Loading of elements and anions to the St. Lawrence River from tributaries in St. Lawrence County, New York

Report[‡]

June 25, 2014

[‡] Adapted from the Senior Year Thesis of Roselyne Laboso

TABLE OF CONTENTS

ABSTRACT

A year-long sampling event (June 2011 to June 2012) was conducted on four tributaries flowing into the St. Lawrence River Basin—Oswegatchie, Grasse, Raquette, and St. Regis. The headwaters of all these rivers originate in the acidified Adirondack Highlands (crystalline acidic bedrock) and flow across the Adirondack Lowlands (marble-rich metasedimentary sequence) and early Paleozoic sedimentary rocks (sandstone and dolostone) of the St. Lawrence River Valley. Sampling was conducted close to US Geological Survey gauging stations in the St. Lawrence River Valley so that loading of the analytes could be determined. In general, the waters were dilute: OSW (128.02±37.40), GRA (125.27±40.55), RAQ (73.76±58.51), and STR (96.10±38.23) µS. Their mean pH was 7.11±0.52, 7.62±0.66, 7.22±0.50, and 7.33±0.50 respectively. The most abundant cations were Ca, Na, Si, Mg, and K. The chief anions were CO_3^{2-}, Cl^-, and SO_4^{2-}. Mean calculated ANC values in the four rivers are 41.13±6.63, 43.24±8.59, 23.65±27.49, and 30.90±6.90 (mg/L) respectively. The chemistry of the rivers varies from West to East and is influenced by the nature of the bedrock. The chemistry of the Raquette River was clearly anomalous and has the least amount of total dissolved solids and the least seasonal variability in nearly every analyte. This homogeneity is likely related to a number (n = 17) of hydropower reservoirs along its length. Runoff from a dolostone quarry upriver is also investigated to determine effects on chemistry of Raquette River. The combinations of physical and chemical characteristics of water quality, along with U.S. Geology Survey data, were used to reveal trends and correlations relating to each of the four rivers. Geological and anthropogenic factors were used to explain the analyzed data.

1. INTRODUCTION

St. Lawrence County is located in northern New York State with a large southern portion situated within the Adirondack Park (Figure 1) and a northern portion bounded by the St. Lawrence River. St. Lawrence County, NY has low population density in most of its area (Figure 2) particularly within the higher elevation areas within the Adirondack blue line (Figure 3). The land within the Adirondack Park is highly forested (Figure 4) and sparsely populated. The Adirondack Park is known to have the most stringent environmental laws in northeastern U.S. in efforts to preserve its pristine lands and wildlife. The Adirondack Park is also a major tourist attraction and allows for winter as well as summer recreational opportunities. Northwards of the Adirondack Park are mostly pasture lands, crop farms, and settlement areas (Figure 4) where the terrain is gently sloping and soils better for farming. There are also forest and non-forest wetlands, lakes, and streams found in the Adirondack Lowlands and St. Lawrence Valley.

Four rivers in St. Lawrence County including the Oswegatchie, Grasse, Raquette, and St. Regis Rivers were sampled weekly in Heuvelton, Chase Mills, Raymondville, and Brasher Center, NY respectively for a period of one year (Figure 1). The rivers flow northwards over three distinct bedrock terranes including the Adirondack Highlands, Adirondack Lowlands, and St. Lawrence Valley before draining into the St. Lawrence River (Chiarenzelli et al., 2012).

Research for acid precipitation began early (1970s) in the Adirondacks due to their high elevation, high rainfall, and igneous bedrock that are sensitive to acid rain and have low buffering capacity. However, most of the research was performed on lakes and soils and observed effects extrapolated onto stream and river systems. By mid-1970s due to the observed impact on ecosystems, it was noted that sulfur and nitrogen oxides were major culprits in atmospheric acidification. Major sources include combustion of fossil fuels for power generation, transportation, heating, and industrial purposes. The Adirondack region receives significant amounts of acid precipitation and deposition via wet and dry deposition, caused by sulfur dioxide and nitrogen oxide (Jenkins et al., 2007; Driscoll et al., 1991). Driscoll et al (2001 & 2004) states that acidic deposition in northeastern US has resulted in decrease in pH and acid neutralizing capacity (ANC), the capacity of solutes and particulates in an aqueous system to neutralize acid (USGS TWRI Book 9, 2012), Additional effects include the depletion of plant nutrient in soils, including Ca^{2+}, Mg^{2+}, K^{+}, increasing inorganic monomeric Al concentration in surface water and accumulation of S and N in the soils. However, an 8 year study (1992 – 2000) of 48 Adirondack lakes by Waller et al. (2012) showed some recovery in ANC. Waller et al (2012) suggests that there has been some evidence of long-term recovery of lakes in the Adirondack region due to decrease in acid deposition, after a control on SO_2 and NO_x emission through market-based cap and trade systems by the Acid Rain Program and Nitrogen Budget Program.

River/stream chemistry information in the Adirondack region is limited (Lawrence et al., 2004). However, some studies of river chemistry have been performed in the past through the Episodic Response Project funded by the U.S. Environmental Protection Agency as well as the Adirondack Lakes Survey Corporation (Wigington et al., 1996; Lawrence et al., 2004). Previously, Chiarenzelli et al (2012) examined the variation in elemental composition and geochemical nature of the four rivers (Oswegatchie, Grasse, Raquette, and St. Regis Rivers) while comparing two summer multi-element sampling events and physiochemical parameters including temperature, precipitation, discharge, and time. O'Connor et al (2010) determined a good correlation between geologic units and groundwater geochemistry, a conclusion that can be extended towards surface water chemistry. Murphy (2011) also investigated stream chemistry of watersheds in central St. Lawrence County and their impact on large water bodies, spatial variability in elemental and physical parameters, and relative anthropogenic factors on basins.

The goal of this study is to determine the loading of elements and anions from rivers draining northern New York into the St. Lawrence River. As a consequence of this sampling regime, the overall quality and annual variation in river chemistry has also been evaluated. Interaction of river water with the bedrock and anthropogenic impacts from farming, mining, and atmospheric deposition in the watersheds are investigated to determine variation of water chemistry in St. Lawrence County. Likewise, the impact of a high number of hydroelectric dams (n=17) along Raquette River on river chemistry will be evaluated Chiarenzelli and Skeels (*in review*). The buffering capacities of Adirondack Rivers are tested as well using alkalinity and ANC. Finally, I also investigate the role of a dolostone quarry along the Raquette River in altering the chemistry of this river during runoff events (Figure 5).

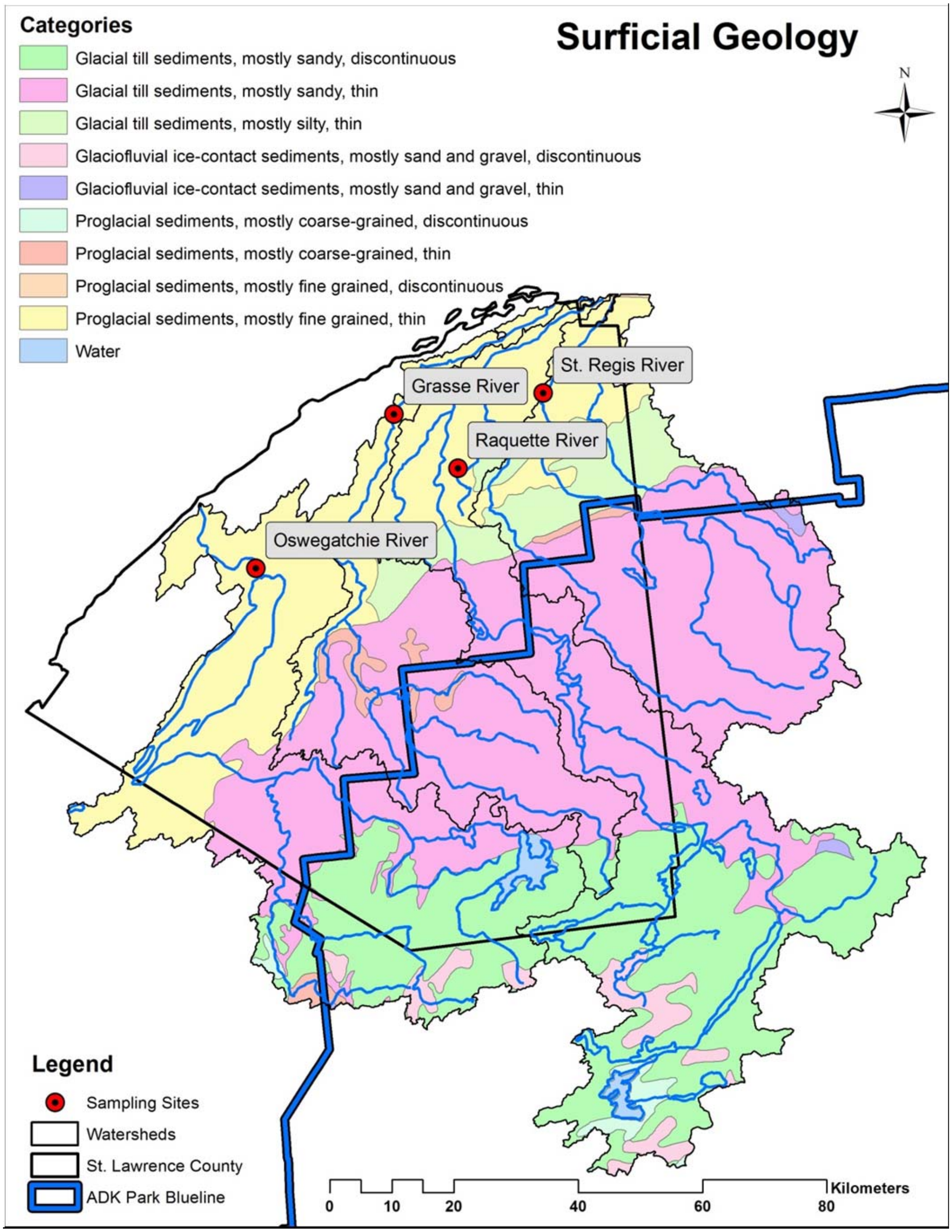


Figure 1: Generalized Surficial Geology map of St. Lawrence County Showing major rivers, watersheds, and the Adirondack Park Boundary (blue line)

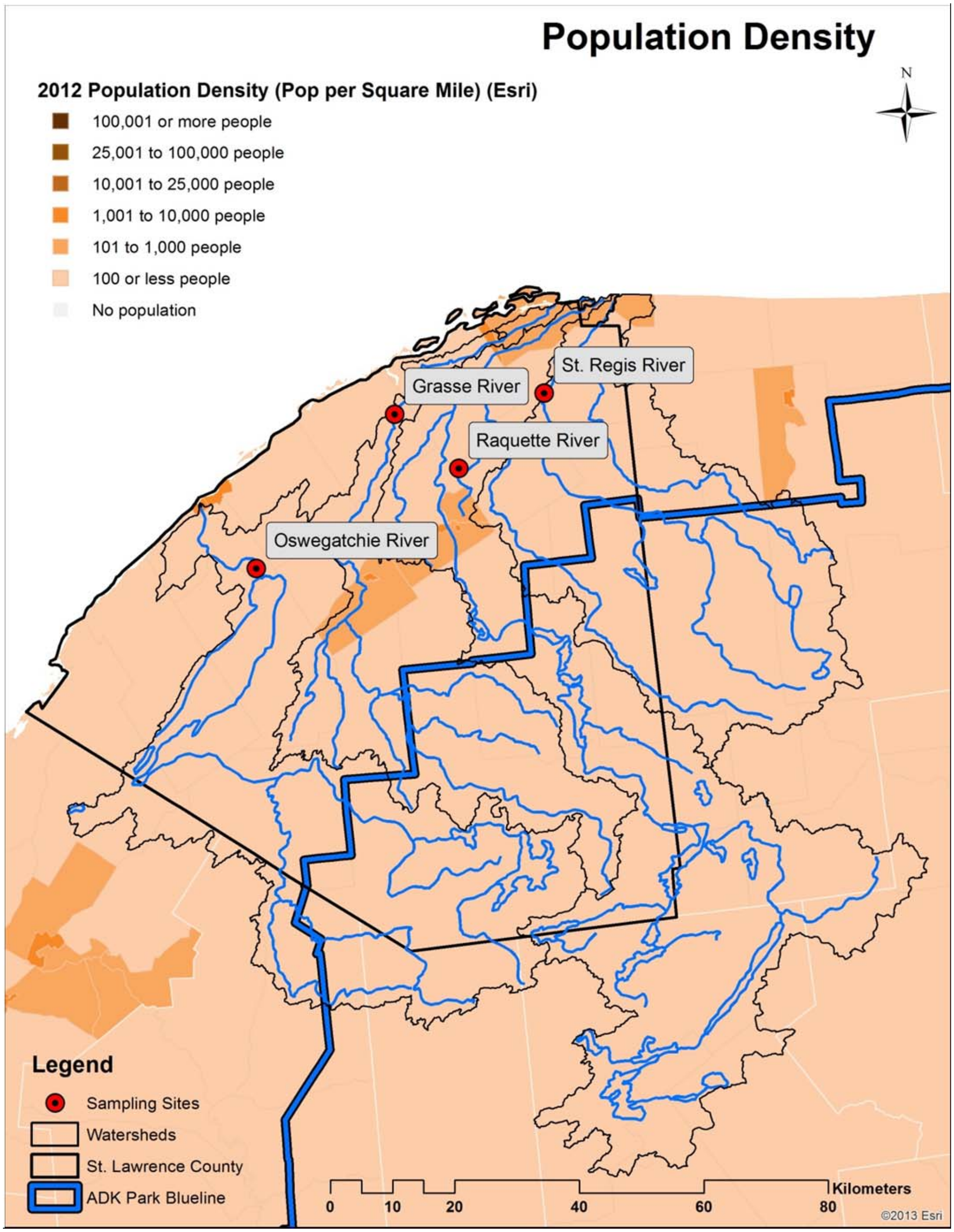


Figure 2: Map of population density of St. Lawrence County, NY also showing major rivers, and watersheds

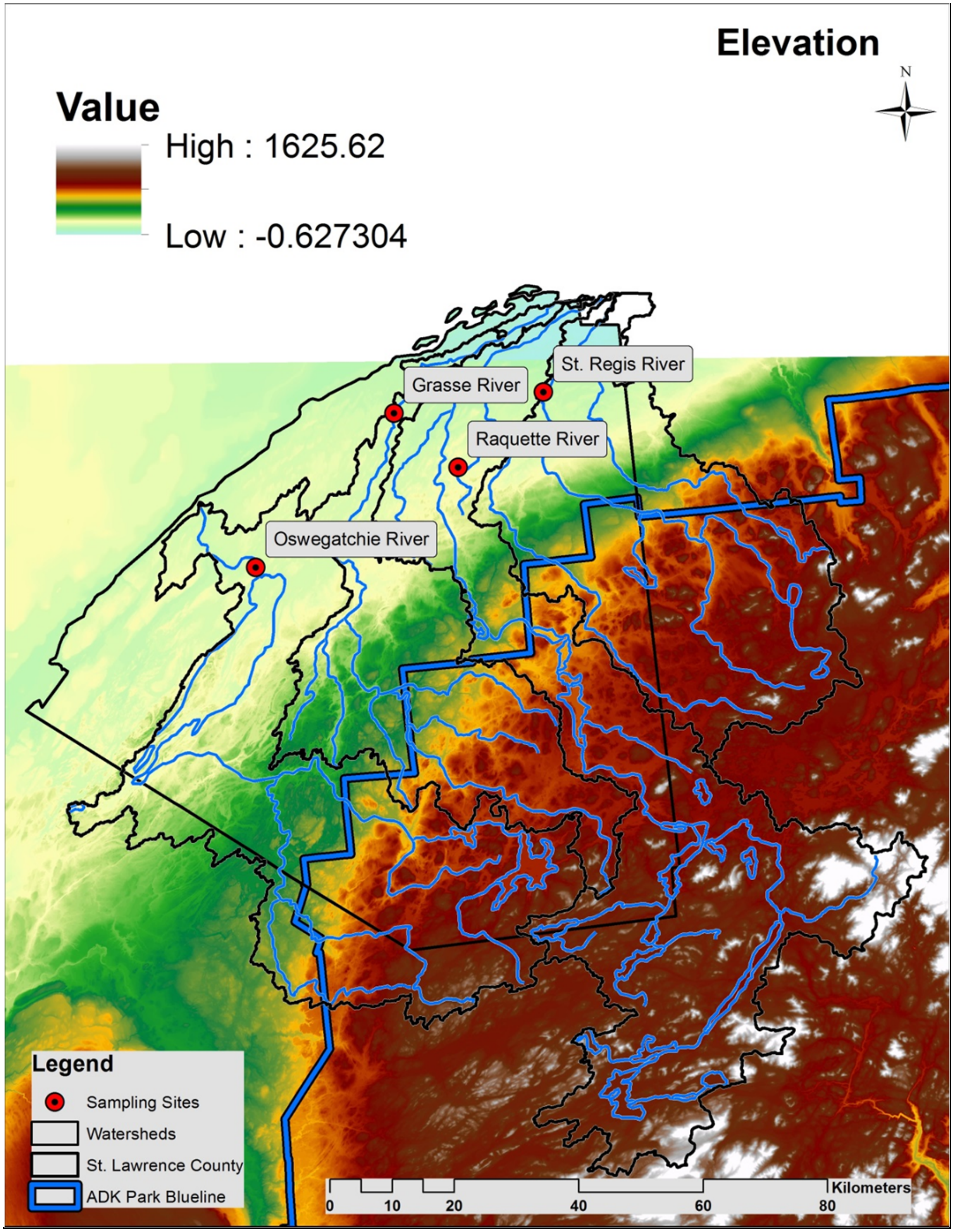


Figure 3: Map showing elevation in St. Lawrence County, NY, major rivers, and watersheds

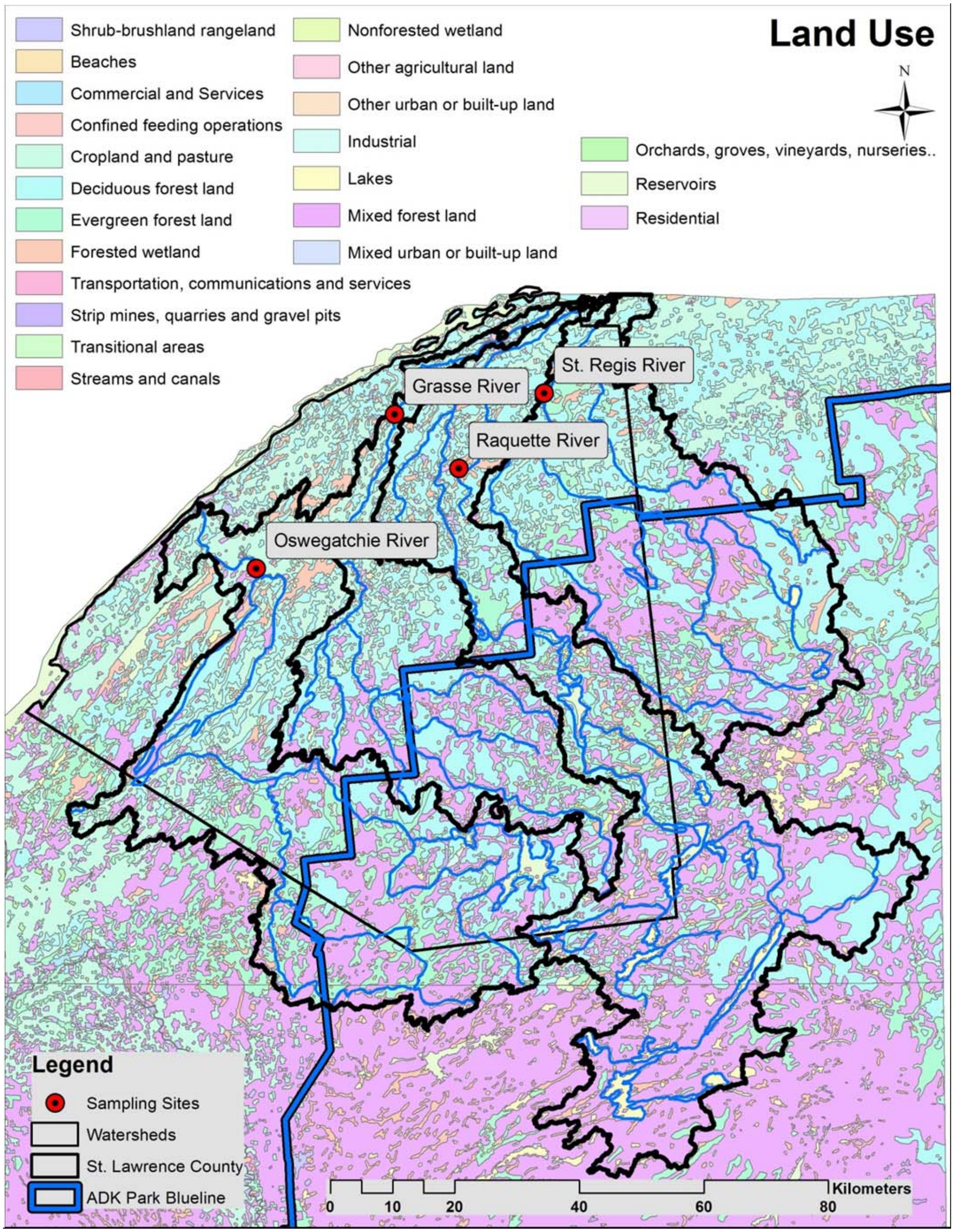


Figure 4: Map of St. Lawrence County land use, as well as major rivers, and watershed. Pink and light blue patches within Adirondack blue line indicates areas covered with mixed forest, deciduous and evergreen forest lands. Region within Adirondack Lowlands and St. Lawrence Lowlands are covered by farming and pasture lands, urban and built up area, and commercial spaces.

