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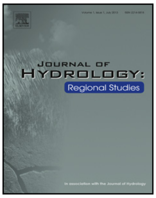

End-member river water composition in the acidified Adirondack Region, Northern New York, USA

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ABSTRACT

Study region: From its headwaters in the Adirondacks to its confluence with the St. Lawrence River, the Raquette flows across acidic crystalline rock, a marble dominated metasedimentary sequence, and Paleozoic sedimentary rocks with increasing capacity to neutralize acidity. Although its drainage basin is largely forested and has a limited population, seventeen hydroelectric reservoirs occur along its mid to lower reaches.
Study focus: The goal of the study was to document the geochemistry of Raquette River waters during discharge events. The river was sampled for 69 elements and 7 anions, along its length during stormflow associated with Tropical Storm Irene. One year later the same sites were sampled during a drought with a flow-duration percentage was 98.65.
New hydrological insights for the region: Samples collected during average discharge volumes documented chemical gradients corresponding to bedrock spatial distribution. These trends were muted during both stormflow and baseflow, and imply that other factors influence water chemistry during high and low-flow events. Our study documents an example of event river chemistry responding less to extremes of flow or variation in underlying geology than anticipated. During the stormflow sampling one sample had elevated specific conductance (160.4 $\mu S\,cm^{-1}$) and pH (8.21). This data, anomalous geochemistry, and images from Google Earth suggest that the river chemistry is sporadically impacted by discharge from a dolostone quarry located 6 km upstream during runoff events.

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1. Introduction

1.1. Problem statement

Drever (1997) listed five major influences on the chemistry of natural waters including: climate, lithology, relief, rock/water interaction, and vegetation. Rock/water interaction, influenced by the proportions of runoff (overland flow) to baseflow is an important factor in the variation documented within individual hydrologic systems (Inamdar et al., 2013). Perturbations of natural hydrologic systems are common and numerous examples of anthropogenic factors, both intra- and extra-basinal, resulting in a strong impact on river water chemistry have been documented in the literature (e.g. Rothwell et al., 2007; Sanchez Espana et al., 2005).

Here we investigate water chemistry during both stormflow and baseflow at seventeen localities in the acidified (Jenkins et al., 2007), but largely undeveloped (Jenkins and Keal, 2004), Raquette River drainage basin within the Adirondack Region. Previous work (Chiarenzelli et al., 2012) has demonstrated that during near average discharge volumes water chemistry is distinct in stretches of the river underlain by three different bedrock terranes (Adirondack Highlands, Adirondack Lowlands, and St. Lawrence River Valley), which vary widely in their chemical composition and capacity to buffer acidity. Our primary goal is to characterize and compare the water composition down the length of the river during conditions of high and low discharge approximating end member compositions. Second, we discuss the factors that exert primary control on the variation in water chemistry within the drainage basin. Third, we present evidence for the unanticipated episodic impact of a dolostone quarry on river water chemistry in the lower reaches of the river.

1.2. The Raquette River

The Raquette River originates in the Central Adirondack Region near Raquette Lake, New York and has a drainage basin of 2900 km^2. It flows north approximately 280 km and drops more than 457 m in elevation to its confluence with the St. Lawrence River near Massena (Fig. 1). During most of its length it flows within the Adirondack Park, a sparsely populated region of private and public lands with limited and highly regulated development, extensive forest cover, and limited agricultural use (Jenkins and Keal, 2004). A system of dams, some built more than a century ago, were used to raise water levels in pre-existing lakes (e.g. Raquette, Forked, Long, and Tupper lakes) and to facilitate spring logging runs. Large reservoirs (e.g. Carry Falls, Blake, Rainbow Falls, Five Falls, and Higley Flow), below the USGS gauging station at Piercefield, were built in the 1950s to provide water storage capacity for hydropower in the river's mid to lower reaches, where seventeen hydropower dams with a generating capacity of 181 MW occur (Supplemental Table 1). In addition to its importance as hydropower resource, the Raquette River serves as a water source for several communities along its banks, as a recreational resource, and as an important cultural resource for the Native American community at Akwesasne.

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1.3. Geology of the Raquette River drainage basin

Along the course of its length the river traverses three very distinct geological terranes including the Adirondack Highlands, Adirondack Lowlands, and St. Lawrence River Valley (Chiarenzelli et al., 2012). The approximate center of the Adirondack topographic dome, the High Peaks Region, is east of the Raquette River drainage basin and underlain by the large Marcy Anorthosite massif. The anorthosite is surrounded by a complex assemblage of highly metamorphosed Precambrian crystalline bedrock lithologies ranging in age from about 1.00 to 1.35 billion years old that make up what is referred to as the Adirondack Highlands (Regan et al., 2011). In addition to its domal topographic expression, this area is characterized by highly deformed and metamorphosed igneous rocks, many of which were intruded along with the anorthosite deep into the roots of an ancient mountain belt. This mountain belt was part of a global system of continental collisions (i.e. orogenic events) that resulted in the formation of the supercontinent of Rodinia by 1.0 billion years ago. The Adirondacks are part of a

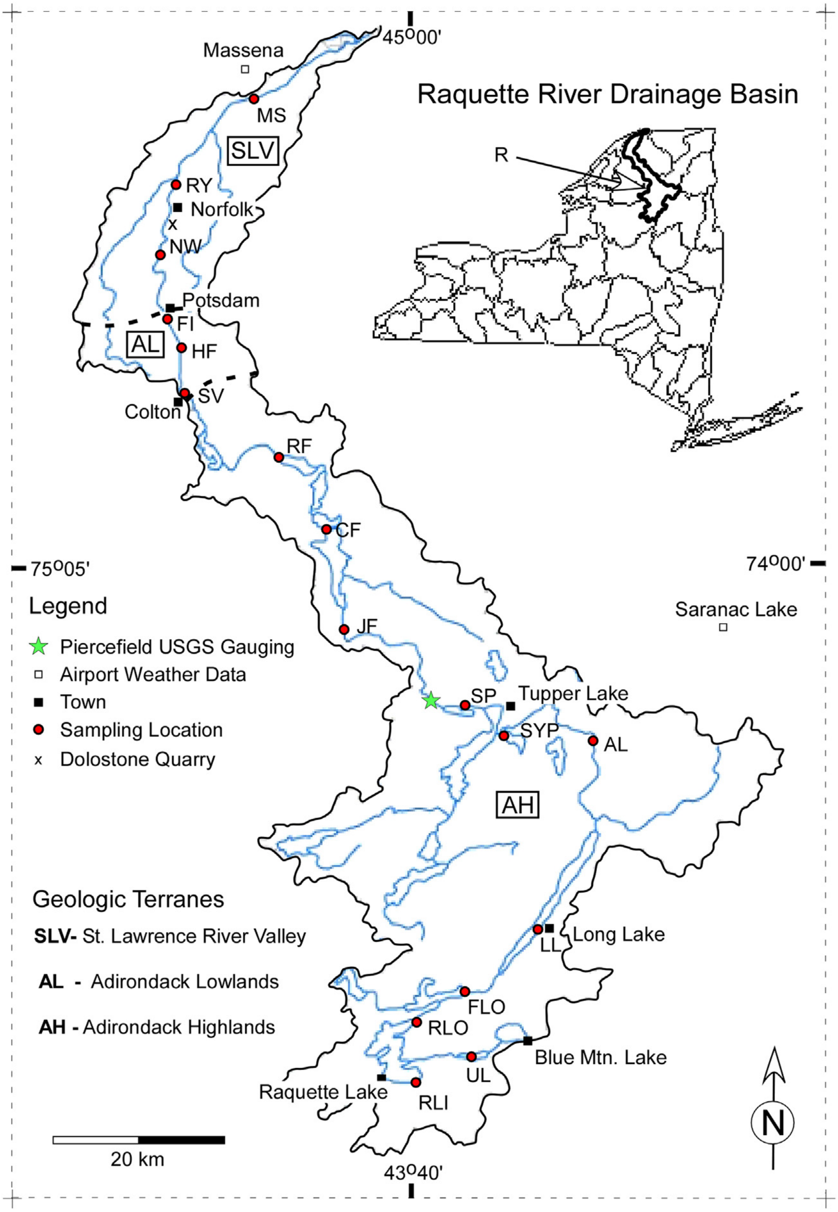

Fig. 1. Map showing the location of the Raquette River drainage basin, lakes and hydropower reservoirs, towns, sampling sites, USGS gauging station at Piercefield, and airports for which precipitation data was available. Major geologic terranes are also shown (Adirondack Highlands, Adirondack Lowlands, St. Lawrence River Valley). Sampling locations from south to north: RLI – Raquette Lake Inlet; UL – Utowana Lake; RLO – Raquette Lake Outflow; FLO – Forked Lake Outlet; LL – Long Lake; AL – Axton Landing; SYP – Symmonds Pond; SPD – Setting Pole Dam; JF – Jamestown Falls; CF – Carry Falls; RF – Rainbow Falls; SV – Stone Valley; HF – Hannawa Falls; FI – Fall Island; NW – Norwood; RY – Raymondville; and MS – Massena Springs.

continental-scale belt of highly eroded crystalline rocks of similar age and origin, known as the Grenville Province, which can be traced in North America from Greenland to Mexico and beyond. With minor exceptions, the rocks in the Adirondack Highlands generally have moderate to limited capacity to buffer acidity (Colquhoun et al., 1981).

The Adirondack Lowlands are located northwest of the Adirondack Highlands and are separated from them by a ductile fault known as the Carthage-Colton Shear Zone. In the Lowlands rocks have been dropped down into their present position after the cessation of mountain building at about 1.0 billion years ago. While still highly deformed and metamorphosed, they record slightly lower metamorphic conditions indicating a position higher in the crust during mountain building than the Highlands. The Lowlands are composed predominantly of less resistant metamorphosed sedimentary rocks developed from a sequence of limestones, sandstones, shale, and evaporitic rocks (Chiarenzelli et al., 2011). They have been intruded by several suites of meta-igneous rocks which comprise a relative small percentage of the current surface area of the Lowlands. The metasedimentary rocks exposed in the Lowlands are also present in the Highlands. However, in the Highlands they are less abundant, occur in narrow, near vertical belts, and are more intensely deformed and disrupted due to deformation and intrusion of igneous rocks on all scales. The high proportion of marble bedrock in the Adirondack Lowlands allows strong buffering of acidic waters (Colquhoun et al., 1981), in contrast to most rocks in the Highlands that have a limited capacity for buffering.

