Trends, Patterns, and Drivers of Freshwater Aluminium Concentrations: Revisiting the Conceptual Model of Freshwater Acidification

by

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Submitted in partial fulfilment of the requirements
for the degree of Master of Science

at

Dalhousie University
Halifax, Nova Scotia
August 2020

Great work is never done in isolation. This thesis is dedicated to the wonderful family and friends which supported me throughout its writing. Thank you for your encouragement, wise words, and unwavering belief in my ability; I could not have done this without you.

“You cannot get through a single day without having an impact on the world around you. What you do makes a difference, and you have to decide what kind of difference you want to make.” — *Jane Goodall*

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Abstract

Aluminium (Al) is toxic to freshwater and terrestrial flora and fauna. Al can cause reduced primary productivity, species mortality and extirpation, reduced bird nesting success, reduced forest health resulting in reduced carbon dioxide uptake, and human neurological and osteological diseases. In Europe and North America, base cation (C_B) depletion due to acid deposition is the primary cause of elevated freshwater Al concentrations. Since legislation reducing the emission of precursors to acid deposition was passed, several local scale studies documented freshwater acidification recovery. However, three recent continental and global scale studies on freshwater acidification recovery patterns indicate that acidification recovery may not be as widespread as once thought. Furthermore, the existing model of freshwater acidification does not explain the recovery patterns observed in these studies. Despite the threat of Al to ecosystems, local scale studies often do not focus on this element, resulting in an incomplete understanding of the drivers of freshwater Al concentrations. Additionally, global scale analyses have not examined Al, and global Al trends and concentrations remain unknown. My research focusses on filling these knowledge gaps by examining the trends, concentrations, and drivers of Al at both the regional and global scale. This thesis presents the identification, characterization, and causal attribution of short-term temporal fluctuations of Al and its species in Nova Scotia, Canada; it presents the creation of a global scale database of surface water chemistry and a use case of this database to identify, characterize, and attribute of the cause of long-term increasing Al trends across acidified regions; lastly, it presents how the aforementioned findings are used to update the existing 1983 model of freshwater acidification. Globally, two hotspots are identified where ecosystem health is threatened by increasing Al concentrations: Nova Scotia and Sweden. Contrary to existing conceptualizations, Al is predominantly predicted by freshwater organic carbon concentrations in these hotspots and other chronically acidified (low C_B) regions. My research contributes empirically and theoretically to the field by changing and enhancing our understanding of freshwater acidification recovery, and by providing a high quality, openly available, global dataset of acidification-related surface water chemistry.

List of Abbreviations Used

Table 1 List of abbreviations used throughout this thesis. Please note, charges of chemical elements and molecules are not used in the main text, with the exception of hydrogen ions and hydroxide ions. Table continued on next page.

Abbreviation	Full name
AIC	Akaike Information Criterion
Al	aluminium
Al_d	dissolved aluminium
ALD	above the West River lime doser
Al_{ext}	extractable aluminium
Al_i	inorganic monomeric aluminium
Al_o	organic aluminium
Al_{poly}	polymeric aluminium
Al_t	total aluminium
ANC	acid neutralization capacity
BLB	Brandon Lake Brook
Ca	calcium – Ca^{2+}
C_B	base cation: Ca, Mg, K, and Na
CC	Colwell Creek
CES	cation exchange site
Cl	chloride – Cl^-
CO_2	carbon dioxide
CRS	coordinate reference system
DOC	dissolved organic carbon
ECCC	Environment and Climate Change Canada
EIFAC	European Inland Fisheries Advisory Council
F	fluoride – F^-
Fe	iron
GEMStat	United Nations International Centre for Water Resources and Global Change's Global Water Quality Database and Information System
GIS	geographic information system
GLMM	generalized linear mixed model
GloRiCh	Global River Chemistry Database

Abbreviation	**Full name**
H^+	hydrogen ion
H_2S	hydrogen sulphide
H_2SO_4	sulphuric acid
HERC	Health and Environmental Research Centre
HNO_3	nitric acid
ICP-MS	inductively-coupled plasma mass spectrometry
ICP-OES	inductively-coupled plasma optical emission spectroscopy
ICS	ion-chromatography cystem
ISO	International Organization for Standardization
K	potassium – K^+
KB	Keef Brook
LR	Little River
MB	Maria Brook
Mg	magnesium – Mg^{2+}
MPB	Moose Pit Brook
MR	Mersey River
Na	sodium – Na^+
NH_4	ammonium – NH_4^+
NO_2	nitrite – NO_2^-
NO_3	nitrate – NO_3^-
NO_x	nitrogen oxide gasses
NS	Nova Scotia
NS Gov.	Nova Scotia Government
NS_A	acid-sensitive areas of Nova Scotia, Canada
NSERC	Natural Sciences and Engineering Research Council Canada
NSGS	Nova Scotia Graduate Scholarship
NSTD	Nova Scotia Topographic Database
OH^-	hydroxide ion
OLS	ordinary least squares
P	phosphorus
PLS	partial least squares
PMB	Pine Marten Brook
PO_4	phosphate – PO_4^{3-}
S	sulphur
S^{2-}	sulphide ion
SEO	search engine optimization

Abbreviation	**Full name**
SI unit	International System of Unit
SO_2	sulphur dioxide gas
SO_4	sulphate – SO_4^{2-}
SWatCh	surface water chemistry database
TOC	total organic carbon
UKR	Upper Killag River
US EPA	United States Environmental Protection Agency
USA	United States of America
WGS 84	World Geodetic System 1984

Acknowledgements

Thank you to Drs. Shannon Sterling, Lawrence Plug, and Rob Jamieson for their feedback, suggestions, and guidance throughout the writing of this thesis. Thank you to Dr. Kevin Keys, Dr. Keith Thompson, Denis Parent, and Heather Daurie answering my soils, statistics, and chemistry questions. Thank you to Lilian Barraclough for her feedback on the draft of this thesis.

Chapter 2. Thank you to Franz Heubach for his support with data analysis and Jon Petter Gustafsson for the Visual MINTEQ geochemical equilibrium model. This research was funded by the Natural Sciences and Engineering Research Council Canada (NSERC) through the Canadian Graduate Scholarship-Master's program and the Nova Scotia Government (NS Gov.) through the Nova Scotia Graduate Scholarship (NSGS) program.

Chapter 3. Thank you to the United Nations International Centre for Water Resources and Global Change, Environment and Climate Change Canada (ECCC), the United States of America (USA) National Science Foundation and National Water Quality Monitoring Council, the European Environment Agency, and Jens Hartmann, Ronny Lauerwald, and Nils Moosdorf for making the data collected by their contributing agencies, laboratories, researchers, and technicians openly available data for research. Thank you to Dr. Rob Jamieson for his feedback on the draft of this manuscript. Thank you to Abby Millard and Lilian Barraclough for assistance with compiling site data. This research was funded by the NS Gov. through the NSGS program.

Chapter 4. Thank you to our colleagues at L'Unité Mixte de Recherche Milieux environnementaux, transferts et interactions dans les hydrosystèmes et les sols for their feedback and administrative support, Jeff Minnichiello for his assistance with exploratory analysis, and Lilian Barraclough for her assistance with manuscript formatting and compilation of Table A3.1. Thank you to Lilian Barraclough and Abby Millard for assistance with compiling site data. This research was funded by NSERC, the NS Gov., the Salamander Foundation, and the Atlantic Salmon Conservation Foundation. The long-term analyses in this paper were made possible by monitoring programs conducted by ECCC in partnership with Nova Scotia (NS) Environment, the United States Environmental Protection Agency (US EPA) , the New York State Energy Research and Development Authority, the National Science Foundation through the Hubbard Brook Long-term Ecological Research program, the New York State Department of Environmental Conservation through the Buck Creek monitoring program, the Czech Science Foundation, and the Czech National Sustainability Program I.

Appendix 1. Thank you to two anonymous referees for their feedback on the manuscript, and Marley Geddes, Siobhan Takla, Franz Heubach, Lorena Heubach, Emily Bibeau, and Ryan Currie for their assistance with data collection. This research was funded by the Atlantic Salmon Conservation Foundation, Atlantic Canada Opportunities Agency, the NS Salmon Association, and Fisheries and Oceans Canada.

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Chapter 1 - Introduction

1.1 Background

1.1.1 Environmental Significance of Al

Aluminium (Al) threatens ecosystem and societal health. Elevated Al causes species extirpation (Brodin, 1995), reduced forest health (Collignon et al., 2012) and carbon sequestration, reduced crop success (Parker et al., 1987), increased cost of water treatment (Letterman & Driscoll, 1988), and threatens human health (World Health Organization, 2010). In this thesis, I focus on freshwater (that is, lacustrine and riverine) Al species (Table 2) and their associated threats (Table 3). Past research on freshwater Al has predominantly focussed on inorganic monomeric species of Al (Al_i) (for example, Exley et al., 1991; Kroglund et al., 2007; Kroglund & Staurnes, 1999; Kure et al., 2013; Lacroix & Townsend, 1987; Nilsen et al., 2013; Staurnes et al., 1996) and has neglected to examine other species, thereby failing to fully quantify the threat of Al to aquatic ecosystems.

Table 2 Abbreviations and operational definitions of Al species. Al species can be defined (1) functionally, aiming to identify Al species of known biological significance; (2) operationally, aiming to identify labile or inert Al species; or (3) classically, aiming to identify Al species based on chemical form (Namieśnik & Rabajczyk, 2010). Most previous research on freshwater Al operationally defines Al species; thus, I adhere to this convention.

Abbreviation	**Name(s)**	**Opperational definition**	**Example species**
Al_{mono}	monomeric Al	species with one Al atom per complex	aquo Al (Al^{3+})
Al_{poly}	polymeric Al	species with more than one Al atom per complex	Al oxide (Al_2O_3)
Al_t	total Al	all species	Al phosphate ($AlPO_4$)
Al_p	particulate Al	species ≥ 0.45 μm in diameter	kaolinite ($KAlSi_3O_8$)
Al_d	dissolved Al	species < 0.45 μm in diameter	Al fluoride (AlF_2^+, AlF^{2+}, AlF_4^-, AlF_3)
Al_o	non-labile Al, organic Al	organic monomeric species < 0.45 μm in diameter	Al oxalate ($Al(C_2O_4)_3^{3-}$)
Al_i	labile Al, cationic Al, inorganic Al	inorganic monomeric species < 0.45 μm in diameter	Al hydroxide ($Al(OH)_2^+$, $Al(OH)^{2+}$)

Table 3 Threats associated with Al species. Al species definitions are listed in Table 2; other chemistry abbreviations are listed in Table 1. Effects of Al species may be indirect; for example, total Al may be converted to more bioavailable Al$_i$ via acid digestion in the stomach (Martin et al., 1987). Table adapted from Rotteveel & Sterling (2020).

	Al Specie(s)	**Threat**
Aquatic nutrient cycling	Al$_d$/Al$_i$	Reduced freshwater Ca availability due to co-precipitation with sulphato-Al species, reducing nutrient bioavailability (Hindar & Lydersen, 1994).
	Al$_d$/ Al$_i$	Reduced freshwater P due to co-precipitation with hydroxy-Al and fluoro-Al species, reducing nutrient bioavailability (Driscoll & Schecher, 1990; Kopáček et al., 2001; Scheel et al., 2008).
	Al$_d$/ Al$_o$	Reduced freshwater DOC due to complexation with Al, reducing nutrient bioavailability, increasing light penetration, and reducing water temperature (Driscoll & Schecher, 1990; Scheel et al., 2008).
Algae	Al$_d$/ Al$_i$	Reduced acidophilic phytoplankton growth (for example, *Asterionella ralfsii*), reducing resources for higher trophic levels (Gensemer, 1991)
	Al$_d$	Increased green algae (*Mougeotia Temnogametum*) growth and decreased cyanobacteria (*Anabaena Lyngby*), and diatom (*Achnathes*) growth (Lacoul et al., 2011).
Invertebrates	Al$_t$/ Al$_d$	Reduced macroinvertebrate species richness (Beneš et al., 2017). Decreased taxa richness in headwater streams, with extirpation of molluscans, crustaceans, and Ephemeroptera (Guerold et al., 2000).
	Al$_{poly}$	Reduced egg laying and behavioural scores in *Lymnaea stagnalis* snails, reducing survival rates (Papathanasiou et al., 2011).
Amphibians	Al$_d$	Reduced fertilization success and larval growth, increased offspring mortality and larvae deformities, and increased development time for smooth newt (*Lissotriton vulgaris*) and palmate newt (*Lissotriton helveticus*) larvae; reduced feeding and mobility for Anuran larvae (Brady & Griffiths, 1995). Reduced Na intake causing toxic Na imbalance, reducing species density and richness (Wyman & Jancola, 1992). Decreased survival of Jefferson salamanders (*Ambystoma jeffersonianum*) and spotted salamanders (*Ambystoma maculatum*) (Horne & Dunson, 1995).
Fish	Al$_{poly}$	Recently-formed Al polymers are highly toxic to fish (Gensemer et al., 2018; Teien et al., 2004).
	Al$_i$/ Al$_{poly}$	Binding/deposition on gills disrupts: 1) ion transport, 2) osmoregulation, 3) acid-base balance, 4) nitrogen excretion, and 5) respiration (Lacroix, 1999) (Fivelstad et al., 2003; Lacroix, 1989). Increased mucus coating of salmonid gills, reducing brown trout (*Saamo trutta*) survivorship (Bulger et al., 1993; Hesthagen et al., 2016)
		Reduced at-sea survival for Atlantic salmon (*Salmo salar*) (Kroglund et al., 2007; Poléo & Hytterød, 2003). Amplified epithelial hyperplasia, hypertrophied Cl cells, Cl cell necrosis in rainbow trout (*Salmo gairdneri*) (Evans et al., 1988).
Water -foul	Al$_t$	Poorer regulation of Ca and P (Lacoul et al., 2011).
Humans and Society	Al$_t$	Potential neurotoxin; may contribute to development of Alzheimer's disease (Parkinsonism dementia), dialysis encephalopathy, and amyotrophic lateral sclerosis (World Health Organization, 2010). May cause conformation changes of Alzheimer's amyloid-beta protein, may cause tau and amyloid-beta protein accumulation, can induce neuronal apoptosis (Kawahara, 2005).
	Al$_t$	May cause bone disease such as osteoporosis and osteomalacia (D'Haese et al., 1999) by causing development of secondary hyperparathyroidism due to a decrease in osteoblasts (Cannata Andía, 1996). Al exchanges with Ca in bones (Namieśnik & Rabajczyk, 2010).
	Al$_t$	May cause anemia in dialysis patients due to decreased red blood cell production (Bia et al., 1989). May reduce Fe metabolism (Cannata Andía, 1996).
	Al$_t$	Increases cost of water treatment (Letterman & Driscoll, 1988).

1.1.2 Sources of Al

Al is the most abundant metal in the Earth's crust (7.8 % by weight) (Namieśnik & Rabajczyk, 2010) and is exported to freshwaters from soils and bedrock where it is present as the product of mineral weathering and podzolization.

1.1.2.1 Mineral Weathering

Most soil Al originates from the weathering of aluminosilicate minerals such as feldspars (Driscoll & Schecher, 1990; Schnoor & Stumm, 1986). Aluminosilicate minerals have slow dissolution kinetics (Bloom, 1983) and poor solubility at circumneutral pH, but are weathered under acidic ($pH < 6$) or alkaline ($pH > 8$) conditions and in the presence of complexing ligands (Kummert & Stumm, 1980; May et al., 1979). This includes dissolution by carbonic acid (H_2CO_3) produced via the hydration and disassociation of carbon dioxide (CO_2) (Driscoll & Schecher, 1990; Schnoor & Stumm, 1986), dissolution by strong acids like sulphuric acid (H_2SO_4) produced via the weathering of sulphidic bedrock (Hindar & Lydersen, 1994), and chelation by organic acids such as citric, oxalic, tartaric, and salicylic acids produced by soil microbes and plant roots (Kummert & Stumm, 1980; Stumm et al., 1983). For example, the dissolution of orthoclase, a potassium feldspar, can produce gibbsite (Eq. 1) and kaolinite (Eq. 2), where gibbsite is produced above pH 4.3 and below silica concentrations of $10^{-4.6}$ mol L^{-1} (Gardner, 1972).

$$KAlSi_3O_{8(s)} + 7H_2O_{(l)} + H^+_{(aq)} \rightarrow K^+_{(aq)} + Al(OH)_{3(s)} + H_4SiO_{4(aq)} \qquad (1)$$

$$2KAlSi_3O_{8(s)} + 9H_2O_{(l)} + 2H^+_{(aq)} \rightarrow 2K^+_{(aq)} + Al_2Si_2O_5(OH)_{4(s)} + 4H_4SiO_{4(aq)} (2)$$

1.1.2.2 Podzolization

Al-containing secondary minerals undergo further weathering and are distributed throughout the soil profile during the process of podzolization. Here, Al and iron (Fe) are solubilized from Al-containing minerals in the acidic upper soil horizons via congruent dissolution and are precipitated as amorphous Al hydroxides in lower soil horizons (Johnson et al., 1981; Lawrence et al., 1995; Schnoor & Stumm, 1986). Further, a gradient of Al concentration develops throughout the soil profile due to pH dependent Al speciation and electrostatic charge (Bloom et al., 1979; Cronan et al., 1986; Driscoll & Schecher, 1990; Helliweli et al., 1983; Lydersen, 1995). Soil organic matter concentration decreases with soil depth, while pH increases, resulting in an increase of positively-charged Al occupation of negatively-charged organic matter and clay surfaces (cation exchange sites; CESs) from the O to B horizons and decreasing occupation from B to C horizons (Ross et al., 2008). In podzols, Al occupation of CESs is at a maximum in the B horizons at soil pH 4.5 (Ross et al., 2008).

1.1.2.3 Al Mobilization from Soils

Al can be exported from soils via two soil pH buffering mechanisms: cation exchange and Al buffering (Keys, 2015). Cation exchange is the main soil buffering mechanism in the pH 4.2 to 5 range (Grennfelt et al., 1990). Under non-acidified conditions, positively charged base cations (C_B: calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na)) bound to CESs are leached together with acidic anions such as sulphate (SO_4) and nitrate (NO_3) to maintain soil solution neutrality (Grennfelt et al., 1990). If C_B's are not replenished by mineral weathering, they are replaced by positively-charged Al species and hydrogen ions (H^+) through a process called C_B depletion (Keys, 2015). Acid anions then cause Al and H^+ ions to be leached from CESs in place of C_B's (Grennfelt et al., 1990). Once soil base saturation (the percent of CESs occupied by C_B's) drops below 15-20 % Al release from CESs and concentration in soil leachate is increased (Reuss & Johnson, 1985). Al has a higher affinity for organic CESs than C_B's (De Coninck, 1980); thus, increased C_B inputs into the soil may not necessarily reverse this process. Al buffering occurs at soil solution pH < 4.2, where excess acidity is buffered by the dissolution of amorphous Al hydroxides (Eq. 3) (Grennfelt et al., 1990; Keys, 2015).

$$3H^+ + Al(OH)_3 \leftrightarrow Al^{3+} + 3H_2O \tag{3}$$

Al buffering limits the pH decrease in soils, but results in Al export and increases the concentration of high affinity Al available to replace C_B's on CESs (Keys, 2015).

Al may also undergo co-transport from soils with complexing ligands, including organic carbon, SO_4, and fluoride (F), all of which are environmentally significant (Driscoll & Schecher, 1990). The relative concentrations of these various Al species are dependant on pH, temperature, and concentrations of individual ligands (Driscoll & Schecher, 1990; Namieśnik & Rabajczyk, 2010; Santore et al., 2018; Schnoor & Stumm, 1986) (Figure 1). Al forms stable organo-Al complexes with a range of organic acids including low molecular mass acids (for example, acetic and oxalic acid), hydroxycarboxylic acids (for example, lactic, tartaric, and citric acids), polysaccharides, and high molecular mass acids (for example, humic and fulvic acids) (Ščančar & Milačič, 2006). Organo-Al complexes tend to be strongly-bonded and resistant to hydrolysis and polymerization, and are thus resistant to re-precipitation (Hagvall et al., 2015). Organo-Al complexation is reduced at low pH, as organic acids are instead protonated by H^+ (Driscoll & Schecher, 1990; Tipping & Carter, 2011). Sulphato-Al complexes are less common than fluoro-Al species, as they are less stable (Namieśnik & Rabajczyk, 2010). In extreme environments, where pH is low and F concentrations exceed those of Al, F outcompetes hydroxide ions (OH^-) and organic acids for binding sites with Al and fluoro-Al species (mainly AlF_2^+ and AlF_3) dominate (Berger et al., 2015).

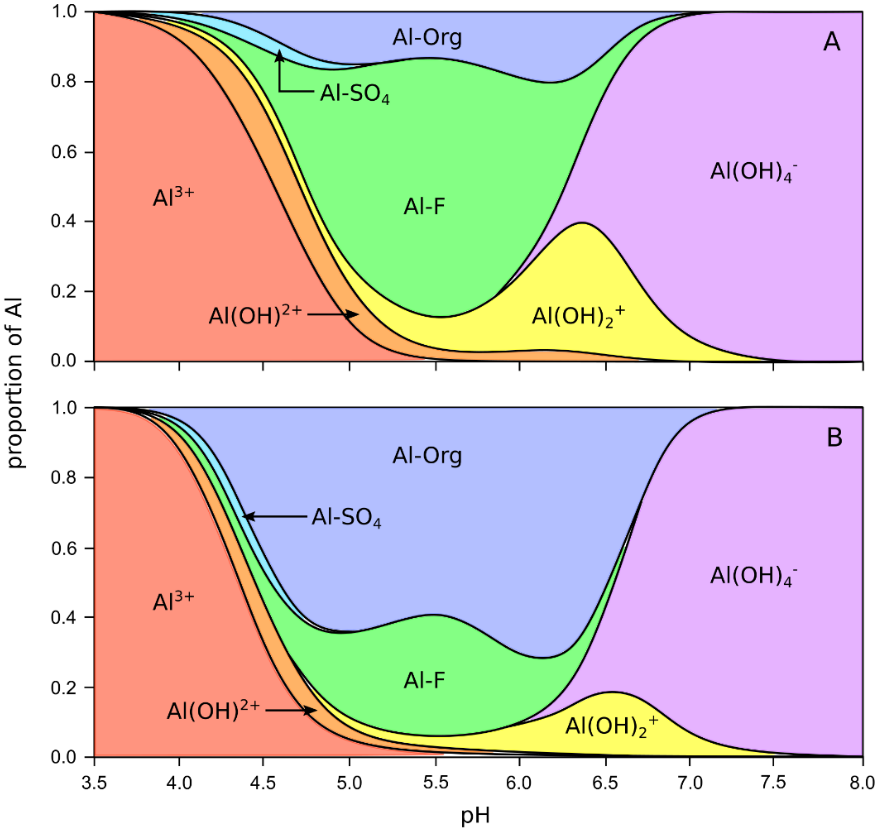

Figure 1 pH and ligand dependant Al speciation in low dissolved organic carbon (DOC) waters (1.2 mg L^{-1}*; A) and high DOC waters (12.0 mg* L^{-1}*; B). Calculations made with Al in equilibrium with* $Al(OH)_3$*,* $F = 0.1$ *mg* L^{-1}*, and* $SO_4 = 9.6$ *mg* L^{-1}*, as is typical of acid-sensitive waters in the Adirondack mountains, New York state, USA. The influence of temperature is not depicted, but shifts the distribution approximately one pH unit lower for a 20 °C decrease in temperature (Lydersen, 1995). Figure adapted from Driscoll & Schecher (1990).*

1.1.3 Anthropogenic Acid Deposition

Anthropologic acid deposition causes increased Al mobilization from soils, with elevated freshwater Al being one of the most lethal effects of this phenomenon (Gensemer & Playle, 1999). The burning of coal and other fossil fuels and metal smelting emits sulphur and nitrogen oxides, which form H_2SO_4 and nitric acid (HNO_3) in the atmosphere which enter ecosystems in the form of wet and dry acid deposition (Driscoll et al., 2001). Excess acid input causes soil C_B depletion and enhanced Al export in areas with sensitive mineralogy via the mechanisms discussed above (Keys, 2015). Regions with sensitive mineralogy have bedrock and overburden which is C_B poor due to low C_B bedrock and/or slow mineral weathering, and include northeastern North America and northern Europe (Schnoor & Stumm, 1986). The C_B depleting effects of anthropogenic acid deposition can be exacerbated by forest harvest, as discussed in section 1.1.4 (Drivers of Spatial and Temporal Al Variability).

Anthropogenic acid deposition was widely recognized as a problem during the acid rain crisis of the 1970s and 1980s (Driscoll et al., 2001). In response to the threat, governments across Europe and North America implemented legislation limiting the emission of precursors to acid rain, for example, the 1990 Canada-USA Clean Air Act Amendments (Environment and Climate Change Canada, 2016). Widespread reductions in SO_4 emission (Environment and Climate Change Canada, 2016) and deposition coincided with reductions in freshwater acidity (Driscoll et al., 2001, 2016; Stoddard et al., 1999). Reductions in sulphate deposition were partially countered by reductions in C_B deposition, predominantly Ca, in many areas (Hedin et al., 1994). C_B deposition, an important source of C_B for sensitive soils (Hedin et al., 1994), has remained low in recent years (Keys et al., 2016). However, with several regions reporting increasing freshwater C_B concentrations and some reporting decreasing Al concentrations (for example, Driscoll et al., 2016; Hesthagen et al., 2011), the problem of freshwater acidification was widely considered solved. However, research on Al response to anthropogenic acid deposition has been limited since the 1990s, and recent trends and concentrations of freshwater Al remain unknown across many regions.

Areas where C_B's increased relatively rapidly following emission reductions are recovering in adherence to the freshwater acidification model proposed by Galloway, Norton, and Church (Figure 2). This conceptual model was developed in 1983, and to my knowledge, has not been updated since. In the 1983 model, increased deposition of acid anions initially causes an increase in freshwater C_B concentrations as cation exchange from CESs buffers acid anions (Stage 2). As CESs are increasingly depleted of C_B's, acid anions are buffered by H^+ and Al, decreasing freshwater pH and increasing Al concentrations (Stage 3). In Stage 4 (steady-state acidification), soil C_B's are depleted, and soils undergo Al buffering, stabilizing pH declines. When acid deposition starts to decline, fewer acid anions are exported to freshwaters and pH increases (Stage 5); this process may be delayed in soils where SO_4 is reversibly adsorbed and is thus exported when acidity declines. C_B's may decrease further in Stage 5 because C_B scavenging occurs due to pH-dependant shifts in adsorption reactions within soils. In Stage 6, the rate of C_B addition to soils via mineral weathering is greater than the rate of export, allowing soil and freshwater C_B concentrations to increase and the system to return to pre-acidification conditions (Stage 7) (Galloway et al., 1983).

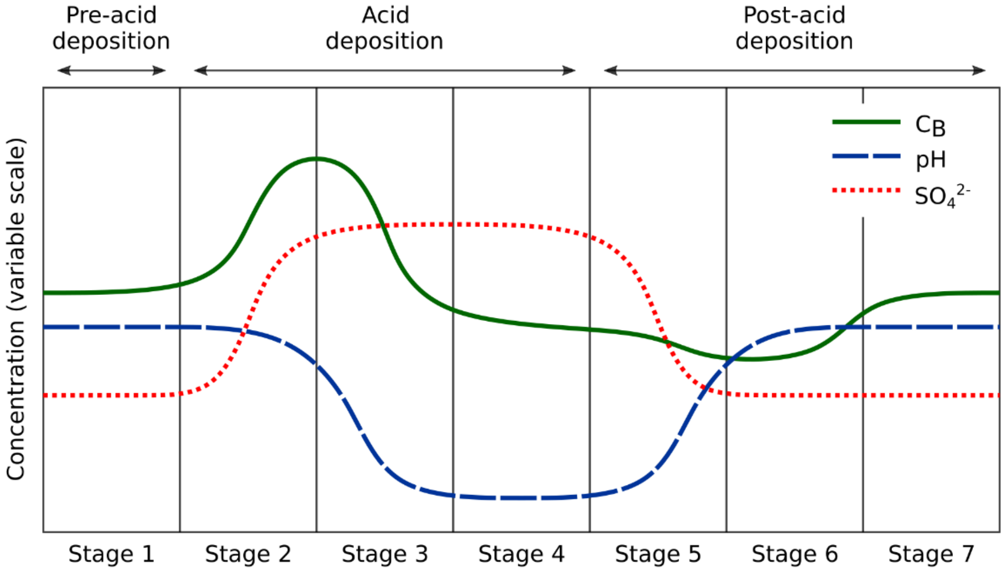

Figure 2 1983 conceptual model of freshwater acidification. Figure adapted from Galloway et al. (1983).

The 1983 model was developed prior to freshwater acidification recovery in most regions, and recent observations depart from those predicted by Galloway and colleagues. For example, C_B concentrations remain low (Warby et al., 2005) or are decreasing further (Jeziorski et al., 2008; Weyhenmeyer et al., 2019) in many regions where SO_4 emissions have decreased. Some of these declines in C_B export may be explained by decreased C_B deposition, which explains between 85% (Driscoll et al., 1989) and 0 - 30% of decreased C_B export (Watt et al., 2000), dependant on the region and time period examined. More recent studies indicate that atmospheric deposition of C_B contributes little to freshwater C_B concentrations (Likens et al., 1996; Watt et al., 2000), and do not propose reduced C_B deposition as a cause of the decreasing trends (Jeziorski et al., 2008; Weyhenmeyer et al., 2019). The inconsistencies of recent observations with the 1983 model indicate the model may be incomplete or incorrect.

The 1983 model may also be outdated; to my knowledge, it has not been updated since its creation. There are several potential reasons for this, most notably: 1) water chemistry responses to acid deposition in many established long-term monitoring sites, such as those in the Adirondack region of New York state, are behaving as predicted by the 1983 model (for example, Driscoll et al., 2003, 2007; Waller et al., 2012); 2) the validity of the model has is difficult to assess in many regions due to a lack of long-term monitoring data; and 3) sites where water chemistry response is not behaving as predicted by the 1983 model are deemed to have "delayed recovery" (for example, Clair et al., 2004; Likens et al., 1996; Likens & Buso, 2006).

The 1983 model does not account for the effects of organic carbon on Al export from soils, despite it being one of the most notable complexing ligands of Al (Santore et al., 2018). Organic carbon, present in soil organic matter, is affected by acidification through the acidity change mechanism. At lower pH, H^+ protonates the carboxylic functional groups of organic matter, neutralizing their negative change, reducing their charge density, and making them less hydrophilic, thus reducing their solubility and export from soils (Hruška et al., 2003; Tipping & Hurley, 1988; Tipping & Woof, 1990). Further, organic matter acts as a buffer from pH 3.5 to 5.0, and an acid at circumneutral pH due to the pH dependant dissociation of acidic functional groups (Hruška et al., 2003). By neglecting the pH-dependant solubility of organic carbon, a strong complexing ligand of Al, in response to acidification, key drivers of Al remain unaccounted for in the 1983 model.

1.1.4 Drivers of Spatial and Temporal Al Variability

In addition to anthropogenic acidification, watershed processes and characteristics influence Al export from soils, and thus its spatial and temporal variability. A non-exhaustive summary of processes known to drive soil Al export and the mechanisms through which this occurs are summarized in Table 4. Many of the processes identified in Table 4 are interlinked; for example, increased microbial nitrification, decomposition, and hydrogen sulphide (H_2S) oxidation during the warm summer months may cause an organic acid flush during the first fall rains, during which there is also C_B dilution, resulting in high freshwater Al concentrations (Dennis & Clair, 2012; Karimian et al., 2017; Wigington et al., 1996).

Once Al has been mobilized to freshwaters, it may undergo further speciation changes. These include photodecomposition of organo-Al (Kopáček et al., 2001, 2006; Porcal et al., 2009, 2010), and precipitation of amorphous hydroxy-Al and phosphato-Al via the mixing of waters with variable pH and phosphorus (P) concentrations, respectively (Kopáček et al., 2001). These speciation changes occur on the order of second to hours and may occur more than once during Al transport from headwaters to oceans (Gensemer & Playle, 1999).

Table 4 Summary of catchment processes known to drive freshwater Al concentrations. Chemistry abbreviations are listed in Table 1. Upward arrows and downward arrows indicate “increase” and “decrease”, respectively. Table continued on next page.

