

A FIRST INVESTIGATION OF GROUNDWATER GEOCHEMISTRY IN THE CRYSTALLINE BEDROCK AROUND LAKE SAINT-JEAN, QUÉBEC

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ABSTRACT

The purposes of this study of groundwaters in the Precambrian bedrock of the Saguenay-Lake-Saint-Jean region are to identify occurrences of mineralised groundwater, to evaluate hydrogeochemical variations, to correlate geology with groundwater geochemistry, and to propose hydrogeochemical models. A total of 46 wells were sampled either once, twice or three times. Samples were analysed for major and minor inorganic components and stable isotopes (^2H and ^{18}O). The results show a strong variability of *in situ* measured parameters, but also of some of the laboratory-analyzed components. Three main groundwater types are found in the study area: Na-Ca- HCO_3 , Na-Ca-Cl- HCO_3 - SO_4 , and Na-Ca-Cl. Lower concentration in Ca and higher concentration in Na seem to characterize a marine clay environment. Most of the samples show higher concentration in bromide than sea water. Isotope results show a trend that is similar to saline waters observed elsewhere in than Canadian Shield.

RÉSUMÉ

Les buts de cette étude des eaux souterraines dans le socle précambrien de la région du Saguenay Lac-Saint-Jean sont d'identifier des secteurs présentant des eaux souterraines minéralisées, d'évaluer les variations hydrogéochimiques, de corrélérer la géologie et la géochimie, ainsi que de proposer des modèles explicatifs. Au total, 46 puits ont été échantillonnés de une à trois fois. Les échantillons ont été analysés pour les composantes inorganiques majeures, mineures et traces, et pour les isotopes stables ^2H et ^{18}O . Les résultats montrent une forte variabilité de certains paramètres mesurés *in situ* et en laboratoire. Trois types d'eau sont identifiés: Na-Ca- HCO_3 , Na-Ca-Cl- HCO_3 - SO_4 , et Na-Ca-Cl. Une teneur faible en Ca et élevée en Na semble caractéristique des environnements d'argile marine. La majorité des échantillons montre une concentration plus élevée en bromure que l'eau de mer. L'étude isotopique révèle une évolution semblable aux eaux salines observées ailleurs dans le Bouclier Canadien.

1. INTRODUCTION

In the Saguenay-Lake-Saint-Jean region (Figure 1), nearly 28% of the population of about 290 000 uses groundwater as a source of drinking water, and more than 32% of them use private wells (MENVQ, 1999). Very little information is available on the groundwater quality in this region despite the fact that there are approximately 6,400 private wells.

Simard and Des Rosiers (1979) presented an overview of several aquifers in the southern part of Quebec, with a special emphasis on the drinking water quality based on 216 samples. The two occurrences with excessive fluoride content (>1.5 mg/l) out of the 20 samples collected from the Precambrian bedrock, as well as the only occurrence with an excessive concentration of chloride (>250 mg/l), and the one with a significant salinity value (>1000 mg/l) were all found in the Saguenay-Lake-Saint-Jean region. In the only

hydrogeological study available for this area, Dessureault (1975) noticed the presence of salt water in the fluvio-glacial deposits and in the bedrock. He suggested that the major natural source of groundwater contamination of the Lac-Saint-Jean area is the salt content of quaternary silty clay deposits from the Laflamme Sea that covered a considerable portion of this area by the end of the last glaciation.

This paper presents the results of the first hydrogeochemical study of groundwater in that region. The goals of this study are to locate occurrences of mineralized groundwater, to evaluate hydrogeochemical variations, to correlate geology with groundwater geochemistry, and to propose hydrogeochemical models.

2. GEOLOGICAL SETTINGS

2.1. Bedrock geology

The Saguenay-Lake-Saint-Jean region is located in the Grenville Province of the Precambrian Shield (Figure 1; Laurin and Sharma, 1975). The main Precambrian lithologies are plutonic rocks ranging in composition from felsic to intermediate, a gneissic complex of orthogneiss and paragneiss (Hébert and Lacoste 1998), and several phases of mesoproterozoic magmatic injections (~1500 and 1000 Ma) of anorthositic bodies. A few remnants of an Ordovician platform sedimentary rock are found in the Lake Saint-Jean and Saguenay lowlands. The Grenvillian bedrock is cut by the Phanerozoic Saguenay graben, which is about 30 km wide and bounded by two WNW fault systems. (Figure 2; Du Berger et al. 1991).