After formation, the Grenville Province (i.e. mountain belt), including the Adirondack region, was worn down to sea level over a period of 500 million years. Renewed uplift and doming of the Adirondack Region began nearly 200 million years ago (Roden-Tice and Tice, 2005) and continues to this day. Sedimentary rocks of Lower Paleozoic age, which currently rim the dome, were once continuous across the region. The renewed erosion has stripped back the Paleozoic cover rocks and created the radial drainage pattern that developed on the flanks of the dome. In the St. Lawrence River Valley sedimentary rocks of Cambrian and Ordovician age overlie the older Grenville basement rocks and record deposition near the shoreline of an ancient ocean. These rocks consist of undeformed and unmetamorphosed sandstones, sandy dolostones, dolostone, and limestones. Aside from relatively pure quartzose sandstones, these rocks have a considerable buffering capacity because of their calcium and magnesium-rich composition (Colquhoun et al., 1981) and yield relatively hard ground water (O'Connor et al., 2010).

1.4. Geochemistry of the Northern New York River waters

The geochemistry of water from several rivers, including the Raquette River, in northern New York has been characterized by Chiarenzelli et al. (2012). Their findings match those of Lawrence et al. (2008) for headwaters of rivers draining the western Adirondacks. The waters were found to be dilute with generally <50 mg/L total dissolved solids (TDS) and strongly influenced by the bedrock within their drainage basin. While the headwaters regions within the Adirondack Highlands are acidified, all of the rivers are quickly buffered upon passing into the Adirondack Lowlands with its abundance of marble bedrock. During long-term, average, summer flow volumes both the TDS and pH of the river water increases downstream. These changes are accompanied by changes in river water chemistry including the decrease in nearly insoluble trivalent cations (Taylor and McLennan, 1985) such as Al, Fe, and REEs (rare earth elements) and the increase in more soluble divalent cations (e.g. Ca, Mg). All the Adirondack rivers have a characteristic tea-like coloration attributed to tannins and other organic compounds derived from their forested drainage basins.

2. Methods

2.1. Opportunity for sampling during high and low discharge

Relative unique meteorological conditions in late summer of 2011 and 2012 presented the opportunity for sampling during periods of high and low discharge. Hurricane Irene (Category 1) tracked along the east coast of the United States in late August of 2011 and although eventually downgraded to a tropical storm it caused severe damage in the eastern Adirondacks, Vermont, and along the East

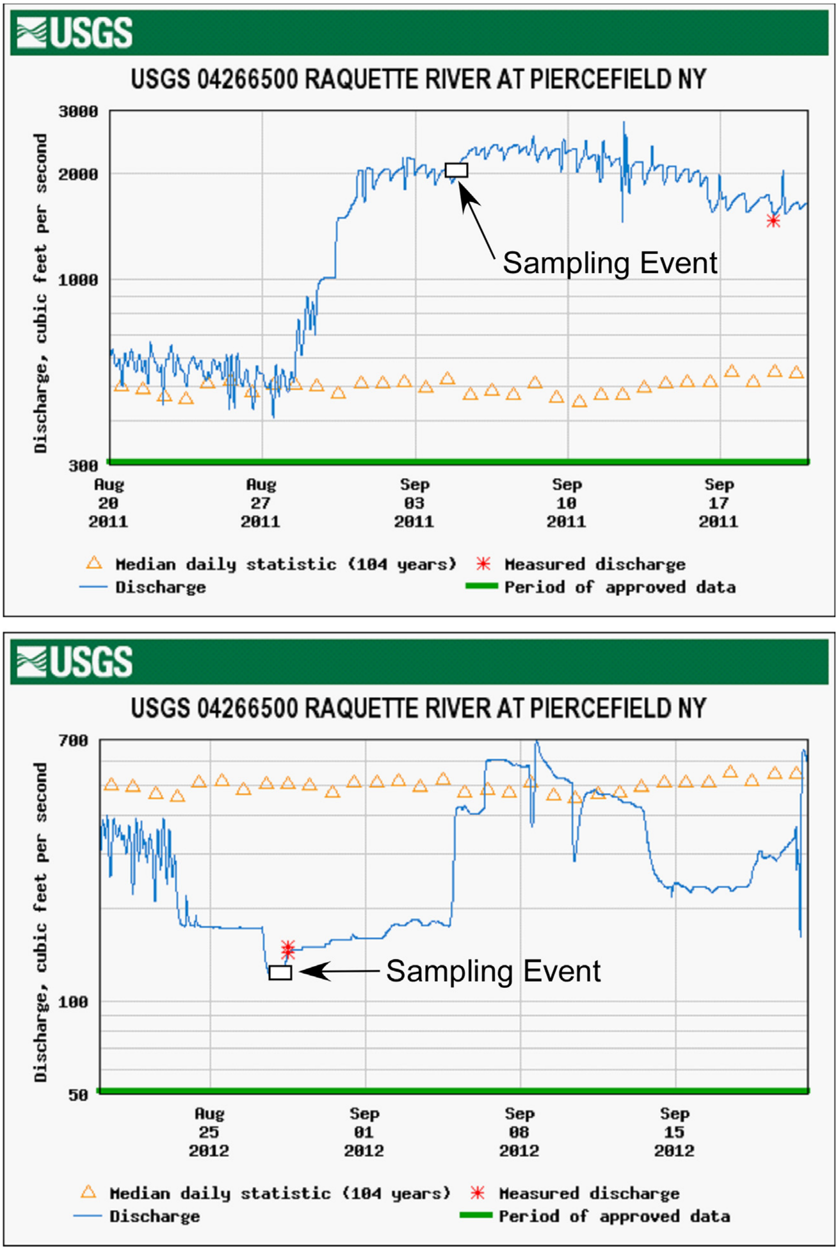

Fig. 2. Hydrographs for the USGS gauging station at Piercefield, New York for the periods August 20th to September 20th, 2011 and August 20th to September 20th, 2012.

Coast. While spared most of the devastation, according to precipitation maps of the Northeast Regional Climate Center, the Raquette River drainage basin received 2–4 in. of rain between August 27 and 29. We sampled on September 4th, 2011 (Fig. 2).

A relatively dry early spring during 2012, combined with less than average rainfall during summer months, resulted in summer drought conditions across much of the U.S. By late August in the

Adirondack Region, abnormally dry to drought conditions were recorded (www.droughtmonitor.unl.edu/) and the discharge in local rivers fell. We sampled on August 27th, 2012 after ten days or more of little to no rain in the drainage basin (Fig. 2; Supplemental Table 2).

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2.2. Sample collection

Water samples were collected on two different occasions from seventeen localities (Supplemental Table 2) along the Raquette River from Utowana Lake along the Marion River (tributary to Raquette Lake) to Massena Springs near its confluence with the St. Lawrence River. A total of 44 samples, including those used to monitor quality control, were analyzed. Sampling sites were selected for legal access (public lands) and spaced at approximately equal intervals as much as possible (Figure 1). Because much of the Raquette River is located in remote areas without road access, some sections of the river have wider sample spacing than others (e.g. Long Lake to Axton Landing). Care was taken to avoid areas with eddies, stagnant waters, anthropogenic structures (excepting dams) where possible, and where disturbance of the bottom sediments was likely.

Samples analyzed for this study were collected on two different dates, approximately one year apart, by reoccupying the same sampling sites. The sampling dates were selected to represent near peak discharge conditions (stormflow) related to precipitation that fell in the Raquette River drainage basin during Tropical Storm Irene (September 4th, 2011) and baseflow conditions associated with an extended period of drought (August 27th, 2012).

Samples were collected in pre-cleaned and metals-certified, plastic 150 mL Wheaton Clean-pak® containers which were filled directly from the river at a depth of ~5 cm. Samples were sealed and placed in a plastic cooler with ice packs. A dedicated plastic beaker was utilized to measure select physical and chemical parameters including water temperature (T_{H_2O}), specific conductivity, pH, and dissolved oxygen. The beaker was immersed in the river and successively filled and emptied three times downriver from the sampling site before measurements were taken. These parameters were measured by dedicated probes controlled by a Vernier Labpro interfaced to a TI-84 handheld calculator running EasyData® 4.0. All data, including time of sampling, was noted in a standard geological field book.

2.3. Quality assurance

Along with the samples, trip and method blanks, and duplicate water samples were collected and analyzed. All samples were run with a certified lake water standards (cations: TMDA-70, Environment Canada) and certified prepared standards for anions (Fluka). Samples for elemental analysis were shipped to ACME Analytical Laboratories in Vancouver, British Columbia and analyzed by Inductively Coupled Plasma (ICP) methodology. An aliquot of each sample was held for anionic analysis and done in house in the Analytical Chemistry Laboratory at St. Lawrence University on a Dionex ICS-2000 Reagent-Free™ Ion Chromatograph (RFIC) System. Ion chromatography (IC) has been approved for monitoring of primary and secondary anions in dilute waters since the mid-1980s per US EPA Method 300.0 (USEPA, 2007). Dionex application note 154 (AN154) describes a validated method meeting, and exceeding EPA method 300.0 for use on their RFIC system. Samples for RFIC analysis are filtered using a 0.45 μ filter and the first 300 μL of effluent discarded. Potassium hydroxide is used as an eluent and is generated electrolytical, eliminating the need to manually prepare eluents. This results in increased automation, greater ease of use of the IC system, and data reproducibility. All samples were run in accordance with AN154 along with method blanks and certified reference standards (as noted below).

A subset of the first round (stormflow) of samples was filtered (0.45 μm nylon 25 mm luer lock syringe filters, Whatman GD/XP) and analyzed with corresponding unfiltered samples to demonstrate the impact of filtration on geochemistry. Filters were used as received without cleaning. Based on three paired filtered and unfiltered samples, filtration had little effect on most elements and concentrations varied by less than 10%, similar to the variation observed in duplicate samples. However, filtration added Cu (90.5%), K (44.0%), Mn (27.6%), Rb (21.2%), and Zn (80.3%). Published studies on the possible impact of filtration on sample chemistry (Reimann et al., 1999; Rodushkin et al., 2010; Chiarenzelli et al., 2012) and the low total dissolved solids concentrations of Raquette River waters (Chiarenzelli et al., 2012; range ~10–110 mg/L), prompted us to simplify sample handling. Neither acidification nor filtration was employed in the field in an effort to minimize introduced sources of contamination. Samples were shipped via courier and acidified upon receipt, and analyzed within two weeks. The loss of metals due to delayed acidification (Benoit et al., 1997; Subramanian et al., 1978) was not investigated, but is thought to be relatively minimal.

