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Hydrogeochemical Characterization of Groundwater in the Outaouais Region (Québec, Canada) – A Regional Scale Study



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ABSTRACT

As part of the Québec regional groundwater characterization program (PACES), a detailed groundwater quality survey was undertaken in the Outaouais Region (Québec, Canada). During the summers of 2011 and 2012, 139 samples were taken from municipal and private wells which were analysed for major ions, nutrients, metals and sulphides. About 70% of the samples were obtained from bedrock wells, mainly in the Canadian Shield and the remainder from wells screened in Quaternary deposit aquifers. Analysis quality was evaluated by calculating the anion-cation balance. As a result, 127 samples with anion-cation charge balance errors within $\pm 10\%$ were used for the determination of hydrogeochemical facies. The classification by facies is also supported by multivariate statistical analysis, namely Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA). The study has identified Champlain Sea invasion, cation exchange and freshwater recharge as the main geochemical processes affecting groundwater chemistry in this region.

RÉSUMÉ

Dans le cadre du Programme d'Acquisition de Connaissances sur les Eaux Souterraines du Québec (PACES), une étude hydrogéochimique a été menée dans l'Outaouais (Québec, Canada). Pendant les étés 2011 et 2012, 139 échantillons ont été prélevés dans des puits municipaux et privés et ont été analysés pour les ions majeurs, les nutriments, les métaux et les sulfures. Environ 70% des échantillons proviennent de puits au roc, principalement dans le Bouclier Canadien, et le restant provient de puits localisés dans les dépôts du Quaternaire. La qualité des analyses a été évaluée par le calcul de la balance ionique. Le facies hydrogéochimique a été déterminé pour les 127 échantillons ayant une balance entre $\pm 10\%$. La classification par les facies est étayée par une analyse statistique multivariée incluant une Analyse en Composantes Principales et une Analyse Hiérarchique. L'invasion par la Mer de Champlain, l'échange cationique et la recharge par des eaux peu minéralisées sont les principaux processus géochimiques affectant la région.

1 INTRODUCTION

This study is part of the Québec regional groundwater characterization program, initiated by the Quebec Ministry of Environment. The main objectives of this study are to identify the primary processes responsible for groundwater quality in the study area using multivariate statistical analysis.

The Outaouais Region is located in the south-western part of Québec, close to the national capital of Ottawa. Only 40% of the Outaouais Region is part of the study, which covers the most populated area. Thus, the study area covers 13,762 km² with a population of over 340,000, of which one-third rely on groundwater via municipal networks or individual wells (Comeau et al. 2011). Elevation varies from 550 (Lac Ste Marie) to 22 meters along the Ottawa River (southern limit of the study area), which is the discharge zone for all the rivers of the study area (Figure 1).

2 GEOLOGICAL AND HYDROGEOLOGICAL CONTEXTS

2.1 Bedrock geology

90% of the study area is located in the Grenville Province of the Canadian Shield (Figure 2), dating from the

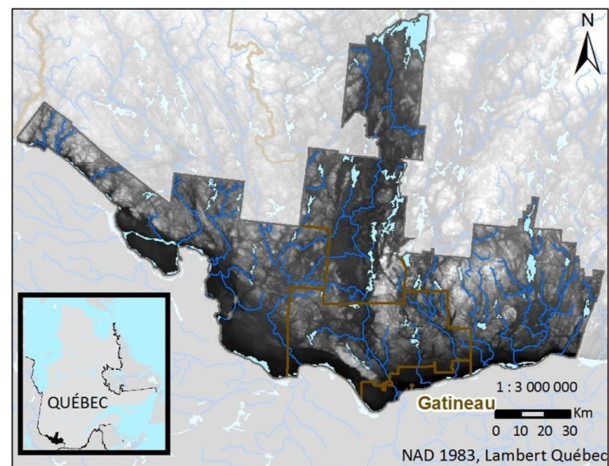


Figure 1. Location of the study area. The major rivers and the digital elevation model are shown.

Proterozoic (Precambrian). According to their origins, three types of rocks can be defined: intrusive (felsic, mafic and ultra-mafic), migmatic and metasedimentary. These rocks are mainly silicates as well as carbonate rocks (Comeau et al. 2011).