Figure 5: Aerial photograph courtesy of Google Earth of Norwood Asphalt Plant and Quarry upriver from RAQ sampling site that mines aggregate (NYSDOT approved crushed limestone, granite, and gravel, sands, and stone fill items). Note the discoloration of the Raquette River due to runoff containing powdered dolostone from the quarry.

2. GEOLOGIC SETTING

Sampling events were conducted within St. Lawrence County, encompassing three distinct physiographic regions of northern New York namely: Adirondack Highlands, Adirondack Lowlands, and St. Lawrence Valley (Figure 6).

The Adirondack Highlands are a regionally elevated elliptical dome exposing metamorphosed igneous rocks of the Grenville Province (Chiarenzelli et al., 2012) of granulite facies grade (Mezger et al., 1992. The Adirondack Lowlands are dominated by mid-upper amphibolite facies metasedimentary rocks including marbles, calc-silicates, pelitic gneisses, and minor quartzite and evaporates intruded with subordinate felsic to intermediate metaigneous rocks (Streepey et al., 2011; Chiarenzelli et al., 2012). Separating the Adirondack Highlands and Lowlands is the Carthage-Colton Mylonite Zone (CCMZ). The CCMZ is a composite (reverse/normal) fault with a known minimum length of about 1000 km (Mezger et al., 1992) associated with high angle faults and fault breccia (Isachen and Fisher, 1970). An unconformity lies between Adirondack Lowlands and Paleozoic rocks of the St. Lawrence Valley marking change in rock texture, grain size, composition, and origin. The St. Lawrence Valley is underlain by Cambrian to Ordovician sandstones, and carbonates (Chiarenzelli et al., 2012) composed of Potsdam sandstone, Theresa formation, and the Beekmantown group (limestones and dolostones).

Bedrock in the county is covered by a thin layer of soil and other loose material that originated from weathering of surface rocks. Most of these loose materials remain in place but some of it may be eroded, transported, and deposited by water, wind, or glacial ice. Surficial geology of St. Lawrence County varies from the Adirondack Highlands to the Lowlands due to past glacial activity in the area.

The Highlands are mostly dominated by bedrock mantled with rock debris, glacial till, and lacustrine or marine sediments, outwash sand and gravel, kame deposits, and lacustrine sand. Some glacial features prominent in the Adirondack Highlands are eskers. The Adirondack Lowlands on the other hand is dominated by lacustrine silt and clay, swamp deposits, glacial till, and undifferentiated marine and lacustrine sand. Glacial features found in the lowlands include till moraine (Pair and Cadwell, 1991). The Laurentide Ice Sheet due to Wisconsin glaciation (most recent major ice sheet advance) is thought to be responsible for glacial deposits, and features in this area as well as the whole of Northern U.S. (Pair and Rodrigues, 1993; O'Connor et al., 2010). Detailed surficial mapping has allowed for identification of ice-marginal landforms throughout the western St. Lawrence Lowlands (Pair and Rodrigues, 1993).

Waters of the four rivers (Oswegatchie, Grasse, Raquette, and St. Regis Rivers) flow over crystalline granitoid rocks of the Adirondack Highlands that have low buffering capacity, then across metasedimentaty rocks (mostly calcitic and dolomitic marbles) of the Adirondack Lowlands with high buffering capacity, then over sedimentary rocks of the St. Lawrence Valley before exiting into the St. Lawrence River.

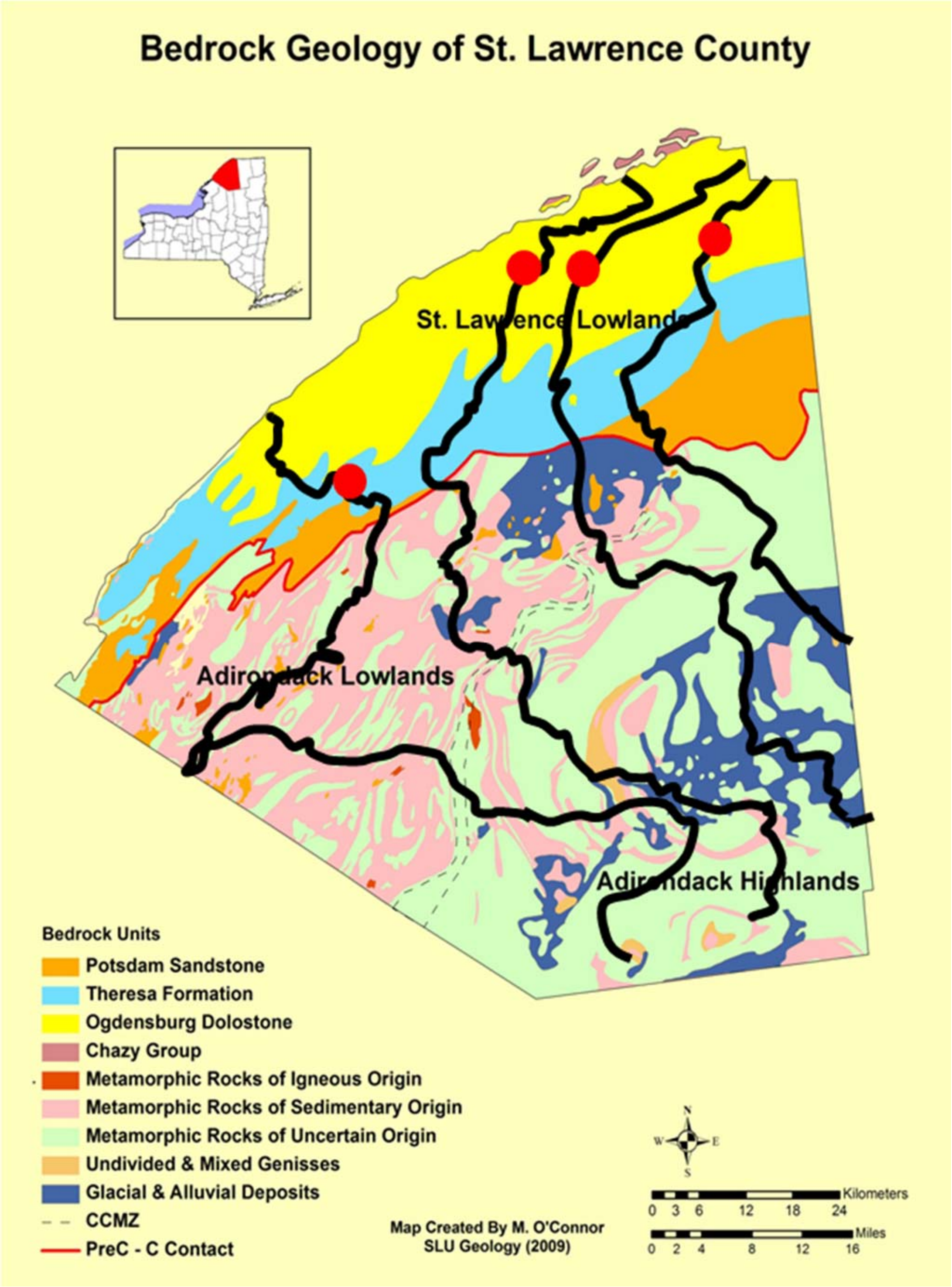


Figure 6: Generalized bedrock geology of Oswegatchie, Grasse, Raquette, and St. Regis watershed areas (adapted from O'Connor et al., 2010).

3. METHODS

3.1 Instrument calibration

Temperature, pH, conductivity, and dissolved oxygen probes via a portable Vernier LabPro were used to determine the physical parameters on site. A two point calibration was performed for the pH probe, using 4 and 10 buffer solutions. A two point calibration was also performed for the conductivity probe. Deionized water served as the zero point, and a KCl solution of 100µS provided the second point. Another KCl solution of 74µS was used as a quality control both in the lab and in the field. A two point calibration was performed for the dissolved oxygen probe. A sodium sulfite calibration solution serves as 0mg/L. The second point calibration was derived from measuring tap water poured back and forth between two 150 mL beakers ten times at room temperature. The values measured were compared to values listed on a table of dissolved oxygen concentrations which vary according to temperature (Table 1) as noted by United States Environmental Protection Agency (USEPA) (USEPA, 2012).

Table 1: Maximum Dissolved oxygen concentrations vary with temperature as shown in EPA website under Sampling and Equipment Considerations (USEPA, 2012)

Temp (˚C)	DO (mg/L)	Temp (˚C)	DO (mg/L)	Temp (˚C)	DO (mg/L)	Temp (˚C)	DO (mg/L)
0	14.6	12	10.76	24	8.4	36	6.82
1	14.19	13	10.52	25	8.24	37	6.71
2	13.81	14	10.29	26	8.09	38	6.61
3	13.44	15	10.07	27	7.95	39	6.51
4	13.09	16	9.85	28	7.81	40	6.41
5	12.75	17	9.65	29	7.67	41	6.41
6	12.43	18	9.45	30	7.54	42	6.22
7	12.12	19	9.26	31	7.41	43	6.13
8	11.83	20	9.07	32	7.28	44	6.04
9	11.55	21	8.9	33	7.16	45	5.95
10	11.27	22	8.72	34	7.16		
11	11.01	23	8.56	35	6.93		

3.2 Sampling Collection

Sample sites were located near USGS gauging stations listed on the USGS web-site and identified via Google Earth along the course of each of the four rivers. Each gauging station was the final gauging station on each tributary and was located within a few miles of the confluence of each of the rivers with the St. Lawrence River. (Figure 1)

Access to gauging station at the Raquette (RAQ) and St. Regis (STR) sites were inaccessible therefore sampling sites along these rivers were chosen at a slight distance (a few hundred meters) from the gauging stations. At the sample sites, air and water temperature, pH, dissolved oxygen, and conductivity readings were taken using Logger Pro software and measurement probes. The stable and final readings from the probes were recorded in a notebook and later transferred into an Excel file at the lab. Water samples were collected in 250 mL, pre-cleaned, Wheaton I-Chem Nalgene Bottles with a duplicate sample taken each week at a different river in a rotating manner. Other water samples were collected weekly alongside river samples as control from a deionized water source in lab (Table F1). Control water samples were treated the same was as river water samples in order to get a general and fairly accurate comparison between the waters.

3.3 Instrument and chromatographic conditions

IC analyses were performed on a DIONEX IC with a LC25 Chromatography Oven, an EG50 Eluent Generator, a CD25 Conductivity Detector, a GP50 Gradient Pump, and an AS40 Automated Sampler. The flow rate of the mobile phase, KOH, was maintained at 1.0mL/minute with an injection volume of 25.0µL. A Fluka analytical: Multielement Ion Chromatography Anion Standard Solution (PCode 220021080) was used as a positive control while deionized water was a negative control. Multiple positive controls were run throughout the sampling event as well as negative controls to ensure stable and consistent readings.

3.4 Standard preparation for Ion Chromatography

Individual stock solutions of fluoride, chloride, nitrite-N, bromide, sulfate, nitrate-N, and phosphate-P were prepared, and serial dilutions were carried out to prepare four standard solutions for the IC. Appendix B displays the concentration of anions in the multi-ion standards. A separate stock solution of carbonate was prepared, and serial dilutions were performed to obtain four carbonate standards, also shown in Appendix B.

3.5 Acid Neutralizing Capacity and Alkalinity

Acid Neutralizing Capacity (ANC) and Alkalinity analysis were performed according to the validated method of U.S. Geological Survey (TWRI Book 9 Chapter A6 Field Measurements). A sulfuric acid titrant solution was prepared by adding 0.5mL concentrated H_2SO_4 to approximately 950 mL deionized water, mixing, and diluting to 1L mark. This resulted in an acid concentration of roughly 0.018N (Eq/L) by calculation (Equation 1). This solution was standardized with a 0.01639N primary standard sodium carbonate solution. This was prepared by weighing out 0.8686g of primary standard grade Na_2CO_3, adding it to a 1L volumetric flask, mixing, and diluting to 1L mark. The sulfuric acid was then standardized by pipeting 25mL of sodium carbonate standard solution into a 100mL beaker, and titrating with the sulfuric acid solution. The pH and volume of titrant added was recorded (Figure xx) and the normality of the acid was determined using a Gran Function Plot (USGS TWRI Book 9 Chapter A6 Field Measurements).

$$ANC\left(\frac{meq}{L}\right)=\frac{B(mL)\times C_a\left(\frac{meq}{L}\right)}{V_s(mL)\times\left(\frac{1L}{1000mL}\right)}$$

B = *volume of acid titrant (milliliters)*
C_a = *concentration of acid titrant (milliequivalents per milliliter)*
V_s = *volume of sample (milliliters)*

Equation 1: Formula used to calculate acid neutralizing capacity and alkalinity of river water

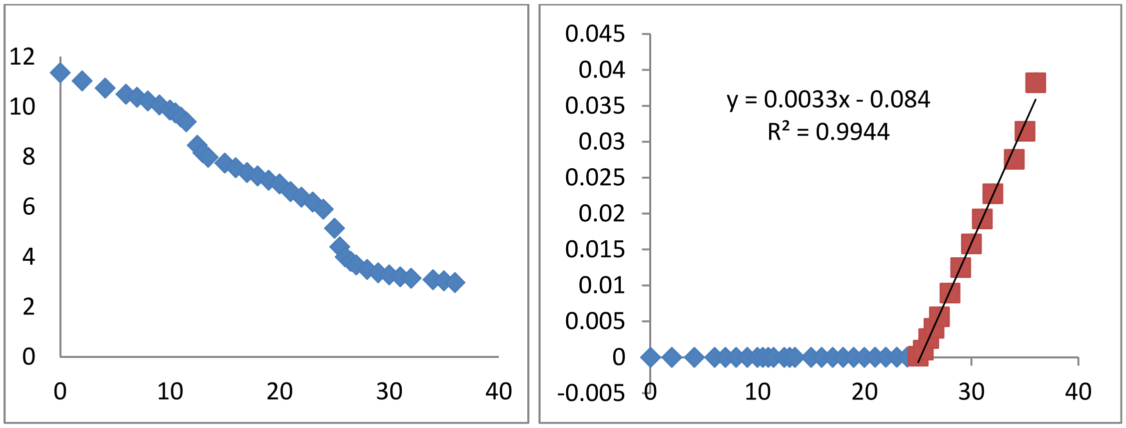


Figure 7: **Standardization of sulfuric acid solution.** Graphs of of pH (y-axis) versus volume of titrant in mL (x-axis) and Gran Function versus volume of titrant (mL) respectively for standardized sulfuric acid as created by Microsoft Excel (5/6/12 Trial 4)

A Hamilton MicroLab 500 Series Auto Titrator was used to perform the ANC and Alkalinity titrations for each sample. Alkalinity samples were prepared by filtering samples with a Nylon 25mm syringe filter-0.45um, while ANC samples were left unfiltered. A bulb pipette was used to accurately transfer 50mL of each sample to a 100mL beaker. The pH of the samples was allowed to equilibrate for 10 minutes followed by a titration of approximately 30 minutes. A Gran Function Plot was once again used to determine final ANC and Alkalinity values (Figure x)

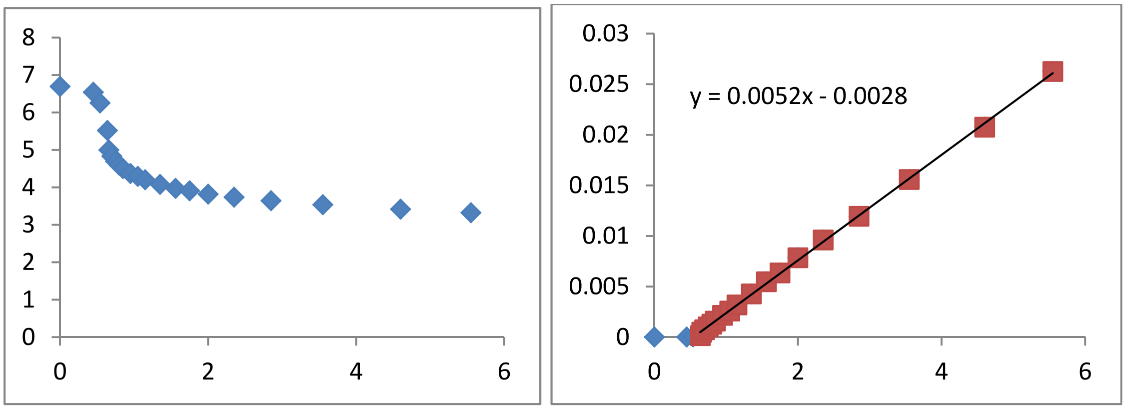


Figure 8: **Example of alkalinity titration.** Graphs of pH (y-axis) versus volume in mL (x-axis) and Gran Function (y-axis) versus volume in mL (x-axis) respectively for ALK (Sample: RAQ 2)

3.6 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis

Weekly samples of river water, their duplicates, and control were shipped to ACME Analytical Laboratories in Vancouver, British Columbia for analysis of 72 elements, primarily at the parts per billion (ppb = µg/L) or parts per trillion level (ppt = ng/L). Before being sent to ACME, water samples were stored in a dark refrigerator at 4˚C.

3.7 Quality Assurance analysis

Quality assurance analysis was determined by use of control, duplicates, blanks, and standards. ACME reports for every set of samples submitted for analysis included sample concentrations, their duplicates, ACME blanks and standards (as reference materials). Appendix F contains all the quality assurance data produced from ICP-MS analysis.

(a) Blank Values

ACME blanks were generated in ACME labs to be analyzed alongside our collected samples for 72 elements (Appendix F). These were to help determine any sources of contamination and impurities brought into our samples during transportation, storage, and/or analysis.

Control samples (method blanks) were deionized water from a lab source. These samples were treated similarly to river water samples in that they were analyzed, stored, and transported in a similar manner. Control samples were used for both element and anion analysis. Detected elements from our control samples are shown in Table 5. The aim of the control was to serve as a method blank in order to assess if preparation, handling, and analysis of water samples added any impurities and contaminants into the samples (USGS TWRI Book 9, 2006). The most frequently detected element is Zn at 35 detects out of 52 control samples, followed by Ba at 34 detects. Mn, Sr, and Ni are other elements detected within our control samples. ACME prepared blanks were also reported to help determine possible contamination from analytical methods (Table 6). Only 8 elements were detected and the highest number of detects was Ru at 4 detects. There is an overlap of detectable elements in control and ACME blanks; Ba, Mn, Sr, and Zn. However, Gd, Li, P, and Ru are introduced in the labs though infrequently and at low concentrations (<4 detects).

In general, our samples may have had some affect by analyses and sample methods. However, we cannot at this point determine the exact cause of some of our introduction of contamination/impurities. We determine this by obtaining sample versus blank ratio where values >10 is good, >100 better, and >1000 best. A few of our samples fall below 10, majority between 10 and 100, and few above 1000. Given that some of our samples and method blanks were below detection limit, majority of our data did not give back actual values for the ratios.

(b) **Accuracy**

ACME certified standards were also analyzed against measured values run with our samples batches (Figure 10). Both certified and measured values closely agree indicating the analyses were accurate.

