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Multi-Element Analysis and Geochemical Spatial Trends of Groundwater in Rural Northern New York

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Abstract: Samples from private wells (n = 169) throughout St. Lawrence County, NY were analyzed by ICP-MS multi-element techniques. St. Lawrence County spans three diverse bedrock terranes including Precambrian crystalline rocks of the Adirondack Lowlands (mostly paragneisses) and Highlands (mostly orthogneisses), as well as Paleozoic sedimentary rocks of the St. Lawrence Valley. An ArcGIS database was constructed and used to generate contour plots for elements across the county. Strontium isotopes and unique geochemical signatures were used to distinguish water from various geologic units. The results were consistent with a large (7,309 km^2), sparsely populated (~110,000), rural region with diverse bedrock and glacial cover.

1. Introduction

Purpose of the Study—St. Lawrence County is a large (7,306 km^2) and sparsely populated, rural, heavily forested county in northern New York (Figure 1a). The southeast half of the county lies within the Adirondack Blue line (Adirondack Park boundary) and is sparsely populated (Figure 1b). Due to its large area and rural nature, much of the region's population utilizes private groundwater wells for potable water. Encompassing two major physiographic provinces (Adirondack Mountains and St. Lawrence Valley), the bedrock geology of St. Lawrence County varies significantly from north to south (Figure 1c). Additionally, the county spans the Carthage-Colton Mylonite Zone (CCMZ) which subdivides the Adirondacks into the Highlands and Lowlands [1]. While the Adirondack Highlands are underlain by large areas of metamorphosed, acidic, igneous crystalline bedrock (orthogneisses), in the Lowlands metasedimentary rocks (paragneisses), including a large proportion of marble and calc-silicate gneisses, predominate [2]. Interacting with these diverse bedrock units, groundwater geochemistry is variable and influenced by rock-water interactions and dissolution from these various lithologies, as well as widespread glacial deposits.

St. Lawrence County has a long and diverse mining history (Figure 1c) and is known widely for world-class mineralization and unique mineral deposits. To determine the geochemical characteristics of private wells in St. Lawrence County, 92 water samples were collected and analyzed for 72 inorganic elements by inductively coupled plasma—mass spectrometry (ICP-MS) in 2008. Additional samples and analyses were supplied by M. Zabik [3] and J. Chiarenzelli who conducted a pilot study during 2007. In total, 169 well water, and additional associated quality control, samples were collected and analyzed.

The purpose of this study was to document the influence of bedrock lithology on groundwater geochemistry and determine if geospatial analysis tools could be employed to estimate spatial trends in groundwater chemistry in St. Lawrence County. The effects of diverse geology and mining history of the county are of special interest. This data set can be used to establish baseline concentrations, identify areas of potential concern, and for future planning in St. Lawrence County including the protection and/or development of water resources and provides a model for similar studies in other areas.

Our approach was to employ multi-element ICP-MS analyses to determine elemental concentrations in groundwater. This approach has been widely used in regional and national surveys and as an exploration technique, and reported in the peer-reviewed literature [4-6]. In addition, a pilot study of Sr isotopic compositions was carried out to determine its utility in distinguishing bedrock signatures in common aquifer types.

Geological Setting—St. Lawrence County includes three general areas with distinct bedrock lithologies (Figure 1d). The northern region of St. Lawrence County is part of the St. Lawrence Lowlands, characterized by flat-lying sequences of sedimentary rocks formed during the Cambrian through the Lower Ordovician Periods [2,7]. Formations include the Potsdam Sandstone (quartz arenite), Theresa Formation (interlayered sandstones and carbonates), and the Ogdensburg Dolostone.

Figure 1. GIS maps of St. Lawrence County, New York including: (a) major highways and populated areas; (b) population density and groundwater sampling locations; (c) geology and mine locations; and (d) samples collected for Sr isotopic analysis.
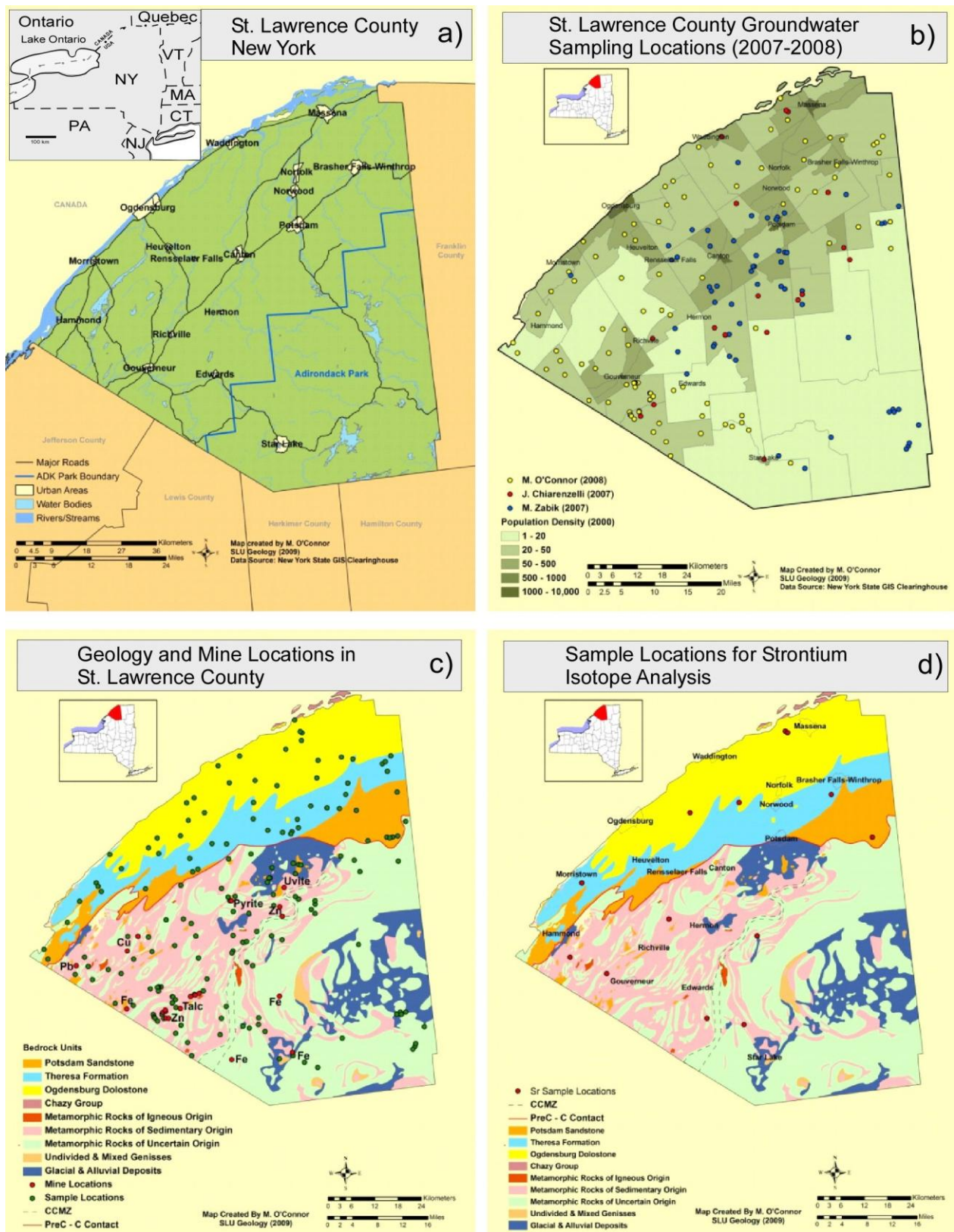
The rest of the county encompasses the Adirondack Mountains Physiographic Province which is subdivided into the Adirondack Highlands and Adirondack Lowlands. Both sub-provinces are composed of Grenville-age crystalline rocks but differ in the proportion of various lithologies. The Adirondack Highlands in the southeast are characterized by Precambrian crystalline granulite facies orthogneisses that range in age from ~1.0–1.35 billion years old [7,8]. In contrast, the Adirondack Lowlands located in the western and southwestern portions of the county are predominantly highly deformed mid to upper amphibolite facies metasedimentary rocks, intruded by meta-igneous plutonic rocks ranging in age from 1.15–1.20 billion years old [2,8]. The boundary between the two regions is a northeast-trending zone of brittle and ductile deformation known as the Carthage Colton Mylonite Zone [1,7,9].

