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Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system

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Summary The study of groundwater hydrogeochemistry of the Paleozoic Basses-Laurentides sedimentary rock aquifer system in Québec produced a large geochemical dataset. Groundwater samples were collected at 153 sites over a 1500 km² study area and analyzed for major and minor ions. The large number of data can lead to difficulties in the integration, interpretation and representation of the results. Two multivariate statistical methods, hierarchical cluster analysis (HCA) and principal components analysis (PCA), were applied to a subgroup of the dataset to evaluate their usefulness to classify the groundwater samples, and to identify geochemical processes controlling groundwater geochemistry. This subgroup consisted of 144 samples and 14 parameters (Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, SO₄²⁻, Fe²⁺, Mn²⁺, Br⁻, Sr²⁺, F⁻, Ba²⁺, HS⁻). Seven geochemically distinct clusters, C1–C7, resulted from the HCA. Samples from clusters C3, C4, C6 and C7 are mostly located in preferential recharge areas. The majority of these samples have Ca–Mg–HCO₃ recharge groundwater (C3, C6, C7) and Na–HCO₃ evolved groundwater (C4). Samples from the other three clusters (C1, C2, C5) are characteristic of an aquifer system under confined conditions. The majority of these samples have Na–HCO₃ evolved groundwater (C1, C5) and Na–Cl ancient groundwater that exhibits elevated concentrations in Br⁻ (C2). In addition to recognizing the importance of hydrogeological conditions on groundwater geochemistry, the distribution of clusters also showed the importance of the geological formations on minor and trace elements, such as Fe²⁺, Mn²⁺, Sr²⁺, F⁻ and Ba²⁺. The first five components of the PCA account for 78.3% of the total variance in the

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dataset. Component 1 is defined by highly positive loadings in Na^+ , Cl^- and Br^- and is related to groundwater mixing with Champlain Sea water and solute diffusion from the marine clay aquitard. The high positive loadings in Ca^{2+} and Mg^{2+} of component 2 suggest the importance of dissolution of carbonate rocks in this aquifer system. From their characteristic loadings, the first two components are defined as the "salinity" and "hardness" components, respectively. Components 3–5 are related to more local and geological effects. The integration of the HCA and the PCA, with conventional classification of groundwater types, as well as with the hydrogeological and geological contexts, allowed the division of the region into four main geochemical areas, providing an improved regional picture of the aquifer system dynamics and hydrogeochemical evolution of groundwater. The following factors were recognized as influencing the evolution of groundwater identified in every geochemical area: (1) geological characteristics including sedimentary rock type and till mineralogy; (2) hydrogeological characteristics represented by the level of confinement and the hydraulic gradient; and (3) the geological history including the latest glaciation and the Champlain Sea invasion. With its integrated approach, this hydrogeochemical study contributes to the characterization and understanding of complex groundwater flow systems, and provides an example of the long-term geochemical evolution of hydrogeological systems after a major perturbation, in this case seawater invasion.

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Introduction

The study area is located on the North shore of the St. Lawrence River, northwest of Montréal, in a geographical region named the Basses-Laurentides (Fig. 1). Groundwater hydrogeochemistry of the Basses-Laurentides aquifer system was studied extensively as part of a regional hydrogeological characterization project (Savard et al., in press). Cloutier et al. (2006) presented results of the regional groundwater hydrogeochemical characterization and the relationship between groundwater types and geological as well as hydrogeological contexts, with the specific objective of identifying the origin of groundwater in the aquifer system.

The hydrogeochemical characterization of the Basses-Laurentides aquifer system involved groundwater sampling

at 153 sites over a 1500 km² study area and groundwater analysis for 47 parameters including in situ field measurements, inorganic constituents and isotopic indicators (Cloutier, 2004; Cloutier et al., 2006). In this previous work, we used different maps and graphical representations to classify and interpret the geochemical data, such as: dot map of chemical parameters, Piper diagram (Piper, 1944), Stiff pattern diagram, box plots and scatterplots of chemical parameters. The knowledge, the understanding and the particularities of the hydrogeochemistry of this aquifer system represent a great opportunity to further apply multivariate statistical analysis, a quantitative approach allowing to classify groundwater samples, to study correlations between the variables (chemical parameters), and to evaluate the similarity between the observations (groundwater sampling sites).