Water analysis by ACME Analytical Laboratories (Method S0200) uses both ICP and ICP-MS (Mass Spectrometry) methodology. The Mass Spectrometers utilized include models ELAN 900, ELAN 6000, and Nexion 300. Spectro Ciros Vision and Spectro Arcos were utilized for ICP analysis. Interference, calibration, and data validation are completed using proprietary standards and software developed over decades of analysis. Detection limits are calculated based research findings, repeat analysis, the methodology employed, and the measured equipment sensitivity for each element. Elements with significant peak interference are denoted by an asterisk and no concentration is reported; however, none of the samples analyzed in this study has significant interference. ACME Laboratories is ISO 9001 certified.

Four method blanks were analyzed during this study and several elements were detected at concentrations just above detection limits in one of the four method blanks. They included Ba (0.07 ppb), Be (0.06 ppb), Ru (0.07 ppb), S (1 ppm), and Sr (0.05 ppb). Four pairs of duplicate samples were analyzed and the average relative percentage difference (RPD) for Al, Ca, and K was <1%. For Ba, Cl, Na, Nd, Rb, Si, and Sr the RPD varied between 1–5%. For Cr, Ce, La, Li, and Zn the RPD varied between 5 and 10%. Elements with higher average RPD include B (13.3%), Cu (22.2%), Fe (14.3%), Ni (14.3%), S (22.2%), Y (35.6%), and Zr (28.6%). In general, the RPD between duplicate samples of each element was inversely proportional to their overall concentration. Repeat analysis of a certified lake water standard (TMDA-70) indicated major components of the water were accurate well within 20% with one exception Si (23.3%).

Prior to ion chromatography analysis certified reference standards were run. Standards included Fluka multi-anion standard (89886-50 mL-F) for F, Cl, Br, NO_3, PO_4, SO_4, Fluka (72784-1 L-F) for CO_3, and Fluka (36427-100 ml-F) for NO_2. If the values determined for the reference standard differed from the accepted value by more than 5% for each analyte the instrument was recalibrated until this limit was achieved. The method detection limits were calculated by performing seven replicate injections of nanopure water fortified at a concentration of three to five times the estimated instrument detection limits then adjusted downwards. Duplicate samples indicate reported values for each anion had a RPD of 10% or less. None of the anions were found above detection limits in blank samples. Recovery of standards based on seven injections ranged from 95.1 (CO_3) to 106% (NO_2-N).

The data were compiled and summarized in Excel® spreadsheets. Standard statistical parameters (mean, standard deviation, relative percent difference, etc.) were determined through the use of an Excel spreadsheet and used to determine the quality and range of the data and display relevant results. Correlation coefficients (r^2) were calculated to determine the potential correlation between various analytes and other parameters and concentration trends with distance downriver.

3. Results

3.1. Physical and chemical data measured in the field

During the September 4th, 2011 Tropical Storm Irene stormflow sampling event the pH of water in the Raquette River ranged from 5.20 to 6.47, with the exception of a single sample collected at Raymondville which had a pH of 8.21 (Supplemental Table 3). Because this was clearly an outlier, the pH was measured several times for verification with the same result. The specific conductance during this sampling event ranged from 22.98 to 65.06 $\mu S\,cm^{-1}$, with the sole exception of the Raymondville sample which was anomalous at 160.44 $\mu S\,cm^{-1}$. Water temperature ranged from 21.2 to 25.1 °C; while air temperature varied from 22.1 to 28.0 °C during the sampling. Dissolved oxygen varied from 5.2 to 11.1 mg/L. The water was darkly colored, as is typical for northern Adirondack rivers enriched in tannin.

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During the August 27th, 2012 baseflow (drought) sampling event the pH ranged from 6.70 to 7.36; with the exception of 5.71 which was recorded at the most southern sampling site at the inlet to Raquette Lake (RLI – Fig. 1 and Supplemental Tables 2 and 3). Specific conductance varied from 20.67 to 83.51 $\mu S\,cm^{-1}$. Water temperature ranged from 23.0 to 25.8 °C; while air temperature varied from 21.0 to 26.4 °C during the sampling. Dissolved oxygen was not measured in the field during the second round of sampling due to a faulty probe. During this sampling event the river was unusually clear and the water samples were uncolored.

3.2. Meteorological and hydrological conditions

Precipitation data is not available for most localities in the Raquette Lake drainage basin during the time of interest; however, daily historic data for airports in Saranac Lake (~10 km northeast of the drainage basin) and Massena (Fig. 1; Supplemental Tables 5 and 6) was found on the web-site www.wunderground.com. These airport-based weather stations serve as a close approximation for the headwaters of the Raquette River (southwest of Saranac Lake) and its confluence with the St. Lawrence River (east of Massena).

The discharge measurements utilized in this study come from the USGS gauging station at Piercefield (green star on Fig. 1). Although effected by diurnal variations related to hydropower plant at Piercefield, the station is above the hydropower reservoirs and dams capable of significant water storage and alteration of flow. Thus, the gauging station at Piercefield provides a direct measurement of flow variations in the drainage basin upriver of its location.

3.2.1. Stormflow sampling

Precipitation records for May–August 2011 (Supplemental Tables 4 and 5) prior to Tropical Storm Irene indicate that Massena had 13.52 in. of rain vs. the long-term average of 13.58 in. Saranac Lake received less than average amounts of rainfall in 2011 during the same period prior to the stormflow sampling event (16.30 vs. 18.44 in.). Daily records indicate that on August 28th, 2011 Massena received 0.87 in. of rain while Saranac Lake received 2.67 in. of rain associated with Tropical Storm Irene. These values show the general increase in the effects of Hurricane Irene toward the south indicating that the headwaters of the Raquette River received the greatest rainfall associated with the event. Flooding, and associated damage, was recorded in the eastern Adirondacks especially within the Ausable River drainage basin and in the Green Mountains of Vermont. Before and after the 28th of August, relatively little rain fell in either area until the sampling date of September 4th, 2011 when 0.20 in. of rain fell in Saranac Lake and 0.49 in. fell in Massena.

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The mean daily discharge for USGS gauging station at Piercefield, New York on September 4th, 2011 was 573 cubic feet per second (cfs). This figure is based on a minimum of 104 years of record keeping. During sampling after Tropical Storm Irene (September 4th, 2011), the discharge varied from 1870 to 2050 cfs during the period of sampling (10 am–5 pm), well above the long-term average (Fig. 2). This corresponds to flow-duration percentile value of 20.26% based on over 36,000 data points of daily average discharge measurements. While well below flood stage, these values represent the near peak values in discharge (~1990 cfs) during the storm ~4× greater than discharge volumes typical for this time of year and this sampling event is taken to approximate high flow conditions.

3.2.2. Baseflow sampling

The May–August records for 2012 (Supplemental Table 5) prior to the baseflow sampling event indicate that both Massena and Saranac Lake rainfall totals were lower than average by 3.19 and 5.18 in., respectively, in agreement with the low discharge values measured in the Raquette River at Piercefield during this period. Daily records for August 2012 (Supplemental Table 4) indicate that very little rain fell in Saranac Lake or Massena from the 18th of August until the sampling date of August 27th, 2012. An exception is 0.17 in. of rain that fell on August 23rd in Massena. This lack of precipitation occurred in addition to what was a very dry spring and summer and, as noted above, the summer rainfall total was several inches below normal at both locations (Supplemental Table 5).

The mean daily discharge for USGS gauging station at Piercefield, New York on August 27th, 2011 was 568 cfs (Fig. 2). The mean discharge above is based on a minimum of 104 years of record keeping. The discharge recorded at the gauging station on August 27, 2012 ranged between 140 and 120 cfs during our sampling trip that occurred between 11 am and 6 pm on that day. Compared to a long-term discharge average (568 cfs) this represents very low flow in agreement with precipitation records summarized above and drought conditions noted that summer (Fig. 2). This corresponds to a flow-duration percentile value of 98.65% based on over 36,000 data points of daily average discharge measurements. Thus sampling on August 27th, 2012 is taken to approximate baseflow conditions within the Raquette River drainage basin.

3.3. *Stormflow and drought baseflow samples*

Of the 69 elements (Supplemental Tables 4a and 4b) routinely reported during standard ICP-MS analysis of dilute natural waters only Al, Ba, Ca, Cl, Fe, K, La, Mg, Mn, Na, Nd, Rb, Si, Sr, Y, and Zn were detected at all seventeen sampling locations during at least one of the two sampling events (Fig. 3; Table 1

; Supplemental Table 6). Some of the lower solubility trivalent cations (e.g. REE^{3+}, Al^{3+}, Fe^{3+}; Taylor and McLennan, 1985) were not detected any of the baseflow sample locations, but were detected in all of the stormflow samples. For example iron, although detected in all stormflow samples, was found above the detection limit of (10 ppb) in only twelve water samples collected during baseflow conditions. The following elements were not detected in either sampling event: Ag, Au, Bi, Cd, Ga, Ge, Hf, Hg, In, P, Pd, Pt, Re, Rh, Ru, Se, Ta, Te, Ti, and Tl (Table 1).

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In accord with USEPA Method 300.0, concentrations of NO_3, NO_2, and PO_4 are given as nitrogen in the form of nitrate, nitrogen in the form of nitrite, and phosphorous in the form of phosphate, respectively. Bromine was not found above the detection limit (6.5 μg/L) in any of the samples analyzed (Fig. 4; Supplemental Table 7). Nitrite was detected in 6 of 17 samples during the Tropical Storm Irene stormflow sampling event and ranged from 2.1 to 3.2 μg/L. Phosphate was detected in samples from all but two baseflow sampling sites but in none of the stormflow samples. Fluoride, Cl, SO_4, NO_3, and CO_3 were detected at nearly all sites during both sampling events. Average NO_3 concentrations in stormflow were ~3× times those in baseflow samples; average CO_3 concentrations were ~2× in baseflow samples compared to stormflow samples.