Largely the product of the Wisconsinan glaciation during the Pleistocene Epoch, surficial deposits distributed intermittently throughout the county include till, moraines, eskers, outwash, deltas, and lacustrine deposits. Furthermore, clay-rich marine sediments deposited by the Champlain Sea, after glacial retreat approximately 14 thousand years ago, are located in topographically low-lying areas of the St. Lawrence Lowlands [2]. These deposits form a thin to thick (up to 100 m or more in deep paleovalleys) veneer of heterogeneous and unconsolidated surficial sediment where bedrock is not exposed at or near the surface.

St. Lawrence County also possesses a rich mining history and a variety of resources were recovered in the past. In the western part of the county talc has been mined since the 1860s at Balmat and Talcville in narrow belts of Proterozoic schist [2,7]. Metal resources are also present in St. Lawrence County and most of New York's metal mining has occurred in the Adirondack region [2]. Metal resources included the mining of Fe in the Adirondack Highlands, such as Benson Mines (magnetite and martite) in Star Lake, and small hematite deposits from many localities in St. Lawrence and adjacent Jefferson counties. Abundant Zn, Pb, and minor amounts of Ag, associated with sphalerite and galena mineralization have been mined extensively in St. Lawrence County [2,10,11]. In the late 1800s and early 1900s pyrite was mined for sulfur in several locations in the Adirondack Lowlands [12]. Aside from the extraction of dolomitic marble, dolostone, and sandstone from quarries, and numerous sand and gravel pits, there are currently no hard rock mining operations in St. Lawrence County. Nonetheless, the mining history further illustrates the diverse range of lithologies that occur throughout the region that may influence groundwater chemistry in St. Lawrence County. Additionally, many of the mines are associated with large piles of tailings left over from mining operations which may further influence groundwater chemistry.

St. Lawrence County also possesses some extraordinary mineral deposits. Among them, tourmaline is found throughout Precambrian rocks in the region as an accessory mineral in granitic rocks and also is widely associated with metasedimentary units [10]. Among the most notable are black uvite tourmaline vein deposits at Power's Farm in Pierrepont. Other important widespread minerals found in St. Lawrence County include tremolite, diopside, and a wide variety of amphiboles of unusual composition, and rarer minerals, including the lavender Mn-tremolite, known as hexagonite.

Literature Review—Several studies on multi-element analysis of private wells near and in the St. Lawrence County region have been conducted recently. Chiarenzelli *et al.* [13] analyzed the inorganic geochemistry of 154 well water samples from private wells on the St. Regis Mohawk Nation (Akwesasne) located to the northeast in Franklin County, adjacent to St. Lawrence County. Part of the

St. Lawrence Lowlands Physiographic Province, the Ogdensburg dolostone is the prominent aquifer in the region [13-16]. In the study elevated concentrations of As, Fe, Hg, and Pb were noted at one site while Al, Mn, and TDS were found at elevated concentrations at 3, 19, and 24 sampling locations respectively and were determined to be primarily associated with shallower wells [11].

Chiarenzelli *et al.* [13] also reported on groundwater with a distinct geochemical composition in Louisville, located in the northeast region of St. Lawrence County just southwest of Massena. Four samples within a 1 mile radius, collected from wells drawing water from the Ogdensburg dolostone, revealed elevated levels of soluble elements including enhanced concentrations of Sr and Li. They hypothesized that the high Sr and Li concentrations could be attributed to an interval or stratigraphic horizon within sections of the Ogdensburg dolostone enriched in soluble evaporite minerals, such as strontianite ($SrCO_3$) and celestite ($SrSO_4$). Groundwater of nearly identical composition was found 15 kilometers to the northeast in private wells on Cornwall Island [13].

Nystrom [16] reported on the quality of groundwater and surface water for the St. Lawrence River Basin, which includes St. Lawrence County. Water samples from 14 domestic and 11 production wells were collected and analyzed for 229 constituents. Similarly to Chiarenzelli *et al.* [11], elevated concentrations of Al, Fe, and Mn were noted by Nystrom.

Zabik [3] conducted the initial pilot study on the quality and geochemistry of groundwater in St. Lawrence County. Sixty samples from private wells were collected in the county, predominantly in the greater Canton area. Although analysis for concentrations of inorganic elements from these samples provide preliminary data for the county and possible areas of concern, groundwater quality and geochemistry trends for several large sections of St. Lawrence County were not analyzed, and the current study was carried out and combined with these data to fill in these spatial gaps.

Hydrogeology—Relatively little information on the hydrogeology of St. Lawrence County or adjacent areas exists in the literature [14-16]. Aside from overlying glacial deposits, the bedrock consists of rocks of Precambrian to Ordovician age which, in general, lack significant primary porosity and permeability. This is particularly true for crystalline rocks of the Adirondack Highlands and Lowlands in which porosity and permeability is entirely secondary and related to fractures. Even the Potsdam sandstone is thoroughly indurated with optically continuous quartz overgrowths that seal off all pore space. Carbonate rocks including Precambrian marbles and Phanerozoic limestones and dolostones have significant amounts of dissolution porosity and tend to be the most prolific bedrock aquifers in the region [14]. Based significant local relief, complex folding and faulting, and the large amount of surface water (streams, rivers, lakes, bogs, swamps, marshes, *etc.*) in the region, groundwater paths in shallow bedrock aquifers are likely to be fairly localized in areas underlain by Precambrian rock. Flat-lying Paleozoic rocks, located in a band along the St. Lawrence River, however, may have longer flow paths with groundwater flow along bedding parallel fractures, unconformity surfaces, and within limited pore space. Many of the lithologies in the county are not particularly soluble and contain waters with low TDS concentrations. Conversely, carbonate lithologies, evaporitic rocks, and various ores may be highly susceptible to dissolution and weathering and can locally, and regionally in some instances, exert a strong influence on groundwater composition.

2. Experimental Section

A sampling protocol based on those established by the USEPA [17] was utilized in this study to ensure accuracy, reproducibility, and quality control. Well water samples were collected from taps preceding water filtration and/or treatment systems. This was crucial for the study to provide an accurate representation of the natural inorganic geochemistry and water quality influenced by bedrock interaction but lessens the relevance for health related studies.

Water was purged for at least 2 minutes to ensure that residual water within the plumbing system was not being sampled. Water samples were collected directly into pre-cleaned 125 mL Wheaton Cleanpak® sample containers. A supplementary sample was collected at 13 sample locations in 500 mL Wheaton Cleanpak® sample containers for Sr isotope analysis. Several duplicate samples and 2 method blanks were also analyzed during the study. Method blanks were transported in the field and filled with deionized water from the St. Lawrence University Geology Department and treated as the other samples. Duplicate samples and blanks were included to ensure the accuracy of the analytical methods employed during the collection process. Additionally, ACME Analytical Laboratories analyzed wastewater standards and replicate analysis for each sample batch to determine the accuracy and precision of ICP-MS analyses (Table 1).

Duplicate and replicate samples possessed correlation coefficient (R^2) values greater than .999. Copper (0.8 and 2.5 ppb) and Cl (1 and 2 ppm) were detected in both sample blanks analyzed while small concentrations of Cr (3.6 ppb), Mn (0.15 ppb), Na (62 ppb), Pb (0.2 ppb), Si (96 ppb), and Zn (1.9 ppb) were also detected in one of the sample blanks. For most groundwater samples, the concentrations of these elements are well in excess (>10–100x) of blank values. Duplicate, replicate, and blank samples illustrate that the concentrations reported for the vast majority of elements accurately represent the water from each well.

pH was measured in the field for each water sample immediately upon collection using a pH meter when available (n = 64). pH values ranged from 6.37 to 9.09 with a mean value of 7.46. After collection samples were sealed, labeled, and stored in a cooler to avoid contamination. Global Positioning System (GPS) coordinates were recorded at each sample location. To avoid contamination, samples were personally transported from the storage cooler to a refrigerator in a locked room in the St. Lawrence University Geology Department until they were shipped for analysis. Samples were shipped directly to ACME Analytical Laboratories in Vancouver, British Columbia, Canada in batches of 20 or more to be analyzed for 72 inorganic elements by inductively coupled plasma—mass spectrometry (ICP-MS).