Our scientific objective was to better identify the processes controlling the geochemical evolution of groundwater in the study area by using two well-proven multivariate methods to analyze the geochemical data, hierarchical cluster analysis (HCA) and principal components analysis (PCA). Given the relatively complex setting and geological history of the study area, our hope was that HCA and PCA could help distinguish the role of geological and hydrogeological contexts on this evolution. A methodological objective of the study was also to assess the relative applicability and complementarity of HCA and PCA in achieving the scientific objective, compared to conventional geochemical grouping. Finally, as an aid to management and future development of groundwater resources in the region, these approaches were also applied to divide the territory in areas with distinct groundwater quality.

Multivariate statistical analysis has been successfully applied in a number of hydrogeochemical studies. Steinhurst and Williams (1985) used multivariate statistical analysis of water chemistry data in two field studies to identify groundwater sources. In their application of multivariate analysis to chemical data, Usunoff and Guzmán-Guzmán (1989) demonstrated the usefulness of the approach in

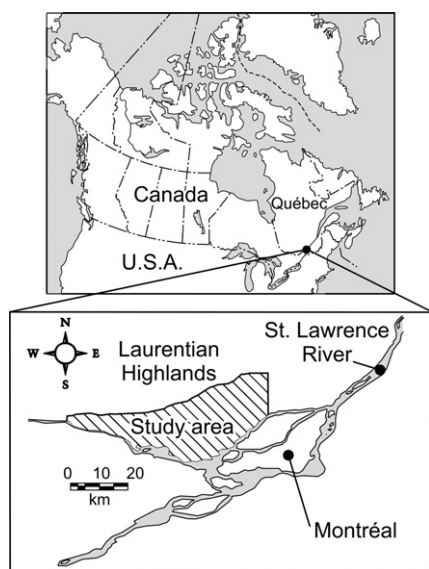


Figure 1 Location of the Basses-Laurentides sedimentary rock aquifer system.

hydrogeochemical investigations when considering the geological and hydrogeological knowledge of the aquifer. Meloul and Collin (1992) used PCA to supplement classical geochemical methods such as Scholler and Piper diagrams and successfully identified major water groups and factors affecting groundwater quality in an aquifer. Schot and van der Wal (1992) applied principal components and clusters analysis to hydrochemical data to show the regional impact of human activities on groundwater composition. In the study of Farnham et al. (2003), the application of multivariate statistical analysis to trace element chemistry of groundwater helped identify rock–water interaction processes and groundwater redox conditions. All the hydrogeochemical studies mentioned above show that multivariate statistical analyses significantly help to classify groundwater and identify major mechanisms influencing groundwater chemistry. When the hydrogeochemical interpretation is combined with the knowledge of the geological and hydrogeological setting, multivariate statistical methods can also help understand groundwater flow in complex aquifer systems (Farnham et al., 2000; Stetzenbach et al., 2001).

Context of the study area

Geology and hydrogeology

The Basses-Laurentides belong to the St. Lawrence Lowlands, a physiographic region having a generally flat topography, with the exception of the Monteregian Hills related to Cretaceous intrusions. The Laurentian Highlands, part of the Grenville Province of the Canadian Shield, border the study area to the North. The southwest, south and southeast borders are surface water limits, namely the Outaouais River, the Deux Montagnes Lake and the Mille îles River. To the East, the study area ends in the watershed of the Mascouche River (Fig. 2a).

The Basses-Laurentides aquifer system consists of nearly horizontal Cambrian–Ordovician sedimentary formations lying unconformably on crystalline basement of the Precambrian Grenville Province (Fig. 2a). The Cambrian Potsdam Group is divided into two formations; the Covey Hill, a reddish feldspathic sandstone, locally conglomeratic and poorly cemented, and the Cairnside, a well-cemented, pure, quartz arenite sandstone (Globensky, 1987). Salad Hersi et al. (2003) subdivide the Ordovician Beekmantown Group into three formations; the dolomitic sandstone and sandy dolostone of the Theresa, the sandy to pure, massive, dolostone of the Beauharnois, and the pure dolostone with sommital limestone of the Carillon. Following are the sandstone of the Lower Chazy, and the limestone and shale of the Upper Chazy Group, the dolostone, shale and limestone of the Black River Group and the limestone and shale of the Trenton Group (Globensky, 1987). More details on the lithology, mineralogy and fracture filling of the sedimentary formations are provided by Cloutier (2004).

