Increasing Concentrations in Aluminum in Southwest Nova Scotia from 1980 to 2011

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Abstract

Elevated aluminum levels in rivers is known to be toxic for aquatic species, in particular *Salmo salar*; however it was only recently aluminum has been identified as a potential threat to *Salmo salar* populations in South Western Nova Scotia, Canada (SWNS) (Dennis and Clair 2012). Previously, it was thought SWNS rivers contained enough DOC to render the aluminum in rivers inactive. A key remaining question is whether aluminum levels are declining following atmospheric pollution reductions. Here we make a first assessment of long-term (1980-2011) aluminum concentration trends in three watersheds located in SWNS, as measured by weekly grab samples. Our results show that total aluminum levels have significantly increased from 1980-2011 in all three sites. Estimates of ionic aluminum levels indicate that the ionic aluminum concentration frequently exceeds the threshold for the level of aquatic health determined by the European Inland Fisheries Advisory Commission (Howells et al. 1990). Data also indicate that calcium levels have yet to recover even with declining concentrations of riverine sulfate. This new knowledge that aluminum is at toxic levels and is worsening will have implications for policy on acidification mitigation in SWNS; this is an urgent issue as the local salmon population numbers currently are declining to near extirpation levels.

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1. Introduction

1.1.   Problem and Motivation

South-West Nova Scotia (SWNS) has observed widespread acidification of its watersheds since the early 1950s (Gorham, 1957; Watt et al., 1979; Watt, 1987; Clair et al., 2004; Dennis and Clair, 2012). SWNS is downwind of sulfate (SO_4^{-2}) release in areas such as eastern United States, and central Canada (Clair et al., 2002; Clair et al., 2004). Reductions of SO_4^{-2} emissions began the 1990s resulting in many watersheds recovering from acidification in eastern North America and Europe (Clair et al., 2004; Clair and Hindar, 2005). This has not been the case in SWNS where water chemistry has not improved (Clair et al., 2002). SWNS is considered one of the most sensitive areas for acidification in Canada (Watt et al., 2000; Clair et al., 2011).

Diminishing and extirpated Atlantic salmon (*Salmo salar*) stocks have been linked with low pH, and high aluminum levels (Lacoul et al., 2011; Gensemer and Playle, 1999). Currently pH values are stable, but are not recovering to pre-acidification levels in SWNS (Clair et al., 2002; Clair et al., 2004). The acid-neutralizing capacity (ANC) in SWNS is directly related to the composition of bedrock and its slow weathering rates. Limited soil development following the previous glacial period (15,000 ka BP) has left SWNS with thin soils (Clair et al., 2008). The low levels of calcium (Ca) found in the soils was stripped with the onset of $SO4^{-2}$ deposition (Freedman and Clair, 1987; Clair et al., 2004). Recovery for Ca in soils to pre-acidification levels is predicted to occur by 2100 with 10% reductions to $SO4^{-2}$, using the Model of Acidification of Groundwater in Catchments (MAGIC) (Clair et al., 2004).

1.2. Background

1.2.1. Ionic Aluminum and Total Aluminum

Aluminum is the most abundant metallic element found in the lithosphere (Driscoll and Schecher, 1990). In neutral conditions (6.0-8.0 pH) aluminum is insoluble whereas in response to acidic or alkaline environments aluminum becomes soluble and bioavailable (Driscoll and Schecher, 1990). Total aluminum (Al_t) is the sum of all forms of aluminum -- soluble, insoluble or aluminum complexed with organics (Al_o) (Driscoll and Schecher, 1990; Dennis and Clair, 2012). Ionic aluminum or inorganic monomeric aluminum (Al_i) is a soluble form of aluminum found at pH below 6.0 (Dennis and Clair, 2012), and found to increase exponentially by a function of pH below 5.5 (Driscoll et al., 1984). As Al_i increases with decreasing pH, Al_o inversely decreases with decreasing pH (Driscoll and Newton, 1985; Driscoll et al., 1987). Al_i is affected by both the availability of organic carbon (OC) and pH (Dennis and Clair, 2012). If Al_i is exposed to OC in high enough concentrations, the OC bonds with the Al_i to create Al_o. To calculate Al_i, the difference between Al_t and Al_o was taken (Dennis and Clair, 2012). Al_i is associated with negative effects on aquatic life at concentrations >15 µg/L at pH between 6.0—5.0, and >30 µg/L at pH below 5.0 (Howells et al., 1990).

1.2.2. Aluminum Generation in Acidified Watersheds

The source of aluminum for aquatic and biological environments are minerals such as alumino-silicates and gibbsite (Driscoll and Schecher, 1990). Large portions of the aluminum found in the lithosphere is insoluble and biologically unavailable because it is tied up in alumino-silicate minerals (Driscoll and Schecher, 1990). As alumino-silcate minerals break down, a portion

can react through biogeochemical reactions (Driscoll and Schecher, 1990). The environmental processes that include aluminum are poorly understood, but it is generally believed that soils are the main source of soluble aluminum found in aqueous environments (Driscoll and Schecher, 1990).

In environments without acidic inputs aluminum mobilization is considered to be caused by organic acids from decomposing foliage. This transports the aluminum as Al_o and mobilizes iron from mineral soil horizons (Driscoll and Schecher, 1990). Bicarbonate can also help to mobilize aluminum in soils (Driscoll and Schecher, 1990).

Environments with strong acidic inputs experience increased mobilization of aluminum, and more so in locations underlain by granites with soils characterized by low base cations because of their limited ability to buffer solutions (Driscoll and Schecher, 1990). When acids, sulfuric acid and nitric acid, are in excess of base cations the acids will not be neutralized (Driscoll and Schecher, 1990; Clair et al., 2004). In these conditions acidic cations such as Al_i can be mobilized from the soils into the streams to act as a buffer (Driscoll and Schecher, 1990). As waters become more acidified aluminum becomes a dominant buffering agent in the watershed (Driscoll and Bisogni, 1984). Al_i in acidified watersheds can also be mobilized by organic acids by the same reactions found in none acidified watersheds (Driscoll and Schecher, 1990). Generally acidified watersheds in Europe and North America experience elevated levels of Al_i in watersheds (Driscoll and Schecher, 1990).

A comparative study of samples taken in northeastern USA between 1986 and 2001 following the reduction of acidic deposition in northeastern USA showed decrease to the concentrations of Al_t, Al_i, and Al_o in lake water (Warby et al., 2008). In Czech Republic and Slovakia a lake water quality study from 1980 to 2000 observed decreased emissions of SO_4^{-2}, nitrate, and ammonium, linked to recovery from acidification (Kopacek et al., 2001). As the recovery from acidification occurred aluminum played less of a role as a buffering agent in the lakes, and the decrease of average aluminum concentrations was 16 ± 13 µg/L per year (Kopacek et al., 2001). This paper also found a strong positive correlation between Al_t and SO_4^{-2} (Kopacek et al., 2001). In the United Kingdom following reductions in acid rain a noticeable recovery in pH and decreasing Al_t concentrations was found in soil solutions during a 12 year study from 1995 to 2006 (Vanguelova et al., 2010). A comparison study between two close watersheds the West Bear, and the East Bear, in Maine, where the West Bear received additions of ammonium and SO_4^{-2}, the results show aluminum acting as a buffer and Al_t increased four-folds over the sampling period of 1989 to 2007 in the treated watershed (Fatemi et al., 2012).

In Birkenes, Norway, a 30 year study looked at acid episodes during recovery from acidification (Wright, 2008). This study did not directly look at aluminum concentrations, although it did look at other important water quality parameters associated with acidification such as ANC, and SO_4^{-2} (Wright, 2008). This study found that, in the 1990s, SO_4^{-2} levels dropped as the ANC rose, and the frequency and severity of acidic episodes decreased (Wright, 2008). Under these conditions it is mostly likely the case that Al_t concentrations would have decreased along with the SO_4^{-2} reductions, but this was not reported.

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1.2.2.2.   Seasonal Patterns of Aluminum

Abundance of Al_t varies throughout the year in stream water (Meranger, 1989). Average Al_t levels in stream discharge in Shelburne NS, show a seasonal variation of high Al_t, 380 μg/L, in the fall, and lower Al_t, 200 μg/L, in the spring (Meranger, 1989). The solubility of Al_t is highly dependent DOC content and pH levels (Driscoll and Schecher, 1990). DOC in SWNS has a bimodal trend with peaks in spring and fall associated with snowmelt and heavy rains respectively (Clair et al., 2008). Umemura et al (2003) observed low pH and peaks of Al_t occurring simultaneously in Japanese soil solutions. A similar trend was also observed in Central Europe with Al_t reaching elevated levels in the spring and fall, concurrently with low pH levels (Kopacek et al., 2000).

1.2.2.3.   Aluminum Episodes

Aluminum episodes are the occurrence of elevated Al_t and Al_i levels over a short period, such as days. Areas effected by aluminum episodes generally have soils and bedrock that do not contain abundant of base cations (Monette and McCormick, 2008). Aluminum episodes occur concurrently with storm events, and usually have a drop in pH associated with them (Soulsby et al., 1995). These episodes usually take place during spring snow-melts and fall storms (Monette and McCormick, 2008). The drop in pH allows for an increased mobilization of Al_t and Al_i (Monette and McCormick, 2008). Short-term exposures of acidic pH and high Al_i have been found to be detrimental to *Salmo salar* especially so when in the smolt life phase (Monette and McCormick, 2008; Magee et al., 2003). Al_i episode is very damaging to *Salmo salar* populations

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in acidified watersheds, as the smolt phase occurs in the spring, when a substantial amount of aluminum episodes occur (Monette and McCormick, 2008).

1.2.3. Acidification Trends in SWNS

1.2.3.1.   Limited pH Recovery

Acidification in SWNS has yet to recover to pre-acidification levels (Watt et al., 1979; Clair et al., 2002; Clair et al., 2004; Korsi et al., 2013). Even with decreases in SO_4^{-2} deposition since the early 1980s, pH in SWNS has not recovered and is the only studied location in North America and Europe not to have seen recovery (Clair et al., 2004; Clair et al., 2011). Extended acid rain deposition has leached the base cations from the soils, and the anions must be neutralized by an oppositely charged cation (Driscoll and Newton, 1985; Clair et al., 2004). The slow weathering rate found in the underlying bedrock, has limited the amount of base cations reintroduced into the soils (Clair et al., 2004). With the absence of base cations, aluminum acts as a replacement in conditions where it is soluble (Clair et al., 2004). Clair et al (2004) found that the pH in SWNS was in equilibrium with SO_4^{-2} deposition and neutralization capacity (Clair et al., 2004). In SWNS pH is expected to recover to pre-acidified levels only if there is continued reduction of SO_4^{-2} (Clair et al., 2004).

1.2.3.2.   Projected Calcium Levels

In SWNS Ca is the main contributing base cation in calculating ANC (Clair et al., 2011). The bedrock in SWNS is characterized by generally having little buffering capacity as well as low

levels of Ca (Clair et al., 2007). The bedrock found in SWNS comprises three main units, the South Mountain Batholith, the Goldenville Group and the Halifax Group, which all have low levels of Ca (Watt et al., 1983). In SWNS bedrock has slow weathering rates, which results in limited amounts of cations being reintroduced into the soils (Bobba and Lam, 1989; Clair et al., 2004).

Clair et al (2004) projected Ca, pH and ANC in Nova Scotian rivers using the model MAGIC, with three scenarios, no change to SO_4^{-2} deposition, a 10% reduction of SO_4^{-2} per decade, or a 20% reduction of SO_4^{-2} per decade. Even with the reduction of 20% of SO_4^{-2} per decade, Ca levels were not predicted to recover to pre-acidified levels in most rivers in the next 100 years (Clair et al., 2004). This limits the ability to neutralize acidic deposition of watersheds in Nova Scotia. With reductions of 10% per decade pH is predicted to recover to pre-acidified levels by 2070 in most Nova Scotian rivers (Clair et al., 2004). Recoveries to Ca and pH are not expected to occur in the near future in Nova Scotian watersheds.

1.2.4. *Salmo salar* Trends in SWNS

The Southern Upland *Salmo salar* population in Nova Scotia was recommended to be listed as endangered by Committee on the Status of Endangered Wildlife in Canada in 2010 (COSEWIC, 2011). This population has been declining over the past century (Watt el al, 1983; COSEWIC, 2011; DFO, 2013)). A 2008 study to observe juvenile *Salmo salar* populations detected their presence in only 20 of 51 rivers surveyed which once held populations (COSEWIC, 2011). Acidification is thought to be the leading cause in the decline of the Southern Uplands *Salmo salar* population (COSEWIC, 2011; Dennis and Clair, 2012).

Watt et al (1983) looked at historical angling records in SWNS of rivers underlain with the South Mountain Batholith (SMB), the Goldenville Group, and the Halifax Group. Since the 1940s there have been declining angled *Salmo salar* in SWNS (Watt et al., 1983). The Nova Scotia Southern Upland *Salmo salar* population has declined by 61% of mature individuals in the three previous generations (COSEWIC, 2011). Two major rivers, the Gold River and the St Mary's River, have seen declines in *Salmo salar* populations of 88% and 99% respectively since the 1980s (DFO, 2013).

1.2.4.1. *Mechanisms for Aluminum Toxicity in Salmo salar*

When *Salmo salar* is exposed to Al_i life expectancy decreases (Monette, 2007; Magee et al., 2003). It is believed that Al_i is an issue because it is only biologically available under conditions where the majority of life did not evolve (Driscoll and Schecher, 1990). There are multiple mechanisms for aluminum toxicity for Atlantic salmon. The epithelium of *Salmo salar* gills are vulnerable to Al_i, positively charged Al_i bonds with the negatively charged gills causing mucous build-up resulting in suffocation (Monette, 2007; Dennis and Clair, 2012). A laboratory experiment has shown that episodic exposure to Al_i is not as detrimental for *Salmo salar* smolts as constant exposure to Al_i (Magee et al., 2003), although they do require more than two weeks to recover from exposure to Al_i (Nilsen et al., 2013).

The substantial change which occurs to the physiology of *Salmo salar* during the parr-smolt transformation is one of the most susceptible times for aluminum toxicity (Rosseland and Skogheim, 1984; Rosseland et al., 2001). This is the period when the salmon are preparing to move from freshwater to saltwater (Monette, 2007). Multiple changes to physiology occur, and these natural pressures with the additional stress from aluminum toxicity leaves the juvenile salmon

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vulnerable (Monette, 2007). The European Inland Fisheries Advisory Commission (EIFAC) suggests that 15 µg/L of Al_i not be exceeded where pH is between 5.0 and 6.0, for safety of fish species and macroinverebrates, and at pH below 5.0 show not surpass 30 µg/L Al_i (Howells et al., 1990).

1.3. Knowledge Gaps

In SWNS studies examining aluminum influence on watersheds are limited, which leaves knowledge gaps in this area. Firstly, there have not been any studies conducted in SWNS which look at increasing trends of aluminum. Finally, the chemical influences on aluminum peaks are still not fully understood (Driscoll and Schecher, 1990). A greater understand of the occurrences of aluminum peaks in SWNS would be beneficial to Al_i predictions.

1.4. Research Questions and Objectives

Here we use the analysis of long-term data from Environment Canada to observe long-term trends and seasonal patterns at our three sites in SWNS. This study aims to answer the following four research questions:

1. Are there long-term trends in total aluminum in SWNS?

2. How do trends in aluminum relate to Ca, DOC, SO_4^{-2} and pH?

3. What is the reliability of existing models to predict Ali? What are the limitations of the model produced by Dennis and Clair (2012) in predicting Al_i? How do other empirical models using same data perform?

4.   What do these models predict for ionic aluminum values, and what is there

relationship to the Al_i EIFAC threshold for aquatic life?

2. Methods

2.1. Study Area

Water quality data was collected at three site locations across SWNS within close proximity to Kejimkujik National Park (KNP), approximately 60 km inland from the Atlantic Ocean (Figure 2.1). The three sites are Mersey River (MR), Moose Pit Brook (MPB) and Pine Marten Brook (PMB). The area is found in a temperate climate, experiencing 1352 mm of mean annual precipitation, with 56% occurring between November and April (Clair et al., 2001). This area was recently glaciated in the last 15 ka, which created drumlins and left the area with limited soil development (Clair et al., 2008). The bedrock is comprised of Meguma Group slate, Goldenville greywackes and South Mountain Batholith. All of these rock units are characterized by their low levels of Ca. The soils around KNP in pre-acidified times had base cations which reflected proportions found in the underlying bedrock. These base cations were stripped from the soils through wet deposition of acid as precipitation hit the area. The study area surrounding KNP has seen a reduction in sulfur deposition from the 1980s of approximately 45% (Clair et al., 2008). All three of the sites experienced low levels of human development, with some forest harvesting and roads in the catchments.