Thirteen additional samples were analyzed for Sr isotope data using a ThermoFinnigan Triton thermal ionization mass spectrometer (TIMS) at Carleton University in Ottawa, Ontario, Canada. One gram of water from each sample was dried down at 125 ℃ in an ultraclean fume hood. Dried samples were redissolved using 2 mL of 2.5N HCL. Samples were then transferred using a pipette into a 14 mL Bio-Rad borosilicate glass chromatography column containing 3.0 mL of Dowex AG50-X8 cation resin. Strontium was eluted using 2.5N HCl. Strontium eluted from each sample was loaded onto a Ta filament with H_3PO_4. Filaments were then loaded onto a magazine and placed in a ThermoFinnigan TIMS running at filament temperatures of 1,480–1,520 ℃ for Sr isotope analysis. Isotope ratios were normalized to $^{86}Sr/^{88}Sr = 0.11940$ to correct for fractionation. A standard (NBS987) was analyzed with

the samples to ensure accuracy of the analysis. The $^{87}Sr/^{86}Sr$ ratio for the NBS987 standard was 0.710218 +/− 0.000012 and falls within the range of the average value for the NBS987 standard reported over a six month period (0.710230 +/− 0.000017).

Table 1. Table listing the elements reported, the detection limit, statistical, and quality assurance parameters for the groundwater analyzed during this study.

	Detection Limit	% Detected	High Value	Low Value	Mean Value	Std. Dev. ±2σ	Duplicate RPD (n = 10)	Standard RPD (n = 5)	Method Blank Avg.
	ppb								
Ag	0.05	1.3	0.1	0.07	0.1	0.0	ND	6.5	ND
Al	1	23.1	205	2	22.3	39.3	3.4	9.4	ND
As	0.5	53.8	10.2	0.6	2.3	2.2	2.9	6.4	ND
Au	0.05	5.0	0.58	0.06	0.1	0.2	ND	ND	ND
B	5	84.4	2,053	6	97.1	234.4	5.3	5.3	ND
Ba	0.05	99.4	704.65	0.1	87.1	97.8	5.6	3.0	ND
Be	0.05	7.5	0.37	0.06	0.1	0.1	ND	8.1	ND
Bi	0.05	0.0	0	0	ND	ND	0.0	ND	ND
Br	5	90.6	3,432	6	79.2	313.8	4.3	ND	ND
Ca	50	98.1	265,656	191	59,111	42,930	1.9	16.2	ND
Cd	0.05	7.5	3.36	0.06	0.6	1.0	0.0	4.6	ND
Ce	0.01	13.8	7.93	0.02	0.6	1.7	7.7	ND	ND
Cl (Cl⁻)	1,000	98.8	231,700	1,000	63,601	203,781	25.4	ND	1500
Co	0.02	57.5	1.23	0.03	0.1	0.2	17.4	5.0	ND
Cr	0.5	93.1	18.6	0.7	8.9	3.9	6.3	6.4	1.8
Cs	0.01	63.1	0.48	0.02	0.1	0.1	19.7	ND	ND
Cu	0.1	94.4	1,435.1	0.2	29.1	148.0	35.7	2.9	1.65
Dy	0.01	18.8	1.94	0.02	0.2	0.4	6.5	ND	ND
Er	0.01	18.8	1.05	0.02	0.1	0.2	11.4	ND	ND
Eu	0.01	5.6	0.29	0.02	0.1	0.1	0.0	ND	ND
Fe	10	36.3	463	11	41.4	65.7	35.4	3.1	ND
Ga	0.05	0.6	0.2	0.2	0.2	ND	ND	ND	ND
Gd	0.01	18.8	2.49	0.02	0.2	0.5	23.0	ND	ND
Ge	0.05	18.1	0.78	0.06	0.2	0.2	ND	ND	ND
Hf	0.02	0.0	0	0	ND	ND	ND	ND	ND
Hg	0.1	3.1	0.3	0.2	0.2	0.1	0.0	ND	ND
Ho	0.01	9.4	0.37	0.02	0.1	0.1	3.4	ND	ND
In	0.01	0.0	0	0	ND	ND	ND	ND	ND
Ir	0.05	23.8	0.69	0.06	0.2	0.2	24.4	ND	ND
K	50	100.0	20,136	67	3,110	3,095	4.7	ND	ND
La	0.01	18.1	9.53	0.02	0.7	1.8	2.7	ND	ND
Li	0.1	94.4	189.3	0.3	9.2	20.3	4.2	ND	ND
Lu	0.01	7.5	0.14	0.02	0.0	0.0	40.0	ND	ND
Mg	50	98.8	106,111	52	23,790	17,259	2.9	ND	ND
Mn	0.05	83.8	11,884	0.06	106.9	1,026	33.2	5.8	0.075
Mo	0.1	88.1	25.1	0.2	2.4	3.3	ND	4.4	ND
Na	50	100.0	1,246,937	777	40,617	113,288	1.7	ND	31

Table 1. *Cont.*

Nb	0.01	37.5	0.11	0.02	0.0	0.0	27.5	ND	ND
Nd	0.01	21.9	14.51	0.02	1.0	2.6	4.2	ND	ND
Ni	0.2	28.1	14.3	0.3	1.4	2.2	0.0	4.7	ND
Os	0.05	0.0	0	0	ND	ND	ND	ND	ND
P	20	7.5	438	24	104.0	122.0	ND	ND	ND
Pb	0.1	16.9	6.3	0.2	1.0	1.4	40.0	4.1	0.1
Pd	0.2	0.0	0	0	ND	ND	ND	11.8	ND
Pr	0.01	12.5	3.41	0.02	0.4	0.8	5.0	ND	ND
Pt	0.01	0.0	0	0	ND	ND	ND	ND	ND
Rb	0.01	100.0	12.37	0.04	2.7	2.6	4.3	ND	ND
Re	0.01	5.6	0.08	0.02	0.0	0.0	0.0	ND	ND
Rh	0.01	2.5	0.49	0.02	0.2	0.2	ND	ND	ND
Ru	0.05	0.6	0.06	0.06	0.1	ND	ND	ND	ND
S (SO_4^{2-})	1,000	100.0	198,000	1,000	18,050	30,282	6.3	ND	ND
Sb	0.05	22.5	4.02	0.06	0.4	0.8	6.6	3.9	ND
Sc	1	82.5	7	2	3.2	1.3	12.0	ND	ND
Se	0.5	14.4	16.7	0.6	2.0	3.4	5.9	3.2	ND
Si	1	100.0	14,243	2,630	7,061	2,387	3.6	7.8	48
Sm	0.02	11.3	2.79	0.03	0.4	0.7	21.7	ND	ND
Sn	0.05	10.6	17.73	0.06	1.3	4.3	18.2	ND	ND
Sr	0.01	100.0	18,566	0.09	781.4	1,928	3.1	4.1	ND
Ta	0.02	5.6	0.08	0.03	0.0	0.0	0.0	ND	ND
Tb	0.01	6.3	0.33	0.02	0.1	0.1	4.0	ND	ND
Te	0.05	4.4	0.2	0.06	0.1	0.1	ND	ND	ND
Th	0.05	3.1	0.1	0.06	0.1	0.0	0.0	ND	ND
Ti	10	0.0	0	0	ND	ND	ND	ND	ND
Tl	0.01	12.5	0.19	0.02	0.0	0.0	0.0	4.2	ND
Tm	0.01	5.0	0.15	0.02	0.1	0.0	0.0	ND	ND
U	0.02	94.4	30.63	0.03	1.9	4.4	9.2	ND	ND
V	0.2	43.1	11.2	0.3	1.0	1.6	10.6	2.2	ND
W	0.02	60.6	5.38	0.03	0.2	0.6	20.3	9.6	ND
Y	0.01	48.8	11.29	0.02	0.6	1.6	0.3	ND	ND
Yb	0.01	20.6	0.99	0.02	0.1	0.2	25.8	ND	ND
Zn	0.5	71.3	1,810	0.6	77.3	258.6	14.1	5.4	0.95
Zr	0.02	14.4	0.6	0.03	0.1	0.1	2.2	9.5	ND

Sample results from ICP-MS analyses were incorporated into a preexisting geodatabase produced by Zabik [3] in ESRI ArcGIS 9.2. Spatial interpolation techniques using ArcGIS were conducted to estimate inorganic metal and trace element concentration trends throughout St. Lawrence County. Spatial interpolation is a method that predicts values at unsampled areas by comparing actual measured values that are in close proximity to one another [18]. The spatial interpolation method utilized in this study was kriging interpolation. Kriging is a method grounded in theoretical principals that compares data located in close proximity to a reference point being examined, determines general properties on the surface from these measured values, and then extrapolates values for unsampled areas based on

those properties [18]. Due to the variable geologic nature and sample distribution in the study area, the number of reference points evaluated during kriging of each sample location was set at five.

