Lake Recovery in Nova Scotia:
A Longitudinal Review of Water Chemistry Data

by

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LIST OF ABBREVIATIONS USED

AAS – Atomic Absorption Spectroscopy

ALET - Atlantic Laboratory for Environmental Testing

ANC – Acid Neutralizing Capacity

AU – Arbitrary Units

CAPMon - Canadian Air and Precipitation Monitoring

CCME - Canadian Council of Ministers of the Environment

cps - Counts Per Second

DOC – Dissolved Organic Carbon

EC - Environment Canada

kDa – Kilo Daltons

kg – Kilogram

ha – Hectare

HDPE – High Density Polyethylene

HPLC – High Performance Liquid Chromatography

IC - Ion Chromatography

ICAP-MS - Inductively Coupled Argon Plasma-Mass Spectroscopy

ICP-MS – Inductively Coupled Plasma-Mass Spectroscopy

yr – Year

L – Litre

LRTAP – Long Range Transport of Air Pollutants

NS – Nova Scotia

OC – Organic Carbon

NOM – Natural Organic Matter

SEC – Size Exclusion Chromatography

SIC - Suppressed Ion Chromatography

eq – Equivalents

g – grams

MAGIC - Model of Acidification of Groundwater in Catchments

UV – Ultra Violet

ABSTRACT

Emission control policies aimed at reducing the emission of sulfur oxides have been effective at reducing acid deposition, thereby allowing lakes to recover from acidification (as indicated by decreasing sulfate and increasing pH and alkalinity). In addition to improvements in pH and alkalinity, increasing dissolved organic carbon (DOC) content has also been observed in lakes recovering from acidification.

This work used long-term precipitation and lake water chemistry data from over 50 lakes in Nova Scotia (NS) to assess trends in precipitation and lake water chemistry to evaluate the recovery of NS lakes from acidification. Lakes in NS had some of the lowest recorded pH and alkalinity of lakes in Canada and previous research investigating the recovery of lakes in NS found little improvement in pH or alkalinity but did note increasing DOC concentrations in many of the lakes.

Trend testing revealed that precipitation sulfate decreased by approximately 66% between 1985 and 2016 and that recovery from acidification (decreasing sulfate, increasing alkalinity and pH) has occurred in most of the study lakes. In addition to increasing pH and alkalinity, widespread increases in NOM content (using colour as a proxy) and total phosphorus concentrations were found.

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To Melissa for her constant support. And to Liam who tried his best to keep me from finishing this.

CHAPTER 1 INTRODUCTION

The combustion of fossil fuels results in emissions of oxidized sulfur and nitrogen that react with atmospheric water to form acidic compounds, namely sulfuric acid (H_2SO_4) and nitric acid (HNO_3). These acids are eventually deposited on the surface of the earth (acid deposition) via precipitation (wet deposition) or gravitational settling (dry deposition).

The negative impacts of acid deposition on freshwater ecosystems gained public attention in the 1970s when it became clear that surface water acidification was detrimental to fish populations (Schofield 1976). In response to growing concerns about the damage caused by acid deposition, changes to emission policies in both North America and Europe were passed throughout the 1980s and 1990s. These policy changes greatly reduced sulfate deposition in both continents, and it was expected that this would allow lakes to recover from acidification, with recovery defined as decreasing sulfate concentration and increasing pH and alkalinity (Skjelkvåle et al., 2005; Stoddard et al., 1999).

While precipitation sulfate concentrations did decline in response to emission control policies, the impact of these changes on lake water chemistry were not always as expected. For example, in certain regions, declines in precipitation sulfate were not met with corresponding decreases in lake sulfate concentrations (Stoddard et al., 1999; Skjelkvåle et al., 2005) or improvements in lake acid/base status (Evans et al., 2006; Lawrence et al. 2011; Monteith et al. 2007). Eastern Canada was one of the regions in which changes in precipitation chemistry were not matched with corresponding changes in surface water chemistry. In Nova Scotia (NS), acid deposition and poorly weathering bedrock created conditions where surface waters became some of the most acidified in Canada (Dupont et al., 2005).

Despite substantial reductions in the sulfate concentration of precipitation in the region, little to no improvement in the acid/base status of NS lakes was found even in the late 2000s (Clair et al., 2011). Of particular concern in NS were the high levels of toxic aluminum, associated with acidified waters, that posed risks to salmon populations in the province (Dennis and Clair 2012).

Additionally, it has been discovered that recovery from acidification involved changing water chemistry beyond decreasing sulfate concentrations and increasing pH and alkalinity. In the late 1990s and early 2000s, many researchers began to note increasing levels of natural organic matter (NOM) and more specifically, dissolved organic carbon (DOC), in lakes recovering from acidification across the northern hemisphere (Skjelkvale et al., 2005; Evans et al., 2006; Monteith et al., 2007). These increases in NOM concentrations have been linked to a variety of issues including both increasing (Kopacek et al., 2015) and decreasing (Huser et al., 2018) phosphorus concentrations, increasing primary productivity (Thrane et al., 2014; Seekel et al., 2015a; Seekel et al., 2015b), changes to light regime (Strock et al., 2017), and changes to lake thermal structure (Strock et al., 2017). Furthermore, increased NOM poses a significant problem for water utilities by increasing treatment costs – an issue that has already gained attention in NS (Anderson et al., 2017).

A long-term surface water monitoring program was established in NS in the early 1980s to monitor the effect of emission control policies on acid-sensitive lakes in the province. The most recent research that thoroughly explored changes in NS surface water chemistry was published in 2011, using data up to and including 2007 (Clair et al., 2011). Since that time, further reductions in sulfur oxides emissions have been reported by Environment Canada (Environment and Climate Change Canada, 2017). It remains to be seen whether the additional decade of data will show improvements in lake water chemistry that were expected, but not seen, in previous research.

1.1 Research Objectives

The goal of this research project was to use long term data to assess the changes in precipitation chemistry and to determine how these changes have affected the water chemistry of NS lakes. Recent observations of changes in NS lake water chemistry have been linked to increased treatment costs (Anderson et al., 2017) and similar changes in lake water chemistry have been documented in other parts of the world. A better understanding of changes in NS lake water chemistry may provide insight to the various stakeholders who rely on NS freshwater resources and will allow for more informed decision making. To accomplish the research goal, the following tasks were undertaken:

1. Long-term precipitation chemistry trends were analyzed using data collected at two NS precipitation monitoring stations;
2. Long-term lake water chemistry trends were analyzed using data collected from two NS lake monitoring programs;
3. Relationships between key water chemistry parameters were explored to better understand the changes observed through trend analysis; and
4. Size exclusion chromatography with inductively coupled plasma-mass spectroscopy was used to examine interactions between aluminum, iron, and NOM in samples collected from three of the study lakes.

1.2 Organization of Thesis

This thesis is organized into four chapters.

Chapter 1 provides introductory information regarding the research project and outlines the objectives of the study.

Chapter 2 provides background information and context for this work. A literature review of relevant work outlines the findings of similar research conducted to date.

Chapter 3 outlines the methods used to complete this research and details the data used.

Chapter 4 presents summaries of the water chemistry of the lakes included in the monitoring programs and presents the findings of the trend analysis work and work done to explore interactions between chemical parameters identified by trend analysis.

Chapter 5 presents brief conclusions.

CHAPTER 2 BACKGROUND

2.1 Acid Deposition

Acidic compounds are formed in the atmosphere when strong-oxidizing agents like sulfur- and nitrogen-oxides react with atmospheric water to form sulfuric acid and nitric acid. The subsequent transport of these compounds to the earth through either precipitation or gravitational settling is referred to as wet deposition or dry deposition, respectively (Reuss and Johnson 1986). Sources of oxidized sulfur and nitrogen include both natural and anthropogenic processes, however anthropogenic processes are the largest source (Driscoll et al., 2007). Anthropogenic processes that contribute to emissions of oxidized sulfur and nitrogen include burning of fossil fuels (power generation and transportation) and smelting of metals (Stoddard et al., 2003).

Research on acid deposition began in the mid-1600s when scientists began to study the movement of pollution and its effect on plant life. Throughout the 1700s and 1800s much work was done to analyze both air and rainwater. In several instances, conclusions were drawn regarding the contents of sulfur in rainwater and dew in areas of industrialization. In the mid-1800s, acidity of urban air was linked to discoloration of textiles and corrosion of metals (Smith, 1852). In 1857, the term "acid rain" was coined by Robert Smith in his book *Air and Rain: The Beginnings of a Chemical Climatology* (Smith, 1857), where he detailed the results of his work regarding the effects of farming, coal burning, and environmental factors on precipitation chemistry.

Smith's research garnered very little attention, and the topic of acid deposition was largely forgotten until the mid-1900s when several papers (Gorham, 1955; 1958; 1961) discussing the causes of acidic precipitation and its effect on aquatic ecosystems were published. This work showed that (1) precipitation acidity in industrial areas is largely caused by emissions generated through the combustion of fossil fuels, (2) that acidic precipitation decreases the alkalinity of surface water, and (3) that free acid found in the soil of regions with acidic precipitation is mainly sulfuric acid. It was in the 1970s that the issue gained public attention (Likens et al., 1972), due in part to recognition of the impacts of acidification on fish habitat (Schofield, 1976). This public attention spurred governments to act and resulted in the establishment of both national (United States Clean Air Act, Canada-Wide Acid Rain Strategy for post 2000) and international (1991 Canada-United States Air Quality Agreement) emission control policies aimed at reducing acid deposition.

2.2 Effects of Acid Deposition

The sensitivity of a surface water to acidification is largely dependent on the ability of the surrounding watershed to provide buffering capacity (Charles 1991; Reuss and Johnson 1986; April and Newton 1985; Gorham 1958). This varies greatly from region to region and is determined by surficial geology (April and Newton 1985; Cronan and Schofield 1990). The model of acidification of groundwater in catchments (MAGIC) developed by Cosby et al. (1985) and based on the conceptual acidification model developed by Galloway et al. (1983) has accurately modelled the effects of and subsequent recovery from acidification of many of surface waters (i.e. Ferrier et al., 1995; Jenkins et al., 1998; Cosby et al., 1995; Wright et al., 1998; Cosby et al., 2001; Wright et al., 2005).

The MAGIC model explains acidification of surface water through five main processes that take place in watershed soils in response to acid deposition: (1) sulfate adsorption, (2) soil cation exchange, (3) alkalinity generation through carbonic acid dissociation, and (4) mineral weathering (Cosby et al., 1985). According to the conceptual model, the acidification process begins with the adsorption of deposited sulfate within the soil system. This depends on the soils sulfate adsorption capacity (typically through ligand exchange of sulfate with metal-hydroxides (Nodvin et al., 1986)); once this capacity has been reached, further deposition of sulfate (and associated H^+) results in increased surface water sulfate concentrations. To maintain charge balance, increased surface water sulfate concentrations must be matched by equivalent decreases in anion concentrations (i.e. HCO_3^-) or increases in cation concentrations (H^+, base cations, or aluminum ions). Base cations have less affinity for soil cation exchange sites than do hydrogen ions, so initially, exchangeable base cations will balance the sulfate anions in surface water. Once the pool of exchangeable cations is sufficiently depleted, the hydrogen ion concentration in surface water increases (Cosby et al., 1985), which has implication to metal transport through dissolution.

The response of a lake to acid deposition is largely dependent on both topography and geology. Lakes that rely heavily on precipitation as an input (perched seepage lakes) tend to experience greater decreases in pH, whereas lakes that depend on overland flow (drainage lakes) tend to experience acidification impacts more in line with the MAGIC model: increases in base cations and/or aluminum (Charles, 1991). The role of geology on the response to acid deposition is clear, as the rate of depletion of soil base cations is largely dependent on weathering rates of surficial geology (Reuss and Johnson, 1986; April and Newton, 1985; Cronan and Schofield, 1990; Likens et al., 1996).

2.3 Impacts of Acid Deposition on Biota

Acidification has been linked to numerous ill-effects on both terrestrial and aquatic biota. In terrestrial ecosystems, the depletion of base cations (particularly calcium) from forest soils has been shown to affect forest health (Bernier and Brazeau, 1988; Shortle and Smith 1988; Watmough

2002) and has even been linked to reduced food availability for forest bird species (Hames et al., 2002; Pabian and Brittingham, 2007). In a 2001 review paper, Driscoll et al. (2001) outlined the body of research looking at the impact of soil acidification on red spruce and sugar maple (two species commonly researched in Northeastern North America). Their review found multiple lines of evidence linking calcium depletion and aluminum mobilization to dieback of these two species.

Research on the effects of acid deposition on aquatic biota has largely focused on fish, as declines in fish stocks were noted in several regions of North America (e.g. Watt et al., 1981, 1983, 2000; Bowlby et al., 2013; Dennis and Clair, 2012). As previously discussed, acidification resulted in the mobilization of aluminum from watershed soils. Furthermore, at lower pH, aluminum speciation is dominated by monomeric, ionic aluminum (Figure 2.1) which poses greater risk to fish populations as it readily binds to fish gills and causes respiratory distress (Gensemer and Playle, 1999).

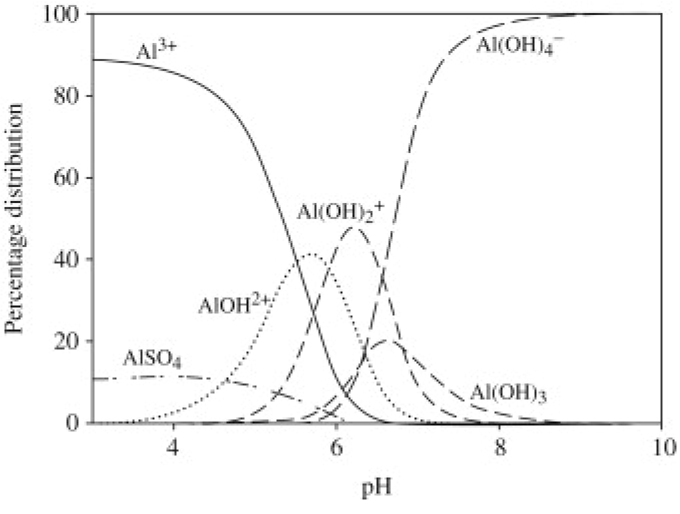

Figure 2.1 - Aluminum speciation in water and sulfate (from Wilson, 2011)

2.4 Emission Control Policies

Changes to emission control policies over the past several decades have been successful in reducing emissions of sulfur dioxide throughout North America and Europe. A large part of the impetus for these policy changes was observations of freshwater acidification and the consequences of freshwater acidification on aquatic biota. Policy changes regarding the emissions of acid producing compounds in North America include The United States Clean Air Act and subsequent Clean Air Act Amendment, the 1991 Canada-United States Air Quality Agreement, and the Canada-Wide Acid Rain Strategy for Post-2000. In addition to these policies, more recent shifts away from the use of high sulfur fuels sources for both energy generation and marine fuels has led to continued reductions in the emission of sulfur oxides. These changes have been evidenced by steady declines in Canadian sulfur oxide emissions since the early 1990s (Figure *2.2*).

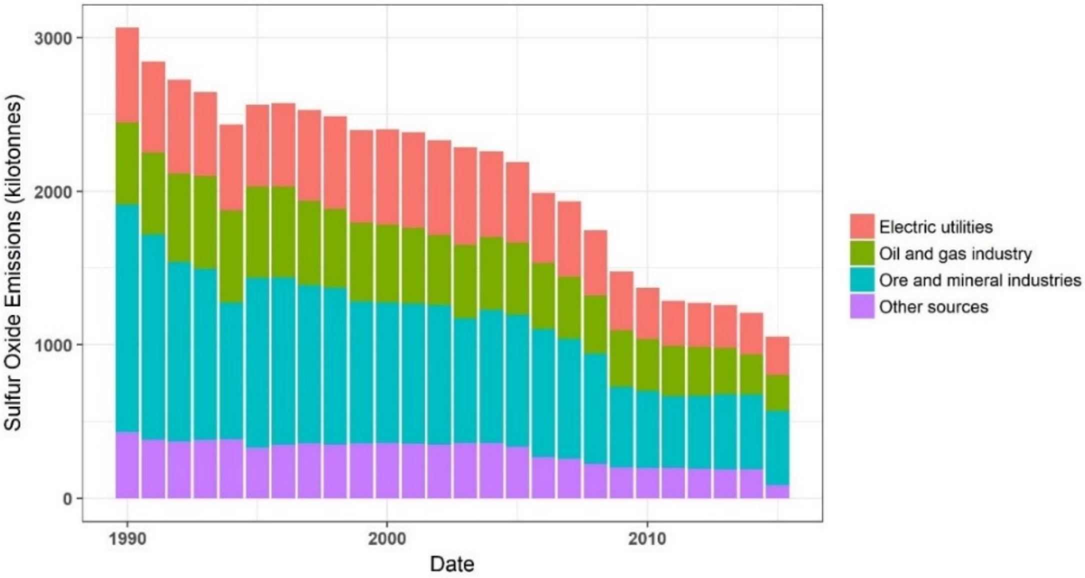

Figure 2.2 - National Sulfur Oxide Emission in Canada by Industry (Data source: Environment and Climate Change Canada, 2017)

2.5 Recovery from Acidification

As implementation of emission policies began, so did monitoring programs aimed at evaluating the efficacy of policy changes. The results of these monitoring programs have highlighted the importance of geology and other regional factors in the recovery of lakes from acidification. Generally, lakes across both North America and Europe responded to reduced acid deposition as predicted by the MAGIC model: lake sulfate concentrations decreased and pH and alkalinity (or ANC) increased (Skjelkvåle et al., 2005; Stoddard et al., 1999). In addition to these predicted changes, increased DOC concentrations were also observed in both Europe and North America (Evans and Monteith 2001; Monteith et al., 2007; Skjelkvåle et al., 2005).

These increases in DOC have slowed recovery of pH and buffering capacity (ANC/alkalinity) in some regions (Evans et al., 2006; Lawrence et al., 2011; Monteith et al., 2007). Long term data (Evans et al., 2006, 2008, Monteith et al., 2007, Driscoll et al., 2007) and experimental studies (Haaland et al., 2010; Ekström et al., 2011; Erlandsson et al., 2008; SanClements et al., 2012) showed that soil OC has become more soluble as a result of reduced acid deposition. This mechanism is explained by the relationship between soil organic matter and soil porewater pH. At lower porewater pH, increased protonation of NOM functional groups and charge neutralization result in less hydrophilic and therefore less soluble NOM (Oulehle et al., 2009; Ekstrom et al., 2011; Tipping et al., 1988). With increased soil porewater pH these effects are reversed, and NOM solubility is increased. The role of NOM in the chemical recovery process is one of weak organic acids replacing the strong mineral acids introduced through sulfate deposition (Evans et al., 2008, Monteith et al., 2014). In this way organic content can be viewed as a buffering mechanism that was depleted by anthropogenic acidification and is now being replenished as sulfate deposition is reduced (Monteith et al., 2014).

2.6 Acidification and Recovery in Nova Scotia

Nova Scotia is a province on the eastern coast of Canada. Being mostly surrounded by waters of the Atlantic Ocean, temperatures in the province are moderated. The 30-year mean daily temperature for the province is approximately 6.5 °C and average yearly rainfall is approximately 1.50 m (Environment Canada, 2018). Geology in the region consists of thin, glaciated soils atop poorly weathering granite and slate bedrock that offers little buffering capacity (Shilts 1981). It is for this reason, as well as high levels of organic acidity (Clair et al., 2007), that lakes in NS are particularly sensitive to acid deposition. Despite relatively low amounts of acid deposition compared to most of North America (Vet et al., 2005), lakes in NS had some of the lowest recorded pH and ANC values in Canada (Dupont et al., 2005; Clair et al., 2007). In a Canadian Acid Deposition Assessment survey of lake acidity, 52% of the survey lakes in NS were found to be acidic (as defined by gran alkalinity ≤ 0 μeqL^{-1}), whereas in Ontario, Quebec, New Brunswick, and Newfoundland less than 13% of lakes were acidic (Dupont et al., 2005).

Reductions in sulfate deposition in NS have been documented (Clair et al., 2011; Anderson et al., 2017; Macleod 2016), but the most recent assessment of long-term lake water chemistry trends (using data from the LRTAP monitoring program) did not find evidence of substantial recovery from acidification (Clair et al., 2011). The issue of freshwater acidification in Eastern Canada gained attention due to declines in Atlantic salmon populations observed in the region. Much of the risk to Atlantic Salmon populations was the result of high ionic aluminum concentrations in NS surface waters (Dennis and Clair, 2012). During the 1980s it was hypothesized that aluminum was not a substantial risk to fish species in NS because the high levels of NOM in NS surface waters complexed aluminum thus rendering it organically-bound and non-toxic. However, Dennis and Clair (2012), using new measurement methods, showed that seven rivers in Southwest NS, continued to have ionic aluminum concentrations at levels considered toxic to aquatic biota (15 μgL^{-1} at pH levels between 5.0 and 6.0). They concluded that the relationship between NOM and aluminum in NS waters may be more complex than in other regions.