In the study area, the sedimentary formations rarely outcrop, as Quaternary sediments cover them. During the deglaciation, the retreat of the Laurentide Ice Sheet of the St. Lawrence Valley, combined with the depression of the continent due to the glaciation, allowed a marine invasion from the St. Lawrence Gulf which created the Cham-

plain Sea. The Champlain Sea water was a mixture of continental waters, including meltwater from the Laurentide Ice Sheet and local precipitation, and salt water from the St. Lawrence Gulf (Hillaire-Marcel, 1988; Cloutier et al., 2006). The Champlain Sea episode left marine sediments, mainly clayey-silts to silty-clays, that can reach a thickness of more than 80 m (Bolduc and Ross, 2001). The Champlain Sea clay is overlying till or glacio-fluvial sand and gravel units of variable thickness. The till is also found at ground surface, above the rock sequence, in elevated topography areas. The composition of the till relates mainly to the glacial erosion of Paleozoic sedimentary formations, such as sandstone, dolostone and limestone, with some influence of Precambrian rocks (Ross and Bolduc, 2001).

Groundwater recharge preferentially occurs where unconfined or semi-confined conditions prevail due to a thin Quaternary cover (Fig. 2b). On the remaining territory, thick low permeability Champlain Sea clays confine the aquifer system (Fig. 2b). These conditions prevail in three southwest–northeast trending buried valleys, and in the eastern region of Ste. Anne-des-Plaines where the clay reaches a thickness of more than 30 m. The main groundwater flow paths of the regional rock aquifer are generally from North to South (Fig. 2c). The potentiometric surface follows the bedrock or surface topography, and is higher in the preferential groundwater recharge areas. Cross-section A–A' illustrates the groundwater flow conceptual model and presents the main hydrostratigraphic units adapted from Savard et al. (in press) (Fig. 2d). The unconfined conditions, that characterize areas of preferential groundwater recharge, are generally areas of elevated topography, sometimes with rock outcropping or with thin to thick permeable surface sediments, generally till. At distance from the recharge zone, the aquitard unit, consisting of thick low permeability Champlain Sea clays, confines the rock aquifer such as for buried valleys. Based on hydrogeological and geological properties, the aquifer system is divided into two distinct units: (1) the highly fractured and (2) the fractured rocks. The highly fractured rock consists of the first few meters of the sedimentary units that are more weathered, with a more developed and better interconnected fracture network than in the underlying rock. A mixed unit, consisting of highly fractured rock in hydraulic connection with sand and gravel, is also observed in the buried valleys (Nastev et al., 2005).

Hydrogeochemistry

Cloutier et al. (2006) identified groundwater types according to major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (HCO_3^- , Cl^- , SO_4^{2-}) and showed that the Basses-Laurentides aquifer system has a highly variable groundwater geochemistry. Four main groundwater groups were identified, G1–G4 (Cloutier, 2004) and their distribution in the study area indicates that the hydrogeological conditions exert an important control on the geochemistry of the groundwater. The preferential recharge areas are characterized by Ca–Mg– HCO_3 modern groundwater (G1) as well as Ca– SO_4 and Na– SO_4 groundwater (G4). Submodern Na– HCO_3 groundwater (G2) and Na–Cl groundwater (G3) characterizes the aquifer under confined conditions.