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The Raquette River, during both sampling events, had average specific conductance values that average about 40 $\mu S\,cm^{-1}$ indicating that the waters sampled are dilute. They also differed little in terms of their total dissolved solids content (Supplemental Table 3). The major cations were Ca, K, Na, and Si and likely reflect the weathering of both plagioclase and potassium feldspar, by far the dominant minerals in the mid to upper parts of the drainage basin (Adirondack Highlands), via hydrolysis (Chiarenzelli et al., 2012). Carbonate is by far the most abundant anion, particularly during the baseflow sampling event.

The samples collected after Tropical Storm Irene were enriched in the elements commonly found in the trivalent cation state including Al, Ce, Fe, La, Mn, Nd, and Y, compared to samples collected during baseflow conditions one year later (Fig. 3). Conversely elements that take on the divalent state including Ba, Ca, Mg, Si, Sr, and Zn had greater concentrations during the baseflow sampling event (Table 2, Fig. 3).

Several sampling locations showed anomalous water chemistry. The sample from Raquette Lake Inlet had the lowest pH value of the baseflow samples and the largest concentrations of trivalent cations. These features may be a consequence of its small, highly acidified, headwaters south of Raquette Lake and relatively short flow paths to the river. Three sample sites in the Adirondack Highlands

Table 1

Summary of ICP-MS elemental analysis of water from the Raquette River sampling sites.

Stormflow (September 4th, 2011)

Element	Ag	Al	As	Au	B	Ba	Be	Bi	Br	Ca	Cd	Ce	Cl	Co	Cr	Cs	Cu	Dy
Unit	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L
D.L.	0.05	1	0.5	0.05	5	0.05	0.05	0.05	5	0.05	0.05	0.01	1	0.02	0.5	0.01	0.1	0.01
Above DL	0	20	1	0	3	20	1	0	5	20	0	20	19	11	11	2	20	20
Mean	nd	58.55	0.50	nd	6.33	8.70	0.05	nd	8.00	4.31	nd	0.17	3.32	0.03	0.96	0.01	0.38	0.03
SD	nd	41.16		nd	1.15	1.65		nd	3.54	3.11	nd	0.20	2.50	0.01	0.84	0.00	0.08	0.03
Max.	nd	212.00	0.50	nd	7.00	13.56	0.05	nd	14.00	16.91	nd	0.90	11.00	0.06	3.40	0.01	0.50	0.15
Min.	nd	14.00	0.50	nd	5.00	5.46	0.05	nd	5.00	2.32	nd	0.02	1.00	0.02	0.60	0.01	0.30	0.01

Stormflow (September 4th, 2011)

Element	Er	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	In	K	La	Li	Lu	Mg	Mn	Mo
Unit	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
D.L.	0.01	0.01	10	0.05	0.01	0.05	0.02	0.1	0.01	0.01	0.05	0.01	0.1	0.01	0.05	0.05	0.1
Above DL	19	1	20	0	19	0	0	0	2	0	20	20	20	1	20	20	3
Mean	0.03	0.01	145.95	nd	0.04	nd	nd	nd	0.02	nd	0.32	0.14	0.45	0.01	1.01	2.38	0.20
SD	0.02		74.13	nd	0.03	nd	nd	nd	0.01	nd	0.08	0.13	0.12		1.18	1.32	0.10
Max.	0.10	0.01	261.00	nd	0.15	nd	nd	nd	0.03	nd	0.64	0.61	0.70	0.01	5.82	4.90	0.30
Min.	0.01	0.01	20.00	nd	0.01	nd	nd	nd	0.01	nd	0.24	0.04	0.20	0.01	0.46	0.59	0.10

Stormflow (September 4th, 2011)

Element	Na	Nb	Nd	Ni	P	Pb	Pd	Pr	Pt	Rb	Re	Rh	Ru	S	Sb	Sc	Se	Si
Unit	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L
D.L.	0.05	0.01	0.01	0.2	10	0.1	0.2	0.01	0.01	0.01	0.01	0.01	0.05	1	0.05	1	0.5	40
Above DL	20	1	20	2	0	4	0	20	0	20	0	0	0	12	2	10	0	20
Mean	2.82	0.01	0.16	0.25	nd	0.18	nd	0.04	nd	0.74	nd	nd	nd	1.17	0.05	1.10	nd	2088.65
SD	1.58		0.13	0.07	nd	0.15	nd	0.03	nd	0.12	nd	nd	nd	0.39	0.00	0.32	nd	457.42
Max.	7.78	0.01	0.65	0.30	nd	0.40	nd	0.17	0.00	1.05	nd	nd	nd	2.00	0.05	2.00	nd	3576.00
Min.	1.21	0.01	0.04	0.20	nd	0.10	nd	0.01	0.00	0.42	nd	nd	nd	1.00	0.05	1.00	nd	1578.00

Stormflow (September 4th, 2011)

Element	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Unit	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
D.L.	0.02	0.05	0.01	0.02	0.01	0.05	0.05	10	0.01	0.01	0.02	0.2	0.02	0.01	0.01	0.5	0.02
Above DL	16	1	20	0	2	0	1	0	0	1	5	3	2	20	19	19	20
Mean	0.04	0.09	18.47	nd	0.02	nd	0.06	nd	nd	0.01	0.03	0.27	0.05	0.23	0.03	2.57	0.04
SD	0.03		10.99	nd	0.01	nd		nd	nd		0.02	0.12	0.00	0.20	0.02	1.21	0.01
Max.	0.13	0.09	63.13	nd	0.02	nd	0.06	nd	nd	0.01	0.06	0.40	0.05	1.01	0.10	6.20	0.09
Min.	0.02	0.09	10.06	nd	0.01	nd	0.06	nd	nd	0.01	0.02	0.20	0.05	0.08	0.01	0.80	0.02

Baseflow (August 27th, 2012)

Element	Ag	Al	As	Au	B	Ba	Be	Bi	Br	Ca	Cd	Ce	Cl	Co	Cr	Cs	Cu	Dy
Unit	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	μg/L	μg/L	mg/L	μg/L	μg/L	μg/L	μg/L	μg/L
D.L.	0.05	1	0.5	0.05	5	0.05	0.05	0.05	5	0.05	0.05	0.01	1	0.02	0.5	0.01	0.1	0.01
Above DL	0	20	0	2	3	20	5	0	6	20	0	14	19	1	1	2	20	1
Mean	nd	15.65	nd	0.13	7.67	7.44	0.07	nd	6.50	4.00	nd	0.04	4.05	0.04	0.60	0.02	0.44	0.03
SD	nd	18.38	nd	0.06	2.31	1.22	0.01	nd	1.97	0.87	nd	0.08	2.27	nd	nd	0.00	0.13	
Max.	nd	90.00	nd	0.17	9.00	9.27	0.08	nd	9.00	5.61	nd	0.31	11.00	0.04	0.60	0.02	0.70	0.03
Min.	nd	2.00	nd	0.09	5.00	5.18	0.05	nd	5.00	2.24	nd	0.01	2.00	0.04	0.60	0.02	0.30	0.03

Baseflow (August 27th, 2012)

Element	Er	Eu	Fe	Ga	Gd	Ge	Hf	Hg	Ho	In	K	La	Li	Lu	Mg	Mn	Mo
Unit	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
D.L.	0.01	0.01	10	0.05	0.01	0.05	0.02	0.1	0.01	0.01	0.05	0.01	0.1	0.01	0.05	0.05	0.1
Above DL	1	0	14	0	3	0	0	0	1	0	20	16	20	0	20	20	3
Mean	0.04	nd	74.25	nd	0.03	nd	nd	nd	0.01	nd	0.45	0.03	0.41	nd	0.97	0.67	0.17
SD		nd	60.01	nd	0.03	nd	nd	nd		nd	0.05	0.05	0.14	nd	0.31	0.59	0.06
Max.	0.04	nd	251.00	nd	0.06	nd	nd	nd	0.01	nd	0.53	0.21	0.60	nd	1.73	2.84	0.20
Min.	0.04	nd	24.00	nd	0.01	nd	nd	nd	0.01	nd	0.36	0.01	0.10	nd	0.53	0.05	0.10

Table 1 (*continued*).

Baseflow (August 27th, 2012)

Element	Na	Nb	Nd	Ni	P	Pb	Pd	Pr	Pt	Rb	Re	Rh	Ru	S	Sb	Sc	Se	Si
Unit	mg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	mg/L	μg/L	μg/L	μg/L	μg/L
D.L.	0.05	0.01	0.01	0.2	10	0.1	0.2	0.01	0.01	0.01	0.01	0.01	0.05	1	0.05	1	0.5	40
Above DL	20	0	17	10	0	1	0	1	0	20	0	0	10	19	3	0	0	20
Mean	3.82	nd	0.05	0.30	nd	0.40	nd	0.05	nd	0.88	nd	nd	0.10	1.26	0.10	nd	nd	2249.38
SD	1.52	nd	0.06	0.07	nd	nd	nd	nd	nd	0.12	nd	nd	0.05	0.42	0.02	nd	nd	532.71
Max.	8.40	nd	0.28	0.40	nd	0.40	nd	0.05	nd	1.03	nd	nd	0.17	2.00	0.12	nd	nd	3610.00
Min.	2.05	nd	0.02	0.20	nd	0.40	nd	0.05	nd	0.50	nd	nd	0.05	1.00	0.09	nd	nd	1173.00

Baseflow (August 27th, 2012)

Element	Sm	Sn	Sr	Ta	Tb	Te	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn	Zr
Unit	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
D.L.	0.02	0.05	0.01	0.02	0.01	0.05	0.05	10	0.01	0.01	0.02	0.2	0.02	0.01	0.01	0.5	0.02
Above DL	1	0	20	0	0	0	1	0	1	0	0	1	0	19	1	19	4
Mean	0.04	nd	18.67	nd	nd	nd	0.05	nd	0.01	nd	nd	0.20	nd	0.07	0.04	2.31	0.03
SD		nd	4.16	nd	nd	nd		nd		nd	nd		nd	0.08		0.81	0.02
Max.	0.04	nd	28.16	nd	nd	nd	0.05	nd	0.01	nd	nd	0.20	nd	0.38	0.04	3.80	0.05
Min.	0.04	nd	11.27	nd	nd	nd	0.05	nd	0.01	nd	nd	0.20	nd	0.02	0.04	0.80	0.02

nd – not detected.

Table 2
Comparison of major cations, anions, and other parameters during stormflow and baseflow.