(c) **Reproducibility**

Reproducibility is determined by examining duplicate samples collected. Duplicate samples were collected on a weekly rotational basis for the entire sampling period. General reproducibility is determined in Appendix F (Table ?) using calcium concentration for three selected sample events per river. The highest relative percentage difference is at 25.07% for STR 31. Most of our samples were below 5% relative difference. Some samples however showed up to 0% difference in duplicate values. Generally, our handling methods were good in terms of reproducibility and handling of samples.

Table 2: Table showing detected elements in 52 control samples (DI water from a lab sources) of the 72 detectable elements. Also given are mean and standard deviation values for detected elements. Appendix F gives control sample values analyzed.

Method	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**
Analyte	**Ag**	**Al**	**Au**	**Ba**	**Br**	**Ca**	**Cl**	**Cs**	**Cu**	**Fe**	**Hg**	**K**	**La**
Unit	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPM**	**PPM**	**PPB**	**PPB**	**PPB**	**PPB**	**PPM**	**PPB**
MDL	**0.05**	**1**	**0.05**	**0.05**	**5**	**0.05**	**1**	**0.01**	**0.1**	**10**	**0.1**	**0.05**	**0.01**
Control													
Mean	15.90	1.60	0.07	0.18	18.60	0.09	15.00	0.06	0.43	12.00	0.17	19.51	0.02
Std Dev	13.91	0.89	0.02	0.11	11.84	0.00	9.18	0.04	0.31	0.00	0.06	10.96	0.01
Detects	8.00	5.00	3.00	34.00	5.00	1.00	8.00	7.00	11.00	1.00	3.00	8.00	4.00

Method	**2C**	**2C**	**2C**	**2C**	2C	2C	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**
Analyte	**Mn**	**Na**	**Nd**	**Ni**	**Pb**	**Pt**	**Rb**	**S**	**Sn**	**Sr**	**W**	**Zn**	**Zr**
Unit	**PPB**	**PPM**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPM**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**
MDL	**0.05**	**0.05**	**0.01**	**0.2**	**0.1**	**0.01**	**0.01**	**1**	**0.05**	**0.01**	**0.02**	**0.5**	**0.02**
Control													
Mean	0.23	29.46	0.02	0.35	0.53	0.11	0.84	1.00	0.07	0.05	0.04	2.23	0.19
Std Dev	0.19	65.79	0.01	0.13	0.32	0.18	0.48	0.00	0.03	0.04	0.00	1.96	0.25
Detects	20.00	10.00	4.00	13.00	4.00	7.00	8.00	3.00	3.00	20.00	1.00	35.00	3.00

Table 3: Table showing detected elements in ACME prepared blanks run together with our water samples. All other 72 elements were analyzed for and are shown in Appendix F.

Method	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**	**2C**
Analyte	**Ba**	**Gd**	**Li**	**Mn**	**P**	**Ru**	**Sr**	**Zn**
Unit	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**
MDL	**0.05**	**0.01**	**0.1**	**0.05**	**20**	**0.05**	**0.01**	**0.5**
Blank								
Mean	0.12	0.01	0.17	0.17	65.00	0.08	0.02	1.07
Std dev	0.12	0.00	0.06	0.00	0.00	0.03	0.01	0.60
detects	3.00	1.00	3.00	1.00	1.00	4.00	4.00	6.00

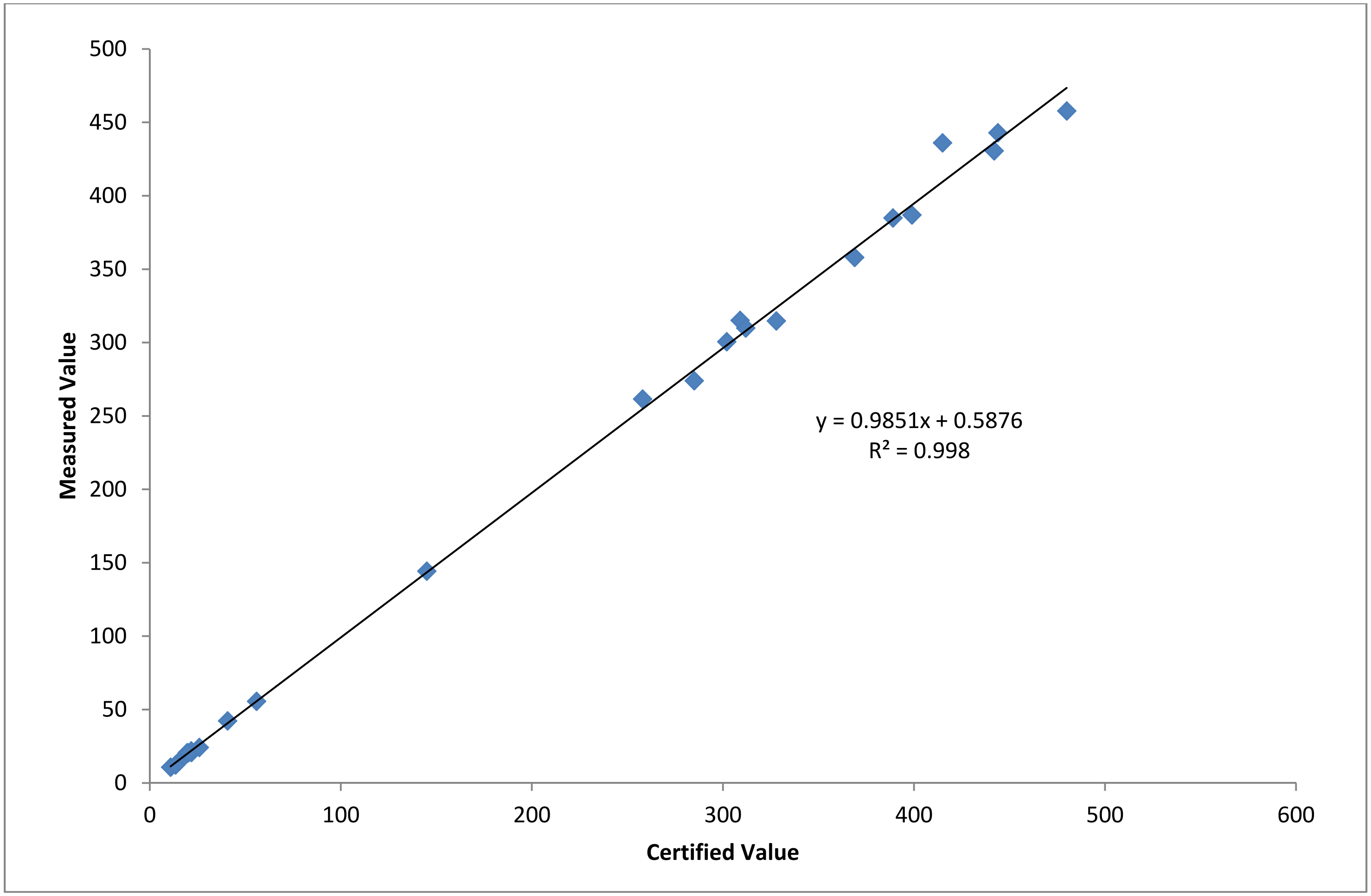


Figure 8: Graph of ACME prepared standards versus samples collected. Measured values (y-axis) represent elements measured from our samples whereas certified values (x-axis) are the expected values as per ACME standards. Measured values were obtained from first and last sets of analyzed samples (weeks 1-4 for first set and weeks 48-52 for last set).

4. RESULTS

4.1 Physical Parameters

Several physical parameters: air temperature, water temperature, conductivity, pH, and dissolved oxygen, were measured in the field to indicate conditions in which sampling was conducted between the sampling period June 2011 and May 2012. Acid neutralizing capacity/alkalinity was measured in lab, whereas discharge data was acquired from USGS gaging station and website. The physical parameters summaries and readings are represented in Tables 7-10 and Appendix A.

Air temperature

The range of overall air temperature recorded in the entire sampling event varied from 33.4˚C (RAQ; 7/21/2011) to -13°C (OSW; 1/5/2012). These values correspond to summer and winter conditions respectively. The air temperatures measured were generally consistent throughout the four sampling sites during each sampling event (Figure A1). Sampling events were generally conducted from late morning to early afternoon and a variety of weather conditions were encountered.

Water temperature

As noted with air temperature, water temperature trends were similar in all four rivers. The range of water temperature varied from 28.5˚C (STR; 7/21/2011) to 0.1°C (GRA; 12/29/2011). In the winter months, there were missing values due to inaccessibility of water as a result of thick ice covering rivers at the sample sites (Figure A2).

Conductivity

The overall range of conductivity is 355.52 (12/8/2011) to 33.45 µS (6/3/2011) (RAQ). OSW and GRA seem to have the highest conductivity values throughout the year. Average conductivity for all the four rivers were as follows: 128.02±37.40 (OSW), 125.27±40.55 (GRA), 73.76±58.51 (RAQ), and 96.10±36.23 µS (STR). The general conductivity trend seems to be increasing in the summer months, a spike some time in fall, a decrease and increase later in fall, and finally a gradual decrease for the rest of winter and spring months (Figure A3).

pH

pH in the four rivers is variable. GRA seems to be the most basic river with highest pH values of 9.06 in the summer and lowest value of 6.26 in spring. The lowest recorded pH of the four rivers was 5.73 (OSW) in early fall. pH in GRA seems to be decreasing throughout the entire sampling event whereas those of OSW, RAQ, and STR seemed to be increasing before leveling out in the winter and spring months (Figure A4).

Dissolved oxygen

Overall range of dissolved oxygen in the rivers recorded were 20.5 mg/L (GRA) to 6.1 mg/L (OSW and RAQ). The observed trend in dissolved oxygen values is increase in summer months, and decrease in the spring months. Highest and lowest values for all rivers seem to occur in the fall months. Missing values are a result of instrument malfunction while in the field (Figure A5).

Acid neutralizing capacity (ANC)/Alkalinity (ALK)

ANC and ALK trends are similar. Throughout sampling year, ANC and ALK range between 5.0 and 60.0 ppm except for significantly high values in RAQ in weeks 25, 27, and 28 of 164.71, 96.27, and 124.18 ppm. Except for these three weeks, RAQ ANC and ALK values are well below those of OSW, GRA, and STR (Figure A6 and A7).

Discharge

Discharge data was variable for all four rivers for the entire sampling event. The overall range of discharge values is 4884 ft^3/s (RAQ) to 344 ft^3/s (GRA). Discharge data decreases during the summer and increases during the fall. From fall to spring, discharge is quite variable with highs and lows fairly evenly spaced out. In general, RAQ appears to have the highest discharge among the other three rivers (Figure A8).

Table 4: Summary table of physical parameters for Oswegatchie River for entire sampling event

OSW								
	Air Temp. (°C)	**Water Temp. (°C)**	**Conductivity (µS)**	**pH**	**Dissolved Oxygen (mg/L)**	**Discharge (ft^3/s)**	**ANC (ppm)**	**ALK (ppm)**
No. of Detects	45.00	44.00	46.00	46.00	44.00	52.00	51.00	51.00
Average	14.05	12.93	128.02	7.11	11.09	1821.67	41.13	41.74
maximum	32.20	26.90	234.06	8.20	17.50	4596.00	53.98	56.98
Minimum	-13.00	0.30	69.30	5.73	6.10	591.00	29.82	29.62
Std dev	10.68	9.17	37.40	0.52	3.03	1052.91	6.63	6.58

Table 5: Summary table of physical parameters for Grasse River for entire sampling event

GRA								
	Air Temp. (°C)	**Water Temp. (°C)**	**Conductivity (µS)**	**pH**	**Dissolved Oxygen (mg/L)**	**Discharge (ft^3/s)**	**ANC (ppm)**	**ALK (ppm)**
No. of Detects	45.00	44.00	46.00	46.00	43.00	52.00	51.00	49.00
Average	13.41	13.14	125.27	7.62	12.76	1128.60	43.24	43.10
maximum	30.80	27.80	245.65	9.06	20.50	3502.00	58.96	60.53
Minimum	-12.00	0.10	68.89	6.26	6.80	344.00	20.37	21.10
Std dev	10.39	9.79	40.55	0.66	3.56	821.77	8.59	9.32

Table 6: Summary table of physical parameters for Raquette River for entire sampling event

RAQ								
	Air Temp. (°C)	**Water Temp. (°C)**	**Conductivity (µS)**	**pH**	**Dissolved Oxygen (mg/L)**	**Discharge (ft^3/s)**	**ANC (ppm)**	**ALK (ppm)**
No. of Detects	44.00	43.00	45.00	45.00	42.00	52.00	52.00	52.00
Average	14.73	13.09	73.76	7.22	12.29	2411.02	23.65	22.37
maximum	33.40	27.00	355.52	8.15	20.10	4884.00	164.71	158.11
Minimum	-8.80	0.20	33.45	6.12	6.10	775.00	6.39	8.40
Std dev	10.41	9.19	58.51	0.50	3.49	1081.33	27.49	24.31

Table 7: Summary table of physical parameters for St. Regis River for entire sampling event

STR								
	Air Temp. (°C)	**Water Temp. (°C)**	**Conductivity (µS)**	**pH**	**Dissolved Oxygen (mg/L)**	**Discharge (ft^3/s)**	**ANC (ppm)**	**ALK (ppm)**
No. of Detects	44.00	43.00	45.00	45.00	42.00	52.00	52.00	52.00
Average	14.27	13.16	96.10	7.33	12.01	1090.50	30.90	30.36
maximum	33.30	28.50	213.10	8.06	20.30	3233.00	49.80	45.61
Minimum	-9.90	0.20	40.10	6.09	6.70	328.00	12.00	14.33
Std dev	10.65	9.56	36.23	0.50	3.39	668.76	6.90	6.70

4.2 Ion Chromatography

Ion chromatograph was used to determine anion concentration in river water samples collected. The anions tested included fluoride, chloride, nitrite, bromide, nitrate, sulfate, phosphate, and carbonate. Concentration trends and average values with standard deviation, maximum and minimum values of anions are given in Appendix B and Tables 11-14 respectively.

Fluoride

The range of fluoride concentrations in all four rivers is 397.28 ppb (GRA) to 33.29 ppb (STR). OSW and GRA seem to have high concentration of fluoride as compared to RAQ and STR. The general trend in OSW and GRA is a slight increase in the summer, decrease in the fall and winter months, and finally spiking in the spring months. RAQ and STR on the other hand had fairly uniform trend throughout the year (Figure B1).

Chloride

Chlorine trends in all four rivers appear to be similar. Highest chloride concentration recorded was 31997.68 ppb (STR) and the lowest concentration was 948.71 ppb (RAQ). The overall trend in chloride concentration seems so be fairly uniform and straight except for peaks in RAQ and STR in late winter/early spring, a few dips on OSW, GRA, and STR in winter and spring months, and several peaks in GRA between fall and spring months. RAQ appears to have relatively lowest fluoride concentrations of all the four rivers (Figure B2).

Nitrite-N

Throughout the year, nitrite was not detected in almost all weeks of sampling in STR. Highest concentrations of nitrite were recorded on GRA with the highest value of 21.41 ppb and the lowest value of 1.44 ppb. Peak concentrations were recorded on GRA between winter and spring months and on STR in the spring (Figure B3).

Bromide

Bromide concentration in all four rivers fell below detection limits except for one sampling event on RAQ with the highest values of 24.78 ppb in spring (Figure B4).

Nitrate-N

Nitrate concentrations increased and decreased rapidly in the summer to a high of 1407.47 ppb (GRA). Lowest values of NO_3 were reported at 3.40 ppb on OSW, GRA, and STR. In the following months, nitrate concentration remained between 600 to 0 ppb. RAQ appears to have the highest nitrate concentration of all the four rivers (Figure B5).

Sulfate

The average trend for sulfate concentration is a decrease in the summer months with a dip in the fall to winter months and a peak in the late winter and early spring times. Highest recorded sulfate concentration is 14299.04 ppb (STR) and the lowest concentration is 359.30 ppb (RAQ). Sulfate concentration is higher in OSW than in the other four rivers except the peak from STR (~week 28). The general trend of sulfate concentration is otherwise fairly consistent throughout the sampling year (Figure B6).

Phosphate-P

Throughout the sampling event, phosphate concentration in all four rivers was below detection limit except for a few weeks where significant concentrations of phosphate were recorded. Highest concentration of 95.04 ppb (GRA) in late summer and lowest concentration of 0.83 ppb (STR) in the spring were recorded (Figure B7).

Carbonate

Carbonate concentration is variable in all four rivers. Highest and lowest concentration of 200534.80 and 200.00 ppb was recorded on OSW. There was a general decrease then increase in carbonate concentration in the summer months, a general increase in the later summer months and a drop towards the fall months. Higher concentrations of carbonate were also recorded in the winter and spring months with peak recordings from each of the rivers occurring at this particular time (Figure B8).

Table 8: Summary table of Oswegatchie River anion data as from ion chromatograph

OSW								
	Fluoride (ppb)	**Chloride (ppb)**	**Nitrite-N (ppb)**	**Bromide (ppb)**	**Nitrate-N (ppb)**	**Sulfate (ppb)**	**Phosphate-P (ppb)**	**Carbonate (ppb)**
No. of Detects	51.00	51.00	51.00	51.00	51.00	51.00	51.00	50.00
Average	132.71	6121.51	2.91	12.50	219.84	7977.73	12.33	57069.82
Maximum	363.15	9045.81	4.00	12.50	781.91	11283.22	38.57	200534.80
Minimum	59.96	2815.81	1.47	12.50	3.40	4267.03	2.34	200.00
Std dev	49.00	1260.04	0.56	0	127.86	1513.02	5.31	33431.68

Table 9: Summary table of Grasse River anion data as from ion chromatograph

GRA								
	Fluoride (ppb)	**Chloride (ppb)**	**Nitrite-N (ppb)**	**Bromide (ppb)**	**Nitrate-N (ppb)**	**Sulfate (ppb)**	**Phosphate-P (ppb)**	**Carbonate (ppb)**
No. of Detects	51.00	51.00	51.00	51.00	51.00	51.00	51.00	51.00
Average	140.05	6663.30	3.86	12.50	339.17	5695.83	12.21	55207.48
Maximum	397.28	12093.87	21.41	12.50	1407.47	8352.14	95.04	166928.83
Minimum	70.47	3608.46	1.44	12.39	3.40	3369.17	1.25	23396.29
Std dev	83.93	1844.66	2.89	0.02	301.12	1256.39	12.14	28928.93

Table 10: Summary table of Raquette River anion data as from ion chromatograph

RAQ								
	Fluoride (ppb)	**Chloride (ppb)**	**Nitrite-N (ppb)**	**Bromide (ppb)**	**Nitrate-N (ppb)**	**Sulfate (ppb)**	**Phosphate-P (ppb)**	**Carbonate (ppb)**
No. of Detects	51.00	51.00	51.00	51.00	51.00	51.00	51.00	51.00
Average	58.62	5563.17	2.92	12.74	265.50	3886.64	11.30	20955.93
Maximum	88.31	23264.20	4.50	24.78	1077.02	6751.34	11.50	144402.48
Minimum	39.00	948.71	1.47	12.50	94.01	359.30	1.40	2381.50
Std dev	11.25	2997.05	0.67	1.72	146.57	1008.60	1.41	22544.61

Table 11: Summary table of St. Regis River anion data as from ion chromatograph

STR								
	Fluoride (ppb)	**Chloride (ppb)**	**Nitrite-N (ppb)**	**Bromide (ppb)**	**Nitrate-N (ppb)**	**Sulfate (ppb)**	**Phosphate-P (ppb)**	**Carbonate (ppb)**
No. of Detects	51.00	51.00	51.00	51.00	51.00	51.00	51.00	51.00
Average	56.22	6399.53	3.22	12.50	275.26	4387.37	10.72	40792.68
Maximum	91.19	31997.68	10.16	12.50	918.47	14299.04	11.50	129188.83
Minimum	33.29	3113.91	1.83	12.50	3.40	2386.76	0.83	13809.41
Std dev	12.71	3870.98	1.04	0	154.09	1597.13	2.71	24745.95

4.3 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Analysis

Seventy-two elements were analyzed by ICPMS at ACME Analytical Laboratories, Vancouver, British Columbia, Canada (Appendix C and Tables 15-18). Duplicate, control, and blank samples were also analyzed alongside water samples for similar elements.