The remaining 10% is composed of rocks from the St Lawrence Lowlands Platform along the Ottawa River (east of Gatineau) and from the Hudson Bay Platform (in

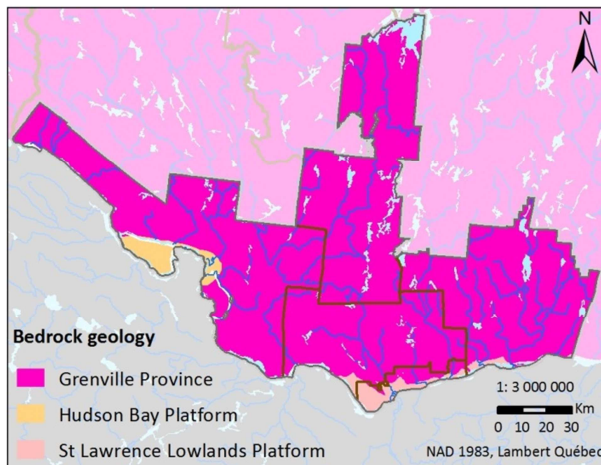


Figure 2. Bedrock geology of the study area.

the area of Île-aux-Allumettes, an island in the Ottawa River, in the western part of the region) (Figure 2). The St Lawrence Lowlands Platform rocks, dating from Cambrian to Ordovician, form a series of sedimentary rocks including sandstone, dolostone, shale and limestone. Rocks from the Hudson Bay Platform include limestone, dolostone, chert, gypsum and anhydrite (Comeau et al. 2011).

2.2 Quaternary deposits

The Quaternary period was affected by several glacial-deglacial cycles. Due to erosion processes, however, only the sediments from the last cycle have been identified in the region.

The bedrock is covered by a discontinuous layer of till, overlaid by fluvio-glacial sediments, a consequence of glacial erosion.

During deglaciation about 12,000 years ago, the depression of the continent due to the ice weight allowed invasion of the Champlain Sea into the main valleys. The Champlain Sea left a layer of clay which is quite thick in some areas (up to 100m in thickness).

Due to glacial isostatic rebound, the Champlain Sea was flushed away which left deltaic sediments, littoral and pre-littoral sediments (sand and gravel).

Along the main rivers, this sequence is buried by ancient and more recent alluvium.

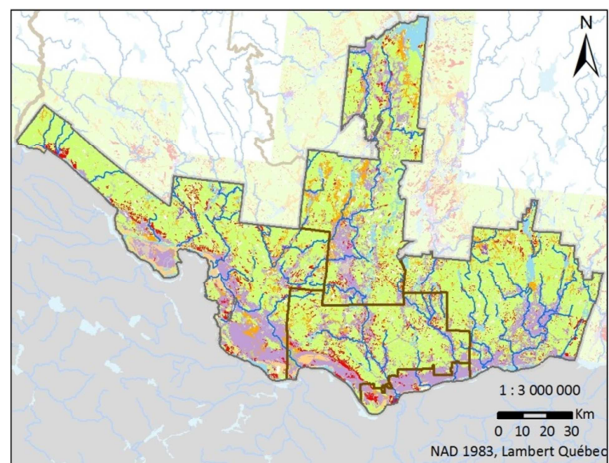
2.3 Hydrogeology

As a result of the geological history of the region, the distribution of the Quaternary sediments is as follows (Figure 3):

- In the areas of elevated topography, the bedrock is covered by a discontinuous layer of till, meaning that the bedrock outcrops in some areas. There, the recharge is elevated and the aquifers are located in the bedrock under unconfined to semi-confined conditions. The recharge occurs mainly in these areas (northern part).
- Fluvio-glacial sediments outcrop only in the higher parts of the major valleys, where the Champlain

Sea did not invade. Depending on their thickness, these deposits, made of sand and gravel, are good aquifers. They are even better in the lower parts of the valleys, if not washed out by the Champlain Sea, where the marine clays are responsible for the aquifer confinement (along the Ottawa River and the main lower valleys).

- Glacio-marine sediments, like deltaic plains and littoral sediments, are generally coarse-grained and are also good aquifers.
- Locally, alluvial sediments are potentially good superficial aquifers.



Quaternary sediments

- | | |
|------------------------|-----------------------------|
| Post-glacial sediments | Glacio-marine sediments |
| Organic sediments | Glacio-lacustrine sediments |
| Eolian sediments | Fluvio-glacial sediments |
| Alluvial sediments | Till |
| Lacustrine sediments | Outcropping bedrock |

Figure 3. Spatial distribution of the Quaternary sediments.

The main groundwater flow paths in the bedrock aquifer can be deduced from the piezometric map realized using about 15,000 water table levels (Comeau et al. 2011). The regional groundwater flow path is from north to south, towards the Ottawa River which is the discharge area for all the rivers of the study area. However, the main rivers, flowing from north to south also serve as watershed-scale discharge areas towards which intermediate groundwater flow paths are directed (along primarily east-west directions).

3 METHODOLOGY

The approach used in this study is similar to those applied to other regional groundwater studies (for studies in Québec, see Blanchette et al. 2010 and Cloutier et al. 2006).

After collection of the samples, analysis quality was checked and water types were determined for samples with a balance charge within $\pm 10\%$, before preparing the dataset for subsequent statistical analysis.

3.1 Selection of the sampled wells

During the summers of 2011 and 2012, 139 groundwater samples were collected from municipal and private wells which were analyzed for major ions, nutrients, metals and sulphides. The sampling protocol followed was standard and assurance quality was ensured by taking 10% duplicates and blanks.