	Driver	**Mechanism**	**Soil solution acidity**	**Soil C_B availability**	**Complexing ligands**	**Reaction time for neutralization**
geologic	C_B poor bedrock	Low C_B input from bedrock weathering results in low C_B soils which are more susceptible to C_B depletion (Whitfield et al., 2006).		↓		
	F rich bedrock	Leaching of F from fluorine-rich granite bedrock provides a complexing ligand to Al, forming fluoro-Al species (Berger et al., 2015).			↑	
	acid rock drainage	Disturbance of S-containing rock such as gneiss and slate causes leaching and oxidation of S^{2-} to H_2SO_4 (Hindar & Lydersen, 1994).	↑			
pedologic	acid sulphate soils	Increased presence of acid anions decreases pH and depletes C_B stores (Ivarsson & Jansson, 1995).	↑	↓		
	soil composition	Poor vertical permeability prevents cation exchange in mineral soil horizon (Schnoor & Stumm, 1986).		↓		
	soil flow paths	Variable Al availability and speciation throughout the soil profile (Ryan et al., 2012; Schnoor & Stumm, 1986).	↕			
	soil moisture content	High moisture content reduces redox potential and soil solution pH (Ryan et al., 2012).	↑			
topographic	hillslope	Increased hillslope steepness reduces time for ion exchange and buffering of precipitation (Schnoor & Stumm, 1986).				↓
	wetlands	Increased organic acid production by microbial decomposition of organic matter (Ivarsson & Jansson, 1995).	↑		↑	
hydrologic	groundwater-dominated flow	Groundwater tends to have higher C_B concentrations due to prolonged contact with mineral soil and bedrock (Wigington et al., 1996).	↓			↑
	increased discharge	Dilution of soil solution C_B concentration (Wigington et al., 1996).	↑			
	organic acid pulse	Flushing of accumulated organic acids and NO_3 during the first rainfall event following a prolonged dry period (Kopáček et al., 2016; Wigington et al., 1996).	↑		↑	
	rapid throughflow	Decreased contact of throughflow with mineral soils and bedrock (Wigington et al., 1996).				↓
Meteorologic	North Atlantic Oscillation	NO_3 leaching rates increase during cold and wet years due to reduced assimilation by biota (Davies et al., 2005; Monteith et al., 2000; Veselý et al., 2003).	↑			
	sea-salt episodes	Sea salt (NaCl) deposited during on-shore storms disassociates, forming Na, which replaces C_B and Al on CESs, and Cl, facilitating soil cation export (Harriman et al., 1995).	↑	↓		

	Driver	**Mechanism**	**Soil solution acidity**	**Soil C_B availability**	**Complexing ligands**	**Reaction time for neutralization**
Meteorologic	temperature	Microbial nitrification rates increase with temperature (Kopáček et al., 2016).	↑			
	temperature	Microbial decomposition rates increase with temperature (Kopáček et al., 2016).	↑		↑	
microbial	nitrification	Production of acid anions (Stumm et al., 1983).	↑			
	denitrification	Consumption of acid anions (Schindler et al., 1986).	↓			
	decomposition	Microbial decomposition of organic matter produces weak organic acids (Clair et al., 2011; Collignon et al., 2012; Ryan et al., 2012).	↑		↑	
	decomposition	Microbial decomposition of vegetation produces organic matter CESs (Collignon et al., 2012; Ryan et al., 2012).		↑		
	H_2S oxidation	Microbial oxidation of H_2S to SO_4 when wetlands dry out, potentially creating acid sulphate soils (Karimian et al., 2017).	↑			
	SO_4 reduction	SO_4 reduction and precipitation as iron sulphides or binding as organic S consumes acid anions (Schindler et al., 1986).	↓			
vegetative	growth	C_B uptake by growing vegetation reduces soil C_B availability (Federer et al., 1989; Keys et al., 2016; Ryan et al., 2012).		↓		
	particle scavenging	Enhanced interception of acid deposition via increased air turbulence (Ryan et al., 2012).	↑			
	root respiration and exudates	Root respiration products and exudates contain organic acids (Collignon et al., 2012).	↑		↑	
	soil throughflow	Faster throughflow through soil macropores created by roots reduces time for neutralization reactions (Ryan et al., 2012).				↓
disturbance	acid deposition	H_2SO_4 and HNO_3 disassociate, forming H^+, which displaces C_B on CESs, and SO_4 and NO_3, which facilitate soil cation export (Borg & Sundbom, 2014; Clair et al., 2007, 2011; Galloway et al., 1983; Hinderer et al., 1998; Stoddard et al., 1999; Wright et al., 1988).	↑	↓		
	acid deposition	Reversibly adsorbed SO_4 in soils from deposition of H_2SO_4 is desorbed following reductions in acid deposition (Fölster & Wilander, 2002).	↑			
	forest fire	High C_B content of ashes temporary decreases soil acidity following forest fires (Lydersen et al., 2014).	↓			
	forest fire	Combustion and aerosolization of soil organic carbon (to CO_2), organic SO_4 (to SO_2), and organic nitrogen (to NO_x) produces localized acid deposition; these acids are mobilized upon rewetting of soils (Lydersen et al., 2014).	↑			
	forest harvest	Long-term soil C_B depletion through removal of C_B fixed in tree biomass (Harriman et al., 2003; Keys, 2015; Keys et al., 2016; Lahey, 2018).		↓		
	forest harvest	Nutrient pulse: a temporary increase in soil C_B availability due to reduced vegetation demands following forest harvest (Harriman et al., 2003).		↑		
	forest dieback	Increased NO_3 export due to reduced vegetation demand (Kopáček et al., 2017; Oulehle et al., 2019).	↑			
	forest dieback	Decomposition of dead vegetation returns C_B to soils, provided it is not removed (Oulehle et al., 2019).		↑		

Results of catchment scale studies such as those reported in Table 4 are often variable or contradictory across regions and the generalizability of these findings across regions is largely unknown. For example, short-term increased Al_i concentrations are caused by SO_4 export and base cation dilution in northeastern USA (DeWalle & Swistock, 1994) and NO_3 export in the Czech Republic (Kopáček et al., 2016). Even within a one geographic region (the Adirondack mountains, Catskill mountains, and Northern Appalachian Plateau in northeastern United Sates of America), the main drivers of short-term increased Al_i concentrations vary per site and throughout time (Wigington et al., 1996). Thus, despite the extensive catchment scale research on Al, there remains an incomplete understanding of drivers behind the spatial and temporal variability of Al concentrations and speciation.

1.2 Problem Statement and Research Questions

Most research on Al has been local in scope, resulting in an incomplete and incongruent understanding of the drivers of this ecologically harmful element at both the regional and global scale. Further, recent trends and concentrations of Al are unidentified across many regions, and it is unknown if these recent patterns correspond with those predicted by the existing 1983 model of freshwater acidification. In my thesis I aim to address these knowledge gaps by answering the following research questions:

RQ_1: What are the spatial, seasonal, and temporal patterns of Al concentrations in acidified regions? This question is addressed in Chapters 2, 4, and Appendix 1.

RQ_2: What are the chemical, meteorological, hydrological, land use/land cover factors associated with elevated and increasing total and cationic Al concentrations in acidified regions? This question is addressed in Chapters 2, 4, and Appendix 1.

RQ_3: What are the main limitations associated with global scale research on Al concentrations? This question is addressed in Chapter 3.

RQ_4: Does the 1983 model of freshwater acidification explain recent observations of Al concentrations, trends, and their drivers? This question is addressed in Chapter 4.

1.3 Research Objectives

The overarching objective of my thesis is to advance the scientific understanding of regional and global scale patterns of changes in Al concentrations due to freshwater acidification. I aim to fulfill this goal by meeting the following sub-objectives:

O_1: To identify where, when, and under what conditions Al and its species pose a threat to aquatic ecosystems. This objective is addressed in Chapter 2 and Appendix 1.

O_2: To create a database facilitating research on the trends, patterns, and drivers of Al concentrations at the global scale. This objective is addressed in Chapter 3.

O_3: To re-evaluate and update the existing 1983 model of freshwater acidification to account for recent Al observations. This objective is addressed in Chapter 4.

1.4 Outline and Interrelationship of Chapters

My thesis has three chapters and one appendix, aside from the introduction (Chapter 1) and conclusion (Chapter 5). Each chapter addresses one or more gaps in the scientific knowledge of the trends, patterns, and drivers of freshwater Al concentrations and culminates in my contribution to changing the theoretical model of freshwater acidification recovery (Chapter 4). Chapters 2, 3, 4, and Appendix 1 are based on published articles or in-preparation manuscripts; figure formats and headings for these chapters reflect the guidelines for the journal the article/manuscript was/will be submitted to and differs per chapter. Below, I provide a brief description of each chapter, and the journal, publication, and authorship details. I discuss the contributions of the authors in detail in the preamble to each chapter.

Chapter 2: *Five Aluminum Seasonality Regimes Identified in Chronically Acidified Rivers of Nova Scotia*. This chapter presents my research on the seasonal patterns of Al concentrations and their drivers across 16 rivers in NS, Canada. The article on which this chapter is based was published in December 2019 in Environmental Science and Technology. Lead author: Lobke Rotteveel. Co-author: Dr. Shannon Sterling.

Chapter 3: *The Surface Water Chemistry (SWatCh) database: A Standardized Global Database of Water Chemistry to Facilitate Large-Sample Hydrological Research*. This chapter presents the global database of freshwater acidification-related surface water chemistry which I developed to identify trends, patterns, and drivers of Al concentrations at a global scale. The manuscript on which this chapter is based is in preparation for submission to Earth Systems Science Data. Lead author: Lobke Rotteveel. Co-author: Dr. Shannon Sterling.

Chapter 4: *Unexpected Increases in Aluminium in Northern Lakes and Rivers*. This chapter presents trends of Al across Europe and northeastern North America between 2000 and 2015 and a new conceptual model of freshwater acidification recovery explaining the observed increasing Al concentrations. The manuscript on which this chapter is based is in preparation for submission to Nature. Lead authors: Dr. Shannon Sterling, Lobke Rotteveel, Sarah MacLeod. Co-authors: Scott W. Bailey, Caroline Björnerås, Douglas Burns, Tom A. Clair, Irena Creed, Heleen de Wit, Charles T. Driscoll, Chris Evans, Ivan Fernandez, Kristin Hart, Franz Heubach, Jim Kellogg, Pirkko Kortelainen, Hjalmar Laudon, Gregory Lawrence, Iain Malcom, Steve Norton, Filip Oulehle, Antti Räike, Gunnhild Riise, and Gesa Weyhenmeyer.

Appendix 1: *Ionic Aluminium Concentrations Exceed Thresholds for Aquatic Health in Nova Scotian Rivers, Even During Conditions of High Dissolved Organic Carbon and Low Flow*. This chapter presents the spatial and temporal patters of toxic Al_i in NS over a four-year period. The article on which this chapter is based in in press at Hydrology and Earth Systems Sciences. Lead author: Dr. Shannon Sterling. Co-authors: Lobke Rotteveel, Sarah MacLeod, Kristin Hart, Thomas A. Clair, Edmund A. Halfyard, Nicole L. O'Brien.

Chapter 2 - Five Aluminum Seasonality Regimes Identified in Chronically Acidified Rivers of Nova Scotia

2.1 Preamble

Lobke Rotteveel and Shannon Sterling

This chapter forms the basis of an article published in December 2019 in Environmental Science and Technology. I conceived the original idea, compiled the data, conducted the data analysis, conceptualized and prepared the figures and tables, and was the principal author. Dr. Shannon Sterling (supervisor) provided ideas, advice, and supervision, and co-edited the article. This article is reprinted with permission from Rotteveel, L. and Sterling, S. (2020) Five Aluminum Seasonality Regimes Identified in Chronically Acidified Rivers of Nova Scotia, Environmental Science and Technology, 54, 807−817. Copyright 2020 American Chemical Society.

2.2 Abstract

Despite reductions in acid deposition, high freshwater Al concentrations continue to threaten acidified ecosystems across the northern hemisphere. Seasonally elevated Al concentrations may pose a particular threat to freshwater organisms. Despite this threat, there is a lack of understanding about the timing and drivers of seasonal Al fluctuations. Here, we address this knowledge gap by identifying seasonal patterns of Al and their drivers in 16 rivers across NS, Canada. We identify five distinct Al regimes with different timing of seasonally elevated Al concentrations. Regimes are distinguished by correlation strength and direction between Al and C_B's, total organic carbon (TOC), turbidity, and river discharge. Most notably, regimes are distinguished by a gradient of Al – C_B decoupling as Ca and Mg concentrations approach 1.4 mg L^{-1} and 0.6 mg L^{-1}, respectively. Seasonally elevated Al concentrations exceeded the 0.1–0.2 mg L^{-1} World Health Organization drinking water guidelines in all regimes, and Al_i is projected to exceed the 15 µg L^{-1} threshold for aquatic health in most rivers. This research highlights the complexity of

seasonal Al dynamics and the importance of understanding seasonal variation of Al to quantify the impact of Al on human health, water treatment, and aquatic organisms.

2.3 Introduction

High freshwater Al concentrations continue to threaten acidified ecosystems. Following sulphur emission reduction legislation enacted in the 1990s and 2000s, several studies in Europe and North America demonstrated chronically acidified ecosystems had recovered; for example, (Hesthagen et al., 2011). However, recently and unexpectedly, high and increasing freshwater Al concentrations were identified across the northern hemisphere (Sterling et al., 2019).

Increased freshwater Al is caused by chronic acidification. Chronically acidified rivers are usually defined by decreased pH, acid neutralization capacity (ANC), and C_B concentrations (Driscoll et al., 2001). However, this definition is evolving due to delays in recovery where pH increases while C_B's remain low (Weyhenmeyer et al., 2019). For example, pH and ANC have significantly increased in some rivers in NS, Canada, between 1990 and 2007 (Clair et al., 2011), yet acid deposition is above critical loads in some portions of these catchments (Forest Mapping Group, 2007) and the rivers remain at risk of decreased C_B's and increased Al.

Ecosystem acidification and associated elevated Al (Clair et al., 2007) is harmful to terrestrial (Clark & Hall, 1985; Eriksson et al., 1989; Feller, 2005) and aquatic (Clair et al., 2007; Lacoul et al., 2011; Lacroix, 1985; Smith et al., 1990) flora and fauna, is a potential human neurotoxin (World Health Organization, 2010), and increases the cost of water treatment (Letterman & Driscoll, 1988). Bioavailable Al_i pose the greatest threat to aquatic biota. However, colloidal and precipitated species of Al were recently identified as a threat in water chemistry transition zones and at higher pH levels (Gensemer et al., 2018; Santore et al., 2018).

Studies have identified four mechanisms that mobilize Al from soils through increased acidity (Galloway et al., 1983) or charge imbalances (Lawrence et al., 1995): dilution of

C_B's during high flow (Borg & Sundbom, 2014), flushing of accumulated SO_4 and non-organic acids during rainfall following summer droughts (Clair et al., 1995), sea salt-driven H^+ leaching in coastal soils (Heath et al., 1992), and mobilization by dissolved organic carbon (DOC) in soil solutions through formation of organometallic colloids and increased acidity from organic acids (SanClements et al., 2018). These drivers may have seasonal patterns.

NS is a hotspot area of increasing Al (Sterling et al., in prep.). Here, average dissolved Al concentrations exceed the 0.1–0.2 mg L^{-1} threshold (Sterling et al., 2019) for human drinking water set by Health Canada (Health Canada, 2019) and the World Health Organization (World Health Organization, 2010). In addition, Al_i concentrations already exceed the European Inland Fisheries Advisory Council threshold for freshwater health, 15 µg L^{-1} at pH 5–6, and 30 µg L^{-1} at pH < 5 (Dennis & Clair, 2012; Howells et al., 1990; Sterling et al., 2019) with particular threats to local wild Atlantic salmon populations (Committee on the Status of Endangered Wildlife in Canada, 2011; Lacroix, 1985). As Al concentrations increase (Sterling et al., 2019), more tolerant freshwater fish species such as perch (*Perca fluviatilis*) and brown trout (Poléo et al., 1997) may also be harmed.

There is a lack of consensus in prior research on the timing of seasonally elevated Al concentrations. Most prior studies have focused on patterns of Al_i, which were found to be elevated during high flow events (Collignon et al., 2012; Kopáček et al., 2016; Ryan et al., 2012; Tipping & Carter, 2011; Wigington et al., 1996). These events occurred in the spring (Ryan et al., 2012; Wigington et al., 1996), fall (Dennis & Clair, 2012), and winter (Collignon et al., 2012; Harriman et al., 1995; Kopáček et al., 2016; Ryan et al., 2012). The processes regulating Al_i differ from those regulating total Al (Al_t) and are, thus, unreliable indicators of seasonal variation of Al_t concentrations. Further, most prior research has focused on Al fluctuation in response to short-term episodic events (for example, Collignon et al., 2012; Kopáček et al., 2016; Ryan et al., 2012; Tipping & Carter, 2011; Wigington et al., 1996)) as opposed to longer-term seasonal drivers.

Our motivation for examining seasonal Al concentrations is three-fold: to identify seasonal-specific threats to Al sensitive species, to better design and interpret sampling schemes, and to understand the mechanisms driving Al concentrations in rivers. This will allow us to better characterize the threat of Al to human health (World Health Organization, 2010), water treatment (Letterman & Driscoll, 1988), and aquatic organisms (Clair et al., 2007; Lacoul et al., 2011; Lacroix, 1985; Smith et al., 1990), including species at risk (Committee on the Status of Endangered Wildlife in Canada, 2011). Here, we aim to address the above knowledge gaps by detecting and examining seasonal patterns of Al concentrations and its drivers between January 1st, 2000 and December 31st, 2018 in 16 spatially distributed rivers across NS, Canada. Specifically, we aim to answer the following two research questions: what chemical, meteorological, hydrological, land use/land cover factors are associated with elevated Al concentrations? And in which seasons do elevated Al concentrations occur?

2.4 Materials and Methods

2.4.1 Study Area

The 55,284 km^2 province of NS on the Atlantic coast of Canada is particularly sensitive to freshwater acidification due to low ANC, high concentrations of naturally occurring organic acids, and historic atmospheric deposition of SO_2 and NO_x (Clair et al., 2007). pH and ANC have not significantly increased in most rivers since the 1980s (Clair et al., 2011; Watt et al., 2000), and most monitored rivers across the province are considered acidified (Clair et al., 2004; Dennis & Clair, 2012).

Bedrock in acid sensitive areas of the province is dominated by slow-weathering, C_B poor granite (Aitkenhead-Peterson et al., 2005). Overlying the bedrock are loamy humo-ferric podzols, ortstein podzols on deep sandy tills, peaty gleysols, fibrisols on raised and flat bogs, and organic mesisols on fens (Aitkenhead-Peterson et al., 2005). Small areas of sulfide-bearing slates produce acid rock drainage when exposed to air and water, resulting in a natural non-point source acidification (Clair et al., 2007). Acid sulphate soils are uncommon and are limited to coastal areas (Neily et al., 2011). The province has a moderate climate, with average air temperatures ranging between -10 °C during the winter to 25 °C during the summer. Hydrographs across the province are characterized by the spring freshet and rainfall events concentrated in the spring and fall (Figure A2.1).

2.4.2 Site Selection

We selected 16 rivers (Figure 3; Table 5) from the ECCC Long Term Water Quality Monitoring database (Table A2.1). Monitoring at our study sites was established under the ECCC Long Range Transport of Airborne Pollutants monitoring program, due to risk of acidification (Parent, 2019), or under the ECCC NS Surface Water Monitoring Program to support the Canadian Environmental Sustainability Indicator Water Quality Index reporting (Parent, 2019). Sites established under the latter program were selected to be representative of different land use/land cover conditions, including potential risk of acidification, and different ecoregions within NS (Parent, 2019).

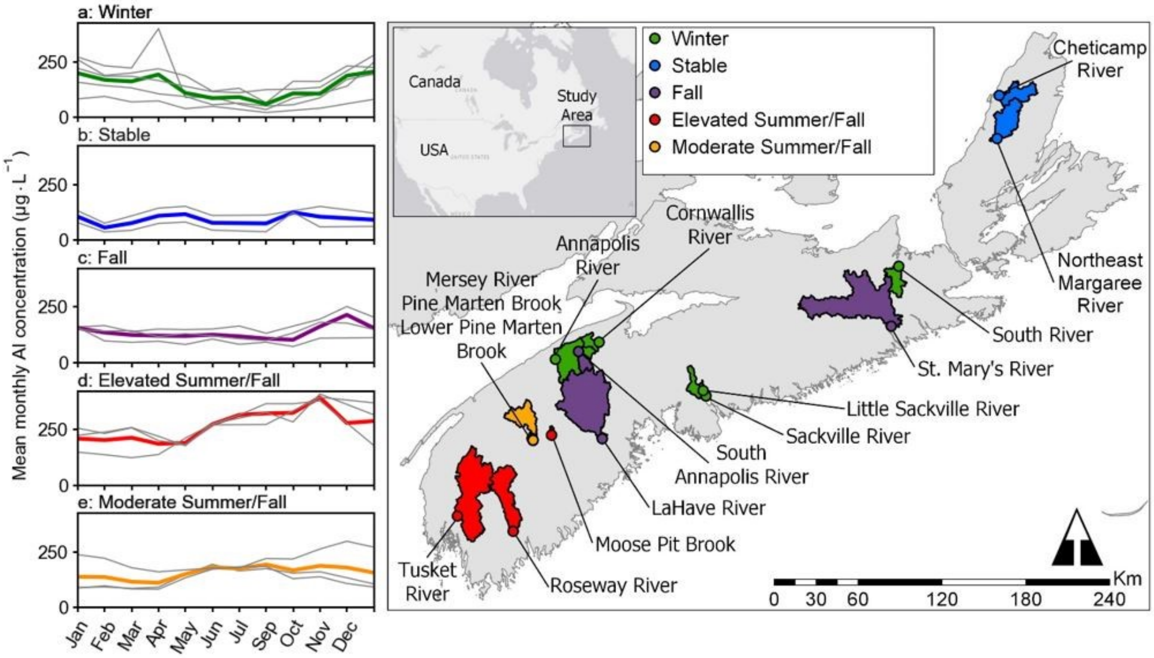

Figure 3 Map of sampled catchments (polygons), and sample site locations (points), coloured to represent seasonal Al regime clusters. Monthly median Al concentrations between January 1st, 2000 and December 31st, 2018 are plotted in gray for individual sites and in colour for the average monthly median concentration for each regime. Basemap sources: Esri, DeLorme, HERE, MapmyIndia.

Table 5 Watershed characteristics. Land use/land cover values may not sum to 100% due to overlap of features and presence of lakes, exposed bedrock, and harvested areas.

Site Name	**Latitude**	**Longitude**	**Regime**	**Watershed Size (km²)**	**Percent Cover (%)**			**Climate**	
					Forest	**Wetland**	**Anthro-pogeinc**	**Temp. (°C)**	**Precip. (mm)**
Annapolis River	44.9492	-65.0292	winter	551.17	70.7	3.2	7.6	7.7 ± 8.9	96 ± 44
Cornwallis River	45.0647	-64.6358	winter	86.31	41.3	2.0	7.1	8.3 ± 8.8	104 ± 45
Little Sackville River	44.7636	-63.6889	winter	13.21	46.0	1.9	8.6	7.0 ± 8.8	118 ± 60
Sackville River	44.7303	-63.6631	winter	150.49	72.1	5.3	6.9	7.0 ± 8.8	118 ± 60
South River	45.5578	-61.9039	winter	178.08	84.7	1.6	1.1	7.1 ± 8.7	94 ± 46
Cheticamp River	46.6428	-60.9439	stable	240.14	82.1	10.7	0.1	6.9 ± 8.4	132 ± 71
Northeast Margaree River	46.3656	-60.9750	stable	368.26	97.0	2.2	1.0	7.2 ± 8.3	121 ± 66
LaHave River	44.4467	-64.5917	fall	1255.84	88.4	4.5	4.9	7.6 ± 8.7	122 ± 63
Saint Mary's River	45.1739	-61.9800	fall	1339.09	91.9	3.0	4.6	7.1 ± 8.7	94 ± 46
South Annapolis River	45.0017	-64.8223	fall	101.51	86.5	4.3	0.9	7.7 ± 8.9	96 ± 44
Moose Pit Brook	44.4619	-65.0483	elevated summer/fall	17.13	99.0	3.0	0.1	7.6 ± 8.7	122 ± 63
Roseway River	43.8381	-65.3694	elevated summer/fall	496.42	85.3	9.9	0.5	7.4 ± 6.0	103 ± 53
Tusket River	43.9242	-65.8667	elevated summer/fall	1062.65	85.4	7.9	2.2	7.5 ± 7.2	110 ± 52
Lower Pine Marten Brook	44.4236	-65.2133	moderate summer/fall	1.10	96.9	5.4	0.0	7.6 ± 8.7	124 ± 63
Mersey River	44.4367	-65.2228	moderate summer/fall	292.43	88.4	5.6	0.7	7.6 ± 8.7	123 ± 63
Pine Marten Brook	44.4264	-65.2128	moderate summer/fall	0.68	96.2	3.8	0.0	7.6 ± 8.7	124 ± 63

Rivers were selected based on Al data which met our sampling criteria: a minimum of four samples per year, as per federal guidelines (Task Force on Water Quality Guidelines, 2007), for a minimum of ten consecutive years between January 1st, 2000 and December 31st, 2018. These criteria eliminated all lakes, which were usually sampled twice per year and most smaller rivers which were sampled less frequently by ECCC. If sites had two non-consecutive ten-year timeseries, we used the most recent one. Timeseries length ranged from 10 to 18 years (average: 12.7 years), with an average of 204 samples per site per variable (range: 59–790 samples; Table A2.2).

2.4.3 Water Chemistry Data

We extracted Al_t, total C_B: Ca, Mg, K, Na, dissolved anions: chloride (Cl), SO_4, NO_3, and TOC, turbidity, and pH from the ECCC Long Term Monitoring database (Table 6). F, ammonium (NH_4), DOC, dissolved cation, total anion, and speciated Al data were not included, as they were measured too infrequently. Water chemistry samples were analyzed at ECCC Atlantic Laboratory for Environmental Testing in Moncton, New Brunswick (Clair et al., 2007). To compensate for pH changes during transport from field to laboratory, we converted laboratory pH to field pH equivalent using a calibration curve (Eq. 4) calculated using ordinary least squares (OLS) regression ($n = 754$, $r^2 = 0.993$, p-value < 0.001).

$$pH_{field} = 0.9361(pH_{lab}) \tag{4}$$

Table 6 Average water chemistry concentrations (mean ± standard deviation). Cations measured as total concentration, anions as dissolved concentration.

Site name	**Regime**	**Al** (µg L^{-1})	**Ca** (mg L^{-1})	**Mg** (mg L^{-1})	**Na** (mg L^{-1})	**Cl** (mg L^{-1})	**NO_3** (mg L^{-1})	**SO_4** (mg L^{-1})	**TOC** (mg L^{-1})	**Turbidity** (NTU)	**pH** (unit)
Annapolis River	winter	155 ± 111	9.8 ± 4.5	1.7 ± 0.5	8.5 ± 3.1	13.6 ± 4.9	0.4 ± 0.2	8.1 ± 3.8	6.6 ± 2.6	2.4 ± 1.6	6.9 ± 0.3
Cornwallis River	winter	112 ± 143	28.3 ± 9.0	3.5 ± 0.7	15.3 ± 3.8	27.3 ± 8.2	2.0 ± 0.7	24.0 ± 11.7	4.8 ± 1.8	3.9 ± 4.3	7.2 ± 0.2
South River	winter	50 ± 44	12.0 ± 5.9	1.7 ± 0.5	45.6 ± 36.8	71.0 ± 60.5	0.2 ± 0.1	18.2 ± 12.5	3.6 ± 1.1	1.3 ± 1.0	7.0 ± 0.2
Sackville River	winter	146 ± 75	4.7 ± 1.2	0.9 ± 0.1	16.1 ± 5.2	24.6 ± 8.6	0.1 ± 0.1	5.8 ± 1.2	6.2 ± 1.7	1.9 ± 1.4	6.5 ± 0.2
Little Sackville River	winter	97 ± 96	16.5 ± 7.0	2.5 ± 0.9	42.6 ± 23.6	67.7 ± 40.3	0.3 ± 0.1	14.5 ± 4.7	5.5 ± 1.5	2.8 ± 1.7	7.1 ± 0.2
Northeast Margaree River	stable	47 ± 37	10.9 ± 4.7	1.3 ± 0.3	12.9 ± 6.6	18.5 ± 9.4	0.1 ± 0.1	18.3 ± 8.5	2.4 ± 1.5	0.4 ± 0.3	6.9 ± 0.2
Cheticamp River	stable	110 ± 61	2.0 ± 0.5	0.8 ± 0.2	4.7 ± 0.7	6.8 ± 1.5	0.0 ± 0.0	2.1 ± 0.4	5.8 ± 2.5	0.4 ± 0.2	6.3 ± 0.4
South Annapolis River	fall	135 ± 42	1.9 ± 0.6	0.7 ± 0.1	3.5 ± 0.5	4.7 ± 0.8	0.0 ± 0.0	1.6 ± 0.4	7.4 ± 2.6	0.8 ± 0.4	6.3 ± 0.3
LaHave River	fall	160 ± 47	1.6 ± 0.3	0.6 ± 0.1	3.9 ± 0.5	5.5 ± 1.0	0.0 ± 0.0	2.0 ± 0.4	7.9 ± 2.1	0.8 ± 0.4	5.9 ± 0.3
Saint Mary's River	fall	88 ± 41	1.3 ± 0.2	0.6 ± 0.1	3.6 ± 0.5	5.3 ± 0.9	0.0 ± 0.0	1.9 ± 0.3	5.6 ± 1.9	0.8 ± 0.4	6.0 ± 0.3
Tusket River	elevated summer/ fall	275 ± 91	1.0 ± 0.3	0.5 ± 0.1	3.8 ± 0.4	5.5 ± 1.1	no data	2.3 ± 0.7	12.4 ± 3.4	0.8 ± 0.3	4.5 ± 0.2
Roseway River	elevated summer/ fall	280 ± 76	0.4 ± 0.1	0.3 ± 0.1	3.2 ± 0.4	4.3 ± 0.7	no data	1.2 ± 0.3	15.7 ± 4.6	0.7 ± 0.3	4.2 ± 0.1
Moose Pit Brook	elevated summer/ fall	223 ± 108	0.8 ± 0.3	0.4 ± 0.2	2.7 ± 0.5	3.4 ± 0.7	no data	1.3 ± 0.8	15.5 ± 8.0	0.4 ± 0.2	4.4 ± 0.2
Mersey River	moderate summer/ fall	212 ± 68	0.8 ± 0.2	0.4 ± 0.1	3.5 ± 0.5	5.7 ± 1.2	no data	1.7 ± 0.6	10.4 ± 3.1	0.8 ± 0.4	4.7 ± 0.2
Lower Pine Marten Brook	moderate summer/ fall	128 ± 63	0.8 ± 0.3	0.5 ± 0.2	2.9 ± 0.4	3.9 ± 0.8	no data	1.8 ± 0.8	7.2 ± 3.7	0.5 ± 0.5	5.2 ± 0.4
Pine Marten Brook	moderate summer/ fall	118 ± 52	0.7 ± 0.2	0.5 ± 0.1	2.7 ± 0.3	3.7 ± 1.0	no data	1.3 ± 0.9	6.5 ± 3.4	0.4 ± 0.2	5.2 ± 0.4

Prior analysis by Clair et al. show no significant effect of ECCC analysis protocol changes between 1983 and 2007 (Clair et al., 2011); we also did not observe effects of analysis protocol changes (Table A2.3) made between 2000 and 2018. We removed K and NO_3 data for Pine Marten, Mersey River (MR), Moose Pit Brook (MPB), Roseway River, and Tusket River due to a high frequency of below detection limit values. To reduce error in statistical calculations, we replaced below detection limit values for the remaining variables (n = 33,094, 8.2 % of samples) in accordance with Equation 5 (Verbovšek, 2011).

$$value = {}^{detection\ limit}/_{\sqrt{2}} \tag{5}$$

Because ECCC does not filter cation samples prior to analysis, extreme outliers were present (n = 817, 2.21 % of samples) and were removed using a four-times median absolute deviation cut-off value (Eq. 6). Median absolute deviation is preferred for outlier removal because this method is more robust against strong outliers than other methods such as Interquartile Range (Rousseeuw & Hubert, 2011).

$$MAD = \frac{1}{n}\sum_{i=1}^{n} |x_i - \tilde{x}| \ where\ i = 1, \ldots, n \tag{6}$$

Here, MAD is median absolute deviation, x_i an observation, and $\tilde{x}$ the median (Rousseeuw & Hubert, 2011).