Kriging was determined to be the best method for interpolation because it is a statistically-based estimation of spatial patterns. Predictions are based on a regionalized variable theory based on direction, distance from other sample points, and random, stochastic variation [19]. Inverse distance weighting (IDW) interpolation was investigated for use in this study; however, IDW applies an arbitrary and more imprecise weighting scheme and therefore was considered ineffective when trying to estimate spatial trends for the influence of highly variable bedrock lithologies on groundwater geochemistry.

The variability of bedrock units across the county makes it difficult to recognize a deterministic trend; therefore, ordinary kriging was utilized as this method is based on such a scenario [19]. The semivariogram chosen for the study was the spherical model. The spherical model shows a progressive decrease of spatial autocorrelation and an equivalently increase in semivariance until some distance, beyond which autocorrelation is zero [19]. Since sample location distances were not taken at regular intervals, choosing a distance for autocorrelation was not ideal. For this reason, a set number of reference sample points were chosen for spatial interpolation. Several scenarios were tested including using three, five, seven, and ten reference points. Five reference points was determined to produce the best trend maps given the distance between sample points and variable geological units. Although less reference points would theoretically be ideal for determining spatial trends in an area of highly variable geological units, lack of sample points in less populated areas would result in heavy weighting of a single sample point, which would result in erroneously high concentrations.

Kriging interpolation in this study is not meant to be an absolute prediction method that is why sample points on the GIS maps are color coded to give actual concentration values for the inorganic elements evaluated in this study. Kriging analysis is meant only to be used as an estimation tool to get a better understanding of what patterns might be expected based on the sample data over broad regions. Having a greater sample density and a more balanced spatial cover of the county would provide the best data for kriging to be most effective, but it proved useful for this study for identification of some basic concentration trends and shows a strong correspondence to known variations in geology.

From a practical standpoint, geological relationships, complex hydrologic flow, and variability of well depth place strong limitations on the interpretation of the GIS concentration plots on the local level. In addition, the relatively sparse sampling density (one sample per 46 km^2) and lack of wells in the southern and southeastern part of the county place additional limitations. For example, the lack of wells within the Adirondack Blue line (Figures 1 and 3) limit usefulness of the contour plots in the southeastern region of the County. Nonetheless, the influence of bedrock chemistry on groundwater on both the regional and local scale is clear and we were able to correlate known geologic lithology with groundwater chemistry and general trends as determined by kriging.

3. Results and Discussion

3.1. Limitations of the Study

This study has several limitations. Unfortunately due to the age of many of the wells, transfer of property over time, and lack of record keeping, the depth and well construction details of most of the wells are unknown. Visual inspection and consultation with local well drillers indicates that most wells were drilled and cased, although a small number of shallow dug wells and springs were also sampled. Where bedrock is not exposed at or near the surface, shallow aquifers composed of glacial materials are locally important, but tend to yield water of inferior aesthetic properties [13,16] and thus most private wells penetrate glacial cover and are drilled and cased into bedrock. Exceptions include thick sand and gravel aquifers with high transmissivity and hydraulic conductivity that follow large rivers and buried glacial channels. For purposes of our study we assumed that: (1) the vast majority of wells draw from bedrock; (2) bedrock maps of the area provide an excellent guide to the two-dimensional distribution of these units; (3) because of local relief, the complex structure of bedrock, and abundant discharge points (streams, lakes, swamps) most flow pathways in Precambrian basement rocks are relatively short; and (4) given the low water usage of individual private wells, the capture zones of most wells are also limited. Even if these assumptions are largely valid, the possibility exists that the chemistry of many of the groundwater samples reflects a mixture of several sources and is influenced primarily by the most soluble unit in which it comes in contact with.

In addition, this study represents a snap shot in time. The elemental compositions of natural waters are known to vary significantly with time and seasonal variation. Repeat analysis on a seasonal and annual basis of some of the samples in this study indicates that unlike surface water, which shows rapid and drastic changes in composition, the effect on groundwater is less pronounced. In general, except where influenced by anthropogenic activities, seasonal changes in groundwater composition in this area vary primarily in the amount of dissolved solids while their proportions remain fairly constant throughout the year. In addition, deeper wells tend to show the least amount of temporal variation.

3.2. Multi-Element ICP-MS Analysis

Samples were analyzed for 72 inorganic elements by ICP-MS at ACME Analytical Laboratories in Vancouver, British Columbia, Canada. Sixty-six elements were detected in the 169 water samples analyzed (Table 1). Bismuth, In, Os, Pd, Pt, and Ti were not detected in any of the samples. Silver, Au, Ga, Hf, Ru, Te, and Th were detected in less than 10 samples. There is a large range in TDS (13–1,259 ppm). Major elements (>10,000 ppb) making up the vast majority of the dissolved components are Ca, Cl, Mg, Na, and S. Minor elements (100–10,000 ppb) include K, Si, and Sr. Trace elements (10–100 ppb) include B, Ba, Br, Cu, Fe, Mn, and Zn. A summary of the results and detection limits are given in Table 1, complete results in Table 1R of the data repository.

3.3. TIMS Analysis of Strontium Isotopes

Thirteen samples also underwent strontium isotope analysis by thermal ionization mass spectrometry (TIMS) at Carleton University in Ottawa, Ontario, Canada. Strontium isotope analysis

was utilized to determine the extent of interaction between various lithologies and groundwater in St. Lawrence County. $^{87}Sr/^{86}Sr$ ratios ranged from 0.709000 +/− 0.000003 to 0.715468 +/− 0.000007 (Table 2).

Table 2. Isotopic ratios, concentrations (Rb and Sr), and rock unit represented for each groundwater sample analyzed for strontium isotopes.

Samples	Bedrock Unit	Symbol	$^{87}Sr/^{86}Sr$	SD*	Rb (ppm)	Sr (ppm)	Rb/Sr
MEO-131	Beekmantown Group	Obk	0.70900	0.00003	1.72	586	0.0029
MEO-138	Beekmantown Group	Obk	0.70923	0.00005	2.32	642	0.0036
MEO-201	Beekmantown Group	Obk	0.70961	0.00008	12.05	18,566	0.0006
MEO-202	Beekmantown Group	Obk	0.70937	0.00006	1.36	2,530	0.0005
MEO-147	Theresa Formation	OCth	0.71137	0.00008	6.34	870	0.0073
MEO-156	Theresa Formation	OCth	0.71000	0.00005	1.1	676	0.0016
MEO-162	Potsdam Sandstone	Cp	0.71286	0.00005	2.91	17	0.1712
MEO-170	Lower Marble	cs	0.70998	0.00010	9.92	4,662	0.0021
MEO-167	Lower Marble	mb	0.71215	0.00010	0.86	975	0.0009
MEO-150	Migmatite	mu	0.71088	0.00005	7.18	151	0.0475
MEO-165	Migmatite	mu	0.71079	0.00006	3.14	118	0.0266
MEO-154	Popple Hill Gneiss	garb	0.71424	0.00007	7.39	241	0.0307
MEO-163	Popple Hill Gneiss	garb	0.71547	0.00007	0.81	59	0.0137
NBS987	Standard		0.71022	0.000012	NA	NA	NA
NBS987	Standard		0.71023	0.000017	NA	NA	NA

NA: not analyzed; * Standard deviation ±2σ

Strontium isotope data in the study area correlates with values from Paleozoic and Precambrian lithologies [20,21]. This indicates that the dominant influence on groundwater composition is interaction with, and dissolution of, underlying lithologic units. Because of the relatively impermeable nature of many of the units, particularly Precambrian units, interactions that occur in bedrock fractures likely predominate.