The elements Ca, Cl, K, Mg, Na, and S were recorded in parts per million (ppm) while the rest of the elements were recorded in parts per billion (ppb). Elements reported to have quantities below detection include Ag, As, Au, Bi, Cd, Cs, Eu, Ge, Hf, Hg, Ho, In, Lu, Nb, P, Pd, Pt, Re, Rh, Ru, Sc, Sn, Ta Tb, Te, Th, Ti, Tl, Tm, and V. Elements with the highest concentrations measured include Al, Ca, Fe, K, Mg, Na, and Si and are reported in Tables 15-18 and Figures C1, C5, C12, C15, C18, C21, and C31. These major elements were detected throughout the sampling event. Concentrations in other elements are reported in Appendix C.

Table 12: Summary tables for Oswegatchie River showing selected elements from ICP-MS analysis

OSW							
	Al	**Ca**	**Fe**	**K**	**Mg**	**Na**	**Si**
	PPB	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**
No of Detects	52.00	52.00	52.00	52.00	52.00	52.00	52.00
Mean	34.27	12480.00	162.29	757.12	3670.19	4395.79	2731.50
High	84.00	16160.00	448.00	1430.00	5080.00	6790.00	3444.00
Low	13.00	8640.00	13.00	450.00	2510.00	2859.00	1824.00
Std dev	16.27	1816.34	112.99	209.57	691.83	793.97	389.64

Table 13: Summary table for Grasse River showing selected elements from ICP-MS analysis

GRA							
	Al	**Ca**	**Fe**	**K**	**Mg**	**Na**	**Si**
	PPB	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**
No of Detects	52.00	52.00	51.00	52.00	52.00	52.00	52.00
Mean	45.06	11928.46	248.45	730.96	4287.69	4594.69	2968.31
High	119.00	16550.00	752.00	1150.00	6110.00	7250.00	4160.00
Low	10.00	8420.00	32.00	430.00	2530.00	2892.00	1561.00
Std dev	25.60	1938.54	200.80	180.88	842.37	1029.78	587.48

Table 14: Summary table for Raquette River showing selected elements from ICP-MS analysis

RAQ							
	Al	**Ca**	**Fe**	**K**	**Mg**	**Na**	**Si**
	PPB	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**
No of Detects	52.00	52.00	52.00	52.00	52.00	52.00	52.00
Mean	43.85	7015.19	120.92	464.04	2338.85	4188.50	2603.25
High	80.00	42910.00	241.00	1830.00	17610.00	16042.00	3785.00
Low	5.00	3510.00	24.00	290.00	970.00	2520.00	648.00
Std dev	14.72	7069.97	57.09	298.57	3074.60	2336.98	695.37

Table 15: Summary table for St. Regis River showing selected elements from ICP-MS analysis

STR							
	Al	**Ca**	**Fe**	**K**	**Mg**	**Na**	**Si**
	PPB	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**	**PPB**
No of Detects	52.00	52.00	51.00	52.00	52.00	52.00	52.00
Mean	42.52	8657.50	233.16	1083.65	3147.31	4226.92	3434.60
High	114.00	11800.00	556.00	30420.00	4900.00	5734.00	5346.00
Low	8.00	5200.00	28.00	300.00	1700.00	2183.00	1937.00
Std dev	22.35	1517.95	150.91	4151.11	760.31	789.84	820.08

4.4 Loading

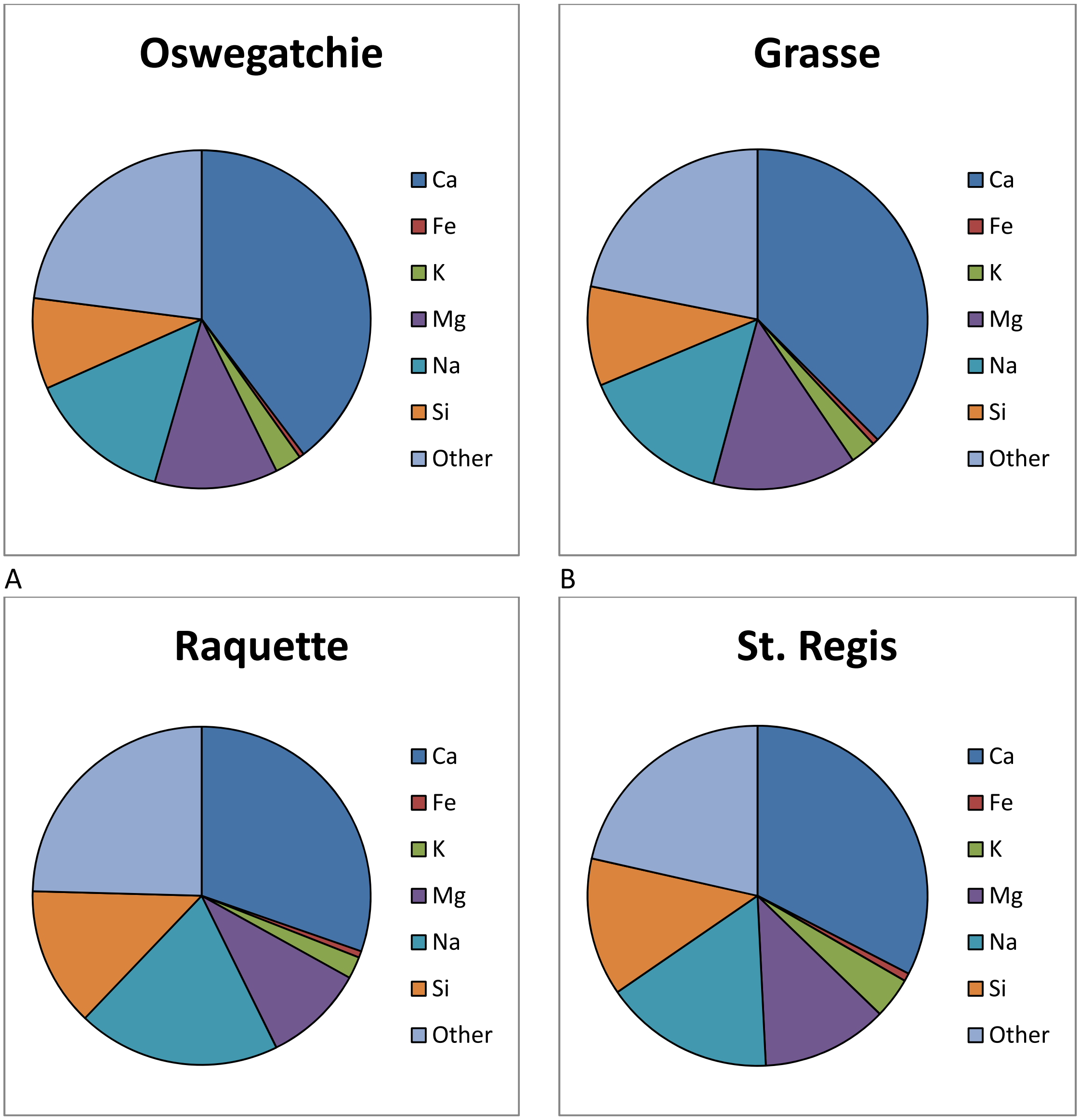
Loading was determined as a function of elements and anion concentrations, and weekly average discharge (Equation 2). Appendix D (Figures D3 & D4) represents seasonal variation of selected cation and anion loading values together with their logarithmic scale values.

The cation loading values were normalized to the total of selected cations and expressed as a percentage: Ca, Fe, K, Mg, Na, Si, and all the other cations grouped as Other (Figure 11; Table 19). Anion loading values were normalized to total loading values of anions expressed as a percentage. All anions included were F, Cl, NO_2, Br, NO_3, SO_4, PO_4, and CO_3 (Figure 12; Table 20).

$$Loading\ \left(\frac{kg}{week}\right) = C\ \left(\frac{\mu g}{L}\right)\left(\frac{1kg}{10^9\mu g}\right) \times Q\left(\frac{ft^3}{s}\right)\left(\frac{28.3168L}{1ft^3}\right)\left(\frac{604800s}{1week}\right)$$

Equation 2: Formula used to calculate loading of elements and anions with units of kg/week

Ca has the highest loading values. Other cations with relatively high loading values are Na, Mg, and Si throughout the four rivers. Carbonate has the highest loading of all eight anions tested. Sulfate and chloride have relatively high loading compared to the rest of the anions (Figures 10 and 11; Appendix D)



A B C D

Figure 9: Graphs 21 A-D represent normalized loading of selected elements to the respective rivers

Table 16: Summary table of normalized loading of selected cations as a percentage

%	Ca	Fe	K	Mg	Na	Si	Other
OSW	39.69	0.46	2.54	11.78	13.85	8.69	22.98
GRA	37.50	0.56	2.45	13.70	14.46	9.44	21.89
RAQ	30.33	0.62	2.11	9.66	19.40	13.30	24.57
STR	32.57	0.76	3.89	12.01	16.19	13.12	21.47

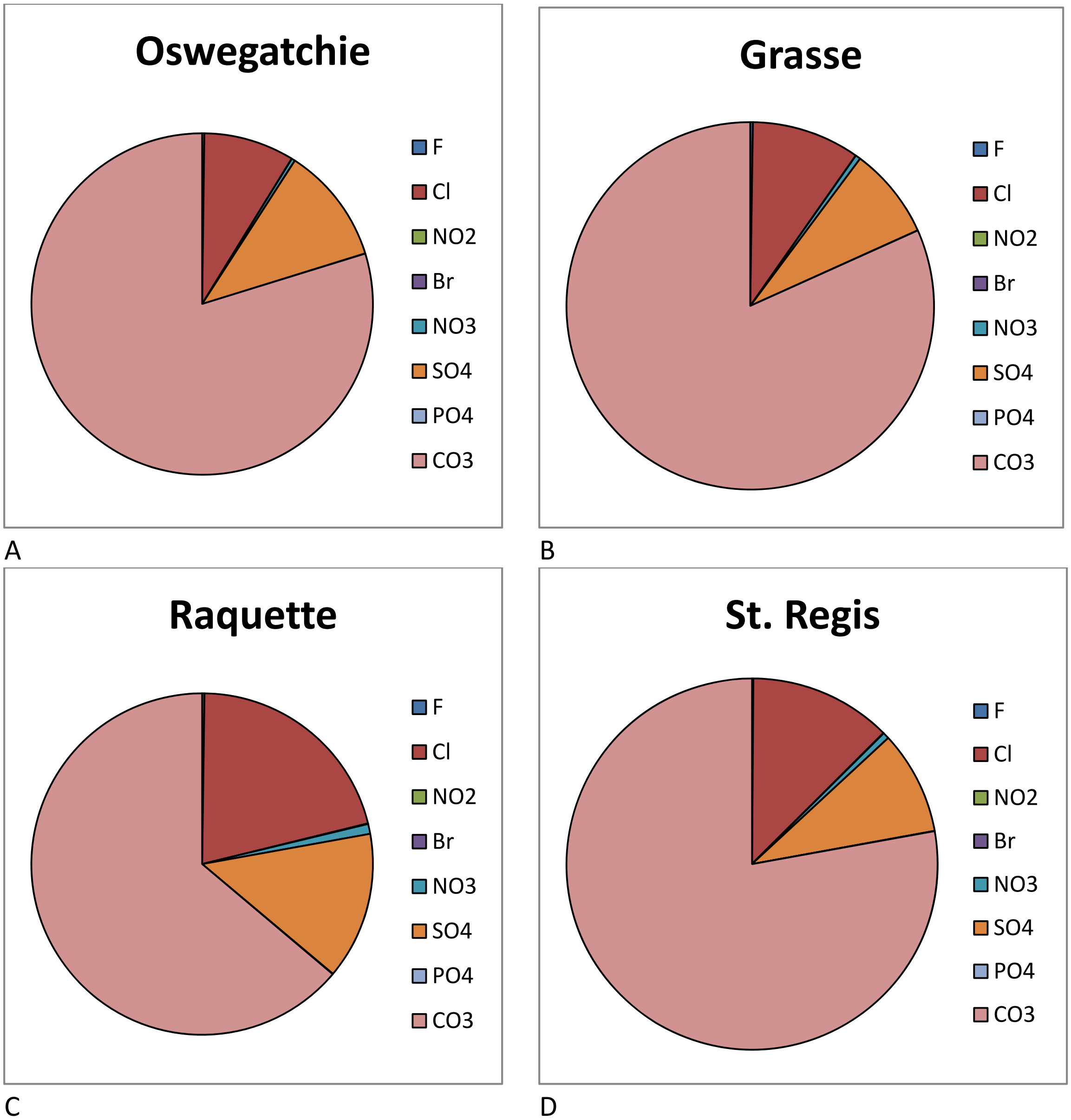


Figure 10: Graphs 22 A-D represent normalized loading of all tested anions by their respective rivers.

Table 17: Summary table of normalized loading of all anions as a percentage

%	**F**	**Cl**	**NO_2**	**Br**	**NO_3**	**SO_4**	**PO_4**	**CO_3**
OSW	0.20	8.58	0.00	0.02	0.32	11.08	0.02	79.77
GRA	0.23	9.51	0.01	0.02	0.44	8.05	0.02	81.73
RAQ	0.21	20.96	0.01	0.05	0.93	13.96	0.04	63.84
STR	0.11	12.40	0.01	0.03	0.56	9.03	0.02	77.84

Table 18: Loading values for selected major cations in all four rivers

	Al (kg/year)	Ca (kg/year)	Mg (kg/year)	Na (kg/year)	K (kg/year)	Fe (kg/year)	Si (kg/year)
OSW	52621.38	18281312.24	5425340.73	6380627.92	1171264.53	212180.30	4003328.77
GRA	41667.84	11728276.95	4285612.91	4526495.50	760164.84	175836.31	2927600.36
RAQ	97407.08	12504167.23	3982073.48	8001337.88	869922.89	254924.20	5483692.43
STR	47201.83	8227542.78	3032848.26	4089420.01	507650.94	191705.01	3313867.21

Table 19: Loading values for all major anions tested during sampling event in all four rivers

	F (kg/year)	Cl (kg/year)	NO_2 (kg/year)	Br (kg/year)	NO_3 (kg/year)	PO_4 (kg/year)	SO_4 (kg/year)	CO_3 (kg/year)
OSW	202931.67	8516374.45	4378.24	18221.34	317173.82	11002787.33	17753.85	82492596.32
GRA	158782.71	6519295.47	4074.47	12390.67	302487.33	5521900.85	11667.52	56055621.33
RAQ	119952.87	11791966.14	5811.74	25596.74	524688.27	7853103.40	22676.29	35921116.42
STR	53008.04	5852174.59	3271.18	12172.39	263551.10	4259861.26	10455.38	36723654.58

4.5 Seasonal Trends

Cosine trends of anion and cation concentration, and anion and cation loading values were plotted using Rstudio software. The cosine trends compare weekly concentrations and loading to sample weeks (seasons) and gives trend lines with respect to the particular rivers. All anions and major cation concentrations and loading values are represented in figures in Appendix D (Both normal and logarithmic scale plots are given).

Cation Concentration

Aluminum

Highest Al concentration appears to be at about 12.0 ppb (GRA). OSW, GRA, and RAQ follow the average trend for Al concentration throughout the year. High Al values are seen in summer. Al concentration decreases in the fall months and reaches low values in the winter before rising again in the spring. RAQ in this case behaves opposite to OSW, GRA, and STR trends, with lowest concentrations in late summer and early fall, and highest concentrations in early spring. Of all the four rivers, OSW appears to have drastic changes, presenting both highest and lowest dips in trend. OSW trend also happens to be entirely below the average trend (Figure D1 given in solid red line) throughout the sampling year.

Calcium

Highest calcium values were recorded on three separate weeks in RAQ (>20 ppm). However, RAQ trend remained below the average Ca concentration trendline as well as STR, OSW, and GRA trend lines were well above the average concentration trend (Figure D1 given in solid red line). The Average trend line has a fairly gradual slope indicating very little change across the entire year in Ca concentration. RAQ on the other hand displayed a bell shape with a significant peak in early winter.

Iron

Iron on the other hand displays drastic seasonal changes throughout the sampling event. As expected, OSW, GRA, and STR trend are similar with a peak in late summer/early fall and lowest values in the winter months. Highest Fe concentration values are from OSW (>600 ppb) (Figure D1). RAQ has a gradual change throughout the year. High RAQ values are noted in fall months and low values noted in late winter/early spring months.

Potassium

Average K concentration has a slight bell-shape with at peak at late fall. RAQ trend is well below the average trend line with a prominent bell shape as compared to the average trend. STR trend appears below the average trend as well, however with a more gradual slope. Highest K values are found in RAQ at values greater than 1.5 ppm in late fall/early winter (Figure D1).

Magnesium

Magnesium trends appear to be similar to calcium trends such that RAQ has a bell-shape to it with a peak in early winter. The other three rivers appear to follow the average trend line pattern with gradual slope (Figure D1 given in solid red line). A slight peak is noticed in early winter. Three highest Mg values seem to correlate to the three highest Ca (>10 ppm).

Sodium

Sodium concentration within the four rivers appears to be within the average trend values. RAQ has its characteristic bell-shape with a peak in early winter and three highest values (>10 ppm) at the same time. The peak of the bell-shape goes over the average trend line. GRA and STR have similar trend as the average values. OSW on the other hand is opposite of the other rivers with a higher values in summer and slight decrease in concentration in early winter (Figure D1).

Silicon

Peak Si concentration values are in winter months for all four rivers. RAQ has a significant Si decrease in late summer as compared to the other rivers and a later peak in late winter. Majority of RAQ trend remains below the average until later in winter. STR has the highest Si concentrations with some values greater than 5000 ppb. OSW and GRA trends begin above the average and later decrease below the average trend (Figure D1).

Anion concentration

Bromide

Bromide was not detected in majority of the water samples for the entire sampling event. Half-detection limits (12.5 ppb) were reported instead (see method section). One highest and lowest value was detected (RAQ and GRA respectively) (Figure D2).

Carbonate

Highest carbonate values was noted at 20000 ppb (OSW) in winter. OSW, GRA, and STR follow the average values, showing a dip in concentration in fall. This is opposite to RAQ which has a peak instead at this time (fall). RAQ and STR values mostly lie below the average concentration trend line (Figure D2).

Chloride

Chloride trends tend to lie well within average concentration values. Highest noted concentration values in STR was at >3000 ppb. Gradual peak appears in winter months (Figure D2).

Fluoride

OSW and GRA concentration values lie above the average trend line while RAQ and STR lie below it. RAQ and STR have nearly flat slopes. GRA had a dip in fall and peak in spring, whereas OSW has a gradual dip in early winter months. Highest values are observed in GRA of up to 400 ppb (Figure D2).

Nitrate-N

Nitrate-N values lie well within average values. GRA has a slightly different trend with peak in summer and dip in early winter. Highest nitrate values are observed in summer months (>1150 ppb) (Figure D2).

Nitrite-N

Similarly to nitrate, nitrite-n values lie within average concentrations. However, GRA shows a peak in winter and the largest concentration of >20 ppb (Figure D2).

Phosphate-P

Phosphate-P values lie within average values except for GRA that noticeably has peak and dip values in summer and winter respectively. Highest value recorded is at >80 ppb (GRA) (Figure D2).

Sulfate

OSW sulfate values are higher compared to the other rivers. However, highest value is ~14000 ppb (GRA). RAQ and STR fall below the average trend line. GRA and STR have peaks in winter, OSW in summer, and RAQ has a dip in fall (Figure D2).

Cation and Anion Loading

Cation and Anion loading trends are similar to those of cation and anion concentration. The only difference is that discharge values play a major factor in loading values. All cation and anion loading values follows average trend line (solid red line in Figures D3 and D4) with only a slight trend difference in RAQ as earlier observed.

Figure D3 shows cation loading trends for selected major elements. Aluminum average loading is at about 1200 kg/ week. RAQ Al loading appears to be greater than the average values. OSW, GRA, and STR loading are below average consistently. Ca loading on the other hand ranges between 300000-400000 kg/week. OSW Ca loading is above the average, followed by RAQ at various times of the sampling year. GRA and STR fall below average loading. Ca loading appears to decrease in the summer and fall months and increase in the winter to spring months. Fe loading increases in the summer to fall months and decreases in summer to spring months. RAQ Fe loading appears to be generally above average loading as compared to OSW, GRA, and STR. K loading ranges between 1000 and 2000 kg/week. OSW K loading falls above average values while GRA and RAQ follow the average trend closely, and STR falls below it. Mg average values are below 100000 kg/week. A few outliers are observed in RAQ with highest values of >300000 kg/week. The loading trends of all four rivers are similar to that of the average with STR below average and OSW above average. Likewise to Ca, Mg loading decreases in the summer and fall months and increases in winter and spring months. Na loading average is within 5000 and 150000 kg/week. RAQ Na loading falls above average values while GRA and STR loading fall below average values. Na loading also decreases in summer and fall months and increases in winter and spring months. OSW closely resembles average trend. Si average loading lies between 10.5 and 11.5 kg/week. RAQ Si loading falls above average values while GRA and STR fall below. Si loading decreases in summer and fall months before increasing in winter.