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Figure 2.1 Site locations with respect to Kejimkujik National Park. Black box with white center indicates sampling station in MR. Grey box with black center indicates the sampling location of PMB, and the Canadian Air and Precipitation Monitoring Network (CAPMoN) Site. After Clair et al., 2008.
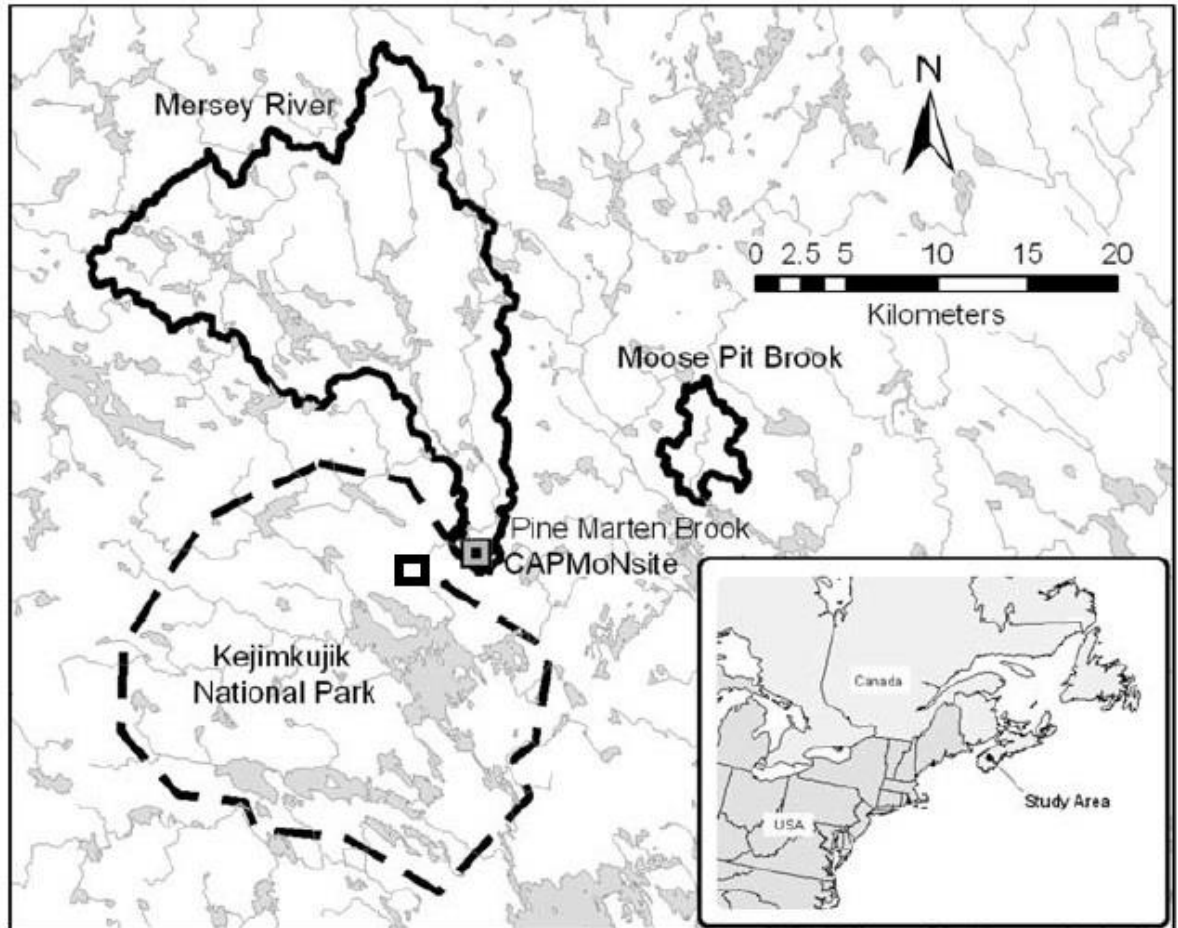
2.1.1.   Mersey River

The MR site is the largest of the three sites encompassing 297 km^2. The sampling site for MR is upstream of Kejimkujik Lake. The geologic makeup of the catchment is South Mountain Batholith granite, Halifax Group slates with some quartzites, and Goldenville Group greywacke (Bobba and Lam, 1989). The catchment's soils are primarily glacial tills made of acidic sandy loams or organic peat and are low in Ca (Bobba and Lam, 1989). The MR drainage is dominated by coniferous forest (94%) with minimal hardwood and mixed forests (Bobba and Lam, 1989). The sampling site is located one kilometer SW of the Maitland Bridge on Nova Scotia Trunk 8 Highway, just below Mill Falls.

2.1.2.   Moose Pit Brook

MPB is located east of the MR catchment (Fig 2.1) occupying 17 km^2 (Clair et al., 2008), and shares the same rock units as MR. The structural layout of the rock units at the MPB and PMB catchments (Figure 2.2). The MPB soils are defined as the Gibraltar Series characterized by extremely permeable sandy loam with granitic pebbles to cobbles (MacDougall et al., 1969). Forests found in MPB are similar to those found at the nearby MR (Clair et al., 2008).

2.1.3.   Pine Marten Brook

Pine Marten Brook (PMB) is the smallest of the three site locations and encompasses 1.3 km^2. The catchment is located along the north eastern boundary of KNP with 42% of the catchment lying outside the park (Fig 2.1). At this catchment there are two sampling sites, Upper Pine Marten

and Lower Pine Marten (Fig 2.3). The upstream site is located above a gravel road with a culvert, and the lower site is below a bog, allowing for observations of inputs of natural acids associated with wetlands. PMB catchment has minimal outcrops. Digging soil pits revealed that the catchment is underlain by the Greenfield Formation and the Cunard Formation of the Halifax Group (Bachiu, T., 2010). The soils and tills found at PMB are defined as part of the Bridgewater Series (MacDougall et al., 1969), characterized by sandy clay loams with low permeability and steep drumlins with minimal soil development (Bachiu, T., 2010).

Figure 2.2 Geologic map of area that includes MPB and PMB from White, 2007.

LEGEND

LATE DEVONIAN

SOUTH MOUTAIN BATHOLITH

biotite monzogranite; medium to course grained

hornfels with andalusite, biotite and cordierite porphyroblasts

LATE CAMBRIAN TO EARLY ORDOVICIAN

HALIFAX GROUP

Greenfield formation: black slate to metasiltstone; locally contains abundant sulphide minerals

Cunard formation
black slate to metasiltstone interbedded with metasandstone; locally contains abundant sulphide minerals

LATE NEOPROTEROZOIC TO MIDDLE CAMBRIAN

GOLDENVILLE GROUP

Moshers Island formation
coticule beds interlayered with green-grey slate and metasiltstone; minor metasandstone

Government Point formation
metasandstone interbedded with green-grey metasiltstone and slate; overall fining upward sequence

SYMBOLS

Inferred syncline

Inferred fault zone

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Figure 2.3 Location of upper and lower sampling sites, and the CAPMoN site in PMB catchment with respect to Hwy-8, and MR (Bachiu, T, 2010).
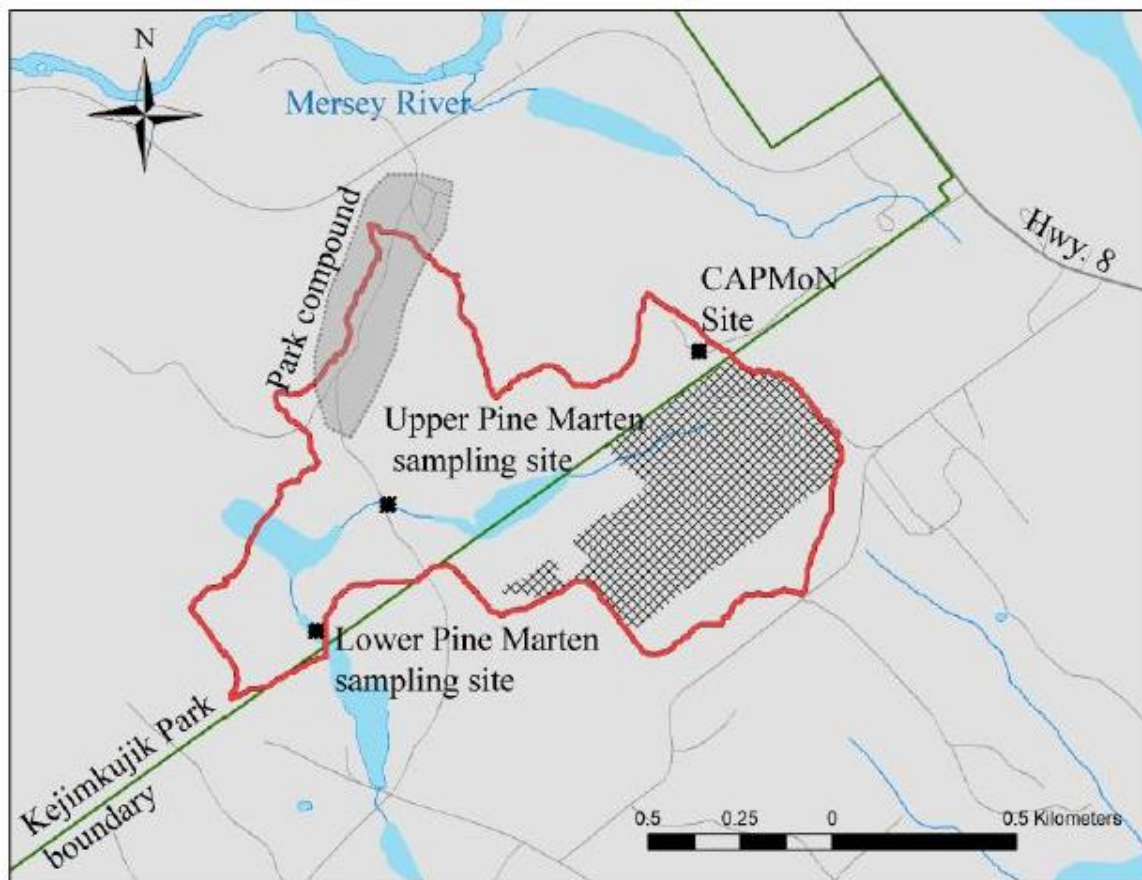
2.2. Data Sources

2.2.1. Water quality Sampling Frequency and Duration

Each site has a different length of data collection. Water samples at MR began to be taken weekly or more frequently starting in 1980, while samples at MPB began to be gathered in 1983. Sampling in the PMB catchment started at the end of 1990. Water sampling continued until July 2011 for all three sites. Samples were analyzed in Moncton, New Brunswick at the Environment Canada laboratory. The laboratory has accreditation by the Canadian Environmental Analytical Laboratory Association (CAEL), and the Environment Canada Acid Precipitation program inter-calibration (Clair et al., 2008).

2.2.2. Total Organic Carbon

Total organic carbon (TOC) is the combination of dissolved organic carbon (DOC), and suspended organic carbon. In SWNS rivers it is assumed that TOC is within 5% of DOC (Clair et al., 2007, Dennis and Clair, 2012). For this reason TOC is considered equivalent to DOC in the study. When analyzing for TOC prior to March 1995, an automated UV-persulfate wet oxidation method (Clair et al., 2008) was used. This method was found to be consistently under calculating by ~28% (Koprivnjak et al., 1995). TOC measurements calculated prior to March 1995 were adjusted by 28% to account for this error. From March 1995 onwards a Shimadzu HTC instrument was used for analyses of TOC (Clair et al., 2008).

2.2.3. Laboratory Analysis of Aluminum

2.2.3.1. *Total Aluminum*

During the study two methods to calculate Al_t were used, from 1980 to 2008 Atomic Absorption Spectroscopy (AAS) was used, and from 2008 to 2011 Inductively Coupled Plasma Optical Emission Spectrometry (ICP/-OES) was used. AAS can be used to find trace metals from water samples by exciting the elements to emit an electron, which will have a given wavelength depending on the element (Walsh, 1955). ICP/-OES measures the emission of photons from atoms and ions when exposed to radiofrequency (Mermet, 2005; Hou and Jones, 2000). Water samples are vaporized, when photons are excited the wavelength was measured (Hou and Jones, 2000). Wavelength of a photon is associated with an element or ion, and the number of photons is directly proportional to the concentration of the elements which they were emitted from (Mermet, 2005; Hou and Jones, 2000).

2.2.3.2. *Ionic Aluminum.*

In the study Al_i was not measured directly, instead it was estimated through empirical formulas. An empirical formula was created by Dennis and Clair (2012) who also did not measure Al_i directly, but estimated it by calculating Al_t and Al_o and taking the difference of the two parameters. Measuring Al_i has been problematic in the past, resulting in variable results (Dennis and Clair, 2012). Sampling reported in Dennis and Clair (2012) took place during the fall, 2006 using samples from 97 rivers in Atlantic Canada with minimal disturbance by anthropogenic sources.

Dennis and Clair (2012) created a formula to predict Al_i using linear regression with the independent predictors Al_t, pH, and TOC. Their linear model predicating Al_i is shown in Equation 2-1, with a resulting $r^2 = 0.68$,

$$Al_i = -166.5 + 0.5 * Al_t - 5.06 * TOC + 23.5 * pH \quad \text{2-1}$$

The majority of values in our sites have pH values, >98%, are below 6.0 (Figure 3.2). Many papers summarized in Driscoll and Schecher (1990) found Al_i levels above 4-8 µg/L to be detrimental to a variety of aquatic species, for this reason we found it suitable to apply the threshold for aquatic life of 15 µg/L of Al_i set by for the sampling period (Howells et al., 1990).

2.2.4. Laboratory Analysis of ANC

ANC is used to predict a solutions buffering ability (Wright, 2008). There are two commonly used methods to calculate ANC gran titration (ANC_g) and calculated ANC (ANC_c). The ANC_c method used for ANC values, which takes the difference between the base cations and anions (Equation 2-2). Negative values have limited buffering capacity from the excess of anions compared with cations.

$$ANC_c = Ca^{+2} + Mg^{+2} + Na^+ + K^+ - SO_4^{-2} - NO_3^- - Cl^- \quad \text{2-2}$$

2.2.5. Laboratory Analysis of pH

The electrometric method was used through the sampling period to calculate pH (EPA, 2004).

2.2.6.   Laboratory Analysis of Sulfate

Analysis of SO_4^{-2} in the laboratory used Ion Chromatography (IC) through the sampling period. This process is calculated by running a sample solution through column, depending on the ion's charge strength, they will adhere to the column (Weiss, 1995). The concentration of the ions can then be calculated by how many ions bonded with the column (Weiss, 1995).

2.2.7.   Laboratory Analysis of Calcium

Analytical calculation of Ca from the start of the sampling period in 1980 to November 2001 used AAS. From November 2001 to November 2011 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used to calculate Ca concentrations. ICP-MS detects trace elements by ionizing a sample with an inductively coupled plasma, in this case argon, and then running mass spectrometer on the sample to find the concentrations (Beachemin, 2008).

2.2.8.   Discharge

Discharge calculations at MR began in 1968 while MPBs began in 1981. Clair et al. (2008) calculated the discharge at PMB using the ForHyM2 hydrological model. Yanni et al. (2000) modeled the discharge at the MR and MPB catchments and found that discharge rates were similar, and concluded that the hydrogeological conditions have limited spatial variability in this area, and was used to predict PMB discharge. This technique has given similar results throughout the Kejimkujik area with the exception of storm flow events being occasionally misrepresented with low values (Clair et al., 2008).

2.3. Methods Used to Determine Long-Term Patterns of Total Aluminum and Ionic Aluminum

Using the R Statistical Package, the time-series data was analyzed to find long-term trends of Al_t and Al_i and major water quality parameters. For trend analysis, water quality values were averaged to generate weekly values and we used interpolation if a week was not sampled. Monthly averages were calculated on a site dependent basis over the sampling period. To eliminate seasonal trends from the data the overall monthly averages were also subtracted from samples collected in the respective month. This removed the seasonal fluctuation, and examined the underlying trend. We applied the gls function to the updated time series data to determine the overall trend in Al_i. The gls function allows for a correlation structure to be included, which we used first order autoregressive correlation structure, to allow for a time-dependence structure, and remove any violations of independent residuals. Using this model we were able to determine the overall trend in Al_t and Al_i through time. The gls function is contained in the 'nlme' package (Pinheiro et al. (2013).

Testing for trend significance was done using two tests, significance by fitting the generalized least squares with the gls function trend-line and by the Mann Kendall test. Using either tests, a result was found significant if p<5%.

2.3.1.   *Preliminary Data Analysis*

To ensure that any faulty samples were not included in the data, we plotted water quality parameters against discharge to ensure that they occur during a flooding event, as there would be no justification for values that physically high without a flooding event. If this critierium was met, values were excluded on the basis that they were most likely were the result of machine-error.

2.4.   Evaluation of existing Empirical models to estimate Ali

To evaluate the linear model generated by Dennis and Clair (2012) for estimates of Al_i, we requested their original data. We examined the range of these original data values for the predictor variables used in the Dennis and Clair (2012), model (Alt, DOC, pH) with those measured in our Keji catchments, and we examined the residuals of their model to determine if they violated any linear model assumptions, or were the best possible fit to these data.

2.5.   Creation of New Al_i Empirical Model

To create an alternate empirical model for Al_i prediction we used a process to determine the best predictors, which used the Bayesian Information Criterion (BIC). Adding additional parameters will always increase the R^2 term, and thus using the BIC, which allows for a penalization of terms better to determine the fit, was a more robust method for fitting these data

(Kadane and Lazar, 2004). We used all the parameters which both Dennis and Clair (2012) and our study shared in common as possible predictors when using this analysis.

2.5.1.   *Preliminary Data Analysis of New Model*

After applying our new model to the dataset, we found that in limited instances predicted values of Al_i were unrealistic. In these cases the predicted Al_i was larger than Al_t. There was four occurrences of this happening over the sampling period. These instances were removed from all data analysis to have a consistent, and comparable dataset.

3. Results

3.1.   Long-term Al_t Trends

After removing the seasonal variation, there was an increase in Al_t over time at all sites (Table 3.2). The trend was significant at all sites as determined by the Mann Kendall test, and was significant at MR and MPB determined by which significance test when fitting the generalized least squares. There was a strong seasonal pattern associated with Al_t, with the highest levels seen at summer and fall at all sites (Figure 3.1). When the analytical method for calculating Al_t changed from AAS to ICP/-OES in 2008, there was not an observable change in calculated values as a results.