Despite field constraints (sparse population, water supply networks, inaccessible protected areas, non-uniform well-owner cooperation), special care was taken in the choice of the wells to be sampled. The wells were selected to be homogeneously distributed in the study area and to be representative of the different types of aquifers (bedrock vs Quaternary deposits) and of the various degrees of confinement (unconfined vs semi-confined vs confined) (Figure 4).

As a result of the spatial distribution of the Quaternary deposits, about 70% of the samples were obtained from bedrock wells, mainly in the Canadian Shield (83 samples), and in carbonate rocks (10 samples) in the southern part, along the Ottawa River. The remainder was from wells screened in Quaternary deposit aquifers (40 samples).

3.2 Analysis quality

Assessment of analysis quality is the first step in the interpretation of groundwater analysis and involves calculation of the charge balance (Hounslow 1995). Many software codes are available for this calculation. Here, PHREEQC 2.18 (Parkhurst and Appelo 1999) was used to infer bicarbonate and carbonate concentrations from alkalinity and pH and other species in solution from total concentrations. For one of the samples, in-situ parameters could not be measured: the pH value was not available and was calculated by the program.

According to Hounslow (1995) and other authors, a charge balance error within $\pm 10\%$ is considered acceptable. Results show that 127 samples had a cation-anion balance between $\pm 10\%$. The remaining 12 samples were rejected for the determination of groundwater types and statistical analyses.

3.3 Data treatment for multivariate statistical analysis

Since many parameters were measured for each sample (9 parameters in the field and 39 species by a commercial laboratory), multivariate statistical analysis was used to identify groups of parameters showing similar trends and to classify samples according to these trends. Processes controlling groundwater chemical trends can then be inferred.

Figure 5 presents the methodology applied for the preparation of the dataset for statistical analysis.

Different aspects account for the parameter exclusion. All redundant parameters (including hardness, which is the sum of calcium and magnesium, total dissolved solids (TDS) which is the sum of all constituents, and alkalinity) were dismissed (Güler et al. 2002). Except for the pH, all parameters taken in the field were discarded due to uncertainty and influence of the surface conditions,

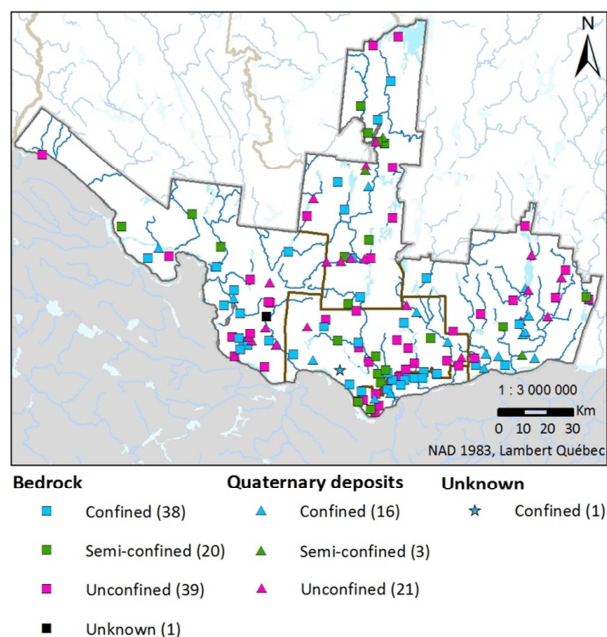
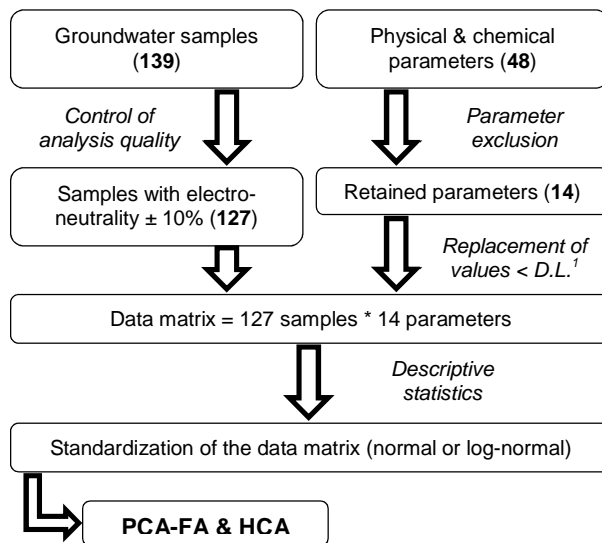


Figure 4. Spatial distribution of sampled wells.



¹D.L.: Detection Limit

Figure 5. Procedure for preparing the chemical dataset for multivariate statistical analysis (modified from Cloutier et al. 2008).

as well as redundancy but they might be included in the interpretation if relevant. Finally, all parameters with more than 15% of their values below the detection limit were not selected for the statistical analysis. Fourteen parameters were retained: the major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- and SO_4^{2-} as well as minor and trace elements B, Ba^{2+} , F^- , Mn^{2+} , pH, Si and Sr^{2+} .