CHAPTER 3 MATERIALS AND METHODS

3.1 Precipitation Data

Daily wet deposition data for the period 1985 to 2016 were obtained from Environment Canada. The data were collected by Environment Canada through the Canadian Air and Precipitation Monitoring (CAPMon) program. Two monitoring stations in NS, Kejimkujik (44°26’01“N, 65°12’21”W) and Jackson (45°35’35“N, 63°50’30”W), were used to represent historical deposition across NS. At each monitoring station, daily precipitation was collected in a Type B Rain Gauge. Samples were stored at 4°C until delivery to the CAPMoN laboratory, where ion chromatography and inductively coupled plasma-mass spectrometry were used to measure anions and cations, respectively. Samples were analyzed for precipitation depth, pH, sulfate, chloride, calcium, magnesium, potassium, sodium, nitrate, and ammonium.

3.2 Lake Water Chemistry Data

3.2.1 Lakes with Minimal Anthropogenic Impact

Data provided by Environment Canada (EC) comprised twice yearly sampling, during spring and fall turnover, of 56 lakes monitored through the Long Range Transport of Air Pollutants (LRTAP) monitoring network (Figure 3). This monitoring network was established in the early 1980s to evaluate the effects of acid deposition on NS surface water. The lakes included in the LRTAP monitoring program were selected based on the results of previous lake surveys. Lakes with undisturbed, forested catchments (60-100% of catchment area); low base cation concentrations; and buffering capacity (alkalinity) were chosen as lakes in which the impact of acid deposition would be more pronounced (Clair et al., 2001). The LRTAP lakes are clustered in four areas (Figure 3.1), three of which are in southwestern NS: Yarmouth (n=11), Kejimkujik (n=31), and

Bridgewater (n=7); and one of which is on the eastern shore of Halifax County (n=7).

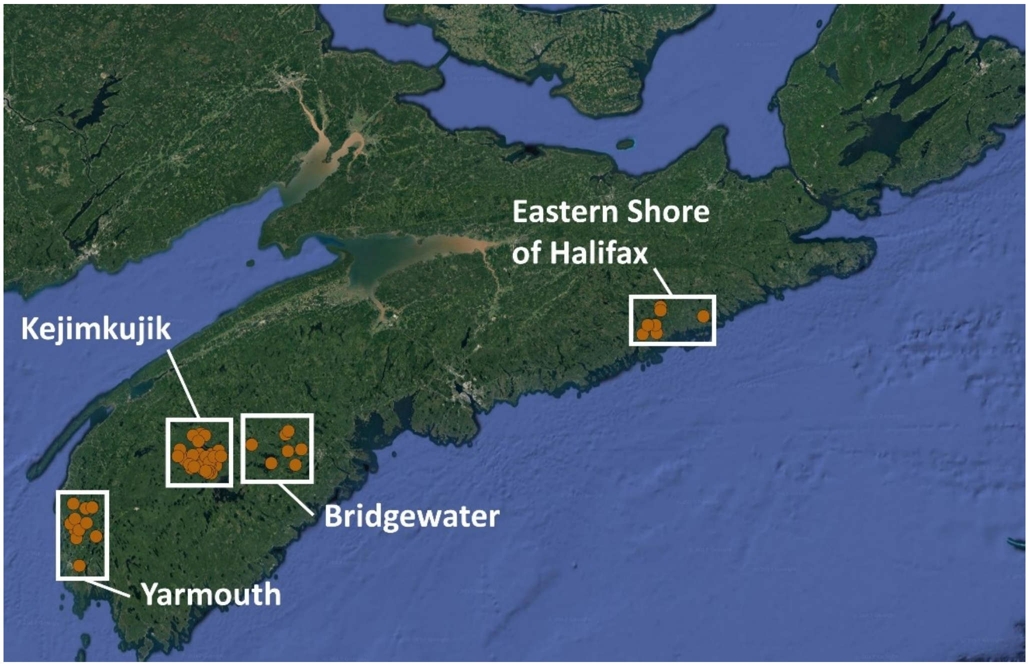

Figure 3.1 – Map of study region showing lakes sampled through the Long Range Transport of Air Pollutants (LRTAP) monitoring program.

Originally, the monitoring program included only the lakes in Yarmouth and Kejimkujik, but additional lakes were added around 1990 to improve spatial coverage (Clair et al., 2001). All the lakes are within 50 km of the ocean, and as such, are influenced by marine aerosols (sea-salt). The lakes are heterogeneous in size, with lake areas ranging from 0.04 to 24.8 km^2, and catchment areas ranging from 0.6 to 756.3 km^2. Retention times range from 0.32 to 168.90 years, with a median retention time of 4.58 years. Detailed information, provided by EC, on lake morphology, geological setting, soil type, vegetative cover, and phyto/zooplankton presence is presented in Table 1, Appendix A.

Samples were collected from helicopter, stored on ice, shipped to Environment Canada's Atlantic Laboratory for Environmental Testing (ALET) in Moncton, New Brunswick, and analyzed for an array of physical and chemical parameters. A detailed description of the sampling program and analytical methodology is provided in Clair et al. (2002). Sampling began with lakes in Yarmouth and Kejimkujik in the 1970s and early 1980s with additional lakes (Bridgewater and eastern shore of Halifax county) added around 1990.

For many of the analytes measured in this monitoring program, multiple changes in analytical methods occurred over the period of record (Table 3-1). Descriptions of analytical methods were provided by Environment Canada and were used to determine comparability of analytical methods. Where it was deemed that methods were not comparable, the analytical method with the most complete data was used for trend testing.

Table 3-1 - Summary of Analytical Methods Used in LRTAP Monitoring Program

Parameter	Method	Years Used
Alkalinity	Potentiometric titration (Gran $CaCO_3$)	1980 to 2016
Aluminum	Flame Atomic Absorption Spectroscopy (AAS) with solvent extraction	1983 to 1999
	Inductively Coupled Argon Plasma-Mass Spectrometer (ICAP-MS) with in bottle nitric acid digestion	1999 to 2007
	ICAP Spectroscopy with in bottle nitric acid digestion	2008 to 2016
Calcium	AAS filtered through 0.45 µm filter and digested in bottle with nitric acid	1983 to 2000
	Suppressed Ion Chromatography (SIC) filtered through 0.45 µm filter and digested in bottle with nitric acid	2001 to 2007
	ICAP extractable with in bottle nitric acid digestion	2008 to 2010
	ICAP with in bottle nitric acid digestion	2011 to 2016
Chloride	Specific ion meter filtered through 0.45 µm filter	1983 to 1985
	Ion Chromatography (IC) filtered through 0.45 µm filter	1986 to 2016
Colour	Automated determination using platinum cobalt standard unfiltered	1980 to 2015
Iron	Flame Atomic Absorption Spectroscopy (AAS) with solvent extraction	1983 to 1999
	Inductively Coupled Argon Plasma-Mass Spectrometer (ICAP-MS) with in bottle nitric acid digestion	1999 to 2007
	ICAP Spectroscopy with in bottle nitric acid digestion	2008 to 2016
Magnesium	AAS filtered through 0.45 µm filter and digested in bottle with nitric acid	1983 to 2000
	Suppressed Ion Chromatography (SIC) filtered through 0.45 µm filter and digested in bottle with nitric acid	2001 to 2007

	ICAP extractable with in bottle nitric acid digestion	2008 to 2010
	ICAP with in bottle nitric acid digestion	2011 to 2016
pH	Electrometric measurement in lab	1980 to 2016
Phosphorus	Colourimetry with ammonium molybdate and $SNCl_2$ boiled for 90 minutes	1983 to 2005
	Colourimetry with ammonium molybdate and $SNCl_2$ autoclaved for 30 minutes	2006 to 2016
Potassium	AAS filtered through 0.45 µm filter and digested in bottle with nitric acid	1983 to 2000
	Suppressed Ion Chromatography (SIC) filtered through 0.45 µm filter and digested in bottle with nitric acid	2001 to 2007
	ICAP extractable with in bottle nitric acid digestion	2008 to 2010
	ICAP with in bottle nitric acid digestion	2011 to 2016
Sodium	AAS filtered through 0.45 µm filter and digested in bottle with nitric acid	1983 to 2000
	Suppressed Ion Chromatography (SIC) filtered through 0.45 µm filter and digested in bottle with nitric acid	2001 to 2007
	ICAP extractable with in bottle nitric acid digestion	2008 to 2010
	ICAP with in bottle nitric acid digestion	2011 to 2016
Sulfate	Ion Chromatography (IC) filtered through 0.45 µm filter	1983 to 2016

3.2.2 Anthropogenically Impacted Lakes

Lake water chemistry data for lakes in King’s County, NS were provided by the King’s County Lake Monitoring program. This monitoring program was started in 1997 over growing concerns about the water quality of these lakes. The sampling was conducted by community volunteers and consisted of one monthly sample from each lake during the summer months. Samples were collected from a boat and consisted of composite samples representing two depths – 0.25 m from the surface and either twice the Secchi depth or 1 m above lake bottom (whichever was shallower).

Samples were analyzed for alkalinity, pH, colour, chlorophyll-a, total phosphorus, total nitrogen, dissolved organic carbon, turbidity, conductivity, phaeophytin, and orthophosphorus. Analyses were performed at the Environmental Science (ES) Lab at the QEII Health Sciences Centre, except for chlorophyll-a and total phosphorus analyses, which were performed at both the ES lab and the New Brunswick Department of Environment Analytical Services (AS) lab. Total phosphorus was originally analyzed at the ES lab but was sent to the AS lab between 2005 and 2011. It was determined that despite improved accuracy obtained through the AS lab, the lower detection limit obtained at the ES lab was more appropriate, so samples were once again analyzed at the ES lab beginning in 2011. Chlorophyll-a analysis was originally analyzed at the ES lab but was switched to the AS lab in 2006. Dalhousie and Stantec (2009) found that the AS lab overestimated chlorophyll-a and therefore recommended analysis again be performed at the ES lab. Analysis was performed at the ES lab from 2009 to 2011 when the ES ceased to offer this analysis. Since 2012, the ES lab has prepared samples for chlorophyll-a analysis and forwarded them to the AS lab. These issues as well as others identified by Dalhousie and Stantec (2009) brought into question the reliability of some of the data generated through this monitoring program. For this reason, only pH and colour data were included in this analysis.

Nine of the monitored lakes were included in the analysis. These lakes are Aylesford, Black River, Gaspereau, George, Hardwood, Little River, Loon, Lumsden, and Murphy. The other lakes were not included because they lacked complete records.

3.3 Statistical Methods

Lake water chemistry trends were evaluated over two different time periods, based on the dates at which lakes were added to the sampling program. The time frame, 1983 to 2016, was the longest period of record available for these data, but only included thirty-eight lakes in Yarmouth and Kejimkujik. The other time frame, 1990 to 2016, is the period over which all the lakes (52) currently included in the program were sampled.

All data analysis was performed using the open source statistical software R (R Core Team 2016). A variety of packages were used in R, including the tidyverse package (Wickham 2017) for data manipulation, GGplot2 for graphics (Wickham 2009), and Performance Analytics (Peterson and Carl, 2018) for the correlation matrix (Figure 4.19) presented in Section 4.9.

Throughout this work, medians were used instead of means as the measure of centrality because the median is resistant to outliers and is better suited to environmental data (Helsel and Hirsch, 2002).

3.3.1 Censored Data

The LRTAP data contained many left-censored (i.e. below detection limit) values. These censored values were replaced with 90% of the reported detection limit. This replacement was done to ensure that censored values were recognized as being less than values reported at the detection limit, for the purposes of trend testing. This replacement did not affect the results of the trend testing because the trend testing method used (see Section 3.3.5) relied on the sign (i.e. negative or positive) of the difference between each pair of data points and did not rely on the absolute value of the difference.

3.3.2 Missing/Unusable Data

Due to missing observations for multiple water chemistry parameters, four lakes were excluded from analysis. Furthermore, due to a change in censoring methods that began in the early 2000s, two additional lakes were excluded from alkalinity trend testing. The detection limit was changed to censor alkalinity values less than zero, and these lakes had negative alkalinity values for the entirety of the time series. Censoring negative data meant that the later data were artificially higher, and made trend testing meaningless. As a result of these exclusions, 52 lakes were used for all parameters except alkalinity, for which 50 lakes were used.

Missing data between 1993 and 2003 precluded phosphorus trend testing. The Wilcoxon rank sum test (Wilcoxon 1945) was used to compare the distribution of phosphorus measurements for each lake before and after this gap in record. This non-parametric approach assumes independence between groups, an assumption that was not met. However, this method has been used to assess similar statistical problems (e.g. Evans et al., 2006; Garmo et al., 2014). The analysis was performed only on lakes for which there was a minimum of five years of data (10 sampling events) both before and after the gap in record.

3.3.3 Sea Salt Corrections

Both lake water and precipitation concentrations of calcium, magnesium, potassium, sodium, and sulfate were corrected to account for the contribution of marine aerosols. Using the ratio of each of these ions to chloride in seawater, the fraction of each ion resulting from marine aerosol was removed as follows,

$$[Ion_{SSC}] = [Ion] - [Cl^{-}] * Ratio$$

Where $[Ion_{SSC}]$ is the sea-salt corrected concentration, and the ratios used for calcium, magnesium, potassium, sodium, and sulfate were 0.021, 0.067, 0.020, 0.556, 0.139 respectively (Watt et al., 1979). When performing sea-salt corrections, a corresponding chloride observation was required for each ion observation. For precipitation data, there were missing chloride values that were imputed by replacing missing values with the monthly chloride mean. Imputation was not required for lake water chemistry data.

3.3.4 Summary Statistics

To provide context and an understanding of the characteristics of the lakes included in these monitoring programs, basic summary statistics (minimum, median, and maximum) were determined for each water chemistry parameter in each of the lakes. The median values calculated for each lake were then used to calculate regional median values for each parameter.

3.3.5 Trend Detection

Trend detection is a commonly employed statistical procedure in environmental data analysis (Helsel and Hirsch, 2002). Non-parametric approaches to trend detection are superior to parametric methods when used for environmental time series data, as this type of data typically contains missing values, censored values, and seasonality, and is serially correlated (Hirsch et al., 1982; Lettenmaier, 1988). For the purposes of this work, a function was created using R to compute the seasonal Mann-Kendall test (SMKT) with variance correction for autocorrelation (Hamed and Rao, 1998). This function was created because existing trend detection software available for R either did not adjust for autocorrelation or was not capable of computing Theil Sen slope estimates with finer resolution than yearly trend. The data used in this work were not collected on the same date each year, so a finer resolution was required. A brief description of the computation is provided below. A copy of the R-code is provided in Appendix B.

The SMKT statistic (S) is computed separately for each season to remove the effect of seasonality. It is computed for the gth season as,

$$S_g = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} Sgn(y_j - y_i)$$

The slope of the trend is then determined using the Theil Sen slope estimator. The Theil Sen slope is calculated by taking the median of the slopes between each pair of points in each season of the time series.

$$M = median \left\{ \sum_{i=1}^{n-1} \sum_{j>i}^{n} \frac{(y_j - y_i)}{(x_j - x_i)} \right\}$$

The intercept of the Theil Sen estimator is calculated as the median of all the intercepts obtained using each data point and the Theil Sen slope M.

It cannot be assumed that the observations in each season are independent of the observations in other seasons; therefore, the variance of the test statistic is the sum of the variance of each individual season, as well as the covariance between seasons,

$$Var(S) = \sum_{g=1}^{m} \sigma_g^2 + \sum_{\substack{g,h \\ g \neq h}} \sigma_{gh}$$

Where σ_g^2 is the variance of the gth season, and $\sigma_{gh}$is the covariance between seasons. When there are no tied values in the series, the variance of each season is given by

$$\sigma_g^2 = \frac{n(n-1)(2n+5)}{18}$$

When ties are present in the series, the variance becomes

$$\sigma_g^2 = \frac{n(n-1)(2n+5) - \sum_{j=1}^{p} t_j(t_j-1)(2t_j+5)}{18}$$

Where p is the number of ties present in the series, and t_j is the size of the j^th^ tied group. Hirsch and Slack (1984) showed that the covariance between season can be estimated as

$$\sigma_{gh} = \frac{\left[K_{gh} + 4\sum_{j=1}^{n} R_{jg}\, R_{jh} - n(n_g+1)(n_h+1)\right]}{3}$$

Where R_j is the rank of the j^th^ observation, and n_g and n_h are the number of observations in seasons g and h respectively. Tied values are assigned the average rank, and missing values are kept in place. K_{gh} describes the correlation between seasons as

$$K_{gh} = \sum_{i=1}^{n-1}\sum_{j=1}^{n} Sgn\left[\left(x_{jg} - x_{ig}\right)\left(x_{jh} - x_{ih}\right)\right]$$

Autocorrelation is inherent in environmental time series due to the persistence of natural systems. The presence of autocorrelation serves to change the effective sample size, as adjacent values in the time series tend to be linearly dependent. Positive autocorrelation reduces the effective sample size, and negative autocorrelation increases it. Several researchers have illustrated the effect of autocorrelation on detection of monotonic trend using non-parametric techniques (Hamed and Rao,1998; Wang et al., 2015; Yue and Wang, 2004). Their work has shown that if autocorrelation is not accounted for, an inflation in the type I error rate occurs. Several methods to account for autocorrelation in the context of trend detection have been proposed. The procedure used here is based on the findings of Hamed and Rao (1998). They proposed that an effective sample size correction be used to adjust the variance of the test statistic S. The procedure that they put forth involves detrending the data using an appropriate non-parametric slope estimator, then calculating the autocorrelation of the ranks of the detrended observations. The variance of S is then adjusted such that

$$Var(S) = \frac{n}{n^*}\sum_{g=1}^{m} \sigma_g^2 + \sum_{\substack{g,h \\ g \neq h}} \sigma_{gh}$$

Where the adjustment for effective sample size is given by

$$\frac{n}{n^*} = 1 + \frac{2}{n(n-1)(n-2)}\sum_{i=1}^{n-1}(n-i)(n-i-1)(n-i-2)\rho_s(i)$$

Where $\rho_s(i)$is the autocorrelation function at lag i, after non-significant autocorrelations (at the chosen significance level) have been replaced by zero.

3.4 Interactions Methods

3.4.1 Sampling Protocol

In September 2017, I collected water samples from three lakes in Yarmouth County - Breton Lake, Corning Lake, and Cedar Lake. Samples were collected in wide mouth high density polyethylene (HDPE) bottles from the shoreline, stored on ice, and shipped to the Dalhousie Water Lab for analysis.

3.4.2 Analytical Methods

The samples were filtered through 0.45 μm cellulose nitrate membranes within 24 hours of sample collection. Sample filtrate was stored at 4°C until subsequent analysis (within 24 hours of filtration). Samples were passed through a high-performance liquid chromatography (HPLC) column with an agarose and dextran stationary phase (Superdex 200, 10 × 300 mm, 13 µm particle size, GE Healthcare) prior to either SEC-UV or ICPMS analysis. The HPLC-SEC-UV system consisted of a vacuum degasser, pump, autosampler with a 200 ml sample loop, and a UV-vis detector (Series 200, Perkin Elmer). The HPLC-ICP-MS system consisted of a vacuum membrane degasser (SCM1000, Thermo Fisher), autosampler (AS3000, Thermo Fisher) with a 1 ml sample loop (Rheodyne), and ICP-MS instrument (X series II, Thermo Fisher). To remove the interference of $^{40}Ar^{16}O$ on determination of ^{56}Fe, a collision cell with 7% H_2 and 93% He was used. Prior to separation on the HPLC column, all samples were passed through a 2 μm pre-column filter.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 LRTAP Lake Water Chemistry

For each LRTAP lake, the median concentration/value of each parameter was calculated over the duration of the monitoring program. These median values were then summarized by region, giving the regional minimum, median, and maximum values (Table 4-1).

Table 4-1 Summary statistics of water chemistry parameters for LRTAP lakes. The median value of each parameter was calculated for each lake. These were used to calculate regional minimums, medians, and maximums for each parameter.

Parameter	Yarmouth			Kejimkujik			Bridgewater			Eastern Shore		
	Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Sulfate	30.2	41.3	50.4	9.7	27.2	38.0	33.2	37.4	77.8	27.5	30.6	33.4
pH	4.8	6.0	6.6	4.3	5.0	6.0	5.3	5.9	6.7	5.1	5.5	6.2
Alkalinity	-4.0	27.1	69.1	-39.0	2.0	38.0	0.6	22.0	61.3	7.7	13.4	20.9
Colour	5.0	20.0	200.0	5.0	67.5	158.5	5.0	9.0	65.0	8.5	36.0	92.0
Calcium	26.1	52.4	80.4	7.1	19.7	45.8	32.9	46.5	69.4	29.9	37.7	51.5
Magnesium	5.6	20.2	34.8	2.1	5.9	22.3	9.2	18.0	29.0	8.2	8.8	11.4
Iron	19.8	65.0	680.0	20.0	140.0	300.0	20.0	120.0	395.0	29.5	190.0	395.0
Aluminum	29.6	73.5	340.0	30.0	159.8	280.0	9.9	43.5	100.0	31.1	142.6	222.5
Phosphorus	4.0	5.0	20.0	4.0	9.0	13.0	3.0	6.0	17.0	4.0	8.0	10.0

4.1.1 Sulfate

The highest sulfate concentrations were found in the LRTAP lakes in Yarmouth and Bridgewater. The lowest median sulfate concentration was found in a lake in Kejimkujik. Given the west to east reductions in sulfate concentrations (see precipitation sulfate results Section 4.4.1) and the proximity of Kejimkujik lakes to Yarmouth lakes, it was expected that sulfate concentrations would be similar in the two regions. A possible explanation for this difference could be regional soil sulfate adsorption capacity which is related to soil composition and native sulfate concentrations (Harrison et al., 1989).