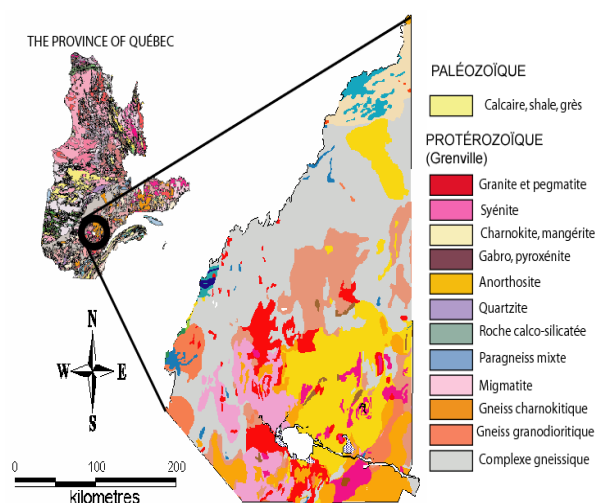


Figure 1: Bedrock geology of the Saguenay-Lake-Saint-Jean region (adapted from Avramtchev, 1993)

2.2 Quaternary geology

In the course of its retreat towards the west-northwest, the last glacier that covered the region left in its way a discontinuous till cover, some terminal moraines and important fluvio-glacial deposits. Thereafter, the lowlands in the area were invaded about 10,000 years ago by the Laflamme Sea. This has resulted in deltaic and shore deposits, as well as deep-water sediments consisting of argillaceous silt with grey silty clay (LaSalle and Tremblay 1978; Bouchard et al. 1983). The fine-grained sea deposits contain salty interstitial water, and they are relatively abundant in the low lands of the Saguenay-Lake-Saint-Jean region (Figure 2).

3. METHODOLOGY

3.1 Location of the sampling sites

The sampling sites were selected on the basis of the high degree of salinity of groundwater (TDS greater than 1000 mg/l). All of the water samples come from the bedrock and most of them were taken from private wells. In other cases, samples were taken from public wells or abandoned wells. The sampling sites (Figure 2) are generally located in areas that can be considered as regional groundwater discharge zones. At each one of the sampling localities shown on Figure 2 correspond between one or up to three sampling sites (or wells).

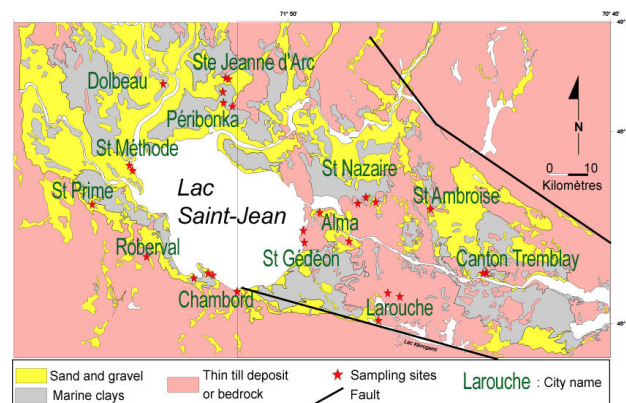


Figure 2: Quaternary geology map showing major faults and sampling localities (adapted from LaSalle et Tremblay, 1978, and McCormack, 1985)

3.2 Groundwater sampling

The sampling protocol included the follow-up of selected physico-chemical parameters during the purging of the well. These parameters are the temperature, the redox potential (Eh), pH, dissolved oxygen, electrical conductivity and TDS. The measurement probe was placed in non-turbulent water in a flow-through cell, and a measure was taken every 5 minutes. Purging was completed when the parameters had reached stability. The water level, the flow rate, and the total volume of pumped water were recorded all through the purging procedure. Moreover, physical parameters such as the colour, the smell, the taste and the turbidity were evaluated qualitatively. The sampled water was filtered through a 0.45 micron filter.