For the statistical analysis, all concentrations are required to be in number format otherwise samples would be excluded. Several methods for replacing values below detection limit are discussed by Farnham et al. (2002)

who demonstrate the effectiveness of replacing values below the detection limit by half the value of the detection limit. This replacement procedure was used for this dataset.

Because of the range of concentration values, especially between major ions (mg/l) and minor ions ($\mu\text{g/l}$), standardization of the data is required for applying multivariate statistical techniques so that each concentration has an equivalent weight (Davis 1986). Descriptive statistics were carried out for each retained parameter as well as histograms to evaluate the concentration distributions. Special attention was brought to the value of skewness, which is an indicator for the symmetry or asymmetry of a distribution and is complementary with the histograms. According to the descriptive statistics (Table 1), all the concentration distributions are positively skewed except pH which can be considered as a normal distribution. Considering the histogram of the Si concentrations and the skewness value calculated on the natural logarithm of the concentration, Si concentrations were assumed to be normally-distributed. The remaining 12 parameters were assumed to follow a log-normal distribution. Standardization was carried out according to the distribution of each parameter. At this point, each distribution has a zero mean and the values are measured in standard deviation units.

Once the standardized dataset was obtained, the multivariate statistical analysis was initiated. Two types of complementary statistical analysis have been chosen which are commonly used for hydrogeochemical data. First, Principal Component Analysis (PCA) combined with Factor Analysis (FA) was carried out to extract interrelations between the parameters (i.e.: parameters behaving the same way). Then Hierarchical Cluster Analysis (HCA), widely used in Earth Sciences, allows the definition of groups that have the most similar chemical analysis results. The results can be displayed as a dendrogram, a kind of tree which links the samples according to their similarities (Davis 1986). Many statistical software codes are available to perform this work; SAS/STAT[®] 9.2 was used in this study (SAS Institute Inc. 2009).

4 DETERMINATION OF WATER TYPES

Water type was defined for all samples having a charge balance within $\pm 10\%$. Basically, water type was determined from the combination of the principal cation and anion based on concentrations expressed in meq/l (see Cloutier 2004 for a complete description of the procedure). Using this method, ten water types were defined for the study area for which the spatial distribution is shown in Figure 6.

Ca-HCO₃ water type is dominant (65%), and is found throughout the study area. This water type is associated with shallow groundwater and with a short residence time, explaining why 76% of Quaternary deposit aquifers are Ca-HCO₃ type. They are recently infiltrated and their chemical signature is not very different from rain water. Sodium dominant types are also important water types in

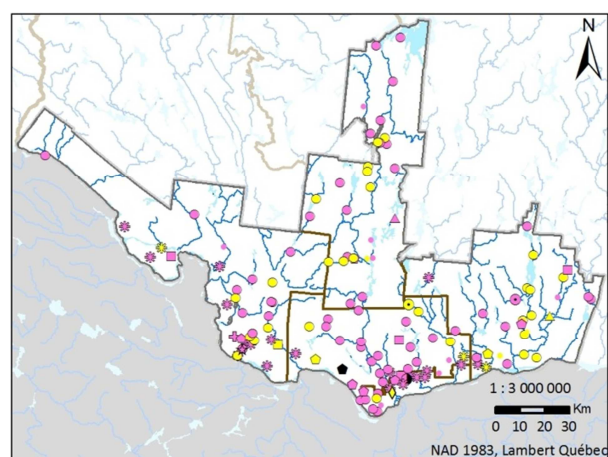
Table 1. Descriptive statistics for the data matrix (units in mg/l).

Parameter	Mean	Median	Min. ¹	Max. ²	Std. ³	Skewness
B	0.163	0.034	0.0025	6.9	0.631	9.9
Ba ²⁺	0.089	0.049	0.001	1	0.144	3.9
HCO ₃ ⁻	188.7	170.4	17.1	572.0	121.2	1.1
Ca ²⁺	47.3	37	1.9	290	39.0	2.7
Cl ⁻	76.71	14	0.39	1100	180.7	3.7
F ⁻	0.52	0.3	0.05	3.6	0.63	2.3
K ⁺	4.27	2.9	0.53	26	4.00	2.4
Mg ²⁺	12.32	7.2	0.71	57	12.33	1.9
Mn ²⁺	0.054	0.011	0.0002	0.63	0.103	3.0
Na ⁺	64.8	12	1.2	860	134.3	3.7
pH	7.93	7.93	5.98	9.66	0.75	-0.2
Si	6.79	6.7	0.05	22	2.44	1.9
SO ₄ ²⁻	43.58	22	0.25	970	97.25	7.8
Sr ²⁺	1.515	0.35	0.032	47	4.797	7.5