The relatively small range of sulfate concentrations in lakes in the eastern shore of Halifax County was also likely the result of the west to east reduction in sulfate concentrations. The maximum concentrations observed in these lakes were similar in magnitude to the median concentrations observed in lakes in the other three regions.

In all four regions, the highest concentrations were observed earlier in the monitoring program (i.e. early- to mid-1980s in Yarmouth and Kejimkujik and early- to mid-1990s in Bridgewater and the Eastern Shore of Halifax County).

4.1.2 pH

The CCME guidelines for the protection of freshwater aquatic life specify a pH range of 6.5 to 9.0 to ensure ecological health (CCME 2018). Most of the LRTAP lakes have pH values below this range. The lowest pH values were observed in Kejimkujik lakes. These lakes are known to be influenced by high levels of organic acidity (Clair et al., 2007). The minimum, median, and maximum pH values observed in the Kejimkujik lakes were lower than those in the other three regions. The greatest range in pH measurements was found in Yarmouth lakes, where there were two lakes with relatively low median pH values (<5.0) and the remaining lakes had median pH values of approximately 6.0.

In all four regions, the maximum pH values were generally observed later in the monitoring period, typically post-2005, and the lowest pH measurements were observed earlier in the monitoring period (i.e. early- to mid-1980s in Yarmouth and Kejimkujik and early- to mid-1990s in Bridgewater and the Eastern Shore of Halifax County). In all four regions there were several lakes where the lowest pH observations were made around the year 2000. In most of the LRTAP lakes there appears to have been a period of low pH observations around this time. The cause of this period of low pH is unknown, however, this period does not correspond to a change in analytical methods.

4.1.3 Alkalinity

Lakes in NS are known to have poor buffering capacity due to poorly weathering bedrock (Shilts 1981) and this was reflected in the low median alkalinity values found for most of the LRTAP lakes. It was particularly apparent in Kejimkujik and Yarmouth where several lakes had median alkalinity values less than zero (***Table 4-1***). Alkalinity, as measured by Gran titration, reflects the balance of hydrogen ions to dissolved carbon dioxide, so the negative alkalinity values indicate an excess ratio of hydrogen ion to carbon dioxide (Wilde 2005).

The low regional median alkalinity found in Kejimkujik lakes was likely due to differences in regional geology and the influence of organic acidity in that region (Clair et al., 2007). In most of the LRTAP lakes, the lowest alkalinity values tended to be near the beginning of the monitoring period, but as was observed with pH, there was a period of low alkalinity in many of the lakes around the year 2000. Again, this period did not correspond to a change in analytical methods.

4.1.4 Colour

There were substantial differences between colour content of lakes in the four regions (***Table 4-1***). Lakes in Bridgewater had the lowest colour and the smallest range of colour. Most of the lakes in that region had median colour below 25 ACU, whereas most lakes in the other three regions had median colour greater than 50 ACU and had multiple lakes with colour greater than 100 ACU. In Bridgewater, there were two lakes with high colour (>100 ACU), but the remainder of lakes in that region had colour below 35 ACU. As was observed for pH and alkalinity, the lowest colour measurement were generally observed early in the monitoring program and the maximum colour was typically observed post-2000.

4.1.5 Calcium and Magnesium

Calcium and magnesium concentrations were of interest in this work because weathering processes exchange hydrogen ions for base cations in catchment soil, meaning that the increased input of hydrogen ions from acid deposition caused greater release of base cations (Reuss & Johnson, 1986). In the LRTAP lakes, calcium and magnesium concentrations were lowest in the Kejimkujik but were similar in magnitude in the other three regions (***Table 4-1***). In Yarmouth, Kejimkujik, and Bridgewater, the lowest concentrations were generally observed later in the monitoring period, and the maximum concentrations were generally earlier in the monitoring period. This was not the case in the eastern shore of Halifax county, where concentrations were relatively steady throughout the monitoring period.

4.1.6 Aluminum

The CCME freshwater aquatic life guidelines for the protection of ecological health specifies a maximum concentration of total aluminum of 5 μgL^{-1} in surface water with pH less than 6.5 (CCME 2018). Additionally, the European Inland Fisheries Advisory Commission advises that concentrations of ionic aluminum greater than 15 μgL^{-1} (for pH between 5.0 and 6.0) are toxic to aquatic biota (Howells et al., 1990). In the LRTAP lakes, median total aluminum concentrations ranged from 9.9 to 340.0 μgL^{-1} and regional median concentrations were all substantially higher than these guidelines (***Table 4-1***).

In most of the lakes, the highest aluminum concentrations were observed in the latter part of the monitoring program. High aluminum concentrations in both Yarmouth and Kejimkujik were consistent with previous finding of high aluminum concentrations in southwestern NS (Dennis and Clair 2008; MacLeod 2016). No information regarding aluminum speciation in these lakes was available, but recent work has showed that in southwest NS rivers, ionic aluminum concentrations exceed the level toxic (15 μgL^{-1} at pH between 5.0 and 6.0) considered to aquatic biota (Dennis and Clair, 2012).

4.1.7 Phosphorus

The CCME uses a total phosphorus concentration of 10 μgL^{-1} as a “trigger range” to distinguish between oligotrophic (total phosphorus < 10 μgL^{-1}) and mesotrophic (total phosphorus between 10 and 35 μgL^{-1}) lakes (CCME 2004). Median phosphorus concentrations in the LRTAP lakes ranged from 3.0 to 20.0 μgL^{-1} with regional medians of 5.0, 9.0, 6.0, and 8.0 μgL^{-1} in Yarmouth, Kejimkujik, Bridgewater, and the eastern shore of Halifax county, respectively, which indicated that most of the lakes in the monitoring program were oligotrophic. The greatest total phosphorus concentrations were generally observed in the latter part of the monitoring program.

4.2 King’s County Lake Water Chemistry

For each of the nine King’s County lakes, the median pH and colour were calculated over the duration of the monitoring program. These median values were then summarized giving the regional minimum, median, and maximum values (Table 4-2).

Table 4-2 Summary Statistics of Water Chemistry Parameters for King's County Lakes.

	Min	Median	Max
Colour	25.0	41.7	50.9
pH	6.2	6.3	6.7

The median pH values for most of the King’s County lakes were just below the minimum pH of 6.5 specified by the CCME guideline for the protection of freshwater aquatic life (CCME 2018) and colour was relatively consistent across the nine lakes. The relatively small variation in pH and colour of these lakes was likely the result of the close proximity of the lakes and therefore the similar geological setting.

4.3 Summary of Lake Water Chemistry

LRTAP lakes encompassed a range of lake water chemistry, but generally, were oligotrophic with relatively low pH, and little buffering capacity. Lakes in Kejimkujik stood out as being low alkalinity lakes, with low base cation concentrations, low pH, and high colour. Also of note, were the high aluminum concentrations in Kejimkujik lakes, a feature of surface water in southwestern NS that has received much attention (Dennis and Clair 2012; Clair et al., 2007; Clair et al., 2011; MacLeod, 2016). Given the limited data available for the King’s County lakes, it was difficult to compare these lakes to the LRTAP lakes, but the pH and colour of the King’s County lakes was most similar to that of lakes in Yarmouth and Bridgewater.

4.4 Precipitation Chemistry Trends

The correlated seasonal Mann-Kendall trend test (Hamed and Rao 1998) was used to identify statistically significant trends ($p < 0.05$) in precipitation. Where statistically significant trends were identified, Sen's slope estimator (Sen 1968) was used to calculate the magnitude of the trend. Trend magnitudes are presented in units of $\mu eqL^{-1}yr^{-1}$ for all chemical parameters, except pH (pH units yr^{-1}), and sulfate and nitrate annual yields (kg $Ha^{-1}yr^{-1}$).

4.4.1 Non-Marine Sulfate

Annual wet deposition of non-marine sulfate decreased at both Jackson and Kejimkujik precipitation monitoring stations since the early 1980s with overall reductions of approximately 66%. (Figure 4.1). Sulfate deposition tended to be lower in Jackson than in Kejimkujik. This west to east reduction in NS precipitation sulfate was observed previously and was attributed to sources of acid deposition in NS being of westerly origin (Clair et al., 2011). The rates of change of annual precipitation sulfate yield for Kejimkujik and Jackson were -0.29 kg $ha^{-1}yr^{-1}$ and -0.25 kg $ha^{-1}yr^{-1}$, respectively between 1983 and 2016. Declines in annual sulfate deposition have been relatively steady since the 1980s (Figure 4.1).

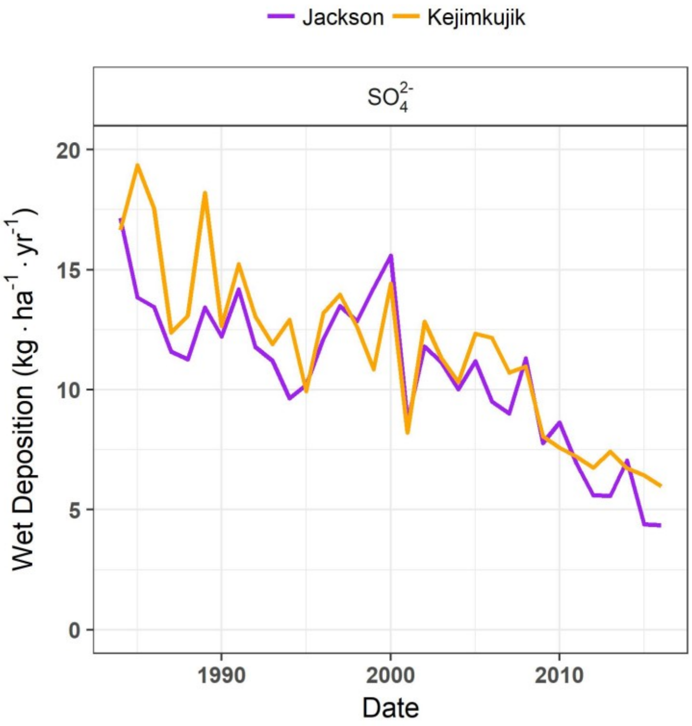

Figure 4.1 - Annual wet deposition of sulfate at Jackson and Kejimkujik weather monitoring stations.

The contribution of sulfate that is of anthropogenic origin (as opposed to marine origin) also decreased at both sites (Figure 4.2). In 1985 over 95% of precipitation sulfate was of anthropogenic origin, whereas after 2010 the proportion of anthropogenic input was nearing 85% and has continued to decline since. These changes were the intended result of national and international emission control policies (see section 2.4) and similar reductions in precipitation sulfate have been observed across North America (Stoddard et al., 1999, 2003; Kahl et al., 2004).

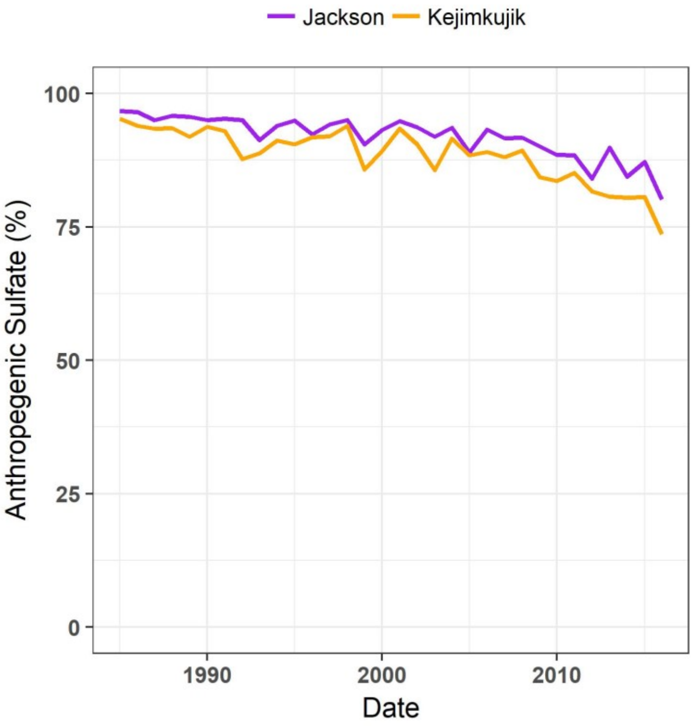

Figure 4.2 - Proportion of precipitation sulfate derived from anthropogenic origins, expressed as a percentage of total sulfate.

4.4.2 Nitrate

Annual wet deposition of nitrate at both Jackson and Kejimkujik precipitation monitoring stations decreased since the early 1980s with overall reductions of approximately 55%. (Figure 4.3). Nitrate deposition tended to be lower in Jackson than in Kejimkujik as was the case for sulfate deposition. The rates of change of precipitation nitrate yield for Kejimkujik and Jackson were -0.13 kg ha^{-1}yr^{-1} and -0.11 kg ha^{-1}yr^{-1}, respectively. Annual nitrate deposition was relatively steady until around 2000, at which point declines became more pronounced. Canadian national nitrogen oxides emissions peaked in 1999 and have declined steadily since. Declines have been largely due to reductions in emissions generated by the transportation and energy production sectors (Environment and Climate Change Canada 2017).

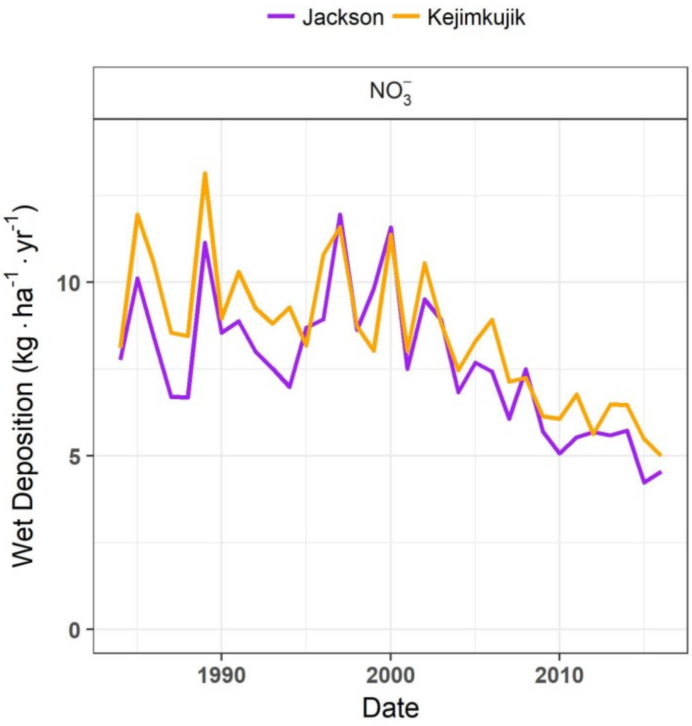

Figure 4.3 - Annual wet deposition of nitrate at Jackson and Kejimkujik weather monitoring stations.

4.4.3 Chloride

No chloride trends were detected at either monitoring station. Chloride is of interest as it has been shown to cause episodic acidification of surface water through the replacement of hydrogen and aluminum ions in soil cation exchange sites with base cations derived from marine aerosols (Wright et al., 1988).

4.4.4 pH

Precipitation pH increased at both Jackson and Kejimkujik (Figure 4.4) with a trend magnitude of 0.014 pH units yr^{-1} at both sites. This equated to an overall change in pH from approximately 4.5 in 1985 to approximately 5.0 in 2016. Precipitation pH was lower in Kejimkujik than in Jackson, which is consistent with the higher precipitation sulfate content observed at Kejimkujik and its proximity to emission sources (Clair et al., 2011). Changes in precipitation pH were minimal until around 2000, at which point pH began to increase more rapidly. Earlier analysis of NS precipitation pH found no statistically significant trends between 1985 and 1997 (Clair et al., 2001).

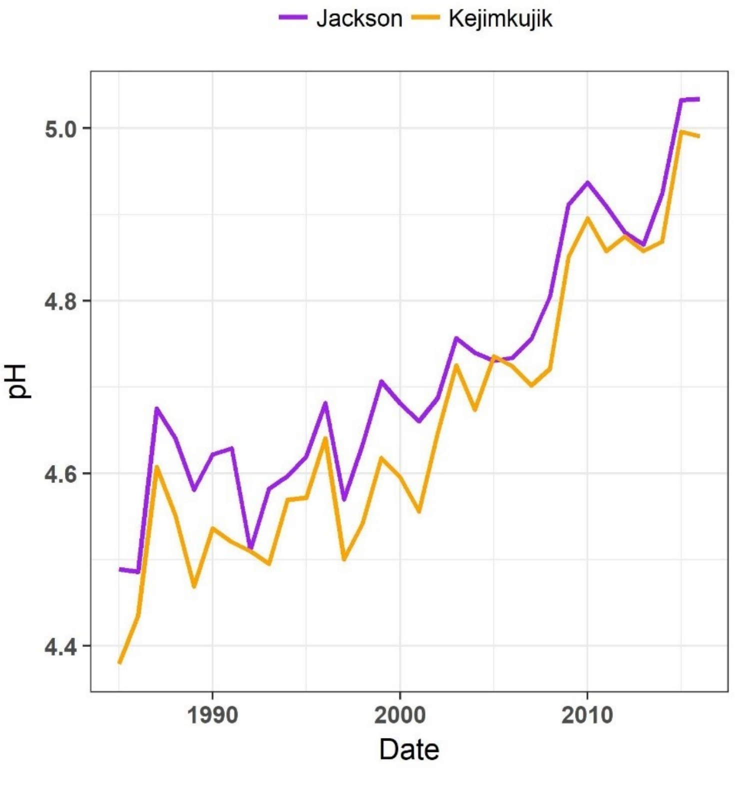

Figure 4.4 - Median annual precipitation pH at Jackson and Kejimkujik weather stations.

4.4.5 Base Cations

No statistically significant trends in precipitation base cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) concentrations were detected at the Kejimkujik monitoring station. At the Jackson monitoring station, a statistically significant increasing potassium trend was found. The magnitude of this trend was 0.006 μeqL^{-1}yr^{-1}.

4.4.6 Summary of Trends in Precipitation Chemistry

At both the Jackson and Kejimkujik precipitation monitoring stations, substantial changes in precipitation chemistry occurred between 1985 and 2016. Sulfate concentrations in 2016 were less than half of what they were in 1985 and there was a marked decrease in sulfate of anthropogenic origin. Reductions in precipitation nitrate were not as substantial as those of sulfate, and did not begin until around 2000s but again, concentrations in 2016 were nearly half of what they were in the early 1980s. These reductions in precipitation sulfate and nitrate concentrations were accompanied by increases in precipitation pH. Between 1985 and 2016, precipitation pH at each of the monitoring stations rose from 4.5 to 5.0.

4.5 Lake Water Chemistry Trends

The correlated seasonal Mann-Kendall trend test (Hamed and Rao 1998) was used to identify statistically significant trends ($p < 0.05$) in water chemistry parameters. Where statistically significant trends were identified, Sen's slope estimator (Sen 1968) was used to calculate the magnitude of the trend. Trend magnitudes are presented in units of μeqL^{-1}yr^{-1} for all chemical parameters, except pH (pH units yr^{-1}), colour (ACU yr^{-1}), iron (μgL^{-1}yr^{-1-}), and aluminum (μgL^{-1}yr^{-1}).

4.6 LRTAP Lakes

When the LRTAP lake monitoring program was established, the lakes included in the program were chosen based on being lake with "minimal anthropogenic impact". This was defined as lakes with undisturbed, forested catchments in which forest area accounted for 60-100% of total catchment area (Clair et al., 2001). The proportion of lakes within each region with increasing or decreasing trends (Table 4-3) and the regional median trend magnitudes (***Table 4-4***) were calculated for sulfate, pH, alkalinity, colour, calcium, magnesium, iron, and aluminum.

Statistically significant trends ($p < 0.05$) identified in both precipitation and lake water chemistry using the correlated seasonal Mann-Kendall trend test (Hamed and Rao 1998) are presented along with trend magnitudes, calculated using Sen's slope estimator (Sen 1968). Trend magnitudes are presented in units of μeqL^{-1}yr^{-1} for all chemical parameters, except pH (pH units yr^{-1}), colour (ACU yr^{-1}), iron (μgL^{-1}yr^{-1-}), and aluminum (μgL^{-1}yr^{-1-}).

Table 4-3 - Proportion of lakes with statistically significant ($p<0.05$) trends. In Kejimkujik, 27 lakes had complete records for the parameters shown (except alkalinity where 25 lakes had complete records*).