2.4.4 Hydrological Data

We selected hydrometric monitoring stations from ECCC Historical Hydrometric databases (Table A2.1) based on Euclidean distance to water chemistry sampling sites (average distance: 136 m, range: 15–375 m; Table A2.2). Daily discharge data are available between 2000 and 2018 for 12 of 16 rivers. Discharge regimes are similar across all sites (Figure A2.1), regardless of catchment size (range: 17.13–1,339.09 km^2; Table 5). Water chemistry data were normalized by discharge using the quotient of concentration and discharge on a daily timestep.

2.4.5 Meteorological Data

Meteorological monitoring stations were selected from ECCC Monthly Climate Summaries database (Table A2.1) based on Euclidean distance to water chemistry sampling sites (average distance: 22.5 km, range: 1.98–53.7 km; Table A2.2). Meteorological data were recorded as monthly average (temperature) or total (precipitation). Ten monitoring stations had data available during the time period in which water quality samples were collected (Table A2.2).

2.4.6 Spatial Analysis

Watersheds were delineated for each water chemistry sample site using the 20 m digital elevation model available from the NS Gov. Department of Lands and Forestry and topographical features available from NS Topographic Database (NSTD). We cross-referenced the delineated catchments with secondary, tertiary, and sub-tertiary catchment shapefiles available from NS Gov. Department of Environment (Table A2.1).

Percent cover of forests, wetlands, roads, agriculture, outdoor recreation, residential, and industrial areas were calculated using land cover data available from the NSTD. For definitions of these categories, please see Table A2.4. Harvested area could not be determined as these data are not openly available for the province of NS. The lack of harvest data is expected to limit the attribution of land use influence on Al concentrations, since most forestry in NS is clear-cutting (Lahey, 2018), which is known to increase freshwater acidity (Feller, 2005).

2.4.7 Speciation Analysis

Although field speciated Al data were unavailable for all our sites, we wanted to expand our examination of Al_i toxicity implications by employing three independent lines of evidence.

We used the Visual MINTEQ version 3.1 geochemical equilibrium model to estimate concentrations of Al_i associated with our data. We are unaware of any prior studies in NS using geochemical equilibrium models, so we follow the methodology of Sjöstedt et al. (2010), who conducted a study on Al speciation in an area of Sweden with similar geochemical characteristics as those common in NS. Our input parameters were Al_t, total Fe (as Fe^{3+}), total C_B (Ca, Mg, and Na), dissolved anions (Cl, NO_3, and SO_4), TOC, and pH. Following Sjöstedt et al. (2010), gibbsite could precipitate out of solution at $\log{}^*K_s$ of 8.29 at 25 °C, temperature was fixed at 10 °C, and the Stockholm Humic Model was used to model TOC.

We also used the statistical model developed by Dennis & Clair (2012) to estimate concentrations of Al_i (Eq. 7).

$$Al_i = -166.5 + 0.50(Al_t) - 5.06(TOC) + 23.5(pH) \tag{7}$$

This model was specifically developed for the Maritime provinces of Canada.

Field speciated Al data are available for five of our study rivers. We compared our modeled Al_i concentrations to these data which were collected between 2015 and 2018 for MR, Pine Marten Brook (PMB), and MPB (Sterling et al., 2019) and in 2006 for the Tusket River, MR, and LaHave River (Dennis & Clair, 2012).

2.4.8 Statistics

We determined the influence of hydrological and water chemistry parameters on Al concentration using Kendall Tau rank correlation for each site, once for non-normalized data and once for discharge normalized data. We use Kendall Tau rank correlation because it is insensitive to discrepancies in the data and is suitable for non-normally distributed data (Kendall, 1975), such as ours. We computed relationships between average water chemistry concentrations and spatial parameters across all sites. Spatial data in the NSTD are updated annually; the data used in this analysis covered the time period from June 1st, 2017 to June 1st, 2018.

We identified the main predictive factors of Al concentration using Mode A partial least squares (PLS) regression. PLS regression is preferred to OLS regression when there is collinearity between predictive variables (Rogerson, 2001) and is preferred to principal component analysis when the goal is to predict a dependent variable (Wold et al., 2001). To select the most parsimonious model, we used an iterative process where variables were individually added to the regression equation, with only the most explanative variable being carried forward into the next iteration (that is, one variable added per iteration). We repeated the iterative procedure until each additional variable added only marginal additional explanatory power (< 0.01 %). Since PLS regression does not handle missing data, we removed observations with missing values, and variables with more than 20 % of data missing during each iteration. We determined the principal components to retain using standard scree plots; the first two principal components were retained. We assessed the goodness of fit of the PLS regression model using the coefficient of determination, and significance using Analysis of Variance. To ensure model robustness, we performed four-fold cross-validation. Maximum difference between model explanatory power was 0.011 %, with the same four variables selected for each cross-validation.

We did not include land use/land cover or geologic data in the PLS regression due to sample size limitations (n = 16); this sample size is too small to draw meaningful conclusions from using PLS regression (Kock & Hadaya, 2018). Instead, we examined the influence of these parameters on Al concentration and its main drivers using Kendall Tau rank correlation. We use Kendall Tau rank correlation because its is more accurate for small sample sizes (Bonett & Wright, 2000).

We identified clusters of catchments with similar drivers of Al using Ward's cluster analysis. Ward's technique is preferred for spatially dependent data and does not require the researcher to pre-define the number of groups (Rogerson, 2001), thereby preventing researcher bias. Clusters were determined using the correlation value between Al and the dominant drivers of Al identified through PLS regression. We identified discharge as a main driver of Al concentration, but these data were not available for all sites. Therefore, two iterations of cluster allocation were performed, one including and one excluding the discharge parameter. Sites without discharge data were allocated to groups identified with discharge data based on correlation strength and direction of the other parameters.

2.5 Results and Discussion

2.5.1 Water Chemistry Drivers of Al

PLS regression identifies TOC and C_B (Ca or Mg) concentration, discharge, and turbidity as the main explanatory parameters of Al variability (82 %) (Table 7; Figure A2.2). Negligible explanatory power (< 0.01 %) is added by including any other parameter in the model. The difference in model fit between Ca and Mg is negligible (Ca: $r^2 = 0.815$; Mg: $r^2 = 0.819$), and is not improved by including both Ca and Mg. Despite pH being a significant indicator of Al for some sites, PLS regression showed pH to be a redundant and less reliable predictor of Al concentration than Ca or Mg concentrations. Therefore, pH was omitted in the PLS regression.

Table 7 Parameter weighting per principal component and C_B model. Principal component is abbreviated as PC and indicates direction of variance. Total variance of Al explained by PLS regression is 82 %.

Base Cation	Parameter	Parameter Weight PC 1 (66 % of variance)	 PC 2 (15 % of variance)
Ca	Ca	-0.454	0.428
	TOC	0.891	0.202
	Turbidity	0.017	0.88
	Discharge	-0.001	0.039
Mg	Mg	-0.413	0.437
	TOC	0.911	0.186
	Turbidity	0.013	0.879
	Discharge	-0.003	0.053

Several mechanisms may cloud the strength of the inverse relationship between pH and Al: Al buffering in C_B-poor soils such as in NS (Keys, 2015), increased DOC solubility at higher pH, increasing Al solubility in soils (Jansen et al., 2003), and increased Al solubility at lower temperatures (Lydersen, 1990).

Our results show Al – C_B coupling strength and sign depends on C_B concentration (Figure 4). Below Ca ~ 5 mg L^{-1} and Mg ~ 1 mg L^{-1} the negative correlation between these C_B's and Al exponentially decreases in strength, and at a threshold of Ca ~ 1.4 mg L^{-1} and Mg ~ 0.6 mg L^{-1} the relationship changes from negative to positive. However, at higher TOC concentration, the threshold is increased, and decoupling occurs at higher C_B concentrations. We term this phenomenon "threshold-dependent decoupling"; the reversal of Al- C_B correlation sign and decrease in correlation strength around the Ca ~ 1.4 mg L^{-1} and Mg ~ 0.6 mg L^{-1} thresholds, where the sign is negative above and positive below. We hypothesize that below these thresholds, C_B concentrations are so low that small increases do not result in decreased Al concentration.

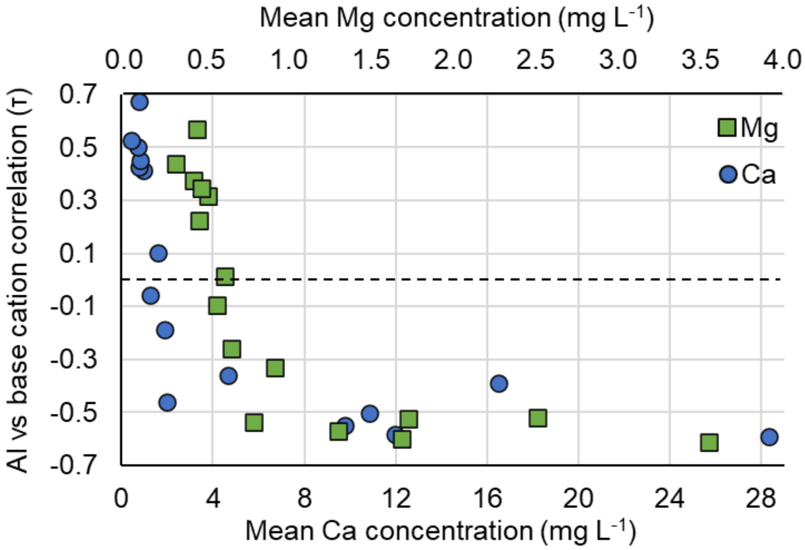

Figure 4 Threshold-dependent decoupling of Al and C_B dynamics at Ca ~ 1.4 mg L^{-1} and Mg ~ 0.6 mg L^{-1} (n = 16 sites). Dashed line indicates correlation value of zero.

To our knowledge, this threshold-dependent decoupling has not been identified in prior research, possibly because C_B concentrations are above Ca ~ 1.4 mg L^{-1} and Mg ~ 0.6 mg L^{-1} in many other areas (Maybeck, 2004; Weyhenmeyer et al., 2019). This threshold-dependent decoupling may become more widespread in the future due to regionally declining Ca concentrations (Bedison & Johnson, 2010; Driscoll et al., 2001; Sterling et al., 2019; Weyhenmeyer et al., 2019). Because stronger decoupling is associated with higher Al concentrations, more rivers may become at risk for elevated Al concentrations.

Since the decoupling behavior of Al from C_B has not been previously identified, further study is required to identify the nature of the C_B threshold, how it is influenced by TOC concentration, and identify other sites with similar patterns.

2.5.2 Land Use/Land Cover Drivers of Al

Kendall Tau rank analysis shows land use and land cover are significantly correlated with water chemistry in NS (Table 8). Wetland area has a moderate positive correlation with Al and TOC concentration and moderate negative correlation with C_B (Table 8). This finding is consistent with past research, which found that the generation of large quantities of DOC in wetlands mobilizes Al (Tipping & Carter, 2011). Specific types of wetlands in NS are known to have low C_B concentrations due to low contact time of surface waters with bedrock, or due to low mineral weathering from bedrock in contact with groundwater (National Wetlands Working Group, 1997).

Table 8 Correlations between water chemistry and catchment land use/land cover. Black bolded values indicate significant correlations ($p \leq 0.05$), and gray values indicate non-significant correlations ($p > 0.05$).

	Agricultural	Forest	Wetland	Recreation	Residential	Industrial	Road
Al	-0.119	0.000	**0.450**	-0.103	-0.103	0.008	0.117
Ca	**0.670**	**-0.483**	**-0.467**	**0.496**	**0.462**	**0.460**	0.133
Mg	**0.633**	**-0.450**	**-0.500**	**0.445**	**0.410**	**0.393**	0.067
Na	**0.523**	**-0.567**	-0.283	**0.530**	**0.530**	**0.544**	0.217
Cl	**0.541**	**-0.600**	-0.317	**0.530**	**0.496**	**0.527**	0.183
NO_3	**0.584**	**-0.600**	-0.378	0.378	0.378	0.422	-0.156
SO_4	**0.578**	**-0.550**	-0.333	**0.427**	**0.393**	**0.427**	0.200
pH	**0.615**	**-0.450**	**-0.500**	**0.445**	**0.410**	0.343	0.033
TOC	-0.358	0.217	**0.500**	-0.274	-0.239	-0.142	-0.100
Turbidity	**0.651**	**-0.583**	-0.267	**0.769**	**0.735**	**0.695**	0.300

Kendall Tau rank correlation shows that anthropogenic land cover, and especially agriculture, is moderately to strongly positively correlated with C_B concentration (Table 8). This association can be attributed to three factors: agriculture selects for productive soils, that is, areas with higher surficial geology C_B content (Stea et al., 1992); agricultural fields are often limed (Forestry and Agrifoods Agency, n.d.), as C_B are limiting nutrients in NS

(Keys, 2015); and increased soil disturbance by agriculture which can cause increased soil erosion (Neupane et al., 2015).

Anthropogenic land use is significantly positively correlated with riverine turbidity levels (Table 8). Anthropogenic land use typically increases soil disturbance and reduces forest cover, both of which can lead to increased runoff erosion (Cavus et al., 2017; Neupane et al., 2015), resulting in elevated turbidity.

Forest cover has moderate negative correlations with C_B concentrations (Table 8). This may be due to several factors: regional bedrock composition, selection of the most productive (that is, C_B-rich) lands for agriculture, and C_B depletion due to past and unknown current harvesting.

2.5.3 Timing and Drivers of Seasonal Al Regimes

Ward's cluster analysis identifies five spatially contiguous clusters of rivers in NS (Figure 3) with different dominant drivers of Al (Table 9) and timing of elevated Al concentrations (Figure 3). PLS regression shows five parameters predict Al concentrations across all groups; but the strength and direction of influence (Table A2.5), and average water chemistry concentrations (Table 6) differ by cluster.

Table 9 Regime characteristics.

Regime	**Base cation concentration**	**Al - base cation correlation**	**Al response to increased discharge**	**Main driver(s) of Al**
Winter	High	Negative	Increase	Turbidity*, discharge, base cations
Stable	High	Negative	Increase	TOC, discharge, base cations
Fall	Moderate	None/weak	Increase at low discharge, leveling off at high discharge	TOC, discharge
Moderate summer/fall	Low	Positive	Increase at low discharge, dilution at high discharge	TOC
Elevated summer/fall	Low	Positive	Decrease	TOC

** Note that due to the strong influence of turbidity on Al, Al_t patterns may not be reflective of bioavailable Al patterns for the winter regime.*

In two regime clusters, the “elevated summer/fall” and “moderate summer/fall” regimes, Al is decoupled from C_B levels. In these rivers Al concentrations are driven by TOC, and seasonally elevated Al concentrations occur in summer and early fall, corresponding to TOC peaks and periods of low flow. These rivers have high TOC and low C_B concentrations, consistent with the numerous wetlands within the catchments, and their underlying granite, slate, and quartzite geology (Table A2.6; Figure A2.3). In the elevated summer/fall regime, increased discharge is associated with low Al, likely due to dilution. Similar patterns of Al dilution at high flow rates have previously been observed in acidified streams in Colorado, USA (McKnight & Bencala, 1988).

Rivers in the “fall regime” have moderate C_B concentrations and have weak correlations between Al and C_B’s. These catchments are predominantly underlain by slow-weathering, C_B poor, granodiorites and shales (Table A2.6; Figure A2.3). Fall regime rivers are characterized by elevated Al concentrations in the fall which coincide with TOC and discharge peaks. For these rivers, we propose the dilution of C_B’s and flushing of TOC during the fall rains results in elevated Al concentrations. Similar patterns of TOC flushing have been previously observed in NS (Lacroix & Townsend, 1987) and near the Czech-German border (Kopáček et al., 2016), and were attributed to accumulation of TOC during the dry summer months due to microbial decomposition and longer soil retention times (Hruška et al., 1996; Jones et al., 2014).

Of the two regimes which have coupled Al – C_B dynamics, the “stable regime” followed Al patterns identified by most prior authors (Collignon et al., 2012; Dennis & Clair, 2012; Kopáček et al., 2016; Ryan et al., 2012; Tipping & Carter, 2011; Wigington et al., 1996). Geology in these catchments is typified by slow weathering and C_B poor granites and conglomerates (Table A2.6; Figure A2.3). Rivers in the stable regime have lower overall Al concentrations, with small, discharge-driven increases of Al in the spring and fall. Here, Al has a strong positive correlation with discharge and TOC, and moderate negative correlation to C_B concentrations. For these rivers, increased discharge is associated with exponential decreases in C_B concentrations and linear increases in TOC, both of which can drive elevated Al concentrations. The stable regime seasonal patterns appear similar to those observed in other areas with similar freshwater geochemistry (Monteith et al., 2007; Weyhenmeyer et al., 2019). For example, three tributaries of the Lofsån River in Sweden were found to have moderate Al_t concentrations (mean: 89 to 151 $\mu g\ L^{-1}$) and small seasonal increases in spring and fall high flow periods, in tandem with C_B dilution (Borg & Sundbom, 2014).

In the fifth cluster, the “winter regime”, the signal, and therefore drivers, of dissolved Al (Al_d) are masked by turbidity. Al samples used in this study are not filtered; thus, Al patterns in the winter regime are more reflective of biogeophysical processes than biogeochemical and likely poorly represent annual variability of bioavailable Al. For these rivers, elevated Al concentrations occur in the winter months and coincide with turbidity peaks. The source of these turbidity-driven Al peaks is likely anthropogenic activity within the catchments, which is associated with increased disturbance and runoff erosion (Cavus et al., 2017; Neupane et al., 2015).

Due to low particulate loads in most rivers across NS, total fractions are often used as proxies for dissolved fractions, especially for TOC and DOC (Clair et al., 2007). However, the high turbidity in our winter regime sites highlights that unfiltered samples should not be used as a proxy for dissolved load in these rivers.

Our findings highlight the complexity of seasonal Al dynamics by demonstrating that five Al seasonality regimes with different timing and drivers of elevated Al concentrations exist in close proximity. The timing of the annual Al peaks for each regime was influenced by the strength and direction of correlation with four influential water chemistry parameters. The variation of these four parameters was driven by their concentrations, discharge, regional geology, and regional land use/land cover. These regional scale influences on water chemistry should be considered when addressing the ecosystem threat of high Al concentrations.

2.5.4 Al_i concentrations

Three independent lines of evidence indicate that Al_i concentrations exceed the toxic threshold for all sites. Mean Al_i concentrations estimated by Visual MINTEQ range from 2 – 65 µg L^{-1} (Table A2.7). Field observations made between 2015 and 2018 in three rivers in the moderate and elevated summer/fall regimes confirm that Al_i concentrations exceed thresholds for aquatic health for 63% of samples (n = 101) and range between 13 – 60 µg L^{-1} (Sterling et al., 2019). Additionally, Dennis and Clair showed that, in 2006, Al_i concentrations exceeded toxic threshold in the Tusket, Mersey, LaHave, and Roseway Rivers, ranging between 25 – 56 µg L^{-1} (Dennis & Clair, 2012).

Model predictions of Al_i show a strong seasonal error component when compared with field observations made by Sterling et al. (Sterling et al., 2019). Underestimation occurs during summer low flows and overestimation occurs during the winter/spring high flow periods (Figure A2.4), closely following discharge patterns (Figure A2.1). Summer low flows correspond to high TOC concentrations; we hypothesize that during this time the models overestimate the proportion of Al bound in organometallic colloids. During winter/spring high flow periods, C_B concentrations are typically low due to dilution effects and dominance of surface runoff pathways. As we discuss above, the classic inverse Al – C_B relationship does not hold for all regimes. We hypothesize that the decoupled Al – C_B relationship potentially causes the models to perform poorly in sites and seasons characterized by high freshwater TOC concentrations. Our results suggest that Al speciation models could be improved by considering distinct regimes and the potentiality of the inverse Al – C_B relationship being decoupled.

Al_t patterns thus may be useful as a first order indicator of toxic conditions in the absence of speciated Al data. Modeled Al_i seasonal patterns (Figure A2.5) resemble those of Al_t (Figure 3), following the five distinct regimes. Further, the high Al_t concentrations we observe coincide with high Al_i concentrations, both of which pose a threat to human and ecosystem health (Table 10).

Table 10 Potential adverse effects of Al species. Note that Al_t *can be converted into more bioavailable forms via acid digestion in the stomach (Ščančar & Milačič, 2006). For species definitions, please see Table 2. Thresholds are presented, where available.*

Al Species	**Affected community**	**Threat**	**Threshold**
Unspecified	Terrestrial	Reduced uptake of Ca and Mg in plants, resulting in reduced root and shoot growth (Rengel, 1992)	
	Terrestrial	Reduced Na intake in amphibians causing toxic Na imbalance, resulting in reduced species density and richness (DeHayes et al., 1999)	
	Terrestrial	Reduced root uptake of Ca, resulting in reduced growth of red spruce (*Picea rubens*) (DeHayes et al., 1999)	
Al_t	Humans	Potential neurotoxin; possible contributing factor in the development of diseases, including Alzheimer's disease and dialysis encephalopathy ((Driscoll & Schecher, 1990; World Health Organization, 2010)	100 to 200 µg L^{-1} (World Health Organization, 2017)
	Humans	Exchange with Ca in bones (Namieśnik & Rabajczyk, 2010); possible contributing factor in the development of osteoporosis and osteomalacia (Driscoll & Schecher, 1990)	
	Humans	Increased cost of water treatment (Letterman & Driscoll, 1988)	
	Aquatic	Reduced acidophilic phytoplankton growth; resulting in reduced resources for higher trophic levels (Gensemer, 1991)	15 µmol L^{-1} (reduced growth), 30 µmol L^{-1} (no growth) (Gensemer, 1991)
	Aquatic	Reduced freshwater Ca due to coprecipitation with sulphato-Al species, resulting in reduced nutrient bioavailability (Hindar & Lydersen, 1994)	
Al_p	Aquatic	Reduced egg laying and behavioural scores in *Lymnaea stagnalis* snails, resulting in reduced survival rates (Papathanasiou et al., 2011)	
	Aquatic	Reduced freshwater P due to coprecipitation with Al-hydroxide species and Al-F species, resulting in reduced nutrient bioavailability (Driscoll & Schecher, 1990; Kopáček et al., 2001; Scheel et al., 2008)	
Al_d	Terrestrial	Reduced nutrient uptake in Norway spruce (*Picea abies*) (de Wit et al., 2010)	
Al_o	Aquatic	Reduced freshwater DOC due to complexation with Al, resulting in reduced nutrient bioavailability (Driscoll & Schecher, 1990; Scheel et al., 2008)	
	Aquatic	Precipitation of DOC out of solution, resulting in increased light penetration and reduced water temperature (Scheel et al., 2008)	
Al_i	Aquatic	Mucus coating of salmonid gills, resulting in reduced brown trout survivorship (Bulger et al., 1993; Hesthagen et al., 2016)	11.34 ± 1.34 µg L^{-1} (Bulger et al., 1993)
	Aquatic	No acidophilic phytoplankton growth, resulting in reduced resources for higher tropic levels (Gensemer, 1991)	1.4 µmol L^{-1} (at pH 6), 23 µmol L^{-1} (at pH 5) (Gensemer, 1991)
	Aquatic	Reduced macroinvertebrate species richness (Beneš et al., 2017)	
	Terrestrial	Tree growth retardation, root tissue damage, and nutrient deficiencies, resulting in reduced forest resilience (Collignon et al., 2012)	
Al_{pm}	Terrestrial	Phytotoxic (Ščančar & Milačič, 2006); reduced wheat root growth, resulting in reduced crop success (Collignon et al., 2012)	

2.5.5 Ecological Implications

Although a wide variety of Al species pose threats to ecosystems (Table 10), elevated springtime Al_i concentrations projected for the winter and stable regimes (Figure A2.5) are particularly concerning, as these coincide with the hatching of Atlantic salmon and their most sensitive life stage (Howells et al., 1990). Further study is required to verify our findings and quantify the impact of Al on freshwater biota in these rivers, most urgently for the economically (Gardner Pinfold Consulting Economists Limited, 2011), biologically (Committee on the Status of Endangered Wildlife in Canada, 2011), and culturally (Parenteau, 1998) important NS populations of wild Atlantic salmon.

Seasonally elevated Al concentrations observed in this study also potentially pose a threat to human health. All rivers have seasonal exceedances of the 0.1-0.2 mg L^{-1} Health Canada (Health Canada, 2019) and World Health Organization guidelines for drinking water (World Health Organization, 2017), and in the elevated summer/fall regime rivers, Al_t concentrations exceed this threshold year-round. These findings indicate that elevated Al is potentially a concern at some point during the year for the 40 % of Nova Scotians who rely on private wells with minimal water treatment prior to consumption (Interdepartmental Drinking Water Management Committee, 2005). Further research is needed into Al concentrations in wells to identify areas where additional water treatment is needed to ensure safety of drinking water. Since rivers with decoupled Al – C_B dynamics have higher Al concentrations, our findings suggest that assessments should focus on areas where Ca and Mg concentrations are below 1.4 mg L^{-1} and 0.6 mg L^{-1}, respectively.

The metric of Al_t encompasses multiple threats to humans and terrestrial and aquatic ecosystems arising from a range of Al species (Table 10). In addition, high Al_t concentrations increase the cost of water treatment (Letterman & Driscoll, 1988). Our study highlights the importance of understanding seasonal dynamics to identify at what time of year threats may be higher and to inform data collection and interpretation to reduce bias from infrequent sampling.

2.5.6 Future Research

To advance our understanding of seasonal Al patterns, this study identifies the following research needs: filtering samples to reduce artifacts from turbidity, speciating Al to identify species-specific threats, and expanding the range and size of study catchments. To advance our understanding of the effects of forest harvest on water chemistry, the NS Gov. could make forest harvest publicly available, as it is in other Canadian provinces. Additional research is also required to predict the impact of increasing DOC (Monteith et al., 2007), earlier annual DOC peaks (Sterling et al., 2019), decreasing Ca (Bedison & Johnson, 2010; Federer et al., 1989; Weyhenmeyer et al., 2019), and climate change on seasonal patterns and drivers of Al because many of these drivers are projected to be altered with changes in meteorological forcing.

Chapter 3 - The Surface Water Chemistry (SWatCh) Database: A Standardized Global Database of Water Chemistry to Facilitate Large-Sample Hydrological Research

3.1 Preamble

Lobke Rotteveel and Shannon Sterling

This chapter forms the basis of a manuscript in preparation to be submitted to Earth Systems Sciences Data. I conceived the original idea, compiled and prepared the data, wrote the data cleaning and processing scripts, conducted the geospatial information systems (GIS) procedures, conceptualized and prepared the figures and tables, and was the principal author. Dr. Shannon Sterling (supervisor) provided supervision and co-edited the manuscript. Dr. Sterling and I hold the copyright for this manuscript.

3.2 Abstract

Openly accessible global scale surface water chemistry datasets are urgently needed to detect widespread trends and problems, to help identify their possible solutions, and identify critical spatial data gaps where more monitoring is required. Existing datasets are limited in availability, sample size/sampling frequency, and geographic scope. These limitations inhibit the answering of emerging transboundary water chemistry questions, for example, the detection and understanding of delayed recovery from freshwater acidification. Here, we begin to address these limitations by compiling the global surface water chemistry (SWatCh) database. We collect, clean, standardize, and aggregate open access data provided by six national and international agencies to compile a database consisting of three relational datasets: sites, methods, and samples, and one GIS shapefile of site locations. We remove poor quality data (for example, values flagged as “suspect”), standardize variable naming conventions and units, and perform other data cleaning steps required for statistical analysis. The database contains water chemistry data across seven continents, 17 variables, 38,598 sites, and over 9 million samples collected between 1960 and 2019. We identify critical spatial data gaps in the equatorial and arid climate regions,

highlighting the need for more data collection and sharing initiatives in these areas, especially considering freshwater ecosystems in these environs are predicted to be among the most heavily impacted by climate change. We identify the main challenges associated with compiling global databases – limited data availability, dissimilar sample collection and analysis methodology, and reporting ambiguity – and provide recommendations to address them. By addressing these challenges and consolidating data from various sources into one standardized, openly available, high quality, and trans-boundary database, SWatCh allows users to conduct powerful and robust statistical analyses of global surface water chemistry.

3.3 Introduction

Globally, 159 million people are reliant on untreated surface water, with only one in three people having access to safely-managed drinking water services (World Health Organization & United Nations Children's Fund, 2017). With two-thirds of the global population (4.0 billion people) already experiencing water shortages at least one month per year (Mekonnen & Hoekstra, 2016), a number projected to increase to 4.8-5.7 billion people by 2050 (Burek et al., 2016), maintaining the quality of these resources is paramount to human health and society. One of the main obstacles to achieving this goal is a lack of openly available, high quality, transboundary data (World Health Organization & United Nations Children's Fund, 2017). Existing large-sample water quality datasets have: 1) limited availability, for example, raw data may not be published with journal articles (Alsheikh-Ali et al., 2011); 2) limited sample size, for example, datasets may only include one water body type (Hartmann et al., 2014); or 3) limited geographic scope, for example, national datasets only include data for one country.

Delayed acidification recovery is an example of a transboundary problem which would benefit from a large-sample dataset. Ecosystem acidification and associated elevated Al concentrations are responsible for the loss of economically-significant fish species (Committee on the Status of Endangered Wildlife in Canada, 2011; Dennis & Clair, 2012), reductions in crop success (Collignon et al., 2012), reduced forest health (Collignon et al., 2012; de Wit et al., 2010; DeHayes et al., 1999) and therefore carbon sequestration, increased cost of water treatment (Letterman & Driscoll, 1988), and may contribute to human osteological and neurological diseases (World Health Organization, 2010). Prior large-sample (Björnerås et al., 2017; Monteith et al., 2007), and global scale (Weyhenmeyer et al., 2019) studies on freshwater acidification indicate that recovery is delayed in some regions. But, so far, there is no openly available global scale database of acidification related water chemistry which includes Al, increased concentrations of which are one of the most biotically toxic effects of acidification (Gensemer & Playle, 1999).

There is a need for harmonized large-sample hydrological research (Blöschl et al., 2019). The majority of water quality research has focussed on catchment scale datasets, which limits our understanding of transboundary processes. Catchment scale analyses make valuable contributions to our understanding of hydrochemical processes, but phenomena observed at the catchment scale may not generalize across regions. For example, with freshwater acidification, catchment response to acid deposition may be altered by its geology and land use/land cover, thus observations made in one watershed may not generalize others. Specifically, regions with slow-weathering bedrock low in C_B's are more strongly effected by acid deposition than those with high C_B bedrock (Stoddard et al., 1999), and watersheds with high-intensity forest harvesting may be more strongly affected by acid deposition than those with less disturbance (Aherne et al., 2008; Feller, 2005).

Obtaining and consolidating water chemistry datasets for transboundary hydrological research is challenging due to limited data access, and disparate (that is, dissimilar) data collection programs and data reporting formats. Access may be limited because data is not published and/or kept confidential, as is the case for some sites within the United Nations International Centre for Water Resources and Global Change's Global Water Quality Database and Information System (GEMStat). Data collection programs are dissimilar largely due to a lack of international variable and analysis method definitions (World Health Organization & United Nations Children's Fund, 2017). For example, Al measurements may not be comparable across different functional, operational, and classical species definitions (Namieśnik & Rabajczyk, 2010; Ščančar & Milačič, 2006). Lastly, disparate variable naming conventions, units, and censored data notation complicates consolidation of datasets from different sources, as these notations must first be standardized.

Here, we aim to address the above limitations by contributing an openly available, standardized, easy-to-use, global water chemistry database. We focus on providing data to address the problem of delayed freshwater acidification recovery by collecting, cleaning, standardizing, and compiling datasets of acidification related water chemistry variables. Specifically, our research goals are 1) to develop a global database of acidification related surface water chemistry, 2) to identify the main limitations associated with compiling this database, 3) to identify and characterize critical spatial data gaps within existing datasets, and 4) to provide recommendations for data reporting and storage to facilitate its easy access and use by other researchers.

3.4 Methods

3.4.1 Data Sources

We obtained input data for SWatCh from openly available datasets published by national and international agencies and from datasets available on open-access servers (Table 11). Our search terms were "water chemistry data" or "water quality data" and "global" and a country name, as listed in the United Nations member countries (United Nations, 2009). We assume that water chemistry data available from these reputable sources have undergone standard laboratory quality assurance and control; spot-checks of available methodology information support this assumption. Our data search did not have a geographic focus, although our sources were limited to datasets available in English. Datasets likely missed by this approach include those hosted on servers or websites without (or without English) Search Engine Optimization (SEO); that is, those which have not been optimized with keywords identifiable by search engines to provide results (Google, 2020). For example, the search "water quality data AND Sweden" does not return a website with Swedish water quality data. This data does exist, it is hosted by the Swedish University of Agricultural Sciences at https://miljodata.slu.se/MVM/, but cannot be found using our English search terms. Please note that this data is included in SWatCh, as it is included in the European Environment Agency's Waterbase, one of our data sources. All datasets were downloaded in September 2019.