¹Min. = minimum

²Max. = maximum

³Std. = standard deviation



Bedrock wells

- Ca-Cl (4)
- Mixed-Cl (1)
- ✦ Na-SO₄ (1)
- Ca-HCO₃ (54)
- ★ Mixed-HCO₃ (1)
- E.B. > $\pm 10\%$ (9)
- Ca-mixed (1)
- Na-Cl (6)
- ▲ Ca-SO₄ (1)
- ✦ Na-HCO₃ (20)

Quaternary deposit wells

- Ca-Cl (1)
- ◇ Mg-HCO₃ (1)
- Ca-HCO₃ (28)
- Na-Cl (2)
- Ca-mixed (1)
- ✦ Na-HCO₃ (3)
- ▲ Ca-SO₄ (1)
- E.B. > $\pm 10\%$ (3)

Unknown aquifer

- Na-Cl (1)

Figure 6. Spatial distribution of water types.

the area (26%) and are found mainly along the Ottawa River and the main tributaries, where the Champlain Sea had invaded inland. Thus, these water types, especially

Na-Cl, seem to be controlled by the remains of the former Champlain Sea.

5 RESULTS OF MULTIVARIATE STATISTICAL ANALYSIS

5.1 Principal Component Analysis (PCA) and Factor Analysis (FA)

From the standardized dataset, a correlation matrix was computed, and eigenvalues and eigenvectors were calculated (Table 2). The eigenvalues represent the weight of each component in explaining the variance within the dataset whereas the eigenvectors are the weight of the parameters on each component. Because the eigenvalues were very similar for the different parameters, the Principal Component Analysis (PCA) results could not be used for the interpretation of the data. For this reason, a factor analysis (FA) was applied.

In the initial stages, FA is very similar to PCA with the calculation of eigenvalues (called factors hereafter). Then, the less important values to explain the variance in the dataset are discarded. There is no consensus in the literature about the choice of the factors to be retained.

Generally, the factors with an eigenvalue greater than one (with a variance greater than the original standardized variables) are kept and are those which explain most of the variance (Davis 1986). In Table 2, the first three factors show eigenvalues greater than one which account for two-thirds of the explained variance.

As mentioned before, the PCA results do not allow the identification of the parameters defining the components (factors). Therefore, a varimax rotation was applied, changing the position of the axis in order to maximize the variance of the loadings on the factors. This results in only a few significant high loadings for each factor, improving the interpretation of the results (Davis 1986).

According to Table 3, the first factor is characterized by high loadings for SO_4^{2-} , Cl^- , Na^+ and Sr^{2+} , which are related to saline water and consistent with the geological history of the region (invasion by the Champlain Sea). The second factor presents high loadings for silica. This factor could be associated with silicate dissolution since the area is mainly covered by silicate rocks. Although silicate weathering is a slow process, it seems to be more important than calcite or dolomite dissolution (although HCO_3^- and Mg^{2+} have higher loadings in Factor 1 and 2). The third factor seems to be associated with the dissolution of F bearing minerals at high pH such as fluorite which is mined in the study area.

Results of the PCA coupled to FA give a preliminary idea of the main chemical processes occurring in the study area and which control the groundwater chemistry.

5.2 Hierarchical Clustering Analysis (HCA)

HCA was applied to the standardized dataset in order to classify samples according to their similarities. A distance matrix is obtained by calculating the similarity between samples. Groups of samples are formed according to their similarities and are joined using a linkage rule. Several

Table 2. Eigenvalues from the PCA.

Factor	Eigenvalue	Difference	Proportion	Cumulative
1	5.828	3.762	0.416	0.416
2	2.066	0.620	0.148	0.564
3	1.446	0.486	0.103	0.667
4	0.960	0.135	0.069	0.736
5	0.824	0.108	0.059	0.795
6	0.716	0.101	0.051	0.846
7	0.614	0.272	0.044	0.890
8	0.342	0.007	0.024	0.914
9	0.335	0.080	0.024	0.938
10	0.255	0.031	0.018	0.956
11	0.224	0.027	0.016	0.972
12	0.197	0.087	0.014	0.986
13	0.110	0.027	0.008	0.994
14	0.083		0.006	1

Table 3. Factor analysis loadings and explained variance after applying varimax rotation.

Parameter	Factor 1	Factor 2	Factor 3
B	0.623	0.156	0.569
Ba ²⁺	0.301	0.595	-0.051
HCO ₃ ⁻	0.544	0.580	0.177
Ca ²⁺	0.464	0.417	-0.646
Cl ⁻	0.807	0.135	0.084
F ⁻	0.334	0.261	0.748
K ⁺	0.522	0.520	0.458
Mg ²⁺	0.602	0.637	-0.139
Mn ²⁺	0.100	0.542	0.089
Na ⁺	0.749	0.169	0.500
pH	0.045	0.005	0.745
Si	-0.260	0.763	0.083
SO ₄ ²⁻	0.848	-0.081	0.058
Sr ²⁺	0.732	0.314	0.055
Explained variance	4.285	2.660	2.396
Explained variance (%)	30.6	19.0	17.1
Cumulative % of variance	30.6	49.6	66.7

distance measure methods as well as linkage rules are available. Güler et al. (2002) tested different combinations of distance measures with linkage rules and concluded that Euclidian distance together with Ward's method for linkage produce the most distinctive groups.