	Al ppb	Ba ppb	Ca ppm	Ce ppb	Fe ppb	K ppm	La ppb	Mg ppm	Mn ppb	Na ppm	Nd ppb	Rb ppb	Si ppm	Sr ppb	Y ppb	Zn ppb
Stormflow[a]																
Mean	53.89	8.25	3.52	0.15	140.55	0.30	0.12	0.72	2.42	2.75	0.15	0.72	2.05	15.85	0.21	2.52
Std. dev.	18.42	1.15	0.76	0.10	71.64	0.04	0.08	0.23	1.31	1.48	0.07	0.11	0.46	3.17	0.08	0.78
r^2	−0.22	0.22	0.70	−0.29	0.84	0.23	−0.30	0.80	0.80	−0.24	−0.23	0.05	−0.09	0.34	−0.26	−0.39
Baseflow																
Mean	16.26	7.50	4.01	0.03	50.41	0.45	0.03	0.99	0.65	3.86	0.05	0.89	2.22	18.84	0.07	2.05
Std. dev.	19.70	1.26	0.98	0.07	65.46	0.04	0.05	0.36	0.64	1.67	0.07	0.11	0.59	4.88	0.09	0.96
r^2	−0.32	0.43	0.67	−0.40	−0.10	0.04	−0.38	0.78	−0.25	−0.01	−0.35	−0.01	−0.03	0.61	−0.40	−0.54
SF/BF	3.31	1.10	0.88	4.85	2.79	0.67	4.44	0.73	3.70	0.71	3.31	0.81	0.92	0.84	3.08	1.23

	F^- mg/L	Cl^- mg/L	NO_2 mg/L	Br^- mg/L	NO_3 mg/L	SO_4 mg/L	PO_4 mg/L	CO_3 mg/L	pH	SpC μS/cm
Stormflow[a]										
Mean	0.071	3.795	0.001	0.000	0.270	2.940	0.000	4.345	5.51	29.50
Std. dev.	0.02	2.59	0.00	0.00	0.19	0.20	0.00	1.87	0.24	10.22
r^2	−0.01	−0.22	0.44		−0.36	0.06	−0.45	0.46	0.65	−0.58
Baseflow										
Mean	0.114	4.290	0.006	0.000	0.074	2.944	0.304	12.443	6.86	41.66
Std. dev.	0.07	3.50	0.02	0.00	0.06	1.06	0.41	6.99	0.36	12.26
r^2	−0.35	−0.18	0.17		0.52	−0.19	0.11	0.32	0.69	0.38
SF/BF	0.62	0.88	0.09		3.64	1.00	0.00	0.35	0.80	0.71

r^2 – correlation coefficient between distance of sampling station downriver and concentration.

[a] Calculated with outliers removed.

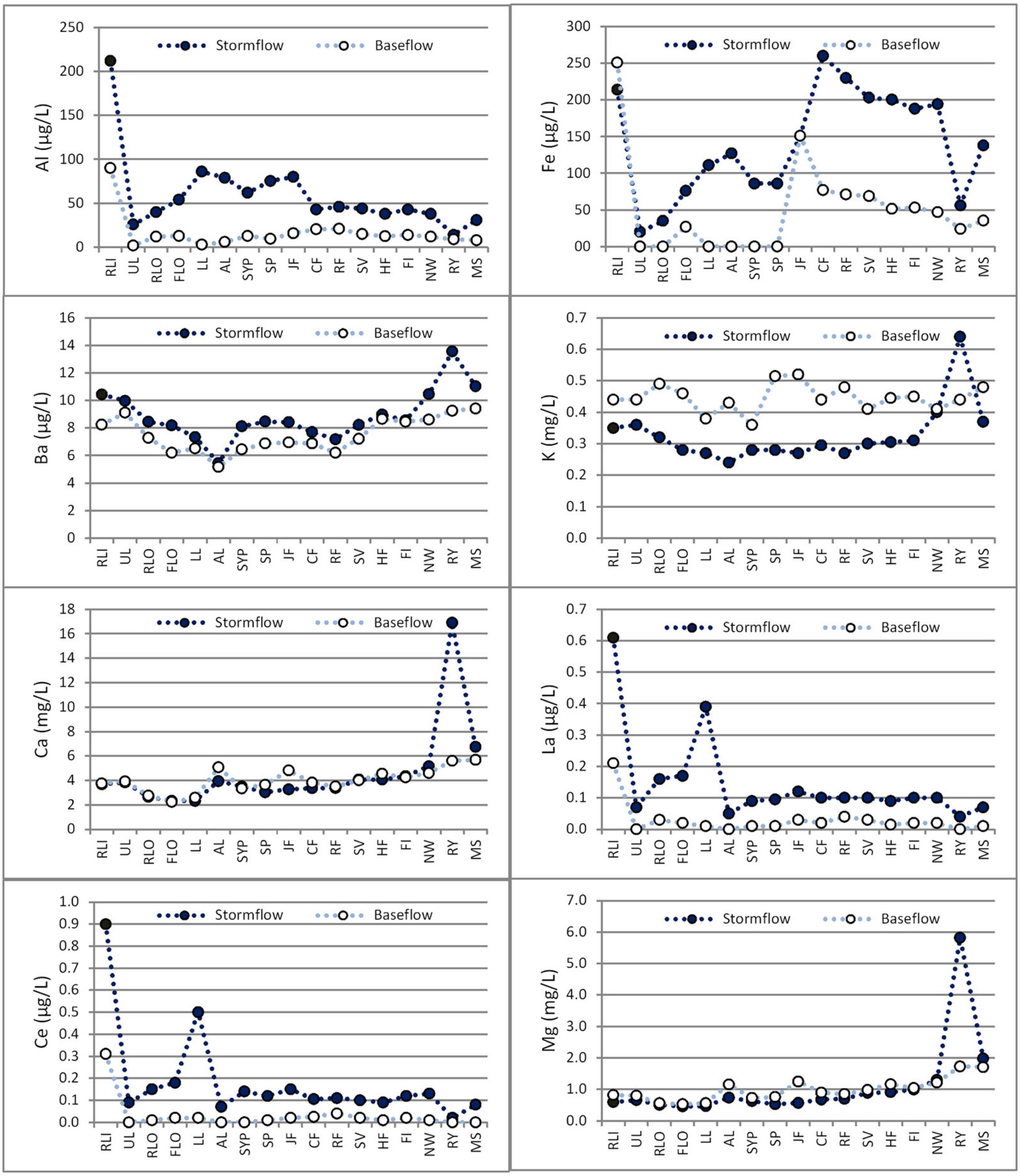

Fig. 3. Concentrations of select elements at 17 sampling sites along the Raquette River during stormflow and baseflow conditions.

(UL, LL, JF) show considerable (3–4×) enrichment in Na and Cl during baseflow over concentrations measured during storm flow (Fig. 3). Because the increase in the two elements is paired, a halite (NaCl) source is suggested. Whether this is a function of local geology or the anthropogenic use and/or storage of salt is unknown. Halite has not been reported from the Adirondack Highlands and its occurrence is restricted to drill core in the Adirondack Lowlands because of its high solubility.

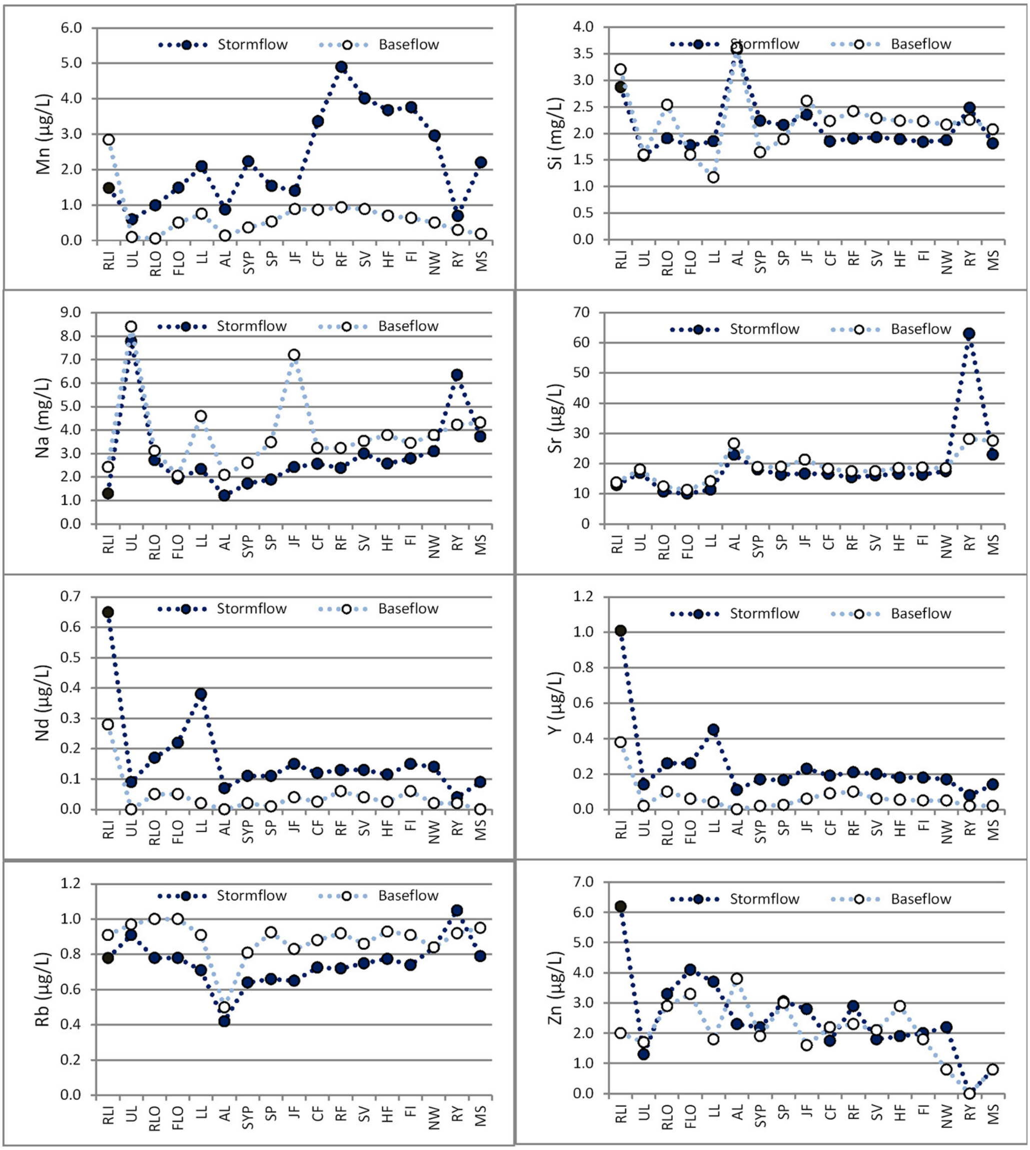

Fig. 3. (*Continued.*)

