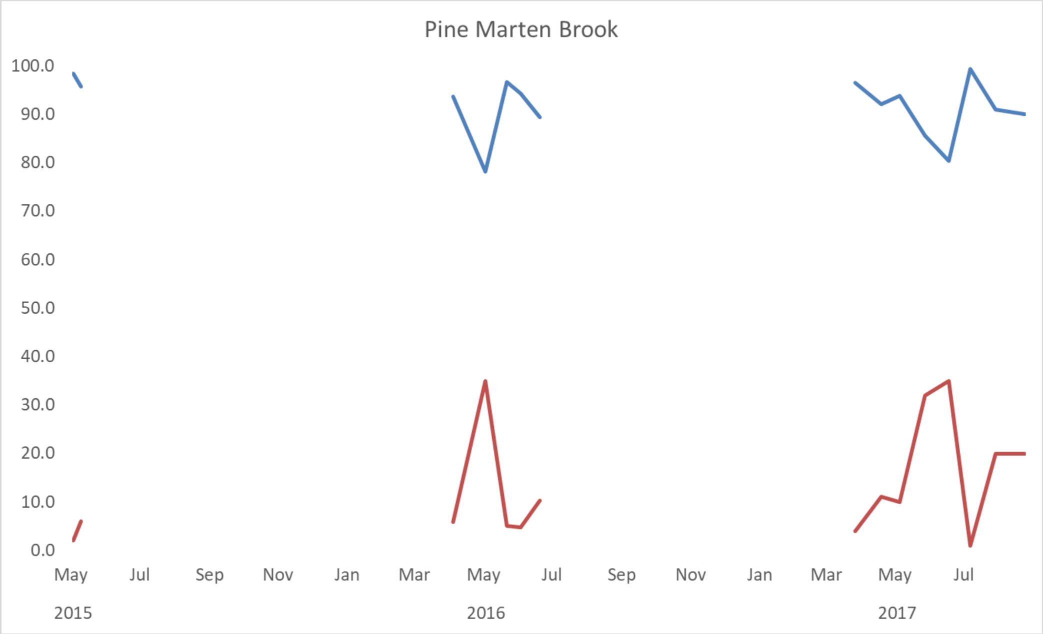

Figure B5 Time series of percentage Al_d comprised of Al_o for PMB, compared to absolute value of Al_i in ug L^{-1}.

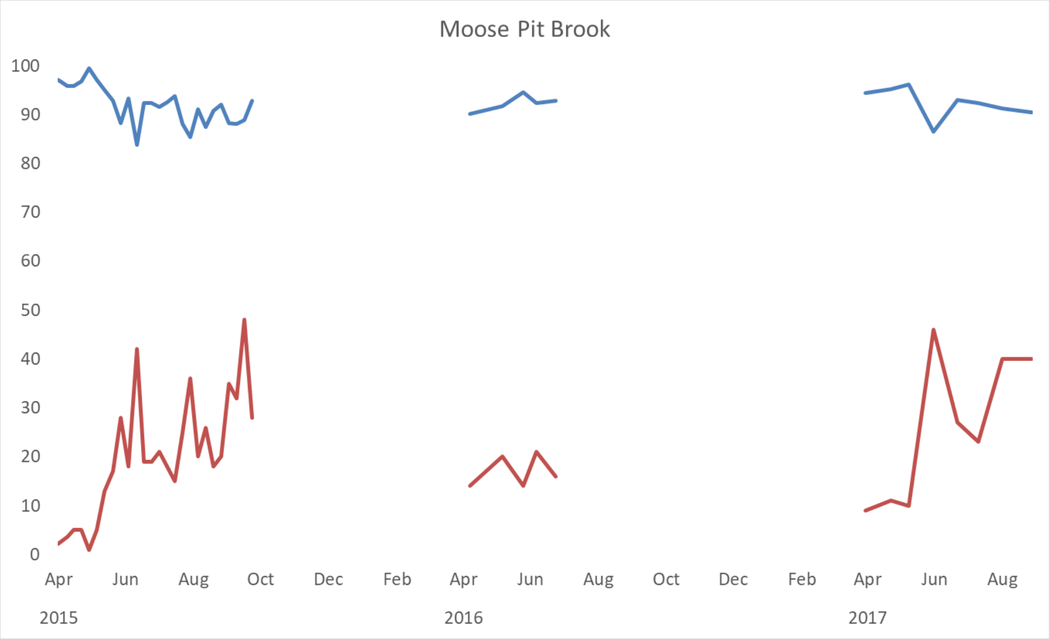

Figure B6 Time series of percentage Al_d comprised of Al_o for MPB, compared to absolute value of Al_i in ug L^{-1}.