The results of the HCA are displayed as a dendrogram (Figure 7). Chemical groups are identified from the tree. To divide the samples into groups, a line, called the phenon line, was drawn for a value of 0.025. Seven clusters were identified with their own characteristics. According to Figure 7, clusters 1 and 2 are quite different from the five other clusters. Clusters 3, 4 and 5 are more similar. Note that cluster 5 is composed of only one sample

On the left side of Figure 7, average Stiff diagrams are represented for each cluster. Stiff diagrams only display

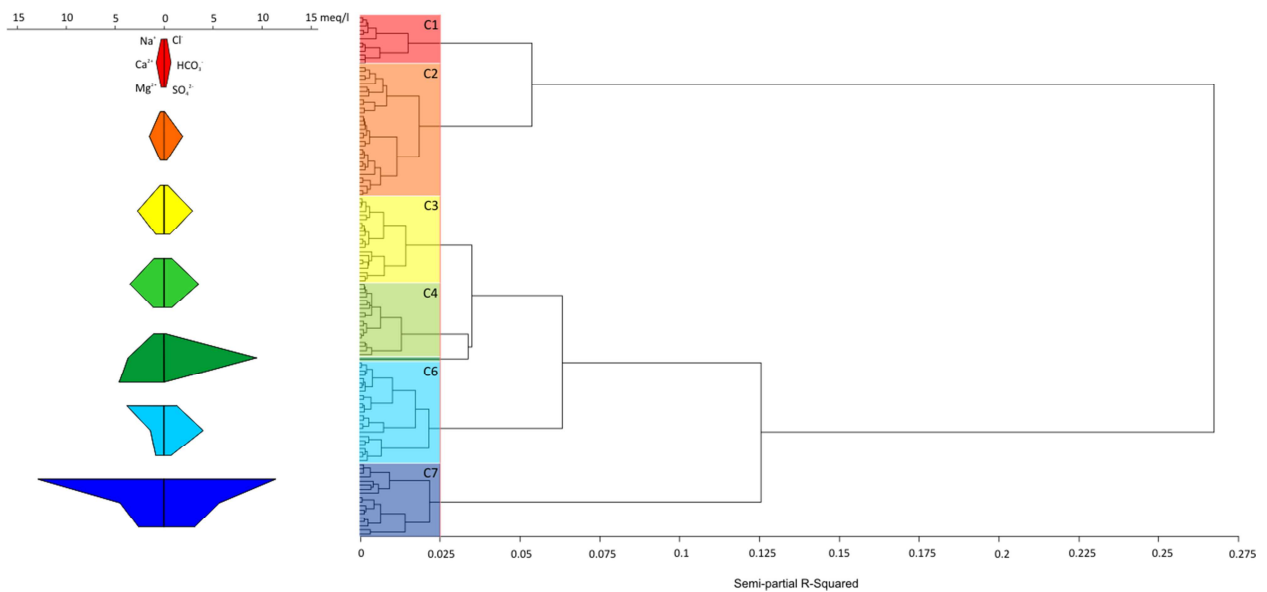


Figure 7. Dendrogram for the groundwater samples (names not displayed for the sake of clarity) and identification of the clusters.

concentrations for major ions in milli-equivalents per liter. The differences and the similarities of each cluster can easily be identified. Stiff diagrams for clusters 1 to 4 show similar shapes, with Ca^{2+} and HCO_3^- as predominant ions. In these groups, Ca- HCO_3^- water type is dominant (Table 4). As mentioned previously, these waters are slightly mineralized and probably have short residence times: most Quaternary deposit wells are in these clusters as are most unconfined aquifer wells. Cluster 1 illustrates very low mineralized waters which have infiltrated very recently. Gradually, these waters become mineralized as they dissolve the rock they are migrating through. Stiff diagrams from C1 to C4 show this trend as a widening at the level of Ca^{2+} and HCO_3^- concentrations and also as increasing values of alkalinity, hardness, TDS and other major ions (Table 4). Note that the average chloride concentration for cluster 1 is greater than that for cluster 2 and 3.

Cluster 1 can be divided into two sub-groups of equal size (see the shape of C1 in Figure 7). These two sub-groups are differentiated by their low chloride concentration of less than 4 mg/l for the first sub-group (similar to cluster 2). Generally, this sub-group is characterized by lower concentrations in major ions compared to the second sub-group (except HCO_3^-). In sub-group 2, chloride concentrations are quite high compared to cluster 2 (next in the chemical evolution). Many explanations for this trend could be invoked: a possible contamination by de-icing salts for wells close to main roads or a mixing between young waters and remaining marine water from the Champlain Sea (with high recharge rates for the infiltrated water) for wells located in deltaic and pro-deltaic sediments.