Of the three sites, MR had the largest rate of increase for Al_t, with an increase of 2.15 µg/L per year, as determined by the slope of the fitted gls line (Table 3.2). Extreme values of Al_t at MR appeared more frequently between 2000 and 2011 (Figure 3.1a). A consistent increase of decade means was observed at MR (Table 3.2).

MPB had a significantly increasing trend of Al_t of 1.4 µg/L per year (Table 3.2). MPB saw no extremely high Al_t values, above the standard seasonal variation (Figure 3.1b). Decadal means also increased at MPB throughout the sampling period (Table 3.2).

The significant increasing trend found at PMB was 1.1 µg/L per year (Table 3.2). PMB frequently had Al_t values peaking above the seasonal patterns between June and August (Figure 3.1c).

3.2. Calcium and its relationship with Sulfate and Al_t

There are significant decreases in Ca for two of the three sites, but no consistent direction of change in Ca concentrations among the sites (Table 3.2). Decadal means do not show a consistent trend for all three sites. Ca does have a seasonal variation, which varied between each site (Figure 3.2).

MR has significantly decreasing Ca concentrations over the sampling period (Table 3.2). Ca levels at MR peak during the fall September through to November (Figure 3.2a). Ca at MPB does not have a significant change (Table 3.2). Peaks of Ca concentrations at MPB occur between August and October (Figure 3.2b). Ca in PMB is significantly declining in concentration (Table 3.2). Ca peaks range in occurrence from July to October (Figure 3.2c).

SO_4^{-2} has a significantly decreasing trend at all site locations (Table 3.2; Figure 3.2). At all sites the occurrence of yearly extreme peaks of sulfate has been reduced in frequency since the early 2000s (Figure 3.2). A strong relationship between SO_4^{-2} and Ca is observable at all sites (Figure 3.2), except there has been a decoupling of SO_4^{-2} and Ca spikes in the last decade.

At MR a strong association was observed between Ca and SO_4^{-2} (Figure 3.2a). Elevated levels of Ca related with higher SO_4^{-2} content (Figure 3.2a). From 2000 to the end of the sampling period, as SO_4^{-2} declined, the values of both parameters became comparable in value (Figure 3.2a).

An association of Ca and SO_4^{-2} is evident at MPB (Figure 3.2b). At MPB, spikes in SO_4^{-2} generally occur concurrently with spikes in Ca, although SO_4^{-2} levels remain elevated for months

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after the Ca levels has dropped after peak events (Figure 3.2b). Spikes of Ca and SO_4^{-2} become decoupled in the last decade (Figure 3.2b).

PMB shares a similar Ca and SO_4^{-2} relationship to MPB (Figure 3.2c; Figure 3.2b). Elevated SO_4^{-2} levels occur simultaneously to peaks in Ca concentrations, with Ca levels quickly declining over the following weeks, with SO_4^{-2} remaining at elevated levels for months (Figure 3.2c). Spikes of Ca and SO_4^{-2} become decoupled in the last decade (Figure 3.2c).

MBP and PMB have strong observable seasonal trends of peaks in fall in the sample period. At PMB similar to MPB, spikes in calcium are closely followed or occur simultaneously with sulfate spikes (Figure 3.2C). Ca levels than drop during the following week, with sulfate plateauing at elevated levels for weeks to months. At MR, elevated levels of SO_4^{-2} also occur concurrently with elevated Ca, although Ca levels remain elevated for as long as SO_4^{-2} is (Figure 3.2A).

The ratio of Ca to Al_t has a significantly negative trend at all site locations (Table 3.2), as a result of the proportion of Al_t increasing as the quantity of calcium is declining, MR and PMB, or remaining constant, MPB (Table 3.2). The ratio of Al_t/Ca also shows a strong seasonal trend in all locations. At all sites there are yearly Al_t/Ca peaks in the summer and late fall (Figure 3.3). At MR along with the peaks in the summer and fall, there are also winter peaks that do not occur annually (Figure 3.3a).

3.3. DOC, ANC_c and pH Trends

3.3.1. DOC

There is a significant increase of DOC at all sites in the study area (Table 3.2). The Mann Kendall test finds all sites significant, $> 95\%$, and PMB is also significant under the generalized least squares. At all sites the decade 1990 – 1999 had the lowest mean (Table 3.2). The following decade 2000-2011 had the highest mean in all sites (Table 3.2). DOC shows a strong seasonal pattern with the highest values in the fall (Figure 3.4). Seasonal DOC trends appear to be strongly associated with Al_t (Figure 3.4). This strong association is also seen in scatter plots between the two variables, DOC and Al_t (Figure 3.5).

3.3.2. ANC_c

All sites have significant ANC_c trends as determined from both the Mann Kendall and generalized least squares. All sites have an increasing ANC_c trend (Table 3.2). All sites have negative mean values in every decade (Table 3.2). MPB has the largest increase, and the closest decade mean to neutral (Table 3.2). MR has the lowest rate of increase, and the lowest decade and overall means (Table 3.2). For the first time after 2000 MR began to observe positive ANC_c values (Table 3.2).

3.3.3. pH

The mean pH found in every decade at all sites is determined to be acidic. Table 3.2 shows the mean pH for all sites is <6.0, a level below which Al_i toxicity is detrimental to aquatic biota

(Dennis and Clair, 2012). MR and MPB have every decadal means close to 5.0, and 4.7 respectively (Table 3.2). The lowest pH value observed, 3.7 on March 3, 1983, was found in MR. There is also a weak positive correlation between pH and Al_t at MR and MPB, and with decreasing levels of pH there are increasing levels of Al_t (Figure 3.6).

3.4. Prediction of Al_i using Existing Model

Samples collected by Dennis and Clair (2012) had Al_t values range from 12.47 to 464.03 µg/L, and Al_i values range from 0.57 to 199.84 µg/L (Table 3.1). When the range of the dataset used to create a linear model exceeds the values used to derive the model, the projections are less reliable, and the values are no longer being interpolated, but extrapolated. Mean levels of all water quality parameters used to predict Al_i fell within the range of data collected by Dennis and Clair (2012) (Table 3.1; Table 3.2).

Table 3.1. The ranges of parameters used in the prediction of Al_i during Dennis and Clair's (2012) sampling period, and our site locations. Al_i values at MR, MPB, and PMB were calculated using the linear model Equation 2-1, the majority of Al_i values calculated using this parameter were negative (**bold**).

	Dennis and Clair (2012)		Mersey River		Moose Pit Brook		Pine Marten Brook	
	Max	Min	Max	Min	Max	Min	Max	Min
Al_t (µg/L)	464.03	12.47	609	20	552	9	796.2	47.7
Al_i (µg/L)	199.84	0.57	200.7	**-111.55**	103.11	**-149.873**	218.9	**-40.698**
TOC (mg/L)	29.1	2.4	28	2.5	43.2	2.6	27.4	1.9
pH	8.25	4.05	6.9	3.7	6	4.28	8.9	4.5
Ca (mg/L)	28	0.49	1.9	0.32	2.35	0.2	4.34	0.3
SO_4^{-2} (mg/L)	21.9	0.5	8.8	0.77	8.23	0.3	25.39	0.27

Upon applying Dennis and Clair's (2012) model (Equation 2-1) to the dataset we found that over 70% of calculated Al_i values were below zero, a physically impossible value (Figure 3.7). By examining the linear model we found that there was a violation of independent random variables. The distribution of the data's residuals was inconsistent with expectations with the distribution being more log-normal than normal (Figure 3.8).

Using the original dataset used to fit the model we were able to refit Dennis and Clair's (2012) model and determine if there were any improvements that could be made. By taking the natural log of the data, and centering the variables we generated a model (Equation 3-1).

$$Al_i = exp\left\{ \frac{1.1(Al_t - 178.24)}{114.78} + \frac{-0.36(TOC - 9.72)}{5.1} + \frac{0.43(pH - 6.77)}{0.95} + 2.94 \right\} \quad \text{3-1}$$

Equation 3-1 has lowered the R^2 value from 0.68 to 0.54, but removed the problems with its residuals. While the R^2 value decreased, the BIC decreased indicating a better fit to the data. This can be observed in Figure 3.9, where the parabolic trend has been removed. The residuals are randomly distributed as is desired, and there are no violations of model assumptions.

3.5.   Prediction of Al_i using a Newly Created Model

We created a new model for Al_i prediction using BIC criterion in a linear model (Appendix B). We used the parameters Ca, TOC, Fe, Al_t, and SO_4^{-2} to predict Al_i. Of the variables previously used in Equation 2-1, it was determined that pH was not a significant predictor of Al_i. We removed the variable Fe from the model, as there was not a known causal relationship between Fe and Al_i. Al_t and Fe are known to react with organic carbon in acidic conditions in a similar fashion (Jansen, 2003), but the lack of a causal relationship between Fe and Al_i does not exist, so the addition of Fe

as a model parameter was unnecessary. After rerunning the model fitting algorithm (Appendix B), with the exclusion of the variable Fe we then created a new formula Equation 3-2.

$$Al_i = exp\left\{\frac{0.94(Al_t-178.24)}{114.78} + \frac{-0.27(TOC-9.73)}{5.1} + \frac{0.32(pH-6.77)}{0.95} + \frac{0.21(SO_4-3.71)}{3.7} + 2.95\right\}\ 3\text{-}2$$

When we examined the residuals of the model (Equation 3-2), we found that they did not violate any model assumptions (Figure 3.10). Equation 3-2 has an R^2 value of 0.57.

When Al_i is predicted using the linear model Equation 3-2 there is significant increase in Al_i at MR, and MPB over the sampling period. All three catchments have Al_i levels higher than the recommended threshold at least once per year during the study period (Figure 3.7). The majority of Al_i episodes occurred in the fall or springtime (Figure 3.7). All site locations have mean value within 5 µg/L of the EIFAC 15 µg/L guideline for aquatic health for Al_i.

MR has the highest rate of increase in Al_i (Table 3.2). In addition to the increase in the annual mean, extreme peaks of Al_i are also increasing in frequency and magnitude over the study period, with much larger extremes in the last decade (Figure 3.7a). Decadal means at MR increased every decade in the sampling period from 10.3 to 14.2 µg/L; the annual mean concentration for Al_i in the last decade is only 1 µg/L below the maximum recommended value for Al_i. In a given year MR is exceedance of the toxic threshold during multiple events (Figure 3.7a). In 1996, for instance, Al_i exceeded guidelines from July1st to December 31st (Figure 3.7a).

MPB exceeded the Al_i threshold on an annual basis, usually once per year (Figure 3.7b). Al_i events occurred from July through to October, peaks remain elevated two to three weeks before decreasing in Al_i concentrations (Figure 3.7b). Decadal means of Al_i at MPB increased each decade during the sampling period (Table 3.2).

PMB is the only site without a significant trend of Al_i (Table 3.2). PMB observed the highest Al_i at 501.7 µg/L on July 29, 2003. PMB

Table 3.2   Site trends, means, and ranges of river water parameters. Bold trend data is significant under Mann-Kendall Test (p<5%). Trend data with * is significant under generalized least of squares (p<5%).

	Mersey River				Trend/yr	Moose Pit Brook				Trend/yr	Pine Marten Brook			Trend/yr
	Concentration [mean (range)]					Concentration [mean (range)]					Concentration [mean (range)]			
	1980-2011	1980-1989	1990-1999	2000-2011	1980-2011	1983-2011	1983-1989	1990-1999	2000-2011	1983-2011	1990-2011	1990-1999	2000-2011	1990-2011
Alt (µg/L)	188 (20-609)	175 (20-370)	187 (60-400)	214 (89-609)	**2.15***	229 (9-552)	211 (61-520)	229 (29-552)	246.4 (9-545)	**1.4***	139 (48-722)	133 (57-650)	144 (48-722)	**1.1**
Eq 2-1 Al$_i$ (µg/L)	-2.9 (-112-898)	-10.3 (-112-78.9)	-0.4 (-46-92.9)	7.9 (-35-898)	0.82	-23.3 (-150-103)	-33.0 (-143-103)	-18.7 (-112-63)	-19.9 (-150-85)	0.46	-5.3 (-41-329)	-9.5 (-41-137)	-1.5 (-41-329)	0.82*
Eq 3-2 Al$_i$ (µg/L)	11.7 (2.1-302.4)	10.3 (2.1 -48.3)	11.9 (4.9-50.2)	14.2 (6.2-302.4)	0.22*	10.4 (1.3-77.6)	8.9 (2.2-77.6)	10.9 (2.8-39.0)	11.3 (1.3-67.1)	**0.07***	11.5 (4.7-501.7)	9.9 (4.7-162)	13.1 (5.4-501.7)	0.27
pH	5.0 (3.7-6.9)	5.0 (3.7-6.1)	5.0 (4.5-6.3)	5.0 (4.2-6.9)	-0.0019	4.7 (4.3-6)	4.7 (4.4-5.5)	4.7 (4.3-6)	4.7 (4.3-5.9)	0.0029	5.3 (4.5-8.9)	5.1 (4.5-6.9)	5.5 (4.6-8.9)	0.042
H+ (meq/L)	11.9 (0.12-198)	11.7 (0.8-198)	11.8 (0.5-31.4)	12.3 (0.1-67.1)	0.057	20.7 (1.0-52.1)	21.4 (3.1-39.5)	20.6 (1.0-52.1)	20.1 (1.3-49.7)	**-0.13**	6.1 (0.001-31.4)	8.2 (0.1-31.4)	4.2 (0.001-26)	**-0.4***
DOC (mg/L)	9.6 (2.5-28)	9.6 (3.4-28)	8.9 (2.5-19.7)	10.4 (4.4-18.3)	0.04	16.3 (2.6-43)	16.2 (4.2-42)	15.3 (2.6-43.2)	17.3 (5-39.1)	0.058	6.7 (1.9-27)	6.0 (1.9-27.4)	7.4 (2.6-27)	**0.16***
ANC$_c$ (mg/L)	-2.7 (-14-0.2)	-2.8 (-14- (-0.3))	-2.7 (-4.9- (-0.1))	-2.6 (-5.3-0.2)	0.034*	-1.1 (-5.4-3.0)	-1.5 (-5.4-1.8)	-1.2 (-4.6-2.8)	-0.6 (-3.5-3.0)	**0.16***	-2.2 (-16.5-5.0)	-2.8 (-16.5-1.4)	-1.52 (-10.8-5.0)	**0.043***
Ca (mg/L)	0.9 (0.3-1.9)	0.9 (0.4-1.8)	0.8 (0.3-1.6)	0.9 (0.4-1.9)	-0.0021	0.85 (0.2-2.4)	0.8 (0.2-2.0)	0.8 (0.3-2.35)	0.9 (0.4-2.0)	0.001	0.7 (0.3-4.3)	0.7 (0.3-4.3)	0.7 (0.4-3.0)	**-0.00078**
SO$_4^{-2}$ (mg/L)	2.5 (0.8-8.8)	2.7 (1-8.8)	2.6 (0.8-5.6)	2.1 (1.0-5.7)	**-0.05***	2.0 (0.3-8.2)	2.2 (0.4-6.6)	2.2 (0.5-8.2)	1.6 (0.3-4.5)	**-0.04***	2.2 (0.3-25.4)	2.6 (0.4-25.4)	1.8 (0.3-14)	**-0.1**
Cl (mg/L)	5.5 (1.4-31)	5.3 (2.2-31)	5.3 (1.4-7.6)	6.2 (3.1-10.3)	**0.03***	3.6 (1.4-7.6)	3.8 (1.7-6.2)	3.4 (1.6-6.7)	3.5 (1.4-7.6)	**-0.02***	4.3 (1.1-8.6)	4.6 (1.2-8.6)	4 (1.1-7.0)	**-0.07***
Ca/Alt					**-0.071***					**-0.018**				**-0.071**