Table 11 Data sources.

Name	Provider	Link
Global Water Quality Database and Information System (GEMStat)	United Nations International Centre for Water Resources and Global Change	https://gemstat.org/custom-data-request/
Global River Chemistry Database (GloRiCh)	Jens Hartmann, Ronny Lauerwald, and Nils Moosdorf	https://doi.pangaea.de/10.1594/PANGAEA.902360
National Long-Term Water Quality Monitoring Database	Environment and Climate Change Canada	http://data.ec.gc.ca/data/substances/monitor/national-long-term-water-quality-monitoring-data/
McMurdo Dry Valleys Long Term Ecological Research Network	The United States of America National Science Foundation	http://mcm.lternet.edu/power-search/data-set
Water Quality Database	The United States of America National Water Quality Monitoring Council	https://www.waterqualitydata.us/portal/
Waterbase	European Environment Agency	https://www.eea.europa.eu/data-and-maps/data/waterbase-water-quantity-11#tab-european-data; https://www.eea.europa.eu/data-and-maps/data/waterbase-water-quality-2

3.4.2 Data Inclusion

SWatCh includes 17 water chemistry variables collected in untreated surface water bodies. We define "untreated" as water that is not wastewater or receiving treatment plant effluent near to the sample collection site. The included water chemistry variables are metals: Al, and Fe; C_B's: Ca, Mg, K, and Na; acid anions: SO_4, NO_3, and nitrite (NO_2); other anions: F, and Cl; nutrients: P, phosphate (PO_4), and NH_4; physical parameters: pH, and temperature; TOC, and DOC. The included water body types are streams, rivers, canals, ponds, lakes, reservoirs, and impoundments. We screened out sites identified as confidential or with other publication restrictions (Figure 5).

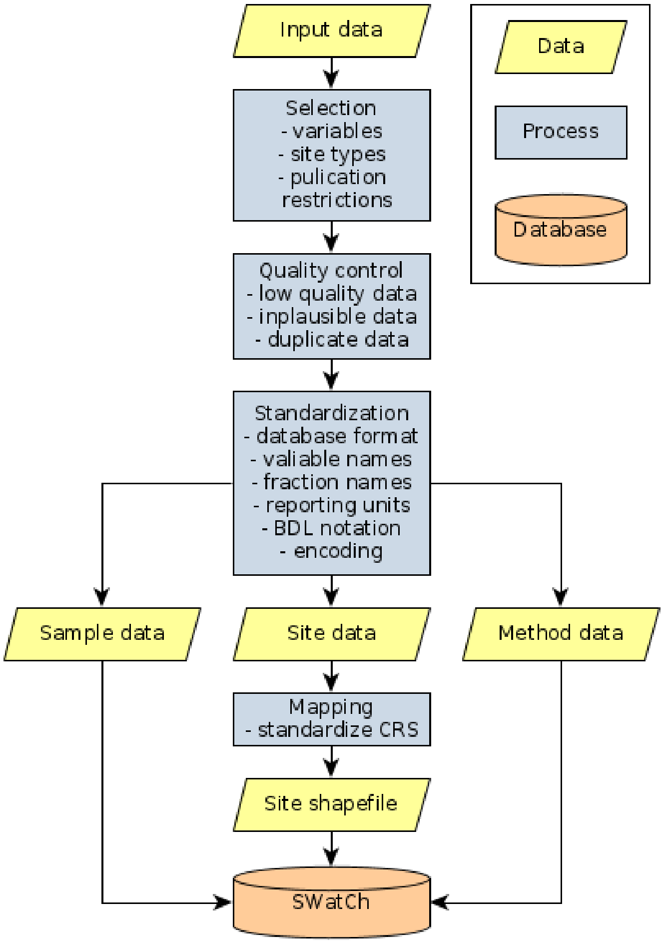

Figure 5 Workflow for creating SWatCh. Below detection limit is abbreviated as BDL and coordinate reference system is abbreviated as CRS.

3.4.3 Data Quality Control

3.4.3.1 Removal of Low Quality Data

We removed low quality data; for example, samples flagged as “unreliable”, “suspect”, or “poor quality”. Additionally, we removed values below zero for all variables except temperature; these values are assumed to be entered incorrectly.

3.4.3.2 Removal of Duplicates

We removed duplicate site and sample data. Three of our source databases, GEMStat, the Global River Chemistry Database (GloRiCh), and Waterbase, are compilations of water chemistry data from several sources, and thus repeat some measurements. We removed duplicated sites based on the site identification code and the country the site was located in. We removed duplicated samples based on the site identification code, country, date, variable name, variable fraction, and sample value. We define "variable fraction" as the component part of a water sample, such as total (unfiltered sample) and dissolved (filtered sample). Country is included as a parameter in the duplicate removal process, as some site codes are replicated across different countries; this primarily occurs for numeric or single-letter site codes.

3.4.4 Data Standardization

3.4.4.1 Database Format

We formatted the SWatCh database to reduce storage requirements and simplify use. To reduce storage requirements, we provide SWatCh as a relational database containing three datasets: 1) sites, 2) methods, and 3) samples. These three datasets are linked via site and method identification codes. We formatted each dataset after the input dataset we found the most straightforward to analyze and manipulate; that is, the sites and methods datasets are modeled after the United Nations' GEMStat, and the samples dataset is modeled after the European Environment Agency's Waterbase.

3.4.4.2 Variable Naming and Measurement Units

We standardized variable naming conventions to prevent confusion due to inconsistent spelling and abbreviation (Table 12). For example, aluminium (British spelling) and aluminum (American spelling) are both abbreviated to Al. We keep variable names separate from variable fractions to simplify analysis examining different fractions simultaneously. In the input datasets, the fractions are not specified for all variables; for these, we denote the fraction as "unspecified".

Table 12 Variable naming and measurement unit conventions in the SWatCh database.

SWatCh variable notation	**Variable name**	**SWatCh unit notation**	**Unit**
Al	aluminium	ug/l	$\mu g\ L^{-1}$
Fe	iron	ug/l	$\mu g\ L^{-1}$
Ca	calcium	mg/l	$mg\ L^{-1}$
Mg	magnesium	mg/l	$mg\ L^{-1}$
K	potassium	mg/l	$mg\ L^{-1}$
Na	sodium	mg/l	$mg\ L^{-1}$
Cl	chloride	mg/l	$mg\ L^{-1}$
F	fluoride	mg/l	$mg\ L^{-1}$
SO4	sulphate	mg/l	$mg\ L^{-1}$
NO3	nitrate	mg/l	$mg\ L^{-1}$
NO2	nitrite	mg/l	$mg\ L^{-1}$
NH4	ammonium	mg/l	$mg\ L^{-1}$
P	phosphorus	mg/l	$mg\ L^{-1}$
PO4	phosphate	mg/l	$mg\ L^{-1}$
OC	organic carbon	mg/l	$mg\ L^{-1}$
pH	pH	unit	unit
temperature	temperature	deg_c	^{o}C

We simplified and standardized measurement units to prevent analysis and encoding errors (Table 12). Several input datasets did not include their encoding type, causing corrupted characters and measurement unit ambiguity. To prevent these errors, we omit non-ASCII (American Standard Code for Information Interchange) characters; for example, micrograms (µg), are denoted as ug. Measurements were reported in different units in the input datasets; we standardized them to the most common International System of Unit (SI unit) we observed for each variable. For example, Ca was reported in $\mu g\ L^{-1}$, $mg\ L^{-1}$, $eq\ L^{-1}$, and Mol, but was most commonly reported as $mg\ L^{-1}$, thus, we standardized the measurement unit to $mg\ L^{-1}$.

3.4.4.3 Censored Data Notation

We standardized censored data notation to facilitate easier handling of these values. Censored data notation varied across the input datasets and included abbreviations such as "bdl", "<", or the numeric value of the detection limit. The input datasets did not distinguish between samples measured at or below the detection limit. Detection limits differed across and within datasets; thus, we standardized below detection limit values by flagging them and providing the detection limit in separate columns, allowing for various approaches of handling these results.

3.4.5 Mapping

We standardized the coordinate reference systems (CRSs) of the sample site locations to simplify geographic analysis. Site location coordinates are provided in various CRSs in the input datasets; thus, we first mapped the sites in their original coordinate systems, then re-projected them to the World Geodetic System 1984 (WGS 84) geographic CRS. We selected WGS 84, as this provides good mean solution across the globe and can easily be projected to local datums (Bajjali, 2018).

3.5 Results

The SWatCh database contains water chemistry data across 17 variables, six fractions, 38,598 sites, and 9,608,026 samples collected between 1960 and 2019 (Table 13). Sample collection frequency ranges from daily to one-time samples, depending on the data source. Not all samples included collection and analysis methodologies; for the samples where this information was available, there are over 600 different methods.

Table 13 The SWatCh database sample sizes by variable and fraction. Field measurements are only applicable to pH and temperature. Temperature is abbreviated as temp.

	Dissolved		**Extractable**		**Recoverable**		**Total**		**Unspecified**		**Field**	
	sites	samples	sites	samples	sites	samples	sites	samples	sites	samples	sites	samples
Al	2,515	27,113	170	5,959	642	2,604	4,144	120,216				
Fe	103	9,866	164	5,941	89	766	277	29,905				
Ca	12,199	591,313	155	5,694	797	5,094	1,433	19,340				
Mg	12,734	590,961	155	5,678	802	5,079	7,708	96,790				
Na	11,639	560,572	161	5,686	589	2,910	6,599	86,296				
K	11,980	549,954	161	5,689	490	2,657	6,205	99,386	189	257		
Cl	12,414	668,247					9,357	144,919	368	6,340		
F	5,567	424,997					901	6,771	25	3,335		
SO_4	13,347	637,383					8,840	117,968	108	3,805		
NO_3	8,434	228,049					4,022	74,668	2,566	65,234		
NO_2	9,148	205,258					2,606	36,721	2,139	51,176		
NH_4	11,241	506,116					5,677	146,000				
P	2,967	103,980					10,306	361,460	35	270		
PO_4	10,351	494,427					968	21,929	13	96		
OC	11,128	301,467					6,642	184,455				
pH									27,183	1,144,310	135	5,853
temp									27,296	849,130	195	6,272

Sites in SWatCh are located across the globe, but are concentrated in North America, South America, and Europe, and encompass a variety of bedrock and land use types (Figure 6).

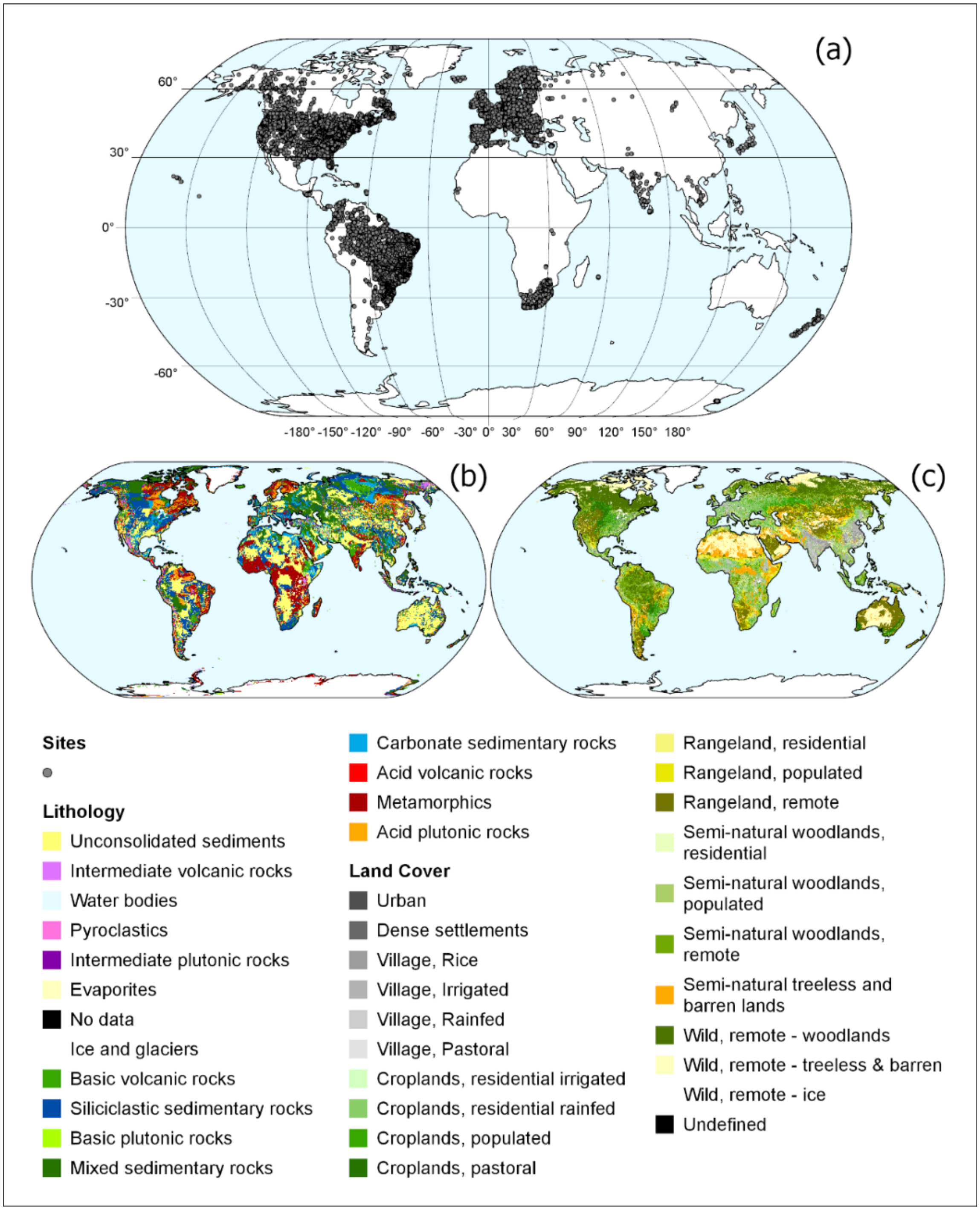

Figure 6 The SWatCh database sample site locations (a), underlying lithology (b), and land cover (c). Points overlap where sites are in close vicinity. Lithology map from GLiM (Hartmann & Moosdorf, 2012), land cover map from HYDE 3.2.1 (Goldewijk et al., 2011). Projection: Natural Earth, scales: a) 1:250,000,000, b and c) 1:400,000,000.

3.6 Discussion

Here, we discuss the main limitations we encounter when compiling and analyzing datasets and provide recommendations for data sharing to facilitate more large-sample and global scale water chemistry research.

3.6.1 Data Availability and Spatial Gaps

Some variables have smaller sample sizes. The number of reported measurements differs greatly per variable, with metals (Fe and Al) and F having the smallest sample sizes and pH and temperature having the largest. This discrepancy is possibly due to the cost of measurement, where pH and temperature can be measured with a variety of field or laboratory-based multiparameter probes, whereas metals and anions require laboratory analysis. What is currently unknown, is if analysis results are under-reported for some variables. Prior research on one of the main variables with low sample size (Fe), includes an openly available research dataset of 340 water bodies in Europe and eastern North America (Björnerås et al., 2017)[1]. These types of published research datasets are uncommon (Alsheikh-Ali et al., 2011) and highlight the potential contribution of unpublished raw research data.

Critical data gaps exist on the African, Asian, Australian, and Antarctic continents, representing mainly the equatorial, arid, and polar climate zones (Kottek et al., 2006). The zones of missing data represent regions where climate change induced alteration of freshwater discharge regimes is projected the greatest by 2050 (Döll & Zhang, 2010). Concentrations of many water chemistry variables are discharge dependant (Moatar et al., 2017); thus, these data gaps may inhibit the detection– and therefore treatment – of emerging climate change induced water quality problems. The observed lower data availability may be because of our reliance on English datasets, less data sharing in these regions due to concerns about "parachute research" (where researchers abscond with local

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[1] These data were not included in SWatCh due to missing site identification codes, variable fraction information, and analysis methodology information.

data to their home countries) (Serwadda et al., 2018), a lack of funding for scientific research (Serwadda et al., 2018), a lack of national data sharing regulations (Serwadda et al., 2018; Thu & Wehn, 2016), outdated information management systems (Thu & Wehn, 2016), or preferential research focus. For example, research on freshwater acidification predominantly focusses on Europe and North America (for example, Björnerås et al., 2017; Holland et al., 2005; Stoddard et al., 1999) where this is an established concern, and focusses less on other regions such as China, where this is an emerging concern (for example, Li et al., 2019).

Alleviating the issue of data availability is complex (Serwadda et al., 2018), but can be facilitated through journals more consistently implementing and enforcing data sharing policies (Alsheikh-Ali et al., 2011), ensuring coherence of and balance between data sharing policies and protecting national interests (Thu & Wehn, 2016), and engaging and crediting the peoples and organizations who collected the data (Serwadda et al., 2018).

3.6.2 Methodology Changes and Dissimilarity

The analysis of timeseries and intercomparison of data collected at different sites is challenging due to dissimilarity of sample collection programs and methodology changes. Methodology changes throughout a timeseries may result in spurious trend test results. For example, spurious negative Al trends may result from changing from inductively-coupled plasma optical emission spectroscopy (ICP-OES) to inductively-coupled plasma mass spectrometry (ICP-MS) if the measured values are at or near the detection limit, as ICP-MS has a lower detection limit than ICP-OES. Spurious positive Al trends may result from changing from extractable Al (Al_{ext}; comprising the dissolved fraction and weakly bound or sorbed molecules) to Al_t (comprising dissolved, weakly bound or sorbed, and particulate molecules), as was done by ECCC in Atlantic Canada in 2011. Similarly, disparate analysis methods across geographic regions may hinder comparability and consolidation of data collected by different sources (World Health Organization & United Nations Children's Fund, 2017). For example, in the USA, Al samples may be analyzed by US EPA method 200.7, with an estimated detection limit of 45 $\mu g\ L^{-1}$ (US EPA, 2015), whereas in Europe, Al samples may be analyzed by International Organization for Standardization (ISO) method 15586:2003, with an estimated detection limit of 1 μg L^{-1} (ISO/TC 147 SC2, 2003); samples analyzed by these two methods cannot be compared if Al concentrations below are 45 μg L^{-1}. To facilitate intercomparison of data, the creation of internationally standardized variable definitions and cross-boundary analysis methodology is needed (World Health Organization & United Nations Children's Fund, 2017).

3.6.3 Ambiguity and Inconsistency

We encounter ambiguity and inconsistency in variable and faction naming conventions, reporting units, analysis methodology, and dataset encoding. Firstly, we find variable and fraction definitions and consistency to be lacking in most input datasets. For example, an Al_d sample may be filtered through a 0.45 or 0.10 μm filter; both samples are considered Al_d but represent a different set of Al molecules. Since naming conventions are variable, and there are no internationally standardized variable definitions (World Health Organization & United Nations Children's Fund, 2017), defining variables and their fractions is required to prevent confusion regarding comparability. Similarly, reporting units and censored data notation should be defined and consistent throughout the dataset; this includes spelling, abbreviations, and capitalization. We also observe ambiguity regarding analysis methodology, where analysis methods are inadequately described or missing entirely. Ideally, analysis method reporting includes all of the following which are applicable: filter size and type, analysis instrument, acid preservative type, location of acid preservation (in field or laboratory), and the analysis/speciation method, method code, its publishing agency, and link to a reference document. Lastly, we encounter corrupted characters due to unknown dataset encoding; to prevent this ambiguity, the encoding of the dataset should be known and published, this is especially important for datasets not encoded in 8-bit Unicode (UTF-8), which preferred for data exchange (ISO/IEC JTC 1/SC 2, 2017).

3.6.4 Limitations and Future Work

In addition to the challenges noted above, the main limitations of SWatCh are a lack of discharge data and information on watershed land use and land cover. We did not include discharge information, as there are numerous openly available global scale river discharge datasets which cover many of the sites available in the SWatCh database. For example, the European Environmental Agency’s Waterbase contains a water quality dataset (used in the SWatCh database) and a water quantity dataset. Further development is needed to integrate existing discharge datasets into SWatCh, allowing discharge-weighted water chemistry concentrations to be computed. Most of the input datasets to SWatCh do not include watershed land use and land cover information; thus, we do not include these data in the SWatCh database. Some of these data are available in the GloRiCh database (Hartmann et al., 2014). Delineating the watersheds and computing land use and land cover information is beyond the scope of this research; but is a key area of improvement for future research and updates to the database.

3.7 Conclusion

Prior research demonstrates that despite variability in sample size, geographic coverage, and analysis methodology, large-sample datasets facilitate the understanding of global water chemistry processes and the identification of transboundary problems (for example, Björnerås et al., 2017; Monteith et al., 2007; Weyhenmeyer et al., 2019). Despite these clear benefits, there are few global scale water chemistry datasets. We created SWatCh to begin to fill this gap; it is a global database of surface water chemistry focussed on freshwater acidification-related variables. This database contains water chemistry data across 17 variables, six variable fractions, 38,598 sites, and 9,608,026 unique samples collected between 1960 and 2019. The numerous available variables and large sample sizes in SWatCh allows users to conduct powerful and robust statistical analyses to answer emerging global surface water chemistry questions. To facilitate data use in databases like SWatCh and by other researchers, we recommend making research data openly available, standardizing analysis methodology, and avoiding ambiguity/inconsistency in variable and fraction names, reporting units, censored data notation, analysis method descriptions, and dataset encoding. Future work should focus on filling the spatial data gaps identified in Asia, Africa, and Australia, adding discharge data, and adding catchment land use/land cover information. With more people experiencing decreased water quantity (Burek et al., 2016; Mekonnen & Hoekstra, 2016), maintaining water quality is paramount. By facilitating the global exchange of their data, researchers can contribute toward this goal.

Chapter 4 - Unexpected Increases in Aluminium in Northern Lakes and Rivers

4.1 Preamble

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This chapter forms the basis of a manuscript in preparation to be submitted to Nature which requires has an unconventional format where the sections are ordered as follows: abstract, main text (with no subsections), and methods. This manuscript is written for non-specialist audience. Dr. Shannon Sterling (supervisor) conceived and supervised the study. Drs. Caroline Björnerås, Scott W. Bailey, Douglas Burns, Tom A. Clair, Irena Creed, Heleen de Wit, Charles T. Driscoll, Chris Evans, Ivan Fernandez, Pirkko Kortelainen, Hjalmar Laudon, Gregory Lawrence, Iain Malcom, Steve Norton, Filip Oulehle, Heather Pembrook, Antti Räike, Gunnhild Riise, and Gesa Weyhenmeyer (co-authors) provided data. I assembled the data with assistance from Drs. Shannon Sterling and Caroline Björnerås. I led and conducted the data analysis, with technical support from Franz Heubach and contributions from Kristin Hart and Sarah MacLeod (co-authors). Dr. Tom Clair (co-author) provided technical advice. Dr. Shannon Sterling wrote the first draft; subsequent versions were led by Dr. Shannon Sterling with close input from myself, support from Kristin Hart, and contributions from all authors. Dr. Shannon Sterling developed the conceptual model; I contributed to revisions. Figures and tables were prepared by myself, Kristin Hart, Sarah MacLeod, and Dr. Shannon Sterling. The co-authors and I hold the copyright to this manuscript.

4.2 Abstract

One of the most lethal effects of terrestrial acidification is increased mobilization of toxic forms of Al from soils to soil solutions and freshwaters (Burrows & Hem, 1977; Gensemer & Playle, 1999). Al toxicity caused the extirpation of sensitive species and a decrease in forest and aquatic productivity in Europe and North America at the end of the last century (Brodin, 1995). Following reductions in acid emissions in Europe and North America in the 1980s and 1990s, acidification status has generally improved (Borg & Sundbom, 2014; Monteith et al., 2007), and the Al problem was widely regarded to be solved. However, continuing environmental measurements show that acidification recovery is delayed in many sensitive forest and aquatic ecosystems (Clair et al., 2011; Houle et al., 2010; Kowalik et al., 2007; Warby et al., 2009; Watmough et al., 2016). At present, it is not known whether a decline in freshwater Al concentrations might also be delayed. To fill this knowledge gap, we examine trends in Al concentrations from 2000-2015 in nearly 400 rivers, lakes, and streams in previously acidified areas across North America and Europe. We found that, in contrast to recovery model predictions, Al concentrations are increasing in many of these freshwaters, particularly in Sweden and NS. These results bring to light an unforeseen recovery response that is preventing a return to pre-acidification conditions in some regions. We propose that recent increases in Al are caused by rapid increases in DOC and slow or delayed increases in C_B concentrations in response to reductions in acid deposition. These drivers of Al mobilization can be exacerbated by prior soil C_B depletion, climate change and forest biomass removal. We tested this conceptual model with data from 461 waters. The trends we observe illuminate an enduring water quality problem in some areas, where, despite reductions in acid deposition and increases in pH, Al concentrations are increasing, with potentially severe implications for freshwater and forest ecosystem health and biodiversity.

4.3 Main Text

Over the last century, acid deposition has mobilized Al in soils, increasing its concentrations in streams and lakes. In some regions, such as eastern North America

(Campbell et al., 2009; Driscoll & Schecher, 1990) and Europe (Seip et al., 1991), the elevated Al concentrations have caused declines in fish populations, such as the economically significant Atlantic salmon (Hesthagen et al., 2011; LaZerte, 1984; Schofield & Trojnar, 1980; Watt et al., 2000), and have threatened aquatic (Gensemer, 1991; Hörnström et al., 1984; Lacoul et al., 2011) and terrestrial (Lawrence et al., 2016) flora and fauna (Table A3.1). Despite being the most abundant metal in the Earth's crust, Al is normally immobilized in clays or hydroxide phases in soils (Figure 7a, Stage 1) (Nilsson & Bergkvist, 1983). Acid deposition accelerates export of C_B's from soils (Figure 7b, Stage 2) (Galloway et al., 1983; Lawrence et al., 2007), depleting exchangeable soil C_B content (Federer et al., 1989). This results in increased Al export from soils into rivers and lakes (Figure 7c, Stages 3 and 4) (Fernandez et al., 2003; Lawrence et al., 1995, 2013; Reuss & Johnson, 2012).

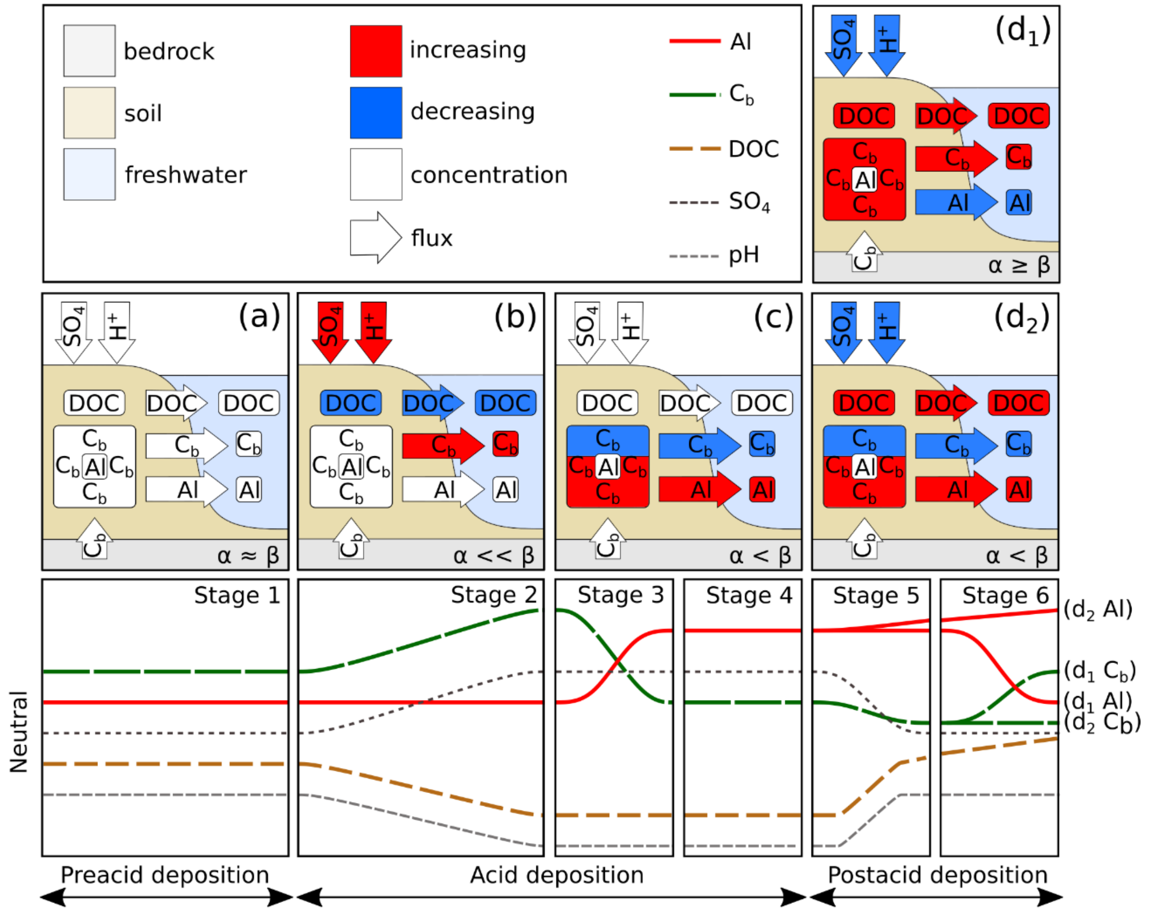

Figure 7 Conceptual models of Al response to changes in acid deposition. Acidification stages are adapted from those identified by Galloway, Norton, and Church (1983). Input rates of C_B via mineral weathering (assuming negligible deposition) are denoted as α, and rates of loss of C_B from the soil system to drainage waters as β. Arrows represent fluxes and boxes represent stores. Increasing and decreasing refer to change relative to the previous stage. Acid deposition is symbolized as SO_4 and hydrogen ions (H^+), but this model may apply to other acid anions (for example, NO_3).

Following reductions in sulphur dioxide emissions since the 1980s and 1990s and nitrogen oxide emissions in the early 2000s, forest and freshwater ecosystems have shown signs of recovery from acidification, with increases in exchangeable soil C_B, freshwater alkalinity, and soil and freshwater pH (Borg & Sundbom, 2014; Evans et al., 2001; Hinderer et al., 1998; Josephson et al., 2014; Lawrence et al., 2015; Monteith et al., 2014; Skjelkvåle et al., 2005; Strock et al., 2014), and decreases in freshwater Al concentrations, in particular its inorganic monomeric species (Burns et al., 2006; Davies et al., 2005; Monteith et al., 2014).

Thus, ecosystem acidification is conceptualized as a reversible process in the classic freshwater acidification model (Figure $7d_1$, Stage $5d_1$) (Galloway et al., 1983; Lawrence et al., 2016). However, accumulating evidence shows that multiple forest and aquatic ecosystems have delayed C_B recovery, particularly in soil exchangeable Ca (Clair et al., 2011; Jeziorski & Smol, 2016; Warby et al., 2009; Watmough et al., 2016). At present it is not known whether freshwater Al concentrations in previously acidified areas also show widespread delayed recovery. Recently, in NS, Canada, high surface water Al concentrations were reported (Dennis & Clair, 2012; Rotteveel & Sterling, 2020; Sterling et al., 2019), which is of particular concern because Atlantic salmon populations are currently declining to near extirpation levels in this region (Bowlby et al., 2013). Here, we aim to answer the question: how have freshwater Al concentrations responded to reduced acid deposition? We answer this question by examining recent Al concentration trends (predominantly Al_t, but varying by site, see section 4.4 Methods and Table A3.2) in nearly 400 freshwater sites located in acid sensitive regions of Europe and eastern North America.

Our results show that between 2000 and 2015, instead of decreasing as expected, Al concentrations increased in many regions (Figure 8). Of the 394 analyzed sites, Al concentrations increased in approximately half of the sites (49 %), of which 33 % increased significantly ($\alpha = 0.05$). Sites with significant increases in Al concentrations are clustered, with hotspots in eastern and southern Sweden and NS, Canada. In NS, Al concentrations increased in 78 % (n = 64) lakes and rivers, of which 32 % increased significantly. In Sweden, Al concentrations increased in 80 % (n = 83) sites, of which 32 % increased significantly.