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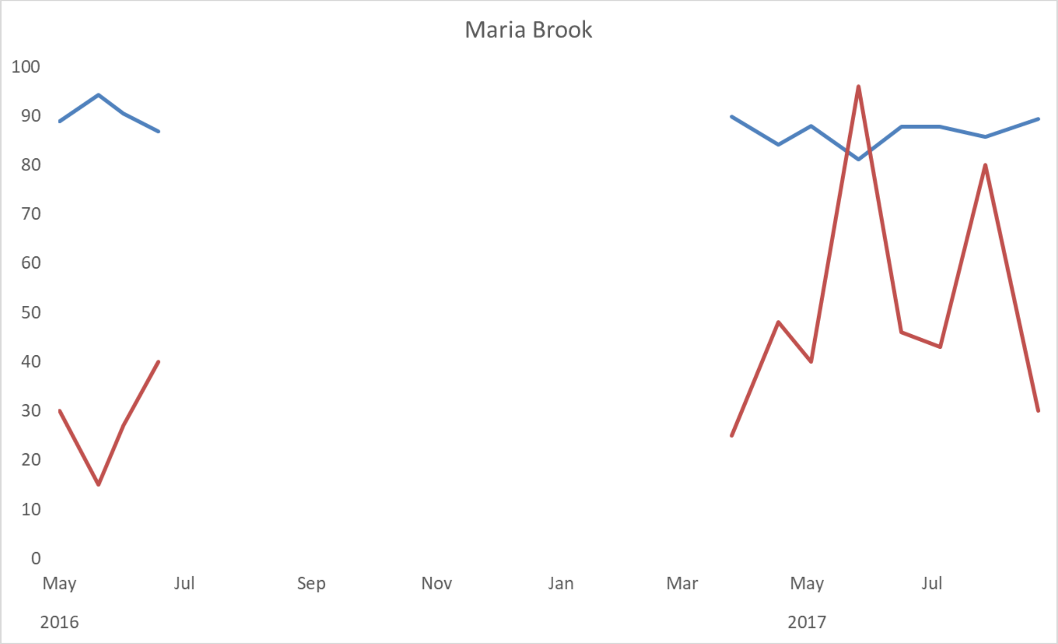

Figure B7 Time series of percentage Al_d comprised of Al_o for MB, compared to absolute value of Al_i in ug L^{-1}.

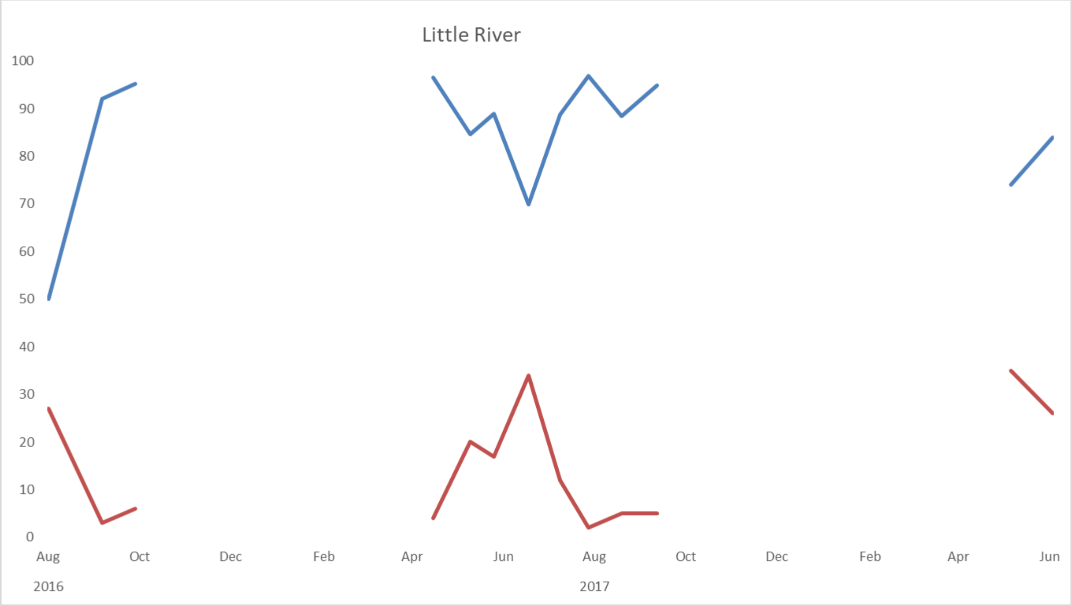

Figure B8 Time series of percentage Al_d comprised of Al_o for LR, compared to absolute value of Al_i in ug L^{-1}.