4. Discussion

While this study focusses on extreme flow conditions, previous work on north-flowing rivers in St. Lawrence County, NY has documented distinct changes in pH, buffering capacity, elemental concentrations and ratios, and total dissolved solids along their length during long-term average summer discharge volumes (Chiarenzelli et al., 2012). Water from each of the four major rivers (from west to east – Oswegatchie, Grasse, Raquette, and St. Regis) was sampled at points within the three geologic terranes (from south to north – Adirondack Highlands, Adirondack Lowlands, and St. Lawrence River Valley) during typical (non-event) summer flow conditions. During these sampling events distinct

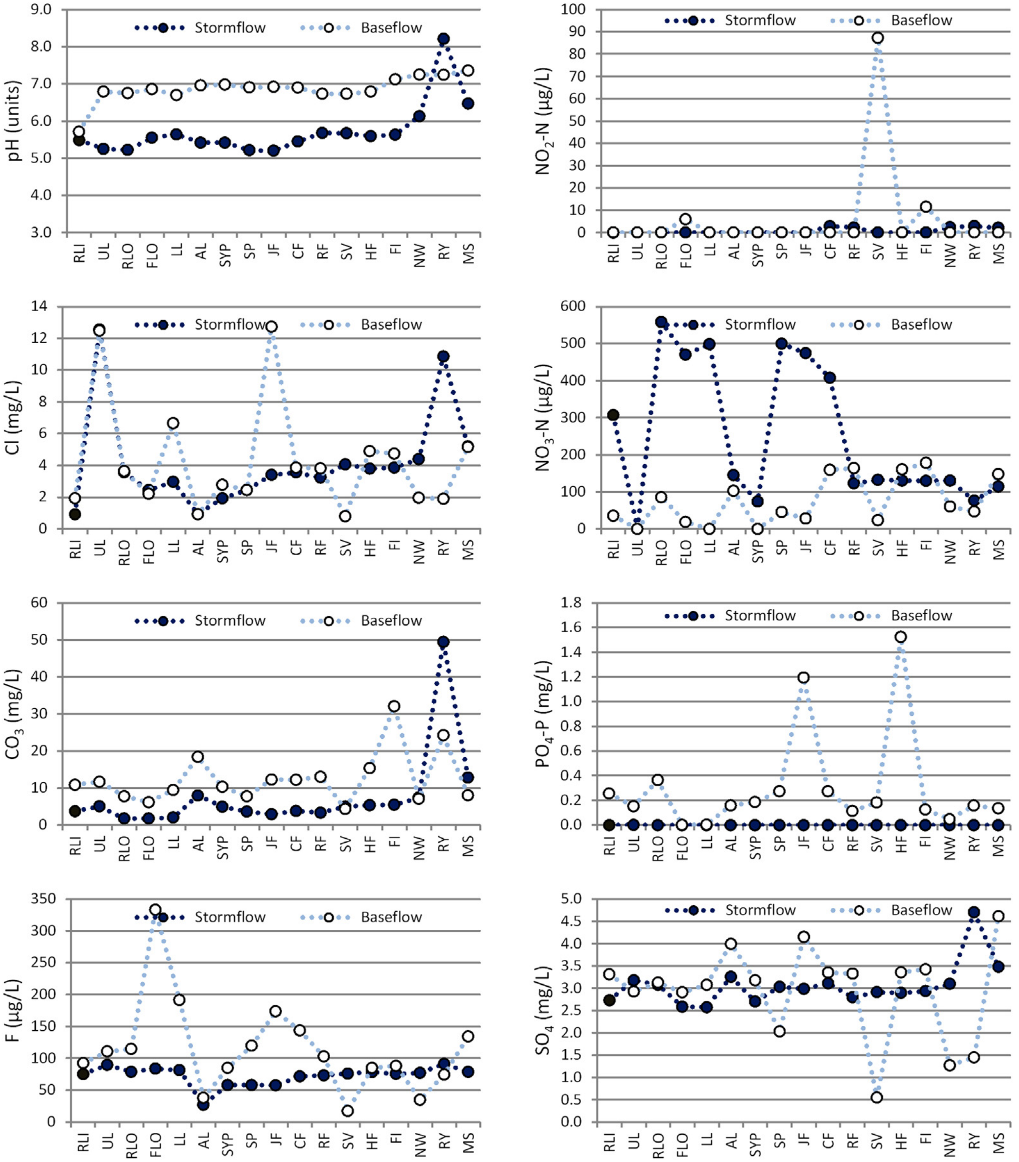

Fig. 4. Variation in pH and specific conductance, and the concentrations of select anions at 17 sampling sites along the Raquette River during stormflow and baseflow conditions.

changes in water chemistry were noted from south to north (i.e. downriver) including an increase in pH (e.g. from 4.67 to 7.49 in the Oswegatchie River watershed), decrease in Al (e.g. 373–25 ppb in the Raquette River watershed), and increase in Ca (e.g. from 4.6 to 47.6 ppm in the Grasse River watershed).

The study concluded that the downriver variation in water chemistry was related to acidification of the headwaters of these rivers, which are underlain by crystalline rocks with limited buffering capacity (Colquhoun et al., 1981), and subsequent buffering by carbonate lithologies downriver in the Adirondack Lowlands (marble and calc-silicate gneisses) and St. Lawrence River Valley (limestone and dolostone). In this follow up study, the control(s) on water chemistry along the length of the Raquette River was investigated during high and low flow events.

4.1. Downriver chemical trends: comparing stormflow and baseflow

Compared to previous work, downriver chemical changes were muted during both stormflow and baseflow conditions (Fig. 5); however, these differences provide additional insight into controls on the hydrogeochemistry of the Raquette River drainage basin. The average specific conductance (Table 2; Fig. 4) was greater during baseflow (41.66 $\mu S\,cm^{-1}$) than stormflow (29.50). Several elements, on the average, are more concentrated in Raquette River water during stormflow conditions (Table 2; Fig. 3) including Al (3.31x), Ce (4.85x), Fe (2.79x), La (4.44x), Mn (3.70), Nd (3.31x), and Y (3.08). In contrast Ca, K, Mg, Na, Rb, and Sr were slightly more enriched (1.14-1.50x) during baseflow conditions.

The downriver concentration trends of elements and anions can be visually estimated from Figs. 3 and 4, and were quantitatively evaluated by determining the correlation coefficients (r^2) between water concentration and the distance of sampling sites downriver (Table 2). During stormflow Ba (0.22), Ca (0.70), Fe (0.84), K (0.23), Mg (0.80), Mn (0.80), Rb (0.05), and Sr (0.34) have positive r^2 values indicating a general, but variable, trends of increasing concentrations downriver. In contrast Al, Ce, La, Na, Nd, Y, and Zn have negative correlation coefficients ranging between −0.22 to −0.39, indicating a slight decrease in concentration downriver. Similar trends are shown during baseflow with the exception that Fe (−0.10) and Mn (−0.25) show slight decreases in concentration downriver rather than steep increases.

In general, these data indicate that the divalent cations (Ba, Ca, Mg, Sr) increase downriver, while trivalent cations (Al, Ce, La, Nd, Y) decrease downriver during both stormflow and baseflow conditions. The behavior of Fe and Mn is more complicated in that they increase significantly in river water downriver during storm flow, but not during baseflow conditions. While the reason for this is unclear, they may be preferential leached from soil profile during precipitation events due to interaction with lower pH waters. Zinc decreases in concentration in river water downriver during both stormflow and baseflow events suggesting the production of zinc hydroxide as the pH rises slightly downstream (Table 2, Figs. 3 and 4).

All anions are found at greater concentrations in baseflow than stormflow river waters, except for nitrate. During storm flow positive correlation coefficients were found for NO_2 (0.44) and CO_3 (0.46) indicating downriver increases in concentration, while NO_3 (−0.36) and PO_4 (−0.45) decrease downriver (Table 2, Fig. 4). During baseflow negative correlation coefficients were found for F (−0.35), Cl (−0.18), and SO_4 (−0.19), indicating a decrease in concentration downriver while the other anions increase, although much variability is seen between sampling sites. The concentration of virtually all anions, except nitrate, and specific conductance were enriched during base flow conditions compared to stormflow (Table 2, Fig. 4). Nitrate was 3.64x more concentrated in river water during stormflow; compatible with an origin from precipitation. In contrast, mean sulfate concentrations in river water were the same during stormflow and baseflow. Taken together with the element data presented above this data suggests the greater rock/water interaction during baseflow conditions enhances bedrock derived anion concentrations and the concentrations of divalent cations in Raquette River waters.

4.2. Comparison of river chemistry during different discharge volumes

Fig. 5 compares the concentration of select elements for three sampling events of varying discharge, including samples taken during low (143 cfs) and high (1990 cfs) flow conditions for this study. The intervening value of 1190 cfs, represents a flow duration percentile of 41.3% ("normal" flow) and was collected on June 5th, 2008. The normal flow samples compared in Fig. 5 were collected at the same sites as the stormflow and baseflow samples representing the Adirondack Highlands (JF), Adirondack Lowlands (FI), and St. Lawrence River Valley (SL) along the Raquette River.

Fig. 5 shows the relatively insoluble trivalent (Al, Ce, Fe) elements generally have the least variation in concentration during periods of "normal" or near average flow (i.e. pinch inwards at 1190 cfs). In contrast, the more soluble divalent and monovalent (Ca, Mg, K, and Na) elements generally show the greatest variation in concentration during "normal" flow conditions (bulge outwards at 1190 cfs).