A total of 96 groundwater samples were collected from 46 wells. From that number, 18 wells were sampled three times: 1) during the months of November and December 2004, 2) in February 2005, and 3) in May 2005. In addition, 13 wells were sampled twice and 16 wells were sampled only once.

3.3 Chemical parameters and analytical procedures

Samples were analysed for 25 major and minor inorganic components and two stable isotopes. Most of the components were analysed at the *Centre d'expertise en analyse environnementale du Québec*, a

division of the *Ministère du Développement Durable, de l'Environnement et des Parcs*. The metallic ions were analysed with ICP-OES; the sulphide by colorimetry with ferric chloride and oxalate of the dimethyl-p-phenylene diamine; and the anions by ionic chromatography. The alkalinity was obtained by titration at the end of each sampling day in the geochemical laboratory at the University of Quebec at Chicoutimi. The isotopes ^2H and ^{18}O were analysed on 43 selected samples using mass spectrometry (IRMS) at the *GG HATCH Isotope* laboratory of the University of Ottawa.

4. ANALYTICAL RESULTS AND WATER QUALITY

All of the samples were analysed for 25 chemical elements and six physico-chemical parameters. Table 1 shows statistics for the 96 analysed samples, namely the arithmetic mean, the coefficient of variation, the lowest value, the highest value, and the median value of the various parameters. Parameters presented in bold in Table 1 are partly repeated in Table 2, along with the CCME (2003) criteria for drinking water quality. The arithmetic mean is an overestimation in a number of cases, since the value of the detection limit is taken for all of the values that are below this limit. In the case of a normal distribution, the median value corresponds to the bias-corrected arithmetic mean. The parameters that are written in bold and italic in Table 1 show maximum values significantly higher than the tolerated maximum for drinking water. The highest differences are observed for the maximum values of TDS, alkalinity, bore, barium, calcium, chloride, fluoride, iron, sulphide, magnesium, manganese, sodium, sulphate and strontium. Data in Table 2 indicate that about half of the 96 samples are above or near the CCME criteria for the considered parameters.

5. VARIABILITY OF THE RESULTS

The variations in the results are analysed at three different levels: 1) the variability during the sample collection, 2) the variability at a sampling site from one campaign to the other, and 3) the variability of a given parameter also from one campaign to the other. For points 2 and 3 above, it is convenient to describe the variation by normalising the values of the difference from one campaign to the other by the arithmetic mean of the considered parameter. Taking the fluoride as an example, the arithmetic mean for the three sampling campaigns is 1.21 mg/l. At site no 10, the fluoride concentration is 1.9 mg/l at the first campaign and 1.0 mg/l at the third one, i.e. a diminution of 0.9 mg/l. This difference represents a variation of 74% (i.e. $(0.9 \times 100) / 1.21$), as defined above.

The following discussion focuses on cases where the above defined variation has a value of 100% or higher. A total of 31 sites are selected, which correspond to those sites that were sampled two or three times, and 21 parameters are investigated.

5.1 *In situ* variability during sample collection

As mentioned above, stability of *in situ* parameters was reached before a water sample was collected. Figures 3, 4 and 5 show three examples of parameter variation with respect to the purged volume of water. This total purged volume was related to the stability of the parameters, but also to the constraints often imposed by the well owner on the volume and duration of purging. The redox potential is not shown on these figures, as its values often appeared highly variable and not reliable. The end of the graph represents the condition of the water at the time of sample collection. The TDS value was calculated by the measuring device using the following relation: $\text{TDS (g/L)} = 0.5 \times \text{conductivity } (\mu\text{S/cm})$. In most cases, the parameters show a satisfying stability. Indeed, Figure 3 shows an example of the most frequently encountered situation where the conductivity decreases only slightly as purging goes along. Figures 4 and 5 show extreme cases where the conductivity suddenly increases (Figure 4) or decreases (Figure 5) significantly after purging 500L and 50L respectively.

5.2 Variability at a sampling site

Figure 6 illustrates the proportion of parameters that vary by 100% or more at the same site from one sampling campaign to the other. Twenty four of the 31 sites that were sampled more than once have at least one parameter (5%) that varies by 100% or more. The most unstable chemistry is observed at site no 18, where 52.5% of the parameters vary by more than 100%. The parameters with a variation higher than 100% at site no 18 are circled in red in Figure 7, and the value of the variation is indicated on the graph.