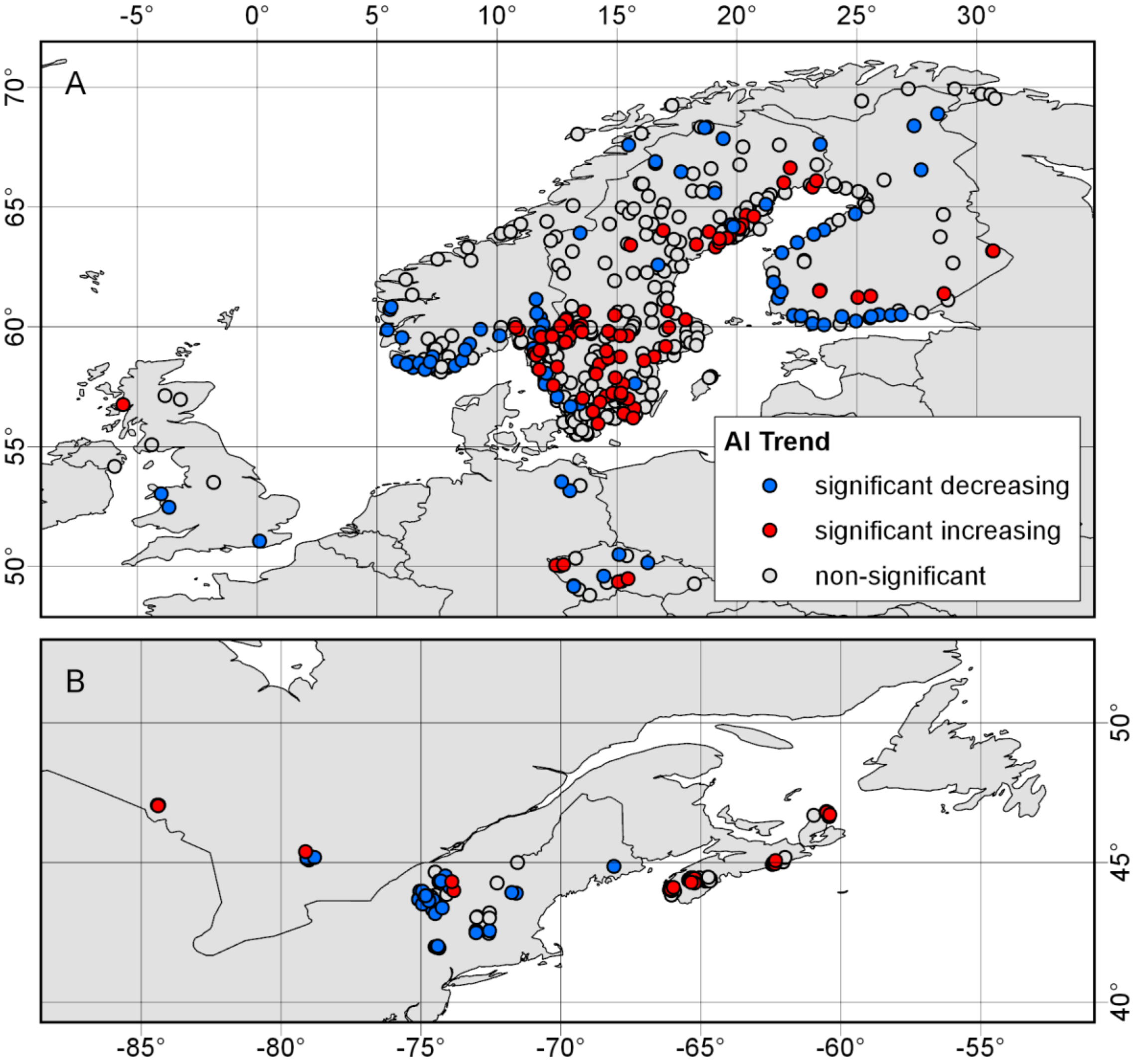

Figure 8 Trends of surface water Al concentrations between 2000 and 2015 in northern Europe (A) and northeastern North America (B). Significance at α = 0.05. Symbols overlap where sample sites are in close proximity, where increasing and decreasing trends are plotted with equal weight. Refer to Table A3.2 for site-specific information.

Increases in Al export rates occurred abruptly in some rivers. For example, in MR, NS, Canada, following one high discharge event between March 26th to 31st, 2003, Al export rates increased by 45 % (from an average of 143 kg day^{-1} during 1992-2003 to 208 kg day^{-1} during 2003-2014) and non-discharge-weighted Al concentrations increased by 17% (from an average of 193 µg L^{-1} during 1992-2003 to 225 µg L^{-1} during 2003-2014) (Figure A3.1; Figure A3.2; Table A3. 3). The increased Al mass exports and concentrations are not accompanied by long-term changes in discharge (Figure A3.1; Table A3. 3). During the

March 26th to 31st, 2003 high discharge event, air temperature surpassed 10 °C for the first time that year and over 110 mm of precipitation fell (not including precipitation from one day with missing data), melting the existing 34 cm snowpack. After the 2003 shift, minimum Al concentrations increased (Figure A3.3), with the largest increases occurring in the summer and autumn, such that the annual autumnal Al peak concentration now occurs earlier in the year (Figure A3.4).

The 1983 acidification model (Galloway et al., 1983) does not predict the increased Al concentrations we observe and therefore needs to be modified. We hypothesize the observed increases in freshwater Al concentrations are driven by increasing DOC mobility in soils with low exchangeable C_B (particularly Ca) (Figure 7, Stage $5d_2$). Reductions in acid deposition increase freshwater DOC concentrations by increasing soil DOC solubility at $pH > 3.5$ and lower ionic strength (Clair et al., 2011; Haaland et al., 2010); these increases can occur rapidly even under small reductions of acid deposition (Watt et al., 2000), and can be exacerbated by land cover change and climate change. On the other hand, replenishment of soil C_B pools via weathering following acid deposition reductions is slow (Clair & Hindar, 2005; Lacoul et al., 2011; Lawrence et al., 2016), and only begins once acid deposition rates decline to below critical load thresholds. Soil C_B recovery can also be delayed by forest biomass removal and climate change. Thus, our conceptual model proposes a hysteresis response of DOC and C_B's to decreasing acid deposition that can cause Al concentrations to increase to above pre-acid deposition levels (Figure 7, Stage $5d_2$). This unforeseen ecosystem response to acid deposition reductions in sensitive ecosystems may be exacerbated by climate change and land use change.

Freshwater chemistry observations from 2000-2015 support our hypothesis that increasing Al concentrations are caused by increasing DOC concentrations in areas of low soil C_B: sites where Al is increasing coincide with those where DOC is increasing and Ca concentrations are low (Figure A3.5). Additionally, the annual timing of the highest Al concentrations coincides with highest DOC concentrations (Figure A3.4) in the low Ca MR (Table A3. 3). When we analyze additional sites located less acid sensitive regions of Europe and North America (please see sections 4.4.3 Trend Analysis and 4.4.4 Regression

Analysis; Figure A3.5), we observe two distinct site groupings based on the drivers of Al: (1) low Ca sites (≤ 2 mg L^{-1}), where Al trends are positively related to DOC trends (τ = 0.299, $p < 0.001$); and (2) high Ca sites (> 2 mg L^{-1}), where Al trends are unrelated to DOC (τ = 0.068, p = 0.143) (Figure 9A). The majority of the variation in Al concentrations (r^2 = 0.57) at the low Ca sites is explained using the main variables in our conceptual model (Ca, DOC, and pH; Figure 9B; Table A3.4); these same parameters are insufficient to explain the variability of Al at the high Ca sites (r^2 = 0.03, Figure 9B, Table A3.4). Other parameters that might contribute to the variability of Al which are unaccounted for in our model include the destabilization of soil organic matter (Krám et al., 2009) and related NO_3 release, strong acid environments in regions underlain by acid-sulphide soils (Palko & Weppling, 1995), and increased runoff (de Wit et al., 2016).

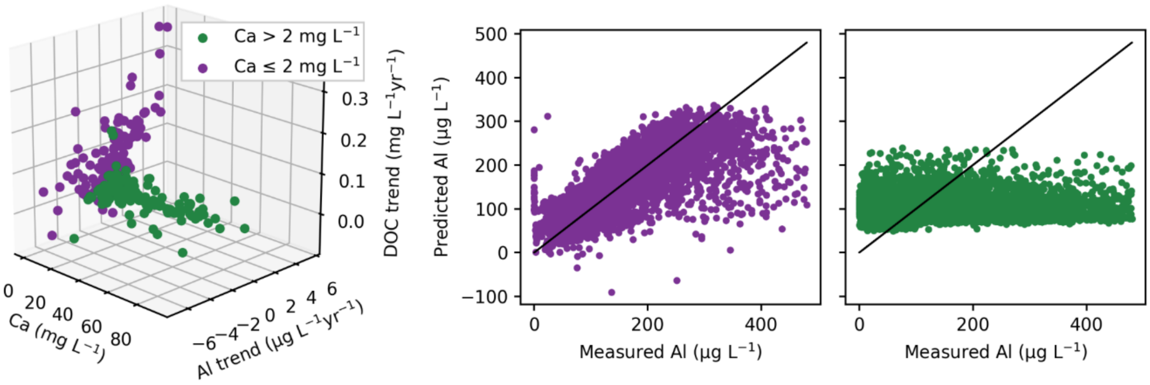

Figure 9 Relationship between Al and DOC trends based on median site Ca concentration (A) and PLS regression prediction of Al concentrations for low C_B sites (i; Ca ≤ 2 mg L^{-1}) and high C_B sites (ii; Ca > 2 mg L^{-1}), using the optimized PLS regression (Table A3.4). Points overlap where they are located in close proximity.

Given the limited spatial coverage of water quality monitoring sites, other areas of high Al concentrations may be undetected thus far. Our conceptual model predicts such sites are more likely to occur in catchments with C_B-poor bedrock (Weyhenmeyer et al., 2019) and increasing DOC (Monteith et al., 2007) such as across the Canadian Shield. Other areas which may have chronically low C_B concentrations and, therefore, increasing Al concentrations, include those with forest harvesting (Achat et al., 2015; Gee & Stoner, 1989; Löfgren et al., 2017; Weyhenmeyer et al., 2019), and areas where acid deposition rates remain above critical thresholds (Borg & Sundbom, 2014). For example, despite reductions in acid deposition (Figure A3.6), extended areas in eastern Canada, including NS, still have deposition rates in excess of critical loads (Forest Mapping Group, 2007; Keys et al., 2016), and soil base saturation levels below 15% (Keys et al., 2016), the minimum threshold needed to prevent harmful "Al stress" in forest soils (Cronan & Grigal, 1995). In NS, median freshwater Ca concentrations between 2000-2015 are as low as 0.2 mg L^{-1}, with 47 sites having median Ca concentrations below 1.0 mg L^{-1}, well below the 2.0 mg L^{-1} threshold required for aquatic health (Figure A3.5; Table A3.2). Further, three lakes have Al concentrations higher than Ca concentrations on a concentration basis (Table A3.2).

Increasing freshwater Al concentrations show no sign of peaking (Figure A3.2); the supply of Al is essentially unlimited. There is no obvious mechanism that will slow Al release until soil C_B levels are replenished or until increases in soil DOC export peak and abate. Climate change is projected to strengthen the C_B and DOC drivers of increasing Al; changes to snowpack (Groffman et al., 2012), rainfall patterns, growing season length, and increased storm frequency and magnitude (Campbell et al., 2009; Clair et al., 2011; Huntington et al., 2009) that are projected in wetter (de Wit et al., 2016) and warmer (Ritson et al., 2014) northern climates are expected to increase DOC concentrations and expedite exchangeable soil C_B depletion (Groffman et al., 2012; Huntington et al., 2009; Mitchell & Likens, 2011). The Al problem may become more widespread because the response to decreasing acid deposition may be delayed in some catchments; response times to disturbances are higher in large catchments with flat topography (Mattsson et al., 2015), which potentially incudes the hysteresis response to acid deposition reductions driving soil Al export. Ongoing timber and biomass harvesting, especially whole tree harvesting, as used in bioenergy generation (Joki-Heiskala et al., 2003), will further deplete soil C_B concentrations (Achat et al., 2015; Löfgren et al., 2017). Lastly, the Al problem may be worsened due to loosened SO_4 and NO_x emission legislation (Keyes et al., 2019), such those limiting emissions from coal burning in the USA.

Elevated concentrations of Al and its species in surface waters pose serious threats to ecosystem productivity (Konôpka & Lukac, 2010; Wang et al., 2007) and biodiversity

(Buckler et al., 1995; Clark & Hall, 1985; Freda, 1986; Hall et al., 1980; Lacroix, 1985; Smith et al., 1990), and negatively impact human health (World Health Organization, 2010) and society (Anderson et al., 2017; Letterman & Driscoll, 1988) (Table A3.1). Although the highly toxic Al_i species, of particular concern for fish populations (Malcolm et al., 2014), have been widely reported as decreasing in recent years, our analysis shows that these studies are in locations where Al_t is not significantly increasing (Table A3.6). Further, although few timeseries of speciated Al exist in catchments with increasing Al, those that are available indicate that Al_i is increasing at some sites where Al_t is increasing (Table A3.6 and Table A3.5), with Al_i having a strong positive correlation with Al_d (Sterling et al., 2019). Increased monitoring of freshwater Al speciation is thus urgently needed in areas at risk for increasing Al concentrations.

Given the serious ecosystem impacts of elevated Al concentrations, prompt solutions are needed. While reducing acid emissions and limiting removal of Ca from ecosystems via forestry are part of the solution, the response of ecosystems to these management actions will take decades to be realized (for example, Clair et al., 2004). The only effective mitigation measure to reduce Al concentrations in the near future is the addition of Ca directly to soils via soil amendments such as liming (Lawrence et al., 2016), but this method is controversial and expensive if required over large areas (Binkley & Högberg, 1997; Lehto & Mälkönen, 1994; Matzner et al., 1985). Alongside accelerating climate change and land use/cover change, acid deposition and its legacy continue to pose serious multinational threats to forest and freshwater ecosystems.

4.4 Methods

4.4.1 Nomenclature

We use Al_t as a proxy for Al_d and refer to them collectively as Al. We operationally define Al_t as unfiltered samples and Al_d as samples passed through a 0.45 μm filter. Al_t can be used as a proxy for Al_d in sites with low concentrations of Al_p, as is the case for sites we examine. Similarly, TOC can be used as DOC in sites with low particulate load; thus we refer to both as DOC, following other studies in comparable areas (Clair et al., 2008; Kortelainen et al., 2006; Mattsson et al., 2005).

4.4.2 Variable Selection

While previous studies focus on Al_i species as response variables, we employ Al_d for five reasons: 1) Al_d encompasses a wide range of aquatic species of Al mobilized from the soil; in contrast, organic Al (Al_o) or Al_i species do not represent the rate of release of Al from the soils because changes in Al speciation are rapid (instantaneous for inorganic species and minutes to hours for organic species) (Gensemer & Playle, 1999) and can occur multiple times during its transport from soil to oceans (Johnson et al., 1981). For example, Al_o may photo-oxidize to Al_i or solid hydrolysis products; the recently hydrolyzed Al may re-dissolve during low pH events (Gensemer & Playle, 1999); and, Al_i speciation may change as a function of pH, temperature, sunlight, DOC, and Al saturation (LaZerte, 1984). 2) Al_d measurements are part of standard analyses and are more easily comparable than Al_i data, due to varying operational definitions of Al_i. 3) Al_i is an important measure of Al toxicity, but is not the only species of environmental or societal concern (Table A3.1); for example, short-lived colloidal and recently hydrolyzed forms of Al also pose serious threats to aquatic life (Gensemer et al., 2018). 4) Al_i and Al_d are positively correlated in environments with elevated Al_d, such as in NS (Sterling et al., 2019). 5) Lastly, Al_i concentrations already chronically exceed aquatic health thresholds (> 15 μg L^-1; Howells et al., 1990) in at least one area of increasing Al_d (Sterling et al., 2019); therefore, any additional increases of Al_d in these locations pose an ecologically relevant threat.

4.4.3 Trend Analysis

We examine Al trends between 2000 and 2015 in two datasets. The first dataset (acidification dataset) consists of 394 rivers, lakes, and streams across Europe and eastern North America that were intensively studied following increased acid deposition during the 1900s. These sites are predominantly forested catchments impacted by acidification, with no major land use /land cover changes in the catchment between 1980-2015 including no changes in nearby anthropogenic sources of Al. The second dataset (extended dataset) contains sites across a wider range of Ca concentrations and is not controlled for land use/land cover. This dataset is described in section 4.4.4 below. Trends computed for sites in the extended dataset are only used for the OLS and PLS regression analyses described below.

Analyzed timeseries meet the following six criteria. 1) Minimum timeseries length of 10 years between 2000 and 2015. Timeseries start and end dates differ by up to five years. We find a difference of 2 % in the proportion of increasing vs. decreasing sites between the earlier (2000 to 2010) and later (2005 to 2015) timeseries; thus, we conclude that differing start and end dates do not bias results. 2) Minimum sampling frequency of four samples per year for fluvial systems and one sample per year for lacustrine systems, provided samples are collected in the same season throughout the record. 3) Minimum dataset completeness of 75 %. 4) Minimum proportion of samples measured above the laboratory detect limit of 50 %. 5) Samples are subject to standard laboratory quality assurance and control procedures; and 6) no major changes in sampling or analysis protocols that affect the ability to determine the presence or absence of a significant trends. Timeseries with substantial analysis changes, such as moving from non-filtered to filtered, are analyzed as separate records. Analysis method changes from ICP-AES to ICP-MS are flagged but analyzed as one record. In the extended dataset there are a small number of sites with higher detection limits (thus, non-detects) early in the timeseries; for these sites, we remove below detection limit values to avoid spurious trend results. Al species (Al_d or Al_t) measured vary among sites but are consistent for each site (Table A3.2).

We use three different monotonic trend analysis methods to account for timeseries seasonality (cyclicity), persistence (auto-regression), and lack thereof, similar to methods used by Clair and colleagues (Clair et al., 1995). We use the seasonal Mann-Kendall test for timeseries with seasonality (Hirsch et al., 1982), the Hamed and Rao modified Mann-Kendall test for timeseries with persistence (Hamed & Rao, 1998), where persistence is defined as a Durbin-Watson statistic less than 1.5 or greater than 2.5 (Durbin & Watson, 1951), and the Mann-Kendall non-parametric test for all other timeseries (Kendall, 1975; Mann, 1945).

4.4.4 Regression Analysis

We use OLS regression and PLS regression to empirically test our conceptual model. For this, we supplemented the acidification dataset with the extended dataset containing additional Al, Ca, Mg, SO_4, pH and DOC data collected in Europe and North America from the publicly available SWatCh database. Using the extended dataset in addition to the acidification dataset allows us to identify how DOC and Ca impact Al trends differently for acidified and non-acidified sites.

The extended dataset contains Al_{ext} in addition to Al_t. Al_{ext} is used by ECCC and is operationally the same as Al_t, provided turbidity values are below 10 NTU (Parent, 2019, pers. com.), as they are for the sites we analyze. ECCC defines Al_{ext} as samples which have been preserved with a dilute mineral acid (most commonly HNO_3) and stored (usually overnight) prior to analysis; ECCC defines Al_t as an unpreserved sample which has been "vigorously digested" with HNO_3. To increase sample size, we use both Al_{ext} and Al_t.

The input data have a positive skew, with several very high Al values. Since we analyze both Al_d and Al_t, we presume these extremely high Al samples contain clay Al particulates and remove them. These values are removed using a > 2.5 times median average deviation cut off. This method is preferred for skewed distributions and is preferred to other methods of outlier removal, such as the interquartile range, as it is more robust against large outliers (Leys et al., 2013; Rousseeuw & Hubert, 2011).

We distinguish between sites with low and high exchangeable C_B using median site Ca concentrations, where we define low C_B sites as ≤ 2 mg Ca L^{-1} and high C_B sites as > 2 mg Ca L^{-1}. We use Ca as the representative C_B because this is the major C_B in freshwaters in most regions (Gaillardet et al., 2003) and 2 mg L^{-1} as the threshold due to its ecological relevance.

We use OLS regression to identify relationships between Al, DOC, and Ca trends, and PLS regression to identify if Al concentrations can be predicted using the main variables in our conceptual model (Ca, DOC, pH, and SO_4). PLS regression is preferred to OLS regression when there is co-variance between predictive variables (Ng, 2013) and is preferred to principle component regression when the goal is to predict a dependent variable (Maitra & Yan, 2008). We do not use PLS regression to examine the relationships between Al and DOC trends due to sample size limitations (Goodhue et al., 2012, 2006). We optimize the PLS regression prediction of Al using 10-fold cross-validation, where the optimized PLS regression is that with the lowest cross-validation mean squared error.

4.4.5 Case Study

We use the MR, NS, Canada as a case study of a river with increasing Al concentrations, as it is located in a hotspot of increasing Al and has among the longest timeseries record with the most frequent data collection. 11,238 unique Al samples were collected since 1980 at a frequency of daily to bi-weekly throughout most of the year. Sample collection and analysis methods are described in a previous study (Clair et al., 2011).

We conduct timeseries decomposition and mass export analysis for the MR timeseries. We decompose the timeseries using a symmetrical, equal weight moving average. We calculate the cumulative water chemistry mass export using a daily time-step. Significance is evaluated using Welch's two-sample t-test ($\alpha = 0.05$). The mass of chemical constituents and flow are linearly interpolated to attain temporal convergence of the discretized measurements.

Chapter 5 - Conclusion

The aim of my thesis is to advance the scientific understanding of regional and global scale patterns of Al concentrations and their changes due to freshwater acidification. I do this by identifying, characterizing, and attributing the cause of the short-term temporal fluctuations of Al and its species at the regional scale, creating a global scale database of surface water chemistry, and using this database to identify, characterize, and attribute the cause of long term increasing Al trends across acidified regions. Through this research, the existing model of freshwater acidification, which has not been updated since 1983, is re-evaluated and updated to account for the observed Al patterns. My research contributes empirically and theoretically to the field by changing and enhancing our understanding of freshwater acidification recovery, and by providing a high quality, openly available, global dataset of acidification-related surface water chemistry.

Elevated Al continues to be a year-round and worsening threat to aquatic ecosystems across acidified regions. This thesis demonstrates that high and increasing Al_t and Al_i concentrations may occur in tandem, with the strongest seasonal and long-term increases occurring in time periods and areas of low C_B concentrations and high/increasing freshwater DOC and TOC concentrations. Specifically, long-term increasing Al concentrations are highest for sites with median Ca concentrations of ≤ 2.0 mg L^{-1}, and seasonal increases of Al are strongest in rivers with median year-round Ca and Mg concentrations below ~1.4 mg L^{-1} and ~0.6 mg L^{-1}, respectively. Across Europe and North America, sites with the highest rates of increasing Al have high freshwater DOC and TOC concentrations and are predominantly located in Sweden and NS, where rivers with the strongest seasonal increases in Al_t and Al_i are located the inland southwestern region of NS.

This thesis shows that across all scales, in sites with low C_B's, the dominant predictors of Al are DOC and TOC: seasons with the highest Al_t and Al_i concentrations also have the highest DOC and TOC, and long-term increasing Al concentrations are predominantly driven by DOC and TOC. Thus, contrary to the existing understanding, high DOC and TOC is not protective against Al toxicity in aquatic environments. Further, this thesis demonstrates that short-term fluctuation in Al concentrations occurs both during periods of high discharge, in agreement with existing research, and during periods of low flow. Sites with elevated Al concentrations during low flow tend to be wetland dominated, which is hypothesized to be because of higher soil organic carbon (and thus Al) export during the summer months due to higher rates of microbial decomposition (Rotteveel & Sterling, 2020).

These unexpected patterns and drivers of Al emphasize the need for ongoing acidification research across a variety of catchment types. Research on Al response to acidification has been limited since the 1990s, thus many of the increasing Al trends we observe have gone unnoticed. By focussing on a select number of long-term research sites, such as the Adirondacks and Catskills in the USA and the Krycklan catchment in Sweden, prior research has inadequately quantified the Al threat and its drivers across other regions. The large-sample and global scale research required to assess the generalizability of these catchment scale results is potentially limited by a lack of data sharing and poor data sharing practices. The SWatCh database begins to address these limitations by providing an easy-to-use, openly available, global dataset of Al and its known drivers.

By using SWatCh and data generously shared by other researchers, the existing 1983 model of freshwater acidification is empirically evaluated and updated. The 1983 model does not predict the persistently high and increasing Al concentrations we observe because it does not account for the influence of DOC and TOC on soil Al export. By including the hysteresis response of C_B (slow) and freshwater organic carbon (fast), we can predict the increasing Al trends we observe in sites with persistently low C_B concentrations.

The problem of high Al continues to threaten ecosystems and may become more widespread due to increased DOC and TOC export from soils or decreasing soil C_B availability. Increased DOC and TOC export from soils may occur due to 1) increased rate of microbial decomposition from atmospheric warming (Clair et al., 2011; Kopáček et al., 2016), 2) delayed response of DOC and TOC to disturbance in large catchments (Mattsson et al., 2015), and/or 3) increased precipitation intensity (Neff & Asner, 2001). Further soil C_B depletion may occur due to 1) forest harvest (Harriman et al., 2003; Keys, 2015; Keys et al., 2016; Lahey, 2018), 2) increased vegetation growth (Federer et al., 1989; Keys et al., 2016; Ryan et al., 2012), and 3) increased intensity and occurrence of on-shore storms (Harriman et al., 1995). Many of these processes are exacerbated by climate change and their influence on Al concentrations and trends remains poorly quantified. Ongoing monitoring and research on long-term Al trends and their evolving drivers is urgently required to protect aquatic ecosystems from further harm.

Despite the increasing availability of research data, the Al problem remains poorly quantified across Asia and Africa. Freshwater acidification is known to occur in these regions (for example, Li et al., 2019); failing to monitor and address the Al threat endangers aquatic ecosystems (Driscoll & Schecher, 1990; Namieśnik & Rabajczyk, 2010), and negatively impacts human health (World Health Organization, 2010) and society (Letterman & Driscoll, 1988). My global database of acidification related water chemistry provides a tool to begin to address this lack of information, but data gaps remain across the continents listed above. Further cross-boundary research and collaborations are required to address these limitations.

C_B concentrations are expected to remain low in many regions with high Al and are not expected to naturally recover within ecologically relevant timescales (for example, Clair et al., 2004). Furthermore, acid deposition is still ongoing in most regions; decreases in SO_4 deposition have leveled off and NO_3 deposition has remained stable across many regions (Driscoll et al., 2001; Environment and Climate Change Canada, 2016). With continued promotion of coal burning and decreased US EPA oversight (Federal Register, 2017), the main cause of soil C_B depletion remains. Terrestrial additions of calcium carbonates (liming) or calcium silicates (enhanced weathering) are geoengineering techniques used to artificially increase soil C_B concentrations and limit Al export which have been successfully used across Europe and North America (Lawrence et al., 2016). Artificial addition of C_B's to soils may be required to prevent further ecosystem damage in regions where acid deposition continues to exceed critical loads, or mineral weathering rates are low, such as in southwestern NS (Forest Mapping Group, 2007). These amendments provide a promising interim solution to the Al problem while soil C_B concentrations recover naturally from mineral weathering while also drawing down atmospheric CO_2 (Beerling et al., 2018). Some limestone application trials have been conducted in NS with variable results (for example, Rotteveel, 2018; Sterling et al., 2014), indicating more study on the viability and effectiveness of soil C_B amendments is needed before they can be applied over large areas.

As freshwater resources diminish in many areas across the globe, maintaining the quality of these resources is paramount to ecosystem and societal health. Ongoing cross-boundary collaborations, data collection, and data sharing are required to monitor Al and its effects in vulnerable regions. My research lays the foundation for these cross-boundary monitoring initiatives by identifying the ongoing threat of Al to ecosystems, identifying regions at risk of high and increasing Al, identifying the drivers of Al concentrations, and providing a database which can be used to monitor Al and associated surface water chemistry at the global scale.

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Appendix 1 - Ionic Aluminium Concentrations Exceed Thresholds for Aquatic Health in Nova Scotian Rivers, Even During Conditions of High Dissolved Organic Carbon and Low Flow

A1.1 Preamble

Shannon M. Sterling, Lobke Rotteveel, Sarah MacLeod, Kristin Hart, Thomas A. Clair, Edmund A. Halfyard, and Nicole L. O'Brien

This chapter forms the basis of a manuscript in in press at Hydrology and Earth Systems Sciences; a prior version of this manuscript was published as a pre-print on Hydrology and Earth Systems Sciences Discussions (Sterling et al., 2019). Dr. Shannon Sterling (supervisor) conceived the idea and led the writing of the article. Sarah Macleod, Tom Clair, Kristin Hart, Nicole O'Brian, Edmund Halfyard, and I (co-authors) contributed to writing the article. Sarah Macleod led the sample collection with assistance from me. Sarah MacLeod and Tom Clair designed the protocol for Al_i sampling. I performed spatial and statistical analysis and produced figures, with assistance from Sarah MacLeod, Kristin Hart, Edmund Halfyard, and Shannon Sterling. Nicole O'Brien led the generalized linear mixed modeling (GLMM) analyses. Tom Clair provided information on analytical and field sampling methods, and sample site selection. Edmund Halfyard contributed samples.

A1.2 Abstract

Acid deposition released large amounts of Al into streams and lakes in northern Europe and eastern North America during the last century. Elevated Al concentrations caused major environmental concern due to its toxicity to terrestrial and aquatic organisms, and led to the extirpation of wild Atlantic salmon populations. Air pollution reduction legislation that began in the 1990s in North America and Europe successfully reduced acid deposition, and the Al problem was widely considered solved. However, accumulating evidence indicates that freshwaters still show delays in recovery from acidification, with poorly understood implications for Al concentrations. Here, we investigate spatial and temporal patterns of toxic Al_i from 2015-2018 in ten catchments in NS, Canada, a region

that was one of the hardest hit by acid deposition, but was not considered to have an Al problem because high DOC concentrations were expected to reduce Al_i concentrations. Surprisingly, our results show widespread and frequent occurrences of Al_i concentrations that exceed toxic thresholds in all sampled rivers despite high DOC concentrations. GLMM results reveal that DOC, instead of being inversely related to Al_i, is the strongest predictor (positive) of Al_i concentrations, suggesting that the recruitment properties of DOC in soil waters outweigh its protective properties in streams. Lastly, we find that contrary to the common conceptualization that high Al_i levels are associated with storm flow, high Al_i concentrations are found during base flow. Our results demonstrate that elevated Al_i concentrations in NS continue to pose a threat to aquatic organisms, such as the biologically, economically, and culturally significant Atlantic salmon.

A1.3 Introduction

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

Al in freshwaters can exist as inorganic monomers, inorganic polymers, amorphous and microcrystalline inorganic forms, and as fast reactive or unreactive organic forms (Chew et al., 1988; Driscoll et al., 1980; LaZerte, 1984). While a variety of Al species in circumneutral waters are toxic to fish (Gensemer & Playle, 1999), including precipitated forms (Gensemer et al., 2018), the cationic species of Al, such as Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$, are considered to be the most labile and toxic to salmonids. Al species bind to the negatively charged fish gills causing morbidity and mortality through suffocation (Exley et al., 1991), reduced nutrient intake at gill sites, and altered blood plasma levels (Nilsen et al., 2010). The effects of sub-lethal exposure to freshwater Al elicits osmoregulatory impairment (Monette & McCormick, 2008; Regish et al., 2018) which reduces survival in the hypertonic marine environment (McCormick et al., 2009; Staurnes et al., 1996). Elevated concentrations of Al_i are also toxic to other freshwater and terrestrial organisms (Boudot et al., 1994; Wauer & 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 ºC and below pH 5.7 at 25 ºC (Lydersen, 1990), with the most toxic Al specie, $Al(OH)_2^+$ (Helliweli et al., 1983), dominating Al speciation between pH 5.0-6.0 at 25 ºC, and 5.5-6.5 at 2 ºC (Lydersen, 1990). Thus, the toxicity of Al increases with pH up to approximately 6.0 at 25 ºC, or 6.5 at 5 ºC, when aqueous Al precipitates, forming amorphous Al hydroxides (Lydersen, 1990; Schofield & Trojnar, 1980), where colder waters will have a higher proportion of toxic species at higher pH values than warmer waters (Lydersen, 1990).

The bioavailability of Al is reduced by the presence of Ca (Brown, 1983), which can occupy the negatively charged gill sites. DOC also reduces bioavailability of Al via the formation of Al_o (Erlandsson et al., 2010; Neville, 1985). High levels of DOC in rivers were believed to be sufficient to protect fish gills from adverse Al effects (Lacroix & Kan, 1986; Vogt & 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 water DOC concentrations. Lower pH increases the solubility of secondary minerals containing Al; Al_i concentrations in streamwater are generally negatively correlated with pH (Campbell et al., 1992; Kopáček et al., 2006; Seip et al., 1991). Low levels of base saturation can cause charge imbalances resulting in the release of Al into soil waters and later into drainage waters (Fernandez et al., 2003); chronic acidification thus shifts available exchangeable cations in the soil water from Ca and Mg towards Al (Schlesinger & 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 water 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 & Van Benschoten, 1990; Jansen et al., 2003). Field studies confirm the Al concentrations are positively correlated with DOC (Campbell et al., 1992; Kopáček et al., 2006).