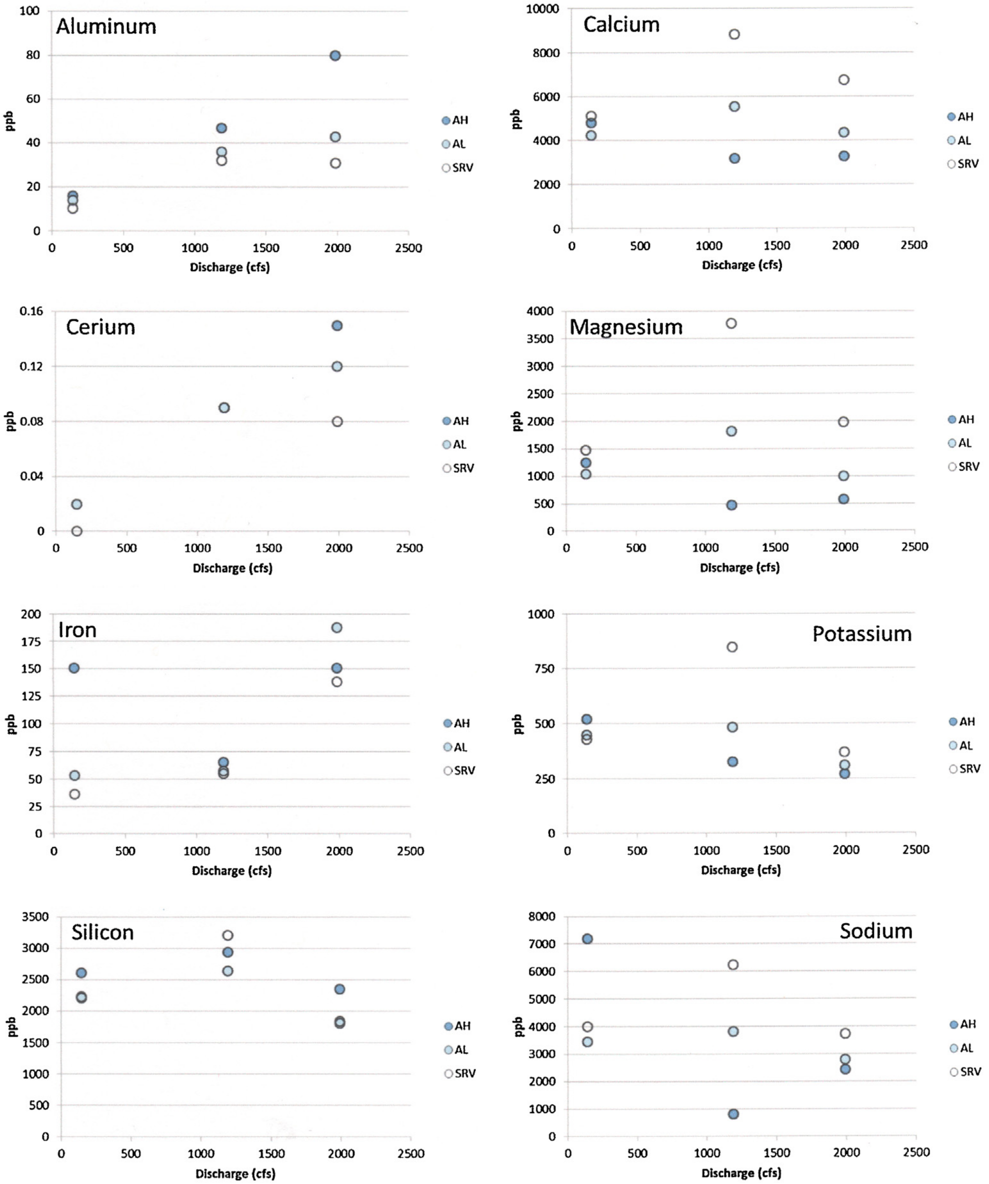

Fig. 5. Concentrations of select elements showing the variation in concentration during periods of low (143 cfs – this study), average (1190 cfs – Chiarenzelli et al., 2012), and high (1990 cfs – this study) discharge. The data comes from sites JF, FI, and MS shown on Fig. 1. AH – Adirondack Highlands, AL – Adirondack Lowlands, SRV – St. Lawrence River Valley.

Silicon, shown for comparative purposes, shows relatively little variation in concentration with discharge values (Table 2, Fig. 5). These data suggest that the chemistry of each of the flow regimes is controlled by different factors and/or combinations of factors.

One plausible explanation for the differences in stormflow and baseflow water chemistry is the chemical variation imparted by differences in river water pH between the two events. The samples collected along the length of the river after Tropical Storm Irene had a mean pH value (5.54 ± 0.32), within analytical error of natural rainfall. Those collected during baseflow conditions are near neutral (6.86 ± 0.33). Both sampling events show relatively little chemical variation along the length of the river (Figs. 3 and 4), however, the slightly enhanced concentration of the relative insoluble elements, like Al, Fe, and the REEs during the stormflow sampling is attributed to this difference in pH. During both sampling events (stormflow $r^2 = 0.65$; baseflow $r^2 = 0.70$) pH increased slightly downriver (Table 2 and Fig. 3) while specific conductance fell during stormflow ($r^2 = -0.58$) but rose during baseflow (0.38).

Another factor which could drive the chemical differences between the two sampling events is the proportion of river water derived by overland versus groundwater flow. The water entering the river via runoff and overland flow after a heavy rainfall would follow shallow flow paths, have relatively little time for buffering and interaction with geologic materials, while discharge volumes would be many times those occurring during baseflow, (∼14× in this comparison). In addition, in the Adirondack region, particularly the western portions, decades of acidic precipitation have leached the soil and sediment of soluble elements. Thus geological materials encountered by runoff and along shallow flow paths, have lost of much of their calcium, magnesium, and capacity to buffer acidity (Jenkins et al., 2007; Lawrence, 2002; Lawrence et al., 2004, 2007, 2008).

During baseflow conditions water in a river system generally has longer and deeper flow paths, and more time to interact with geologic materials; some of which may be much less weathered than those at, or near, the surface. Baseflow should be better buffered and contain more of the elements with enhanced solubility at near neutral pH values, and approximate the composition of groundwater (Soulsby et al., 2003). The higher pH would also serve to limit the concentrations of most metals which have greater solubility in more acidic waters. Greater concentrations of anions (e.g. OH, CO_3, and SO_4) and higher pH would cause precipitation of insoluble phases containing metals such as Al, Fe, and the REEs.

Carbonate dominates the anion population in both sampling events; however, the average concentrations during baseflow are almost twice those of stormflow conditions (12.35 vs. 6.99 mg/L), indicating more extensive interaction with carbonate-bearing geologic materials (Fig. 4). The more extensive interaction of the groundwater with bedrock contributing to baseflow may explain the homogeneity of water chemistry along the length of the Raquette River and the buffered nature of the water along the length of the river, even within the chronically acidified headwaters of the Raquette River drainage basin.

In contrast to baseflow conditions, stormflow waters reflect the acidic nature of precipitation in the region, including NO_3 concentrations derived largely from sources outside the watershed (Fig. 4) and the slightly enhanced solubility of trivalent metals such as Al and the REEs. The concentration of SO_4 is less variable between events and likely controlled by the oxidation of common sulfide-rich minerals such as pyrite.

4.3. *Anomalous water chemistry at the Raymondville sampling site*

As noted above, the Raymondville sampling site (RY on Fig. 1) is intriguing because of its anomalous geochemistry compared with other sampling sites during storm flow (Figs. 3 and 4). This was particularly evident during the stormflow after Tropical Storm Irene, but not apparent during the baseflow sampling event. In particular, the Raymondville sampling site stands out during the stormflow sampling as the only site to have an alkaline pH (8.21), the largest concentrations of the anions CO_3 and SO_4, and the largest concentrations of Ba, Ca, Cl, K, Mg, Na, Rb, Si, and Sr (∼3 times baseflow concentrations; Figs. 3 and 4). Slight decreases in the trivalent cations were also found in the Raymondville stormflow sample when compared to samples collected up- and downriver. These chemical trends have been duplicated in another study which sampled Raquette River waters at Raymondville weekly for an entire year (Laboso et al., 2014), indicating control by a continuing, but sporadic, process.

Review of land use south of the Raymondville sampling site on the Raquette River indicates that a large quarry (∼1.3 km × 0.4 km) exists 6 km upriver at Norfolk (Fig. 6). The quarry is located on east bank of the Raquette River and produces a variety of crushed stone products for construction and other purposes. The rock quarried here is the Ordovician Ogdensburg Dolostone. Previous studies have indicated that evaporitic horizons exist in the dolostone and samples from water wells in nearby

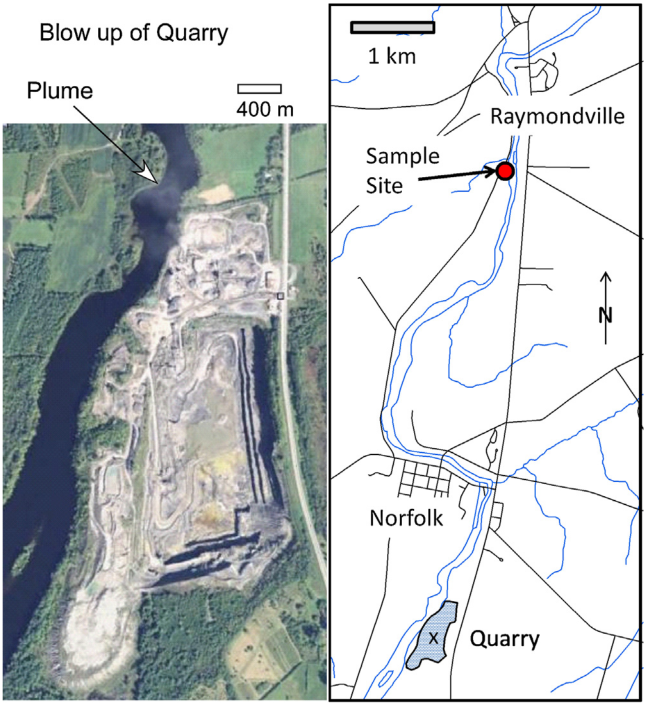

Fig. 6. Google Earth image (May 26, 2011) and sketch map of Raquette River six kilometers south (upriver) of the Raymondville sampling site near Norfolk, New York.