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Fig 3.1 Aluminum concentration in Kejimkujik calibrated catchments as measured from grab samples A) Mersey River (MR), B) Moose Pit Brook (MPB), C) Pine Marten Stream (PMB). Trend lines are calculated from interpolated weekly averages.
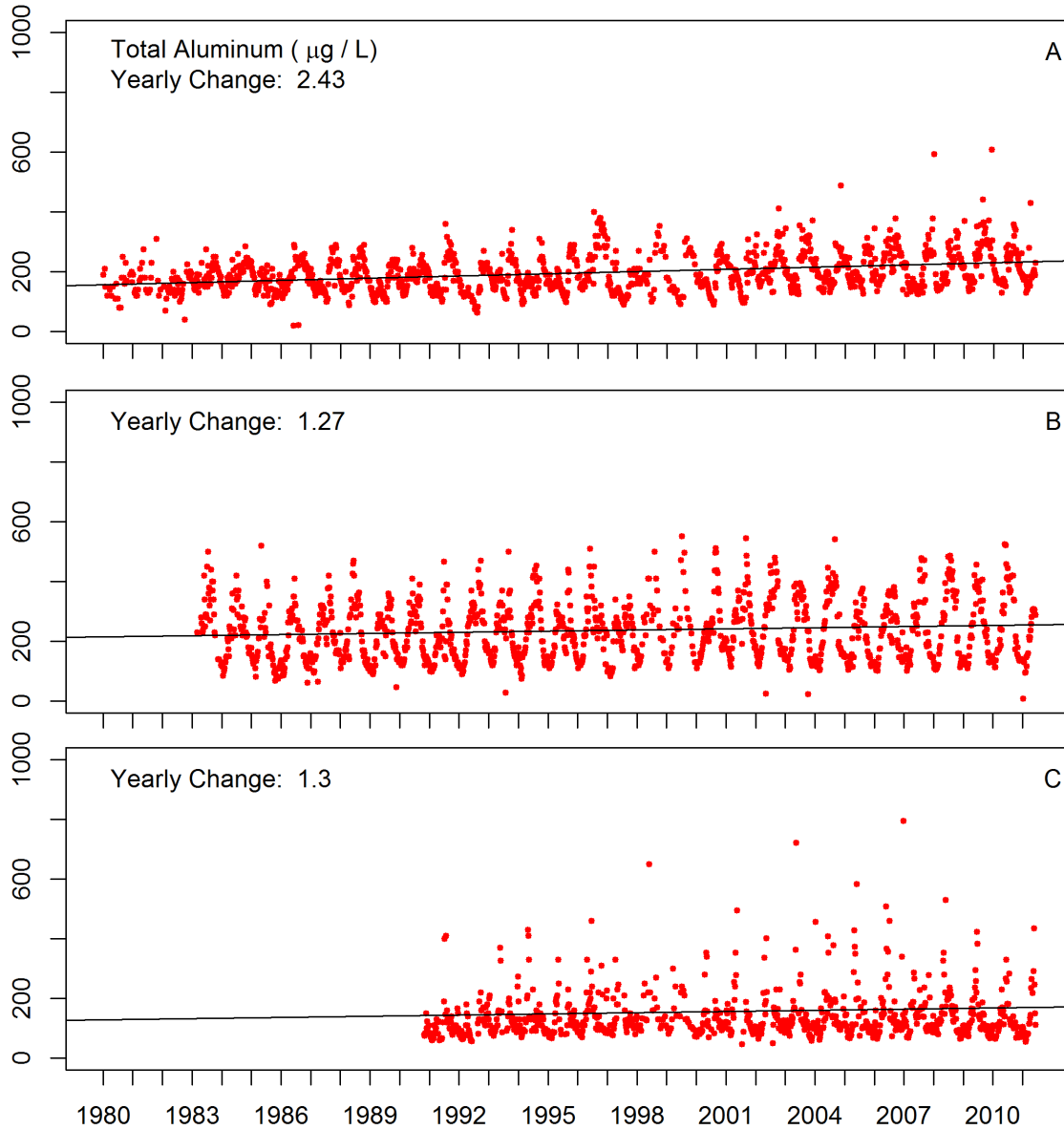
Fig 3.2 Weekly mean interpolated calcium and sulfate calculated from grab samples from Kejimkujik calibrated catchments. A) MR, B) MPB, C) PMB.
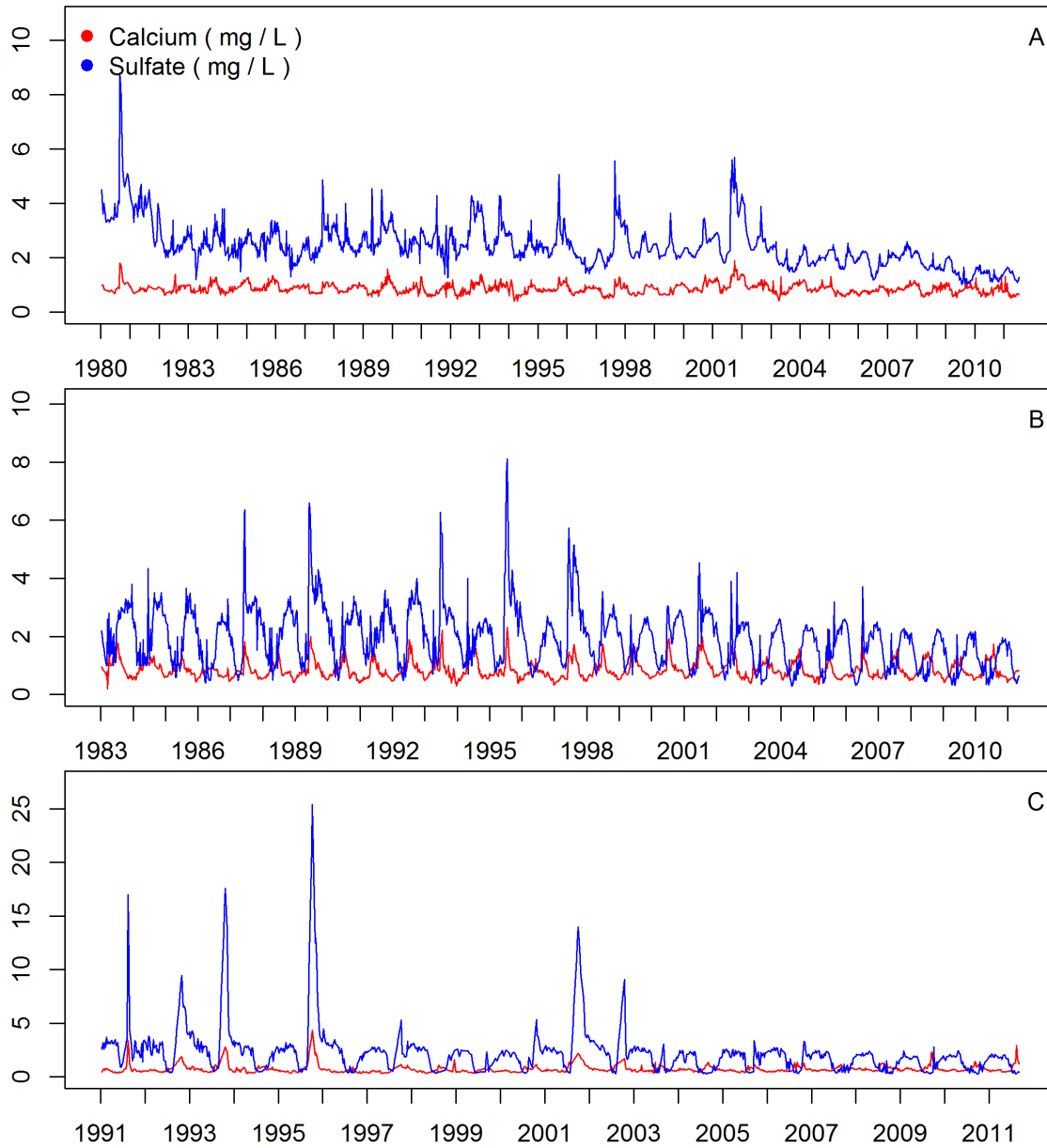
Fig 3.3 Ratio of total aluminum to calcium in Kejimkujik calibrated catchments as measured from grab samples. Trend lines are calculated from interpolated weekly averages of the ratio.
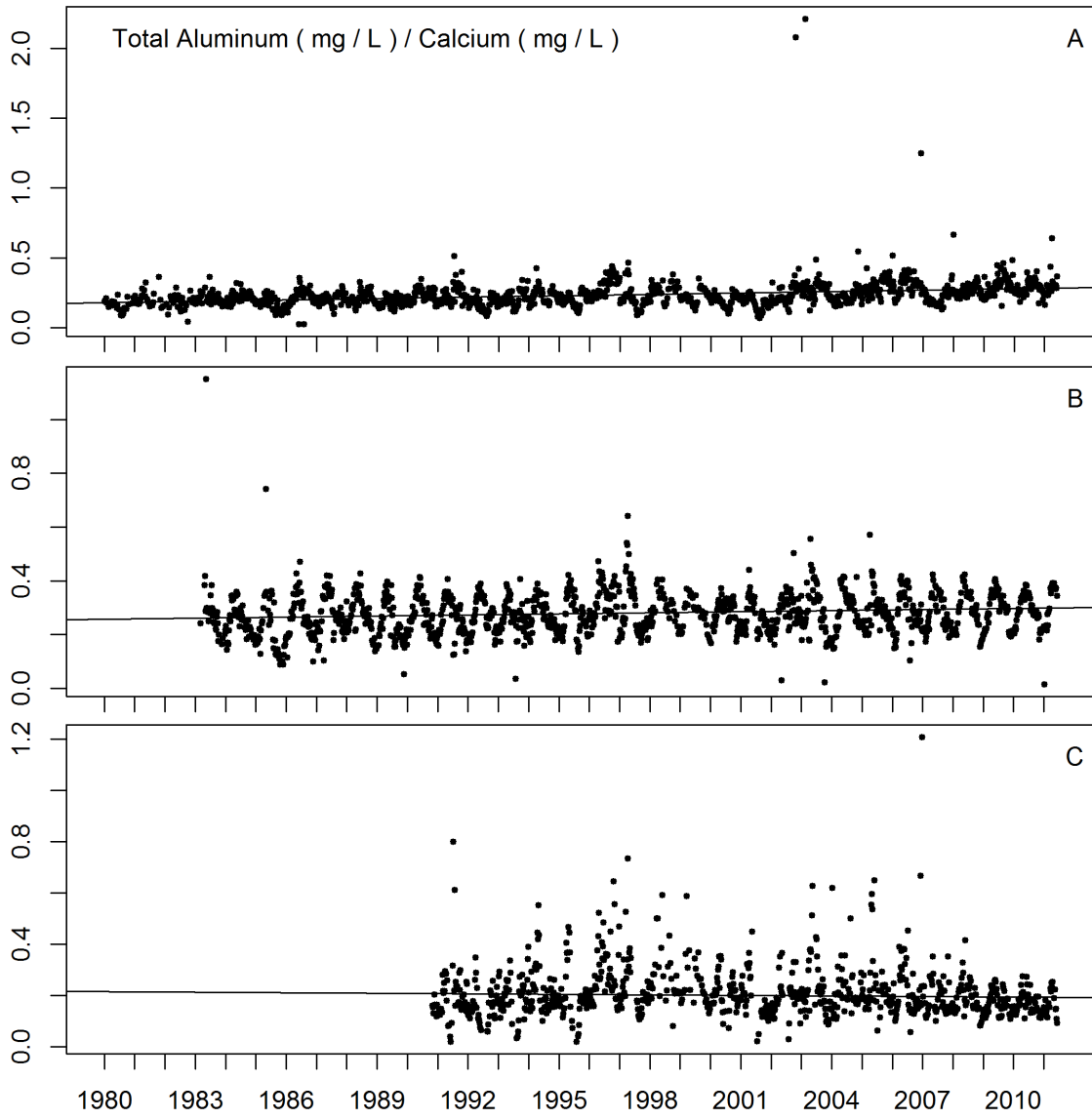
Figure 3.4 Weekly mean total aluminum and DOC as calculated from grab samples from Kejimkujik calibrated catchments. A) MR, B) MPB, C) PMB. DOC trend line calculated from interpolated weekly averages.
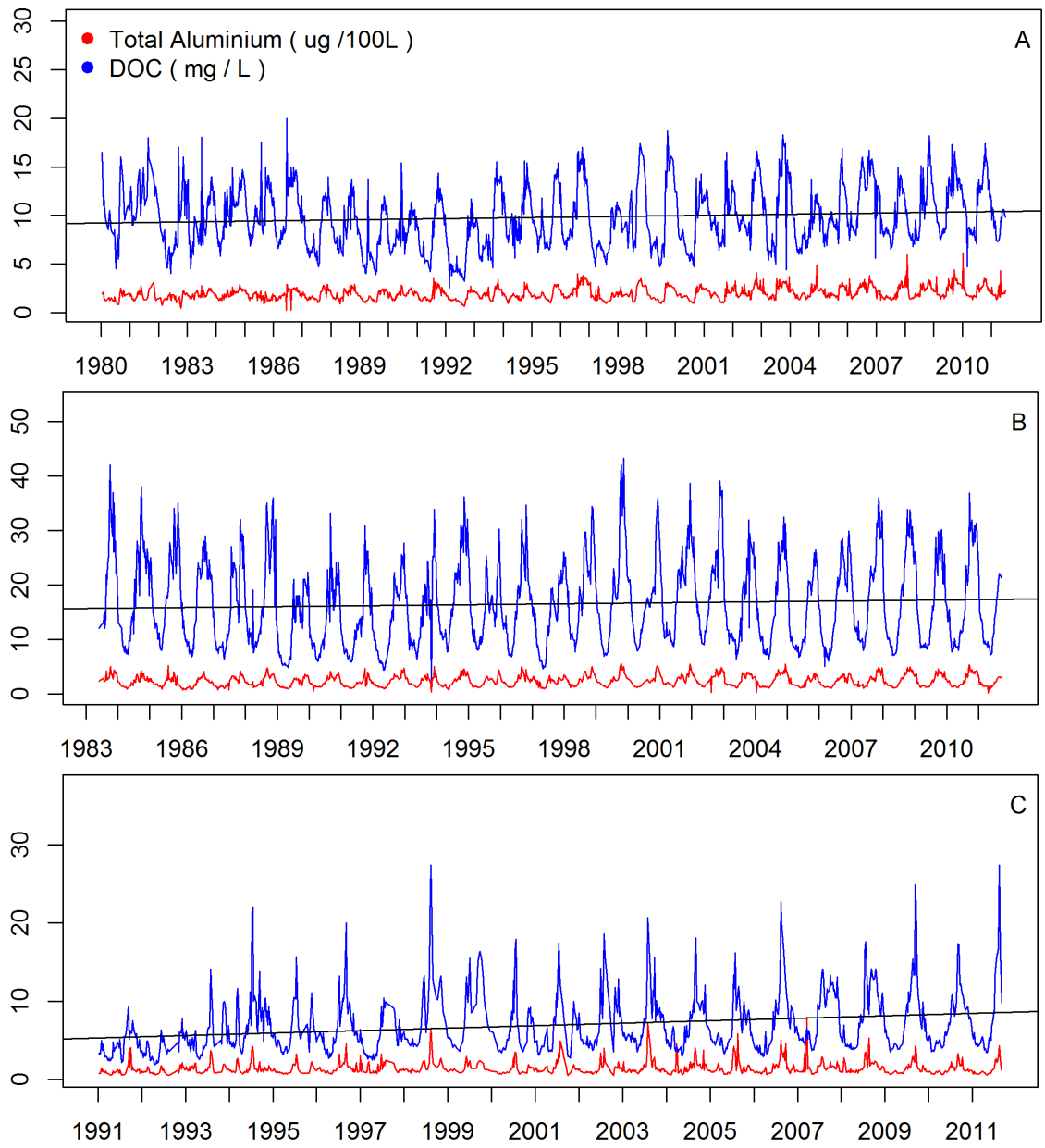
Figure 3.5 Scatter plot of total aluminum and dissolved organic carbon. A) MR, B) MBP, C)PMB.
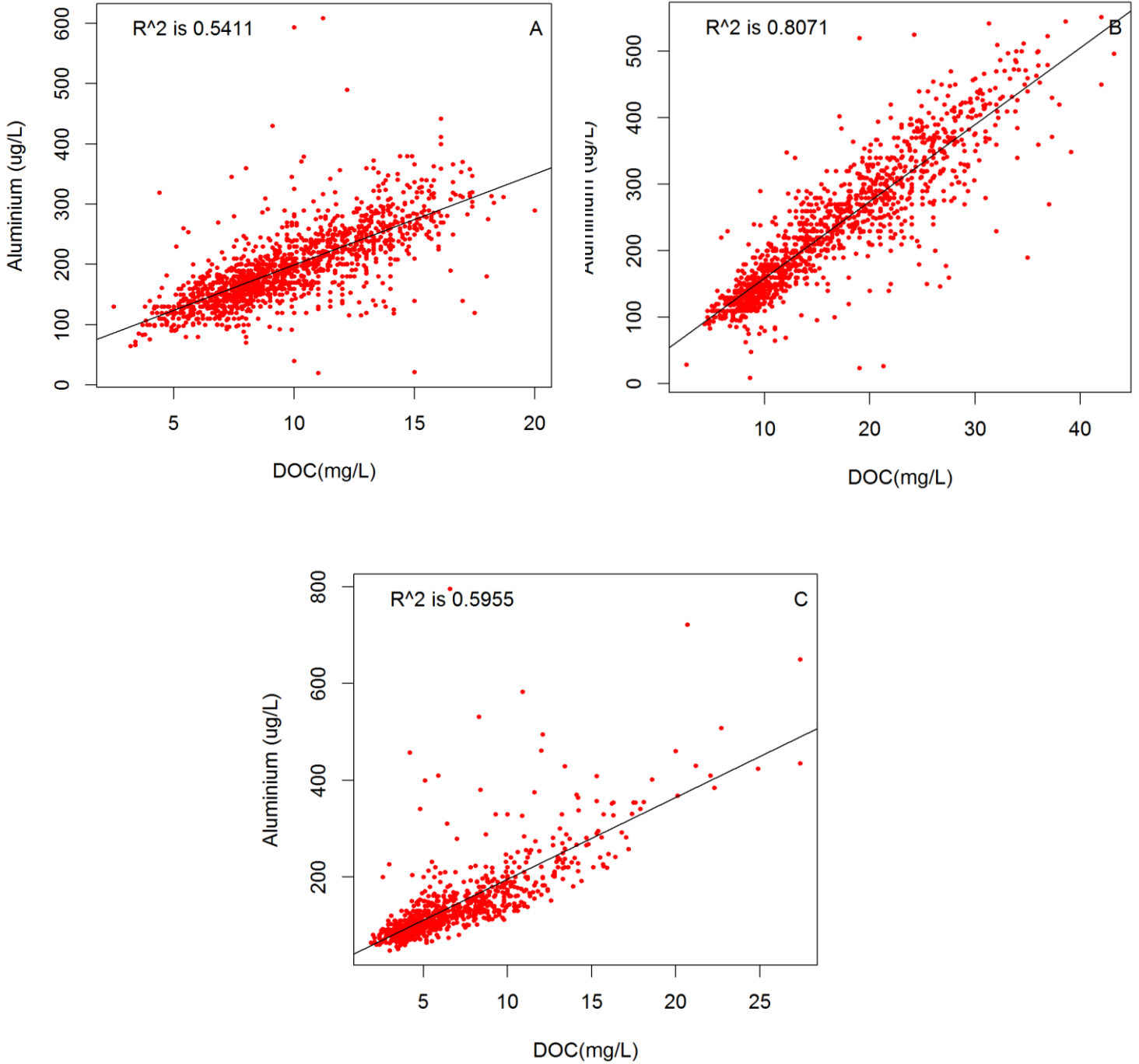
Figure 3.6 Scatter plot of total aluminum and pH in Kejimkujik catchments. A) MR, B) MPB, C) PMB. The horizontal trend seen in B is the result of precision for calculating pH using the electrometric method.
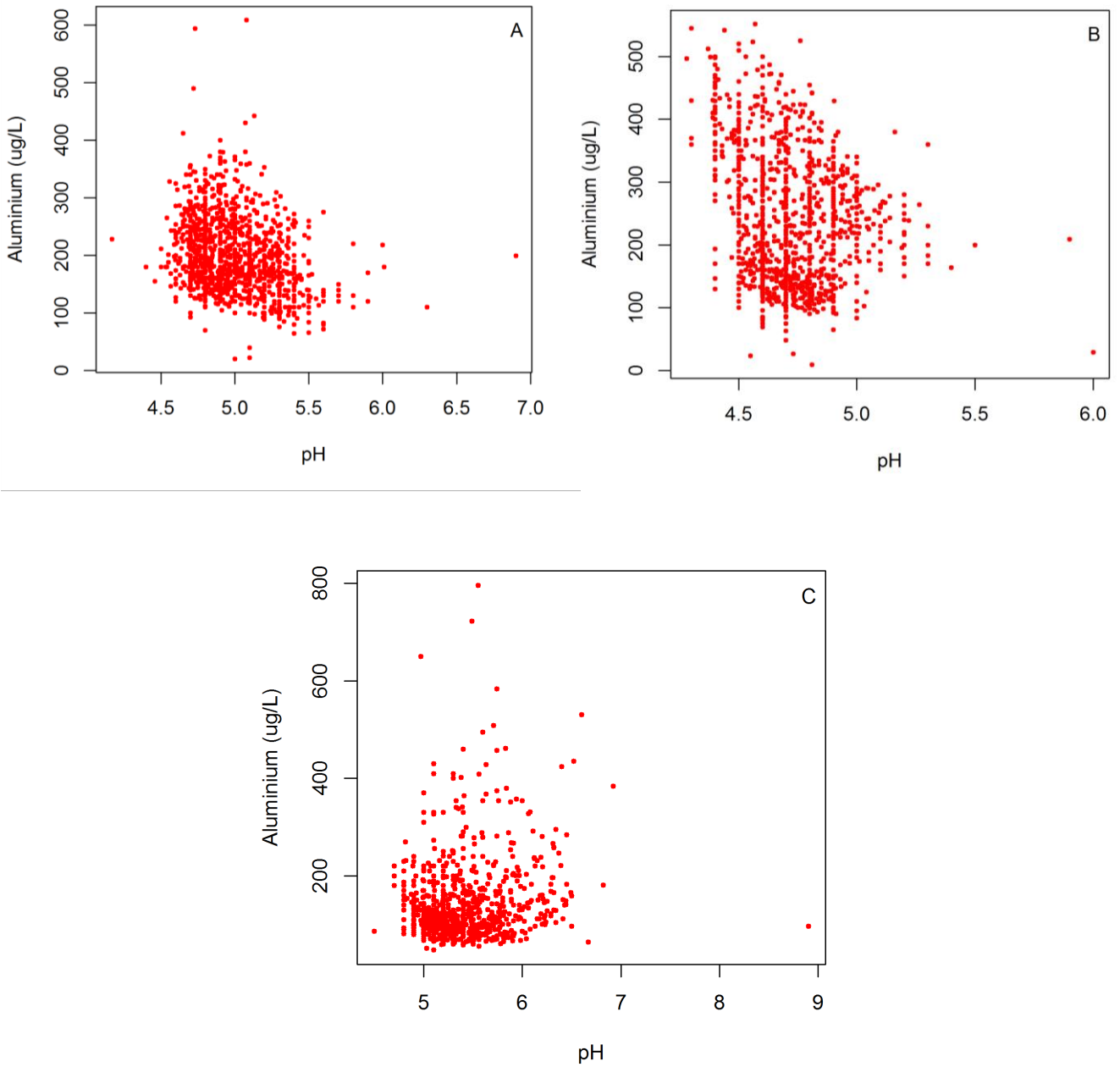
Figure 3.7. Calculated ionic aluminum concentrations in Kejimkujik calibrated catchments. Values calculated by Equation 2-1 are shown in red with blue dashed line showing predicted Al_i of 0 µg/L. Values calculated by Equation 3-2 are shown in blue. A) MR, B) MPB, C) PMB. Black line is the 15 µg/L EIFAC guideline for aquatic biota health.