*3.4. Spatial Analysis: Investigating County-Wide Groundwater Geochemical Trends*

Due to the large size and rural nature of St. Lawrence County, sampling of every well in the county was implausible; therefore, in an effort to develop individual element concentration trend maps for the entire county, including areas between sampling sites, Geographic Information Systems (GIS) software was utilized in this study. Specifically, kriging interpolation in ESRI 9.2 ArcGIS® was utilized to develop regional geochemical trend maps. The geospatial trends for select elements are discussed in this section. Each trend map has color coded symbols (circles) so comparisons between absolute values obtained by analysis of well water and calculated trends can be made at a glance.

3.4.1. Arsenic and Lead

Arsenic has been found associated with moderately calcareous and calc-silicate rocks, desorption from iron oxide minerals, and from the oxidation of sulfide minerals such as pyrite, chalcopyrite,

arsenopyrite, and arsenical pyrite [22-24]. The greatest groundwater As concentrations are primarily located in the St. Lawrence Lowlands, with areas of relatively elevated concentrations located in the Adirondack Lowlands (Figure 2a). Specifically, the highest estimated As concentrations occur in close proximity to the Precambrian-Paleozoic contact. The dominant rock units associated with elevated As concentrations include the Theresa Formation, Ogdensburg dolostone, calcitic and dolomitic marble, and some granitic rock units.

Figure 2. The concentration of groundwater constituents estimated from groundwater samples collected in St. Lawrence County, New York including (a) arsenic; (b) lead; (c) copper; and (d) zinc.
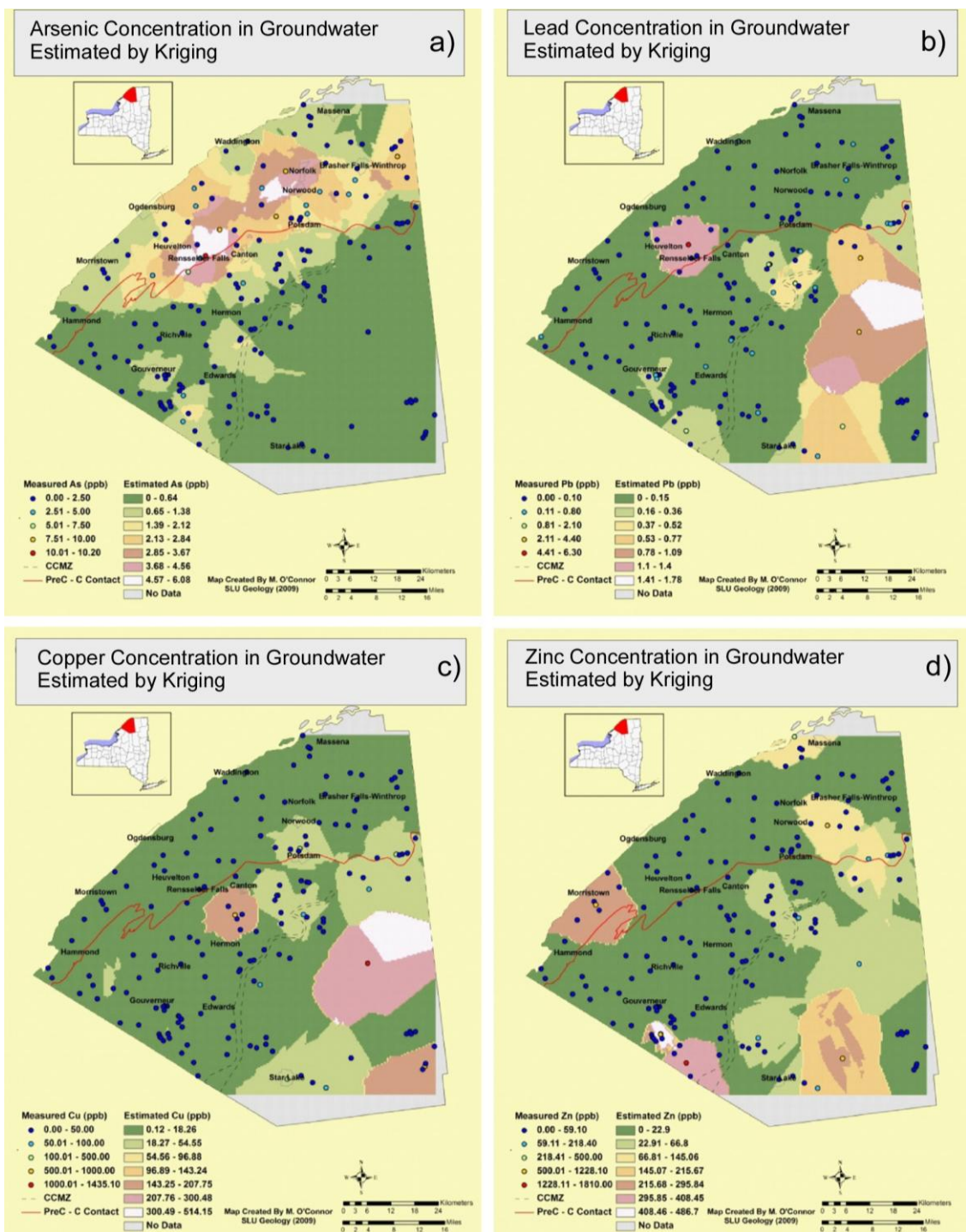
Pyrite is particularly abundant in bedrock units such as the sulfide-rich ore deposits associated with the Balmat zinc mine and in widespread pyritic gneisses [11,12]. Zabik [3] noted that elevated As concentrations should be expected around the villages of Pyrites and Hermon located south of Canton due to the proximity of old pyrite mines and abundant tailings [12]; however, only a minor enrichment of As in groundwater in these areas was measured despite elevated levels of As in the pyrite ore and surface water draining from the tailings [25].

In summary, slightly elevated As concentration trends are notable in the northern portion of the county from Rensselaer Falls northeast to Norfolk in close proximity to the Precambrian-Paleozoic contact. Pyrite and hematite are the most probable sources of As in these regions.

Lead comes from a variety of natural and anthropogenic sources. Mining of Pb occurred from veins of galena hosted in marble at Rossie and galena associated with sphalerite and pyrite in the Balmat-Edwards zinc belt in St. Lawrence County. Somewhat surprisingly, Pb values are minor at all locations sampled. Review of Pb on the groundwater contour diagram (Figure 2b) reveals that the majority of samples contained less than 0.1 ppb. Only near Heuvelton did measured concentrations exceed a few ppb. This data suggests that native Pb mineralization is localized and appears not to have a widespread impact on groundwater chemistry.

3.4.2. Copper and Zinc

Although Cu was found in measurable concentrations in more than 90% of the samples analyzed, the concentrations of most samples were below 10 ppb (Figure 2c). A similar situation was found for Zn; however, Zn concentrations were found to be elevated (>200 ppb) near Morristown and Balmat (Figure 2d). The Balmat area is well known for sphalerite mining and the occurrence of Zn in this area is not surprising. However, the reason for elevated Zn concentrations in Morristown in the St. Lawrence Lowlands is unknown. The anomaly in this area is based on data from a single well. For this reason, and because the sample contains a relatively high concentration of Cu (25.7 ppb), it is thought likely an artifact of antiquated plumbing. A similar source may explain elevated concentrations of Cu (1,435 ppb), Pb (4.4 ppb), and Zn (146.2 ppb) in a well approximately 15 km from the eastern boundary of the county in the Adirondack Highlands.

3.4.3. Iron and Manganese

Iron concentrations in groundwater throughout the region are variable and many wells have non-detectable levels (Figure 3a). The solubility of Fe is highly dependent on its valence state with ferric iron nearly insoluble at near neutral pH values in oxygenated waters. Deeper waters, isolated from the atmosphere, generally contain ferrous iron, which is considerably more soluble. Thus the map pattern shown in Figure 3a is likely strongly influenced by the amount of dissolved oxygen available in the various aquifers (dissolved oxygen was not measured in this study).