Parameter	1983 to 2016				1990 to 2016							
	Yarmouth (n=11)		Kejimkujik (n=27) *		Yarmouth (n=11)		Kejimkujik (n=27) *		Bridgewater (n=7)		Eastern Shore (n=7)	
	Increasing (%)	Decreasing (%)	Increasing (%)	Decreasing (%)	Increasing (%)	Decreasing (%)	Increasing (%)	Decreasing (%)	Increasing (%)	Decreasing (%)	Increasing (%)	Decreasing (%)
Sulfate	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0
pH	63.6	0.0	37.0	0.0	63.6	0.0	37.0	0.0	100.0	0.0	28.6	0.0
Alkalinity	63.6	0.0	36.0	0.0	54.5	0.0	52.0	0.0	85.7	0.0	28.6	0.0
Colour	81.8	0.0	85.2	0.0	72.7	0.0	88.9	0.0	85.7	0.0	28.6	0.0
Calcium	0.0	72.7	3.7	85.2	9.1	27.3	3.7	33.3	14.3	14.3	14.3	0.0
Magnesium	0.0	72.7	0.0	96.3	0.0	45.5	0.0	85.2	0.0	57.1	0.0	71.4
Iron	36.4	0.0	37.0	0.0	27.3	0.0	51.9	0.0	28.6	0.0	28.6	14.3
Aluminum	54.5	0.0	51.9	0.0	36.3	0.0	48.1	0.0	0.0	14.3	0.0	0.0
Phosphorus												

Table 4-4 - Magnitude of regional trends for each parameter, computed as the median of statistically significant ($p<0.05$) trends in each region for each of the two time-frames (* signifies n=1).

Parameter	Units	1983 to 2016		1990 to 2016			
		Yarmouth	Kejimkujik	Yarmouth	Kejimkujik	Bridgewater	Eastern Shore
Sulfate	$\mu eqL^{-1}yr^{-1}$	-1.36	-0.89	-1.56	-1.05	-1.53	-0.63
pH	units yr^{-1}	0.009	0.010	0.013	0.014	0.021	0.012
Alkalinity	$\mu eqL^{-1}yr^{-1}$	0.62	0.46	1.03	0.56	0.93	0.56
Colour	ACU yr^{-1}	0.58	0.95	0.87	1.61	0.35	1.06
Calcium	$\mu eqL^{-1}yr^{-1}$	-0.39	-0.15	-0.29	-0.15	-0.20	0.23*
Magnesium	$\mu eqL^{-1}yr^{-1}$	-0.25	-0.23	-0.32	-0.22	-0.67	-0.24
Iron	mg L^{-1} yr^{-1}	1.27	1.39	2.51	2.50	5.60	1.99
Aluminum	mg L^{-1} yr^{-1}	0.77	1.05	1.33	1.44	-0.21	

4.6.1 Non-Marine Sulfate

Non-marine sulfate concentrations decreased in all LRTAP lakes between 1990 and 2016 (Table ***4-3***) with trend magnitudes ranging from -2.84 μeqL^{-1}yr^{-1} to -0.55 μeqL^{-1}yr^{-1} (Figure 4.5). A gradient of lake sulfate concentration and magnitude of sulfate trends was apparent; lakes in southwestern NS had higher sulfate concentrations and generally experienced greater reductions in sulfate concentration than lakes on the eastern shore of Halifax county.

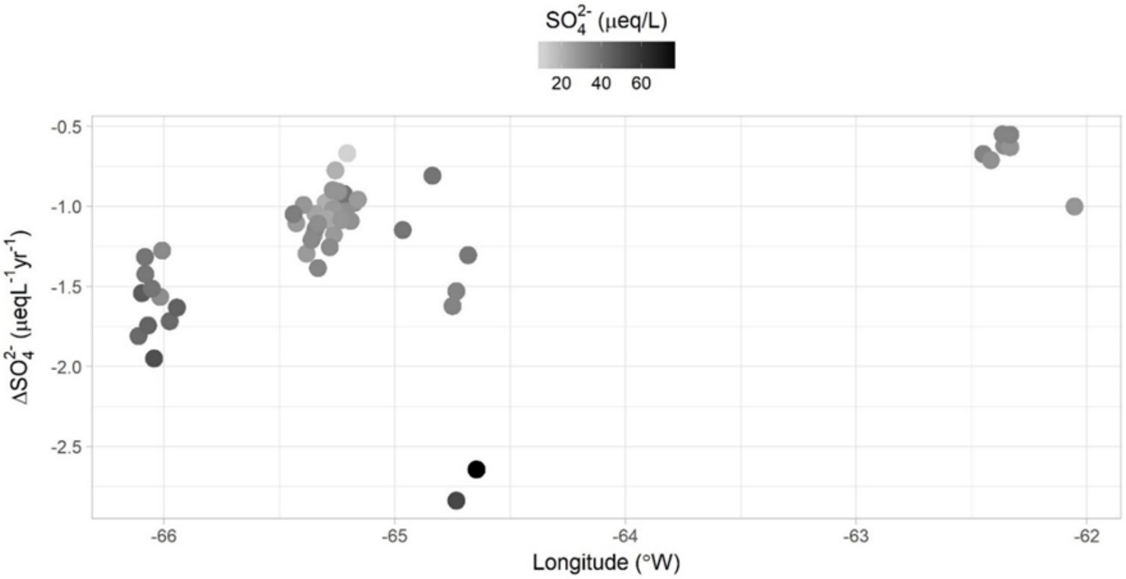

Figure 4.5- Magnitudes of sulfate trends in LRTAP lakes plotted against longitude to show spatial variation. Median lake sulfate concentration is indicated by shading of points.

These differences were likely due to the proximity of lakes in southwestern NS to major sources of atmospheric sulfate which caused lakes in southwestern NS to receive higher rates of acid deposition (Clair et al., 2011). As discussed previously (Section 4.1.1), the maximum sulfate concentrations observed in lakes in the eastern shore of Halifax county were similar in magnitude to the median concentrations observed in lakes in the other three regions. There were, however, two lakes in Bridgewater (Little Wiles Lake and Rocky Lake) where the greatest reductions in lake sulfate concentration were observed; these lakes also had some of the highest median sulfate concentrations (>50 μeqL^{-1}) of all the LRTAP lakes. This relationship between sulfate concentration and trend magnitude was true for most LRTAP lakes; lakes with greater median sulfate concentrations generally experienced greater rates of decline (Figure 4.6).

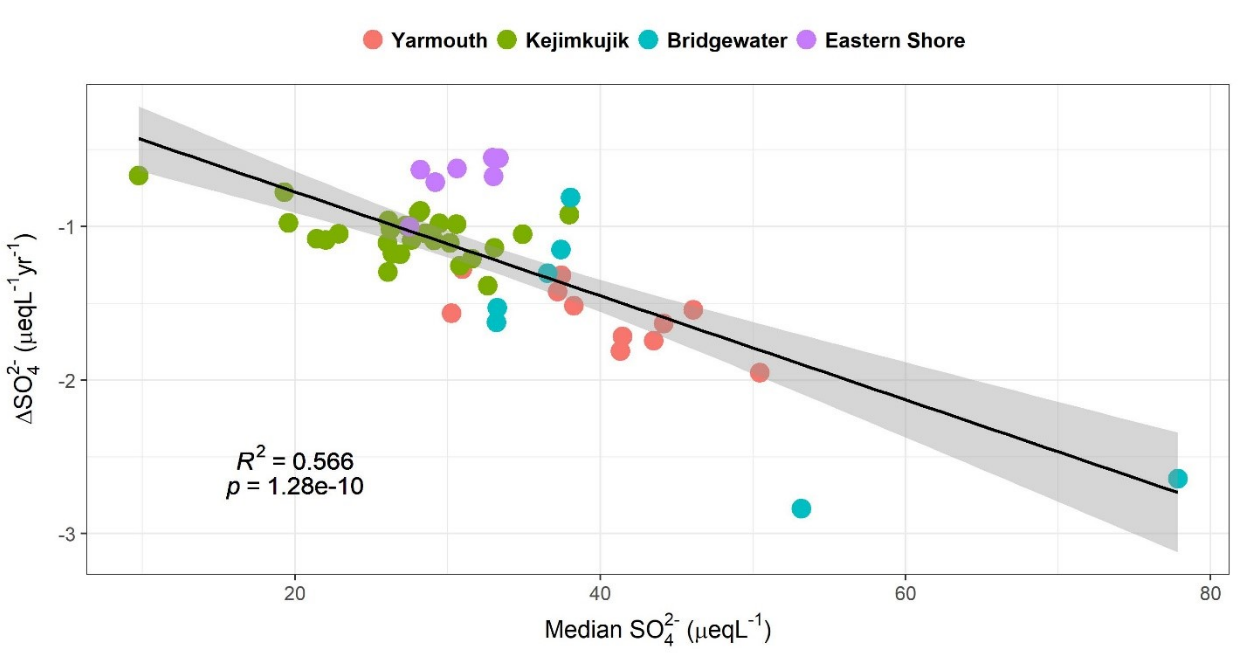

Figure 4.6 - Magnitude of sulfate trends plotted again median lake sulfate concentrations. The colour of the points indicates the region in which each lake is situated. Bands around the regression line represent the 95% confidence interval.

Given the reductions in sulfate deposition observed at both NS precipitation monitoring stations, decreases in lake sulfate concentrations were expected. In a previous assessment of LRTAP lakes, using data up to and including 2007, decreasing lake sulfate trends were found in many, but not all, NS lakes (Clair et al., 2011). Sulfate deposition continued to decline post-2007 (Section 4.4.1) and this led to sulfate decreases in all LRTAP lakes.

4.6.2 pH

pH increased in half of the LRTAP lakes between 1990 and 2016 and did not decrease in any of the lakes (Table 4-3). The proportion of lakes with increasing pH trends was highest in Bridgewater, where pH increased in all 7 lakes; this was followed by Yarmouth where pH increased in 7 of the 11 lakes. Trend magnitudes ranged from 0.007 to 0.031 pH units yr-^{1} (Figure ***4.7***).

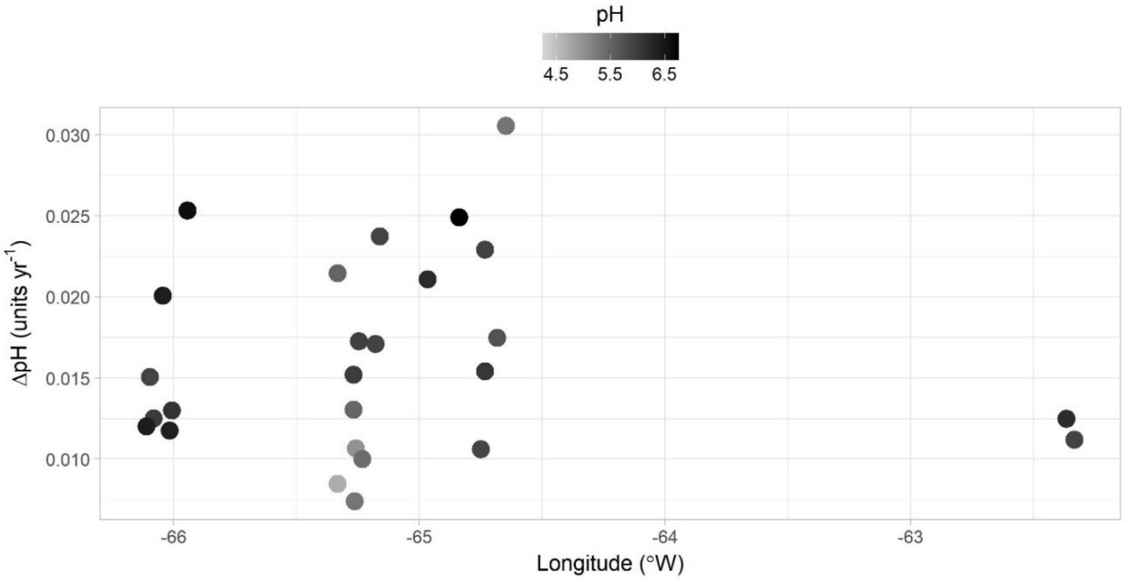

Figure 4.7 - Magnitudes of pH trends in LRTAP lakes plotted against longitude to show spatial variation. Median lake pH is indicated by shading of points.

The five-year median pH between 1990 to 1995 (beginning of the monitoring period) was compared to the five-year median pH between 2011 and 2016 (end of the monitoring period) to provide context for the rates of change observed in these lakes. Prior to 1995, only 2 LRTAP lakes had a pH greater than 6.5, the minimum pH specified by the CCME freshwater aquatic life guidelines; whereas post-2010, 6 lakes had a median pH greater than 6.5. Clearly, the majority of LRTAP lakes continued to have pH levels below the recommended range for ecological health, however, the number of lakes with a median pH greater than 6.0 increased from 12 to 21 lakes.

No spatial pattern was observed in the pH trends (Figure ***4.7***), nor was there a strong relationship between changes in pH and median pH (Figure 4.8). This is likely due to the dependency of pH on site specific factors rather than on regional drivers, as was the case for lake sulfate concentrations. Median rates of change were similar between regions, but there was a substantial range in trend magnitude within each region (except the eastern shore of Halifax county where only 2 trends were found).

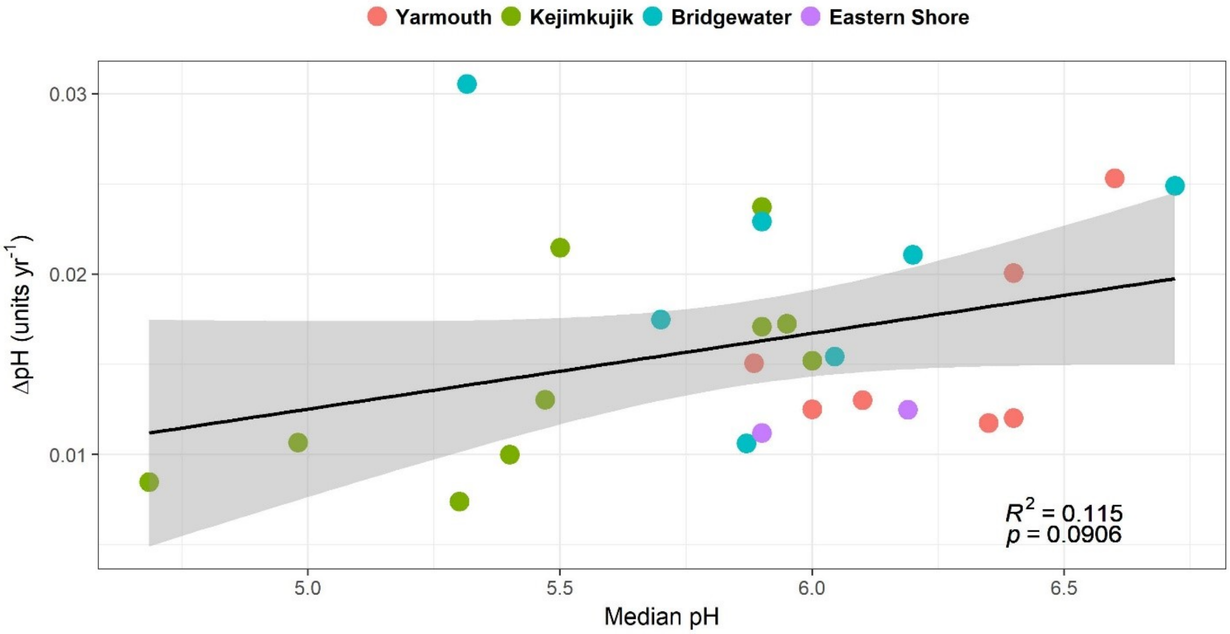

Figure 4.8 - Magnitude of pH trends plotted against median lake pH. The colour of the points indicates the region in which each lake is situated. Bands around the regression line represent the 95% confidence interval.

Previous studies (Clair et al., 2007; Clair et al., 2011; Whitfield et al., 2006) found little evidence of improved acid-base status in NS lakes, despite reductions in sulfate deposition. In the most recent analysis of water chemistry trends in LRTAP lakes, Clair et al. (2011) found that between 1990 and 2007, the number of lakes in southwestern NS (Yarmouth and Kejimkujik) with increasing pH trends was nearly equal to the number of lakes with decreasing pH trends. The current analysis found no lakes with decreasing trends, indicating further recovery from acidification in the LRTAP lakes since 2007.

4.6.3 Alkalinity

Increasing alkalinity trends were found in over half (27 of 50) of the LRTAP lakes and there were no decreasing trends in any LRTAP lakes (Table 4-3). In Bridgewater, alkalinity increased in 6 of

7 (85%) of lakes, whereas in Yarmouth and Kejimkujik increases were found in 6 of 11 (55%) and 13 of 25 (52%) of lakes, respectively. In the eastern shore of Halifax county, alkalinity increases were only found in 2 of 7 (29%) of lakes. Trend magnitudes ranged from 0.26 to 2.38 μeqL^{-1}yr^{-1} (Figure 4.9) and the regional median rates of change (Table 4-4) were highest in Yarmouth (1.03 μeqL^{-1}yr^{-1}) and Bridgewater (0.93 μeqL^{-1}yr^{-1}). There was a general pattern of west to east reductions in alkalinity trends, where greater alkalinity increases occurred in lakes in western NS (Figure 4.9).

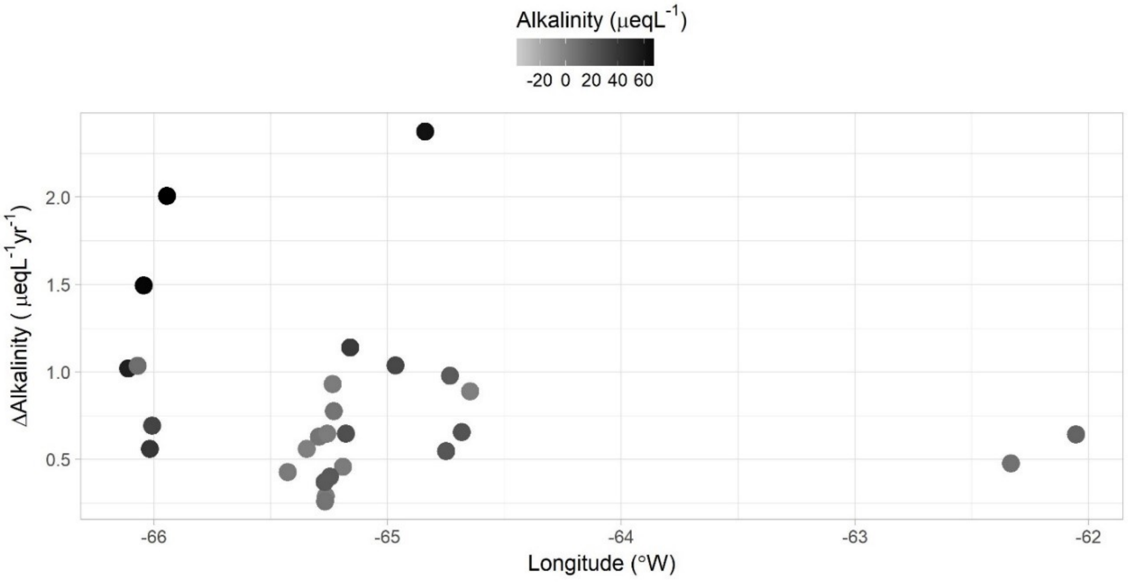

Figure 4.9 - Magnitudes of alkalinity trends in LRTAP lakes plotted against longitude to show spatial variation. Median lake alkalinity is indicated by shading of points.

A relationship between rates of alkalinity increase and median alkalinity concentrations was also observed (Figure 4.10). This was particularly apparent for several lakes in Yarmouth and Bridgewater where rates of increase were greater than 1.5 μeqL^{-1}yr^{-1} and lake alkalinity was greater than 60 μeqL^{-1}.