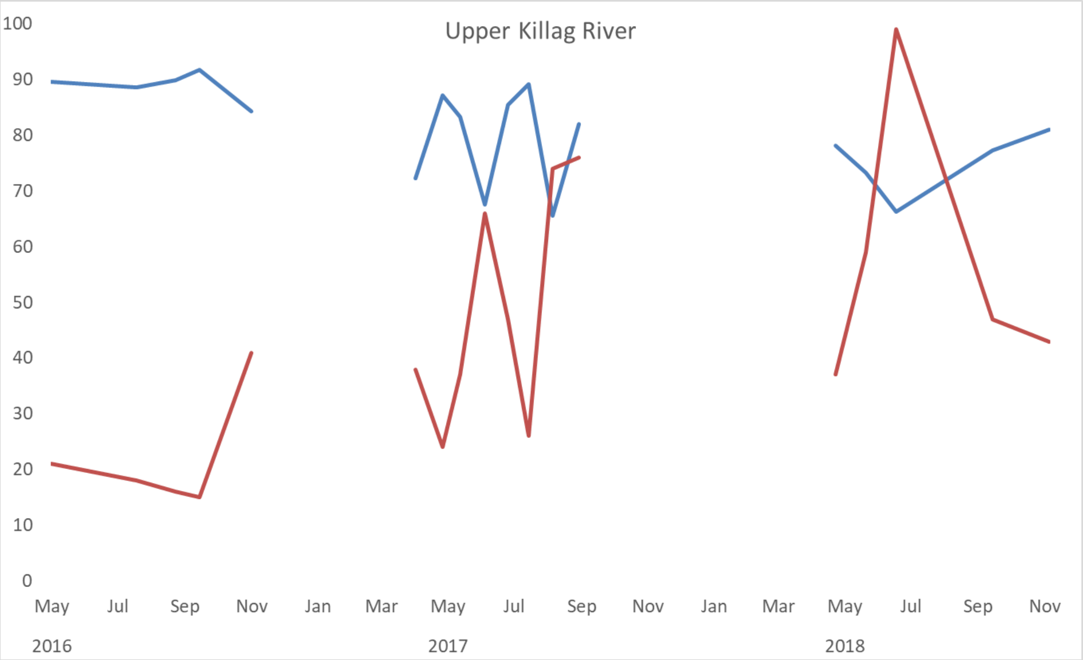

Figure B9 Time series of percentage Al_d comprised of Al_o for UKR, compared to absolute value of Al_i in ug L^{-1}.