Figure D4 gives anion loading trends and values for all detected anions. All anion average loading trends tend to be similar such that the anion loading values decrease in summer to fall months and increase in winter to spring months. Br loading for all rivers is quite similar to average loading without variation. Because bromide was not detected in majority of the samples, half detection values were used instead, hence the similarity in the rivers. CO_3 average loading ranges between 500000 and 1500000 kg/week. CO_3 has the highest loading of the anions. OSW has loading values greater than the average whereas GRA and STR loading closely follow the average loading. RAQ has a fairly constant CO_3 loading throughout the sampling event. Cl average loading lies between 1000-3000 kg/week. RAQ loading lies above average loading values whereas OSW, GRA, and STR fall below. RAQ and STR F loading values appear to be constant throughout the sampling even as CO_3. Other two rivers appear to follow the average loading trend. RAQ NO_3-N loading lies well above average loading other three rivers follow the average closely. There is not much change from the average loading for NO_2-N in the four rivers. However, highest NO_2-N loading values (>80 kg/week) was spotted in GRA in the spring. PO_4-P loading values closely resemble average loading. Likewise to Br, PO_4-P was not detected in majority of water samples. Hence there is not much variation in river trends for PO_4-P. Highest PO_4-P loading values however, was detected in GRA and OSW at (>150 kg/week). SO_4 loading varied within the rivers. Average loading lies between 1500-2500 kg/week. OSW had the highest loading (above average loading) whereas GRA and STR fell below average loading.

5. DISCUSSION

River water chemistry has been noted to vary as the four major rivers flow northwards towards St. Lawrence River. Changes in physical and chemical parameters in river water can be linked to changes in the nature of the bedrock in each drainage basin. Major geologic subdivisions in St. Lawrence County are shown in (Figure 6). Variation in river water chemistry include: 1) changes within the rivers, 2) changes as the rivers flow northwards to St. Lawrence River, 3) changes in properties related to human activity, 4) seasonal variability, and 5) loading of dominant cation and anion species.

The four rivers flow over three major bedrock subdivisions of St. Lawrence County: 1) Mid-Proterozoic crystalline granitoid rocks of the Adirondack Highlands, 2) Mid Proterozoic metasedimentary rocks of the Adirondack Lowlands, and 3) Paleozoic clastic and carbonate rocks of the St. Lawrence River Valley. Over these three zones, buffering capacity of river water varies. Buffering capacity measured as ANC is low in the Adirondack Highlands (predominantly metamorphosed igneous rocks), is moderate and variable in the Adirondack Lowlands (predominantly metasedimentary rocks including large areas of marble), and highest in St. Lawrence Valley (clastic and carbonate sedimentary rocks).

5.1 Elemental and Anion Trends

OSW has the highest mean ANC values of the four sampled rivers (43.24±8.59 ppm) followed by GRA (41.13±6.63 ppm), STR (30.90±6.90 ppm), and finally RAQ (23.65±27.49 ppm). High ANC value in GRA and OSW is due to the fact that the rivers flow across wide portions of the Adirondack Lowland (metasedimentary rocks, mostly marbles) that have high buffering capacity. RAQ and STR lie to the east in St. Lawrence County and cross only over a narrow area underlain by Adirondack Lowland rocks. Mean pH values in all four rivers range within neutral values. All measured water parameters reflect the entire drainage basin of each river up until the sampling location. Figure 13 shows the relationship between pH and ANC in all four rivers. Because the trends for all the rivers on Figure 13 are vertical, there appears to be little correlation between low ANC and pH values. This is as expected as the pH of all rivers is close to neutral.

Aluminum concentration in river water generally is low (in ppb range). Al in OSW is fairly low as compared to other rivers as well (Figures D1 and D5). Al appears to reach its lowest concentration during low flow and highest concentrations during episodes of snowmelt and precipitation for OSW, GRA, and STR. This is so because of lack of sufficient base cations in the watersheds to neutralize the acidity (Lawrence, 2004). High Al concentration in surface water is synonymous to acidic water due to NO_x and SO_x (Driscoll, 1985). Al only dissolves in either highly acidic or basic waters and precipitates in neutral water. Figure 14 shows pH versus Al concentration but significant trends are not seen. In the case of OSW, Al concentrations are fairly low indicating that the waters are not very acidic. Buffering by marble in the Adirondack Lowlands may play a big role in reduced acidity in the waters (Chiarenzelii et al, 2012). Figure D5 shows that Al in GRA has an opposite trend to the other three rivers with decreasing concentration in solution during high flow conditions. OSW, RAQ, and STR have increased concentration with increasing discharge. Another possibility is that Al is transported in colloidal particles and clays in the water. Given that the water samples were not filtered Al may preferably remain as suspended solids especially during runoff events and high discharge events (Figure D5).

When fully oxidized, iron, like aluminum is an immobile element and its mobility is determined by pH levels and redox conditions in natural waters. Figure 15 shows little correlation between pH and Fe, as was also shown for pH and Al. Fe in river waters is also affected by redox and light conditions, and amount and type of dissolved organic matter (Vuori, 1995). Given that the four watersheds are considered natural and not affected by any active iron mines, weathering of bedrock containing iron may be responsible for iron concentration in the rivers. Fe(II) in dissolved state is transported before undergoing oxidation to insoluble Fe(III) that precipitates out as colloidal particles, sinks to the bottom of the stream, is transported as suspended solids, or coats in pebbles and cobbles in rivers. Fe in the river seems to decrease significantly during high discharge and increased runoff except for in RAQ (Figure D5). Vuori concludes that intensified forestry, peat production, and agricultural draining leads to the increase of iron load in many river ecosystems.

Calcium is the most abundant cation. This implies that the river waters of St. Lawrence County are calcic waters. Ca and Mg would have a positive relationship indicating direct correlation between them due to their relatively similar ionic size, radii, and ionic charge (Figure 16). Ca and Mg commonly occur together in marbles (calcitic and dolomitic) prevalent in Adirondack Lowland bedrock (Chiarenzelli et al., 2012). However, Mg concentrations are lower than those of Ca in all river water (Figure D1). Nonetheless, Al and Fe species are able to be buffered by occurrence of Ca and Mg species in the waters. Ca and Al have a negative correlation such that high Ca results in low Al concentration in stream waters (Figure 17). Ca concentrations are much higher (~150x) than Al concentrations in the same waters.

Sodium concentrations are generally higher than K. Na and K appears to increase with onset of low flow seasonally (Figure D1). Comparing Na and K concentration against discharge (Figure D5), both species behave in a similar manner such that overall concentrations decrease with increasing discharge. Na in OSW however, decreases with beginning of low flow conditions. Generally, there is a direct relation in trends for both Na and K and possibly similar sources of both cations. Likewise, Cl concentration in all waters behaves similarly as Na (Figure 18). A likely source for both species would be road salt used widely in removal of snow and ice in U.S. roads, where studies have shown adverse effects on water quality, flora, and fauna (Godwin et al., 2003). On average, Na and Cl concentration increases in the waters during winter months and just before episodes of snowmelt and precipitation within the watershed (Figures D1 and D2). Figure 19 shows Na/Ca ratios that tell us Na and Cl concentrations are correlated. This may indicate that road salt is affecting surface water quality. Na/Ca ratios appear to be smaller indicating halite dissolution into river waters as compared to salting of roads. Lower normalized Na ratios (Na/Ca) indicate drainage of silicate bedrock and that Ca rich minerals are preferentially dissolved making the Na/ Ca ratios much smaller (Gaillarder et al., 1999).

Silicon concentration, likely as silicic acid (H_4SiO_4) is relatively high in all four rivers. Highest concentration appears to be during low flow conditions. Silicon in natural waters is primarily derived from weathering of silicates and alumnosilicate minerals in bedrock and soils (Berner and Berner, 1996). Neal et al (2005) noted two possible processes that result in silicon concentration in surface waters: relative inputs of groundwater enriched in silicon and near surface waters more depleted in silicon, and plankton uptake of silicon during the summer months under low flow conditions. Organisms such as diatoms are known to construct their shells from silica present in waters they live in (Reynolds, 1984).

Carbonate is a major anion in St. Lawrence County Rivers due to calcitic and dolomitic marbles of the Adirondack Lowlands. Since CO_3 is associated with Ca and Mg, its presence and availability contributes to buffering of river waters in the county. CO_3 decreases slightly in cold winter temperatures possibly due to decreased temperatures (onset of winter cold) and solubility into surface waters.

Nitrate and sulfate concentration in the four rivers may have two sources: acid deposition (Jenkins et al., 2007), and land use (Figure 4). Agriculture in St. Lawrence County is common in the Lowlands where there is extensive land for farming and keeping livestock. As a result, fertilizer and animal waste rich in nitrates and sulfate compounds drain into nearby streams and water bodies. Ribbe et al (2008) note that agriculture could have a significant impact on surface and groundwater and as a result cause negative impacts to riverine and coastal ecosystems. High nitrate concentrations in drinking water could also present blue baby syndrome in children. SO_4 concentration appears to be variable in all four rivers whereas NO_3 concentration is fairly uniform in for the rivers. Since SO_4 is derived primarily from acid precipitation, however, in St. Lawrence County pyrite deposits (as in Pyrites, NY) may provide a source of sulfate locally and hence drive the variability. Agricultural practices on the other hand tend to be regular and seasonal hence the uniformity of NO_3 concentrations across all four rivers.