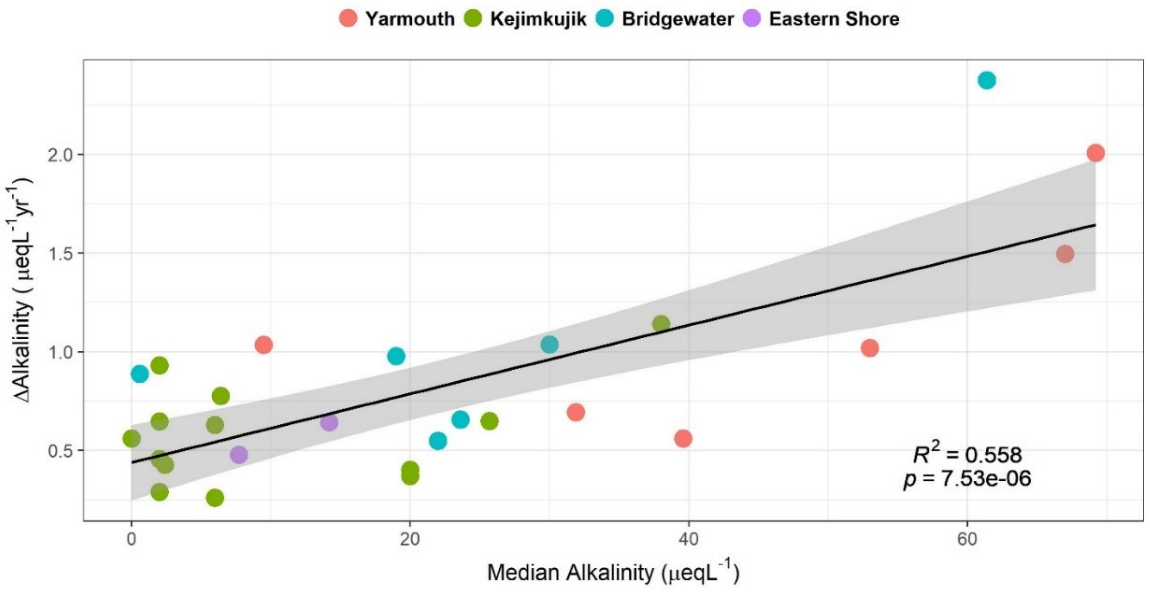

Figure 4.10 - Magnitude of alkalinity trends plotted against median lake alkalinity. The colour of the points indicates the region in which each lake is situated. Bands around the regression line represent the 95% confidence interval.

Previous analysis of LRTAP lakes found that increases in alkalinity were limited to more recent time periods (2000 to 2007), and that longer-term alkalinity trends (1990 to 2007) were mainly negative (Clair et al., 2011). The current analysis showed that inclusion of more recent alkalinity data (i.e. post-2007) resulted in more increasing alkalinity trends. The previous analysis also found that between 1983 and 2007, the number of lakes in western NS (Yarmouth and Kejimkujik) with increasing alkalinity trends was nearly equal to the number with decreasing alkalinity trends., whereas the current analysis found no decreasing alkalinity trends in LRTAP lakes. Clearly, alkalinity has continued to increase in the LRTAP lakes since 2007.

4.6.4 Colour

Colour was used in place of DOC because changes to analytical methods over the course of the monitoring program made DOC measurements incomparable. A strong correlation exists between colour and DOC for lakes in NS (Waller et al., 1996), making colour a suitable proxy for DOC.

Colour increased in most of the LRTAP lakes in Yarmouth (8 of 11 lakes), Kejimkujik (24 of 27 lakes), and Bridgewater (6 of 7 lakes), but only in 2 of 7 lakes in the eastern shore of Halifax County (Table 4-3). Decreasing colour trends were not detected in any of the lakes. Trend magnitudes ranged from 0.01 to 3.50 ACU yr^{-1} (***Table 4-4***) with the greatest increases occurring in Kejimkujik and Yarmouth (Figure 4.11).

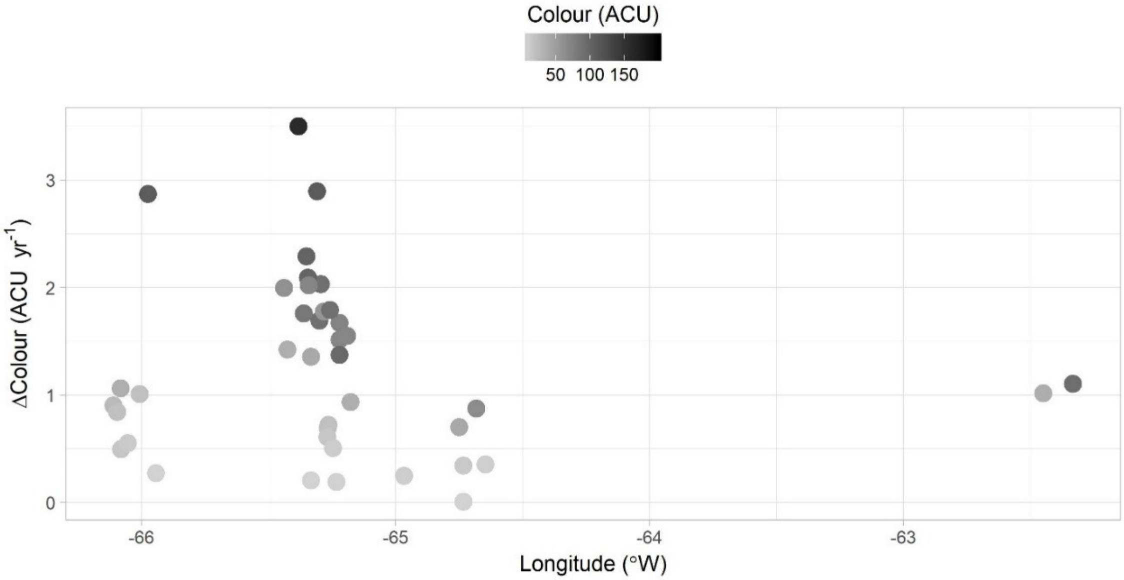

Figure 4.11 - Magnitudes of colour trends in LRTAP lakes plotted against longitude to show spatial variation. Median lake colour is indicated by shading of points.

A strong relationship was found between trend magnitude and median colour, with greater rates of change occurring in lakes with higher colour content (Figure 15). The greatest rates of change were found in highly coloured lakes of Kejimkujik and Yarmouth situated atop peat and sandy loams.

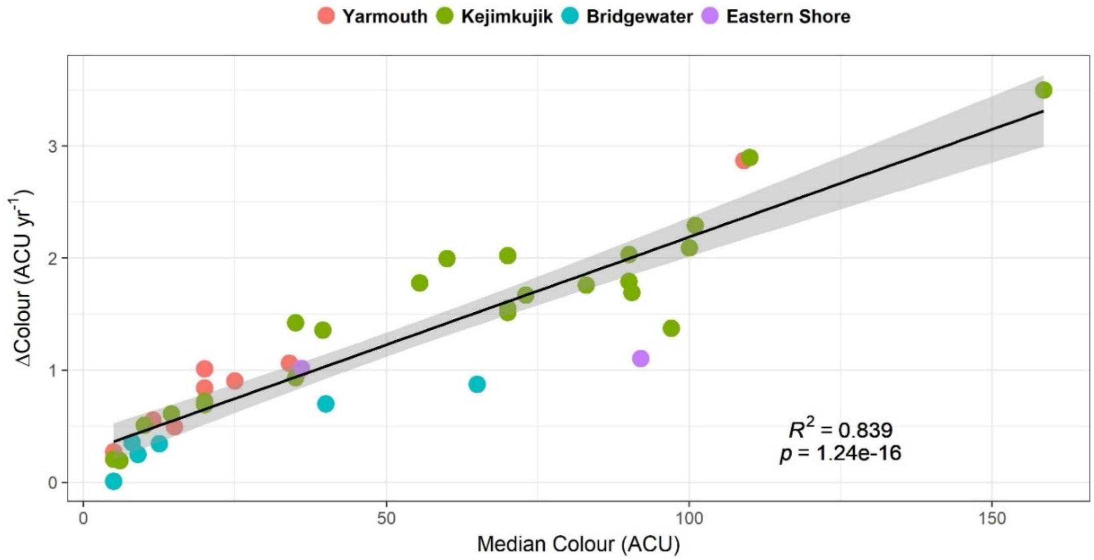

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Figure 4.12 - Magnitude of colour trends plotted against median lake colour. The colour of the points indicates the region in which each lake is situated. Bands around the regression line represent the 95% confidence interval.

Previous analysis of DOC trends in LRTAP lakes found that roughly 75% of LRTAP lakes experienced increasing DOC between 1990 and 2007 (Clair et al., 2011). The inclusion of more recent data (i.e. post-2007) has not majorly impacted the number of lakes for which increasing colour/DOC trends were detected.

4.6.5 Calcium and Magnesium

Calcium concentrations decreased or were unchanged in most LRTAP lakes, except in the eastern shore of Halifax County where no decreasing trends were found. Only one increasing trend was detected in each of the four regions (Table ***4-3***). The greatest proportion of lakes with decreasing trends was found in Kejimkujik where calcium concentrations decreased in 9 of 27 lakes (33%). Trend magnitudes in all the LRTAP lakes ranged from -0.87 to 0.54 μeqL^{-1}yr^{-1} (***Table 4-4***) with the greatest rate of decline found in Bridgewater. Magnesium concentrations also decreased in most LRTAP and did not increase in any (Table ***4-3***). In Kejimkujik, decreasing magnesium trends were found in 19 of 27 lakes (85%). Trend magnitudes ranged from -0.96 to -0.12 μeqL^{-1}yr^{-1} (***Table 4-4***) with the greatest rates of decline found in Bridgewater.

There weren't any apparent spatial patterns for either calcium or magnesium trends, nor were there strong relationships between trend magnitudes and median concentrations. It was clear however, that lakes in Kejimkujik have lower calcium and magnesium concentrations than the three regions, and that the rates of decline in Kejimkujik tended to be smaller (i.e. closer to zero) than in other regions.

Previous analysis LRTAP lakes found that calcium and magnesium decreased at the beginning of the sampling program, but that in more recent years (i.e. 1990 to 2007) there was a relatively even distribution of increasing and decreasing trends (Clair et al., 2011). This current analysis found that including more recent data resulted in more decreasing trends. Acidification of catchment soil increases the flux of base cations from soil to surface water (Reuss and Johnson 1986). Therefore, decreasing calcium and magnesium trends are likely the result of decreased flux from catchment soil due to reduced acidification and/or depletion of calcium from soils. The lack of decreasing calcium trends in the eastern shore of Halifax county may be the result of local geology or may be due to the west to east reduction in acid deposition discussed previously (Section 4.4.1).

4.6.6 Iron

Each of the four regions had several lakes where increasing iron concentrations were found. The only decreasing iron trend was found in a lake in the eastern shore of Halifax county (Table ***4-3***). Trend magnitudes ranged from -0.7 to 6.4 $\mu gL^{-1}yr^{-1}$ (Figure 4.13) and median regional trends in Yarmouth, Kejimkujik, and the eastern shore of Halifax County were all approximately 2.5 $\mu gL^{-1}yr^{-1}$. The median regional trend in Bridgewater was substantially higher (5.6 $\mu gL^{-1}yr^{-1}$) than in the other three regions, but there were only two significant trends found in that region and both were greater than 4 $\mu gL^{-1}yr^{-1}$.

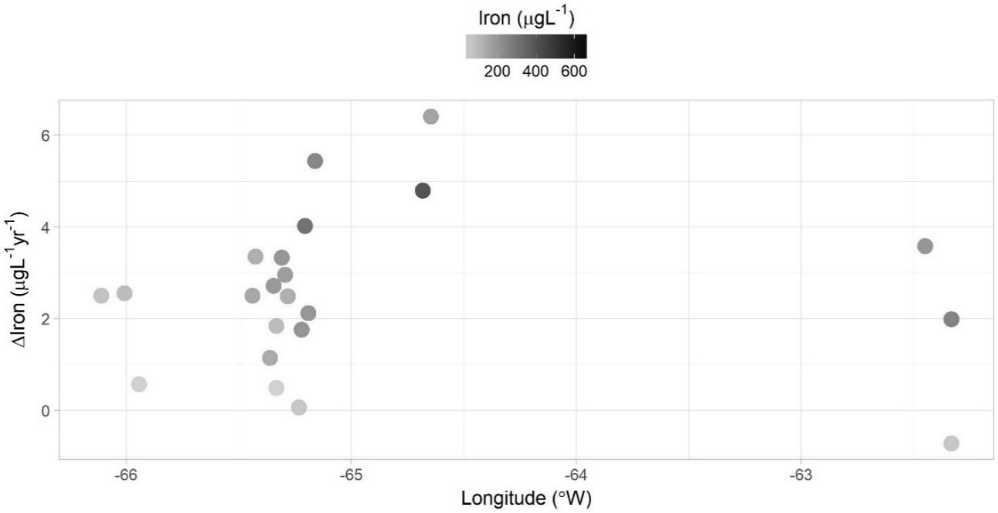

Figure 4.13 - Magnitudes of iron trends in LRTAP lakes plotted against longitude to show spatial variation. Median lake iron concentration is indicated by shading of points.

There was no apparent spatial pattern and, generally, lakes with higher median iron concentrations had greater trend magnitudes. The one lake for which iron concentration decreased was also one of the lakes with lowest median iron concentration (Figure 4.14).

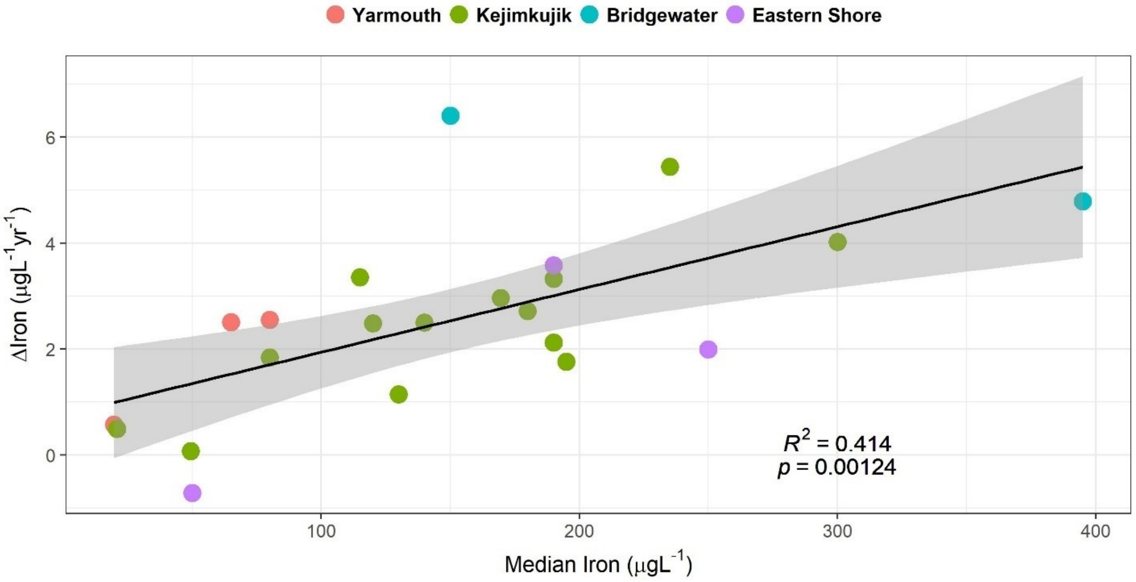

Figure 4.14 - Magnitude of iron trends plotted against median iron concentrations. The colour of the points indicates the region in which each lake is situated. Bands around the regression line represent the 95% confidence interval.

Iron trends were not analyzed in previous assessments of LRTAP lakes. However, recent work has shown that iron concentrations are increasing in lakes recovering from acidification (i.e. Björnerås et al., 2017; Weyenheimer et al., 2014; Kritzberg et al., 2012). Strong correlations between increasing iron and increasing DOC trends throughout North America and Europe suggest that both are responding to regional-scale drivers such as reduced acid deposition or changing hydrological conditions (Björnerås et al., 2017).

4.6.7 Aluminum

Increasing aluminum trends were found in over one-third of the lakes in Yarmouth and nearly half of the lakes in Kejimkujik (Table ***4-3***). In Bridgewater, aluminum decreased in one lake and was unchanged in the rest. In the eastern shore of Halifax county, aluminum trends were not detected in any of the lakes. The greatest increasing trend was 3.28 μg$L^{-1}yr^{-1}$ in a lake in Kejimkujik (Figure 4.15) and the regional median trends in Yarmouth and Kejimkujik were 1.33 and 1.44 μg$L^{-1}yr^{-1}$, respectively (Table ***4-4***).

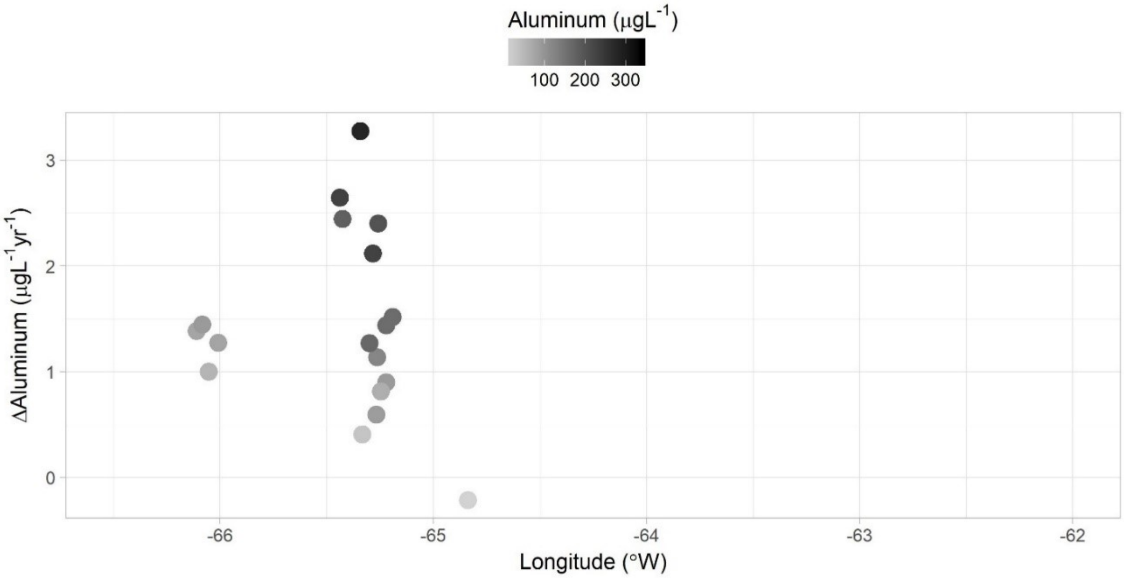

Figure 4.15 - Magnitudes of aluminum trends in LRTAP lakes plotted against longitude to show spatial variation. Median lake aluminum concentration is indicated by shading of points.

A strong relationship between median aluminum concentration and trend magnitude (Figure 4.16***Figure 4.15***) was observed, and five lakes in Kejimkujik with high total aluminum concentrations experienced rates of aluminum increase greater than 2 μg $L^{-1}yr^{-1}$. The lake in Bridgewater with a decreasing aluminum trend also had the lowest median total aluminum concentration of all the LRTAP lakes for which statistically significant aluminum trends were found. However, median aluminum concentrations in lakes of the eastern shore of Halifax county were greater than those in Yarmouth and were similar in magnitude to aluminum concentrations in Kejimkujik, and yet no increasing trends were found in that region. During soil acidification, base cations (Ca, Mg, K, Na) in soil are the first to exchange with hydrogen ions. Once these base cations are depleted, exchange with aluminum increases (Reuss and Johnson 1986). The absence of increasing aluminum trends in the eastern shore of Halifax County may indicate that soil base cations were not depleted to the same extent in that region.

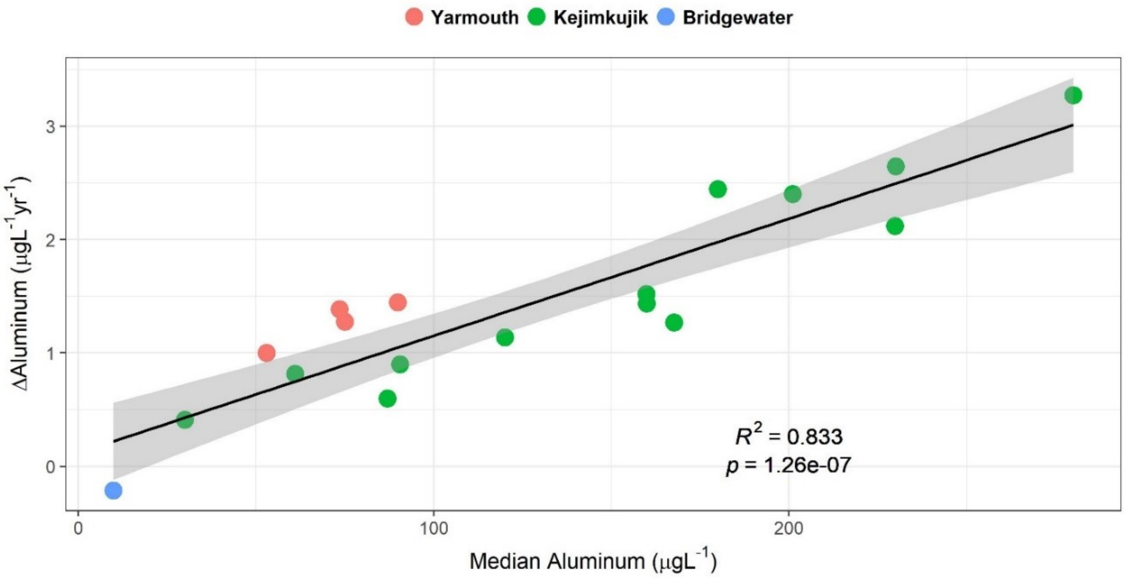

Figure 4.16 - Magnitude of aluminum trends plotted against median aluminum concentrations. The colour of the points indicates the region in which each lake is situated. Bands around the regression line represent the 95% confidence interval.