5.3 Variability of individual parameters

Figure 8 illustrates the percentage of the sites where one parameter varies above 100% or more over two or three campaigns. None of the station shows a variation for the pH and the silica content is less than 100% at all of the sites. However the other parameters show a variation higher than 100% at least at one site (3%). Fluoride is one of the parameters that vary the most. In fact 35.5% of the sites show a variation of 100% and more for this element. The fluoride content is higher during campaign 2 at many of the sites, as illustrated on Figure 7. This is also the case for the other parameters. Site no 1 shows the highest variation in fluoride content, with an increase of 3.2 mg/l between the first and the second campaign. The fluoride content at the same site may meet the drinking water standard - the red line on Figure 9 indicates the Quebec standard - during one campaign but exceed significantly this standard at other campaigns.

Table 1: Statistics for the 96 groundwater samples

Parameters	N Total	Mean	Coefficient of variation	Min.	Max.	Median
Temperature (Celsius)	96	8.068	0.205	4.9	14.1	7.5
Eh (mV)	96	-25.36	-	-375.6	180.4	-13.25
pH	96	7.69	0.145	3.62	9.56	7.73
DO (mg/L)	95	0.727	2.795	0	12.6	0.13
Specific Cond. at 25°C (µS/cm)	96	3219.94	1.093	90	23085	2165
TDS (mg/l)	96	2773.47	1.172	45	20776.5	1948.5
Al (mg/l)	96	0.031	3.475	0.007	0.99	0.007
Alkalinity (mg CaCO₃/l)	95	200.253	0.822	17.64	1335	147
As (mg/l)	39	0.001	0.000	0.001	0.001	0.001
B (mg/l)	96	0.853	4.323	0.004	36	0.33
Ba (mg/l)	96	0.167	1.960	0.001	2.1	0.058
Br (mg/l)	95	8.317	1.544	0.4	99.55	3.76
Ca (mg/l)	96	218.408	2.062	0.04	3700	59.5
Cl (mg/l)	96	696.362	1.268	0.4	4200	375
Cr (mg/l)	39	0.003	0.105	0.003	0.005	0.003
Cu (mg/l)	96	0.004	2.505	0.001	0.063	0.001
F (mg/l)	96	1.209	0.631	0.04	3.2	1.2
Fe (mg/l)	96	0.585	3.484	0.001	17	0.043
HCO₃ (mg/l)	95	244.308	0.822	21.52	1628.7	179.34
H₂S (mg/l)	24	0.19	1.11	0.03	1.4	0.045
K (mg/l)	96	12.286	1.285	0.26	83	5.8
Li (mg/l)	96	0.046	2.172	0.001	0.6	0.01
Mg (mg/l)	96	28.212	1.461	0.04	220	14
Mn (mg/l)	96	0.075	1.749	0	0.77	0.031
Na (mg/l)	96	387.25	1.225	2.9	2500	255
Ni (mg/l)	96	0.001	0.485	0.001	0.003	0.001
Pb (mg/l)	96	0.005	0.381	0.004	0.016	0.004
Si (mg/l)	96	6.125	0.341	1.3	11	5.65
SO₄ (mg/l)	96	106.436	1.305	0.5	700	45
Sr (mg/l)	96	6.562	1.874	0.005	100	1.6
Zn (mg/l)	96	0.011	1.202	0.005	0.099	0.007

Table 2: Mean and median values of parameters written in normal bold in table 1, and CCME (2003) criteria

Parameters	Mean (mg/l)	Median (mg/l)	CCME (mg/l)
TDS	2773.47	1948.5	< 500
Alkalinity	200.253	147	200
Ca	218.408	59.5	200
Cl	696.362	375	250
F	1.209	1.2	1.5
Fe	0.585	0.043	0.3
HCO ₃	244.308	179.34	164
H ₂ S	0.19	0.045	0.05
Mn	0.075	0.031	0.05
Na	387.25	255	270