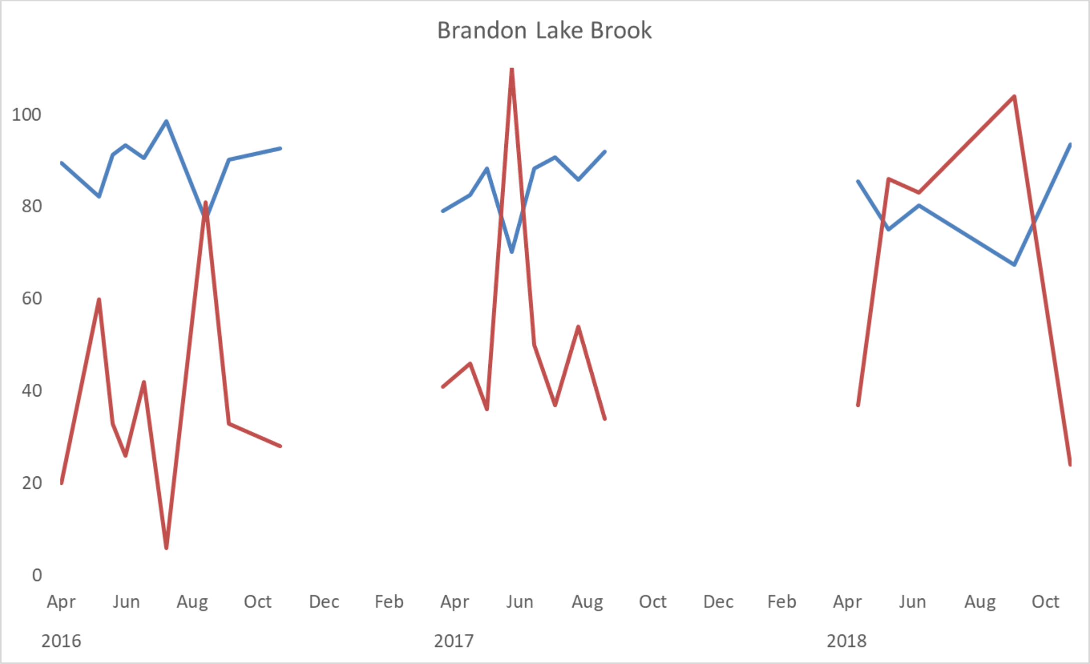

Figure B10 Time series of percentage Al_d comprised of Al_o for BLB, compared to absolute value of Al_i in ug L^{-1}.

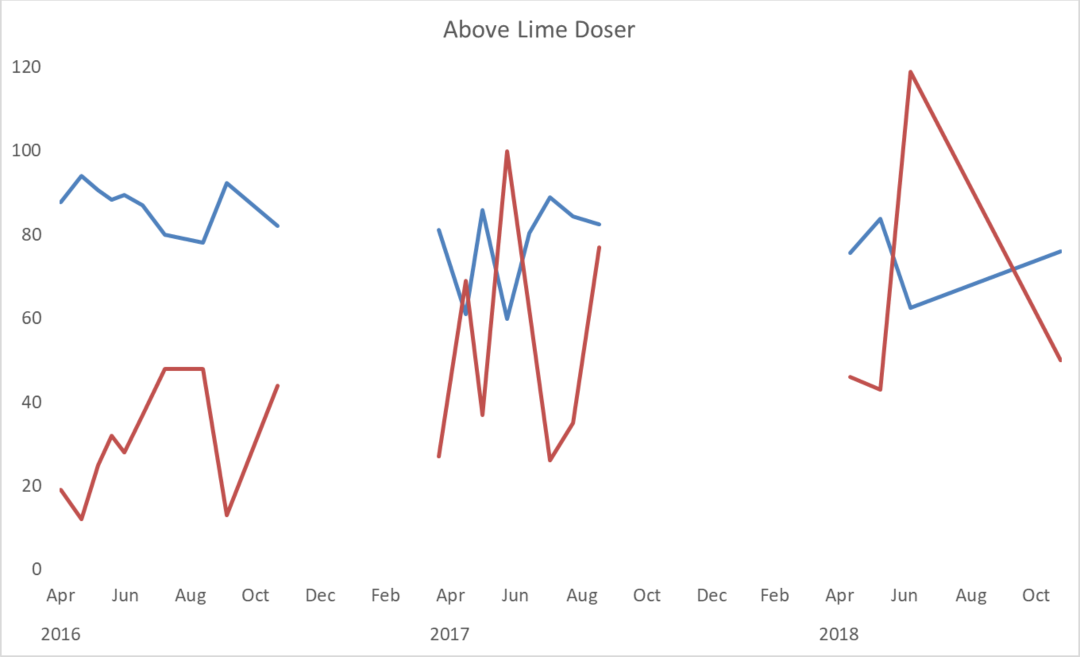

Figure B11 Time series of percentage Al_d comprised of Al_o for ALD, compared to absolute value of Al_i in ug L^{-1}.