Previous work in Southwestern NS identified rivers and streams where ionic aluminum concentrations reached levels that were toxic to aquatic biota (Dennis and Clair, 2012). More recent work has also identified rivers in Western NS that continue to have ionic aluminum in concentrations that pose a risk to aquatic biota (Macleod, 2016).

4.6.8 Total Phosphorus

Total phosphorus concentrations increased in 7 of 11 lakes (64%) in Yarmouth, 23 of 27 lakes (85%) in Kejimkujik, 2 of 7 lakes (29%) in Bridgewater, and 3 of 7 lakes (43%) in the eastern shore of Halifax county (Table ***4-3***). Differences between median pre-1993 and post-2003 concentrations ranged from 1 to 5 μgL^{-1} and total phosphorus concentration did not decrease in any of the LRTAP lakes between the pre-1993 and post-2003 periods (Figure 4.17).

While the differences between median concentrations were small in magnitude, in many cases they represented a change in the trophic status classification of the lake from oligotrophic to mesotrophic (based on CCME trigger ranges [CCME 2004]). The highest total phosphorus concentrations were found in LRTAP lakes in Kejimkujik and it was these lakes that experienced the greatest increases in total phosphorus. Generally, greater increases in total phosphorus were observed in lakes with higher median total phosphorus concentrations (Figure 4.18).

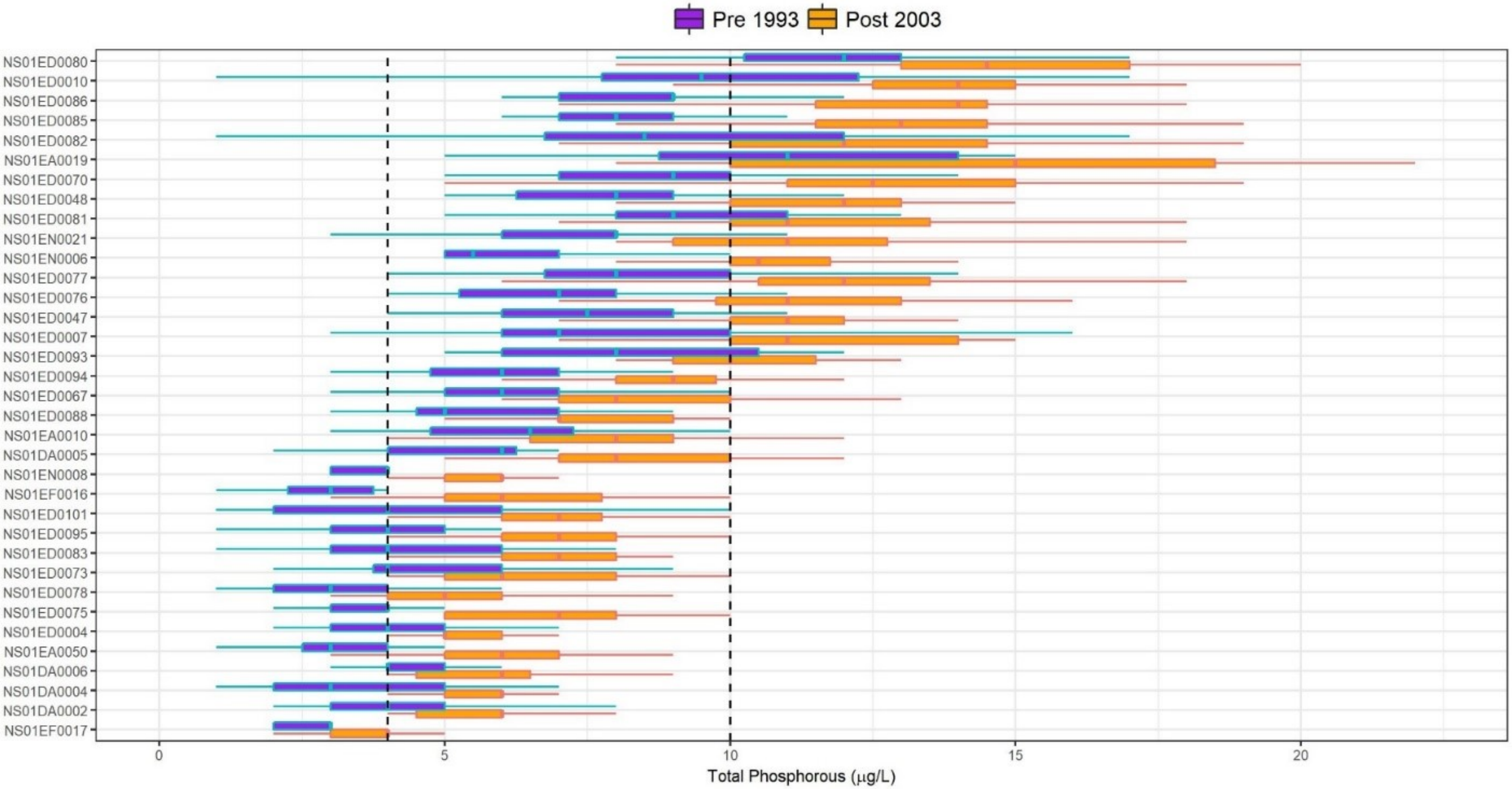

Figure 4.17 - Phosphorus concentrations pre-1993 and post-2003 in LRTAP lakes. The boxplots show the distribution of phosphorus concentrations in each lake in each period. The dashed vertical lines show the phosphorus concentrations used by the CCME to distinguish between ultraoligotrophic (<4 μgL^{-1}), oligotrophic (<10 μgL^{-1}), and mesotrophic (>10 μgL^{-1}) lakes.

Increasing phosphorus concentrations were not anticipated, as the study lakes were minimally impacted by anthropogenic activity (e.g., wastewater discharges, agricultural impacts etc.). However, similar findings have been made in lakes and streams with minimal anthropogenic impacts across North America (Stoddard et al., 2016) and Northern Europe (Kopácek et al., 2015). Previous assessments of LRTAP lakes did not include analysis of phosphorus trends.

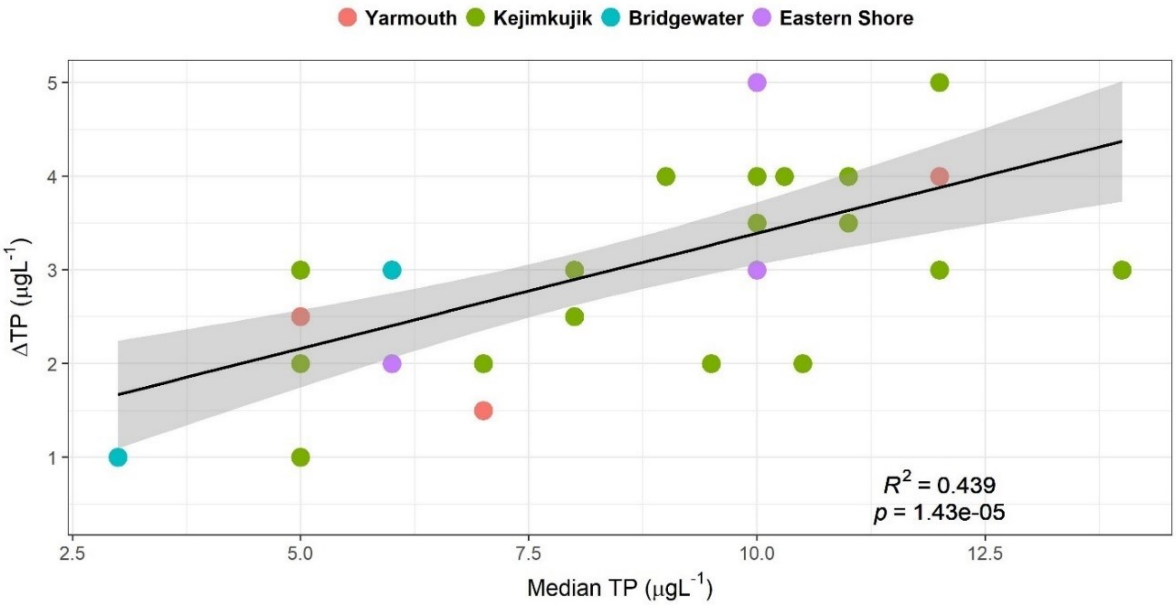

Figure 4.18 - Magnitude of change in phosphorus (post-2003 vs pre-1993) plotted against median lake phosphorus concentration.

4.6.9 Trends 1983 to 2016

The previous results presented trends found using data collected between 1990 to 2016 for LRTAP lakes in all four regions. However, sampling of lakes in Yarmouth and Kejimkujik began in 1983, so additional trend analysis for these two regions was done for the period 1983 to 2016.

Including these earlier data did not affect the proportion of lakes with increasing sulfate or pH trends, and only slightly affected the proportion of lakes with increasing alkalinity, colour, aluminum, and iron trends (Table ***4-3***). It did, however, affect the median trend magnitudes of each of those parameters. Greater rates of declining sulfate and increasing pH, alkalinity, colour, aluminum, and iron were found for the period 1990 to 2016 (***Table 4-4***). Review of the individual lake data for each of these parameters showed that for many of the lakes in these two regions, the concentrations or values of these parameters were relatively steady until the mid- to late-1990s, at which point noticeable trends began to emerge.

The inclusion of these earlier data resulted in more decreasing calcium and magnesium trends in both Yarmouth and Kejimkujik (Table ***4-3***), but did not greatly affect median trend magnitudes (***Table 4-4***). It appears that a steady decline of calcium and magnesium concentrations in most lakes began at, or most likely before, the beginning of the monitoring program and continued until 2016. The smaller proportion of decreasing trends detected in the 1990 to 2016 period suggests that concentrations of calcium and magnesium may have begun to reach a steady state in some of the lakes near the end of the monitoring period.

4.7 King’s County Lakes

Trends in long term water chemistry of anthropogenically impacted lakes monitored through the Kings County Lake Monitoring Program were analyzed to provide further context for the findings of the analysis of the LRTAP lake data. It should be noted, however, that significant issues regarding the accuracy of the data obtained through this monitoring program have been brought forward (Dalhousie University and Stantec, 2009). For this reason, only pH and colour data were included in this work and it was not intended to be a thorough analysis of NS lake water chemistry trends.

Table 4-5- Results of trend analysis for King's County Lakes.

Parameter	King's County (n=9) Increasing (%)	King's County (n=9) Decreasing (%)	Median Trend Magnitude	Unit
pH	66.7	0.0	0.021	units yr^{-1}
Colour	88.9	0.0	0.92	ACU yr^{-1}

pH and colour increased in most of the King's County lakes and did not decrease in any (***Table 4-5***). pH trends ranged in magnitude from 0.011 to 0.025 units yr^{-1} with a median trend magnitude of 0.021 units yr^{-1} which was equal to the median pH trend found for LRTAP lakes in Bridgewater, the group of LRTAP lakes closest to the King's County lakes. Colour trend ranged in magnitude from 0.61 to 1.41 $ACUyr^{-1}$ with a median trend magnitude of 0.92 $ACUyr^{-1}$.

Statistically significant relationships were not found between the trend magnitudes and median colour or pH of the lakes.

4.8 Summary Lake Water Chemistry Trends

Emission control policies aimed at reducing sulfur dioxide emissions successfully reduced wet deposition of sulfate and increased precipitation pH in NS over the past 30 years. The impetus for these policies were observations of freshwater acidification, and the resultant deleterious effects on aquatic biota documented in several regions of Canada. Improvements in the acid/base status (i.e. pH and alkalinity) of lakes was an important metric by which the success of these policies was measured. The LRTAP lake monitoring program was established to evaluate the effect of emission control policies on NS lakes which were deemed to be particularly sensitive to acidification. The improvements in both precipitation and lake water chemistry documented in this research indicate that that these policies have had substantial effect in NS.

Previous assessments of NS precipitation sulfate and LRTAP lake water chemistry found decreases in precipitation sulfate but little evidence of these changes impacting water chemistry in the lakes. The most recent of these assessments used data up to and including 2007 (Clair et al., 2011) and found that despite substantial reductions in lake sulfate concentrations, the number of lakes with increasing pH was nearly equal to the number of lakes with decreasing pH. It was also shown that increases in lake alkalinity were only observed during more recent periods (i.e. late 1990s and early 2000s).

The current assessment has shown that precipitation sulfate continued to decrease after 2007, and precipitation pH continued to increase. It stood to reason that these more recent improvements in precipitation chemistry would lead to further improvements in LRTAP lake water chemistry. This expectation was borne out by the data. No decreasing pH trends were found, and a greater proportion of lakes had increasing alkalinity trends than in the previous assessment. Additionally, most of the lakes included in the King's County Lake Monitoring Program have experienced increases in pH. Despite concerns regarding the reliability of the data from that monitoring program, these findings do indicate that increasing lake water pH was not limited to the LRTAP lakes.

The colour increases observed in LRTAP and King's County lakes were consistent with increasing DOC trends in the last assessment of LRTAP lakes (Clair et al., 2011) and with increasing DOC trends found across North America and Europe in lakes recovering from acidification (Evans and Monteith 2001; Monteith et al., 2007; Skjelkvåle et al., 2005; Evans et al., 2006; Lawrence et al., 2011). While DOC was not used in this work, colour was considered a suitable proxy (as discussed in Section 4.6.4) and it was found to have increased in approximately three-quarters of the LRTAP lakes. The notable exception was the eastern shore of Halifax county, where colour increased in only one of the seven lakes.

The other notable findings of the trend testing were declining concentrations of base cations and increasing concentrations of aluminum, iron, and phosphorus. Declining base cation concentrations in LRTAP lakes were consistent with the model of acidification presented by Galloway et al. (1983) and were also consistent with observations made across North America and Europe (Skjelkvåle et al., 2001; Skjelkvåle et al.,2005; Stoddard et al., 2003; Evans and Monteith, 2001). Loss of calcium from freshwater is an issue that has gained much attention recently and may have substantial impact on aquatic ecosystems (e.g. Jeziorski, et al.,2008; Jeziorski, and Smol, 2016). Replenishment of base cation concentrations in these lakes will depend on soil calcium availability, weathering rates, and export rates.

The increasing aluminum concentrations found in this work support previous findings of high and/or increasing aluminum concentrations in Southwest NS (Dennis and Clair, 2012; Macleod, 2016). The water chemistry data used in this work did not allow for assessment of ionic aluminum trends. However, increased pH coupled with increased DOC concentrations result in non-labile organic aluminum complexes (Driscoll et al., 1985; Gjessing et al., 1989)., suggesting that the observed increases in total aluminum were likely increases in organically complexed aluminum. If this is the case, it could mean that the increased aluminum concentrations do not necessarily pose greater risk to aquatic biota.

Increasing iron trends were found in nearly half of the LRTAP lakes and only one decreasing trend was found. Recent evidence indicates that iron concentrations are increasing in surface waters across North America and Europe (i.e. Björnerås et al., 2017; Weyenheimer et al., 2014; Kritzberg et al., 2012) and strong correlations between increasing iron and increasing DOC trends suggest that both are responding to regional-scale drivers such as reduced acid deposition or changing hydrological conditions (Björnerås et al., 2017). In the LRTAP lakes, it appears that increasing trends in iron and colour occurred concurrently, providing further support for a relationship between the two.

Increasing phosphorus trends were not anticipated given the choice of lakes with minimal anthropogenic impact used in the LRTAP monitoring program. However, similar findings, have been made in minimally impacted surface water in North America (Stoddard et al., 2016) and Europe (Kopacek et al., 2015). Kopacek et al. (2015) reported trends in total phosphorus of 0.04 ±0.08 μgL^{-1}yr^{-1} in their assessment of phosphorus in minimally impacted lakes in Northern Europe, where phosphorus concentrations were similar to those in LRTAP lakes. Trend testing was not possible for total phosphorus in LRTAP lakes, however the observed changes of 2 to 3 μgL^{-1} over a period of 15 to 20 years equate to approximate trends of 0.1 to 0.2 μgL^{-1}yr^{-1}, trends that are greater than those reported by Kopacek et al. (2015). Stoddard et al. (2016) also reported increasing total phosphorus concentrations in surface waters across the continental US. They found that the number of oligotrophic (total phosphorus concentrations <10 μgL^{-1}) lakes and streams decreased from 24.9% to 6.7% between 2007 and 2012.

Reasons for increasing phosphorus in minimally impacted lakes are still unclear. While, atmospheric deposition is a non-trivial source of phosphorus (Brahney et al., 2015; Carbo et al., 2005; Herut, et al., 2002; Homyak et al., 2014), the increased phosphorus concentrations in streams and rivers observed by Stoddard et al (2016) indicate that other mechanisms must exist. Kopácek et al., (2015) proposed that increasing phosphorus concentrations were due to either increased co-transport of phosphorus and organic matter from catchment soil, or increased mobilization of phosphorus from lake sediment as a result of reduced ionic aluminum concentrations. More recently, Nurnberg et al. (2018) assessed the release of phosphorus from sediment of lakes recovering from acidification as a potential cause of increased lake productivity. Their findings provide further support for the theory that decreased ionic aluminum in the water column, following recovery from acidification, is allowing for greater phosphorus release from lake sediment (Nurnberg et al., 2018).

4.9 Correlations Between Lake Water Chemistry Trends

Through the analysis of water chemistry trends, it became apparent that relationships existed between aluminum, iron, colour, and pH trends. These relationships have also been noted by other researchers (as discussed in Section 4.8). To further explore these relationships, correlations between the trends of these parameters in the LRTAP lakes were assessed (Figure 4.19). Statistically significant ($p<0.01$) relationships were found between trends (including magnitudes of both statistically significant and non-significant trends) in aluminum, colour, and pH, with negative correlations existing between trends in aluminum and pH and trends in colour and pH.

Positive correlations were found between trends in aluminum and colour and between trends in iron and colour. It appeared that there was a positive correlation between trends in iron and aluminum as well; however, there were several lakes with high increasing iron trends that affected the correlation.

Strong negative correlations were found between trends in aluminum and pH and between trends in colour and pH. Again, it appeared that a negative correlation existed between trends in iron and pH, but the lakes with high increasing iron trends affected the correlation.

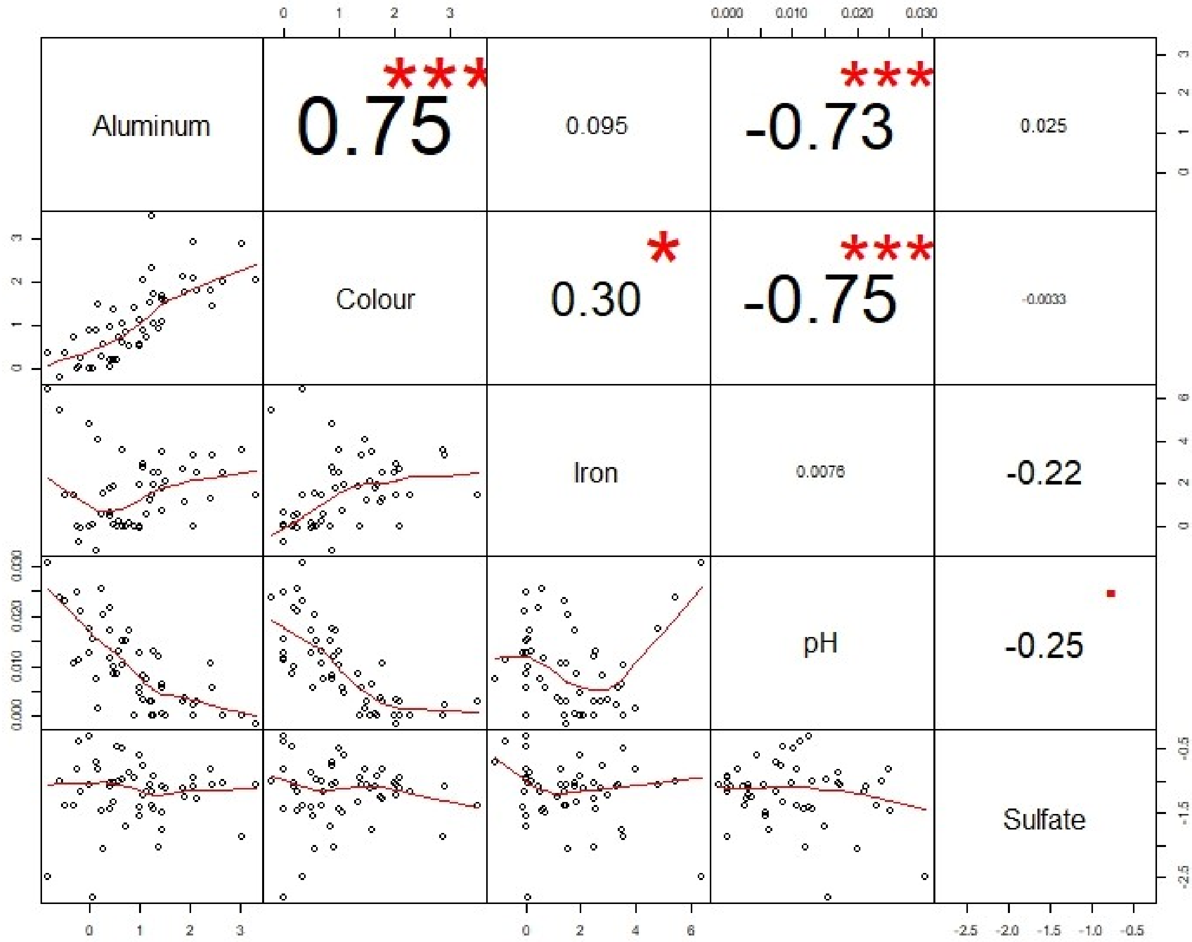

Figure 4.19 - Correlations between magnitudes of aluminum, iron, colour, pH, and sulfate trends for LRTAP lakes. Scatterplots are shown on the lower diagonal and coefficients of determination are shown on the upper diagonal. Statistical significance is indicated in the upper diagonal with p values of <0.1, <0.05, <0.01, and <0.001, indicated by ▪, *, **, and *, respectively. The trend magnitudes are presented in units of μeqL^{-1}yr^{-1} (sulfate), units yr^{-1} (pH), ACU yr^{-1} (colour), and μgL^{-1}yr^{-1-} (aluminum and iron).**

Trends in aluminum, colour, and iron were not correlated with trends in lake sulfate; a weak negative correlation was found between trends in pH and trends in lake sulfate. Similar analysis was conducted to explore relationships between changes in total phosphorus concentrations and trend magnitudes of aluminum, colour, iron, and pH. Changes in total phosphorus concentrations were significantly ($p < 0.01$) correlated ($r^2 = 0.58$) with trends in colour, with greater changes in total phosphorus concentrations occurring in lakes with greater increases in colour.