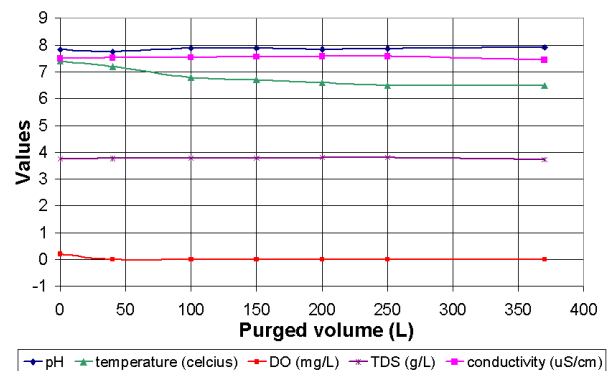


Figure 3: Variation of *in situ* parameters showing a slight diminution of electrical conductivity all through purging procedure

5.4 Sources of variability

Possible sources of the observed variability include actual variations in groundwater chemistry related to hydrogeological or well construction factors. The variability may also be due to a number of sources of error at different stages of the study. At the sampling stage for instance, the purging conditions may vary from one site to the other and from one campaign to the other at the same site. At the analysis stage, sources of error include values below the detection limit, as well as the sample dilution often required in order to reduce the mineral content, etc. Analysis is currently in progress on the sources of the observed variability.

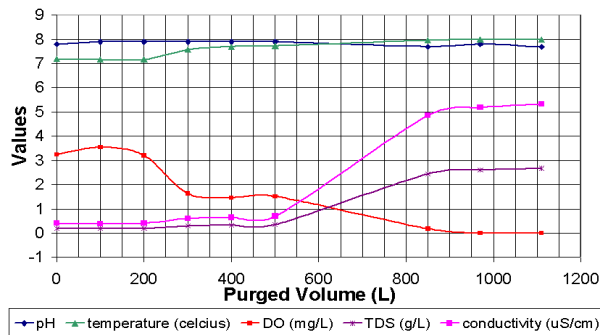


Figure 4: Variation of *in situ* parameters showing an increase of conductivity after 500L of water purging

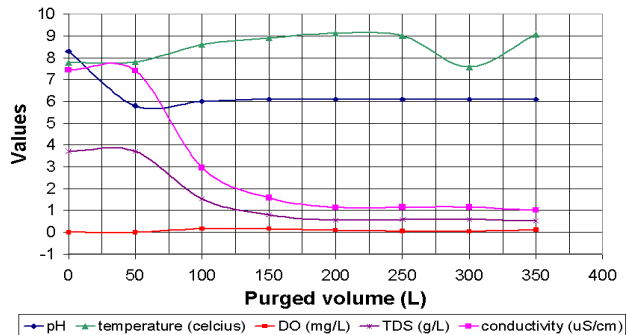


Figure 5: Variation of *in situ* parameters showing a decrease of conductivity after 50L of water purging

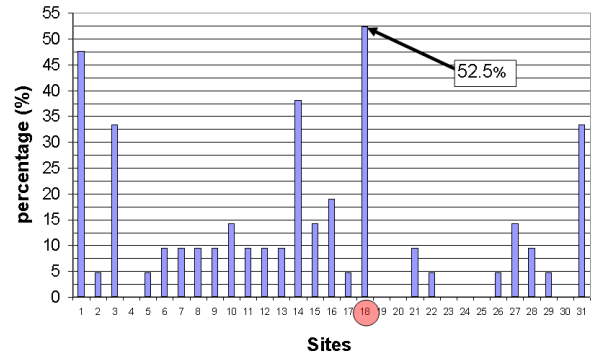


Figure 6: Number of parameters varying by 100% or more at one site, between the two or three campaigns

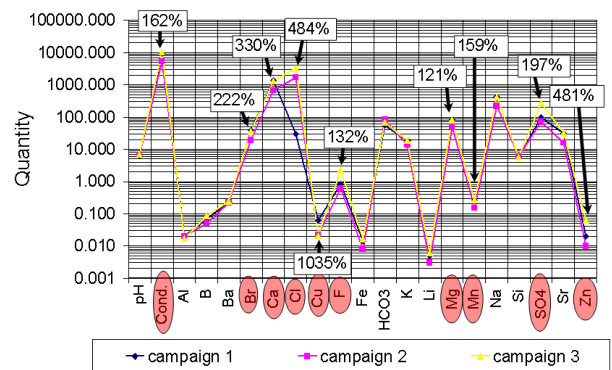


Figure 7: Variation of parameters at site no 18; variations higher than 100% are pointed out