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

Despite much progress in acidification research, the processes affecting Al_i dynamics are not well understood (Mulder et al., 1990). Our understanding of Al_i is limited by the relative paucity of samples; Al_i is not measured as part of standard analyses. Our understanding is also limited by the difficulty in comparing the wide variety of methods for estimating Al_i; different definitions, often operational, of toxic Al include inorganic Al, inorganic monomeric Al, labile Al, Al^{3+}, and cationic Al (Table A1.1).

Acid-sensitive areas of NS, Canada, here abbreviated as NS_A (following Clair et al., 2007), with once-famous wild Atlantic salmon populations, were heavily impacted by SO_4 deposition at the end of the last century, which originated from coal burning in central Canada and northeastern USA (Hindar, 2001; Summers & Whelpdale, 1976). NS_A catchments are particularly sensitive to acid deposition due to C_B-poor and slowly weathering bedrock that generates thin soils with low ANC, extensive wetlands, and episodic sea salt inputs (Clair et al., 2011; Freedman & Clair, 1987; Watt et al., 2000; Whitfield et al., 2006). Al was not considered to be a threat to Atlantic salmon in NS because of the naturally high DOC concentrations (Lacroix, 1989; Lacroix & Townsend, 1987). However, a survey in fall 2006 found that, in seven of 42 surveyed NS rivers, Al_i concentrations exceeded the 15 $\mu g\ L^{-1}$ toxic threshold for aquatic health (Dennis & Clair, 2012). This threshold was determined from an extensive review of toxicological and geochemical literature by the European Inland Fisheries Advisory Council (EIFAC) (Howells et al., 1990). No assessment of Al_i has been done in NS_A since that time, and little is known about the current extent and patterns of Al_i in the region. Here, we conduct a four-year survey of Al_i concentrations in ten streams in NS_A, to test the hypothesis that elevated DOC concentrations are sufficient to protect life from Al_i, and to identify the hydrologic conditions associated with elevated Al_i concentrations.

A1.4 Methods

A1.4.1 Study Area

We surveyed Al_i concentrations at ten study catchments in NS_A, ranging from headwater to higher-order systems: MR, MPB, 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 14; Figure 10). Our study catchments are predominantly forested with a mix of coniferous and deciduous species, and drain slow-weathering, C_B-poor bedrock, producing soils with low ANC (Langan & Wilson, 1992; Tipping, 1989). The catchments have relatively high DOC concentrations (Ginn et al., 2007) associated with abundant wetlands in the region (Clair et al., 2008; Gorham et al., 1986; Kerekes et al., 1986).

Table 14 Study site characteristics. Dominant land cover for all sites is natural forest. Standard deviation reported in backets next to mean concentrations. One Al_i outlier removed for MR (value: 2 $\mu g\ L^{-1}$, date: 30 April 2015).

Site name and abbreviation	Lat-itude	Long-itude	Basin area (km^2)	Dominant bedrock type	Number of samples	Mean Al_d ($\mu g\ L^{-1}$)	Mean Al_i ($\mu g\ L^{-1}$)	Mean Ca ($\mu g\ L^{-1}$)	Mean DOC ($mg\ L^{-1}$)	Mean pH (unit)
Mersey River (MR)	44.437	-65.223	292.8	Granite	47	195 (54.9)	22.5 (11.7)	699 (120)	8.6 (2.7)	5.1 (0.3)
Moose Pit Brook (MPB)	44.462	-65.048	15.8	Granite/ slate	39	249 (85.9)	20.8 (12.2)	826 (344)	15.8 (6.1)	5.0 (0.2)
Pine Marten Brook (PMB)	44.436	-65.209	1.5	Slate	15	149 (43.4)	13.5 (12.0)	969 (536)	8.6 (3.3)	5.1 (0.3)
Maria Brook (MB)	44.779	-64.414	0.2	Granite	12	319 (99.2)	40.1 (23.2)	1292 (286)	9.8 (4.4)	5.1 (0.2)
Brandon Lake Brook (BLB)	45.021	-62.690	1.3	Sandstone/ slate	22	350 (71.0)	48.7 (27.6)	836 (272)	16.0 (8.3)	4.9 (0.1)
Upstream of West River Lime Doser (ALD)	45.054	-62.800	32.3	Sandstone/ slate	22	243 (64.8)	45.3 (26.7)	759 (126)	13.8 (3.7)	5.2 (0.2)
Upper Killag River (UKR)	45.064	-62.705	36.8	Sandstone/ slate	18	224 (68.3)	43.5 (23.5)	739 (230)	12.8 (3.0)	5.3 (0.2)
Little River (LR)	44.952	-62.611	47.1	Sandstone/ slate	13	109 (46.1)	15.1 (11.7)	746 (166)	7.2 (1.9)	5.4 (0.3)
Keef Brook (KB)	45.028	-62.715	2.3	Sandstone/ slate	5	281 (80.4)	28.2 (11.5)	621 (275)	10.8 (3.6)	5.1 (0.1)
Colwell Creek (CC)	45.028	-62.713	1.7	Sandstone/ slate	8	411 (117)	58.9 (41.7)	750 (568)	23.1 (5.1)	5.0 (0.1)

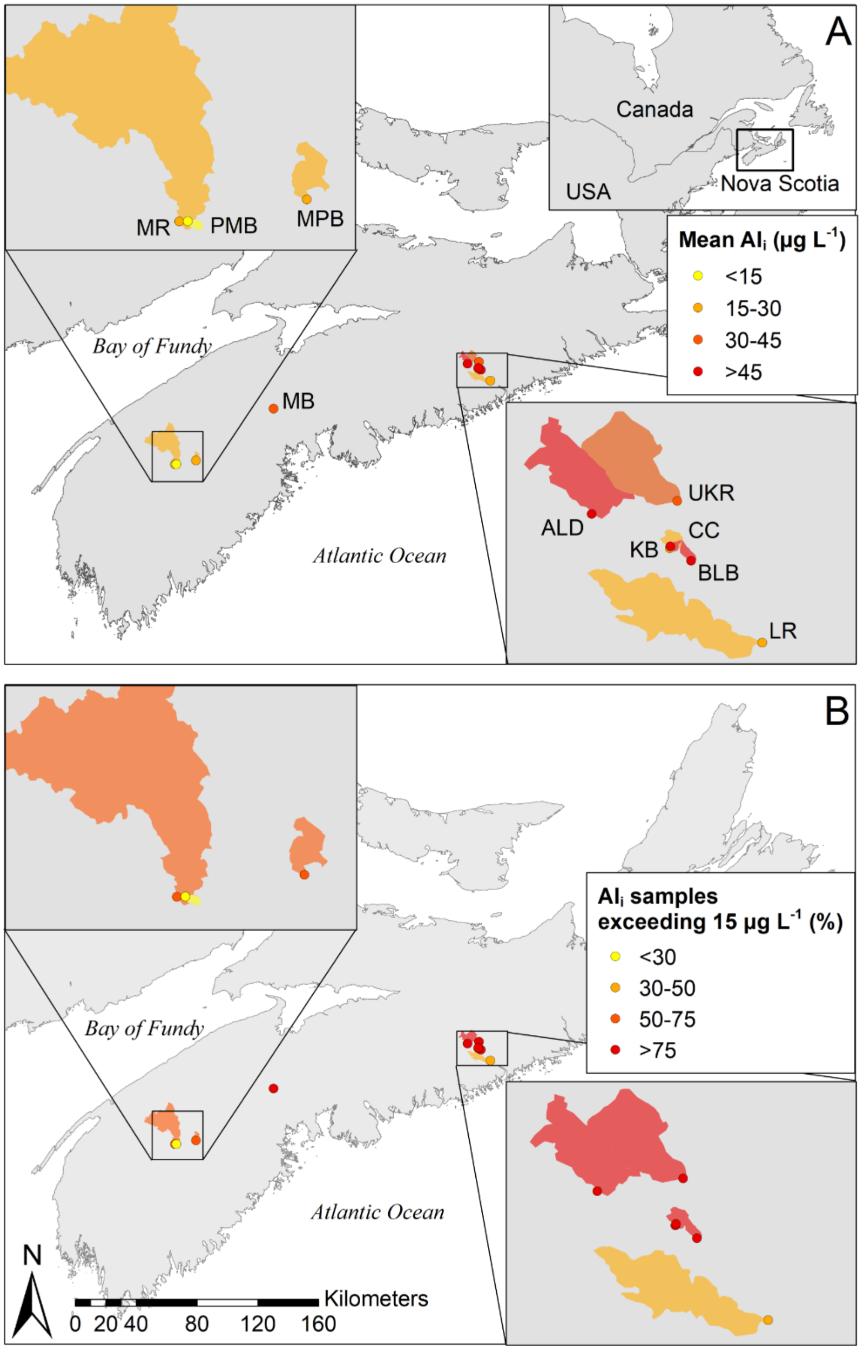

Figure 10 Sample site locations (points) and catchments (polygons) showing mean Al$_i$ concentrations (A) and percent of samples where Al$_i$ concentrations exceeded the 15 µg L^{-1} toxic threshold (B) between spring 2015 and fall 2018.

A1.4.2 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 A1.2). From 2016 to 2018, five other sites were also sampled every two weeks to monthly during the snow-free season. Two sites (CC and KB) were only sampled from June to September 2016 because catchment liming occurred in was conducted in their watersheds in October 2016.

Al_i sampling events comprised of grab samples for lab analysis and in situ measurements of pH and water temperature. We calculate Al_i as the difference between Al_d and Al_o following (Dennis & Clair, 2012; Poléo, 1995) (Eq. 8), separating the species in the field to reduce errors caused by Al species change due to changes in temperature and pH in transport from field to lab.

$$Al_i = Al_d - Al_o \tag{8}$$

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

Al species measured via the cation exchange method thus consist of weak monomeric Al_o complexes (column eluate), monomeric inorganic Al (retained in the column), and colloidal, polymeric, and strong organic complexes that are measured after acid digestion of the sample (Al_d sample) (Gensemer & 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 potentially have a toxic effect (see (Gensemer & Playle, 1999). The eluate is generally considered to be non-toxic; however, there is some evidence that precipitated polymeric Al (Al_{poly}) and colloidal Al can be toxic to aquatic life (Gensemer et al., 2018; Gensemer & Playle, 1999) although the nuances of this toxicity are unclear. To this end, the calculated Al_i reported in this study represents a minimum concentration of toxic Al species. 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 and sterilized polyethylene bottles. Samples for SO_4 analysis were not filtered. Trace metal samples were filtered (0.45 μm) and preserved with HNO_3. Samples for DOC analysis were filtered (0.45 μm) and transported in amber glass bottles containing H_2SO_4 preservative 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°C prior to analysis (section A1.7.3.2 Laboratory Analysis Methods).

We examined correlations between Al_i and water chemistry parameters: Al_d, Ca, DOC, pH, SO_4, water temperature, F, NO_3, and discharge (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 A1.2; section A1.7.3.3Toxic Thresholds of Al_i).

We developed a GLMM to identify the main drivers of Al_i concentration at the study sites. We tested Al_d, DOC, Ca, SO_4, F, NO_3, season, and water temperature as potential drivers. The GLMM analysis was implemented with R version 3.6.2. using the lme4 package (Bates et al., 2014). Due to the nonnormality of the Al_i concentration data, the glmer() function was employed for model fitting; it uses the method of maximum likelihood for parameters estimation through Laplace approximation (Raudenbush et al., 2000). The study sites in the were included as the random effect with fixed effects provided in Table A1.3; Al_d was not included in the GLMM as it results in an over fit model (singularity). The Wald t-Test Statistic and the Akaike Information Criterion (AIC) were used as measures of goodness-of-fit (Akaike, 1974; Bolker et al., 2009). Numerous iterations of fixed effects and interactions were considered in the GLMM development (Table A1.3). Multiple fixed effects were initially considered; however, several of the effects were not significant, although the overall model fit provides a low AIC. GLMMs were applied to assess the influence of season on Al_i concentrations; however, due to the limited amount of seasonal data collected, an analysis of both the site and seasonal random effects could not be carried out due to model singularities.

A1.5 Results and Discussion

A.1.5.1 Prevalence of Al_i

Al_i concentrations exceed toxic levels (15 µg L^{-1}) at all sites during the study period (Table A1.2) despite high DOC concentrations (mean values ranging from 7.2 to 23.1 mg L^{-1}; Table 14). Mean Al_i concentrations across all sites range from 13–60 µg L^{-1} (Table 14), with the highest mean concentrations occurring in the eastern part of the study area (Figure 10A), where one site had 100% of samples in exceedance of the 15 µg L^{-1} threshold (Figure 10B). Al_i concentrations exceed 100 µg L^{-1} (approximately seven times the threshold) at three sites (Table A1.2). The Al_i concentrations we measure are consistent with the 6.9–230 µg L^{-1} range of found across NS_A by Dennis and Clair (2012) and are higher than concentrations measured in Norway from 1987–2010 (5–30 µg L^{-1}) (Hesthagen et al., 2016).

The percent of Al not complexed by DOC (Al_i/Al_d) ranges from a minimum of 0.6 % to a maximum of 50 %, with a median value of 10.7 %, across all sites. These findings are similar to those found in NS_A by Dennis and Clair (2012) of the proportion of Al_i in Al_t (minimum = 4 %, maximum = 70.1 %, median = 12.4 %), and less than those found by Lacroix (1989) (over 90 % Al_o/Al_d). The Al_i/Al_d we find is also quite similar to other diverse environments, such as those for acid sulphate soil environments in Australia (Simpson et al., 2014). However, even when the percentage of Al_i/Al_d is low, Al_i concentrations remain well above thresholds for toxicity (Figure A1.1). Similar to our findings, previous studies show Al_i/Al_d is low during baseflow (Bailey et al., 1995; Murdoch & Stoddard, 1992; Schofield et al., 1985).

The highest concentrations of Al_i (> 100 µg L^{-1}) occur in early summer (late June or early July in 2016-2018) when Al_d, Ca, and DOC concentrations have not yet reached their annual peak (Table A1.2). The spring/summer extreme events occur among the first exceptionally warm days (> 21 °C) of the year, in dry conditions, and when the proportion of Al_o/Al_d are low (approximately 60-70 % compared to 80-90 %) (Figure A1.1). pH was not abnormally low during these events (range: 4.8-6.13), Ca concentrations were low ($\leq$ 800 μg L^{-1}) and DOC concentrations ranged from 15−21 mg L^{-1}.

In the sites with the longest and most frequent data collection (MR and MPB), Al_i concentrations exceed the toxic threshold in consecutive samples for months at a time, particularly in the late summer (Figure A1.1).

A1.5.2 Potential Al_i Drivers

GLMM results reveal, through multiple fixed effect model combinations, that DOC and water temperature are the most significant predictors of Al_i concentrations (Table A1.3). When both DOC and water temperature are 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 water temperature alone. Furthermore, the interaction between DOC and water temperature is not significant in the model and provides a nominally lower AIC. The correlation between DOC and water temperature effects is low (-0.378), indicating that distinct processes are responsible for Al_i concentrations. The strength of the water temperature 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 existing conceptualization that DOC is inversely correlated with Al_i. This suggests that the increased recruitment of Al in soils by DOC may outweigh DOC's protective effects in freshwater, consistent with observations in other studies (for example, 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) (Figure 11; Table A1.4). Ca is significantly and positively correlated with Al_i at two sites (MPB, MR) (Figure 11; Table A1.4). The positive relationship between Ca and Al_i is the opposite of expectations, but has been found in another study in the area (Rotteveel & Sterling, 2020). We hypothesize that the positive correlation is due to the two study sites having very low Ca concentrations (mean < 1 mg L^{-1}) – too low to retard Al release from soils.

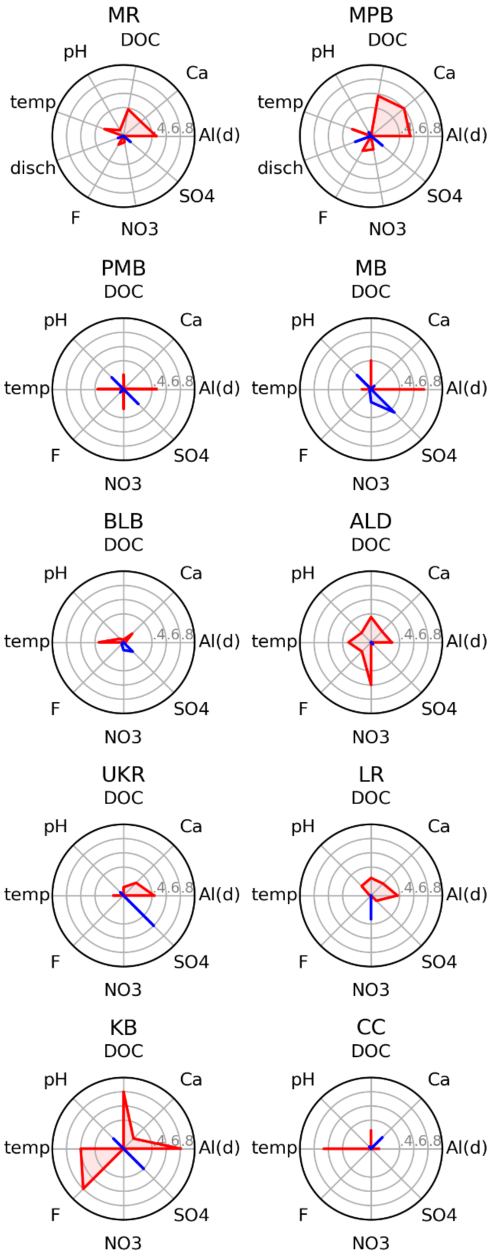

Figure 11 Correlations among water chemistry parameters and Al_i concentration, where red polygons and lines indicate a positive correlation with Al_i, and blue polygons and lines indicate a negative correlation with Al_i. One Al_i outlier removed for MR (value: 2 µg L^{-1}, date: 30 April 2015). Correlation data are listed in Table A1.4.

Discharge is significantly and negatively correlated with Al_i at one site, MPB (Figure 11; Table A1.4), in contrast with previous observations (Hooper & Shoemaker, 1985; Neal et al., 1986; Seip et al., 1989; Sullivan et al., 1986). Discharge data are available for only two of the study sites (MR, MPB); more 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 (Figure 11; Table A1.4). The lack of significant correlation may be due in part to other mechanisms that may obscure the inverse relationship between pH and Al, such as increased DOC solubility at higher pH, leading to increased Al solubility in soils (Lydersen, 1990), pH buffering by Al in the lower pH range (Grennfelt et al., 1990), and by the limited pH range in the data set. We did observe a statistically significant positive relationship between pH and Al_i/Al_d (Table A1.5); thus, it seems that pH may play a more important role in determining the proportion of different Al species rather than the absolute value of Al_i present in stream waters in chronically acidified regions such as NS_A. F is a known complexing agent of Al that affects speciation at low pH levels and 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 at two sites (KB, MPB) (Figure 11; Table A1.4). NO_3 and SO_4 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 and Al_i at MB.

A1.5.3 Possible Seasonal Groupings of Al_i in NS_A

In the two sites with the most samples, MPB and MR, groupings of data are visible that are temporally contiguous, suggesting seasonally dependent Al_i behavior (Figure 12). This is supported by stronger linear correlations (r^2) among variables when grouped by “season” (Table 15; Figure 12). For example, for the correlation between pH and Al_i at MR, r^2 improves from 0.02 for year-round data (Figure A1.1) to 0.78 in season 1 (Table 15; Figure

12). The transition dates between the seasons are similar for the two catchments, but not the same (Table A1.6), and vary by year. Here we propose an initial characterization of potential “seasons”; more research is needed to test these hypotheses on seasonal divisions and their drivers using larger datasets to test for statistical significance among the potential seasonal groupings.

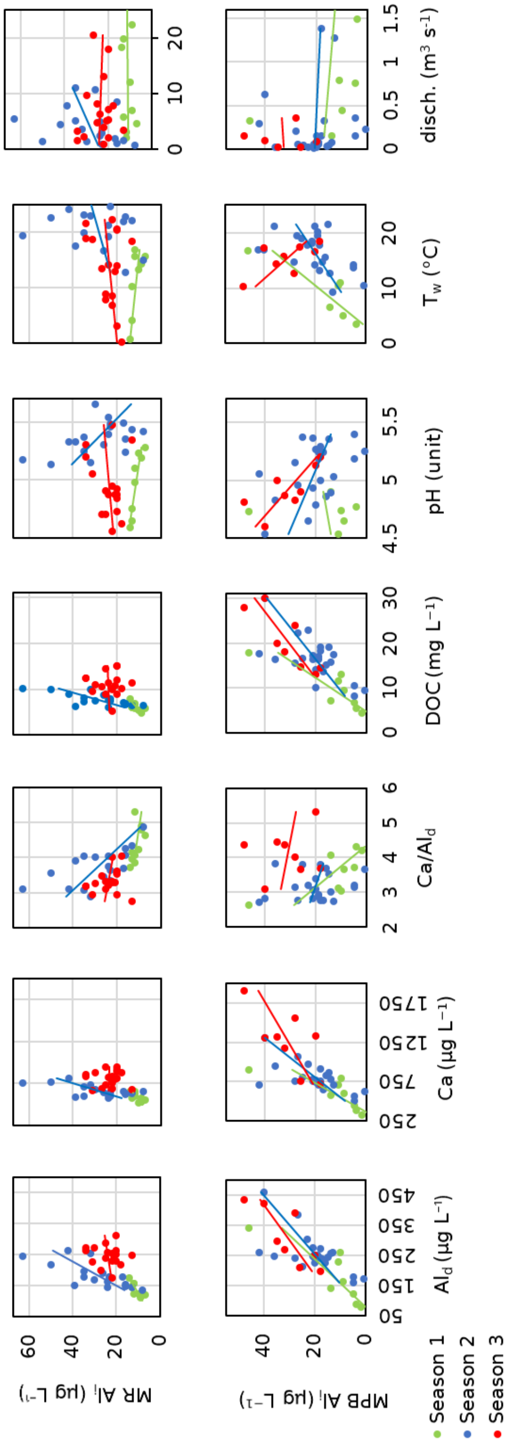

Figure 12 Seasonal relationships between Al_i and other water chemistry parameters for MR and MPB. One runoff outlier removed for MR (value: 17.294 m^3 s^{-1}, date: 22 April 2015) and for MPB (value: 34.994 m^3 s^{-1}, date: 22 April 2015). r^2 values are listed in Table A1.6.

Table 15 Relations between Al_i and other stream chemistry parameters separated by possible seasons. Light and dark shading represent r^2 = 0.4-0.6, and r^2> 0.6, respectively. Orange and blue indicate positive and negative relations, respectively.

Season	**Site**	**Al_i vs. Al_d**		**Al_i vs. Ca**		**Al_i vs. Al_d/Ca**		**Al_i vs. DOC**		**Al_i vs. pH**		**Al_i vs. T_w**	
		slope	**r^2**	**slope**	**r^2**	**slope**	**r^2**	**slope**	**r^2**	**slope**	**r^2**	**slope**	**r^2**
1	MR	0.08	0.67	0.03	0.50	-2.43	0.32	1.78	0.49	-7.67	0.78	-0.26	0.42
	MPB	0.13	0.68	0.05	0.59	-16.64	0.51	2.62	0.71	8.44	0.00	2.66	0.72
2	MR	0.23	0.52	0.13	0.37	-17.03	0.41	7.50	0.51	-53.20	0.27	0.72	0.03
	MPB	0.10	0.42	0.04	0.42	-4.65	0.03	1.40	0.43	-19.60	0.22	1.43	0.23
3	MR	0.02	0.01	0.01	0.00	-3.28	0.04	0.09	0.00	4.57	0.05	0.25	0.09
	MPB	0.09	0.66	0.02	0.49	-2.59	0.03	1.33	0.73	-39.60	0.56	-2.42	0.44

Season 1 (approximately April to May) is coincident with snowmelt runoff and is characterized by relatively low concentrations of Al_i (2-46 µg L^{-1}), low pH (4.5-5.3), and lower concentrations of most constituents, including DOC, and cold temperatures (< 4 °C). During this season, Al_i is strongly coupled with pH, DOC, Al_d and Ca in MR, but less so in MPB. A possible explanation is that season 1 is dominated by snowmelt hydrology in which cation exchange between soil and discharge occurs less efficiently, and can potentially be attributed to ice and frozen soil limiting time for cation exchange (Christophersen et al., 1990). It is important to note that we likely did not capture the first flush effect of increased Al_i as has been noted in other studies (for example, Hendershot et al., 1986). 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, Al_i has a strong positive relationship with DOC in season 2. The highest observed Al_i concentrations of the year occur in season 2 (Figure 12). Al_i relations are weak in MR in season 3 (approximately September to 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 this is only the case for Ca.

There remains limited data for undertaking a robust comparative analysis of seasons via GLMM analysis, but the results are included nonetheless to highlight the seasonal impacts that can be decerned from the limited dataset (Table A1.7). pH and water temperature are 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 water temperature on seasonal Al_i concentrations.

In contrast with the conceptualization that peak Al_i concentrations occur during storm flow (for example, Campbell et al., 1992; Kopáček et al., 2000; Neal et al., 1986; Rodushkin et al., 1995), our data show elevated Al_i concentrations during base flow. These results suggest a new pathway for generating 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) 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 13) (following Nilsson & Bergkvist, 1983). Biological activity further generates DOC which mobilizes Al to drainage waters during summer base flow (Figure 13). Other cases of increased Al_i concentrations occurring during low flow and warming temperatures can be found in the literature in locations such as Ontario and Quebec (Hendershot et al., 1986) and in Virginia, USA (Cozzarelli et al., 1987).

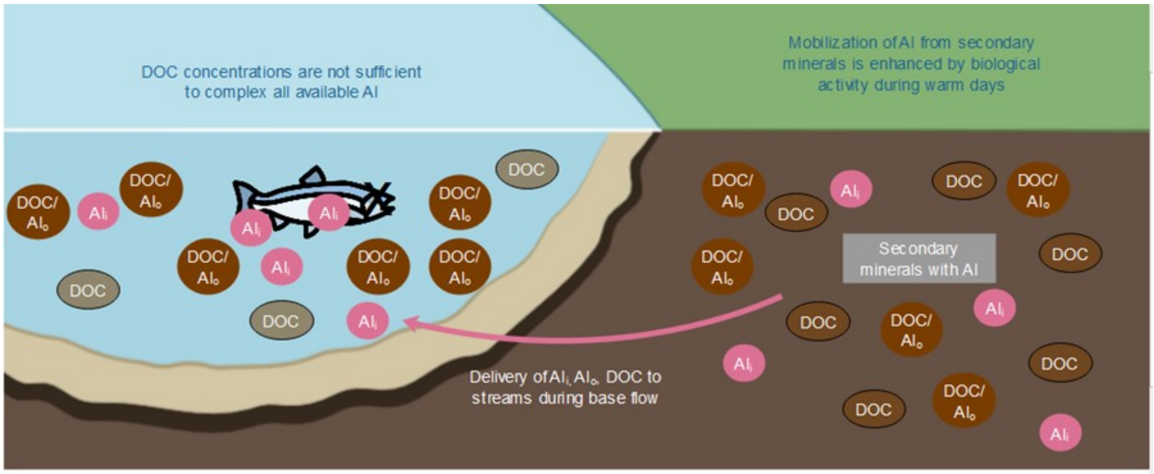

Figure 13 Conceptual model of new mechanism that can produce high concentrations of Al_i *in freshwaters during low flow. Warm days increase biological activity which mobilizes Al from secondary minerals and enhances production of DOC, which in turn reduces pH and reduces Al saturation in soil solution 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.*

A1.5.4 Ecological Implications

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

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

A1.6 Conclusion

Our four-year study of stream chemistry in NS_A has two important findings. First, high DOC concentrations in rivers may not protect aquatic life against Al_i as previously thought; instead, higher DOC concentrations drive higher levels of Al_i, possibly on a seasonal basis. Our study thus reveals that despite high DOC levels, widespread and persistent toxic concentrations of Al_i in NS_A freshwaters pose a risk to aquatic life. Second, our study highlights an overlooked hydrological pathway that is associated with high Al_i concentrations: base flow, suggesting a chronically acidified/Al dynamic, in addition to episodic Al_i peaks associated with storm flow. This base flow pathway suggests that Al_i concentrations are chronically elevated during warmer summer months, and thus that this Al pathway may be exacerbated by atmospheric warming. Our results suggest that the recent 88 to 99 % population decline of the Southern Uplands Atlantic salmon population in NS_A (Gibson et al., 2011) may be partially attributable to Al_i, in contrast to earlier studies which downplayed the role of Al_i in Atlantic salmon mortality (Lacroix & 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 because Ca is protective against Al_i toxicity, and highlighting coincident threats of Ca depletion and elevated Al. Recent work has identified widespread low and declining Ca across the globe (Weyhenmeyer et al., 2019), raising the question of what other regions may also have Al_i concentrations exceeding toxic thresholds. The serious potential consequences of high Al_i highlight the importance of 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 C_B removal and depletion. Addition of C_B's through liming and enhanced weathering of soils and freshwaters may accelerate recovery from acidification.

A1.7 Supplementary Information

A1.7.1 Figures

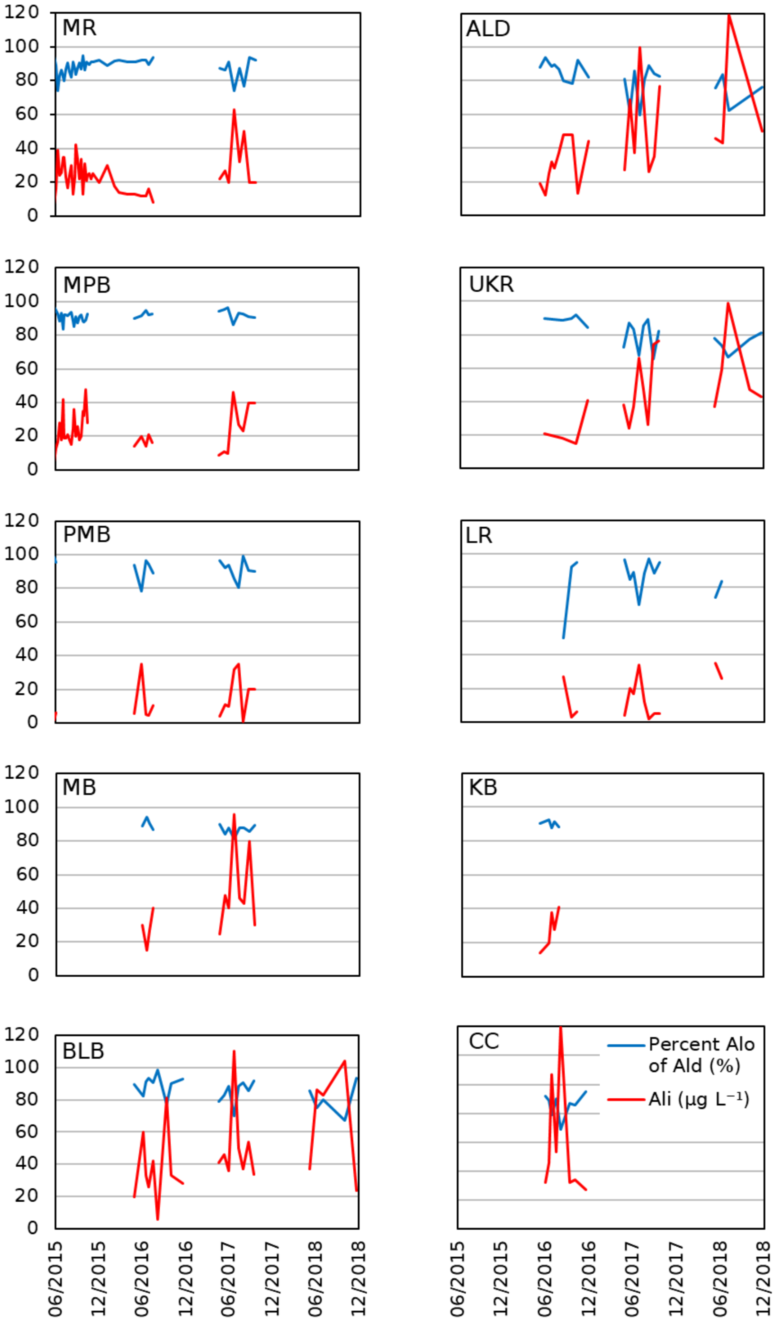

Figure A1.1 Timeseries of percent Al$_o$ of Al$_d$ and absolute value of Al$_i$ for study sites between April 22nd 2015 and November 23rd, 2018.