Some Mn concentration trends are notable in St. Lawrence County (Figure 3b). A majority of elevated Mn Concentrations (>50 ppb) are located within the Paleozoic units of the St. Lawrence Lowlands. Additionally, elevated Mn concentrations occur in dolomitic or calcitic marble, glacial/alluvial deposits, and within close proximity to abandoned mines in the Adirondack Mountains Physiographic Province.

Figure 3. The concentration of groundwater constituents estimated from groundwater samples collected in St. Lawrence County, New York including (a) iron; (b) manganese; (c) hardness; and (d) total dissolved solids (TDS).
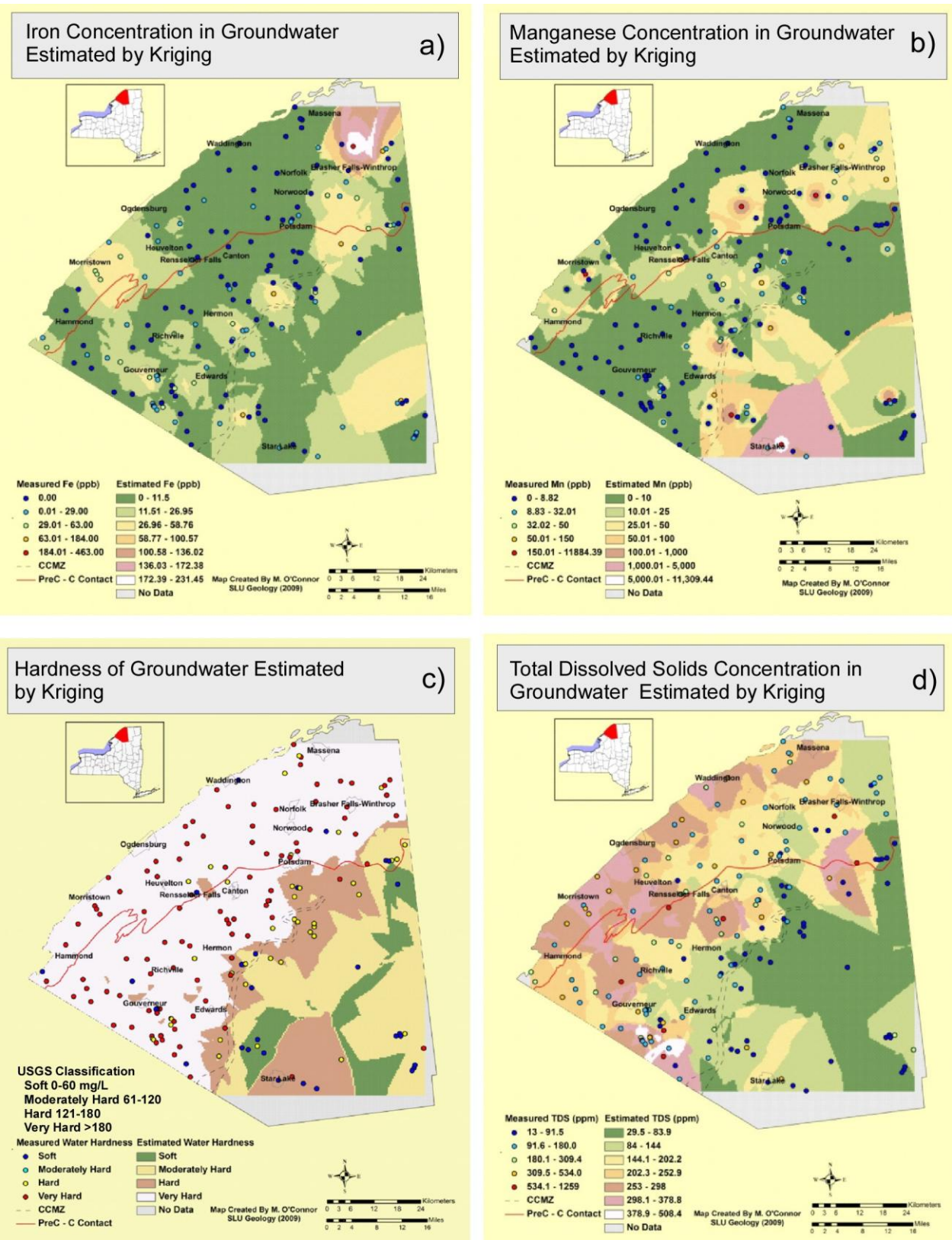
Manganese can substitute for Fe, Mg, and Ca in silicate, oxide, and carbonate mineral structures and is common in small amounts in dolomite and limestone [26]. In addition, local sulfide-rich ores [2,7,11], magnetite mining, and mineralization related to talc-rich rocks are suspected Mn sources. Alternatively Mn may be related to widespread glacial deposits. At Akwesasne, Chiarenzelli *et al.* [13] noted elevated Mn concentrations were associated with wells intersecting the water table and concluded that high concentrations of Mn were prevalent in shallow wells in glacial deposits. Nystrom [16] also noted elevated Mn concentrations were located in shallow bedrock wells in St. Lawrence Valley. Glacial and alluvial deposits are dispersed throughout the region and it is likely that this source is also contributing to elevated Mn concentrations.

A markedly high concentration of Mn (11,884.4 ppb) was recorded by Zabik [3] in a well sampled near Benson Mine in the southern region of St. Lawrence County within the Adirondack Highlands. Benson Mine was the largest open pit magnetite mine in the world before its closure in the mid-1970s [2] and the location of the well is in close proximity to rock tailings associated with mining at Benson Mines; therefore, groundwater interaction with these rock tailings and magnetite mineralization are likely sources for the high Mn concentration measured in this area.

In summary, elevated Mn concentration trends are most prominent in Paleozoic units, including the mixed siliciclastic-carbonate Theresa Formation and Ogdensburg dolostone in the St. Lawrence Lowlands. Additional elevated concentration trends are related to glacial/alluvial deposits, metasedimentary units, and mining areas that occur in the Adirondack Lowlands and Highlands.

3.4.4. Hardness and Total Dissolved Solids

Hardness is an important consideration in the use of water for many purposes. In St. Lawrence County the Carthage-Colton Mylonite Zone is the effective boundary between very hard and soft water (Figure 3c). This change in hydrochemistry corresponds to the abundance or carbonate lithologies (calcitic and dolomitic marble) in the Adirondack Lowlands and their lack in the Highlands. Very hard water is also found in the St. Lawrence Valley where the Paleozoic section contains considerable amount of interstratified sandstone and carbonate (limestone and dolostone). A few individual wells show some variance to this general pattern.

Elevated TDS concentrations are found in the Ogdensburg dolostone within the St. Lawrence Lowlands (Figure 3d). Carbonate rocks associated with the Ogdensburg dolostone and Theresa Formation possess minerals with very soluble elements (e.g., Ca, Mg, Na, and Cl) and are most likely an important source for TDS. Additionally, the presence of proposed evaporitic sequences would also contribute to elevated TDS concentrations in the Ogdensburg dolostone. Nystrom [16] and Chiarenzelli *et al.* [13] noted the degree of elevated TDS concentrations in the St. Lawrence Lowlands and this study confirms those findings.

In the Adirondack Lowlands, elevated TDS concentrations are notably associated with metasedimentary units. Specifically, high TDS concentrations near the Balmat zinc mines reflect gypsum and anhydrite evaporite units, calcitic and dolomitic marbles, and associated sulfides [2,11]. In the Adirondack Highlands, TDS concentrations are considerably lower. This is attributed to more resistant and sulfur-poor meta-igneous lithologies that are much less soluble than the carbonate, metasedimentary, and evaporitic units found elsewhere in St. Lawrence County.

3.4.5. Boron and Chloride

Boron is an essential component in the mineral tourmaline, which generally occurs in granitic rocks, pegmatites, and some metasedimentary rocks [21]. There are some interesting concentration trends for B in St. Lawrence County (Figure 4a), particularly near Massena, Pierrepont, and Balmat. Elevated B concentrations correlate well with tourmaline deposits throughout St. Lawrence County. Robinson and Chamberlin [8] have noted tourmaline deposits in the Balmat-Edwards district, Gouverneur, DeKalb, Macomb, Talcville, and West Pierrepont. Power's Farm, located in Pierrepont, is a world famous mineral collecting locale for black uvite tourmaline. Elevated concentrations of B were detected in all of these regions suggesting that tourmaline deposits are a prominent source for the element's presence in groundwater composition within the study area. Additionally, Li and Sr, which are typically associated with tourmaline, correlate with elevated B concentrations further suggesting the influence of tourmaline on groundwater geochemistry.