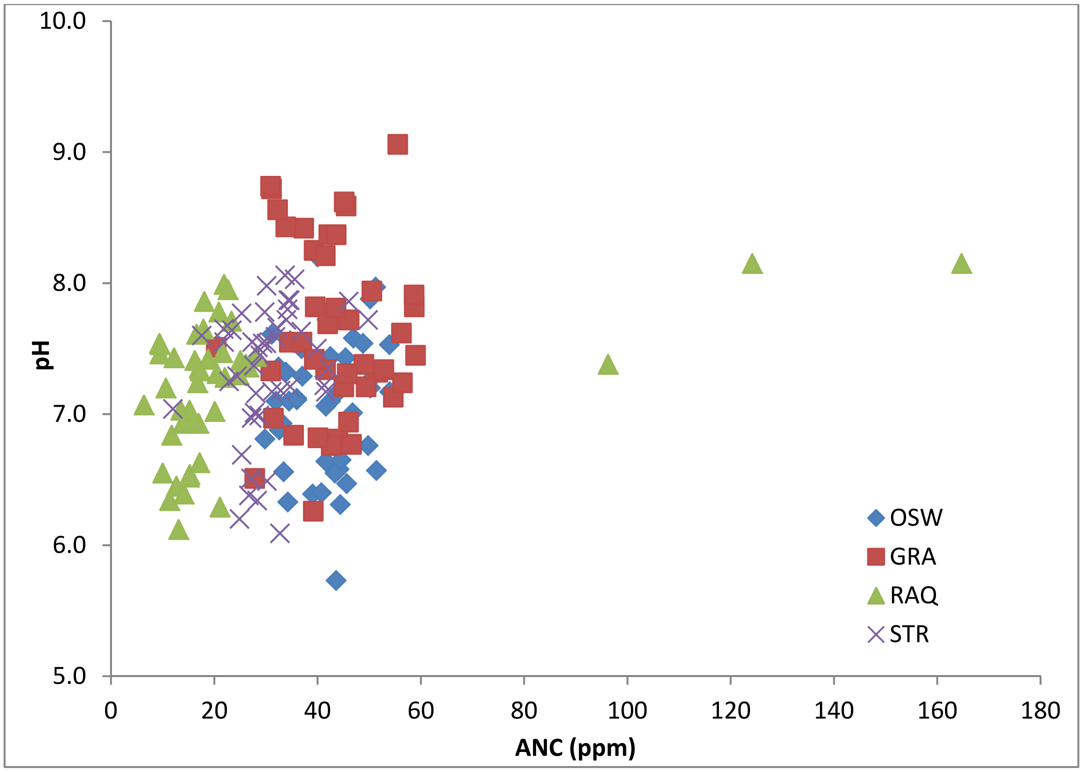


Figure 11: Graph showing pH vs ANC for all four rivers

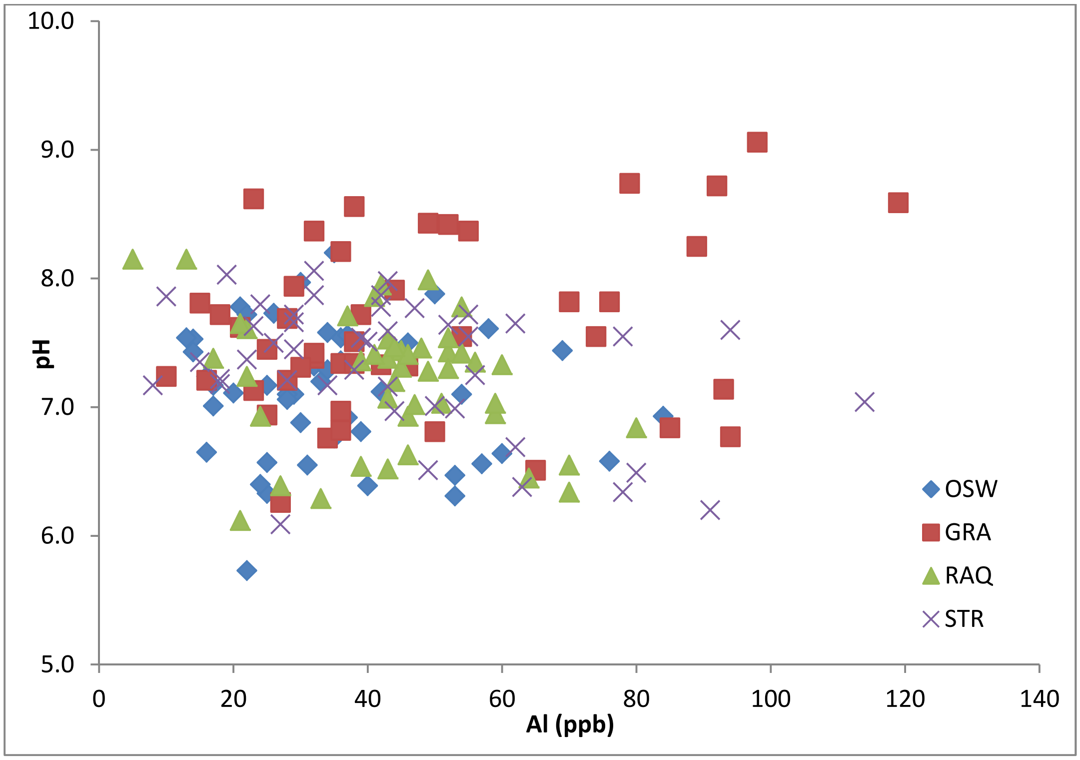


Figure 12: Graph showing relationship between pH and Al for all four rivers

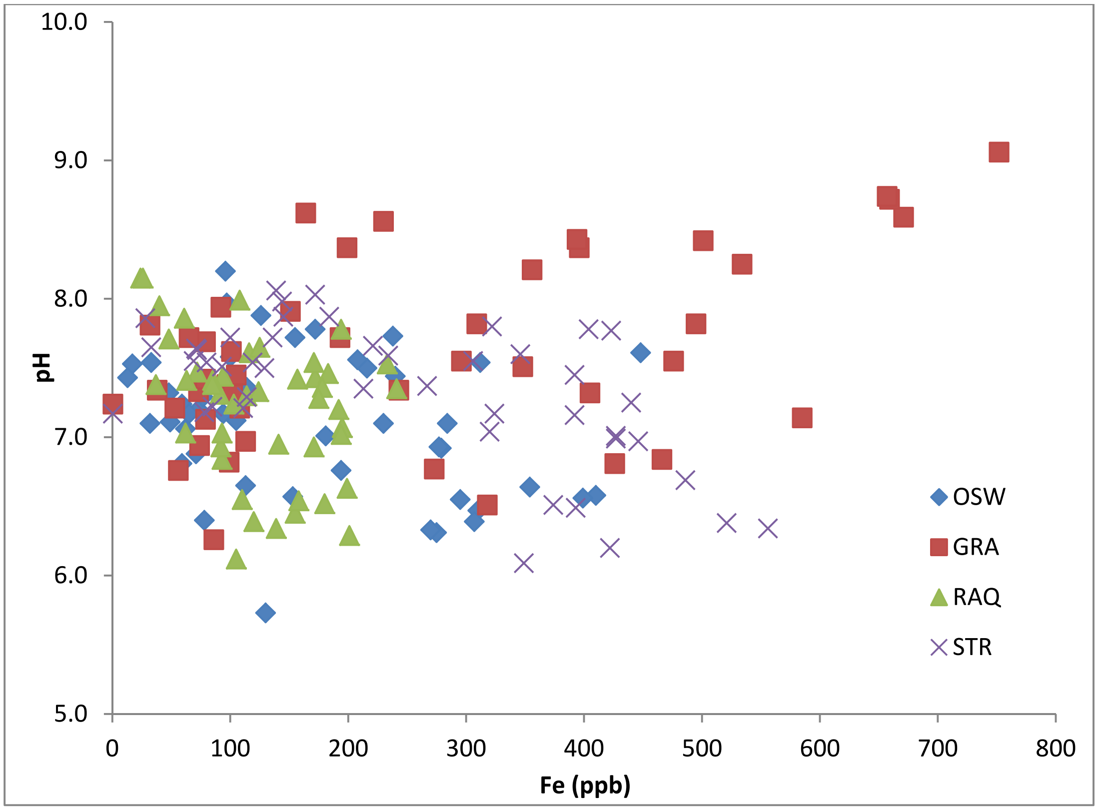


Figure 13: Graph showing relationship between pH and Fe for all four rivers

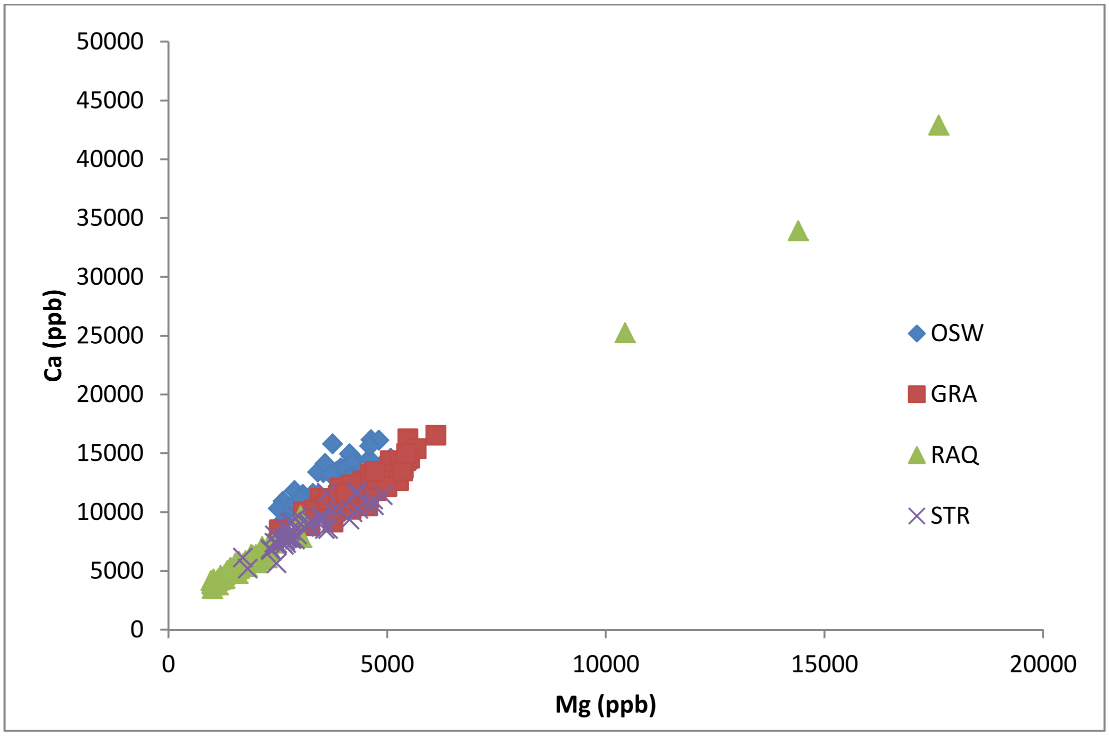


Figure 14: Graph of Ca against Mg

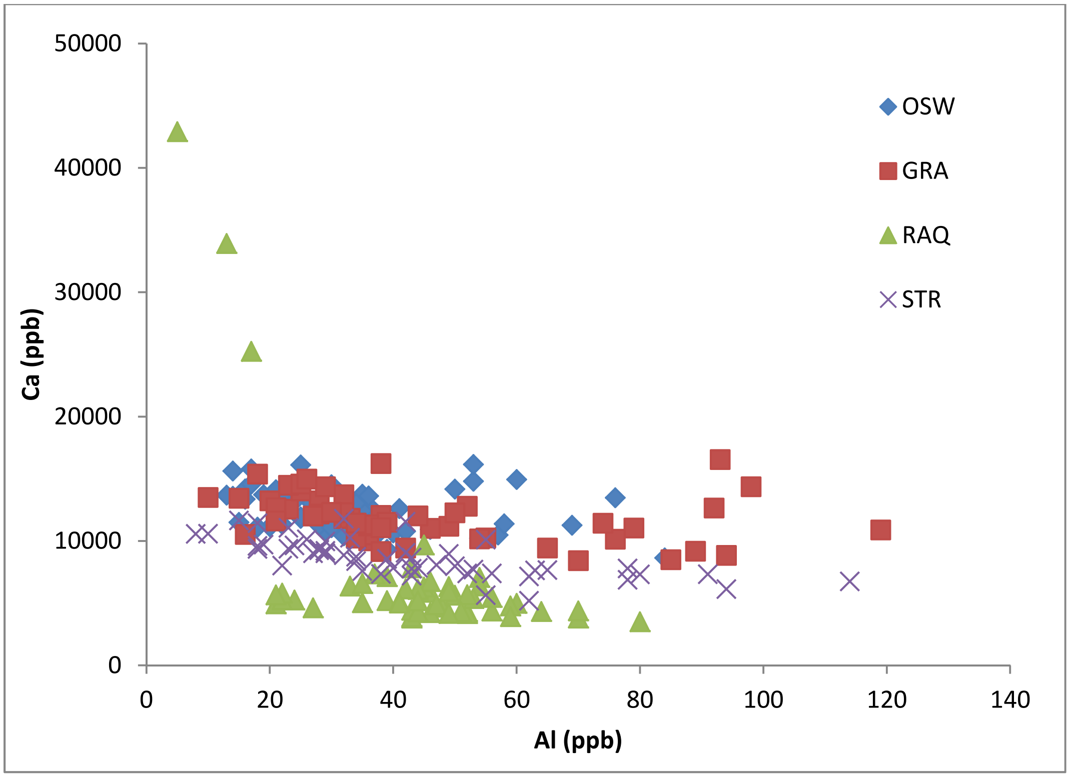


Figure 15: Graph of Ca versus Al

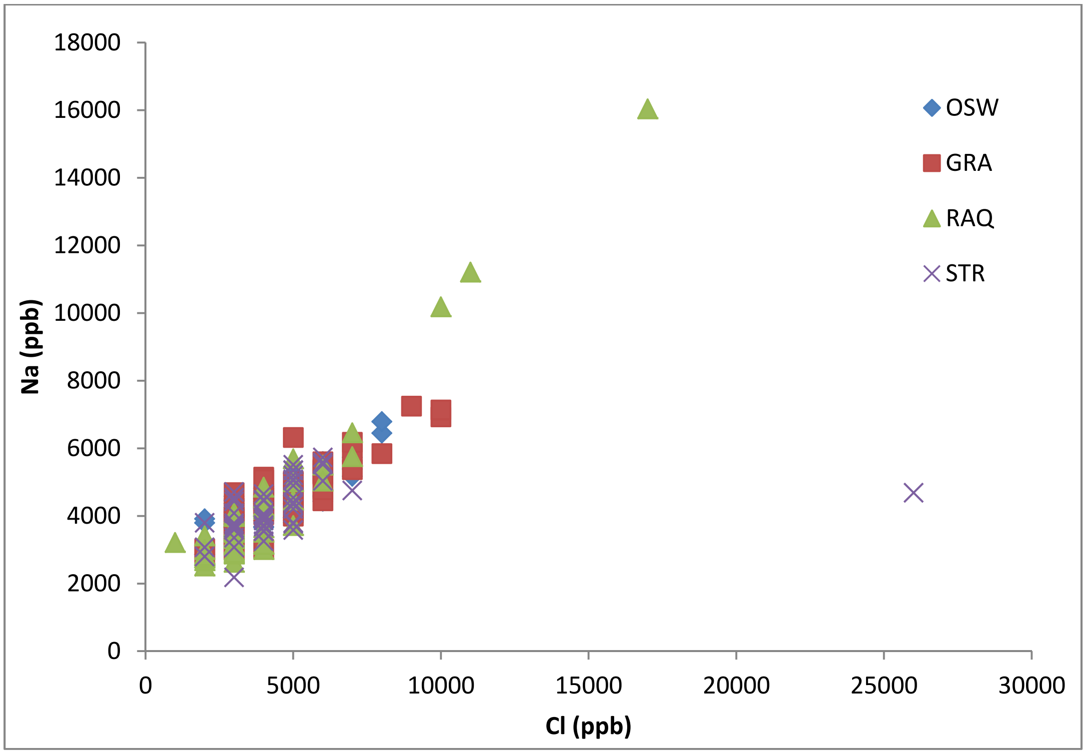


Figure 16: Graph of Na versus Cl

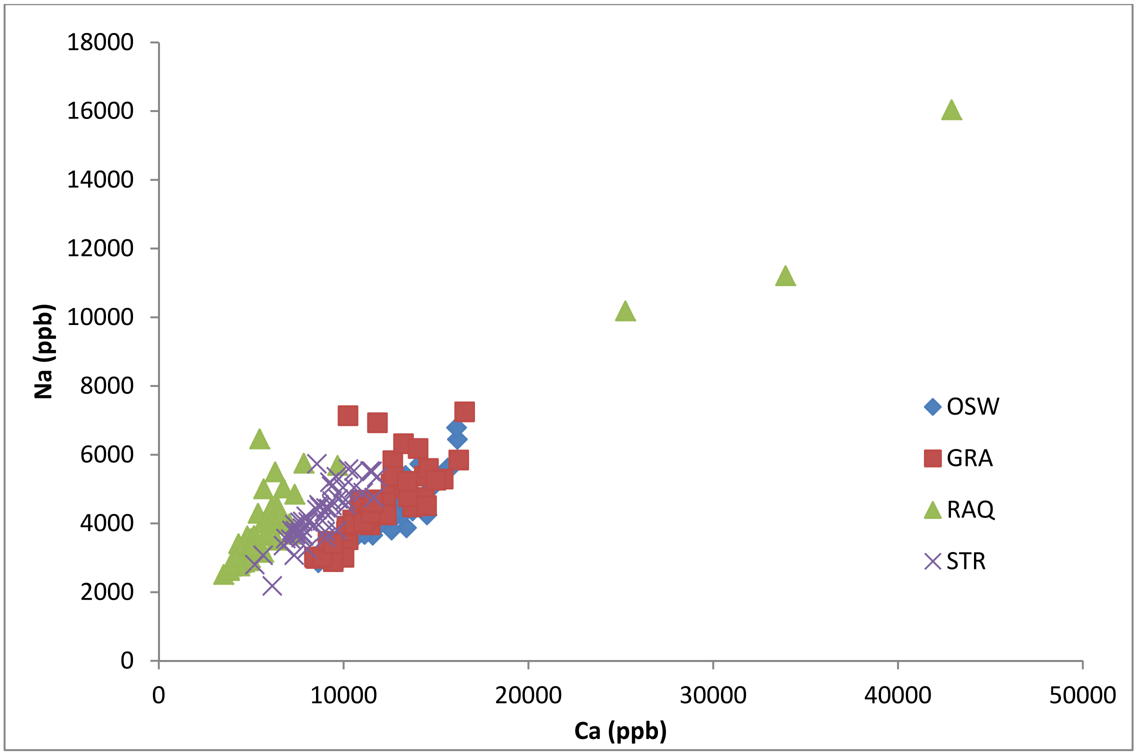


Figure 17: Graph of Na versus Ca

5.2 Elemental and Anion Loading

Element and anion loading was calculated as a function of concentration and river discharge and recorded as mass per unit time. Gaillardet et al (1999) used a similar method to calculate dissolved yield in 60 major rivers from all over the world. Their goal was to determine global silicate weathering and CO_2 consumption rates inferred from chemistry of large rivers. Dissolved yield was calculated from total dissolved loads (calculated as sum of major element concentrations) and water discharges. Given the size and magnitude of the rivers investigated by Gaillardet et al., that is Amazon (the largest) to Seine River (the smallest), weathering fluxes are reported in t/year. Amazon River is reported to have the highest silicate weathering flux of $80 \times 10^6\ t/yr$, Irrawady River at $30 \times 10^6\ t/year$, Zaire River at $16 \times 10^6\ t/year$, and Seine River at the lowest with $0.1 \times 10^6\ t/year$. On a global scale, $300 \times 10^6\ t/year$ of dissolved solids from silicate weathering is transported into the ocean by the 60 rivers, $640 \times 10^6 t/year$ by carbonate weathering, and $144 \times 10^6\ t/year$ by evaporite weathering (Gaillardet et al 1999).

OSW has the highest loading capacity at 32% for cations and 37% for anions (Figures 20 and 21) as per discharge rates for that given sample year. RAQ has the second highest loading capacity for cations at 28%. GRA has the second highest anion loading capacity at 25%. Both rivers OSW and GRA are to the western section of St. Lawrence County. The rivers flow over a large portion of the county that has exposed bedrock susceptible to weathering namely the Adirondack Lowlands (Figure 6) before draining into the St.

Lawrence River. Relatively high concentration of elements and discharge flow results in high loading values in OSW and GRA. Same applies to GRA as it is next to OSW and flows roughly through the same terrain and exposure as OSW.

RAQ and STR have lower loading capacity. RAQ cation and anion loading values are 28% (second highest cation loading value) and 21 % respectively whereas STR has 18% and 17%. Both rivers are to the easternmost section of the county. This region has very little exposure of Adirondack Lowlands bedrock exposure which we assume is the main source of most of the solutes in the river waters. Crystalline rocks of the Adirondack Highlands are fairly resistant to weathering due to the nature of their mineral composition (mostly silicate rocks). Blum et al (1998) attributes silicates to weather out of orthoclase into kaolinite. STR, for example, does not flow over bedrock that is easily weathered that would drive high concentrations of solutes and dissolved solids.

Figure 22-29 show normalized loading for selected cations and all anions by river. Ca and CO_3 are the most dominant cation and anion respectively, in St. Lawrence County river waters. Other cations and anions found in the rivers include Na, Mg, Si, Cl, and SO_4.

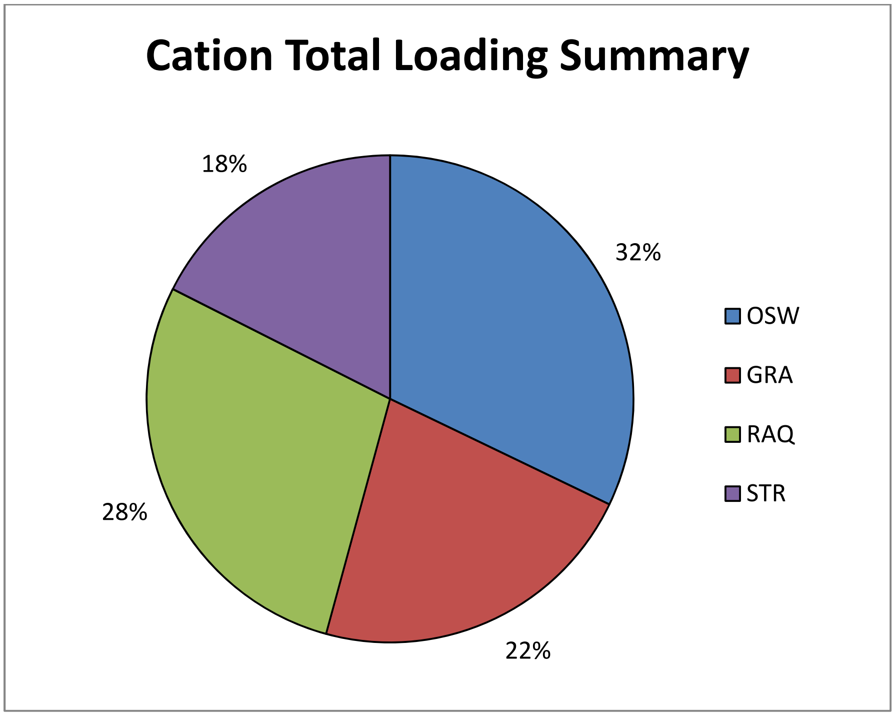


Figure 18: Total element loading for all 72 elements detected represented in kg/year and by river from June 2011 – May 2012.

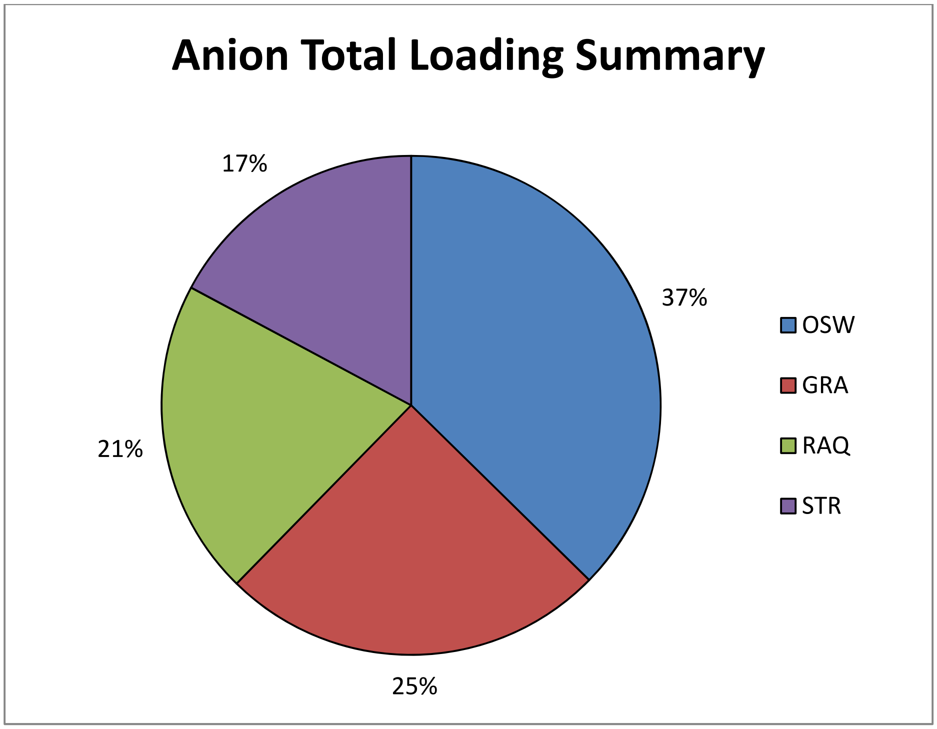


Figure 19: Total anion loading for all 8 anions detected in water samples expressed in kg/year and by river from June 2011 – May 2012.

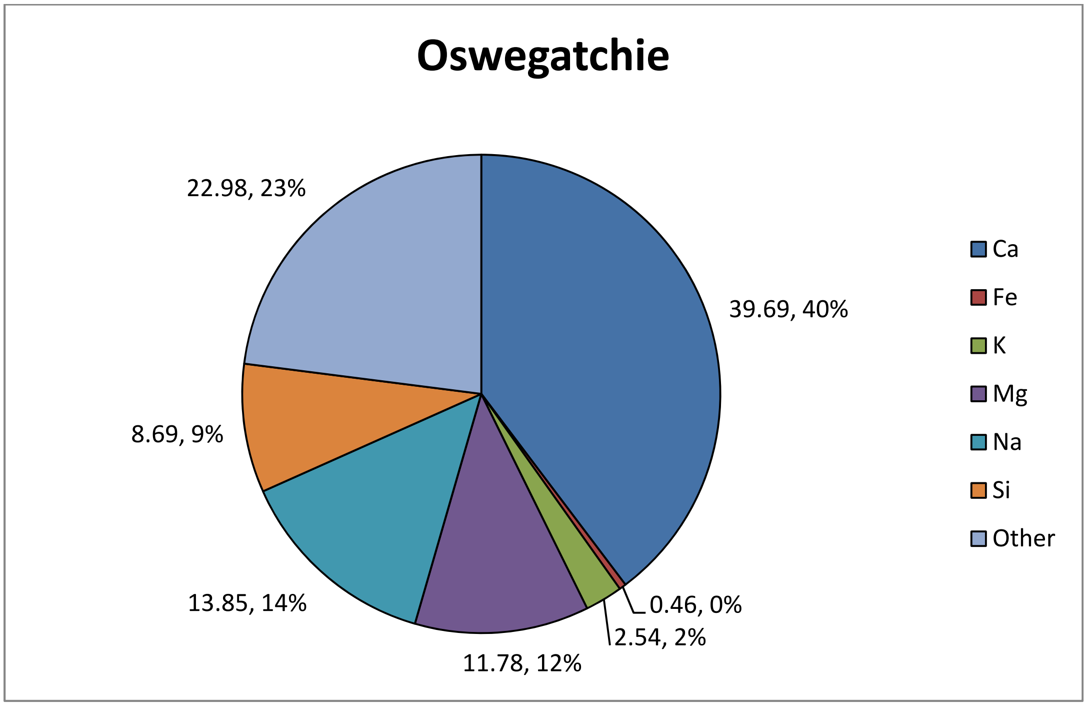


Figure 20: Pie charts representing Oswegatchie River normalized loading of major elements. Ca is the most dominant cation followed by Na, Mg, and Si. Other category represents other 66 elements detected in all sample waters.

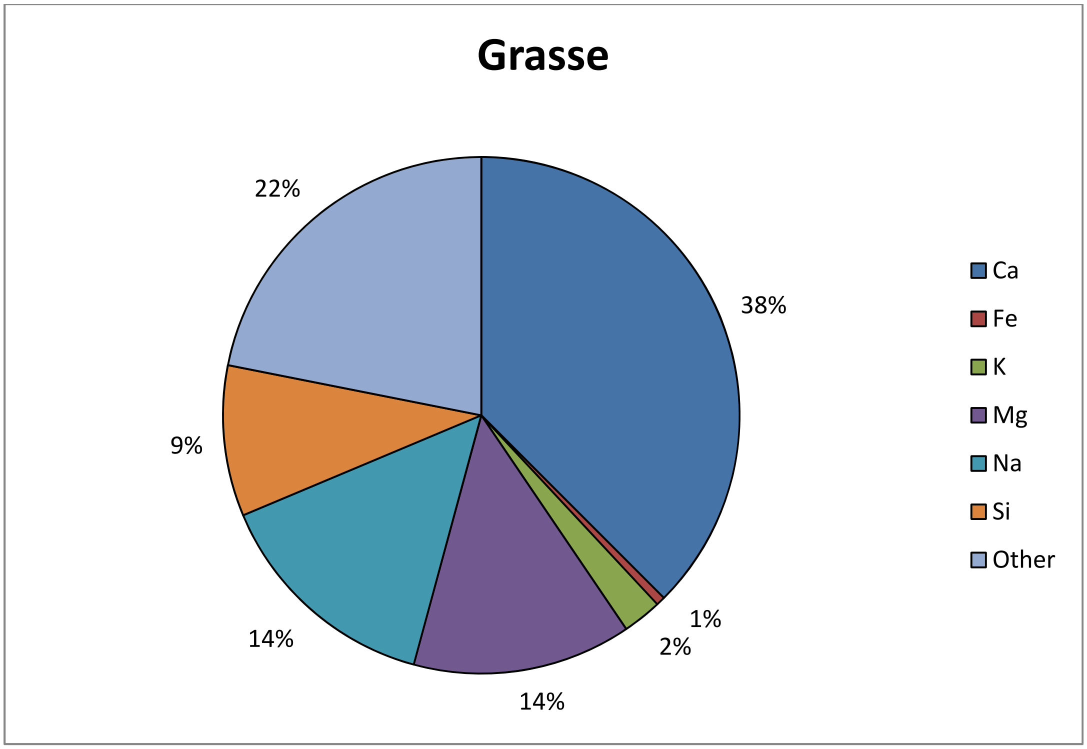


Figure 21: Pie charts representing Grasse River normalized loading of major elements. Ca is the most dominant cation followed by Na, Mg, and Si. Other category represents other 66 elements detected in all sample waters.