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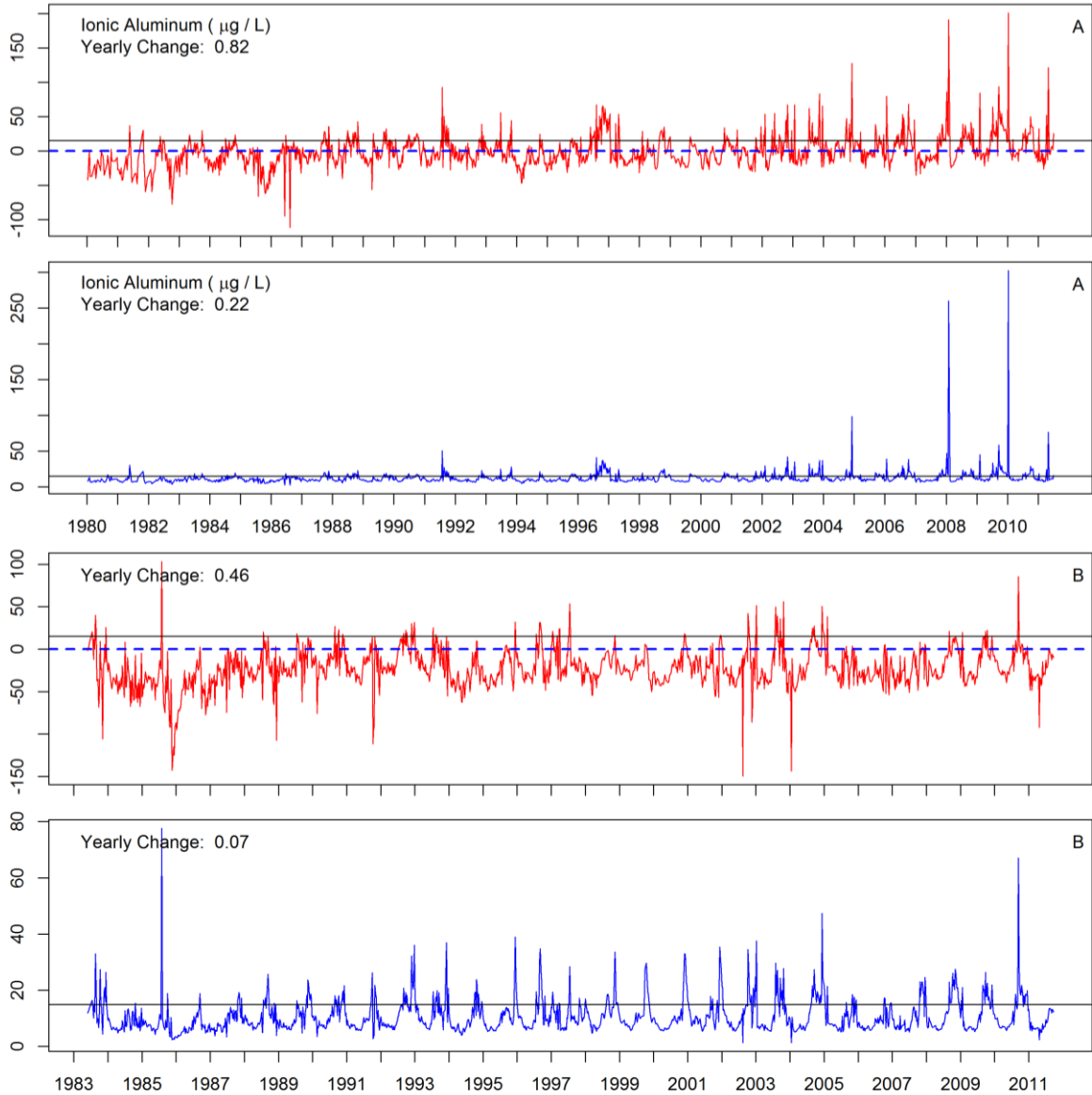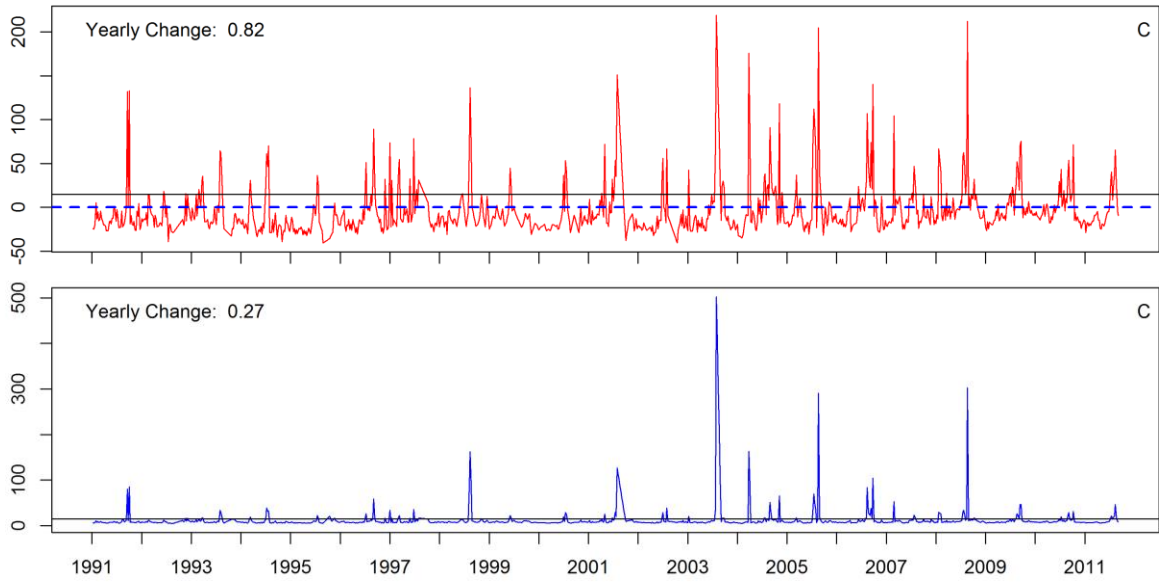
Figure 3.8 Residuals of raw data from Dennis and Clair's (2012) Equation 2-1 with a parabolic trend.
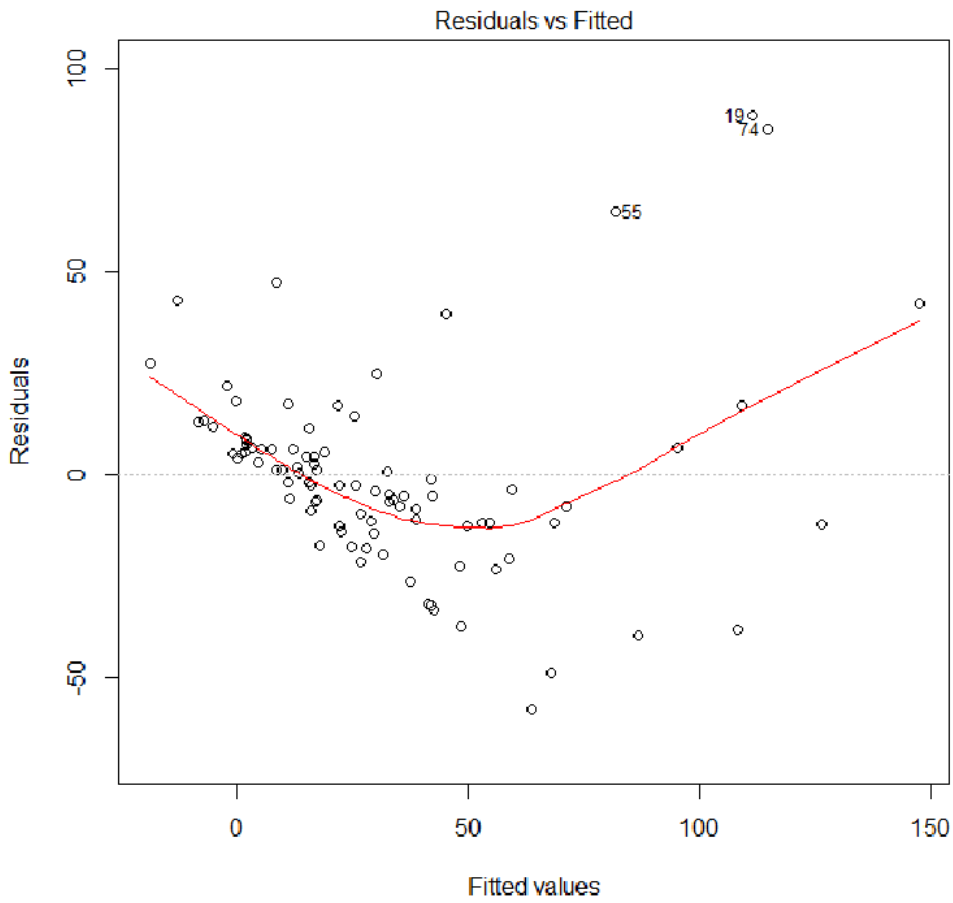
Figure 3.9 Residuals from Equation 3-1 adapted from Dennis and Clair's (2012) formula. Residuals are randomly scattered to create a linear trend
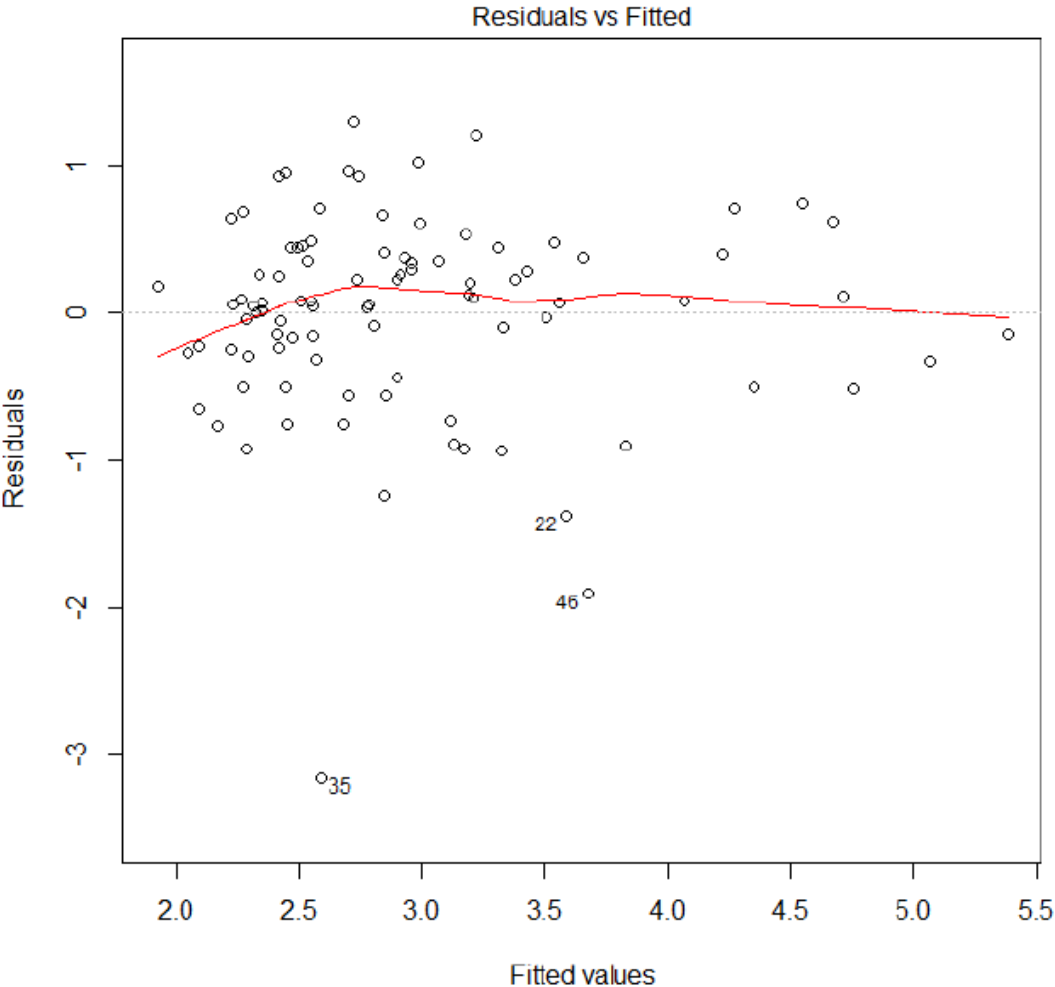
Figure 3.10 Residuals from Equation 3-2 with randomly scattered residuals creating a linear trend line.
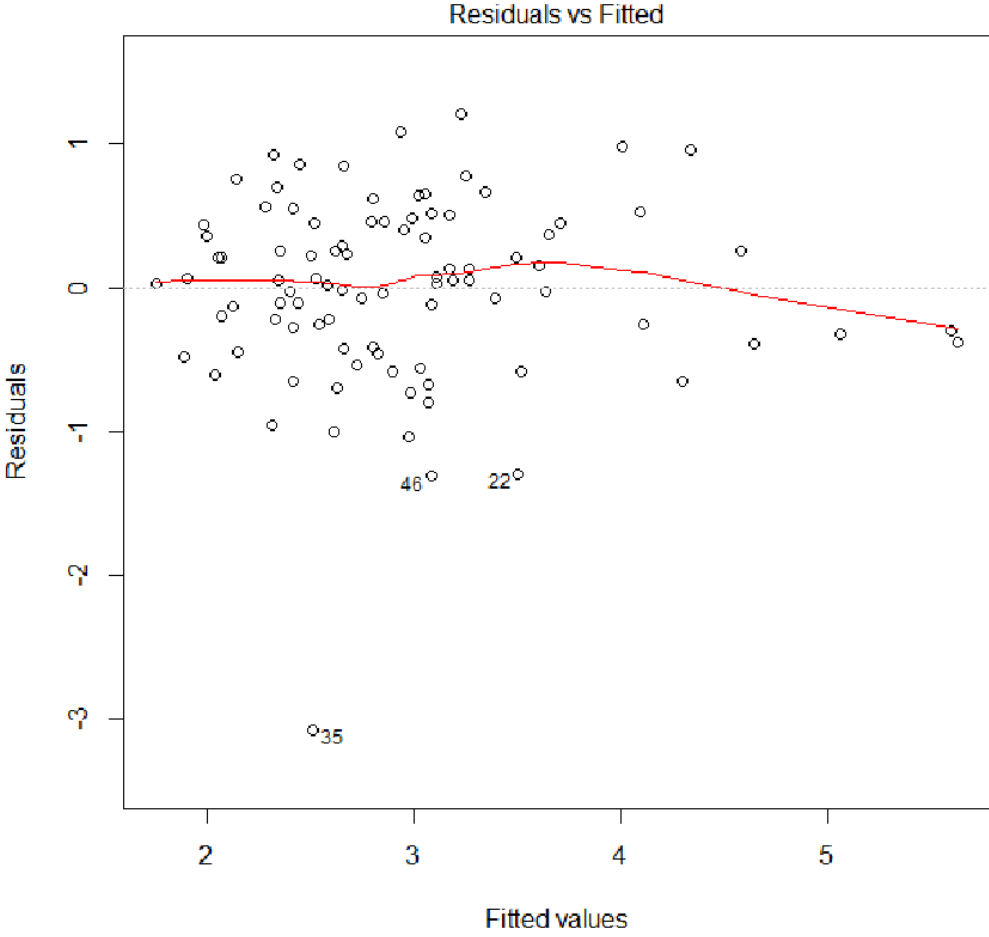
4. Discussion