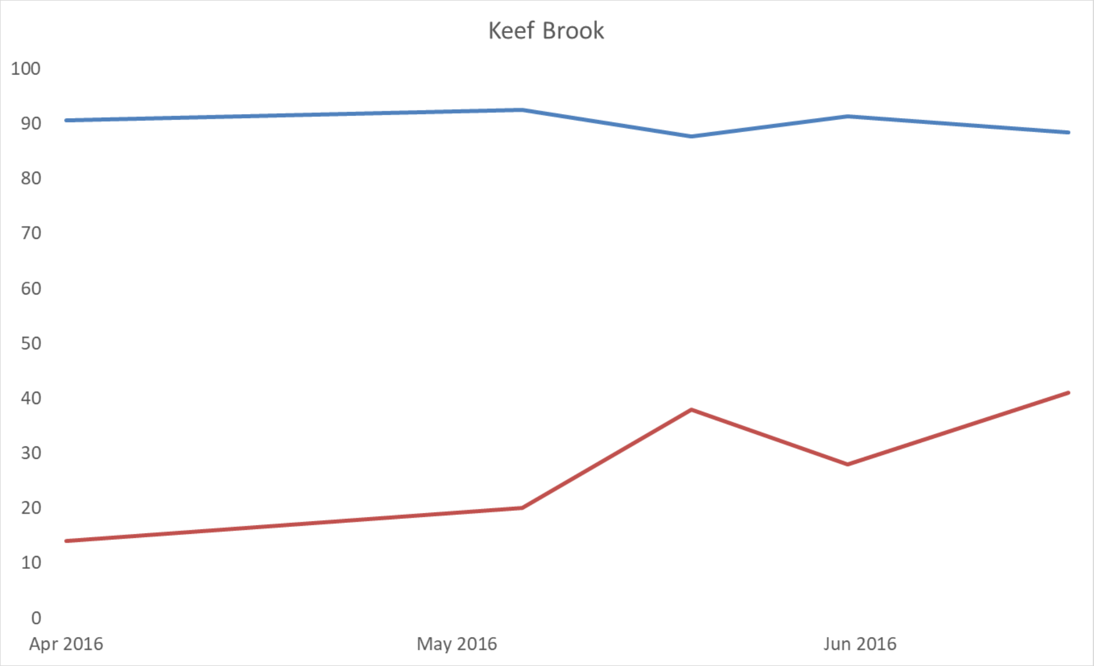

Figure B12 Time series of percentage Al_d comprised of Al_o for KB, compared to absolute value of Al_i in ug L^{-1}.

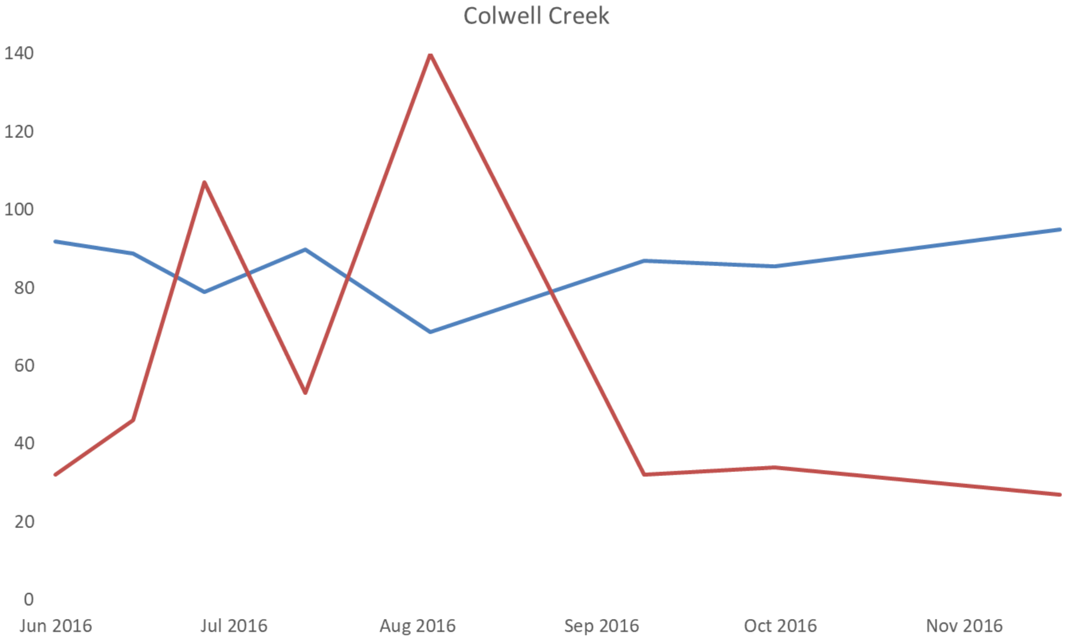

Figure B13 Time series of percentage Al_d comprised of Al_o for CC, compared to absolute value of Al_i in ug L^{-1}