Elevated concentrations of B were also measured near Balmat, New York. Here evaporitic horizons, including halite are found in the Upper Marble. Rather than tourmaline, dissolution of such rocks may provide a source for B in this area. Elevated concentrations of B, Li, and Sr were also measured to the northeast in St. Lawrence County near Massena. No significant tourmaline deposits are known in the area. A possible source for elevated concentrations of these elements may be the evaporitic sequences that have been suggested by Chiarenzelli *et al.* [13]. Although relatively rare, the Sr-bearing minerals strontianite and celestite have been reported in evaporitic sequences [28] and could be present in the Ogdensburg dolostone, explaining the abnormal concentrations of B, Li, and Sr in the region.

Elemental analysis using ICP-MS provides concentrations for elemental chlorine; however, chlorine does not exist freely in nature; therefore, chlorine results are stated as chloride (Cl) since this is the only form of chlorine that would make sense in groundwater. Chloride has a variety of natural and anthropogenic sources including rock salt. Relatively large Cl concentrations are found in groundwater near Balmat (Figure 4b). Here, as mentioned above for B, the dissolution of natural halite may be an important source. Surprisingly high concentrations of Cl and TDS are also found in groundwater about 15 km east of Potsdam, New York. Intensive agriculture, concentrated animal feeding operates (CAFOs; primarily cattle), and the waste generated may be the source of the elevated Cl concentrations in groundwater. A similar belt of higher Cl concentrations can be traced south of Canton eastwards through Rensselaer Falls to Morristown. Because this belt cuts across the general strike of bedrock in the area, intensive agriculture (animal waste) is thought to be the predominant source.

3.4.6. Lithium and Strontium

Lithium concentration trends in groundwater (Figure 4c) tend to follow those of boron (Figure 4a) and strontium (Figure 4d). The highest values of both strontium and lithium are found south and west of Massena. This is in excellent agreement with the groundwater sampling previously done at Akwesasne, Cornwall Island, and southwest of Massena in Louisville where soluble elements like B, Li, Sr and others were found to be elevated in groundwater. Lithium, like B and Sr likely comes from the dissolution of soluble evaporitic minerals [13].

Figure 4. The concentration of groundwater constituents estimated from groundwater samples collected in St. Lawrence County, New York including (a) boron; (b) chlorine (chloride); (c) lithium; and (d) strontium.
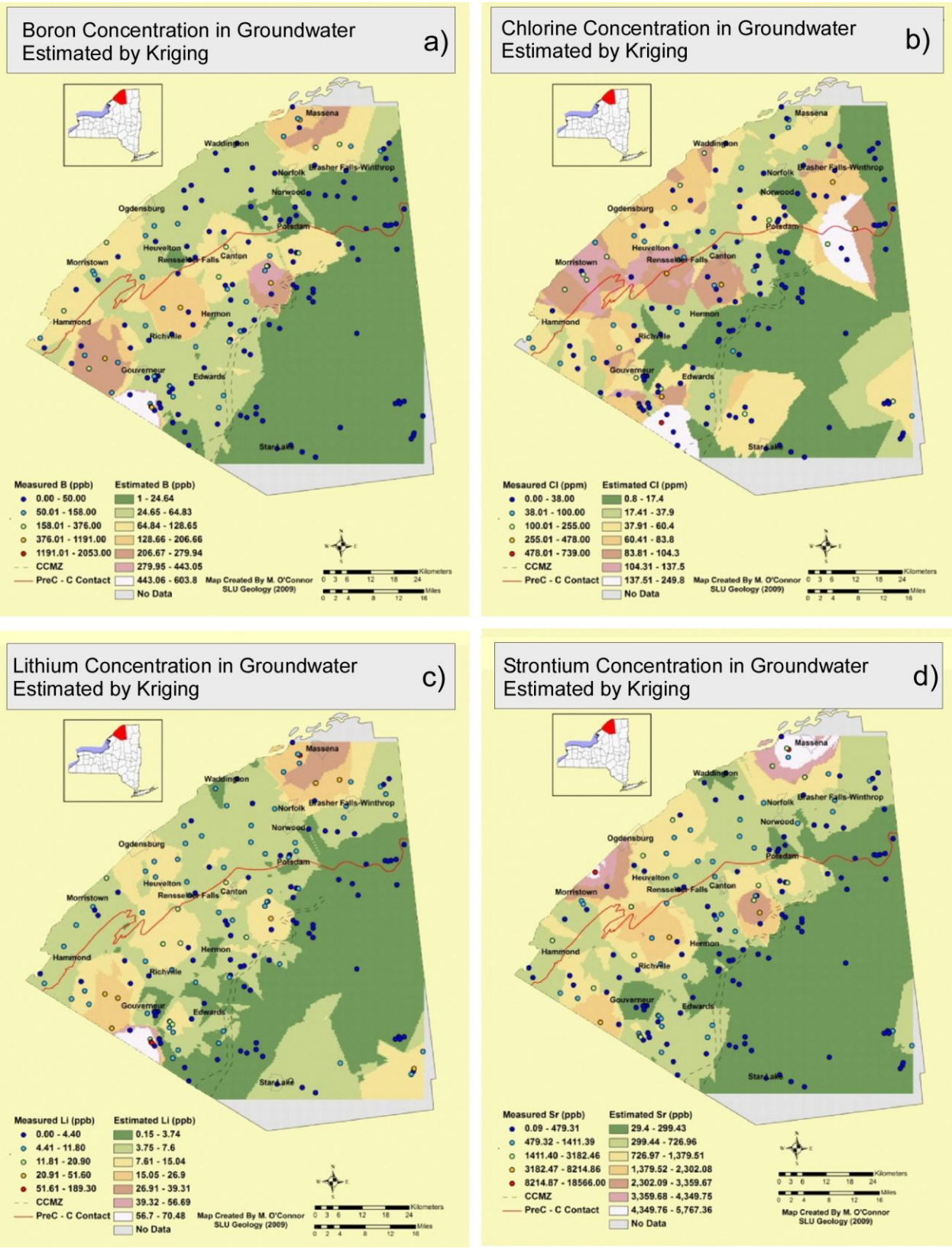
Elevated Sr concentration trends predominate in the Ogdensburg dolostone within the St. Lawrence Lowlands. Similar trends were observed by Chiarenzelli *et al.* [13] in Louisville and east of St. Lawrence County at Akwesasne. Interspersed evaporite deposits within the bedrock unit are believed to be the source for elevated Sr concentrations. Celestite deposits associated with gypsum, anhydrite, and halite have been noted by Robinson and Chamberlain [10] in metasedimentary rocks in the Balmat Mine region and similar associations in the Ogdensburg dolostone may be a source for the elevated concentration trends in the St. Lawrence Lowlands.

3.4.7. Pilot Strontium Isotope Study

Concentration trends of Sr are of geologic interest as minerals with considerable amounts of Sr are relatively rare. Strontium concentrations in the Ogdensburg dolostone may indicate strontianite or celestite layers associated with evaporitic layers within this formation. To help determine the source of elevated Sr concentrations, a Sr isotope pilot study was conducted on 13 additional water samples collected in St. Lawrence County. Sample locations ranged from a variety of bedrock units including Paleozoic lithologies (7 samples), and metamorphic units of the Adirondack Lowlands (4 samples) and Highlands (2 samples).