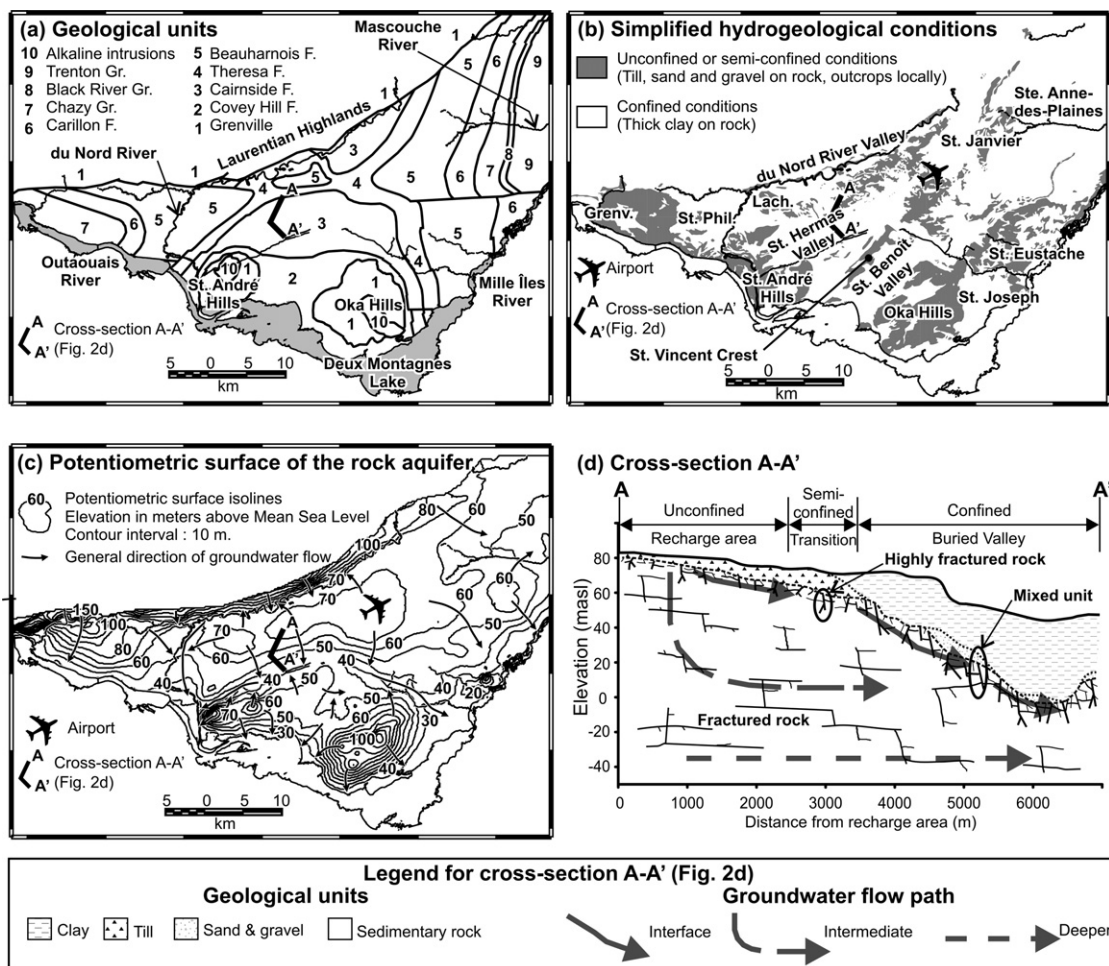


Figure 2 Context of the study area: (a) geology (map modified from Rocher et al., in press), (b) hydrogeological conditions (Grenv.: Grenville; St. Phil.: St. Philippe; Lach.: Lachute) (map modified from Hamel et al., 2001), (c) potentiometric surface (map modified from Nastev et al., 2005) and (d) cross-section A–A' illustrating the groundwater flow conceptual model and the main hydrostratigraphic units (modified from Cloutier et al., 2006).