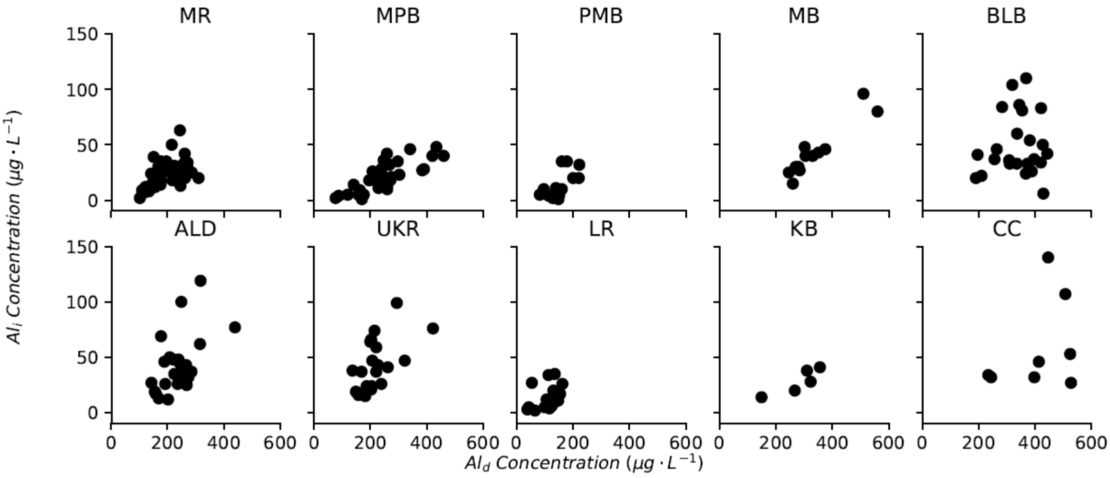

Figure B14 Least-squares linear regression of Al_i versus Al_d for each study site. One Al_i outlier removed for MR

(value: 2 µg L-1, date: 30 April 2015).

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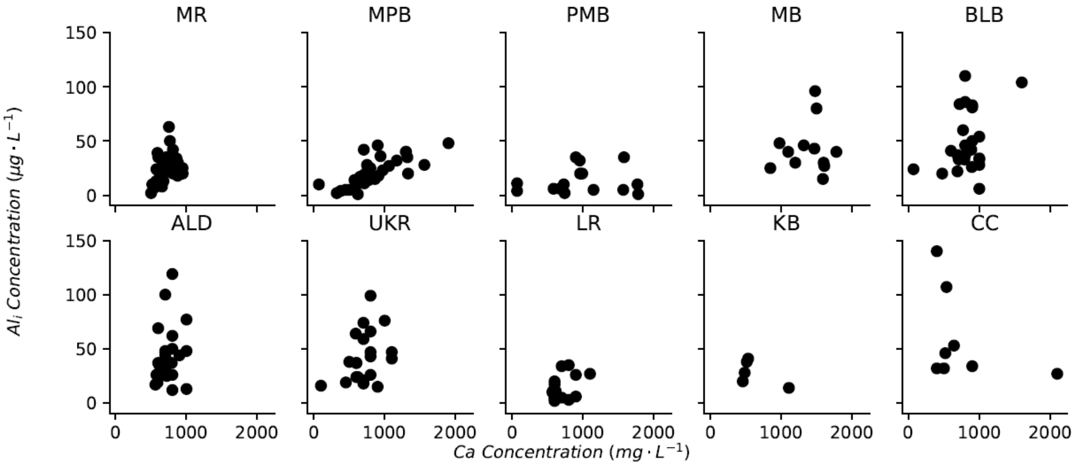

Figure B15 Least-squares linear regression of Al_i versus Ca for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015). One Ca outlier for KB removed (value: 1110 µg L-1, date: 29 April 2016).

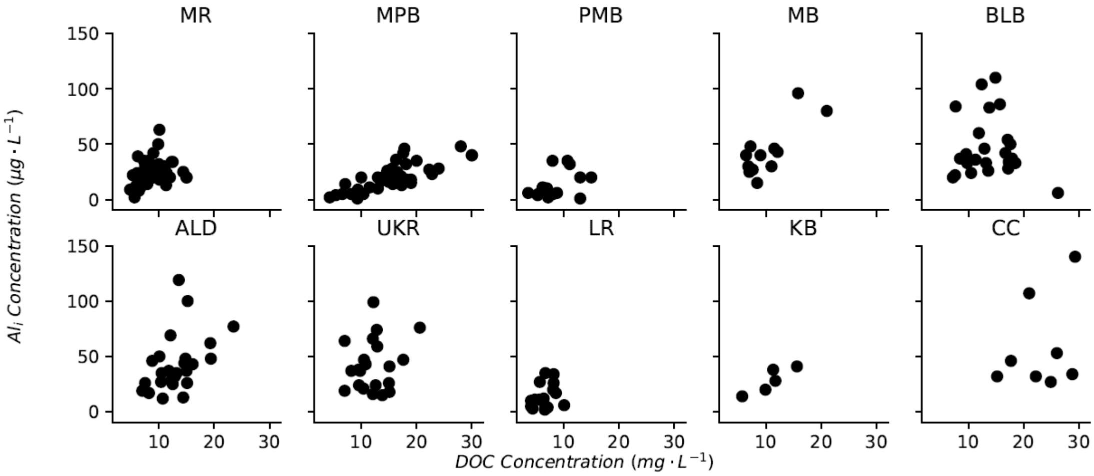

Figure B16 Least-squares linear regression of Al_i versus DOC for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