3.6. Al_t Values and Trends

Al_t was found to be significantly increasing in all of our site locations over the sampling period. This is the only known location worldwide where this is currently occurring except for the West Bear watershed in Maine, where there has been continued artificial inputs of SO_4^{-2} and ammonium from 1989 to 2007, which resulted in increases in Al_t (Fatemi et al., 2012). All other areas in long-term Al_t studies have seen a reduction in Al_t concentrations with decreased emissions of SO_4^{-2}. Watt et al (1983) showed an increase of Al_t in four SWNS rivers from 1954-1981, the Roseway, Medway, LaHave, and Mersey River. We see a continuation of this trend to the end of the sampling period in July 2011.

Table 4.1 Ranges of total aluminum (μg/L) and pH from different acidified watersheds from around the world.

Location	Description	pH	Al_t (μg/L)	Reference
Nova Scotia	MR	3.7-6.9	20-609	
Nova Scotia	MPB	4.3-6.0	9-552	
Nova Scotia	PMB	4.5-8.9	48-722	
Nova Scotia	Maria Brook	4.0-6.0	52-1418	Angelidis et al, 2014
Sweden	Central Sweden	4.6-5.2	159-405	Rosen, 1982
Adirondacks	1977-78	4.0-7.6	81-1160	Driscoll et al, 1984
New England	1978-81	4.1-7.7	13-378	Haines and Kielaszeck, 1983
Catskill Mnts.	Black Brook	5.4-7.0	28-179	Baldigo & Murdoch, 1996
Catskill Mnts.	East Branch Neversink	4.3-5.4	51-746	Baldigo & Murdoch, 1996
France	Northern Vosges	4.4-7.0	56-510	Thiébaut & Muller 1999

Similar positive correlations between the relationship of Al_t and pH found in our study are synonymous to other findings, which indicates at lower pH increased mobilization of aluminum occurs in the soils (Dennis and Clair, 2012; Driscoll and Schecher, 1990).

3.7.   Calcium and Sulfate Predictions in SWNS

Watt et al. (1983) found that in four SWNS rivers including the Mersey River, from 1954-1981 there was a significant increase in sulfate and a decline in calcium. Later Watt et al, (2000) showed that sulfate declined in rivers in SWNS rivers from 1982-1996 following the decline of emissions after the Eastern Canada SO_2 Control Program and the Clean Air Act. We observed a similar trend at all sites. Sulfate is significantly decreasing over the entire sampling period, 1980-2011, in all sites (Figure 3.5). Calcium trends in Mersey River during 1954-1981 were found to be decreasing (Watt et al, 1983), this trend has continued from 1980-1996 (Watt et al, 2000), as well as in our data set. These trends follow the predictions of soil recovery from acidic deposition in NS by Clair et al (2004). With the reductions of sulfate deposition from anthropogenic sources calcium levels are still expected to take 100 years to recover to pre-acidified levels (Clair et al., 2004).

3.8.   DOC Trends

There is a strong relationship between DOC and Al_t at all sites in our study. Dennis and Clair (2012) observed a leveling off of Al_t levels at ~450 µg/L with DOC values at ~15 mg/L (Figure 4.2). This was not observed in our study, where we saw a linear increase of DOC to Al_t, exceeding both the Al_t and DOC values captured by Dennis and Clair (2012) (Figure 3.7). This relationship between Al_t and DOC is well documented, and DOC helps to mobilize Al_t from soil (Jansen, 2003; Driscoll and Schecher, 1990).

3.9. pH Trends

Our study indicates that there are minimal changes over the sampling period of pH levels near Kejimkujik National Park (KNP). Studies of paleolimnology in the KNP area have shown a decrease in pH of ~0.5 ± 0.2 since pre-industrialization (Korosi et al., 2013). Since the 1980s long-term monitoring of pH in Nova Scotia has not observed a recovery of pH, even with large reductions in SO_4^{-2} emissions (Clair et al., 2011).

3.10. Predictive Power of Empirical Models New and Old

Upon analysis of the existing model for Al_i prediction (Equation 2-1), we found issues arising from its ability to predict physically plausible results from our dataset as well as from the original dataset used to create it. We found that this was because the existing model (Equation 2-1) failed to address its violation of independent normally distributed residuals or address that all predicted values should be greater than zero. Our model (Equation 3-2) is an equation that generates normal residuals as well as only positive values, thus not violating any assumptions of least squares. This new model (Equation 3-2) was used to predict Al_i concentrations over the sampling period, which were found to be frequently above the threshold for aquatic biota, and significantly increasing in two of the three sites, MR and MPB (Table 3.2). There are still issues associated with our model. There are physical restraints on the generation of Al_i, and in particular it only exists in pH below 6.0. With this in mind Al_i values which are calculated need to be excluded if the pH is greater than 6.0, there was not a check for this during the prediction for Al_i in this study, which was also absent from the previous model (Equation 2-1).

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3.11. Limitations of the Study

Our site locations only include three watersheds in SWNS, which are in a close proximity to one another (Figure 2.1). They do not necessarily reflect the water quality trends of entire SWNS watersheds.

Dennis and Clair (2012)'s original data was collected during one fall sampling period, in SWNS there is evident seasonal variation associated with water quality parameters, this limited sampling period has limited the range of empirical models created from this dataset. Dennis and Clair (2012)'s collected data has a limited range, which has reduced the ability to effectively predict Al_i values during Al_t events.

Figure 4.1 Scatter plot created by Dennis and Clair (2012) with a negative correlation between pH and Al_t.
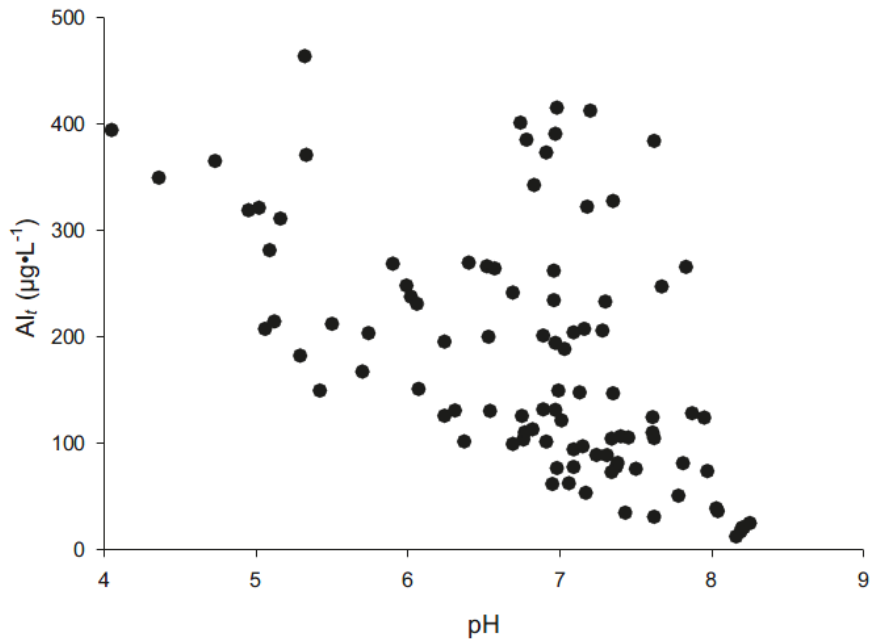
Figure 4.2 Relationship observed by Dennis and Clair (2012) between Al_t and TOC. At TOC values >15 mg/L there is a leveling off of Al_t at values of ~450 µg/L.

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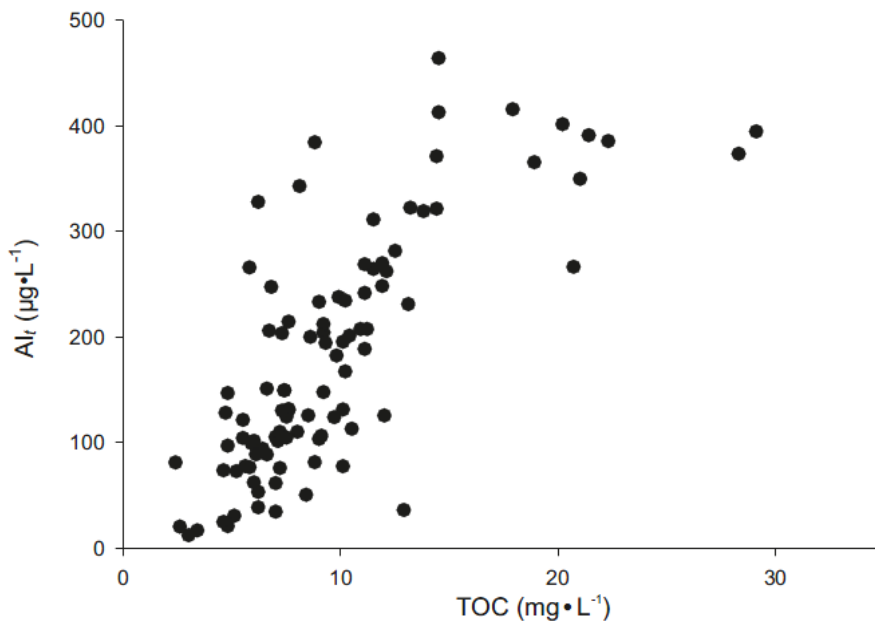
5 Conclusion

Based on the results produced in this thesis I have concluded the following about the three studied watersheds:

1. Al_t has been increasing significantly over the study period in all sites, and historical data suggests it has been increasing at least since the 1950's. Besides a test watershed with artificial inputs of SO_4^{-2}, SWNS is the only known location with increasing Al_t levels presently.

2. Projected levels of Al_i are of concern for *Salmo salar*, because they are above threshold limits but are highly uncertain. Our new model (Equation 3-2) for estimating Al_i indicates Al_i concentrations frequently exceed EIFAC thresholds for aquatic life. Previous models for Al_i (Equation 2-1) prediction was limited because it predicted negative values of Al_i and because the residuals violated assumptions about random distributions.

3. Conditions for the generation of Al_i is met for the majority of the sampling period. Using our model we found Al_i was significantly increasing in MR and MPB between 1980 to 2011, and 1983 to 2011 respectively. Levels of Al_i were found to be at levels which can be detrimental to aquatic life when using both models.

5.1. Recommendation for Future Work

Top priority should be to collect more data on Al_t, Al_i, and DOC, following Dennis and Clair (2012) methods over a wider range of flows and seasons to create an improved empirical model for Al_i prediction. Another study to be conducted similar to Dennis and Clair (2012) over a longer study period. To gain a better understanding of Al_i in SWNS watersheds.