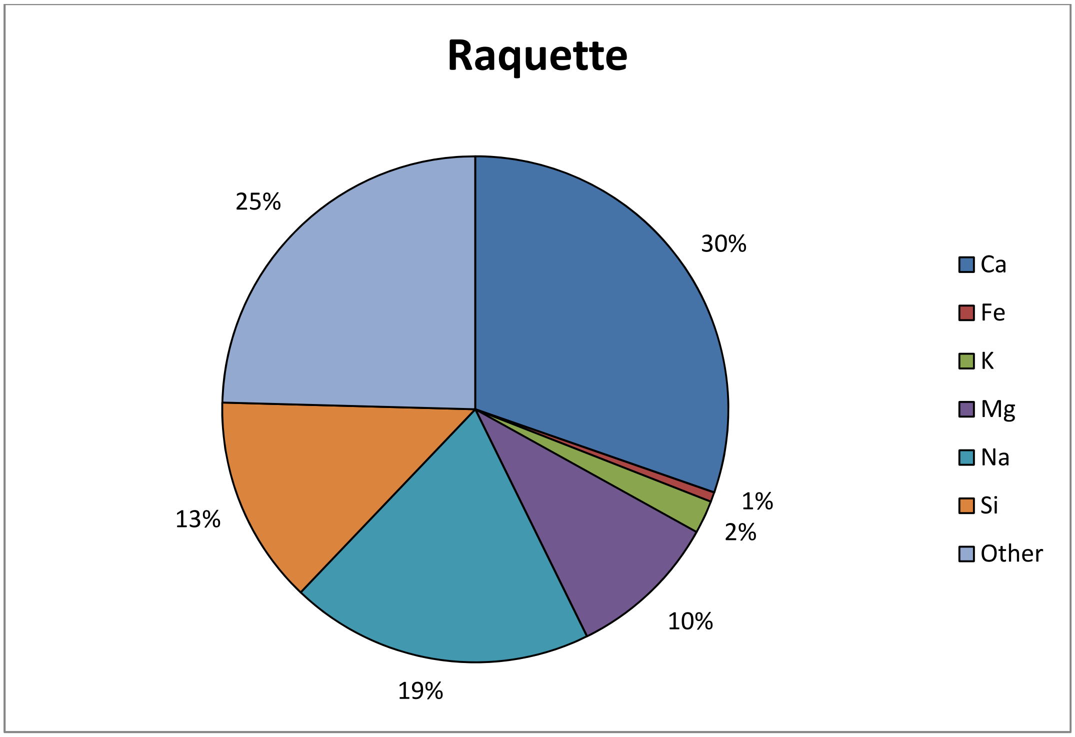


Figure 22: Pie charts representing Raquette River normalized loading of major elements. Ca is the most dominant cation followed by Na, Mg, and Si. Other category represents other 66 elements detected in all sample waters.

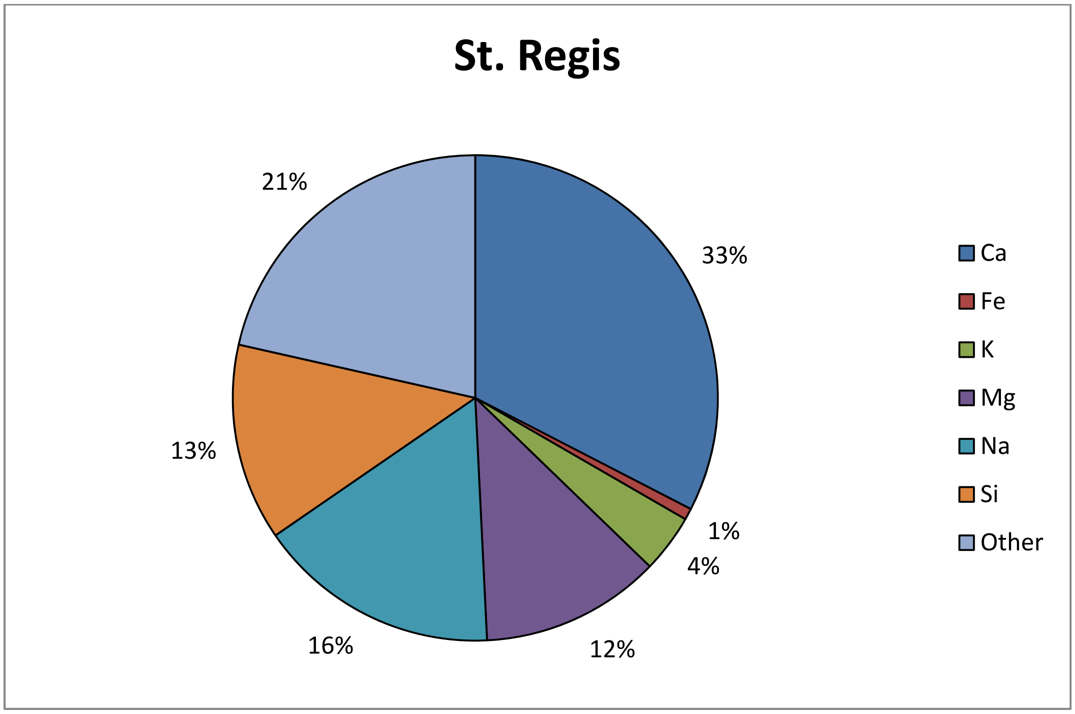


Figure 23: Pie charts representing St. Regis River normalized loading of major elements. Ca is the most dominant cation followed by Na, Mg, and Si. Other category represents other 66 elements detected in all sample waters.

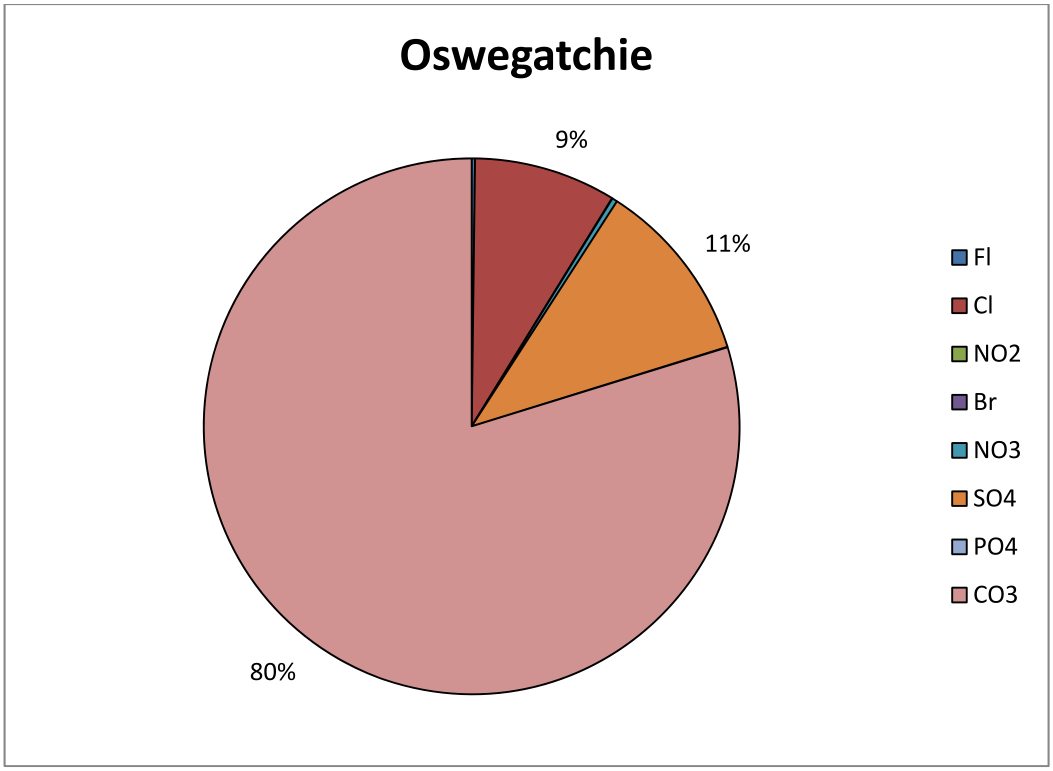


Figure 24: Pie charts representing Oswegatchie River normalized loading of major anions. CO_3 is the most dominant anion followed by SO_4 and Cl.

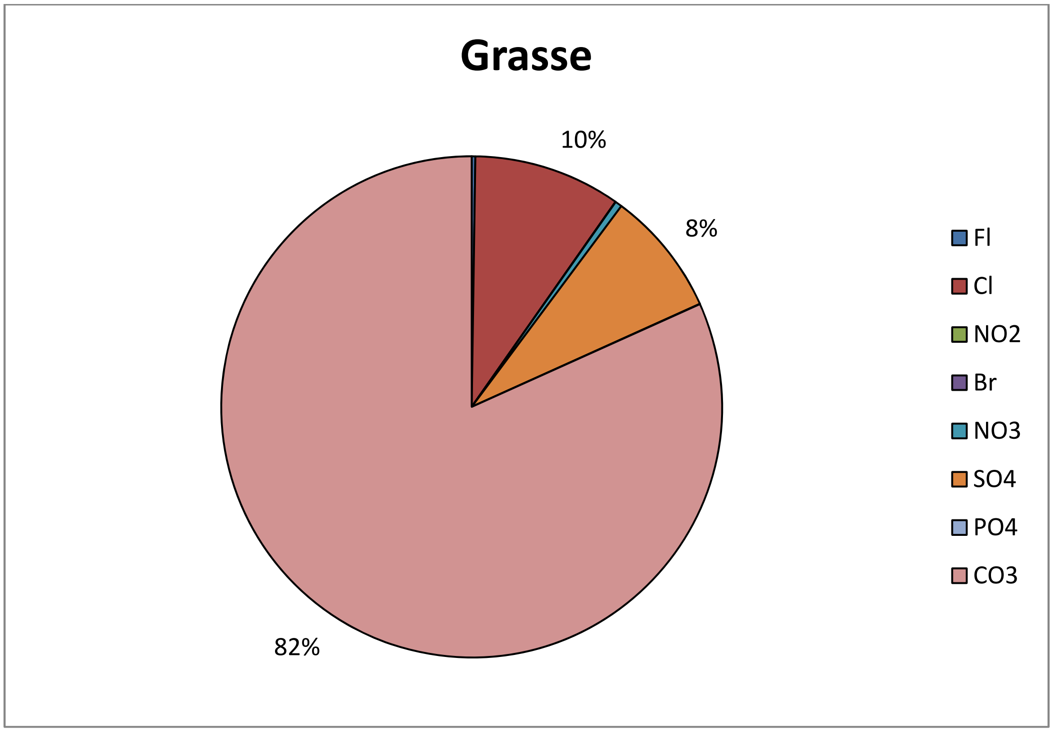


Figure 25: Pie charts representing Grasse River normalized loading of major anions. CO_3 is the most dominant anion followed by Cl and SO_4.

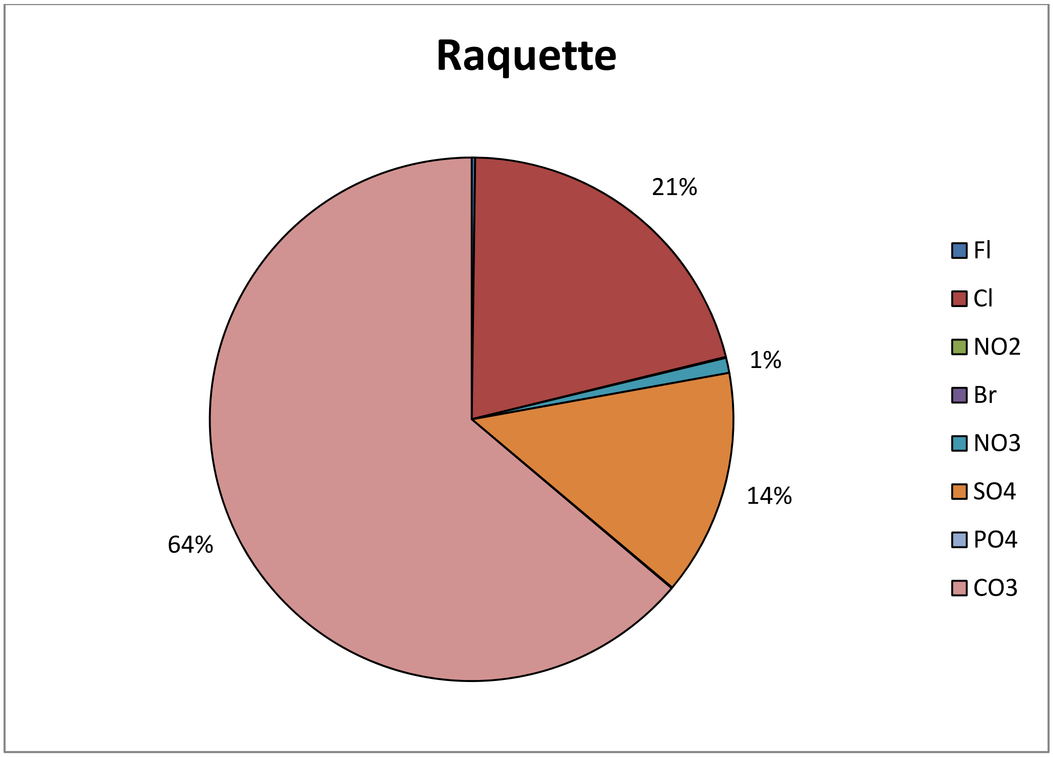


Figure 26: Pie charts representing Raquette River normalized loading of major anions. CO_3 is the most dominant anion followed by Cl and SO_4.

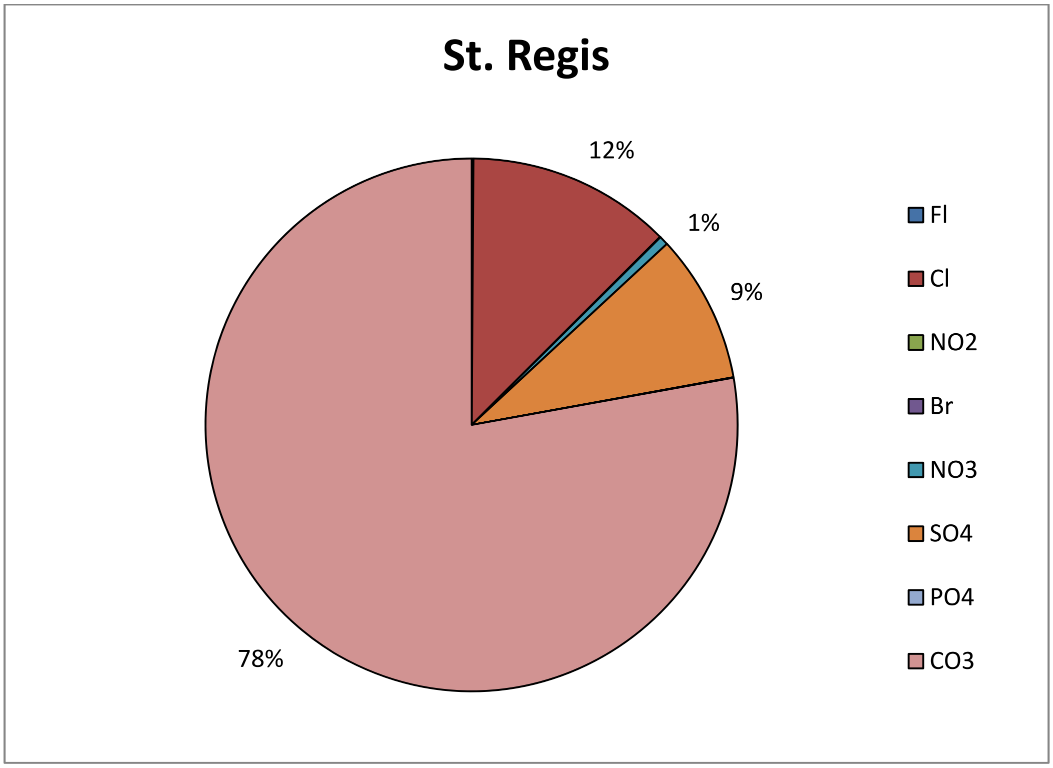


Figure 27 : Pie charts representing St. Regis River normalized loading of major anions. CO_3 is the most dominant anion followed by Cl and SO_4.

5.3 Seasonal and Geochemical Differences among the Rivers

Seasonal geochemical differences among the rivers have been noted in the course of this study. Changes in season and discharge conditions were expected to have an effect on physical parameter as well as chemical properties and characteristics of the rivers. Tipper et al. (2006) discuss seasonal variations in riverine chemistry in the Himalayas especially silicate and carbonate weathering. He postulates the most likely cause of seasonal variation to be increased runoff from precipitation, and glacial melt water that increase discharge rates. High discharge rate is also thought to be the main control for compositional variability within rivers. High discharge rates are noted in the around the following dates: 6/3/2011, 9/8/2011, 10/20/2011, 12/8/2011, 2/2/2012, 3/15/2012, and 4/26/2012 (mostly variable high discharge rates from early fall towards spring) (Figure A8). Similarly, I argue that seasonal variation in river watersheds in the county affect discharge rates, weathering rates, and consequently concentration and dissolution of elements and anions into the rivers. Appendix D shows cosine trends that reflect seasonal variability in selected elements and anions.

During summer (June to August, ~weeks 1-12) Al and Fe are preferentially enriched in the waters than other elements and anions. In some cases, NO_3-N (GRA), PO_4-P (GRA), and SO_4 (OSW) are concentrated (Figures D1 and D2). Given Al and Fe dissolve in non-neutral waters, summer waters tend to be basic and sometimes acidic due to dissolved solids, resulting in enhanced dissolution of Al and Fe. NO_3-N, PO_4-P, and SO_4 are mostly attributed to fertilizing fields with fertilizer and/or manure, which commonly happen in the late spring/early summer times to ready farms for planting. Runoff due to precipitation can wash off loose fertilizers in to the water. Loading in the summer months appear to be decreasing. This could be a function of reduced precipitation. Snow packs and banks will have melted away and not much runoff will be available to replenish the rivers. In general, discharge rates are decreased and consequently loading values as well. An exception is noted in Fe where loading is noted to increase in summer. Fe concentration is brought about by preferential weathering of iron-rich rocks and minerals and redox conditions in the waters (Vuori, 1995). Warmer temperatures appear to be crucial in increased concentration and loading of Fe (Figure D3). Iron on the other hand has been known to pose adverse effects on ecosystems. For example, toxic effects have been noted on rainbow trout due to iron at neutral pH as a result of precipitation of ferric hydroxides on the egg and gill surfaces of their young (Von Luckowicz, 1976). Generally, combined direct and indirect effects of iron contamination decreases species diversity and abundance among fishes and amphibians (Vuori, 1995). Dissolution and precipitation of Fe affects bioavailability, toxic effects, and fate of trace metals and organic toxicants within a food chain.

Through fall months (September to November, ~weeks 14-27) most trends appear to transition to peak or base concentrations. Such elements and anions include Al, Fe, Mg, Na, Si, Cl, NO_3-N, and SO_4 in relatively all rivers. Peak and base concentrations of elements and anions however are Ca (RAQ), K (all rivers), Mg (RAQ), Na (RAQ), Si (all rivers except RAQ), CO_3 (all rivers), F (all rivers), and SO_4 (RAQ and STR) (Figures D1 and D2). Onset of precipitation of the fall appears to facilitate weathering of peak concentration of elements and anions and lack of weathering for more resistant elements and anions under such conditions. Loading of selected elements and anions are noted to increase with increasing discharge rate due to precipitation (Figures D3 and D4). As noted earlier, the exception to this trend is Fe whose loading begins to decrease in the fall. Ferric iron (oxidized from ferrous iron) would appear to precipitate as the waters are now fairly neutral and do not dissolve the iron present in the waters.