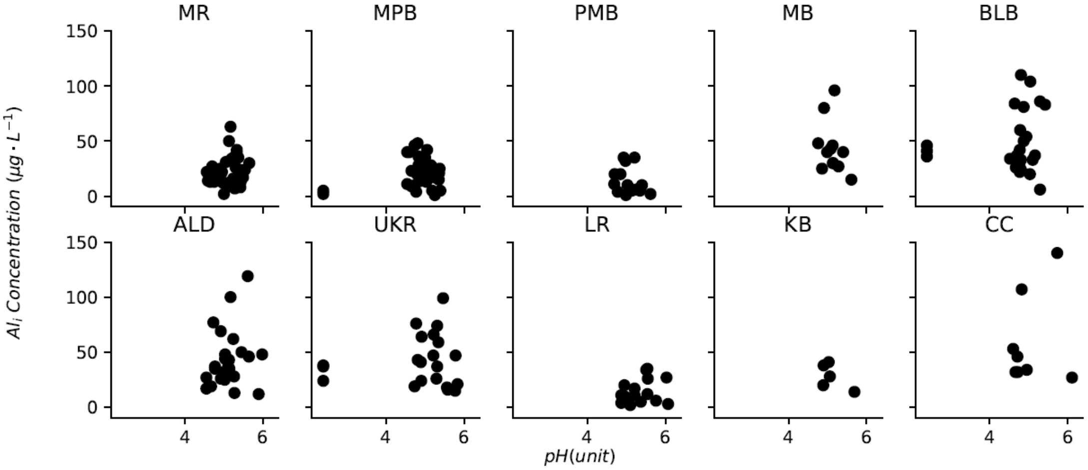

Figure B17 Least-squares linear regression of Al_i versus pH for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

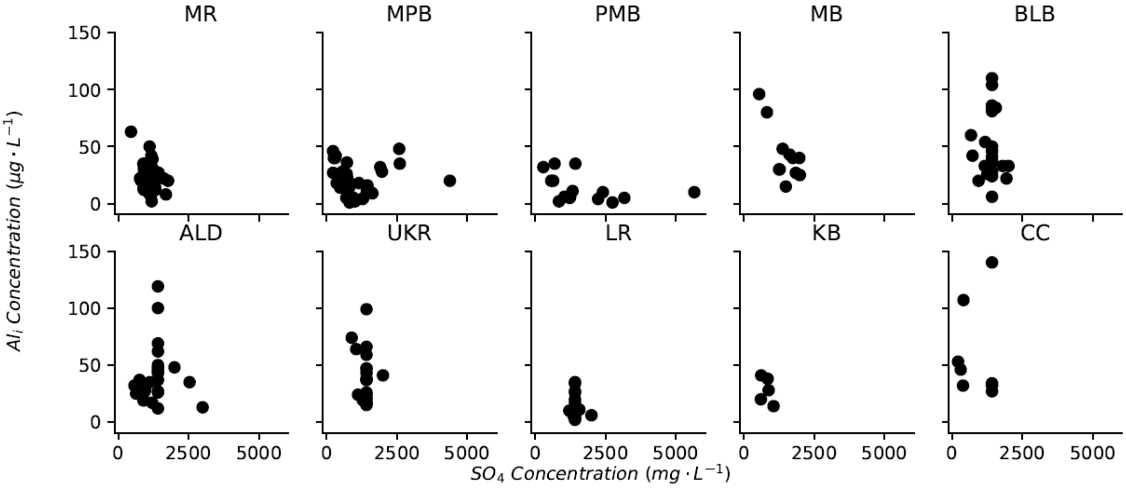

Figure B18 Least-squares linear regression of Al_i versus SO_4^{2-} for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