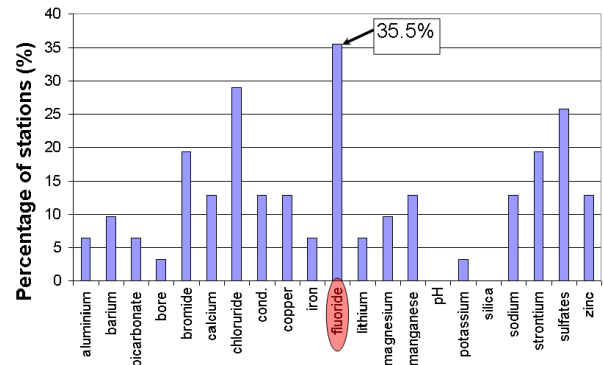


Figure 8: Number of sites where the indicated parameter varies by 100% and more, between the two or three campaigns.

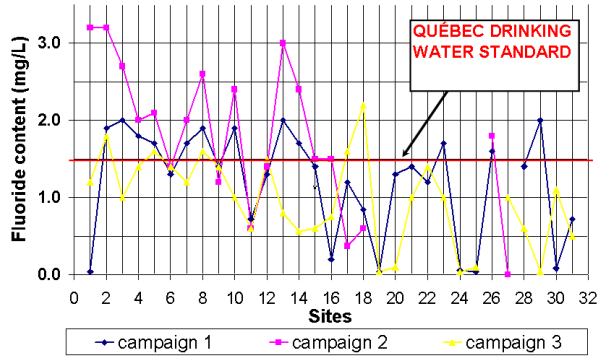


Figure 9: Variability of fluoride content in comparison with Quebec drinking water standard

6. TYPES OF WATER

Three types of water are observed in the study area, as illustrated by the Piper diagrams on Figures 10, 11, and 12. The dominant chemical elements are bicarbonate, calcium, and sodium. The chloride type of water showed on Figure 11 corresponds to the saline end member of our data set. The chemistry of this water is defined by its high content in chloride, as well as in calcium and/or sodium. The third type of water (Figure 12) shows an intermediate composition between the bicarbonate type and the chloride type. A sulphated composition is present in few cases. The dominant constituents for this water type are chlorides, bicarbonate, as well calcium and sodium in cases.