Most minor elements have similar median values for these four clusters. However, clusters 1 and 3 have higher nitrate concentrations. At this level of characterization, it is difficult to provide a reasonable explanation since it cannot be explained by a higher

proportion of unconfined/semi-confined aquifers compared to the two other clusters (C2 and C4). The trend is perhaps related to the location of the wells in relation to farming zones. Cluster 4 is characterized by higher concentrations of Ba^{2+} , Mn^{2+} and Sr^{2+} compared to the three other clusters, suggesting the dissolution of Ba, Mn- and Sr-bearing minerals. Median pH values are acidic for cluster 1 and oxido-reduction potential (ORP) values indicate oxidizing conditions. These characteristics are typical of groundwater in recharge zones.

Cluster 5 includes only one sample and has a quite atypical chemical composition. According to the shape of the Stiff diagram, this sample has a Mg- HCO_3^- water type. This sample also has the highest concentrations in the dataset for the following parameters: HCO_3^- , Mg, Si, Ag, NH_4 and exceedances for Fe, Mn and TDS. Although these high concentrations seem to indicate that the sample has a long residence time, the sample was taken in a shallow sand-point (depth less than 10m). The chemistry of this sample is not yet fully understood.

On the anion side of the Stiff diagram, cluster 6 has the same shape as cluster 4 but on the cation side, a shift can be observed between the concentrations in Na^+ and Ca^{2+} (noticeable in Table 4 as well), indicating cation exchange. Due to Champlain Sea invasion, the superficial part of the bedrock aquifers was invaded by salt water with Na^+ adsorbing onto minerals and retained by clays whose pores were filled with salt water. Since then, these aquifers have been recharged by infiltrated water rich in Ca^{2+} , which replaces Na^+ on minerals and clays. Samples in this cluster present various degrees of cation exchange, are generally Na- HCO_3^- water type and were taken from confined aquifers under reducing conditions (Table 4).

Samples from cluster 7 are characterized by high concentrations in Na^+ and Cl^- and are mainly Na-Cl water type. Most of the Na^+ and Cl^- concentrations are above drinking water standards (200 and 250 mg/l, respectively)

Table 4. Characteristics of the different clusters (C5 not included since it is only one sample the description of which is provided in the text).

	C1 (12)	C2 (32)	C3 (21)	C4 (18)	C6 (25)	C7 (19)
Water type	Ca-HCO ₃ (7) Ca-Cl (2); Ca-SO ₄ (1); Na-HCO ₃ (1); Ca-mixed (1)	Ca-HCO ₃ (30) Na-HCO ₃ (2)	Ca-HCO ₃ (20) Ca-SO ₄ (1)	Ca-HCO ₃ (17) Ca-mixed (1)	Na-HCO ₃ (18) Ca-HCO ₃ (4); Ca-Cl (1); Mixed-HCO ₃ (1); Na-Cl (1)	Na-Cl (8) Ca-HCO ₃ (4); Ca-Cl (2); Na-HCO ₃ (2); Mixed-Cl (1); Na-SO ₄ (1)
Geology						
Q. sed. ¹	10	8	6	5	5	2
St L.L. ²				1	2	7
H. Bay ³		1			2	
Grenville	2	23	15	12	16	8
Unknown						1
Confinement						
Unconfined	8	19	10	6	5	7
Semi-conf. ⁴	1	4	5	7	1	1
Confined	2	9	6	4	19	9
Unknown	1			1		1
Geographic location	Overall study area, a few samples along the Ottawa River (median elevation: 191, 187, 178 and 168 m.a.s.l. respectively)				Mainly along the Ottawa River, a few samples along main river valleys (median elevation: 138 and 100 m.a.s.l. respectively)	
Median conc. ⁵ (mg/l)						
Ca ²⁺	17	29.5	54	68	23	86.5
Mg ²⁺	3.05	4.65	6.6	13	9.4	33
Na ⁺	6.55	5	7.4	17.5	69	225
K ⁺	1.35	1.95	1.9	3	6.8	7.85
HCO ₃ ⁻	42.7	107	158	200	201	346
Cl ⁻	9.05	1.1	8.4	36.5	27	350
SO ₄ ²⁻	8.25	15.5	21	34	25	80.5
B	0.00925	0.017	0.02	0.02	0.14	0.335
Ba ²⁺	0.0145	0.033	0.028	0.18	0.055	0.061
Br ⁻	L.D.	L.D.	0.05	L.D.	0.1	0.375
F ⁻	L.D.	0.25	0.1	0.2	0.8	0.7
Mn ²⁺	0.0016	0.0135	0.00083	0.051	0.019	0.016
NH ₄ ⁺	0.04	0.03	0.02	0.025	0.14	0.165
NO ₃ -NO ₂	0.65	0.05	0.85	0.045	0.03	0.15
Si	5.5	6.4	7.3	6.55	6.6	7.1
Sr ²⁺	0.0905	0.22	0.21	0.435	0.64	1.9
Alkalinity	35	89	130	165	180	285
Hardness	59	90	176	224	104	333
TDS	111	184	304	404	452	1054
pH	6.69	8.3	7.72	7.54	8.6	8.01
ORP (mV)	-1.5	-160	-24	-63	-275	-147
O ₂ (%)	72	4.9	38	5	1.8	12.6