Analysis of $^{87}Sr/^{86}Sr$ was used to provide insight into water-rock interaction (Figures 1d and 5). This ratio is strongly influenced by the age and Rb/Sr ratio of the rock unit it passes through; thus, Sr isotope analysis could help determine if the ultimate source of the groundwater sampled in various areas throughout the county. Well samples that draw water from Paleozoic rocks have $^{87}Sr/^{86}Sr$ ratios (0.70900–0.71286) that fall within the range (0.70946–0.71563) proposed by Wadleigh *et al.* [20] for rivers draining Paleozoic rocks of the Canadian Shield with a mean value of 0.710204 +/− 0.0014 comparable to his average value of 0.71170. The $^{87}Sr/^{86}Sr$ ratios for samples that interact with metamorphic units in the Adirondack Mountains (0.70998–0.71547) are generally lower than the range and mean (0.71307–0.71864; 0.71510) of rivers draining areas of Grenville-aged rocks [20]. Rocks in the Adirondack Lowlands are generally younger (1.15–1.20 Ga) than in other parts of the Grenville Province, which can be up to 1.40 Ga or older. This age difference and the additional time available for isotopic evolution may explain this discrepancy.

In general, rocks derived from clastic sediments and granite tend to have elevated Rb/Sr ratios while those derived from carbonate are smaller (Figure 5). Elevated Rb/Sr and Rb concentrations ratios led to greater production of radiogenic ^{87}Sr and higher $^{87}Sr/^{86}Sr$ ratios over time. Carbonate rocks of the Beekmantown Group (Ogdensburg dolostone) in this study have a fairly narrow range of values (0.709302 ± 0.000255), likely reflecting seawater Sr ratios as their dominant source [21] which matches that (*ca.* 0.7090) of Lower Ordovician brachiopods (seawater surrogate). These isotopic data indicate that groundwater at the locations sampled is interacting with the immediately underlying bedrock in the region. The results suggest that it is less likely that water is transported long distance and/or mixed extensively with that derived from distant lithologies. This provides further support for the theory that evaporitic sequences occur within the Ogdensburg dolostone and result in the elevated Sr concentrations in the St. Lawrence Lowlands [13,29,30].

Figure 5. Results of the strontium isotopic study showing $^{87}Sr/^{86}Sr$ ratio plotted against strontium in parts per million. The Rb/Sr ratio multiplied by 1,000 of each sample is shown in green. Inset shows relative stratigraphic positioning.
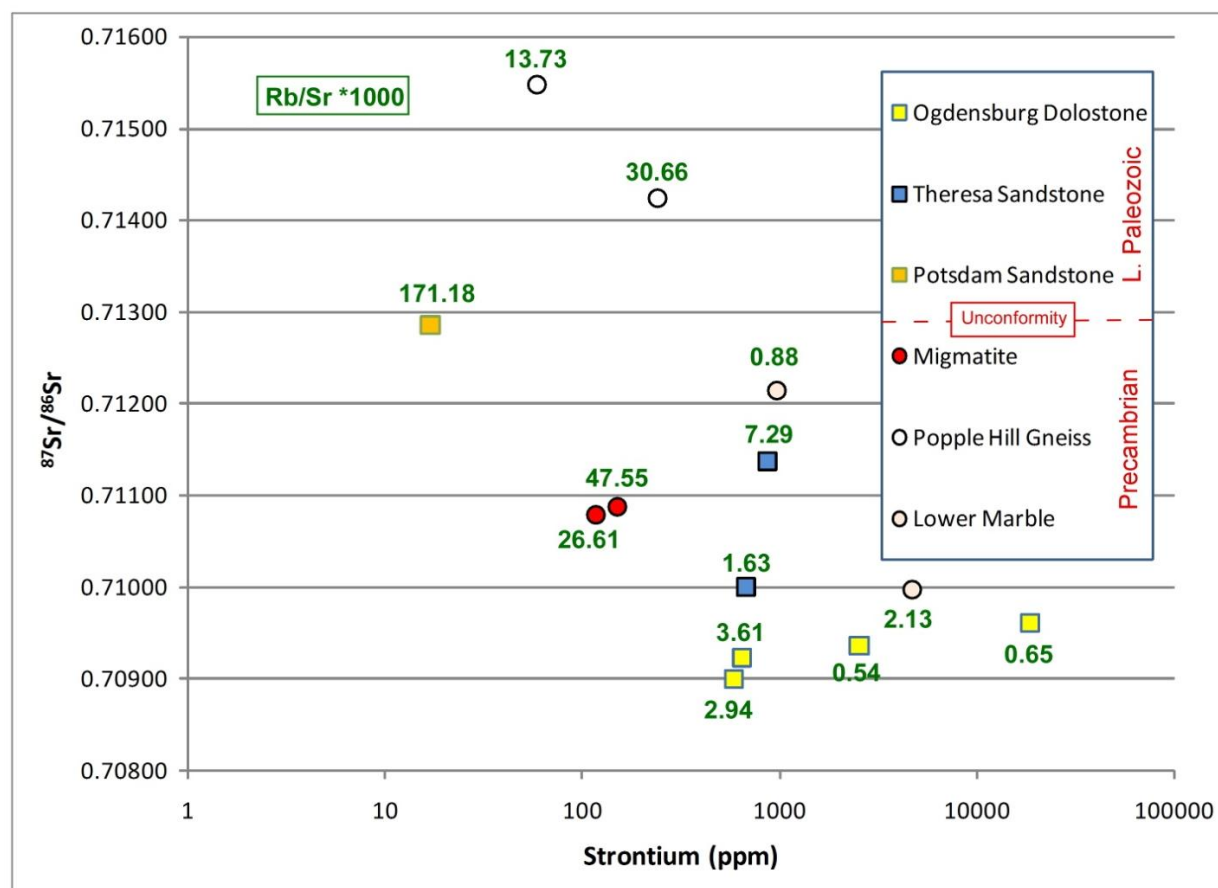
Water from the Potsdam sandstone was found to have a Grenville-like Sr isotopic ratio. The Late Cambrian Potsdam Sandstone is a quartz arenite and has only trace amounts of Sr (Figure 5). However, the Potsdam sandstone was derived from underlying Grenville basement that contains higher Rb/Sr ratios than Ordovician carbonates of the Ogdensburg dolostone. Thus it is believed that much of the Sr isotopic signature is derived from non-quartzose, Precambrian detritus and/or by groundwater flow paths along the unconformity surface or through going fracture networks intersecting the basement rocks. Interlayered carbonate-cemented quartz arenites and dolostones of the Lower Ordovician Theresa Formation plot between samples of Ogdensburg dolostone and Potsdam sandstone.

In general, while there is some scatter, groundwater derived from Precambrian crystalline rocks has higher $^{87}Sr/^{86}Sr$ ratios than samples from the Phanerozoic carbonates. In addition the values reported for each agree well with values given in the literature. The highest $^{87}Sr/^{86}Sr$ ratios come from the Popple Hill gneiss, a metamorphic Precambrian shale unit, one of the oldest rocks in the Lowlands and itself composed of older detritus. The lowest values come from the Ogdensburg dolostone, the youngest bedrock unit in the area. Carbonate rocks tend to have high Sr and low Rb/Sr ratios, while for clastic rocks and granites the opposite is true. Although this study is preliminary, it suggests a good correlation between the chemistry of bedrock and Sr isotopic signatures.

4. Conclusions

Inductively coupled plasma—mass spectrometry (ICP-MS) analyses of 169 well water samples for 72 inorganic elements are presented with estimated concentration trend maps produced using ArcGIS. There is good correspondence between geologic units and groundwater geochemistry and it can be approximated by geospatial analysis tools. An array of trend maps of elements, TDS concentrations, water hardness values, and Sr isotopes are presented to illustrate this contention. Paleozoic units of the St. Lawrence Lowlands and the predominantly metasedimentary rocks of the Adirondack Lowlands appear to have the greatest influence on water chemistry and quality due to high abundances of readily soluble minerals and elements. The Potsdam sandstone and acidic crystalline rocks are only sparingly soluble and yield very little to the groundwater which passes through them.

Elevated concentrations of inorganic elements are most prevalent in the Balmat-Edwards district which is likely influenced by ore-deposits and associated mineralization and evaporitic layers in the metasedimentary rock units. Although even here, where mining has occurred for nearly two hundred years, little impact could be discerned; perhaps because the limited sampling density and distance of mining activities from most private wells sampled.

Sr isotope ratios from TIMS analyses agreed well with the Lower Paleozoic and Precambrian ages of the units indicating that the dominant influence on groundwater is the composition of underlying bedrock units in the immediate area.

Acknowledgements

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