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Appendices

A. R Statistical Package Code

The following is a list of R code which was used to calculate trends, significance, and to produce figures.

```
for(k in 1:3){
data_1=read.csv(paste0("R",k,".u.csv"))


#replace all the ionic values below 0 to 0
data_1[data_1[,2] < 0,2] = 0



#create the julien date
data_1$Jul = julian(data_1$Month,data_1$Date,data_1$Year)-3708
#Creates a week column based off Julien Date
data_1$Week = ceiling(data_1$Jul/7)
#loops through each row of the csv table

#calculate the weekly average
Alt = c()
Ali = c()
pH = c()
DOC = c()
H = c()
week = c()

for(i in 1:min(data_1$Week)){
```

```
      Alt[i] = NA

      Ali[i] = NA

      pH[i]  = NA

      DOC[i] = NA

      H[i] = NA

      week[i] = NA

   temp = NA

   }


for(i in min(data_1$Week):max(data_1$Week)){

      Rnew = data_1[data_1$Week ==i,]


      temp = sd(Rnew[,1])


      Alt[i] = mean(Rnew[,1])

      Ali[i] = mean(Rnew[,2])

      pH[i]  = mean(Rnew[,6])

      DOC[i] = mean(Rnew[,7])

      H[i] = mean(Rnew[,8])

      if(dim(Rnew)[1] <1){

           week[i] = NA}

      else{

           week[i]= Rnew$Week

      }      }


new_Date = data.frame(Alt = Alt, Ali = Ali, pH = pH, DOC = DOC, H = H,
week = week)


Alt.i =interpNA(Alt[min(data_1$Week):length(Alt)])

Ali.i =interpNA(Ali[min(data_1$Week):length(Alt)])

pH.i =interpNA(pH[min(data_1$Week):length(Alt)])
```

```
H.i =interpNA(H[min(data_1$Week):length(Alt)])

DOC.i =interpNA(DOC[min(data_1$Week):length(Alt)])

Week.i = interpNA(week[min(data_1$Week):length(Alt)])


week.new = Week.i-min(Week.i)


if(k==1){start1 = 1980  }

if(k==2){start1 = 1991  } #SA Nov 23

if(k==3){ start1 = 1983}  #SA Nov 23


  if(k==1){ label   = "pH vs Alt MR.png"  }

  if(k==2){ label   = "pH vs Alt PMS.png" }

  if(k==3){ label  = "pH vs Alt MPB.png"  }

  if (k==1){ label2   = "A"  }

  if(k==2){ label2   = "C" }

  if(k==3){ label2  =  "B"}

png(file= label, units="in", width=5, height=5, res=300)


plot(pH,Alt, xlab = "pH", ylab = "Aluminium (ug/L)",  col = "red",pch
= 19,cex = .5,)#main = paste("Aluminium vs pH at",river[k]))   #plots
the first values

     fit <-lm(Alt~pH)

  #abline(fit)

  legend("topright", bty="n", label2)#legend=paste("R^2 is",
format(summary(fit)$adj.r.squared, digits=4)))


     dev.off()}


        ###### Figure 4.1 ######


 if(k==1){ label   = "Fig4.1. test MR.png"}
```

```
if(k==2){ label    = "Fig4.1. test PMS.png"}

if(k==3){ label   = "Fig4.1. testMPB.png"}

if (k==1){ label2   = "A"  }

if(k==2){ label2   = "C" }

if(k==3){ label2   =  "B"}


png(file= label, units="in", width=11, height=4, res=300)

model.t = gls(Alt.i~week.new, corr = corAR1())

  rate.t = 52*model.t$coef[2]

  rate.t = round(rate.t, digits=2)



  plot(Alt,ylim = c(0,1000),ylab = NA, xaxt = "n", xlab = "Date",  col
= "red",pch = 19,cex = .5)    #plots the first values
ylab = "Aluminium(ug/L)"

  axis(1, at = seq(1,1638,52.1), labels = seq(1980,2011, 1))  # adds
the x axis labels to the plot using the dates

  if(k==1){legend("topleft", bty="n", legend=
c(expression(paste("Total Aluminum ( " ,mu, "g / L)")),
legend=paste("Yearly Change: ", rate.t))) }    #

  if(k==2 || k==3){ legend("topleft",bty="n", legend=paste("Yearly
Change: ", rate.t))}

  legend("topright", bty="n", legend=paste( label2) )

  abline(model.t)

dev.off()


  Alt.test = Alt.i/100


  if(k==1){ label   = "Fig 4.3 MR.png"  }

  if(k==2){ label   = "Fig 4.3 PMS.png" }

  if(k==3){ label   = "Fig 4.3 MPB.png"  }


  png(file= label, units="in", width=11, height=4, res=300)
```

```r
    plot(Alt.test, type = "l", ylim = c(min(Alt.test), max(DOC.i+10)),
xaxt = "n",  col = "red", ylab = NA)    #plots the first values
ylab = "Aluminium(ug/L)"

      if (k ==3){axis(1, at = seq(-20,length(Alt.test),52), labels =
seq(start1,2011, 1))}

if (k == 1 || k ==2){axis(1, at = seq(0,length(Alt.test),52), labels =
seq(start1,2011, 1))}

 points(DOC.i, type = "l", col = "blue")

if(k==1){  legend("topleft",legend=c("Total Aluminium ( ug /100L )
","DOC ( mg / L )"),pch=c(19,19),col=c("red","blue"), bty = "n")   }

    legend("topright", legend=c(label2), bty = "n")

    model.d = gls(DOC.i~week.new, corr = corAR1())


    abline(model.d)



dev.off()



#### Figure 4.2 Ali vs time#######


# gls model for ionic
   if(k==1){ label   = "Fig test 4.2 MR.png"  }

   if(k==2){ label   = "Fig test 4.2 PMS.png" }

   if(k==3){ label  = "Fig test 4.2 MPB.png"  }
png(file=label, units="in", width=11, height=4, res=300)



model.i = gls(Ali.i~week.new, corr = corAR1())

  rate.i = 52*model.i$coef[2]

  rate.i = round(rate.i, digits=2)
```

```
plot(Ali.i,  ylim = c(min(Ali.i), max(Ali.i)), xaxt = "n", ylab = NA,
xlab = "Date",  type = "l", col= "red")         #, main = paste("Ionic
Aluminium Trend at ",river[k])

legend("topright", bty="n", legend=paste( label2) )

if(k==1){legend("topleft", bty="n", legend= c(expression(paste("Ionic
Aluminum ( " ,mu, "g / L)")), legend=paste("Yearly Change: ",
rate.i))) }

if(k==2 || k==3){ legend("topleft",bty="n", legend=paste("Yearly
Change: ", rate.i))}

#axis(1, at = seq(1,1638,52.1), labels = seq(1980,2011, 1))

testline = 15

abline(15,0)

if (k ==3){axis(1, at = seq(-20,length(Ali.i),52), labels =
seq(start1,2011, 1))}

if (k == 1 || k ==2){axis(1, at = seq(0,length(Ali.i),52), labels =
seq(start1,2011, 1))}


  dev.off()


#preparing for mann kendal

data_1$Month2 = (data_1$Year-1980)*12 + data_1$Month


#calculate the monthly average

Alt_month = c()

Ali_month = c()

H_month = c()

DOC_month = c()

month = c()


for(i in 1:min(data_1$Month2)){


    Alt_month[i] = NA

  Ali_month[i]= NA
```

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```
  H_month[i] = NA

 DOC_month[i] = NA

    month[i] = NA

    }

for(i in min(data_1$Month2):max(data_1$Month2)){

   Rnew = data_1[data_1$Month2 == i,]

   Alt_month[i] = mean(Rnew[,1])

   Ali_month[i] = mean(Rnew[,2])

   H_month[i] = mean(Rnew[,8])

   DOC_month[i] = mean(Rnew[,7])

    }


AltMonth.i =interpNA(Alt_month[min(data_1$Month):length(Alt_month)])

AliMonth.i =interpNA(Ali_month[min(data_1$Month):length(Ali_month)])

HMonth.i =interpNA(H_month[min(data_1$Month):length(H_month)])

DOCMonth.i =interpNA(DOC_month[min(data_1$Month):length(DOC_month)])


if (k ==1){


   ts_Alt = ts(AltMonth.i, start = c(1980, 2), end = c(2011,7), freq
= 12)

   ts_Ali = ts(AliMonth.i, start = c(1980, 2), end = c(2011,7), freq
= 12)

   ts_H= ts(HMonth.i, start = c(1980, 2), end = c(2011,7), freq =
12)

   ts_DOC = ts(DOCMonth.i, start = c(1980, 2), end = c(2011,7), freq
= 12)

    }


if (k ==2){

   ts_Alt = ts(AltMonth.i, start = c(1989, 2), end = c(2011,7), freq
= 12)
```

```
      ts_Ali = ts(AliMonth.i, start = c(1989, 2), end = c(2011,7), freq
= 12)

      ts_H=   ts(HMonth.i, start = c(1989, 2), end = c(2011,7), freq =
12)

      ts_DOC = ts(DOCMonth.i, start = c(1989, 2), end = c(2011,7), freq
= 12)

      }
if (k==3){

  ts_Alt = ts(AltMonth.i, start = c(1983, 2), end = c(2011,7), freq =
12)

      ts_Ali = ts(AliMonth.i, start = c(1983, 2), end = c(2011,7), freq
= 12)

      ts_H= ts(HMonth.i, start = c(1983, 2), end = c(2011,7), freq =
12)

      ts_DOC = ts(DOCMonth.i, start = c(1983, 2), end = c(2011,7), freq
= 12)

  }


print(SeasonalMannKendall(ts_Alt))

print(SeasonalMannKendall(ts_Ali))

print(SeasonalMannKendall(ts_H))

print(SeasonalMannKendall(ts_DOC))


for(k in 4:6){

data_1=read.csv(paste0("R",k,".u.csv"))


data_1$Jul = julian(data_1$Month,data_1$Date,data_1$Year)

#Creates a week column based off Julien Date

data_1$Week = ceiling(data_1$Jul/7)

#loops through each row of the csv table


#calculate the weekly average

Ca = c()
```

```r
ANC = c()

Mg = c()

Na = c()

K = c()

SO4 = c()

NO3 = c()

Cl = c()

week = c()


for(i in 1:min(data_1$Week)){

    Ca[i] = NA

    ANC[i] = NA

    Mg[i]  = NA

    Na[i] = NA

    K[i] = NA

    SO4[i] = NA

    NO3[i] = NA

    Cl[i] = NA

    week[i] = NA

    }


for(i in min(data_1$Week):max(ceiling((data_1$Jul)/7))){

    Rnew = data_1[data_1$Week ==i,]


    Ca[i] = mean(Rnew[,2])

    ANC[i] = mean(Rnew[,1])

    Mg[i]  = mean(Rnew[,3])

    Na[i] = mean(Rnew[,4])

    K[i] = mean(Rnew[,5])

    SO4[i] = mean(Rnew[,6])
```

```
        NO3[i] = mean(Rnew[,7])

        Cl[i] = mean(Rnew[,8])

        if(dim(Rnew)[1] <1){

        week[i] = NA}

        else{

        week[i]= Rnew$Week

        }       }


new_Date = data.frame(Ca = Ca, ANC = ANC, Mg = Mg, Na = Na,K = K, SO4
= SO4, NO3 = NO3, Cl = Cl, week = week)


## INTERPOLATION OF MISSING VALUES



Ca.i =interpNA(Ca[min(data_1$Week):length(Ca)])

ANC.i =interpNA(ANC[min(data_1$Week):length(Ca)])

Mg.i =interpNA(Mg[min(data_1$Week):length(Ca)])

Na.i =interpNA(Na[min(data_1$Week):length(Ca)])

K.i =interpNA(K[min(data_1$Week):length(Ca)])

SO4.i =interpNA(SO4[min(data_1$Week):length(Ca)])

NO3.i =interpNA(NO3[min(data_1$Week):length(Ca)])

Cl.i = interpNA(Cl[min(data_1$Week):length(Ca)])


Week.i = interpNA(week[min(data_1$Week):length(Ca)])


if(k==4){start1 = 1980

  label2   = "A"

  label   = "Ca SO4 MR.png" }

if(k==5){start1 = 1991

label2   = "C"

label   = "Ca SO4 PMS.png" } #SA Nov 23
```

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```
if(k==6){ start1 = 1983

label2  =  "B"

label  = "Ca SO4 MPB.png"}  #SA Nov 23


   ###### Figure 4.4 ######


png(file= label, units="in", width=11, height=4, res=300)

plot(Ca.i,ylim = c(0, max(SO4.i+2)), type="l", ylab = NA, xaxt = "n",
xlab = "Date",  col = "red",pch = 19,cex = .5,)   #plots the first
values

   axis(1, at = seq(0,length(Ca.i),52), labels = seq(start1,2011, 1))

   points(SO4.i, type= "l",col = "blue",cex = .5, pch = 19)

   legend("topright",legend=c(label2), bty="n" )

   if(k==4){ legend("topleft", bty="n", legend=c("Calcium ( mg / L )",
"Sulfate ( mg / L )"), pch=c(19,19),col=c("red","blue") )   }

dev.off()


  if(k==4){ label   = "Cl MR.png"  }

  if(k==5){ label   = "Cl PMS.png" }

  if(k==6){ label  = "Cl MPB.png"  }

png(file= label, units="in", width=11, height=4, res=300)

Week.model = Week.i-min(Week.i)

model.Cl = gls(Cl.i~Week.model, corr = corAR1())

plot(Cl.i, type = "l", col = "blue",  ylim = c(min(Cl.i), max(Cl.i)),
xaxt = "n", ylab = NA , xlab = "Date")

axis(1, at = seq(0,length(Cl.i),52), labels = seq(start1,2011, 1))

legend("topright",legend=c(label2), bty="n" )

if(k==4){ legend("topleft", bty="n", legend=c("Chloride ( mg / L )" )
) }


abline(model.Cl)

#to see coefficients
```

```
model.Cl$coef


  dev.off()



#for mann kendal

data_1$Month2 = (data_1$Year-1980)*12 + data_1$Month

Ca_month = c()

Anc_month = c()

SO4_month = c()

Cl_month = c()

month = c()

for(i in 1:min(data_1$Month2)){

     Ca_month[i] = NA

     Anc_month[i] = NA

     SO4_month[i] = NA

     Cl_month[i] = NA

     month[i] = NA    #jm edit dec 6

     }

for(i in min(data_1$Month2):max(data_1$Month2)){

     Rnew = data_1[data_1$Month2 == i,]

     Ca_month[i] = mean(Rnew[,2])

     Anc_month[i] = mean(Rnew[,1])

     SO4_month[i] = mean(Rnew[,6])

     Cl_month[i] = mean(Rnew[,8])

     }

CaMonth.i =interpNA(Ca_month[min(data_1$Month2):length(Ca_month)])

AncMonth.i =interpNA(Anc_month[min(data_1$Month2):length(Anc_month)])

SO4Month.i =interpNA(SO4_month[min(data_1$Month2):length(SO4_month)])

ClMonth.i =interpNA(Cl_month[min(data_1$Month2):length(Cl_month)])
```

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```
if (k ==4){

    ts_Ca = ts(CaMonth.i, start = c(1980, 2), end = c(2011,7), freq =
12)

    ts_Anc = ts(AncMonth.i, start = c(1980, 2), end = c(2011,7), freq
= 12)

    ts_SO4 = ts(SO4Month.i, start = c(1980, 2), end = c(2011,7), freq
= 12)

    ts_Cl = ts(ClMonth.i, start = c(1980, 2), end = c(2011,7), freq =
12)


    }
if (k ==5){

    ts_Ca = ts(CaMonth.i, start = c(1990, 12), end = c(2011,7), freq
= 12)

    ts_Anc = ts(AncMonth.i, start = c(1990, 12), end = c(2011,7),
freq = 12)

    ts_SO4 = ts(SO4Month.i, start = c(1990, 12), end = c(2011,7),
freq = 12)

    ts_Cl = ts(ClMonth.i, start = c(1990, 12), end = c(2011,7), freq
= 12)

    }
if (k==6){

    ts_Ca = ts(CaMonth.i, start = c(1983, 5), end = c(2011,7), freq =
12)

  ts_Anc = ts(AncMonth.i, start = c(1983, 5), end = c(2011,7), freq =
12)

  ts_SO4 = ts(SO4Month.i, start = c(1983, 5), end = c(2011,7), freq =
12)

  ts_Cl = ts(ClMonth.i, start = c(1983, 5), end = c(2011,7), freq =
12)

  }
print(SeasonalMannKendall(ts_Ca))

print(SeasonalMannKendall(ts_Anc))
```

66

```
print(SeasonalMannKendall(ts_SO4))

print(SeasonalMannKendall(ts_Cl))


   #Creating scatter plots and Alt/Ca plots


for(k in 1:3){

# for alum/ca/ANC plots

names_1 = c("ANC_Alt_mersey.csv", "ANC_Al_Pinemarten.csv",
"ANC_Al_Moosepit.csv")

names_2 = c("ANC_Alt_Mersey", "ANC_Al_Pinemarten", "ANC_Al_Moosepit")


#This is for ANC_Alt_mersey

data_1= read.csv(names_1[k])

#create the julian date

julian(data_1$Month,data_1$Date,data_1$Year)

data_1$Jul = julian(data_1$Month,data_1$Date,data_1$Year)-3708

#Creates a week column based off Julien Date

data_1$Week = ceiling(data_1$Jul/7)

#loops through each row of the csv table

#calculate the weekly average

Alt = c()

Al = c()

week = c()

Ca = c()

ANC = c()

SO4 = c()

DOC = c()

CL = c()

CB = c()

CaAlt = c()
```

```
for(i in 1:min(data_1$Week)){

      Alt[i] = NA

      Al[i] = NA

      Ca = c()

      ANC = c()

      SO4 = c()

   DOC = c()

   CB= c()

   CL =c()

      #add extra variables here

      week[i] = NA

      CaAlt[i] = NA}



for(i in min(data_1$Week):max(data_1$Week)){

      Rnew = data_1[data_1$Week ==i,]


      Alt[i] = mean(Rnew$Alt)

      Al[i] = mean(Rnew$Al)

      Ca[i]  = mean(Rnew$Ca)

   CB[i] = mean(Rnew$CB)

      ANC[i] = mean(Rnew$ANC)

      SO4[i] = mean(Rnew$SO4)

   DOC[i] = mean(Rnew$DOC)

   CL[i] = mean(Rnew$CL)

   CaAlt[i] = mean(Rnew$CaAlt)


      if(dim(Rnew)[1] <1){

            week[i] = NA}

      else{

            week[i]= Rnew$Week
```

```
        }        }
new_Date = data.frame(Alt = Alt, Al = Al, Ca = Ca, ANC = ANC, week =
week, SO4 = SO4, DOC = DOC, CaAlt = CaAlt, CB = CB, CL = CL)

   if(k==1){ label   = "Scatter plots MR.png"  }

   if(k==2){ label   = "Scatter plots PMS.png" }

   if(k==3){ label  = "Scatter plots MPB.png"  }

   if (k==1){ label2  = "A"  }

   if(k==2){ label2   = "C" }

   if(k==3){ label2  =  "B"}


png(file= label, units="in", width=5, height=5, res=250)


   plot(DOC, Alt , xlab = "DOC(mg/L)", ylab = "Aluminium (ug/L)",  col
= "red",pch = 19,cex = .5, main = paste("Aluminium vs DOC
at",river[k]))   #add DOC to the cvs file

   fit <-lm(Alt~DOC)

   abline(fit)

   legend("topright", bty="n", label2)

   legend ("topleft", bty="n", legend=paste("R^2 is",
format(summary(fit)$adj.r.squared, digits=4)))


     plot(Alt,Ca , ylab = "Calcium(mg/L)", xlab = "Aluminium (ug/L)",
col = "red",pch = 19,cex = .5,main = paste("Aluminium vs Ca
at",river[k]))   #plots the first values

     fit <-lm(Ca~Alt)

   abline(fit)

   legend("topright", bty="n", legend=paste("R2 is",
format(summary(fit)$adj.r.squared, digits=4)))


     plot(Alt,ANC ,ylab = "ANC", xlab = "Aluminium (ug/L)",  col =
"red",pch = 19,cex = .5, main = paste("Aluminium vs ANC at",river[k]))
#plots the first values

   fit <-lm(ANC~Alt)
```

```
  abline(fit)

  legend("topright", bty="n", legend=paste("R2 is",
format(summary(fit)$adj.r.squared, digits=4)))



      plot(Ca,ANC ,ylab = "ANC", xlab = "Calcium (mg/L)",  col =
"red",pch = 19,cex = .5, main = paste("Calcium vs ANC at",river[k]))
#plots the first values     # adds the x axis labels to the plot using
the dates

      fit <-lm(ANC~Ca)

  abline(fit)

  legend("topright", bty="n", legend=paste("R2 is",
format(summary(fit)$adj.r.squared, digits=4)))



  plot(SO4,ANC ,ylab = "ANC", xlab = "Sulfate (mg/L)",  col =
"red",pch = 19,cex = .5, main = paste("Sulfate vs ANC at",river[k]))

  fit <-lm(ANC~SO4)

  abline(fit)

  legend("topright", bty="n", legend=paste("R2 is",
format(summary(fit)$adj.r.squared, digits=4)))



dev.off()