Methodology

Hydrogeochemical dataset

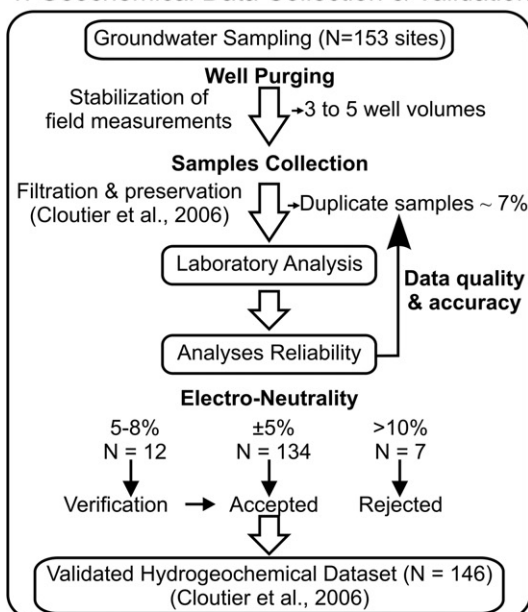
The regional hydrogeochemical characterization of the Basses-Laurentides aquifer system was carried out in 1999 and 2000 with the groundwater sampling of private, municipal and observation wells. The top part of Fig. 3 presents a summary of the sampling protocol and the methodology used for geochemical data collection. Groundwater samples were collected at 153 sites, to a maximum depth of about 140 m. The sampled sites, distributed over the whole region, cover all permeable hydrostratigraphic units: the surface sediments such as till, the sediments under clay deposits, the mixed unit consisting of highly fractured rock and sediments under clay deposits, and the fractured rock units. A rigorous, but conventional and recognized, protocol was used for samples collection and preservation, and the chemical analyses were performed in certified laboratories using standard methods. The complete sampling and analytical protocols are detailed in Cloutier et al. (2006). Of the 153 samples, 7 groundwater samples with an electro-neu-

trality above 10% were rejected as they were generally missing major ions. In situ field measurements were made on water samples for temperature (T), pH, electrical conductivity (EC), dissolved oxygen (DO) and redox potential (Eh). Groundwater samples were analyzed for major, minor and trace inorganic constituents for a total of 36 parameters, plus stable isotopes $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}_{\text{DIC}}$, and some samples were also analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H and ^{14}C of DIC. The complete hydrogeochemical dataset of the 146 sites is presented as electronic supplementary material by Cloutier et al. (2006).

Data preparation for the multivariate statistical analysis

As mentioned, each sampling site is characterized by a large number of chemical and physical variables, making the regional hydrogeochemical study a multivariate problem. The multivariate statistical analysis is a quantitative and independent approach of groundwater classification allowing the grouping of groundwater samples and the making of correlations between chemical parameters and ground-

1. Geochemical Data Collection & Validation



2. Multivariate Statistical Analysis

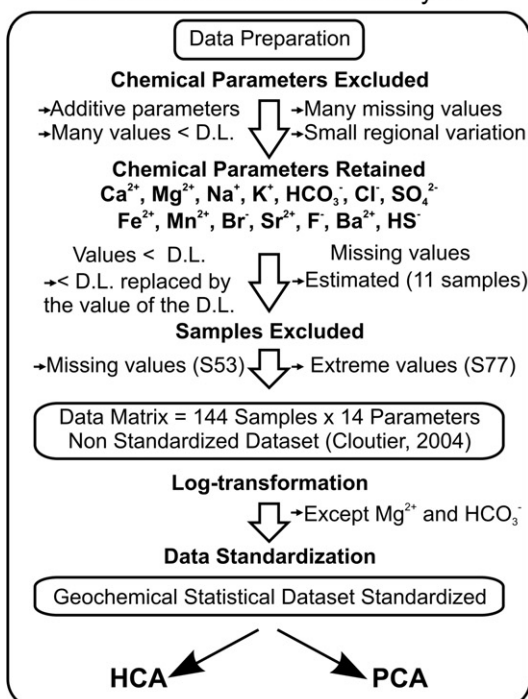


Figure 3 Methodological flow chart, from groundwater sampling to data analysis (D.L.: detection limit).

water samples. In this study, two multivariate methods were applied using Statistica version 6.1 (StatSoft Inc., 2004): the hierarchical cluster analysis (HCA) and the principal components analysis (PCA). The description of HCA and PCA techniques and the methodology used for their application are detailed in Cloutier (2004).