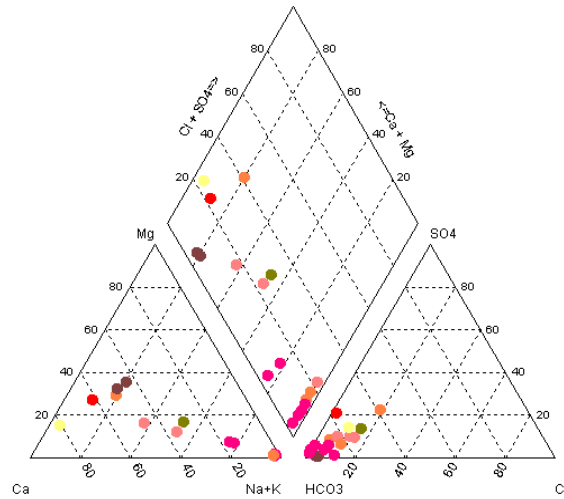


Figure 10: Piper diagram showing bicarbonate type of water

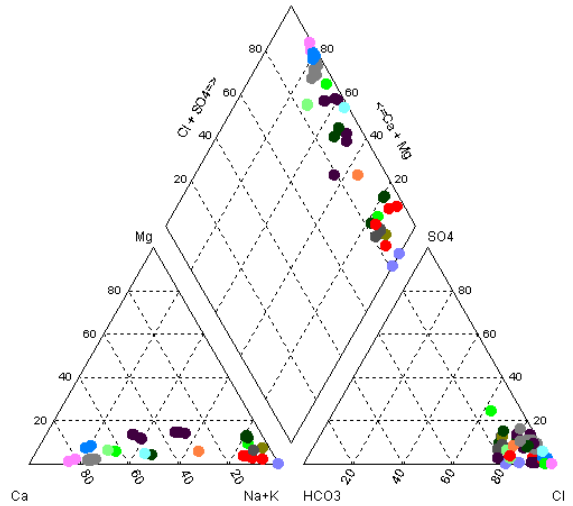


Figure 11: Piper diagram showing chloride type of water

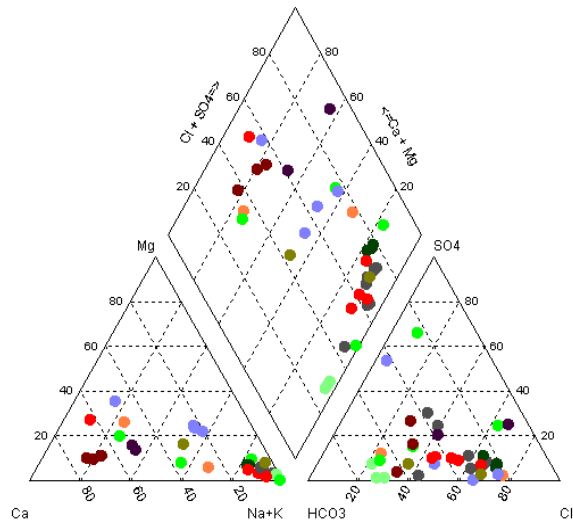


Figure 12: Piper diagram showing intermediate type of water, and some cases of sulphated waters

The different dot colours on Figure 10, 11 and 12 represent the different sampling localities shown by red stars on Figure 2. The same color appears several times, since several sampling sites are generally located in the same locality, as mentioned above, and also many of the sites have been sampled more than once. Some groupings of the same color are apparent, on the Piper diagrams, indicating a similarity of the water chemistry at different sites in the same locality.

7. HYDROGEOCHEMICAL MODELS

A few thoughts are warranted to explain the salinity of the groundwaters described above in comparison with seawater and Precambrian shield brines.

7.1. Water – rock interactions

According to Gascoyne and Kamineni’s model (1994), the recent groundwater corresponds to the bicarbonate type. This water may become sulfated, later on, especially in the presence of sulfide minerals. As it flows deeper, this groundwater turns into the chloride type and its salinity increases. This geochemical evolution of groundwater with depth is observed in the Precambrian Shield, no matter the rock types present in a given area, e.g. granitic, gneissic or gabbroic rocks. We don’t have a clear control on the depth of our sampling points, except that almost all of our sampling wells are shallower than 100m. Nevertheless, the three types of water described in the previous section may correspond to the above model. Furthermore, Tóth (1999) has suggested that the chemical evolution of groundwater is directly related to the residence time of groundwater, to the distance along a flow path, and to the scale of the flow system, i.e. local, intermediate, or regional. Most of the samples sites in our study are located in areas that can be considered as regional groundwater discharge zones.

7.2. Leaching of Laflamme’s marine clays

The chemistry of the waters does not invalidate Dessureault’s (1975) suggestion that the presence of salt bearing clay in the region could explain the salinity of the water both in the fluvio-glacial gravels and in the bedrock. The actual salinity of the interstitial water of the Laflamme Sea clay varies from 0.2 to 16g/L (Bouchard *et al.*, 1993), which indicates that a leaching phenomena and diffusion may take place at the present time.

In general, as shown on Schoeller diagram illustrated on Figure 13, samples from environment where clays are present (Figure 13a) show lower concentration in Ca and higher concentration in Na than samples from other geological environments (Figure 13b).

7.3. Br/Cl ratios; $\delta^{18}\text{O}$ $\delta^2\text{H}$ data

The Br/Cl ratio in most of the samples is higher than in sea water (Figure 14); but the source of bromide is not yet identified. Other samples plot near the dilution line for seawater.

The $\delta^2\text{H}$ - $\delta^{18}\text{O}$ graph (Figure 15) shows two different trends. A number of data points plot on the Global Meteoritic Water Line (GMWL); but most of the other points suggest a mix of shallow fresh water with older saline waters, as observed elsewhere in the Canadian Shield (Frape and Fritz 1982).