As discussed previously (see section 3.6), reductions in sulfate deposition increase soil NOM solubility (Haaland et al., 2010; Ekström et al., 2011; Erlandsson et al., 2008; SanClements et al., 2012), which led to the increasing colour observed in most LRTAP lakes. It is also known that NOM increases aluminum solubility through complexation with organic anions (Driscoll et al., 2003; Schott et al., 2009; Tipping et al., 1988) as well as by buffering against rising pH (Evans et al., 2008; Monteith et al., 2014). This is a likely explanation for the observed aluminum increases in LRTAP lakes, and also explains the strong relationship between color and aluminum trends. Furthermore, organically complexed aluminum was the explanation proposed by Kopacek et al. (2016) for increased sedimentary phosphorus release in Northern European lakes; the same explanation might be used to explain increases in phosphorus concentrations observed in LRTAP lakes.

Recently, increasing iron concentrations in surface waters across the Northern Hemisphere have been observed (Knorr, 2013; Kritzberg and Ekstrom, 2012; Neal et al., 2008; Sarkkola et al., 2013; Weyhenmeyer et al., 2014, Björnerås et al., 2017) and have been correlated with increases in NOM content (Björnerås et al., 2017). The increasing iron trends observed in LRTAP lakes are consistent with these observations. The role of iron rich organic colloids (Pokrovsky et al., 2016; Hassellöv et al., 2008; Baken et al., 2016) and aluminum rich organic colloids (Pokrovsky et al., 2016) as transport vectors also suggests relationships between NOM solubility (resulting from reduced sulfate deposition) and increasing aluminum and iron export from watershed soils. It also appears that increasing phosphorus concentrations are linked to either co-transport with iron and aluminum from catchment soil, or to increased mobilization resulting from less ionic aluminum within lakes.

4.10 Results of SEC-UV with Multi-Element Detection

To better understand the interactions between these parameters in LRTAP lakes, samples were collected from three of the LRTAP lakes in Yarmouth with relatively high colour, iron, and aluminum concentrations and where phosphorus concentrations were shown to have increased. The interactions between these parameters were explored using SEC-UV with multi-element detection (ICP-MS). This approach has been used to explore interactions between iron, OM, and lead in drinking water distribution systems (Trueman and Gagnon, 2016) as well as interactions between heavy metals and OM in riverine ecosystems (Rottman and Heuman, 1994).

No discernible ^{31}P peaks were observed in any of the lake samples, due in large part to a moderately high background in the mobile phase. This, combined with low phosphorus concentrations in the samples resulted in a low signal to noise ratio. Potential polyatomic interferences that may have prevented ^{31}P determination include: $^{14}N^{16}O^{1}H^{+}$, $^{15}N^{15}N^{1}H^{+}$, $^{15}N^{16}O^{+}$, $^{14}N^{17}O^{+}$, $^{13}C^{18}O^{+}$, $^{12}C^{18}O^{1}H^{+}$(May and Weidmeyer, 1998). Several negative peaks were observed in the chromatograms of the lake samples, but were not observed in the mobile phase blanks, indicating that they were artefacts of the sample matrix.

The following figures present the individual aluminum, iron, and UV_{254} chromatograms for each lake. These elution profiles have been scaled vertically to allow each constituent to be shown on one plot. Each profile has vertical axis units of counts per second (cps), for metals, or arbitrary units (AU), for UV_{254}. The axis scales of the various constituents differ by orders of magnitude. It is for this reason than no axis labels were provided. The intent of these figures is to illustrate the elution characteristics of each constituent and to thereby gain some insight into interactions between the constituents. In each figure, a vertical dashed line shows the elution time of thyroglobulin (molecular weight 669 kDa, Stoke's radius 8.5 nm), providing a relative indication of size.

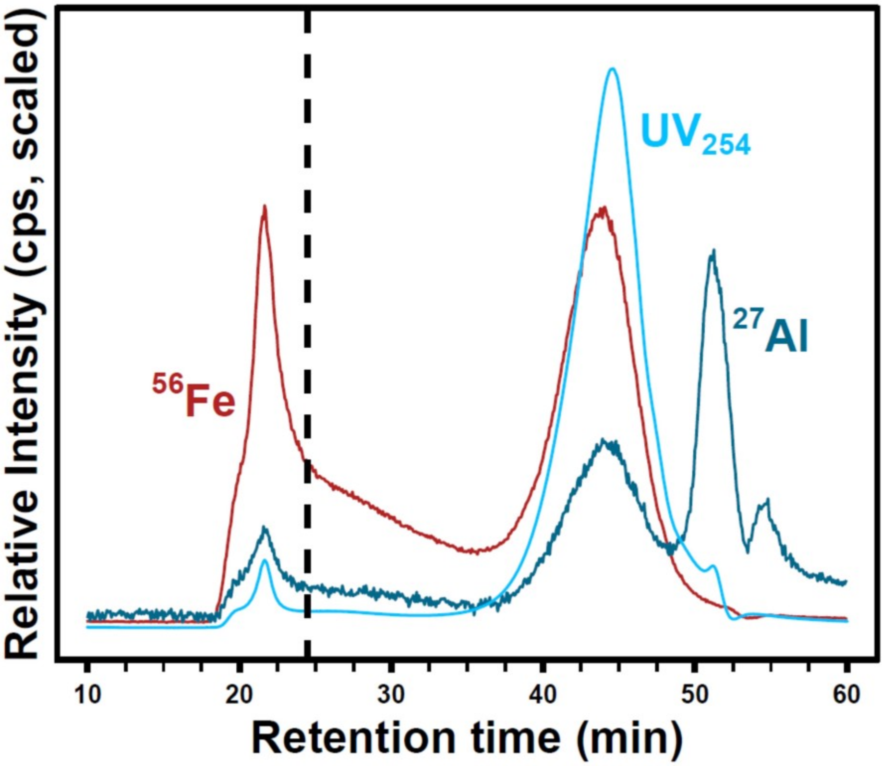

Figure 4.20 - Chromatograms from Breton Lake water sample showing relative intensity of iron (red line), aluminum (dark blue line) and UV254 (light blue line). The vertical dashed line shows the elution time of thyroglobulin (molecular weight 669 kDa, Stoke's radius 8.5 nm).

In the Brenton lake sample (Figure 4.20) aluminum, iron, and UV$_{254}$ co-eluted at retention times of 21 and 42 minutes. Aluminum and UV$_{254}$ also co-eluted at a retention time of 51 minutes, and an additional aluminum peak was observed at a retention time of 55 minutes. The peak at a retention time of 21 minutes eluting, before thyroglobulin (669 kDa, Stoke's radius 8.5 nm) and having narrow total peak width compared to subsequent peaks, suggested high apparent molecular weight colloids composed largely of iron with relatively small proportions of NOM and aluminum. The peak observed at a retention time of 42 minutes consisted of large UV_{254}, iron, and aluminum peaks. The broad total peak area and later elution time suggested low molecular weight iron-aluminum-NOM colloids. The peak observed at a retention time of 51 minutes consisted of a large aluminum peak with a relatively small UV_{254} peak. The late elution time and narrow total peak width suggested low apparent molecular weight aluminum with a relatively small proportion of NOM. The final peak, eluting at a retention time of 55 minutes, consisted solely of an aluminum peak, suggesting dissolved aluminum species.

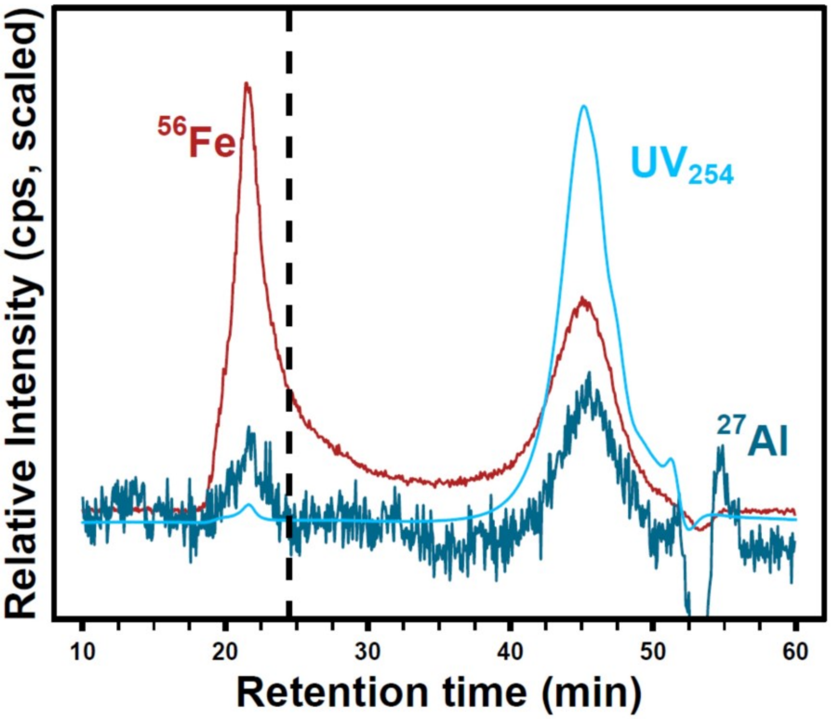

Figure 4.21 - Chromatograms from Cedar Lake water sample showing relative intensity of iron (red line), aluminum (dark blue line) and UV254 (light blue line). The vertical dashed line shows the elution time of thyroglobulin (molecular weight 669 kDa, Stoke's radius 8.5 nm).

In the Cedar lake sample (Figure 4.21), aluminum, iron, and UV$_{254}$ co-eluted at retention times of 21 and 45 minutes. An additional aluminum peak was observed at a retention time of 55 minutes. The peak at a retention time of 21 minutes consisted of a large iron peak with small aluminum and UV$_{254}$ peaks. Eluting before thyroglobulin (669 kDa, Stoke's radius 8.5 nm) and having narrow total peak width compared to subsequent peaks, suggested high apparent molecular weight colloids composed largely of iron with relatively small proportions of NOM and aluminum. The peak observed at a retention time of 45 minutes consisted of moderately sized aluminum, UV$_{254}$, and iron peaks. The broad total peak area and later elution time suggested low molecular weight iron-aluminum-NOM colloids. The final peak (eluting at a retention time of 55 minutes) consisted solely of an aluminum peak, which is indicative of dissolved aluminum that is free from organic colloid. The relative peak size of aluminum at elution times of 21, 45 and 55 min indicate that the concentration of organic bound aluminum is highly relevant in these water samples.

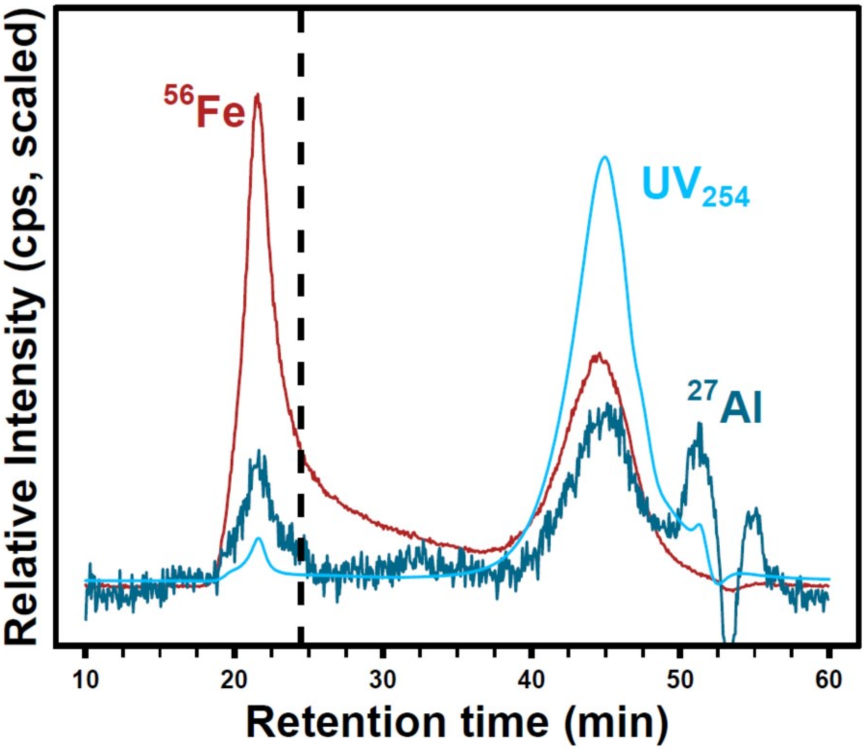

Figure 4.22 - Corning lake chromatograms showing relative intensity of iron (red line), aluminum (dark blue line) and UV254 (light blue line). The vertical dashed line shows the elution time of thyroglobulin (molecular weight 669 kDa, Stoke's radius 8.5 nm).

In the Lake Corning sample (Figure 4.22), aluminum, iron, and UV$_{254}$ co-eluted at retention times of 21 and 45 minutes. Aluminum and UV$_{254}$ also co-eluted at a retention time of 51 minutes, and an additional aluminum peak was observed at a retention time of 55 minutes. The peak observed at a retention time of 21 minutes consisted of a large iron peak with relatively small aluminum and UV$_{254}$ peaks. Eluting before thyroglobulin (669 kDa, Stoke's radius 8.5 nm) and having narrow total peak width compared to subsequent peaks, suggested high apparent molecular weight colloids composed largely of iron with relatively small proportions of OM and aluminum. The peak observed at a retention time of 42 minutes consisted of a large UV_{254} peak and relatively large aluminum and iron peaks. The broad total peak area and later elution time suggested low molecular weight iron-aluminum-OM colloids. The peak observed at a retention time of 51 minutes consisted of a moderate aluminum peak with a small UV_{254} peak. The late elution time and narrow total peak width suggested low apparent molecular weight aluminum with adsorbed OM. The final peak, eluting at a retention time of 55 minutes, consisted solely of an aluminum peak, suggesting dissolved aluminum species.

4.11 Discussion of Chemical Interactions

Strong correlations exist between the trend magnitudes of colour, aluminum, and iron in the LRTAP lakes. Using SEC-UV with multi-element detection, it was possible to gain greater insight into the nature of these interactions. Each of the three LRTAP lakes had similar elution profiles suggesting that each sample contained: 1) high apparent molecular weight iron-rich colloids that were associated with relatively small proportions of aluminum and NOM, 2) low apparent molecular weight iron-aluminum-NOM colloids, and 3) low apparent molecular weight aluminum with a relatively small proportion of NOM.

While only three samples were analyzed, the findings were consistent between samples and also reflected the relationships found between the trend magnitudes of iron, aluminum, and colour in the LRTAP lakes. This provides evidence that the relationships noted between the trend magnitudes of these parameters are based on physical associations in the lakes. It should also be noted that for a given analyte, the recoveries for different size fractions may differ (i.e. a small soluble aluminum peak does not necessarily indicate a small soluble aluminum fraction in the sample). Further work is required to verify these preliminary findings. However, the broad pattern of particulate aluminum speciation being controlled either by larger iron-rich colloids or smaller NOM-rich colloids is consistent with previous research (e.g., Pokrovsky and Schott, 2002; Hill and Alpin, 2001). It was not possible to detect phosphorus in the samples collected from the LRTAP lakes, so the nature of physical interactions between phosphorus and other parameters could not be assessed.

CHAPTER 5 CONCLUSIONS

Annual sulfate deposition in NS has decreased by approximately 66% since the mid-1990s. The impact of this change on NS lakes, particularly those deemed sensitive to acidification was assessed by evaluating long-term trends in lake water chemistry in NS. It was found that recovery from acidification (decreasing sulfate, increasing alkalinity and pH) occurred in most of the lakes included in this study, and that these improvements have been more pronounced in recent years (early 2000s). In addition to increasing pH and alkalinity, widespread increases in OM content were also found in over 75% of the LRTAP lakes and in 8 of the 9 King's County lakes. It appears likely that increasing OM is occurring in lakes throughout NS, and based on previous research (e.g. Monteith et al., 2007; Haaland et al., 2010; Ekström et al., 2011; Erlandsson et al., 2008; SanClements et al., 2012) recovery from acidification is likely the primary driver of these changes. Further research is required to better understand the implications of increasing OM, but this work points to OM as playing a large role in controlling other chemical changes in these lakes, as increasing colour was correlated with slower rates of pH increase, higher rates of aluminum increase, and greater increases in total phosphorus.

Total phosphorus concentrations increased in roughly two-thirds of the LRTAP lakes. This was an unexpected result, but similar findings have been made in both North America and Europe. A theory put forth by Kopacek et al. (2016) suggests that decreased ionic aluminum in lakes is allowing greater release of phosphorus from lake sediment. The increasing aluminum concentrations in the LRTAP lakes seemed to contradict that theory. However, studies exploring aluminum speciation in relation to pH and OC concentrations have shown that increasing pH and increasing OC results in non-labile organic aluminum complexes (Driscoll et al., 1985; Gjessing et al., 1989). Preliminary work using SEC-UV coupled with multi-element detection to explore the relationships between aluminum and organic matter in samples from LRTAP lakes found that aluminum was highly associated with OM. This suggests that the observed increases in total aluminum were likely increases in organically complexed aluminum and provides support for the theory of Kopacek et al. (2016). It was also noted that changes in total phosphorus concentrations in the LRTAP lakes were most highly correlated with increasing colour. This finding provides support for the other possibility put forth by Kopacek et al (2016) that increasing phosphorus concentrations were due to co-transport of phosphorus with OM from catchment soils. It was hoped that by using SEV-UV with multi element detection, it would be possible to explore the interactions between phosphorus, OM, and aluminum content in samples collected from LRTAP lakes to gain greater insight into the nature of these relationships. Unfortunately, it was not possible to detect phosphorus due to the low phosphorus concentrations in the samples and interferences from the mobile phase.

Continued monitoring of LRTAP lakes is required to document the ongoing recovery of these lakes from acidification. The rise in OM observed in these lakes (as measured by colour) warrants close attention. A greater understanding of the implications of increasing OM on lake chemistry is also needed, as OM plays an important role in the transport and speciation of aluminum and iron. No strong conclusions have been drawn as to the reasons for increasing phosphorus concentrations, but the findings of this work have provided further support for existing theories. More research should be conducted to better investigate the theory that co-transport of phosphorus with OM from catchment soils is resulting in increasing phosphorus concentrations.