Winter conditions (December to February, ~weeks 28-41) are expected to have a different effect on dissolution of elements and anions into the rivers. Al and Fe have low concentrations during this time, as well as NO_3-N, PO_4-P, and SO_4 (Figures D1 and D2). Decreased acidity and alkalinity of the waters and lack of fertilizing in fields in the winter may be responsible for the decrease in the above stated elements and anions. Loading of majority of elements and anions increases with onset of winter, while that of Fe decreases. Winter brings about snow, sleet, and frost, all forms of precipitation capable of increasing discharge rates and loading values as well (Figures D3 and D4).

Spring months (March to May, ~weeks 42-52) mostly show change in element and anion concentrations from peak to base conditions and vice versa depending on the rivers. Peak and base concentrations in CO_3 are observed for OSW, GRA, and STR, and RAQ respectively. Other patterns are noticed in F where peak conditions are seen in GRA and base conditions in RAQ and STR. CO_3 and F may be readily weathered with onset of melting of snow packs and increasing temperatures (Figures D1 and D2). Loading values get to their peak values in the spring due to increased discharge with snow melt and precipitation. However, towards the end of spring, loading values begin to decrease with reducing discharge due to decreasing runoff and snowmelt. Fe loading begins to increase in the spring months probably as a result of increased discharge rates.

Vuori (1995) notes observations on discharge and iron concentrations in river waters as contradictory. Vuori points out that Johnson and Thornton (1987) noticed a large fluctuation in fluxes and concentrations of iron in river water occurring particularly during storms and rapid floods. Surface runoff plays an important role in concentration of iron during floods. Heikkinen (1990c) reports decrease in iron concentration with rise of spring flood when pH values decreased. On the other hand, Grieve (1984) suggested that flood induces flushing of iron from dissolved organic compounds. Vuori finalizes that iron mobility ti be determined by the same factors that cause changes in the quality and quantity of organic material transported in rivers.

5.4 Geochemical Characteristics of the Raquette River

The Raquette River lies towards the East in St. Lawrence County. Its waters derive from the Adirondack Highland waters (crystalline granitic rocks), pass through a narrow portion of the Adirondack Lowlands (metasedimentary rocks of high buffering capacity), and then enter the St. Lawrence Lowlands (mostly clastic and carbonate sedimentary rocks. Its path is different from the OSW, GRA, and STR. The Raquette River has the highest number of dams in the County (n=17) for hydropower purposes. The river flows through several large man-made reservoirs in the area such as the Carry Falls and Blake Reservoirs (Figure 30).

RAQ has the least amount of TDS and least variability in nearly every analyte as a result of numerous dams (Chiarenzelli et al., 2012). As a consequence of damming, flow of river water is highly regulated and retention time of the water increased. Increases in retention time allows for organic particles, fine sediments, and other components such as colloids to precipitate out of solution and settle at the bottom of reservoirs. The only time these sediments would be removed from the reservoirs would be during a catastrophic failure.

Water in reservoirs therefore contains those cations and anions that can remain in solution during neutral conditions and those that are not affected by redox reactions and sunlight. The series of pools of standing water because of standing water enhances limnologic processes and produces a variety of geochemical environments in which redox sensitive elements can be precipitated e.g. Fe, Mn, Co, Ni, and V (Chiarenzelli et al., 2012). These redox sensitive elements settle to the bottom of the river as colloidal particles or as a coating to pebbles and cobbles in the river bed. Other concerns for dam construction in rivers include considerable reduction in nutrient loads owing to removal of the nutrients (Si, N, and P) in reservoir sediments, a condition termed as 'artificial-lake effect' (Humborg et al., 1997; Humborg et al., 2002). N, P, and dissolved silica (DSi) are essential nutrients for diatoms and silicoflagellates, which form a major part of the aquatic food chain. In cases where there is decrease DSi in waters, there has been an observed species shift to carbonate-utilizing organisms.

A dolostone quarry (Barrett Paving Materials Inc, Norwood, NY) was noted upriver from RAQ sampling site (Figure 5). White discoloration is noted in the waters as a result of surface runoff from the quarry into the river. Ca, Mg, and CO_3 plots on the Raquette River are fairly similar as they have a broad peak in the fall months. In the fall months, there is considerable surface runoff from precipitation and warm temperatures. These conditions may be responsible for the considerable increase in Ca, Mg, and CO_3 concentration in RAQ waters compared to the other rivers. The proximity the quarry to the river likewise ensures runoff into the rivers. Chiarenzelli and Skeels (*in review*) also investigated effects of the dolostone quarry to the Raquette River. They attributed enrichment of CO_3 and SO_4 to runoff from the quarry during flood events. They also argue that fractured dolostone would allow for considerable seepage into RAQ River. Three outliers noted in Ca, Na, Mg, and CO_3 concentrations are linked to runoff from this particular quarry. Historical rainfall events were noted for three to four consecutive days before the sampling dates – 11/17/2011, 12/1/2011, 12/8/2011 that give unusually high concentrations of $CO_{3,}$ Ca, Mg, and Na (Figures 16-19).

High ANC values also correlate to these three days (Figure 13). pH of RAQ ranges between 6.0 and 8.0 and appears to have the lowest buffering capacity except for the three specified days above. This is unexpected as the RAQ flows over some portion of the Adirondack Lowlands as compared to the STR that flows over almost none of the AL. Damming of the river may be the reason for the decreases buffering capacity of the river as compared to STR. More investigation should be done to further outline the impacts of impounding waters on RAQ to river chemistry and characteristics.

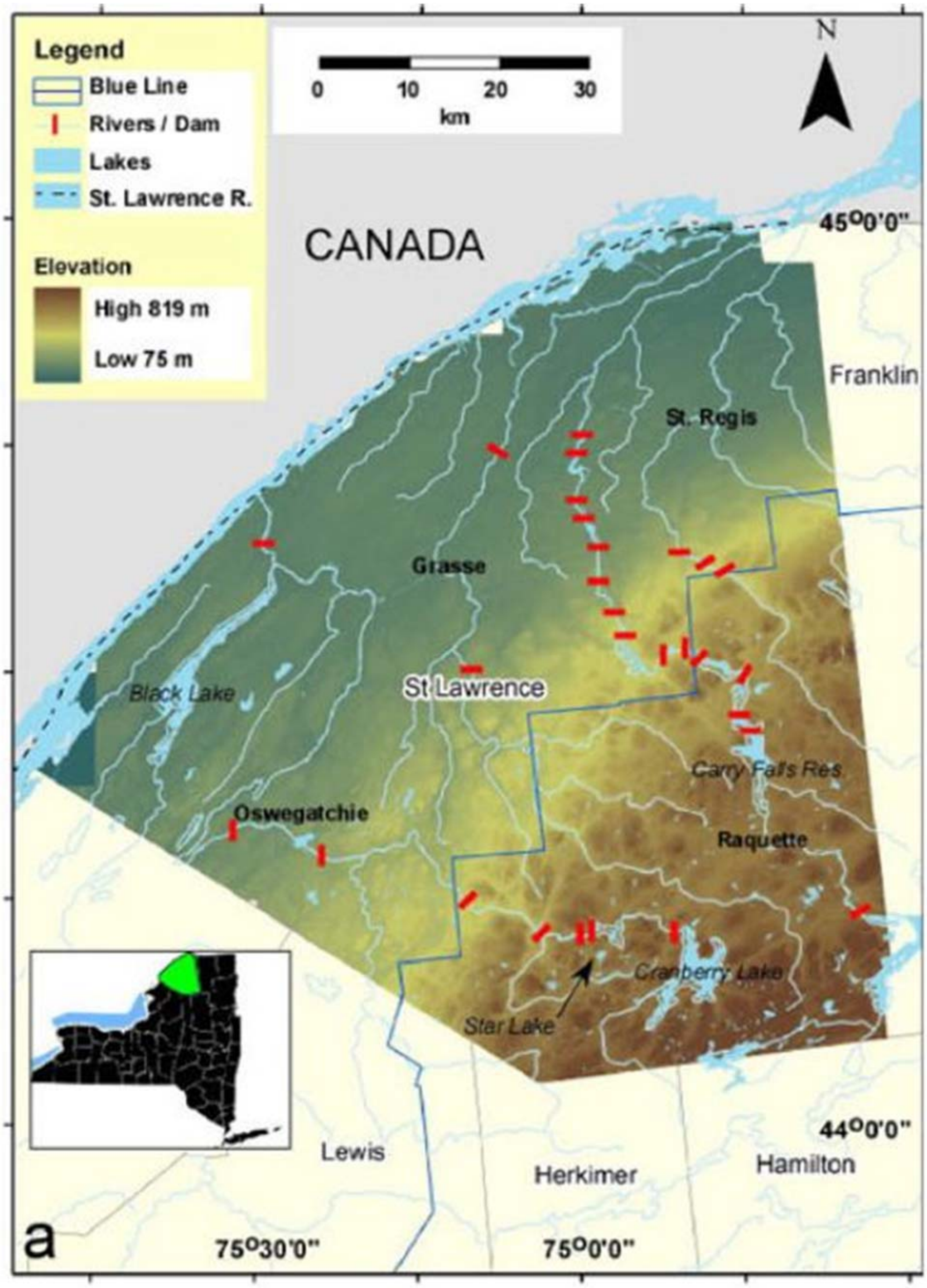


Figure 28: Map showing major rivers in St. Lawrence County and dams along their profile. Note the amount of dams along Raquette River as compare to all other rivers. (Image adapted from Chiarenzelli et al., 2012)

6. CONCLUSIONS

1. Calcium and carbonate are the most dominant cation and anion in St. Lawrence County waters. These soluble minerals are derived from metasedimentary rocks (marble and dolostone) of the Adirondack Lowlands as surface runoff and river waters flow over the region.
2. Nature of bedrock plays a big role in determining river chemistry of an area as preferentially weathered elements (by physical and/or physical processes) from local rocks and minerals end up in the river waters. Metasedimentary rocks are the most soluble rocks besides bedrock containing evaporate minerals. Crystalline metaigneous rocks are not easily dissolved.
3. River chemistry and properties vary from West to East. OSW flows over the most area of the Adirondack Lowlands resulting in its significantly high buffering capacity and concentration of Ca and CO_3. GRA is the second river with high concentrations of Ca, and CO_3 and high buffering capacity. RAQ and STR flow over minimal area of the Adirondack Lowlands hence their low buffering capabilities
4. Acid precipitation from the Adirondack highlands are buffered in the Lowlands and St. Lawrence River Valley due to presence of metasedimentary, clastic, and calc-silicate rocks of the region. The Adirondack Highlands are characterized by crystalline metaigneous rocks that have very little acid neutralizing capacity to acid rain.
5. Other dominant elements in St. Lawrence County river waters are sodium, magnesium, and silicon. Magnesium is common due to presence of Mg-rich minerals such as dolostone in the Lowlands. Sodium is from other soluble minerals in the county such as Na-rich plagioclase (albite), whereas silicon is from silicate minerals that forms majority of minerals on the earth's crust and that of the county.
6. Other dominant anions include chloride and sulfate. Chloride is thought to originate from halite and chlorite minerals found in the county. Another source would be road salt during winter months to improve access to roads. Sulfate on the other hand is due to acid deposition and agricultural land draining. Most of the Adirondack Lowlands and St. Lawrence River Valley have farm lands and pasture lands. Agricultural compounds such as fertilizers, manure, pesticides, herbicides, and other treatments are a good source of sulfates in the waters. Acid deposition over the Highlands is washed down to the Lowlands and Valley from sources such as emissions from commercial industries and vehicular fumes.

7. Oswegatchie River has the highest loading capacity of elements and anions owing to its expanse and drainage in the Adirondack Lowlands and St. Lawrence River Valley. The other rivers in descending order of loading capacity are Grasse, Raquette, and St. Regis. OSW contributes the highest load of elements and anions to St. Lawrence River while STR contributes the least load. Anions contribute the most to total load over the elements. This is due to the nature of charge (small as compared to elements) they carry.

8. Raquette Rivers portrays different characteristics and trends as compared to the other three rivers in the county. RAQ has a numerous (n = 17) hydroelectric dams along its profile. This makes the river appear to be a series of big 'pools' of water with decrease flow velocity, controlled discharge, increased redox conditions, and longer retention time of its waters. As a result some elements and particles are able to precipitate out of the waters while others tend to be concentrated in the waters. Fe (II) may be oxidized to Fe (III) on the RAQ as compared to the other waters among other redox sensitive elements such as Mn, Co, Ni, and V.
9. Runoff from a dolostone quarry upriver from RAQ sampling location has been noted to be the reason for three outlier values in concentration of Ca, CO_3, Mg, and Na. Significant runoff three to four consecutive days prior to sampling events show direct correlation between the rainfall events and unusually high concentration of the above named elements. White discoloration on the river can be noted on the via Google Earth images on days before significant amounts of rainfall.

7. REFERENCES

Berner, E.K., and Berner, R.A., 1996, Global Environment: Water, Air, and Geochemical Cycles. Prentice Hall, Upper Saddle River, NJ, 376p.

Blum, J.D., Gavis, C.A., Jacobson, A.D., and Chamberlain, C.P., 1998, Carbonate versus Silicate Weathering in Raikhot Watershed within the High Himalayan Crystalline Series: Geology, v. 26, p. 411-414.

Chiarenzelli, J.R., and McLelland, J.M., 1991, Age and regional relationships of granitoid rocks of the Adirondack highlands: Journal of Geology, v. 99, no. 4, p.571-590.

Chiarenzelli, J., Lock, R., Cady, C., Bregani, A., and Whitney, B., 2012, Variation in river multi-element chemistry related to bedrock buffering: an example from the Adirondack region of northern New York, USA: Environmental Earth Sciences, v. 67, p. 189-204.

Chiarenzelli, J., and Skeels, M., *in review,* End-Member Water constrained by Event Sampling in and Acidified Drainage Basin, Northern New York, USA: Journal of Hydrology.

Driscoll, C.T., 1985, Aluminum in Acidic Surface Waters: Chemistry, Transport, and Effects: Environmental Health Perspectives, v. 63, p. 93-104.

Driscoll, C. T., Newton, R. M., Gubala, C. P., Baker, J. P., and Christensen, S. W., 1991, Adirondack mountains. Acidic deposition and aquatic ecosystems: regional case studies: Springer-Verlag, New York, 133-202.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., and Weathers, K.C., 2001, Acidic deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and management strategies: BioScience, v. 51, No. 3, p. 180-198.

Driscoll, C.T., Chen, L., 2004, Modeling the response of soil and surface waters in the Adirondack and Catskill regions of New York to changes in atmospheric deposition and historical land disturbance: Atmospheric Environment-North America, v. 38, p. 4099-4109.

Gaillardet, J., Dupre, B., Louvat, P., and Allegre, C.J., 1999, Global Silicate Weathering and CO_2 Consumption Rates deduced from the Chemistry of Large Rivers: Chemical Geology, v. 159, p. 3-30.

Godwin, K.S., Hafner, S.D., and Buff, M.F., 2003, Long-Term Trends in Sodium and Chloride in Mohawk River, New York: The Effect of Fifty Years of Road-Salt Application: Environmental Pollution, v. 124, p. 273-281.

Grieve, I.C., 1984, Relationships among Dissolved Organic Matter, Iron, and Discharge in a Moorland Stream: Earth Surface Processes and Landforms, v. 9, p. 35-41.

Heikkinen, K., 1990c, Seasonal Changes in Iron Transport and Nature of Dissolved organic matter in a Humic River in Northern Finland: Earth Surface Processes and Landforms, v. 15, p. 583-596.

Humborg, C., Blomqvist, S., Avsan, E., Bergensund, Y., Smedberg, E., Brink, J., and Morth, C-M., 2002, Hydrological Alterations with River Damming in Northern Sweden: Implications for Weathering and River Biogeochemistry: Global Biogeochemical Cycles, v. 16, no. 3, 1039.

Humborg, C., Ittekkot, V., Cociasu, A., and Bodungen, B., 1997, Effect of Danube River Dam on Sea Biogeochemistry and Ecosystem Structure: Nature, v. 386, no. 27, p. 385-388.

Isachen, Y.W., and Fisher, D.W., 1970, compilers and editors, Geologic Map of New York: Adirondack Sheet: New York State Museum and Science Service, Map and Chart Series 15, scale 1:250 000.

Jenkins, J., Driscoll, C., Roy, K., and Buerkett, C., 2007, Acid rain in the Adirondacks: an environmental history, 1st Ed.: Cornell University Press, Ithaca, USA, 256 p.

Johnson, C.A., and Thornton, I., 1987, Hydrological and Chemical Factors Controlling the Concentrations of Fe, Cu, Zn, and As in a River System Contaminated by Acid Mine Drainage: Water Resources, v. 21, p. 359-365.

Lawrence, G.B., Momen, B., and Roy, K.M., 2004, Use of stream chemistry for monitoring acidic deposition effects in the Adirondack region of New York: Journal of Environmental Quality, v. 33, p. 1002-1009.

Luckowicz, M.v., 1976, Der Eisengehalt in Wasser und Seine Wirkung auf den Fisch: Fisch Umwelt, v. 2, p. 85-92.

Mezger, K., Van Der Pluijm, B.A., Essene, E.J., and Halliday, A.N., 1992, The carthage-colton mylonite zone (Adirondack Mountains, New York): the site of a cryptic suture in the Grenville Orogen?: Journal of Geology, v. 100, no. 5, p. 630-638.

Murphy, J.T Jr., 2011, An Investigation of Stream Chemistry Variability of Watersheds in Central St. Lawrence County, New York: Undergraduate Thesis; St. Lawrence University, Canton, NY, USA.

O'Connor, M., Zabik, M., Cady, C., Cousens, B., and Chiarenzelli, J., 2010, Multi-Element Analysis and Geochemical Spatial Trends of Groundwater in Rural Northern New York: Water, v. 2, p. 217-238.

Pair, D.L., and Cadwell, D.H., compilers and editors, 1991, Surficial Geology Map of New York: Adirondack Sheet: New York State Museum – Geological Survey, Map and Chart Series 40, scale 1:250 000.

Pair, D.L., and Rodrigues, C.G., 1993, Late Quaternary Deglaciation of the Southwestern St. Lawrence Lowland, New York and Ontario: Geological Society of America Bulletin, v. 105, p. 1151-1164.

Peltola, P., Brun, C., Astrom, M., and Tomilina, O., 2008, High K/Rb Rations in Stream Waters – Exploring Pland Litter Decay, Ground Water, and Lithology as Potential Controlling Mechanisms: Chemical Geology, v. 257, p. 92-100.

Reynolds, C.S., 1984, The Ecology of Freshwater Phytoplankton. Cambridge University Press, Cambridge, 384 p.

Ribbe, L., Delgado, P., Salgado, E., and Flugel, W.-A., 2008, Nitrate Pollution of Surface Water Induced by Agricultural Non-Point Pollution in the Pocochay Watershed, Chile: Desalination, v. 226, p. 13-20.

Streepey, M.M., Johnson, E.L., Mezger, K., and van der Pluijm, B.A., 2001, Early History of the Carhage-Colton Shear Zone, Grenville Province, Northwest Adirondacks, New York (U.S.A.): Journal of Geology, v. 109, no. 4, p. 479-492.

Tipper, E.T., Bickle, M.J., Galy, A., West, A.J., Pomies, C., and Chapman, H.J., 2006, The Short Term Climatic Sensitivity of Carbonate and Silicate Weathering Fluxes: Insight from Seasonal Variations in River Chemistry: Geochimica et Cosmochimia Acta, v. 70, p. 2737-2754.

U.S. Geological Survey TWRI Book 9, 2012, National Field Manual for the collection of water-quality data: Alkalinity and Acid neutralizing Capacity: http://water.usgs.gov/owq/FieldManual/Chapter6/section6.6/ (Revised by S.A. Rounds, version 4.0.

United States Environmental Protection Agency, 2012, Water: Monitoring and Assessment: http://water.epa.gov/type/rsl/monitoring/vms52.cfm (accessed February 2014).

Vuori, K., 1995, Direct and Indirect Effects of Iron on River Ecosystems: Annales Zoologici Fennici, v. 32, p. 317-329.

Waller, K., Driscoll, C., Lynch, J., Newcomb, D., and Roy, K., 2012, Long-term recovery of lakes in the Adirondack region of New York to decreases in acidic deposition: Atmospheric Environment, v. 46, p. 56-64.

Wigington, Jr. P.J., Baker, J.P., DeWalle, D.R., Kretser, W.A., Murdoch, P.S., Simonin, H.A., Van Sickle, J., McDowell, M.K., Peck, D.V., and Barchet, W.R., 1996, Episodic acidification of small streams in the northeastern united states: Episodic Response Project: Ecological Application, v. 6, no. 2, p. 374-388.