¹ Quaternary sediments

² St Lawrence Lowlands Platform

³ Hudson Bay Platform

⁴ Semi-confined

⁵ Median concentrations

⁶ Oxido-reduction potential

as well as all the TDS values (500 mg/l). The median concentrations for the other major ions and for minor constituents are the highest among all clusters (except for Ba²⁺, Mn²⁺ and NO₃-NO₂).

Similar to cluster 1, cluster 7 can be divided into two sub-groups. The first sub-group of 8 samples (higher branch of C7 on Figure 7), has similar amounts of Na⁺/Ca²⁺ and Cl⁻/HCO₃⁻. Most of the samples come from unconfined to semi-confined aquifers and appear to be a

mixture of younger waters (Ca-HCO₃ type) and older waters from the Champlain Sea (Na-Cl type). Indeed, a recharge signature is seen in samples from the St Lawrence Lowlands Platform (Ca-HCO₃), or reflects a mixed water type (Ca-Cl). There are two exceptions: one sample is Na-HCO₃ and the other Na-Cl which might be explained by the prevalence of cation exchange or the degree of mixing between the younger and older waters. The second sub-group, of 10 samples (lower branch of

C7 on Figure 7), includes samples of Na-Cl water type and also Na-HCO₃, Na-SO₄ and mixed-Cl (one sample each). Most samples are from confined aquifers. Due to confinement by marine clays, they represent diluted sea water, with less mixing than in the first sub-group.

One important point to emphasize is the importance of hydrogeological conditions over the geology. This can be illustrated using 10 samples taken from the St Lawrence Lowlands bedrock which is composed mainly of limestone. Therefore, groundwater is expected to be Ca-HCO₃ type. Most of these samples belong to clusters 6 and 7. Half of the samples were taken from unconfined/semi-confined aquifers and the second half from confined aquifers. Samples from unconfined or semi-confined aquifers are all Ca-HCO₃ water type whereas samples from confined aquifers are Na-HCO₃ or Na-Cl water type (except one of Ca-HCO₃ type). The geological history of the region, i.e. Champlain Sea invasion and the presence of marine clays, influence and control the hydrochemistry of these samples.

6 CONCLUSIONS AND PERSPECTIVES

A groundwater quality assessment of the Outaouais Region was carried out thanks to the collection of 139 samples. After discarding analyses of poor quality, water types were defined for the 127 remaining samples. Ca-HCO₃ is the dominant water type in the study area, which characterizes waters with low to medium mineralization, located in recharge areas at higher elevations. Other important water types are Na-HCO₃ and Na-Cl which result from the geological history of the region.

These observations are supported by a multivariate statistical analysis. PCA allows identifying parameters explaining the variance between the samples and grouping them together according to their behavior. The first component was found to be related to salinity parameters (SO₄²⁻, Cl⁻, Na⁺ and Sr²⁺), the second to the silica content (silicate dissolution) and the third to the dissolution of F bearing minerals under high pH conditions. Thus, PCA gives a first idea of the processes involved in the chemical evolution of groundwater. Using HCA, samples were classified into groups according to their similarity. Seven clusters were defined with clusters 1 and 7 divided into two sub-groups. The definition of the clusters closely follows the classification by water types. Samples from clusters 1 to 4 are mainly Ca-HCO₃ water type with increasing mineralization from C1 to C4. The division of cluster 1 into two sub-groups was justified by the higher concentrations in Cl⁻ for sub-group 2, indicating potential contamination by de-icing salts or mixing of young waters with residual marine water whereas sub-group 1 has a signature of recharge waters. Cluster 6 helps in identifying cation exchange between Na⁺ from the marine episode and Ca²⁺ from recharge waters (Na-HCO₃ water type). Finally, cluster 7 can be divided into two sub-groups showing various degrees of marine water dilution according to the unconfined/semi-confined or confined aquifer conditions (Ca-HCO₃ vs Na-Cl).

On-going work is focusing on better identification of the main and minor chemical processes. Nonetheless,

these results are in agreement with conclusions of other studies carried in the Québec region, where the Champlain Sea was also present (Blanchette 2010 and Cloutier 2006).

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