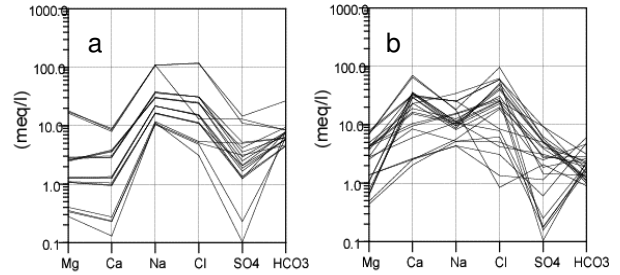


Figure 13: Schoeller diagrams for samples from localities where clays are present (a); and from other geological environments (b)

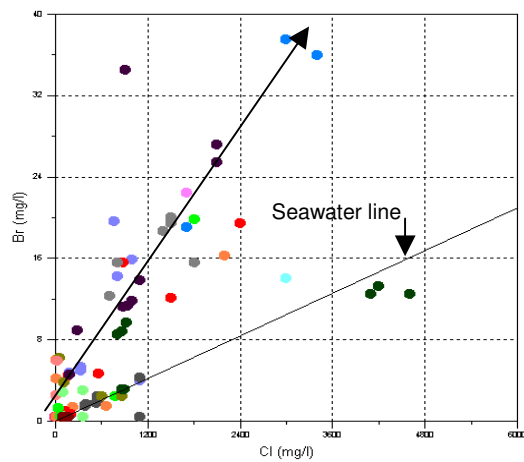


Figure 14: Br and Cl relationship for our groundwater samples, in relation to the dilution line for seawater.

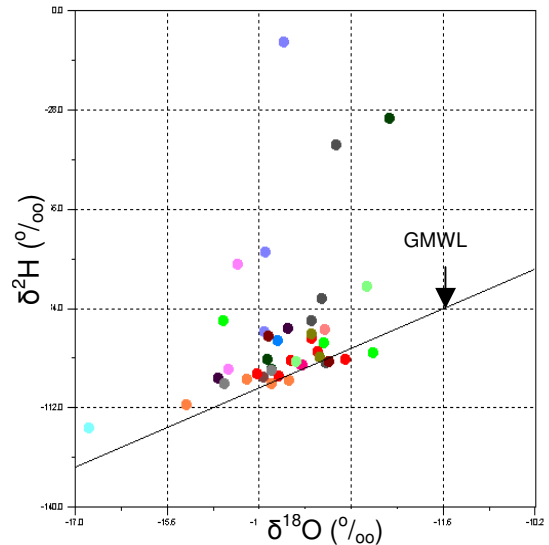


Figure 15: $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ for our groundwater samples, in relation to the Global Meteoritic Water Line

8. SUMMARY AND CONCLUSION

We have presented preliminary results of the first hydrogeochemical study of groundwaters in the Saguenay-Lake-Saint-Jean region, with a special attention on mineralised waters in the bedrock.

About 50% of the 96 samples are above or near the CCME (2003) criteria for the following parameters: TDS, alkalinity, Ca, Cl, F, Fe, HCO₃, H₂S, Mn, and Na.

The parameters measured *in situ* during the sampling procedure generally show a satisfying stability, with a slight decrease in electrical conductivity as well purging goes along. In a few cases, a strong variability is observed for some of the parameters measured *in situ*.

For almost every sampling site, at least one parameter varies by 100% or more with respect to its arithmetic mean, from one sampling campaign to the other. Fluoride is the most variable parameter. The analysis of the sources of variability is in progress, including the natural variability, as well as the sampling, e.g. the well purging, and the analysis procedures.

Three types of water are identified from our data set: 1) bicarbonate type or fresh water, 2) chloride type and salty water, and 3) an intermediate composition between the bicarbonate and the chloride types, with sometimes a sulphated component.

The two main hypotheses that are considered to explain the observed salinity of groundwaters in this study area are: 1) water – rock interactions, after Tóth (1999), and Gascoyne & Kamineni's (1994) models; and 2) leaching of the Laflamme Sea clays as proposed by Dessureault (1975).

Schoeller diagrams, the analysis of the Br/Cl ratio, and isotope studies seem to yield useful clues to further refine the interpretation of the origin of these mineralised groundwaters.

9. ACKNOWLEDGEMENTS

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