} # ends the loop



#Caculates Al/Ca, Ca/Al, Al/ANC

for(k in 1:3){

# for alum/ca/ANC plots

names_1 = c("ANC_Alt_mersey.csv", "ANC_Al_Pinemarten.csv",
"ANC_Al_Moosepit.csv")

names_2 = c("ANC_Alt_Mersey", "ANC_Al_Pinemarten", "ANC_Al_Moosepit")



#This is for ANC_Alt_mersey

data_1= read.csv(names_1[k])

#create the julien date
```

```
#julian(data_1$Month,data_1$Date,data_1$Year)

data_1$Jul = julian(data_1$Month,data_1$Date,data_1$Year)-3708

#Creates a week column based off Julien Date

data_1$Week = ceiling(data_1$Jul/7)

#loops through each row of the csv table

#calculate the weekly average

CaAlt = c()

AlDoc = c()

AlAnc = c()

AltCa = c()

week = c()


for(i in 1:min(data_1$Week)){

  CaAlt[i] = NA

  AlDoc[i] = NA

  AlAnc[i] =  NA

  AltCa[i] = NA

  week[i] = NA}


for(i in min(data_1$Week):max(data_1$Week)){

    Rnew = data_1[data_1$Week ==i,]

    CaAlt[i] = mean(Rnew[,16])

    AlDoc[i] = mean(Rnew[,17])

    AlAnc[i] = mean(Rnew[,18])

    AltCa[i] = mean(Rnew[,20])


    if(dim(Rnew)[1] <1){

        week[i] = NA}

    else{

        week[i]= Rnew$Week
```

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```
        }       }


new_Date = data.frame(CaAlt = CaAlt, AlDoc = AlDoc, AlAnc = AlAnc,
week = week)


CaAlt.i =interpNA(CaAlt[min(data_1$Week):length(CaAlt)])

AlDoc.i =interpNA(AlDoc[min(data_1$Week):length(AlDoc)])

AlAnc.i =interpNA(AlAnc[min(data_1$Week):length(AlAnc)])

AltCa.i =interpNA(AltCa[min(data_1$Week):length(AltCa)])

Week.i = interpNA(week[min(data_1$Week):length(CaAlt)])


week.new = Week.i-min(Week.i)


CaAlt_plot = c(CaAlt[1:min(data_1$Week)-1], CaAlt.i)

AlDoc_plot = c(AlDoc[1:min(data_1$Week)-1], AlDoc.i)

AlAnc_plot = c(AlAnc[1:min(data_1$Week)-1], AlAnc.i)

AltCa_plot = c(AltCa[1:min(data_1$Week)-1], AltCa.i)


model.CaAlt = gls(CaAlt.i~week.new, corr = corAR1())

model.AlDoc = gls(AlDoc.i~week.new, corr = corAR1())

model.AlAnc = gls(AlAnc.i~week.new, corr = corAR1())

model.AltCa = gls(AltCa.i~week.new, corr = corAR1())


  if(k==1){start1 = 1980  }

  if(k==2){start1 = 1991  } #SA Nov 23

  if(k==3){ start1 = 1983}  #SA Nov 23

  if(k==1){ label2   = "A"  }

  if(k==2){ label2   = "C" }

  if(k==3){ label2   =  "B"}


  ###### Figure 4.5 ######
```
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```
  if(k==1){ label   = "Alt-Ca MR.png"  }

  if(k==2){ label   = "Alt-Ca PMS.png" }

  if(k==3){ label  = "Alt-Ca MPB.png"  }



 png(file= label, units="in", width=11, height=4, res=300)

plot(AltCa, , xaxt = "n", ylim = c(min(AltCa.i), max(AltCa.i)) , col =
"black",pch = 19,cex = .5, ylab= NA,  xlab = "Date")

    axis(1, at = seq(1,1638,52.1), labels = seq(1980,2011, 1))

    abline(model.AltCa)

     legend("topright", bty="n", legend=paste( label2) )

    if(k==1){legend("topleft",bty="n", legend=paste("Total Aluminum (
mg / L ) / Calcium ( mg / L )"))}

     dev.off()

    if(k==1){ label   = "Ca - Alt MR.png"  }

    if(k==2){ label   = "Ca - Alt PMS.png" }

    if(k==3){ label  = "Ca - Alt  MPB.png"  }



     png(file= label, units="in", width=11, height=4, res=300)

  plot(CaAlt, ylim = c(0, 50),xaxt = "n", col = "black",pch = 19,cex =
.5, ylab= NA,  xlab = "Date")

    axis(1, at = seq(1,1638,52.1), labels = seq(1980,2011, 1))

     legend("topright", bty="n", legend=paste( label2) )

     if(k==1){legend("topleft",bty="n", legend=paste("Calcium ( mg /
L ) / Total Aluminum ( mg / L )"))}

       abline(model.CaAlt)


       dev.off()



plot(AlDoc, xaxt = "n", col = "black",pch = 19,cex = .5, ylab= "Total
Aluminum / DOC",  xlab = "Date", main = paste("Total Aluminum / DOC vs
Time at ",river[k]))
```

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```
    axis(1, at = seq(1,1638,52.1), labels = seq(1980,2011, 1))

    abline(model.AlDoc)

    legend("topleft", bty="n",  legend=paste("Weekly Change:
",model.AlDoc$coef[2]))



    plot(AlAnc, xaxt = "n", col = "black",pch = 19,cex = .5, ylab=
"Total Aluminum / ANC",  xlab = "Date", main = paste("Total Aluminum /
ANC vs Time at ",river[k]))

    axis(1, at = seq(1,1638,52.1), labels = seq(1980,2011, 1))

    abline(model.AlAnc)

    legend("topleft", bty="n",  legend=paste("Weekly Change:
",model.AlAnc$coef[2]))



  ##Monthly Data calulated


data_1$Month2 = (data_1$Year-1980)*12 + data_1$Month


#calculate the monthly average


CaAlt_month = c()

AlDoc_month = c()

AlAnc_month = c()

AltCa_month = c()

month = c()

for(i in 1:min(data_1$Month2)){

     CaAlt_month[i] = NA

     AlDoc_month[i] = NA

  AlAnc_month[i] = NA

  AltCa_month[i] = NA

     month[i] = NA    #jm edit dec 6

     }

for(i in min(data_1$Month2):max(data_1$Month2)){
```

```
        Rnew = data_1[data_1$Month2 == i,]

        CaAlt_month[i] = mean(Rnew[,16])

        AlDoc_month[i] = mean(Rnew[,17])

        AlAnc_month[i] = mean(Rnew[,18])

        AltCa_month[i] = mean(Rnew[,20])



        }

CaAltMonth.i
=interpNA(CaAlt_month[min(data_1$Month):length(CaAlt_month)])

AlDocMonth.i
=interpNA(AlDoc_month[min(data_1$Month):length(AlDoc_month)])

AlAncMonth.i
=interpNA(AlAnc_month[min(data_1$Month):length(AlAnc_month)])

AltCaMonth.i
=interpNA(AltCa_month[min(data_1$Month):length(AltCa_month)])

if (k ==1){

        ts_CaAlt = ts(CaAltMonth.i, start = c(1980, 2), end = c(2011,7),
freq = 12)

        ts_AlDoc = ts(AlDocMonth.i, start = c(1980, 2), end = c(2011,7),
freq = 12)

        ts_AlAnc = ts(AlAncMonth.i, start = c(1980, 2), end = c(2011,7),
freq = 12)

        ts_AltCa = ts(AltCaMonth.i, start = c(1980, 2), end = c(2011,7),
freq = 12)



        }

if (k ==2){

        ts_CaAlt = ts(CaAltMonth.i, start = c(1989, 12), end = c(2011,7),
freq = 12)

        ts_AlDoc = ts(AlDocMonth.i, start = c(1989, 2), end = c(2011,7),
freq = 12)

        ts_AlAnc = ts(AlAncMonth.i, start = c(1989, 2), end = c(2011,7),
freq = 12)

        ts_AltCa = ts(AltCaMonth.i, start = c(1989, 12), end = c(2011,7),
freq = 12)
```

```
      }
if (k==3){

      ts_CaAlt = ts(CaAltMonth.i, start = c(1983, 5), end = c(2011,7),
freq = 12)

  ts_AlDoc = ts(AlDocMonth.i, start = c(1983, 2), end = c(2011,7),
freq = 12)

      ts_AlAnc = ts(AlAncMonth.i, start = c(1983, 2), end = c(2011,7),
freq = 12)

      ts_AltCa = ts(AltCaMonth.i, start = c(1983, 5), end = c(2011,7),
freq = 12)

  }
print(SeasonalMannKendall(ts_CaAlt))

print(SeasonalMannKendall(ts_AlDoc))

print(SeasonalMannKendall(ts_AlAnc))

print(SeasonalMannKendall(ts_AltCa))

}
```

B. BIC R Statistical Package Code

Used to determine the best predictors for the estimation of Al_i

```
#Creates a lm to calculate ionic aluminium

setwd("S:\\HSRG\\122 - Aluminum Survey EC Data\\Jeff\\R")
data = read.csv("RawData.csv")
data = data[,-c(67:dim(data)[2])]
data = data[-c(93:dim(data)[1]),]
plots = data[,c(9:dim(data)[2])]


##possible variables:


for(i in 1:dim(plots)[2]){
    plots[,i] = as.numeric(as.character(plots[,i]))
}


# completed so iron is NOT included
    selected = data.frame(CA = (plots$CA-mean(plots$CA))/sd(plots$CA)
, CL =  (plots$CL-mean(plots$CL))/sd(plots$CL), TOC = (plots$TOC-
mean(plots$TOC))/sd(plots$TOC),
    PH = (plots$PH-mean(plots$PH))/sd(plots$PH), SO4 =  (plots$SO4-
mean(plots$SO4))/sd(plots$SO4), AL =  (plots$AL_T-
mean(plots$AL_T))/sd(plots$AL_T),IA =  log(plots$AL_F))



#this extracts the variables tom and dennis used
plots$TOC = as.numeric(as.character(plots$TOC))
plots$AL_C = as.numeric(as.character(plots$AL_C))
plots$AL_T = as.numeric(as.character(plots$AL_T))
plots$PH = as.numeric(as.character(plots$PH))
```

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```
#this creates the model tom use, the model with standardised variables
and the model with the log

pdf("Model.pdf")

#raw data

model1 = lm(AL_F ~ AL_T + TOC + PH, data = plots)

summary(model1)

plot(model1)

#very bad residuals


ALT_cen = (plots$AL_T - mean(plots$AL_T)) / sd(plots$AL_T)

TOC_cen = (plots$TOC - mean(plots$TOC)) / sd(plots$TOC)

PH_cen = (plots$PH - mean(plots$PH)) / sd(plots$PH)


#centered data

model2 = lm(plots$AL_F ~ ALT_cen + TOC_cen + PH_cen)

summary(model2)

plot(model2)


#natural log of AL

model3 = lm(log(plots$AL_F) ~ ALT_cen + TOC_cen + PH_cen)

summary(model3)

plot(model3)

dev.off()


#plots each of the variables against the line

#individual plots

pdf("Veriables.pdf")

plot(ALT_cen, log(plots$AL_F), pch = 19)

abline(model3$coef[1], model3$coef[2])
```

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```
plot(TOC_cen, log(plots$AL_F), pch = 19)

abline(model3$coef[1], model3$coef[3])


plot(PH_cen, log(plots$AL_F), pch = 19)

abline(model3$coef[1], model3$coef[4])

dev.off()


#Ionic = exp(2.9464116  + 1.1077030((ALT- 178.2412)/114.7843) -
0.3586587((TOC-9.726087)/ 5.100611) +   0.4271494((PH- 6.770978)/
0.9478038)


#try out the possible combinations

head(selected)

#############################################

#############################################

#This is the code to find the BEST model possible

#############################################

#############################################


 library(nlme)

 #make sure the selected dataframe is run before - or there are erro
with teh words

 rem =
matrix(c(selected$CA,selected$CL,selected$TOC,selected$PH,selected$SO4
,selected$AL), ncol =6)

 colnames(rem) = c("CA","CL","TOC", "PH", "SO4","AL")

 IA = selected$IA

 model = lm(IA~rem)

 BICval =  BIC(model)


  for (i in 1:floor(ncol(rem)/2)){

      select = NULL
```

```
    select = combn(ncol(rem), i)
    iter = length(select)/i


    if (i == 1){
      for (k in 1:iter){
        rem1 = rem[,-select[1,k]]
        rem2 = matrix(rem[,select[1,k]  ], ncol =1)
        colnames(rem2) = c(colnames(rem)[select[1,k]])


        model1 = lm(IA~rem1 )
        model2 = lm(IA~rem2 )
        if (BIC(model1) < BICval){
          BICval = BIC(model1)
          model = model1
          remhold = rem1
          code = colnames(rem1)


          }
        if (BIC(model2) < BICval){
          BICval = BIC(model2)
          model = model2
          remhold = rem2
          code = colnames(rem2)
        }
    }}


  if (i == 2){
    for (k in 1:iter){
      rem1 = rem[,-select[2,k]]
      rem1 = rem1[,-select[1,k]]
```

```r
        rem2 = matrix(c(rem[,select[1,k]], rem[,select[2,k]]), ncol =
2)

        colnames(rem2) = c(colnames(rem)[select[1,k]],
colnames(rem)[select[2,k]] )

        model1 = lm(IA~rem1)

        model2 = lm(IA~rem2)

        if (BIC(model1) < BICval){

          BICval = BIC(model1)

          model = model1

          remhold = rem1

          code = "no" }

        if (BIC(model2) < BICval){

          BICval = BIC(model2)

          model = model2

          remhold = rem2

          code = "no"}

        }}


    if (i == 3){

      for (k in 1:iter){

        rem1 = rem[,-select[3,k]]

        rem1 = rem1[,-select[2,k]]

        rem1 = rem1[,-select[1,k]]

        rem2 = matrix(c(rem[,select[1,k]],
rem[,select[2,k]],rem[,select[3,k]]), ncol = 3)

        colnames(rem2) = c(colnames(rem)[select[1,k]],
colnames(rem)[select[2,k]],colnames(rem)[select[3,k]])

        model1 = lm(IA~rem1)

        model2 = lm(IA~rem2)

        #if (k == 30){print(BIC(model1))}

        if (BIC(model1) < BICval){

          BICval = BIC(model1)
```

```
      model = model1

      remhold = rem1

      code = "no"}

    if (BIC(model2) < BICval){

      BICval = BIC(model2)

      model = model2

      remhold = rem2

      code = "no"}

    }}


  if (i == 4){

    for (k in 1:iter){

      rem1 = rem[,-select[4,k]]

      rem1 = rem1[,-select[3,k]]

      rem1 = rem1[,-select[2,k]]

      rem1 = rem1[,-select[1,k]]

      rem2 = matrix(c(rem[,select[1,k]],
rem[,select[2,k]],rem[,select[3,k]],rem[,select[4,k]]), ncol = 4)

      colnames(rem2) = c(colnames(rem)[select[1,k]],
colnames(rem)[select[2,k]],colnames(rem)[select[3,k]],colnames(rem)[se
lect[4,k]])

      model1 = lm(IA~rem1)

      model2 = lm(IA~rem2)

      if (BIC(model1) < BICval){

        BICval = BIC(model1)

        model = model1

        remhold = rem1

        code = "no" }

      if (BIC(model2) < BICval){

        BICval = BIC(model2)

        model = model2
```

```
        remhold = rem2

        code = "no"}

      }}


  if (i == 5){

    for (k in 1:iter){

      rem1 = rem[,-select[5,k]]

      rem1 = rem1[,-select[4,k]]

      rem1 = rem1[,-select[3,k]]

      rem1 = rem1[,-select[2,k]]

      rem1 = rem1[,-select[1,k]]


      rem2 = matrix(c(rem[,select[1,k]],
rem[,select[2,k]],rem[,select[3,k]],rem[,select[4,k]],rem[,select[5,k]
]), ncol = 5)

      colnames(rem2) = c(colnames(rem)[select[1,k]],
colnames(rem)[select[2,k]],colnames(rem)[select[3,k]],colnames(rem)[se
lect[4,k]],colnames(rem)[select[5,k]])

      model1 = lm(IA~rem1)

      model2 = lm(IA~rem2)

    if (BIC(model1) < BICval){

      BICval = BIC(model1)

      model = model1

      remhold = rem1

      code = "no" }

    if (BIC(model2) < BICval){

      BICval = BIC(model2)

      model = model2

      remhold = rem2

      code = "no"}

    }}}
```

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```
#the best MODEL selected above is called MODEL
summary(model)


pdf("Veriables_35.pdf")
plot(selected$TOC, selected$IA, pch = 19)
abline(model$coef[1], model$coef[3])


plot(selected$AL, selected$IA, pch = 19)
abline(model$coef[1], model$coef[6])


plot(selected$CA,selected$IA, pch = 19)
abline(model$coef[1], model$coef[2])


plot(selected$SO4, selected$IA, pch = 19)
abline(model$coef[1], model$coef[5])


plot(selected$FE_T, selected$IA, pch = 19)
abline(model$coef[1], model$coef[4])
dev.off()
```

C. Original Al$_t$ Time Series Data with Outliers Included

Raw Al$_t$ values without interpolation or outlier removal. A) MR B) MPB C) PMB.