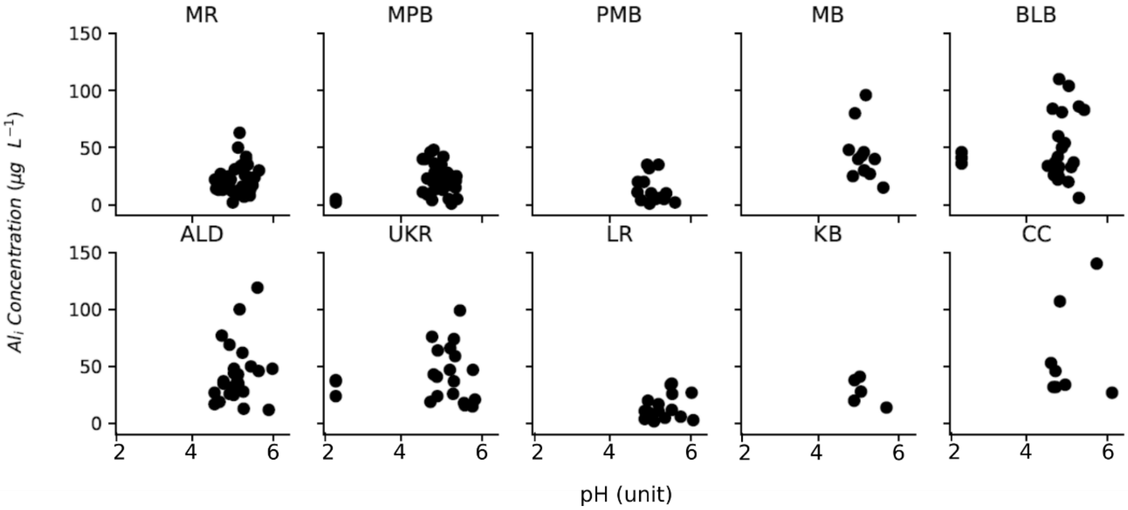

Figure A1.2 Al_i versus pH for each study site. One Al_i outlier removed for MR (value: 2 µg L^{-1}, date: April 30th, 2015).

A1.7.2 Tables

Table A1.1 Al_i terminology, speciation methods, and trends from published studies. Abbreviations are as follows: 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, and AWMN = Acid Waters Monitoring Network, UK = United Kingdom.

Al specie	**Definition**	**Analysis method**	**Trend**	**Location**	**Reference**
Al_i	Inorganic Al	Colourimetry (Al_t-Al_{nl})	Decreasing between 1988-2008	AWMN in UK	Monteith et al., 2014
Al_{im}	Inorganic monomeric Al	Colourimetry (Al_{tm}-Al_{om})	Decreasing between 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^{-1}; Mean New Brunswick Al_i = 31.0 µg L^{-1}	Atlantic Canada	Dennis & Clair, 2012
Al_i	Ionic Al	Colourimetry	Decreasing between 1995-2009	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 % >10 µg L^{-1}	Norway	Kristensen et al., 2009
Al-l	Labile/ cationic/ inorganic monomeric Al	Colourimetry (Al_{tm}-Al_{nlm})	Decreasing between 1988-2000	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^{-1} between 2009-2010	China	Wang et al., 2013
Al_i	Inorganic monomeric	Colourimetry and CEC (Al_m-Al_o)	Decreasing between 1991 & 2007	Czech Republic	Krám et al., 2009
Al_i	Inorganic Al	AAS	Decreasing between 1990-2010	Adirondack Mountains, USA	Strock et al., 2014

Table A1.2 Raw sample data. Hydrograph stages are abbreviated as follows: rising limb: RL, falling limb: FL, base flow: BF. 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 sites, and from 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 sites. Missing T_a data for MR, MPB, PMB, and MB were replaced with data from another local meteorological tower located one kilometer to the northwest of the MPB site (44°28'10.3764" N, 65°3'40.662" W). Table available as an electronic supplement to this thesis.

*Table A1.3 GLMM results for all field data. Parameters significant at $\alpha = 0.05$ are bolded and parameters significant at $\alpha = 0.10$ are italicised. Interaction terms are indicated with a *. Water temperature is abbreviated as T_w.*

Fixed Effect	Parameter Estimate	Wald t Test Statistic	P-Value	AIC
Ca	0.281	1.551	0.121	1316.9
DOC	0.536	3.285	**0.001**	
F	-0.040	-0.790	0.429	
NO_3	0.068	3.269	**0.001**	
pH	-1.123	-0.952	0.341	
SO_4	-0.295	-3.038	**0.002**	
T_w	0.340	1.551	**0.046**	
DOC	0.321	5.647	**0.000**	1946.3
DOC	0.149	4.954	**0.000**	1816.7
NO_3	0.417	2.721	**0.007**	
SO_4	-0.417	-2.667	**0.008**	
DOC	0.256	6.908	**0.000**	1837.2
NO_3	0.120	3.335	**0.000**	
DOC*NO_3	1.100	4.545	**0.000**	
T_w	0.548	4.574	**0.000**	1467.8
DOC	1.135	3.445	**0.000**	1438.2
T_w	0.678	2.215	**0.027**	
DOC*T_w	-0.470	0.109	0.109	
DOC	0.623	6.391	**0.000**	1438.6
T_w	0.240	1.943	*0.052*	

Table A1.4 Kendal-tau correlation and significance (α = 0.05) between Al_i and other water chemistry parameters. One Al_i outlier removed for MR (value: 2 μg L^{-1}, date: April 30^{th}, 2015). Water temperature is abbreviated as T_w.

Variable	ALD		BLB		CC		KB		LR		MB		MPB		MR		PMB		UKR	
	Tau	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**	**Tau**	**P-value**
Al_d	0.29	0.044	0.03	0.852	0.11	0.708	0.80	0.050	0.37	0.047	0.74	0.001	0.55	0.000	0.46	0.000	0.46	0.019	0.34	0.071
Ca	0.22	0.143	0.17	0.238	-0.22	0.451	0.20	0.624	0.24	0.226	-0.06	0.783	0.58	0.000	0.32	0.002	0.01	0.960	0.38	0.053
DOC	0.36	0.013	0.08	0.575	0.25	0.383	0.80	0.050	0.25	0.189	0.40	0.073	0.57	0.000	0.38	0.000	0.21	0.295	0.32	0.086
pH	0.19	0.190	0.07	0.622	-0.04	0.901	-0.20	0.624	0.19	0.319	-0.28	0.214	-0.17	0.146	0.10	0.362	-0.23	0.232	0.35	0.063
T_w	0.32	0.093	0.35	0.099	0.67	0.174	0.60	0.142	0.02	0.937	0.13	0.580	0.28	0.016	0.29	0.007	0.36	0.065	0.14	0.621
Discharge													-0.23	0.042	-0.11	0.291				
F	0.18	0.533	-0.04	0.901			0.80	0.050			-0.03	0.917	0.24	0.042	0.14	0.188	-0.06	0.782		
NO_3	0.60	0.142	-0.11	0.708					-0.33	0.348	-0.18	0.533	0.19	0.160	0.09	0.450	0.28	0.444		
SO_4	-0.04	0.876	-0.18	0.468			-0.40	0.327	0.11	0.801	-0.46	0.050	-0.21	0.067	-0.13	0.215	-0.29	0.135	-0.60	0.142

Table A1.5 Correlation (r^2) and significance ($\alpha = 0.05$) between the percent Al_i of Al_d and other water chemistry parameters across all sites. Water temperature is abbreviated as T_w.

Variable	**Unit**	**Correlation with Al_i/Al_d (r^2)**	**Significance (p-value)**
Al_d	$\mu g\ L^{-1}$	0.007	0.247
Ca	$\mu g\ L^{-1}$	0.001	0.676
DOC	$mg\ L^{-1}$	0.007	0.247
pH	unit	0.077	0.000
T_w	°C	0.114	0.000
F	$\mu g\ L^{-1}$	0.003	0.537
NO_3	$\mu g\ L^{-1}$	0.002	0.624
SO_4	$\mu g\ L^{-1}$	0.000	0.952

Table A1.6 Season ranges for scatterplots of water chemistry relationships shown in Figure 12 and Table 15.

Site	Season	Season range
MR	1	April-May
	2	June-Aug
	3	Sept-Feb
MPB	1	April-June
	2	July-Aug
	3	Sept-Oct

*Table A1.7 GLMM results for seasonal field data. Parameters significant at $\alpha = 0.05$ are bolded and parameters significant at $\alpha = 0.10$ are italicised. Interaction terms indicated with a *.*

Fixed Effect	Parameter Estimate	Wald t Test Statistic	P-Value	AIC
Al$_d$	0.264	6.170	**0.000**	1736.5
Ca	-0.007	-0.183	0.855	
DOC	0.143	3.727	**0.000**	
F	-0.020	-0.207	0.836	
NO$_3$	0.146	0.991	0.322	
SO$_4$	-0.133	-1.129	0.259	
Al$_d$	0.281	6.921	**0.000**	1867.3
DOC	0.078	1.877	*0.061*	
Al$_d$	0.313	7.393	**0.000**	1862.8
DOC	0.158	3.152	**0.002**	
AL$_d$*DOC	-0.076	-2.490	**0.013**	
Al$_d$	0.332	11.490	**0.000**	1868.3
DOC	0.229	9.445	**0.000**	1909.9
DOC	0.247	9.744	**0.000**	1768.4
NO$_3$	0.329	-2.399	**0.016**	
SO$_4$	-0.316	2.515	**0.012**	
DOC	0.287	9.453	**0.000**	1797.3
NO$_3$	0.063	1.733	*0.083*	
DOC*NO$_3$	0.410	1.709	*0.088*	

Table A1.8 Comparison of laboratory detection limits. Variables not analyzed at a laboratory are denoted by n/a.

Variable	**Units**	**Laboratory**		
		HERC	**Maxxam**	**AGAT**
pH	unit	n/a	n/a	n/a
TOC	mg L^{-1}	n/a	n/a	0.50
DOC	mg L^{-1}	n/a	0.50	n/a
SO_4	µg L^{-1}	10.00	n/a	2000
Al_t	µg L^{-1}	n/a	5.00	5
Al_d	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

A1.7.3 Additional Methods

A1.7.3.1 Calibration of pH Measurements

In situ pH measurements were taken using a YSI Pro Plus sonde and confirmed with a YSI Ecosense pH pen. Measurements taken with the YSI Pro Plus sonde deviated from the YSI Ecosense pen, which is known to measure pH accurately. Therefore, we calculated a calibration curve based on simultaneous side-by-side measurements of both instruments (n = 69 pairs) and adjusted the in sonde pH measurements accordingly (Eq. 9).

$$pH_{pen} = 0.595pH_{sonde} + 2.3868 \tag{9}$$

Here, pH_{pen} denotes the equivalent value of the YSI Ecosense pen for a measurement taken by the YSI Pro Plus sonde (pH_{sonde}).

A1.7.3.2 Laboratory Analysis Methods

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

A1.7.3.2.1 Bureau Veritas Laboratory

The protocol at Bureau Veritas Laboratory in Bedford, NS, adheres to methods approved by the US EPA for identifying trace elements in water (US EPA., 1994) and analyzing samples using 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.

A1.7.3.2.2 HERC Laboratory

SO_4 samples were analyzed at HERC Laboratory in Halifax, NS, because they have a lower detection limit than Bureau Veritas 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.

A1.7.3.2.3 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 and anions were measured using ICS. Samples analyzed at AGAT were analyzed for TOC as opposed to DOC and were analyzed using Infrared Combustion.

A1.7.3.3 Toxic Thresholds of Al_i

Identified toxic thresholds of Al_i for Atlantic salmon vary in the literature. Based on toxicological and geochemical studies on Al and Atlantic salmon, the EIFAC suggests a freshwater Al_i toxic threshold of 15 μg L^{-1} for pH between 5.0-6.0, and 30 μg 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 Atlantic salmon are considered negligible, and toxic effects are dominated by other dissolved and precipitated forms (Gensemer et al., 2018). For the purposes of this study, we use the toxic threshold of Al_i at 15 μg L^{-1}, as the majority of our pH observations were greater than or equal to 5.0 (Table A1.2).

Appendix 2 - Supplementary Information for Chapter 2

A2.1 Figures

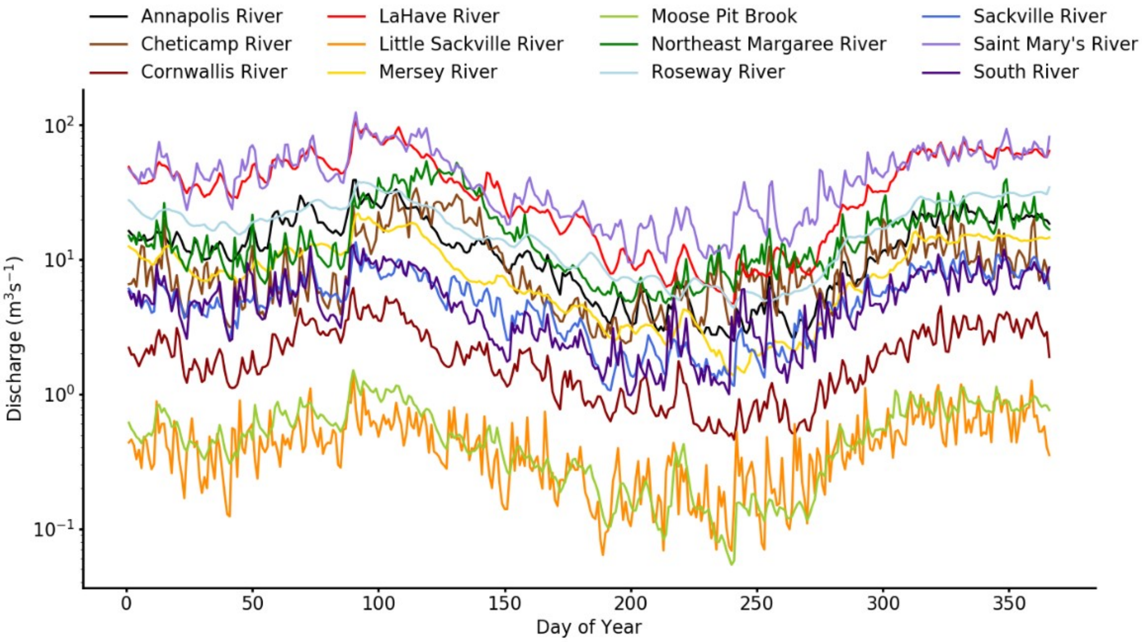

Figure A2.1 Discharge regimes in the study rivers. Data displayed are average daily discharge values between 2000 and 2018 for each site. Y axis is in log scale to accommodate difference in discharge magnitude (catchment size ranges from 17.13 km^2 for MPB to 1,339.09 km^2 for Saint Mary's River).

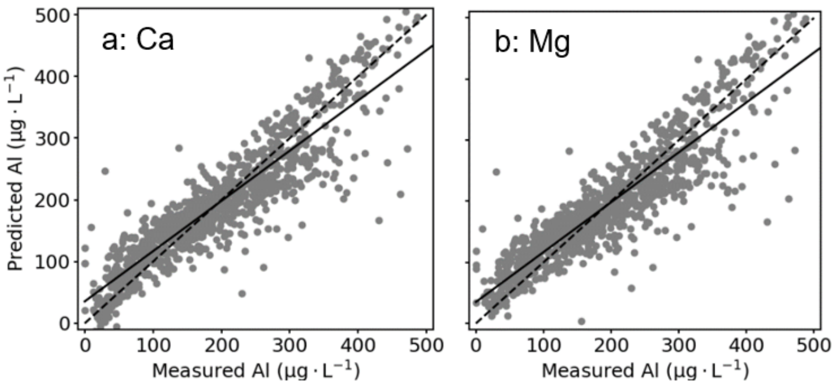

Figure A2.2 PLS regression model fit with TOC, C_B, turbidity, and discharge as explanatory variables in the first two directions of variance (n = 1,101 for each C_B model). Dashed black line indicates the $r^2 = 1$ line, while the solid line indicates the r^2 fit between the predicted and measured Al concentration. 82 % of Al variability is explained.

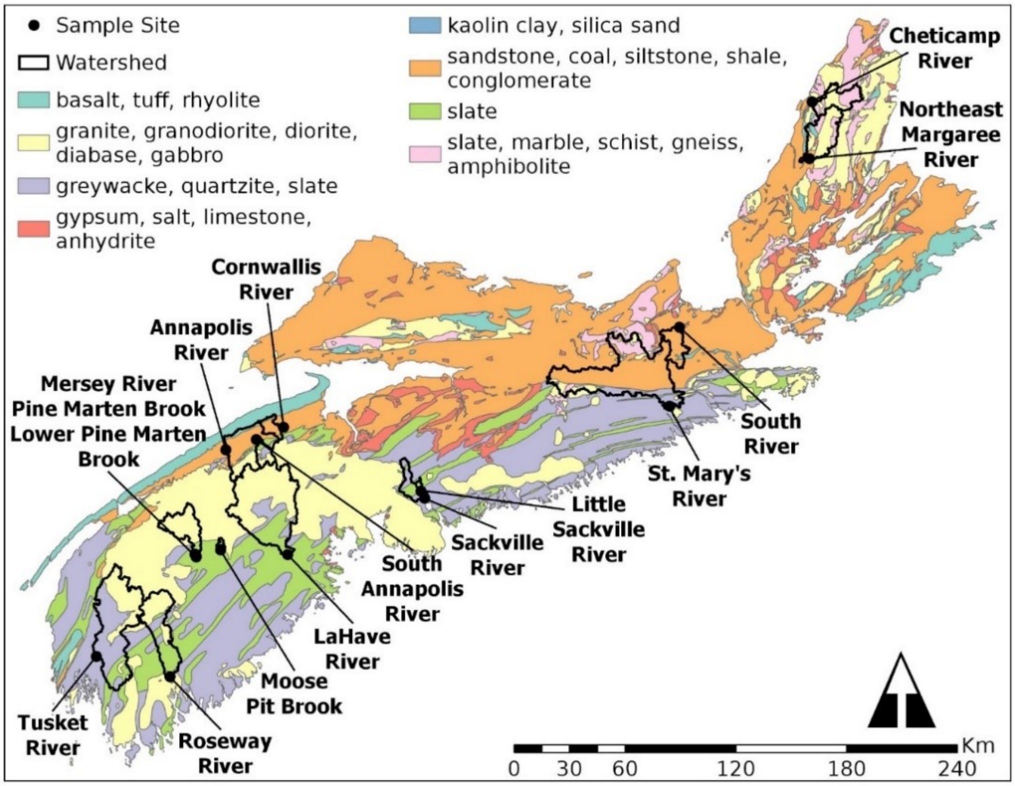

Figure A2.3 Map of geology underlying study catchments. For data sources, please see Table A2.1.

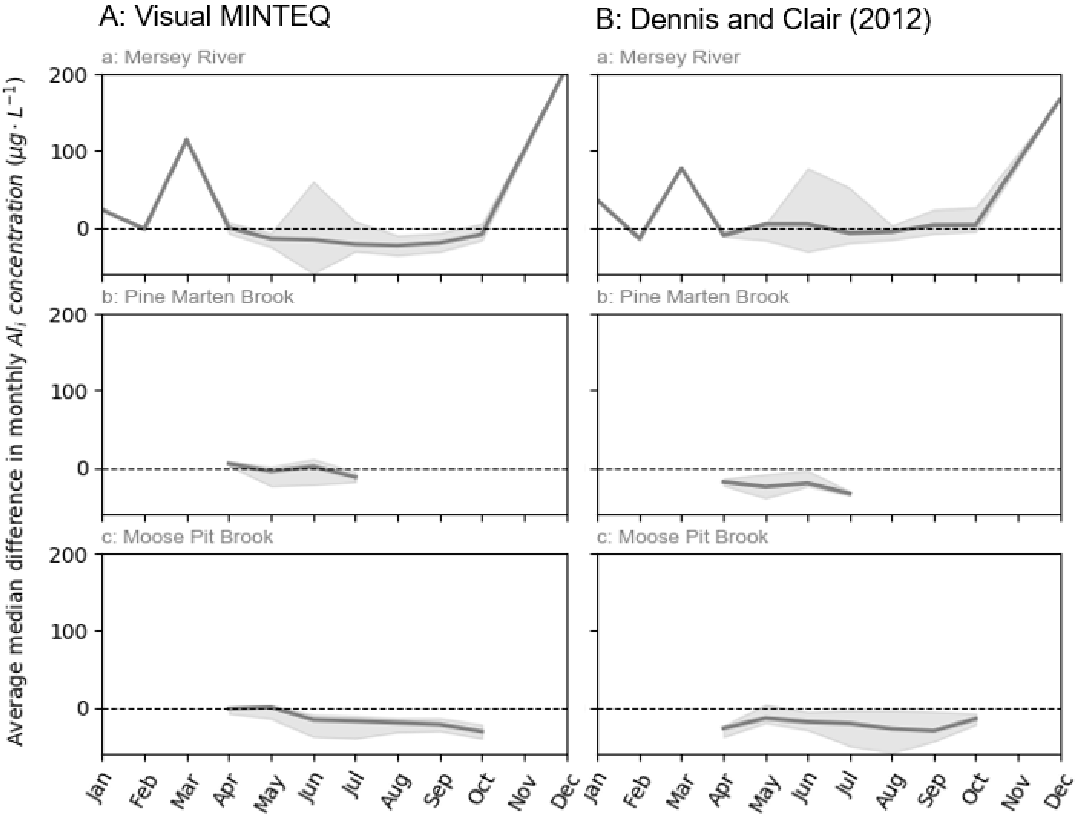

Figure A2.4 Comparison of modeled Al_i concentrations against field observations measured by Sterling et al. (2019). Al_i concentrations predicted by Visual MINTEQ geochemical equilibrium model (A), and Dennis & Clair (2012) statistical model (B). The dark gray line indicates the median difference between the modeled and measured values, and the light gray background indicates the range between minimum and maximum difference. Negative values indicate an underestimation of measured Al_i and positive values indicate an overestimation. The doted black line indicates 0, where modeled Al_i exactly predicts measured Al_i.

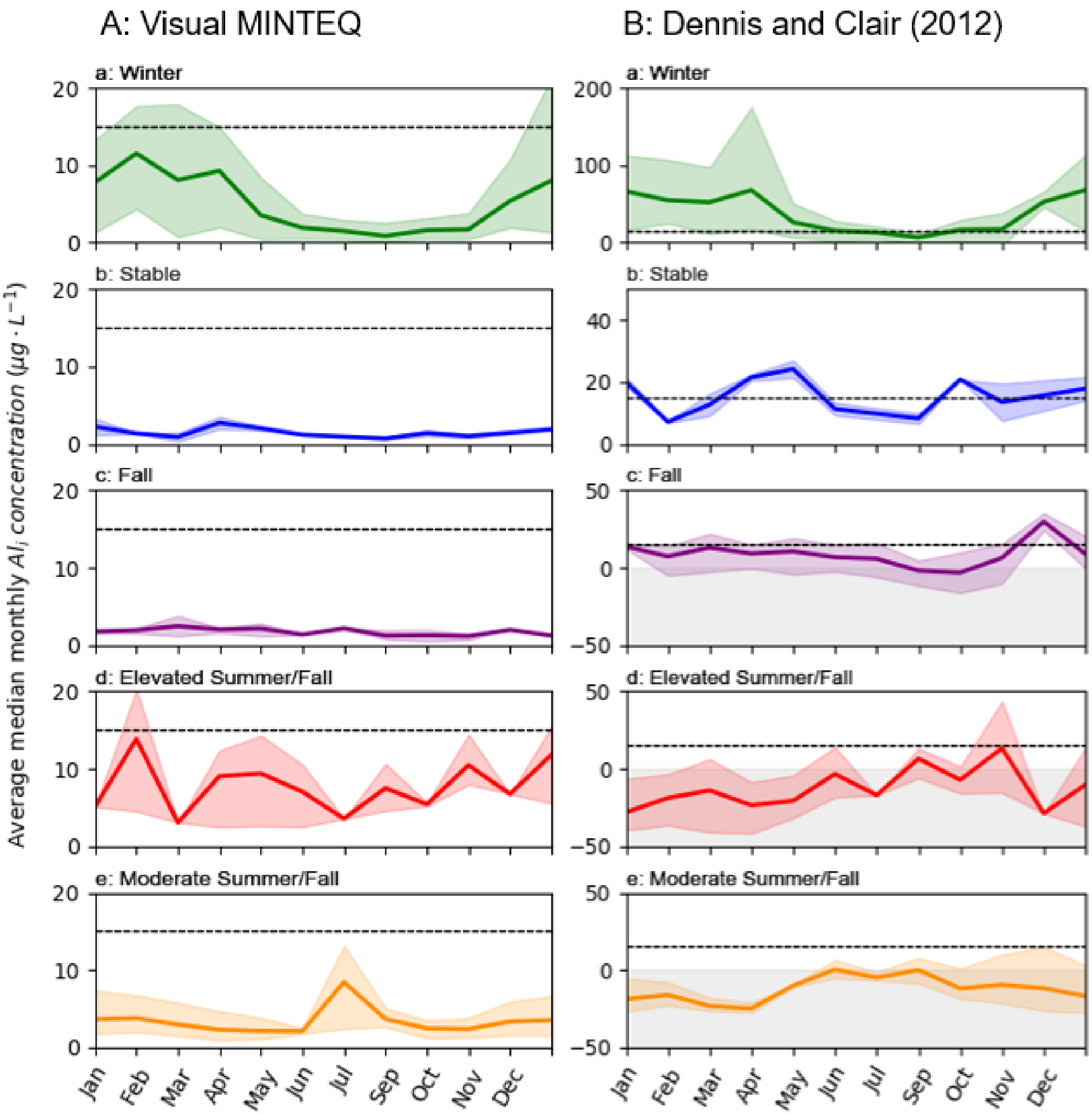

Figure A2.5 Seasonal patterns of modeled Al_i per regime. Al_i predicted by Visual MINTEQ geochemical equilibrium model (A), and Dennis & Clair (2012) statistical model (B). Thick line indicates average monthly median Al_i concentrations across all sites in each regime cluster, coloured range indicates average minimum and maximum values. Gray Background indicates values predicted below 0 µg L^{-1}. The black dotted line indicates the maximum (15 µg L^{-1}) Al_i concentration recommended for aquatic health (Howells et al., 1990). Note the difference in y-axis range.

A2.2 Tables

Table A2.1 Data sources. Abbreviations are listed in Table 1.

Parameter Type	Data	Last Updated	Source	Website
Chemical	Water chemistry	2019	ECCC LTM	http://data.ec.gc.ca/data/substances/monitor/national-long-term-water-quality-monitoring-data/maritime-coastal-basin-long-term-water-quality-monitoring-data/?lang=en
Topographic	Land use/ cover	2018	NS Gov NSTD	https://nsgi.novascotia.ca/gdd/
	Roads	2018	NS Gov NSTD	https://nsgi.novascotia.ca/gdd/
	Old forest	2016	NS Gov NSTD	https://nsgi.novascotia.ca/gdd/
	Water features	2018	NS Gov NSTD	https://nsgi.novascotia.ca/gdd/
	Digital elevation model	2006	NS Gov department of Lands and Forestry	https://novascotia.ca/natr/meb/download/dp055.asp
Geologic	Geochemistry	2006	NS Gov department of Lands and Forestry	https://novascotia.ca/natr/meb/geoscience-online/geochemistry.asp
	Bedrock geology	2006	NS Gov department of Lands and Forestry	https://novascotia.ca/natr/meb/download/gis-data-maps-provincial.asp
	Surficial geology	2006	NS Gov department of Lands and Forestry	https://novascotia.ca/natr/meb/download/gis-data-maps-provincial.asp
Watershed	Primary, secondary, tertiary, and sub-tertiary watersheds	2018	NS Gov department of Environment	https://data.novascotia.ca/Environment-and-Energy/1-10-000-Nova-Scotia-Watersheds/569x-2wnq
Meteorologic	Monthly climate summaries	2019	Government of Canada	http://climate.weather.gc.ca/prods_servs/cdn_climate_summary_e.html

Table A2.2 Site and sampling metadata. Table is available as an electronic supplement to this thesis.

Table A2.3 ECCC analysis methods and their comparability. The "Combined" column indicates the groupings of ECCC analysis types in our study. Table is available as an electronic supplement to this thesis.

Table A2.4 NS Topographic Database features included in land use and land cover categories; only features listed in the database are included. Some category features may not be present in each catchment.

Land use/land cover category (description)	**Included parameters**
Agricultural (areas associated with crops, animal rearing and husbandry, or farms)	Cranberry bog, crop field, fur farm, greenhouse, nursery, orchard, peat cutting area, silo
Forest (un-harvested forested areas)	Game management area, protected area, provincial park*
Industrial (anthropogenic buildings and features associated with increased environmental impact)	Ammunition dump, airport/airstrip, auto salvage yard, chimney, communication dome, construction area, dockyard, dry dock, electrical generating plant, factory, ferry port, gas station, grandstand, heliport, incinerator, kiln, landfill, lumber mill, mine, mine disposal site, petroleum refinery, pile, pipeline, pulp mill, quarry, refinery, sewage settling pond, sewage treatment plant, substation, tank
Recreational (outdoor areas in which anthropogenic recreational activities occur)	Campground, cemetery, exhibition ground, foot bridge, golf range, gun range, historic site, look out, picnic park, ski hill, sports field, trail
Residential (non-industrial or agricultural buildings)	Arena, community center, church, elderly home, fire station, fort, hospital, legislative, library, military reserve, mobile home park, museum, native reserve, outdoor rink, police station, pool, post office, school, storage area, town hall
Road (paved areas associated with increased automobile impact or railways)	Arterial street, bridge, drive-in theatre, driveway, highway, overpass, parking area (paved and unpaved), service lane, tunnel, underpass, racetrack, railway, railway ramp, rest area
Wetland (as identified in the Canadian Wetland Classification System)	Swamp**

** No other forest features specified.*
*** No other wetland types specified.*

Table A2.5 Correlation between Al and dominant drivers identified through PLS regression. Black bolded values indicate significant correlations ($p < 0.05$), and gray values indicate non-significant correlations ($p > 0.05$).

Regime	Site	Non-Discharge Normalized					Discharge Normalized			
		Ca	Mg	TOC	Turbidity	Discharge	Ca	Mg	TOC	Turbidity
Winter	Annapolis River	**-0.548**	**-0.435**	**0.355**	**0.511**	**0.570**	**0.468**	**0.492**	**0.489**	**0.560**
	Cornwallis River	**-0.593**	**-0.517**	**0.326**	**0.730**	**0.576**	**0.176**	**0.189**	**0.189**	**0.618**
	Little Sackville River	**-0.388**	**-0.433**	0.057	**0.560**	**0.600**	**0.580**	**0.602**	**0.617**	**0.739**
	Sackville River	**-0.361**	**-0.257**	**0.197**	**0.388**	**0.545**	**0.781**	**0.804**	**0.800**	**0.611**
	South River	**-0.584**	**-0.509**	**0.296**	**0.565**	**0.684**	**0.533**	**0.533**	**0.522**	**0.485**
Stable	Cheticamp River	**-0.463**	**-0.448**	**0.667**	0.194	**0.542**	**0.489**	**0.474**	**0.569**	**0.487**
	Northeast Margaree River	**-0.504**	**-0.480**	**0.588**	**0.386**	**0.617**	**0.306**	**0.307**	**0.315**	**0.417**
Fall	LaHave River	0.103	0.063	**0.552**	0.014	**0.329**	**0.845**	**0.813**	**0.841**	**0.641**
	South Annapolis River	-0.058	-0.038	**0.542**	0.123					
	St. Mary's River	**-0.187**	**-0.193**	**0.344**	0.164	**0.465**	**0.816**	**0.798**	**0.817**	**0.631**
Elevated summer/ fall	Moose Pit Brook	**0.673**	**0.574**	**0.808**	**0.085**	**-0.273**	**0.891**	**0.862**	**0.797**	**0.731**
	Roseway River	**0.528**	**0.456**	**0.755**	-0.080	-0.132	**0.903**	**0.897**	**0.847**	**0.617**
	Tusket River	**0.413**	**0.256**	**0.724**	0.015					
Moderate summer/ fall	Lower Pine Marten	**0.453**	**0.343**	**0.648**	**0.356**		**0.854**	**0.846**	**0.845**	**0.691**
	Mersey River	**0.427**	**0.397**	**0.646**	**0.097**	**0.225**				
	Pine Marten Brook	**0.503**	**0.370**	**0.682**	**0.332**					

Table A2.6 Study catchment geology. Clastics and organics consist of sandstone, coal, siltstone, shale, and/or conglomerate; evaporites consists of gypsum, salt, limestone, and/or anhydrite; gold-bearing metasediments consist of greywacke, quartzite, and/or slate; intrusives consist of granite, granodiorite, diorite, diabase, and/or gabbro; sulphide-bearing metasediments consist of slate; undivideds consist of slate, marble, schist, gneiss, and amphibolite; volcanics consist of basalt, tuff, and rhyolite.