Louisville and on the Akwesasne Mohawk Nation east of Massena which penetrate it, have an enrichment in soluble elements such as B, Ca, Br, K, Li, Rb, and, particularly, Sr (Chiarenzelli et al., 2007; O'Connor et al., 2010). A view of the quarry from Google Earth on May 26, 2011 (Fig. 6) indicates that it has standing water in low areas and stockpiles of a variety of crushed stone products. In addition, a plume of material, presumably fine rock powder, can be seen entering the river there and is carried downstream. On that day at the Massena airport 0.23 in. of rain fell. The monthly total at that point was 3.96 in. compared to a long-term average of 2.56 in., indicating wetter than normal conditions, and likely greater runoff, in the time leading up to the satellite image.

In addition to fine particles, a considerable volume of water with dissolved components is likely discharged to the river during precipitation events via runoff and dewatering operations. The fractured dolostone bedrock here also likely allows considerable seepage into the river along short flow pathways (i.e. fractures) from the quarry into the Raquette River. These waters would be highly alkaline and contain the soluble elements and anions derived from the dolostone noted above. In particular, the abundance of Sr, a trace metal, is intriguing because highly elevated Sr groundwater concentrations was previously attributed to horizons in the Ogdensburg Dolostone containing celestine (Sr-sulfate) or strontianite (Sr-carbonate), both relatively rare minerals by Chiarenzelli et al. (2007) and O'Connor et al. (2010).

During baseflow conditions, runoff from the quarry and dewatering operations would likely cease or be minimized. Input to the river from the quarry would be negligible and little impact would be measured. These conditions existed when the baseflow sampling event was carried out. During baseflow sampling the pH and specific conductance were significantly reduced compared to the stormflow sampling event and the soluble element concentration of river water was also less. For these reasons, it appears that the quarry at Norfolk exerts a strong influence on the water chemistry of the Raquette

River at Raymondville during times when significant amounts of runoff, water from processing or dewatering, and/or groundwater enters the river from the site.

5. Conclusions

1. Water derived from runoff associated with Tropical Storm Irene was sampled (9/4/2011) at seventeen locations along the length of the Raquette River and geochemically characterized. Nearly one year later (8/27/2012) the same stations were resampled during an extended drought. The two sampling events allow comparison of stormflow and baseflow water chemistry approximating end member compositions throughout the Raquette River drainage basin, an undeveloped and forested area impacted by acidic precipitation.
2. Raquette River waters are dilute Ca-CO_3 waters and, for the most part, show relatively little anthropogenic effect aside from those derived by acidification, in concert with the limited ability of the crystalline bedrock in the headwaters of the Raquette River drainage basin to buffer acidity.
3. Previous studies have shown that during average discharge conditions pH, total dissolved solids, and the concentration of soluble elements increase and trivalent cations decrease, downriver in response to the progressive buffering capacity of the bedrock rock terranes (Adirondacks Highlands < Adirondack Lowlands < St. Lawrence River Valley). These trends were unexpectedly muted in samples associated with both stormflow and baseflow events.
4. The most notable difference between stormflow and baseflow conditions in the Raquette River is the variation in pH; samples taken during the drought had pH values near neutral and on the average 1.2 units above those taken during stormflow conditions associated with Tropical Storm Irene. These geochemical differences are attributed to the longer flow pathways associated with baseflow conditions and interaction with deeper, less weathered materials over longer time intervals.
5. During average flow conditions the Raquette River shows progressive downriver changes related to the interaction of its waters with geologic terranes of distinct chemical composition with increasing capacity to buffer acidity. During stormflow these changes are muted and less apparent because of the minimal buffering due to the high volume and rapid flow-through of water directly derived from precipitation in the system. Conversely, during baseflow conditions deeper flow paths and extended interaction times allow for greater buffering and homogenization of pH values and leaching of soluble elements derived from less weathered materials.
6. Anomalously geochemical characteristics measured at the Raymondville sampling site suggest an impact from a dolostone quarry six kilometers upstream. This impact was observed only during the stormflow when sediment charged waters from the site runoff into the river as documented by satellite images.
7. This study documents an example of event river chemistry responding less to extremes of flow or variation in underlying geology than anticipated. Based on this work, the main controls on river water chemistry in the Raquette River drainage basin during high and low flow regimes is the pH of river water, which itself it controlled by the proportions of over-land flow to groundwater. The longer flow paths of groundwater buffer river waters in the Adirondack Highlands during periods of baseflow despite decades of acidification.

Conflict of interest

We wish to confirm that there are no known conflicts of interest associated with this publication.

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References

Benoit, G., Hunter, K.S., Rozan, T.F., 1997. Sources of trace metal contamination artifacts during collection, handling, and analysis of freshwaters. Anal. Chem. 69, 1006–1011.

Chiarenzelli, J., Lock, R., Cady, C., Bregani, A., Whitney, B., 2012. Variation in river multi-element chemistry related to bedrock buffering: an example from the Adirondack region of northern New York, USA. Environ. Earth Sci. 67, 189–204, http://dx.doi.org/10.1007/s12665-011-1492-z.

Chiarenzelli, J., Hudson, M., Dahl, P., deLorraine, W.D., 2011. Constraints on deposition in the Trans-Adirondack Basin, Northern New York: composition and origin of the Popple Hill Gneiss. Precambrian Res. 214–215, 154–171, http://dx.doi.org/10.1016/j.precamres.2011.10.024.

Chiarenzelli, J., Shrady, C., Cady, C., General, K., Snyder, J., Benedict-Debo, A., David, T., 2007. Multi-element analyses of private wells on the St. Regis Mohawk Nation (Akwesasne). Northeast. Geol. Environ. Sci. 29, 167–175.

Colquhoun, J.R., Symula, J., Pfeiffer, M.H., Feurer, J., 1981. Preliminary Report of Stream Sampling for Acidification Studies, Technical Report 81-2. New York State Department of Environmental Conservation, Albany, USA.

Drever, J.I., 1997. The Geochemistry of Natural Waters, 3rd ed. Prentice Hall, Englewood Cliffs, NJ, pp. 437.

Inamdar, S., Dhillon, G., Singh, S., Duttam, S., Levia, D., Scott, D., Mitchell, M., Van Stan, J., McHale, P., 2013. Temporal variation in end-member chemistry and its influence on runoff mixing patterns in a forested, Piedmont catchment. Water Resour. Res. 49, 1828–1844, http://dx.doi.org/10.1002/wrcr.20158.

Jenkins, J., Keal, A., 2004. The Adirondack Atlas: A Geographic Portrait of the Adirondack Park, 1st ed. Syracuse University Press, Syracuse, USA, pp. 296.

Jenkins, J., Driscoll, C., Roy, K., Buerkett, C., 2007. Acid Rain in the Adirondacks: An Environmental History, 1st ed. Cornell University Press, Ithaca, USA, pp. 256.

Laboso, R., Walsh, E., Lock, R., Skeels, M., Chiarenzelli, J., 2014. Weekly monitoring of river chemistry in St. Lawrence County, vol. 46(2). Northeast Geological Society of America Abstracts with Programs (Abstract), New York, pp. 101.

Lawrence, G.B., 2002. Persistent episodic acidification of streams linked to acid rain effects on soil. Atmos. Environ. 36, 1589–1598.

Lawrence, G.B., Baldigo, B.P., Roy, K.M., Simonin, H.A., Bode, R.W., 2008. Results from the 2003–2005 Western Adirondack Stream Survey. New York State Energy Research and Development Authority, Albany, USA, 141 p.

Lawrence, G.B., Sutherland, J.W., Boylen, C.W., Nierzwicki-Bauer, S.A., Momen, B., Baldigo, B.P., Simonin, H.A., 2007. Acid rain effects on aluminum mobilization clarified by the inclusion of strong organic acids. Environ. Sci. Technol. 43, 93–98.

Lawrence, G.B., Momen, B., Roy, K.M., 2004. Use of stream chemistry for monitoring acidic deposition effects in the Adirondack Region of New York. J. Environ. Qual. 33, 1002–1009.

O'Connor, M., Zabik, M., Cady, C., Cousens, B., Chiarenzelli, J., 2010. Multi-element analysis and geochemical spatial trends of groundwater in rural northern New York. Water 2, 217–238, http://dx.doi.org/10.3390/w2020217.

Regan, S.P., Chiarenzelli, J.R., McLelland, J.M., Cousens, B.L., 2011. Evidence for an enriched asthenospheric source for coronitic metagabbros in the Adirondack Highlands. Geosphere 7, 694–709, http://dx.doi.org/10.1130/GES00629.1.

Reimann, C., Siewers, U., Skarphagen, H., Banks, D., 1999. Influence of filtration on concentrations of 62 elements analyzed on crystalline bedrock groundwater samples by ICP-MS. Sci. Total Environ. 234, 155–173.

Roden-Tice, M.K., Tice, S.J., 2005. Regional scale mid-Jurassic to Late Cretaceous unroofing from the Adirondack Mountains through central New England based on apatite fission-track and (U–Th)/He thermochronology. J. Geol. 113, 535–552.

Rodushkin, I., Engström, E., Baxter, D., 2010. Sources of contamination and remedial strategies in the multi-element trace analysis laboratory. Anal. Bioanal. Chem. 396, 365–377, http://dx.doi.org/10.1007/s00216-009-3087-z.

Rothwell, J.J., Evans, M.G., Daniels, S.M., Allott, T.E.H., 2007. Baseflow and stormflow metal concentrations in streams draining contaminated peat moorlands in the Peak District National Park (UK). J. Hydrol. 341, 90–104, http://dx.doi.org/10.1016/j.jhydrol.2007.05.004.

Sanchez Espana, J., Lopez Pamo, E., Santofomia, E., Aduvire, O., Reyes, J., Barettino, D., 2005. Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): geochemistry, mineralogy and environmental implications. Appl. Geochem. 20, 1320–1356, http://dx.doi.org/10.1016/j.apgeochem.2005.01.011.

Soulsby, C., Petry, J., Brewer, M.J., Dunn, S.M., Ott, B., Malcom, I.A., 2003. Identifying and assessing uncertainty in hydrological pathways: a novel approach to end member mixing in a Scottish agricultural catchment. J. Hydrol. 274, 109–128, http://dx.doi.org/10.1016/S0022-1694(02)00398-0.

Subramanian, K.S., Chakrabarti, C.L., Sueiras, J.E., Maines, I.S., 1978. Preservation of some trace-metals in samples of natural-waters. Anal. Chem. 50, 444–448.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford, pp. 312 pp.

USEPA, 2007. http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_300_0.pdf