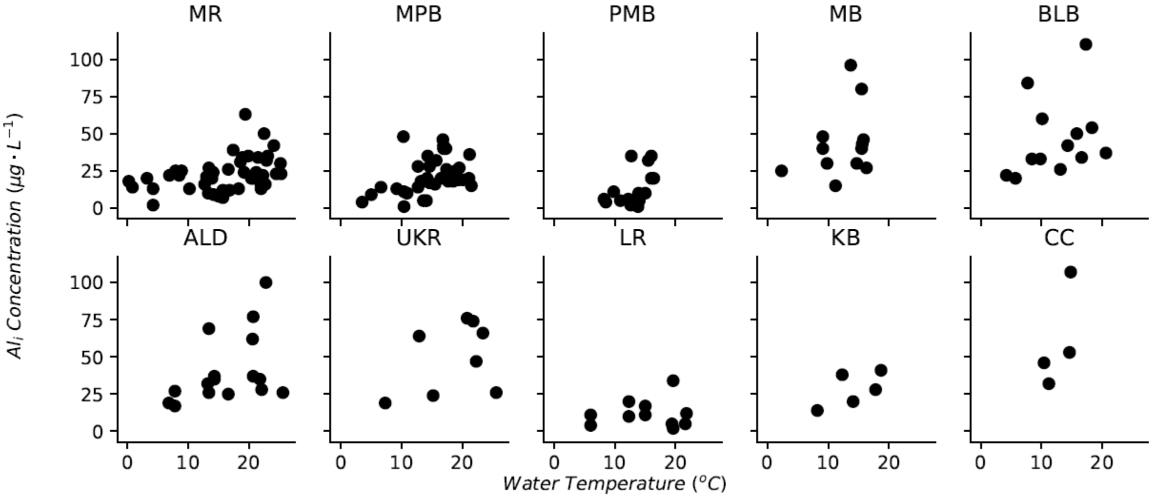

Figure B19 Least-squares linear regression of Al_i versus T_w for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015).

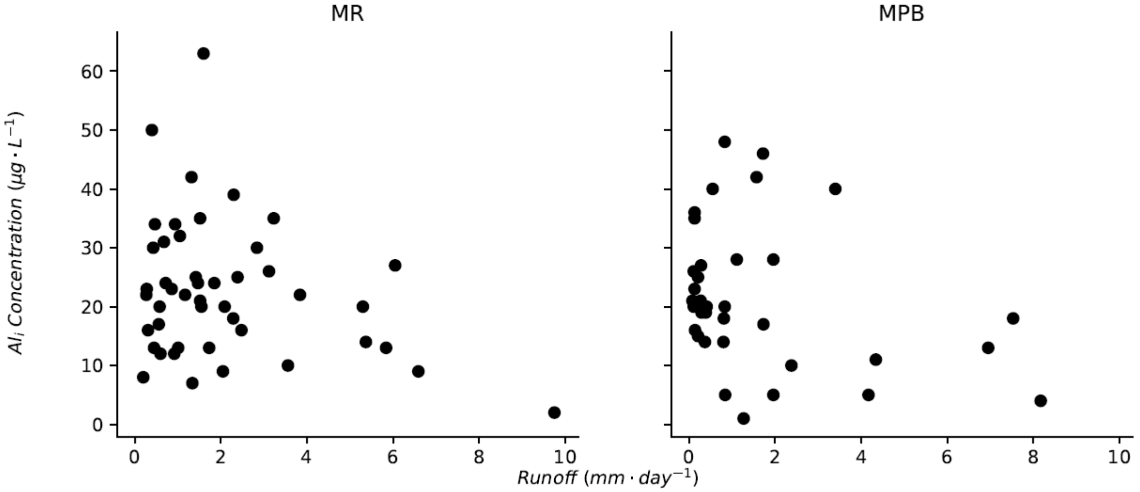

Figure B20 Least-squares linear regression of Al_i versus runoff for each study site. One Al_i outlier removed for MR (value: 2 µg L-1, date: 30 April 2015). One runoff outlier for MR removed (value: 17.294 mm day-1, date: 22 April 2015), and one runoff outlier for MPB removed (value: 34.994 mm day-1, date: 22 April 2015).

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:{}\n'.format(x_col, y_col, Sig))
```

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Appendix D. Additional methods

D.1 Laboratory analysis methods

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

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

SO_4^{2-} 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

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

Blanks were used to assess contamination during the Al_o 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_o and $Al_{filtered}$ or $Al_{unfiltered}$, 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.

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 µg 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

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

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).

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