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APPENDIX A

LRTAP Lake Names, Locations, Physical Characteristics, and Biota

Lake Name	Drainage Basin	Elevation (m)	Lake Area (ha)	Basin Area (km2)	Flushing Rate (yr)	Shorelength (km)	Max Depth (m)	Mean Depth (m)	Geology	Soils
TEDFORD LAKE	Salmon	61	81.56	2.45	2.29	5	4.34	1.24	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX & ASPOTOGAN SANDY LOAMS
KILLAM LAKE	Salmon	30	125	210.7	168.9	6	1.51	0.67	HALIFAX SLATE, SCHIST, MINOR QUARTZITE	BRIDGEWATER, HALIFAX, DEERFIELD SANDY LOAMS
CEDAR LAKE	Salmon	15	100	188.18	3.703704	9	NA	NA	HALIFAX SLATE, SCHIST, MINOR QUARTZITE	HALIFAX, ASPOTOGAN, DEERFIELD, PITMAN SANDY LOAMS. SMALL AREAS OF PEAT
LOWER CORNING LAKE	Salmon	30	82.06	200.1	143.75	5	3.83	1.36	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX, LIVERPOOL, PITMAN & MERSEY SANDY LOAMS
PIERCE LAKE	Salmon	35	37.15	1.2	2.58	2.6	4.19	1.94	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX, LIVERPOOL & ASPOTOGAN SANDY LOAMS
BRENTON LAKE	Ohio Millstream	30	58.42	4.95	0.57	5	3.68	1.18	UPPER SILURIAN QUARTZITE WITH SLATE INTERBEDS, VOLCANIC ROCKS	DEERFIELD, YARMOUTH & PITMAN SANDY LOAMS
TREFRY LAKE	Cheboque	15	29.62	1	0.87	4.5	12.44	3.12	GOLDENVILLE GREYWACKE, QUARTZITE,	LIVERPOOL & PITMAN SANDY LOAMS

									GNEISS, MINOR SLATE	
SNARE LAKE	Tusket	61	64.71	9.1	8.79	5.4	6.69	1.28	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX & DANESVILLE SANDY LOAMS. SMALL AREAS OF SWAMP & PEAT BOG
BIRD LAKE	Tusket	61	30	1.2	2.272727	4.6	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX & YARMOUTH SANDY LOAMS
YARMOUTH MUNICIPAL WATER SUPPLY	Coggins Brook	46	1180	29.65	0.322581	30	NA	NA	UPPER SILURIAN QUARTZITE WITH SLATE INTERBEDS, VOLCANIC ROCKS	YARMOUTH, PITMAN, DEERFIELD, HALFAX & BRIDGEWATER SANDY LOAMS
JESSE LAKE	Tusket	30	26.77	1.85	2.32	4.3	5.7	2.38	UPPER SILURIAN QUARTZITE WITH SLATE INTERBEDS, VOLCANIC ROCKS	MERSEY SANDY LOAM
MOUNTAIN LAKE	NA	111	141.62	8.46	14.28571	8.4	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	GIBRALTAR & HALIFAX SANDY LOAMS
KEJIMKUJIK LAKE	NA	87	2482	717.69	5.555556	7.7	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	BRIDGEWATER SANDY LOAM & PEAT
PUZZLE LAKE	NA	100	35.92	NA	NA	3.5	NA	NA	GOLDENVILLE GREYWACKE,	HALIFAX SANDY LOAM

									QUARTZITE, GNEISS, MINOR SLATE	
PEBBLELOG GITCH LAKE	Mersey River	120	33.4	1.6	2.87	5	2.5	1.42	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	GIBRALTAR SANDY LOAM & PEAT
BEN LAKE	Mersey River	170	20.4	1.7	5.7	2.1	0.74	0.5	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	GIBRALTAR SANDY LOAMS & PEAT
MOUNT TOM LAKE	Mersey River	120	13.96	0.6	1.818182	4.17	NA	NA	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	BRIDGEWATER, MIDDLEWOOD SANDY LOAMS, SURFACE PEAT
GEORGE LAKE	NA	87	107.81	720.4	100	7.7	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	BRIDGEWATER SANDY LOAM & PEAT
LOON LAKE	NA	86	123.33	756.3	100	13.1	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
BACK LAKE	Shelburne River	100	87.1	3.83	2	7.4	2.2	5.8	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
BIG DAM WEST LAKE	Mersey River	120	115.4	40	131	6.5	9.5	2.5	GOLDENVILLE GREYWACKE, QUARTZITE,	HALIFAX & BRIDGEWATER SANDY LOAMS

BIG DAM EAST LAKE	NA	113	52.27	1.98	1.612903	4.5	NA	NA	GNEISS, MINOR SLATE GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX & BRIDGEWATER SANDY LOAMS
PESKOWESK LAKE	Mersey River	105	685	85	2.73	25.5	13	3.85	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	GIBRALTAR & HALIFAX SANDY LOAMS
GRAFTON LAKE	Mersey River	100	270.4	53	6.04	20	10	2.76	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	BRIDGEWATER SANDY LOAM, PEAT
HIGH LAKE	Mersey River	90	3.81	1.1	16.35	1	2.8	1.5	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	ASPOTOGAN & BRIDGEWATER SANDY LOAMS
COBRIELLE LAKE	Mersey River	129	131.8	11.5	3.76	8.3	6.25	1.97	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
NORTH CRANBERRY LAKE	NA	94	38.47	NA	NA	4	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
BIG RED LAKE	Mersey River	160	70.5	8	9.64	5	2.2	1	MIDDLE DEVONIAN	PEAT & GIBRALTAR SANDY LOAMS

MUD LAKE	Mersey River	100	7	6.1	71.8	1	2.2	1	GRANITIC & ALLIED ROCKS HALIFAX SLATE, SCHIST, MINOR QUARTZITE	SANDY LOAMS, PEAT
SNAKE LAKE	Mersey River	90	12.7	4.54	5.4	1.6	2.5	1.36	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	BRIDGEWATER SANDY LOAM & PEAT
LIBERTY LAKE	Mersey River	135	73.4	4.35	1.8	5.2	NA	NA	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	GIBRALTAR, ASPOTOGAN SANDY LOAMS & PEAT
FROZEN OCEAN LAKE	Mersey River	105	228	116	23.2	13.3	7.6	1.9	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM, PEAT, ASPOTOGAN SANDY LOAM, NICTAUX, TORBROOK
CHANNEL LAKE	Mersey River	100	68.4	128	138.6	6.4	1.8	1.14	HALIFAX SLATE, SCHIST, MINOR QUARTZITE	PEAT, BRIDGEWATER & HALIFAX SANDY LOAM
LITTLE RED LAKE	Mersey River	150	19.6	3.8	23	2.2	1.3	0.71	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	SANDY LOAMS & PEAT
POPLAR LAKE	Mersey River	170	84	5.6	2.1	6	NA	NA	EUBOSMINA LONGISPINA, CALANOID COPEPODS	BAYSWATER & GIBRALTAR SANDY LOAMS, PEAT
LUXTON LAKE	Mersey River	135	47.1	4.7	2.8	5	8.5	3	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	PEAT, GIBRALTAR SANDY LOAM

HILCHEMAKAAR LAKE	NA	99	99.08	NA	NA	8.8	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
MCGINTY LAKE	Mersey River	105	4.37	1	13.9	1	4	1.4	HALIFAX SLATE, SCHIST, MINOR QUARTZITE	PEAT
PESKAWA LAKE	Mersey River	120	388.5	66	13.9	13.3	9	3.16	MIDDLE DEVONIAN GRANITIC & ALLIED ROCKS	GIBRALTAR SANDY LOAM
UPPER SILVER LAKE	Mersey River	90	24.3	0.9	1.35	4.8	5.75	2.33	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
LOWER SILVER LAKE	NA	100	24	NA	NA	2.5	NA	NA	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	HALIFAX SANDY LOAM
BEAVERSKIN LAKE	Mersey River	120	39.5	1	1	5	6.3	2.2	GOLDENVILLE GREYWACKE, QUARTZITE, GNEISS, MINOR SLATE	GIBRALTAR SANDY LOAMS
LITTLE TUPPER LAKE	Medway	107	117.82	5.93	1.7	7.48	7.84	2.72	PRECAMBRIAN SLATE	BRIDGEWATER & BRIDGEWATER DRUMLIN SANDY LOAMS, SOME SWAMP
HUEY LAKE	LaHave River	107	13.28	2.62	29.9	1.64	1.26	0.66	PRECAMBRIAN SLATE	BRIDGEWATER & BRIDGEWATER

HIRTLE LAKE	LaHave River	91	445.75	59.7	9.9	16.87	5.57	1.35	PRECAMBRIAN SLATE	DRUMLIN SANDY LOAMS, SOME ROCK LAND, RIVERPORT SANDY LOAM, SWAMP BRIDGEWATER & FARMVILLE SANDY LOAMS, SOME BRIDGEWATER & FARMVILLE DRUMLIN SANDY LOAMS, SWAMP
MATTHEW LAKE	Into Minamkeak Lake	99	16.9	2.59	9.7	2.88	5.16	1.57	PRECAMBRIAN SLATE	BRIDGEWATER & BRIDGEWATER DRUMLIN SANDY LOAMS, SOME SWAMP
ANNIS LAKE	Medway	76	86.99	2.15	0.36	76	15.71	6.47	PRECAMBRIAN QUARTZITE	HALIFAX & HALIFAX DRUMLIN SANDY LOAMS
LITTLE WILES LAKE	West LaHave	122	36.33	3.13	NA	3.19	NA	NA	PRECAMBRIAN SLATE	BRIDGEWATER & BRIDGEWATER DRUMLIN SANDY LOAMS
ROCKY LAKE	LaHave River	99	85.33	7.25	NA	7.39	NA	NA	PRECAMBRIAN SLATE	BRIDGEWATER SANDY LOAMS, SOME SMALL AREAS OF FARMVILLE & FARMVILLE DRUMLIN SANDY LOAMS, SWAMP
HALFWAY BROOK LAKE	Halfway Brook	60	106.61	4.77	1.8	7.5	7.56	2.51	QUARTZITE & PRECAMBRIAN SLATE	HALIFAX & DANESVILLE SANDY LOAMS, SMALL AREAS OF WOLFVILLE SANDY LOAM, PEAT

HOOPER LAKE	Hooper Pond	46	20.72	1.76	NA	3.07	NA	NA	PRECAMBRIAN QUARTZITE	ROCK LAND & HALIFAX SANDY LOAMS, SMALL AREAS OF DANESVILLE SANDY LOAMS
PAUL MORRIS LAKE	Quoddy	30	18.13	1.11	NA	1.61	NA	NA	PRECAMBRIAN QUARTZITE	HALIFAX & WOLFVILLE SANDY LOAMS, SMALL AREAS OF PEAT
NOWLIN LAKE	Salmon Brook	60	59.53	2.46	2.3	4.43	5.11	1.82	PRECAMBRIAN SLATE & QUARTZITE	HALIFAX & WOLFVILLE SANDY LOAMS
ROUND LAKE	NA	78	53.76	NA	NA	3.4	NA	NA	PRECAMBRIAN QUARTZITE AND SLATE	BRIDGEWATER & DANESVILLE SANDY LOAMS, SMALL AREAS OF WOLFVILLE SANDY LOAMS
KELLY LAKE	Moser	85	56.98	2.31	NA	3.89	NA	NA	PRECAMBRIAN QUARTZITE AND SLATE	BRIDGEWATER & DANESVILLE SANDY LOAMS, SMALL AREAS OF WOLFVILLE SANDY LOAMS
SALMON RIVER BIG LAKE	Salmon	46	305.3	81.66	12.4	11.67	7.47	2.16	PRECAMBRIAN QUARTZITE AND SLATE	HALIFAX & DANESVILLE SANDY LOAMS, PEAT, SMALL AREAS OF BRIDGEWATER & WOLFVILLE SANDY LOAMS

APPENDIX B

Seasonal Mann-Kendall Trend Test - R-Code

```
########################################
# Functions used in the main function
########################################

# This function binds columns of differing lengths together and fills the shorter column with NAs
# to make it the same length as the longer column

cbind.fill<-function(...){
 nm <- list(...)
 nm<-lapply(nm, as.matrix)
 n <- max(sapply(nm, nrow))
 do.call(cbind, lapply(nm, function (x)
  rbind(x, matrix(, n-nrow(x), ncol(x)))))
}

# This calculates the slope between each pair of points and stores all the slopes
# in a list

slope.fcn <- function(X){
 slopes = list()
 N = length(X[,2])
 X[,1] <- as.numeric(X[,1])
 S = list()
 for(i in 1:(N-1)) {
  slopes[[i]] = signif((X[(i+1):N, 2] - X[i, 2]) /
   as.numeric((X[(i+1):N, 1] - X[i,1])), digits = 10)
   }
 slopes
}

# using the sign function, a pairwise comparison is done to assign a -1, 0, or +1 to
# each pair of points

signs.fcn <- function(X){
 Sgn=list()
 N = length(X)
 for(i in 1:(N-1)){
  Sgn[[i]] = sign(X[(i+1):N] - X[i])
 }
 Sgn
```

```
}

#############################################
# Correlated Seasonal Mann Kendall Trend Test
#############################################

## Input must be a data frame with first column as Dates, and second as observations
## The groupings input is a list where each member of the list contains two
## numeric elements denoting the start and end of the season : c(start month, end month).
## The number of list members will be the number of seasons

csmk.trend <-
  function(X, groupings){
  library(lubridate)
  library(dplyr)
  csmk.out = list()
  names(X)<- c("Date", "Obs") # Renames columns
  X$Date <- as.Date(X$Date)
  n.groups <- length(groupings) #Calculates number of seasons based on the number of groups specified
in the
                              #input



  ##Theil Sen Estimator is calculated using the slope function created above
  slopes=list()
  for(i in 1:n.groups){
    S.s <- 0
    S.s <- X %>% filter(month(Date)>=groupings[[i]][1] & month(Date)<=groupings[[i]][2])
    slopes[[i]] = slope.fcn(S.s)
  }

  ## Make each season a separate column of data frame x (exclude date column)
  obs.s <- list()
  for(i in 1:n.groups){
    obs.s[[i]]<- X %>%
                filter(month(Date)>=groupings[[i]][1] & month(Date)<=groupings[[i]][2]) %>%
                select(Obs)
  }
  x<- do.call(cbind.fill, obs.s) #Attach seasons using column binding function from above

  # List of column lengths for each season
```

```
n.list <- list()
for(i in 1:n.groups){
  n.list[[i]] <- length(na.omit(x[,i]))
}

n.obs <- dim(x)[1] #Gives length of longest season

# Calculate the S value using the sign function created above. Compute the sum for each season
# and store them in a list
Sgn = list()
S.sum <- rep(0,n.groups)
for(k in 1:dim(x)[2]){
  #Kendall Statistic and ties
  Sgn[[k]] = signs.fcn(x[,k])
  S.sum[k]=sum(unlist(Sgn[[k]]), na.rm=TRUE)
}

# Sum the S values for all seasons
S <- sum(unlist(S.sum))

  #Create a matrix of ranked observations for each season
  #NAs are left as NAs, and tied observations are assigned mean ranks
  Ranks = matrix(NA, ncol = n.groups, nrow = n.obs)
  for(i in 1:n.groups){
    R = rank(x[,i],na.last = 'keep', ties.method="average")
    R[is.na(R)]= (n.obs+1)/2
    Ranks[,i] = R
  }

  #Calculate Kgh matrix by creating a matrix of all S values (rows are observations, columns are seasons)
  #and then taking the inner product to yield a matrix where the number of rows and columns equals the number
  #of seasons. Each element of the matrix is a sum of S values between respective seasons
  K.temp <- do.call(cbind.fill,lapply(Sgn,unlist))
  K.temp[is.na(K.temp)]<-0



  K.mat <- t(K.temp)%*% K.temp

  #####Covariance calculations#####
  # First all the pieces required to compute the covariance between seasons (sigma.gh) are created
```

```
#Inner product of the ranks between each pair of seasons
R.sum <-  t(Ranks) %*% Ranks
n.terms <- matrix(NA, nrow=n.groups, ncol=n.groups)

# n(n_g+1)(n_h+1) term
for(i in 1:dim(x)[2]){
  for(j in  1:dim(x)[2]){
    n.terms[i,j] <- (n.obs*(n.list[[i]]+1)*(n.list[[j]]+1))
  }
}

#Correct for tied observations
correct<- rep(0, n.groups)

for(i in 1:dim(x)[2]){
  runs <- rle(sort(x[,i]))
  ties <- runs$lengths[runs$lengths >1]
  i.ext<-as.numeric(names(table(ties))) #there are ties of extent ...
  ti <- as.numeric(as.character(table(ties))) #how many times a tie of that length occurred

  #If ties exsit do this...
  if(length(ti != 0)){
  for(j in 1:length(ti)){
    cor.temp = ti[j]*i.ext[j]*(i.ext[j]-1)*(2*i.ext[j]+5)
    correct[i] <- correct[i] + cor.temp
    }
  }
  #if no ties exist, no correction is required
  else{ correct[i] <-0}
}


#### Variances of individual seasons sigma.gg #####
var.gg = rep(0, n.groups)
for(i in 1:n.groups){
  var.gg[i] = (n.list[[i]]*(n.list[[i]]-1)*(2*n.list[[i]]+5) - correct[i])/18
}

#### Covariance matrix sigma.gh #####
```

```
  sigma.s <- matrix(NA, n.groups, n.groups)

  #if there is only one season no covariance calculations are required
 if(n.groups==1){
    var.gh <- 0
    sigma.s <- var.gg

    #if there are multiple seasons, compute sigma.gh
    } else{
      sigma.s = (K.mat + 4*R.sum - n.terms)/3 - diag(correct)/18
      var.gh = sum(sigma.s[lower.tri(sigma.s)])
      diag(sigma.s) = var.gg
    }


###########################################
# Slope and intercept calculations
############################################



# create a vector of all the slopes and remove any non-finite slopes that arise if two observations were
# taken on the same day, resulting in division by zero
all.slopes <- unlist(slopes)
sni <- which(is.finite(all.slopes))

#Sen slope is the median of all finite slopes
sen <- median(all.slopes[sni])

#Compute the intercepts of each point when the Sen slope is used
int = list()
for(k in 1:n.groups){
  int[[k]] = X$Obs - sen * as.numeric(X$Date)
}
#The Sen intercept is the median of all intercepts
intercept <- median(unlist(int), na.rm=TRUE)

# Sum variances
var.total = sum(var.gg) + var.gh
```

```
# Calculate significance using critical values from normal distribution given the variance just calculated
# the cacluculation of critical values changes based on the S statistic
if(S>0){Z = (S-1)/sqrt(var.total)}
if(S==0){Z=0}
if(S<0){Z = (S+1)/sqrt(var.total)}

# Compute p-values (these are the uncorrected p values)
Pval = 2*pnorm(-abs(Z))
# Denote this crtical value as the original critical value (uncorrected)
Z.orig <- Z

##############################################
#Detrend and compute effective sample size
##############################################

#Detrend using sen slope and intercept
resids <- X$Obs - (intercept + as.numeric(X$Date)*sen)
residuals <- cbind.data.frame(X$Date, resids)
names(residuals)<- c("Date", "Obs")

## Make each season a separate column of data frame x (exclude date column)
res.s <- list()
for(i in 1:n.groups){
  res.s[[i]]<- residuals %>%
    filter(month(Date)>=groupings[[i]][1] & month(Date)<=groupings[[i]][2]) %>%
    select(Obs)
}
x.detrend <- do.call(cbind.fill, res.s)

#Ranks and acf of residuals for each season. NAs are kept as NAs, ties are assigned mean rank
dt.ranks = matrix(NA, ncol = n.groups, nrow = n.obs)
for(i in 1:n.groups){
  R.dt = rank(x.detrend[,i], na.last='keep',ties.method="average")
  R.dt[is.na(R.dt)]= (n.obs+1)/2
  dt.ranks[,i] = R.dt
}

# find the autocorrelation for lags up to n (total number of observations for each season)
rho <- list()
for(i in 1:n.groups){
```

```
rho[[i]] = acf(dt.ranks[,i], plot=FALSE, lag.max=n.list[[i]]-1)$acf[-1]
}

# store as a matrix
rho.mat <- do.call(cbind.fill, rho)

# compute the significance level of the ACF
sig<- numeric()
for(i in 1:n.groups){
sig[i] = qnorm((1 + .95)/2)/sqrt(n.list[[i]])
}

## This replaces non significant ACFs with 0
for(j in 1:n.groups){
  c.j <- rho.mat[,j]
  c.j[which(c.j< sig[j])] <-0
  c.j[is.na(c.j)]<- 0
  rho.mat[,j] <- c.j
}

#Correction factor based on significant autocorrelations
efss= matrix(NA, nrow=n.obs, ncol=n.groups)
for(j in 1:n.groups){
  for(i in 1:dim(rho.mat)[1]){
    efss[i,j] = (n.list[[j]]-i)*(n.list[[j]]-1-i)*(n.list[[j]]-2-i)*rho.mat[i,j]
  }
}

# Sum the correction factors
ess = apply(efss, 2, function(u) sum(u, na.rm = TRUE))

# compute the effective sample size correction for each season
n.ns <-numeric(0)
for(i in 1:n.groups){
  num <- 2/(n.list[[i]] * (n.list[[i]] - 1) * (n.list[[i]] - 2))
  n.ns[i] = 1 + ess[i]*num
}

### Correct Variances ####
```

```
  # if there is only 1 season
  if(n.groups==1){
    var.gg.cor <- sigma.s *n.ns

    #if there are multiple seasons
  } else{
    var.gg.cor <- diag(sigma.s) %*% n.ns
  }

  # Corrected variance
  var.cor <- var.gg.cor + var.gh

  # Calculate significance
  if(S>0){Z.c = (S-1)/sqrt(var.cor)}
  if(S==0){Z.c=0}
  if(S<0){Z.c = (S+1)/sqrt(var.cor)}

  # Corrected p value
  Pval.c = 2*pnorm(-abs(Z.c))

  #Specify the function output
  csmk.out <- data.frame("p value" = Pval, "Corrected p" = Pval.c, "Slope (units/day)" = sen,
                  "Intercept" = intercept)
  return(csmk.out)
}
```