Site Name	**Clastic and Organic**	**Evaporite**	**Gold-bearing meta-sediment**	**Intrusive**	**Sulphide-bearing meta-sediment**	**Undivided**	**Volcanic**
Annapolis River	45.28	0.00	5.16	32.93	10.03	0.00	6.60
Cheticamp River	0.01	0.00	0.00	44.64	0.00	55.10	0.25
Cornwallis River	80.25	0.00	1.00	0.24	5.09	0.00	13.41
LaHave River	0.00	0.00	14.49	66.64	18.88	0.00	0.00
Little Sackville River	0.00	0.00	6.30	0.00	93.70	0.00	0.00
Lower Pine Marten Brook	0.00	0.00	0.00	0.00	100.00	0.00	0.00
Mersey River	0.00	0.00	0.04	91.36	8.60	0.00	0.00
Moose Pit Brook	0.00	0.00	0.00	53.72	46.28	0.00	0.00
Northeast Margaree River	7.04	1.61	0.00	62.58	0.00	21.99	6.78
Pine Marten Brook	0.00	0.00	0.00	0.00	100.00	0.00	0.00
Roseway River	0.00	0.00	13.40	51.12	35.47	0.00	0.00
Sackville River	0.00	0.00	55.86	0.13	44.00	0.00	0.00
South Annapolis River	5.67	0.00	24.89	53.81	15.63	0.00	0.00
South River	95.38	0.31	0.00	0.00	0.00	0.00	4.31
Saint Mary's River	63.94	0.01	14.09	10.21	1.17	10.59	0.00
Tusket River	0.00	0.00	50.28	39.58	10.14	0.00	0.00

Table A2.7 Modeled Al_i *concentrations for study rivers. Concentrations are reported in µg* L^{-1}.

Regime	**Site**	**Visual MINTEQ**					**Dennis and Clair**				
		Max	**Min**	**Med**	**Mean**	**Std**	**Max**	**Min**	**Med**	**Mean**	**Std**
Winter	Annapolis River	244	0	5	14	33	231	-7	42	51	46
Winter	Cornwallis River	65	0	2	7	12	275	-9	41	63	66
Winter	Little Sackville River	41	0	2	5	8	200	-31	24	38	46
Winter	Sackville River	178	0	10	16	27	160	-68	36	38	34
Winter	South River	132	0	1	5	18	75	-26	8	12	19
Stable	Cheticamp River	13	0	1	2	2	58	-36	16	17	14
Stable	Northeast Margaree River	342	0	1	9	44	47	-13	10	13	12
Fall	LaHave River	268	0	1	6	34	66	-28	15	14	15
Fall	Saint Mary's River	28	0	1	2	4	38	-49	-4	-3	13
Fall	South Annapolis River	92	1	2	4	11	54	-4	10	14	12
Elevated summer/fall	Moose Pit Brook	188	0	4	5	10	140	-157	-29	-26	22
Elevated summer/fall	Roseway River	46	2	12	13	7	33	-46	-7	-6	19
Elevated summer/fall	Tusket River	47	1	11	12	8	96	-40	9	15	26
Moderate summer/fall	Lower Pine Marten Brook	5122	0	2	65	322	105	-53	-20	-14	24
Moderate summer/fall	Mersey River	1019	0	5	16	71	138	-87	-5	0	25
Moderate summer/fall	Pine Marten Brook	368	0	2	9	36	64	-48	-20	-16	17

Appendix 3 – Supplementary Information for Chapter 4

A3.1 Figures

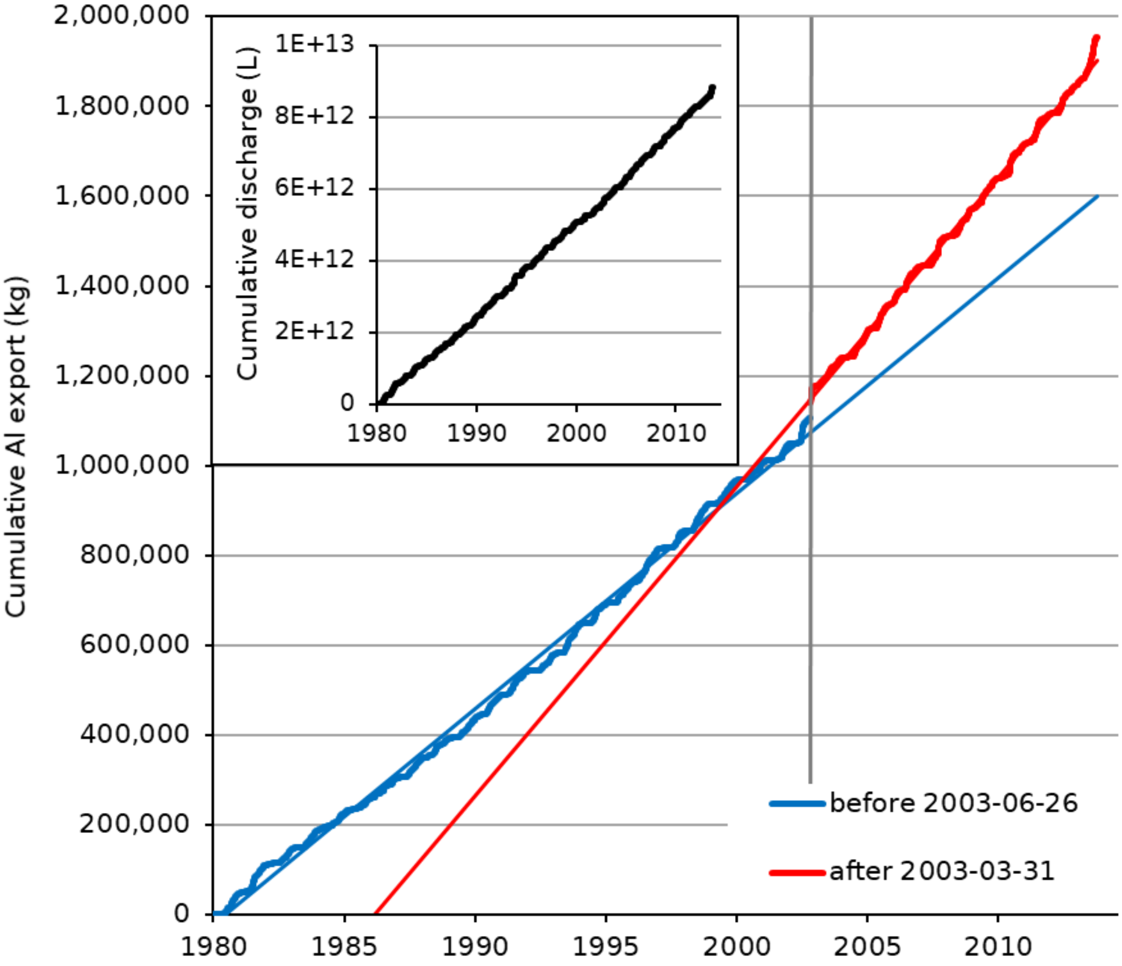

Figure A3.1 Cumulative daily mass exports of Al (main figure) and cumulative daily discharge (inset) in MR between 1980 and 2014. The thin blue line represents average daily cumulative Al export (132 kg day^{-1}) prior to the high-flow event from March 26th to 31st, 2003 (vertical grey line), and the thin red line represents average daily cumulative Al export (189 kg day^{-1}) after the event.

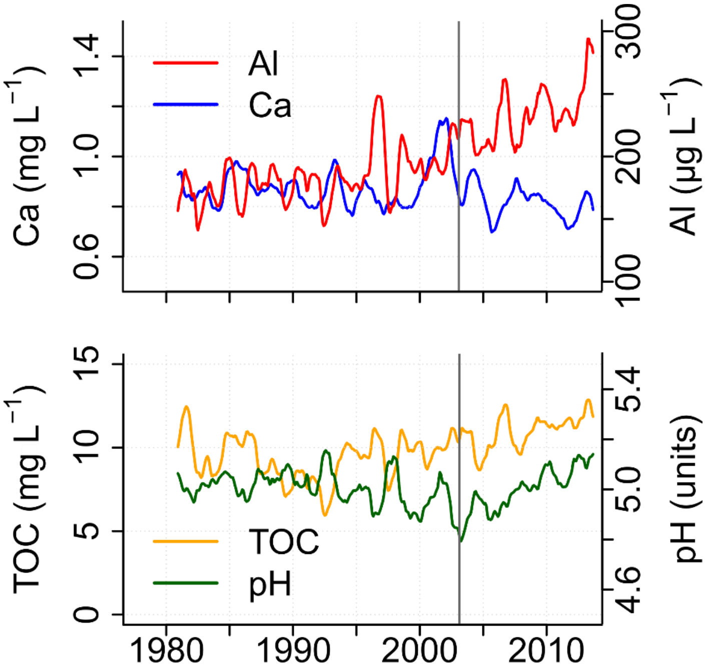

Figure A3.2 Decomposed trends of Al_t*, Ca, TOC, and pH in MR from 1980 to 2014. Vertical gray line indicates the high-flow event from March 26th to 31st, 2003.*

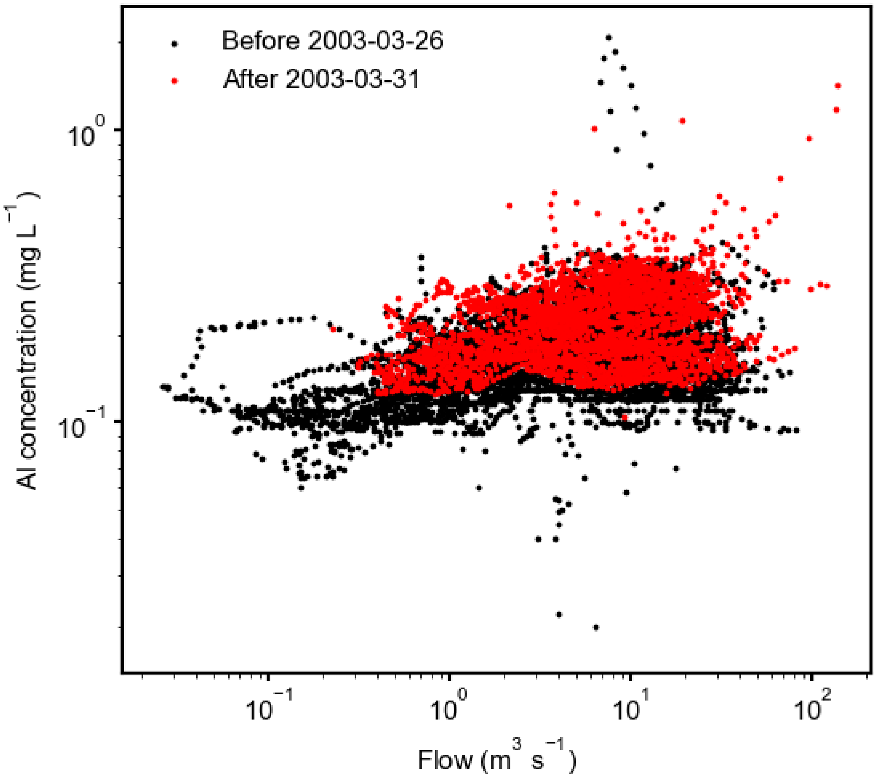

Figure A3.3 Al concentration versus discharge at time of sampling in the MR from 1980 to 2014. Both Al concentration and flow are log transformed. Timeseries is separated into two periods by the high-flow event from March 26th to 31st, 2003.

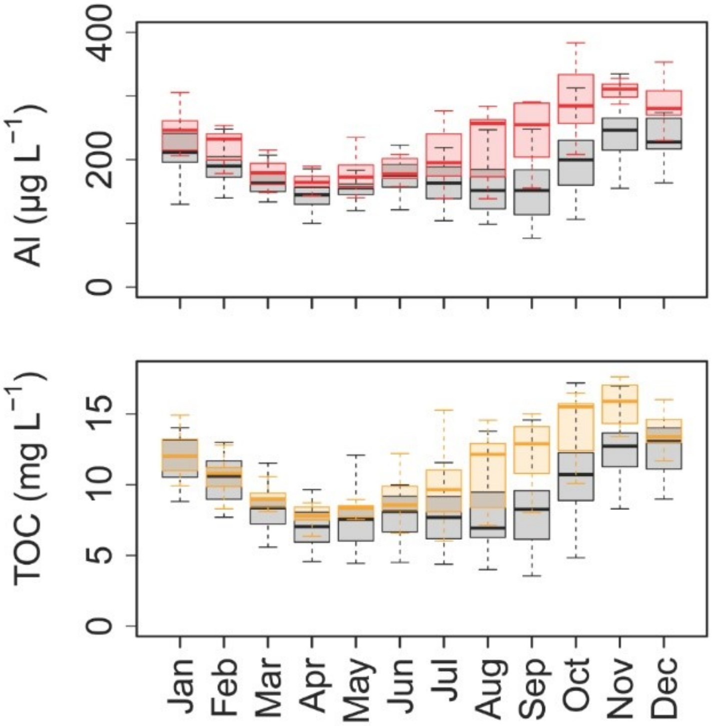

Figure A3.4 Box and whisker plots of monthly average values for Al_t and TOC in MR. Timeseries is separated by the high-flow event from March 26th to 31st, 2003, where grey boxes indicate values prior and coloured boxes indicate values after. Values less than the 25th and greater than the 75th percentiles are not displayed.

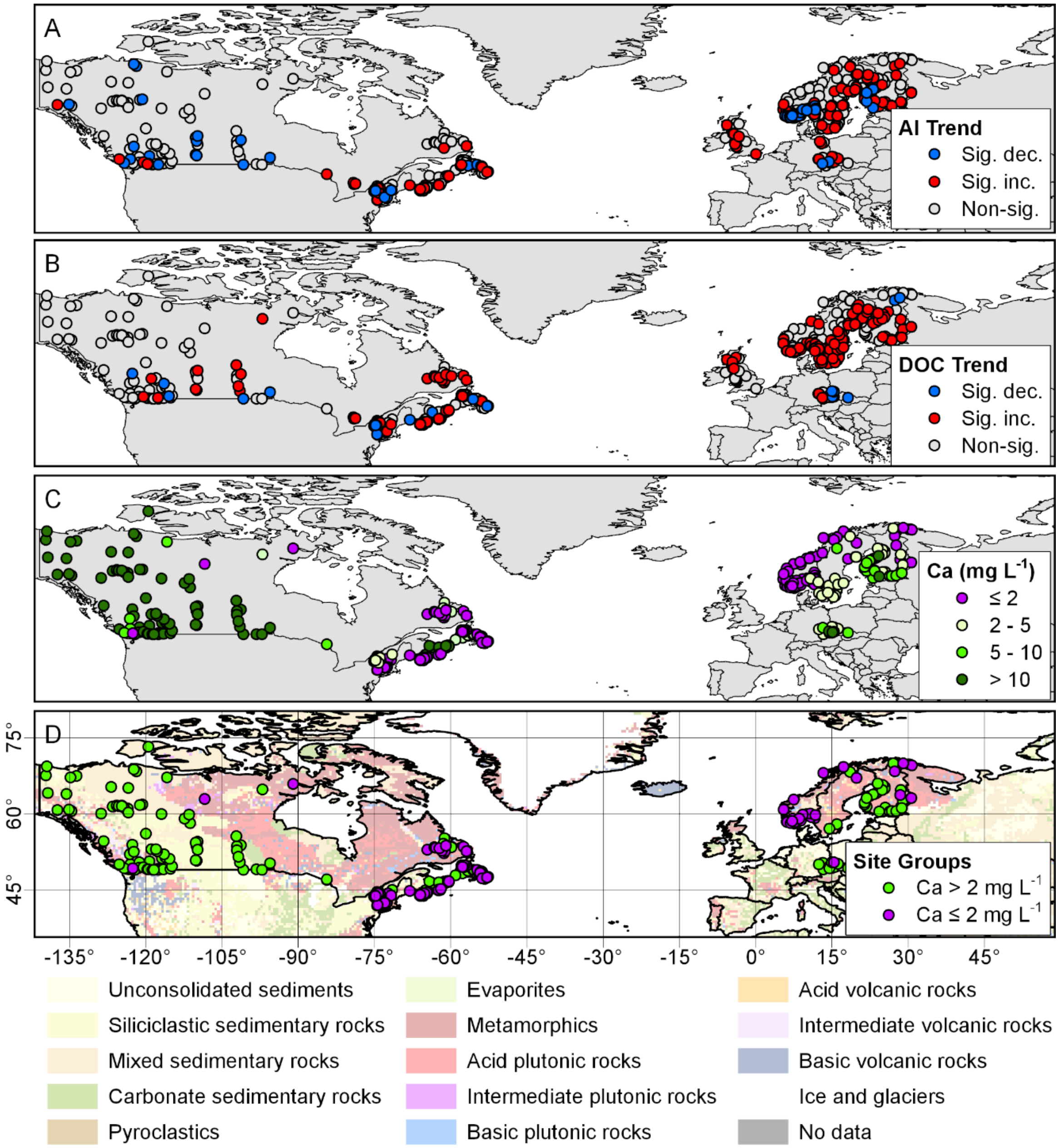

Figure A3.5 Maps of Al trends (A), DOC trends (B), median Ca concentrations (C), and site groups for PLS regression analysis and the underlying geology (D). Sites from the acidification and extended datasets are plotted (please see section 4.4.3 Trend Analysis for details). Statistics calculated between 2000 and 2015. Increasing trends are plotted above decreasing trends and higher Ca concentrations are plotted above lower Ca concentrations; significant trends are plotted above non-significant trends. Significant is abbreviated as sig., increasing as inc., and decreasing as dec. Lithology data from GLiM (Hartmann & Moosdorf, 2012).

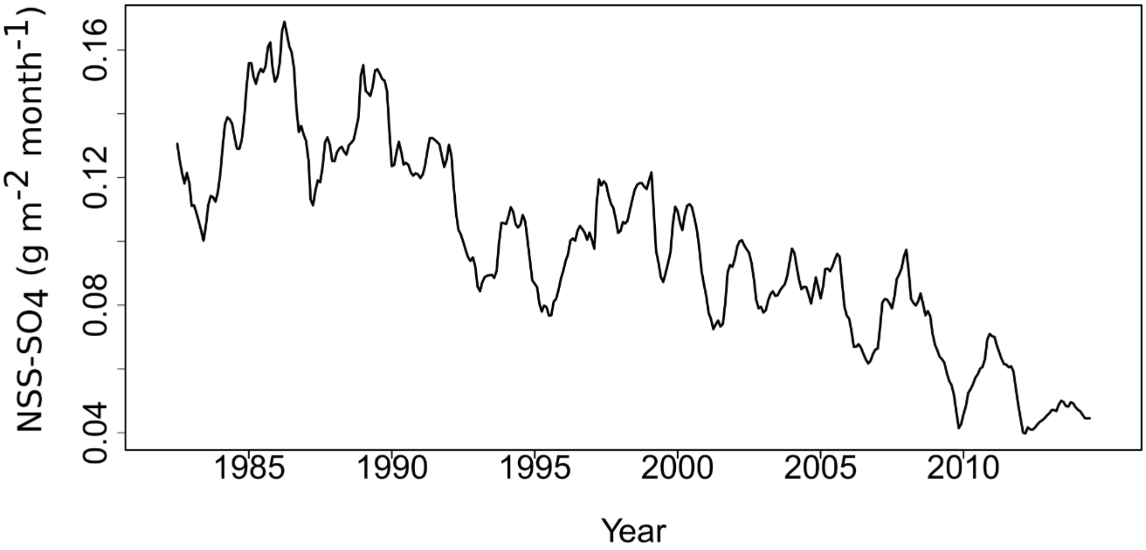

Figure A3.6 Decomposed trend of total wet and dry non-sea salt (NSS) SO_4 deposition from 1980-2014 at the Atlantic Canada Canadian Air and Precipitation Monitoring Network (CAPMoN) station in Kejimujik National Park, Nova Scotia, Canada, located 0.6 km from MR. Deposition rates significantly decreased by $7.9 \cdot 10^{-6}$ g m^{-2} $month^{-1}$ between 1990 and 2014 ($\alpha = 0.05$).

A3.2 Tables

Table A3.1 Potential adverse effects of Al species. Species defined in Table 2. Al_i *is considered equivalent to operationally defined cationic Al (the cation exchange column method of speciating* Al_i *operationally defines it as cationic; thus, able to bind with fish gills). Effects of Al species may be indirect; for example,* Al_t *may be converted to more bioavailable* Al_i *via acid digestion in the stomach (Martin et al., 1987). Table adapted from (Rotteveel & Sterling, 2020) and continued on next page.*

	Al Specie(s)	**Threat**
Humans and Society	Al_t	Potential neurotoxin; may contribute to development of Alzheimer's disease (Parkinsonism dementia), dialysis encephalopathy, and amyotrophic lateral sclerosis (World Health Organization, 2010). May cause conformation changes of Alzheimer's amyloid-beta protein, may cause tau and amyloid-beta protein accumulation, can induce neuronal apoptosis (Kawahara, 2005).
	Al_t	May cause bone disease such as osteoporosis and osteomalacia (D'Haese et al., 1999) by causing development of secondary hyperparathyroidism due to a decrease in osteoblasts (Cannata Andía, 1996). Al exchanges with Ca in bones (Namieśnik & Rabajczyk, 2010).
	Al_t	May cause anemia in dialysis patients due to decreased red blood cell production (Bia et al., 1989). May reduce Fe metabolism (Cannata Andía, 1996).
	Al_t	Increases cost of water treatment (Letterman & Driscoll, 1988).
Birds	Al_t	Poorer regulation of Ca and P (Lacoul et al., 2011).
Terrestrial plants	Al_{poly}/ Al_d	Phytotoxic (Ščančar & Milačič, 2006); reduced wheat root growth, reducing crop success (Parker et al., 1987). Reduced Ca and Mg uptake, reducing root and shoot growth (Rengel, 1992).
	Al_d	Causes retarded growth, root tissue damage, and nutrient deficiencies in trees, reducing forest resilience (Collignon et al., 2012). Reduced nutrient uptake in Norway spruce (de Wit et al., 2010). Reduced root uptake of Ca, reducing growth of red spruce (DeHayes et al., 1999).
Aquatic nutrient cycling	Al_d/Al_i	Reduced freshwater Ca availability due to co-precipitation with sulphato-Al species, reducing nutrient bioavailability (Hindar & Lydersen, 1994).
	Al_d/Al_i	Reduced freshwater P due to co-precipitation with hydroxy-Al and fluoro-Al species, reducing nutrient bioavailability (Driscoll & Schecher, 1990; Kopáček et al., 2001; Scheel et al., 2008).
	Al_d/Al_o	Reduced freshwater DOC due to complexation with Al, reducing nutrient bioavailability, increasing light penetration, and reducing water temperature (Driscoll & Schecher, 1990; Scheel et al., 2008).
Algae	Al_d/Al_i	Reduced acidophilic phytoplankton growth (for example, *Asterionella ralfsii*), reducing resources for higher trophic levels (Gensemer, 1991)
	Al_d	Increased green algae growth and decreased cyanobacteria, and diatom growth (Lacoul et al., 2011).

	Al Specie(s)	Threat
Invertebrates	Al_t/Al_d	Reduced macroinvertebrate species richness (Beneš et al., 2017). Decreased taxa richness in headwater streams, with extirpation of molluscans, crustaceans, and Ephemeroptera (Guerold et al., 2000).
	Al_{poly}	Reduced egg laying and behavioural scores in *Lymnaea stagnalis* snails, reducing survival rates (Papathanasiou et al., 2011).
Amphibians	Al_d	Reduced fertilization success and larval growth, increased offspring mortality and larvae deformities, and increased development time for smooth newt and palmate newt larvae; reduced feeding and mobility for Anuran larvae (Brady & Griffiths, 1995). Reduced Na intake causing toxic Na imbalance, reducing species density and richness (Wyman & Jancola, 1992). Decreased survival of Jefferson salamanders and spotted salamanders (Horne & Dunson, 1995).
Fish	Al_{poly}	Recently-formed Al polymers are highly toxic to fish (Gensemer et al., 2018; Teien et al., 2004).
	$Al_i/$ Al_{poly}	Binding/deposition on gills disrupts: 1) ion transport, 2) osmoregulation, 3) acid-base balance, 4) nitrogen excretion, and 5) respiration (Lacroix, 1999) (Fivelstad et al., 2003; Lacroix, 1989). Increased mucus coating of salmonid gills, reducing brown trout survivorship (Bulger et al., 1993; Hesthagen et al., 2016)
		Reduced at-sea survival for Atlantic salmon (Kroglund et al., 2007; Poléo & Hytterød, 2003). Amplified epithelial hyperplasia, hypertrophied Cl cells, Cl cell necrosis in rainbow trout (Evans et al., 1988).

Table A3.2 Site metadata table. Table contains site names, site types, site locations, data sources, sample analysis methodologies, sample sizes, and statistical analysis results (median, trend, p-value) for Al, Ca, and DOC. This table is available as an electronic supplement to this thesis.

Table A3. 3 Mean water chemistry concentrations and discharge in MR. Standard deviation is noted in brackets. Concentrations are not volume weighted. Timeseries separated by the high-flow event from March 26th to 31st, 2003.

Period	**Discharge (m^3 s^{-1})**	**Al (μg L^{-1})**	**Ca (mg L^{-1})**	**TOC (mg L^{-1})**
1992-2003	7.9 (8.6)	193 (0.1)	0.89 (0.2)	9.4 (3.2)
2003-2014	9.3 (9.9)	225 (0.1)	0.82 (0.2)	10.7 (3.0)

Table A3.4 PLS regression optimization results. Bolded text indicates optimized PLS regression.

Group	**Principle components (n)**	**Coefficients**				**Training**		**Cross-validation**	
		Ca	**OC**	**pH**	**SO_4**	**r^2**	**MSE**	**r^2**	**MSE**
high C_B	1	-19.99	22.23	-2.95	24.70	0.08	9,233	0.03	9,721
	2	-6.76	24.02	-5.82	15.51	0.07	9,325	0.02	9,815
	3	-6.92	19.30	-8.57	5.60	0.06	9,458	0.02	9,862
	1	**-14.21**	**25.35**		**21.23**	**0.08**	**9,260**	**0.03**	**9,702**
	2	-9.03	25.18		7.30	0.06	9,388	0.02	9,797
	1	-7.41	20.67			0.05	9,540	0.01	9,884
low C_B	1	4.81	57.61	-14.22	-2.78	0.57	3,122	0.53	3,467
	2	7.81	55.74	-17.92	-4.33	0.57	3,127	0.53	3,428
	3	-6.60	42.75	-24.87	-2.97	0.51	3,563	0.47	3,850
	1	**7.42**	**56.10**	**-17.36**		**0.57**	**3,141**	**0.53**	**3,403**
	2	-6.60	42.72	-24.86		0.51	3,579	0.48	3,827
	1		45.68	-26.58		0.54	3,391	0.50	3,626

Table A3.5 Trends for Al species: Al_t, Al_d, total monomeric Al, organic monomeric Al, and Al_i. This table is available as an electronic supplement to this thesis.

Table A3.6 Examples of significant Al_i trends reported in the literature.

Study	**Location**	**Date range**	**Al_i trend**	**Al_o trend**	**Al_d or Al_t trend**
Monteith et al., 2014	United Kingdom	1988-2008	decreasing	not reported	not reported
Burns et al., 2006	New York state, USA	1992-2001	decreasing	not reported	not reported
Davies et al., 2005	United Kingdom	1988-2002	decreasing	not reported	not reported
Burns et al., 2008	New York state, USA	1987/1991-2003	decreasing, increasing, and no trend	not reported	not reported
Josephson et al., 2014	New York state, USA	2001-2011	decreasing	not reported	not reported
Hesthagen et al., 2011	Norway	1995-2008	decreasing	not reported	not reported
Evans & Monteith, 2001	United Kingdom	1988-2000	decreasing	increasing	not reported
Krám et al., 2009	Czech Republic	1991-2007	decreasing	increasing	decreasing
Strock et al., 2014	New England, USA	2000-2010		not reported	increasing
Driscoll et al., 2016	Adirondack mountains, USA	1983-2015	decreasing	not reported	not reported
Stoddard et al., 1999	Adirondack mountains, USA	1990-2000	decreasing	not reported	not reported
Malcolm et al., 2014	United Kingdom		decreasing	not reported	not reported

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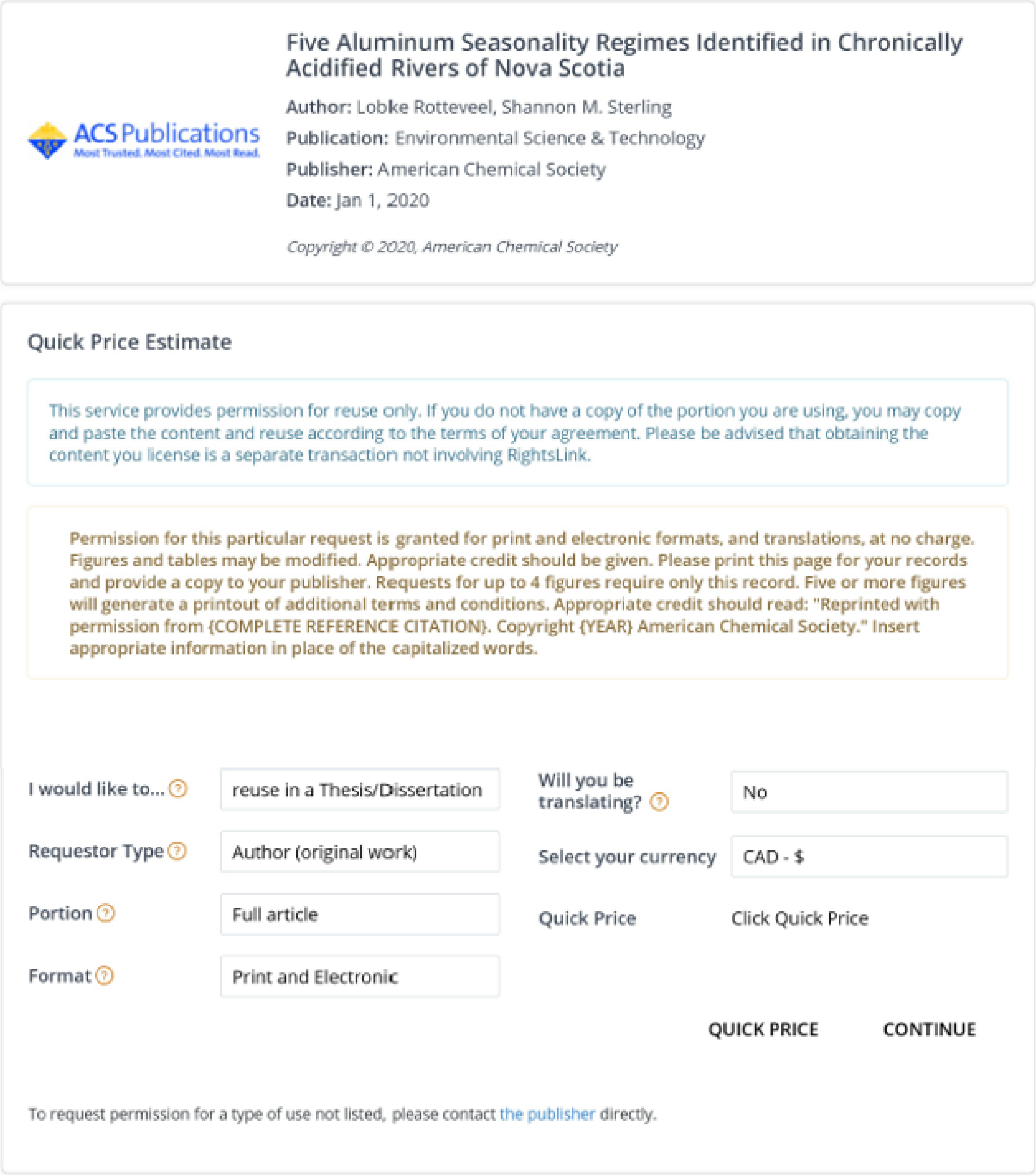

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Publication: Environmental Science & Technology

Publisher: American Chemical Society

Date: Jan 1, 2020

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