The lower part of Fig. 3 is a summary of the methodology used in the preparation of geochemical data for multivariate statistical analysis. The multivariate statisti-

cal methods were applied to a subgroup of the whole hydrogeochemical dataset that consists of 146 groundwater samples and 14 parameters, as presented in Cloutier (2004). These parameters include major constituents Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , HCO_3^{-} , Cl^{-} and SO_4^{2-} , as well as minor and trace constituents Fe^{2+} , Mn^{2+} , Br^{-} , Sr^{2+} , F^{-} , Ba^{2+} and HS^{-} . Thus, a certain number of parameters were excluded from the multivariate statistical analysis for the following reasons: parameters with additive characteristics such as EC and TDS, parameters with an elevated number of samples below the detection limit such as NO_3^{-} , PO_4^{3-} , Al^{3+} and most trace constituents, parameters missing or not analyzed for a large number of sampling sites such as T , DO , Eh , $\delta^{13}\text{C}_{\text{DIC}}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H and ^{14}C of DIC, and parameters that show small regional variation such as SiO_2 , pH , $\delta^2\text{H}$ and $\delta^{18}\text{O}$.

For multivariate statistical analysis, the parameters with values of concentration lower than the detection limit, the censored data, have to be replaced. A number of methods exist to replace censored data (Alley, 1993; Güler et al., 2002). For this study, it was chosen to replace the censored data by the value of the detection limit. Twelve sampling sites have missing values for one or two chemical parameters among the following: SO_4^{2-} , Fe^{2+} , Br^{-} , Sr^{2+} , F^{-} , or HS^{-} . In HCA, a missing value in a chemical parameter will automatically exclude the corresponding sample from the analysis. To avoid sample exclusion, an evaluation was made for the 12 sampling sites to determine if the missing elements could be estimated by averaging values of nearby sampling sites. In the case of two samples with missing SO_4^{2-} , values were estimated from the electro-neutrality of the samples. Estimation of missing values was possible for 11 out of the 12 samples. Güler et al. (2002) discuss different statistical methods and geochemical relationships that can be used to estimate missing values. Site S53 was excluded from the multivariate statistical analysis as the estimation of missing values for Fe^{2+} and F^{-} could not be justified for this sample. A second site, S77, was also excluded from the analysis as its TDS is well above the other samples. Thus, the final dataset used for the multivariate statistical analysis is a data matrix of 144 sampling sites (observations) by 14 chemical parameters (variables). Table 1 compiles the descriptive statistics of the parameters for the 144 groundwater samples.

The distributions of most chemical parameters (in mg/L) are highly positively skewed (Table 1) and their frequency diagrams do not follow a normal distribution. Chemical parameters were thus log-transformed, except for Mg^{2+} and HCO_3^{-} whose distribution is close to normal. Finally, standardization was applied to the 12 lognormal and two normal distributions to ensure that each variable is weighted equally. Standardization of the data (X_i) results in new values (Z_i) that have zero mean and are measured in units of standard deviation (s). The standardized data are obtained by subtracting the mean of the distribution from each data and dividing by the standard deviation of the distribution, $Z_i = (X_i - \text{mean})/s$ (Davis, 1986). Log-transformation of positively skewed chemical parameters as well as data standardization are commonly done in multivariate statistical analysis (Steinhorst and Williams, 1985; Schot and van der Wal, 1992; Güler et al., 2002).

Table 1 Descriptive statistics for the 144 groundwater samples (concentrations in mg/L)

Parameters	Mean	Median	Minimum	Maximum	Standard deviation	Skewness
Ca ²⁺	52.6	44.5	0.2	480	48.8	5.1
Mg ²⁺	26.4	26	0.04	76	13.6	0.6
Na ⁺	114.4	42	1.6	1260	191.0	3.3
K ⁺	7.58	5.25	0.13	34	6.30	1.4
HCO ₃ ⁻	312.3	296.9	40.0	922.0	112.4	1.2
Cl ⁻	129	35	0.1	1900	270	3.8
SO ₄ ²⁻	53.7	27.5	0.5	1200	116.6	7.8
Fe ²⁺	0.4694	0.12	0.0007	15	1.4456	8.0
Mn ²⁺	0.0783	0.0175	0.0003	0.93	0.1426	3.1
Br ⁻	0.608	0.04	0.002	14.2	1.934	5.2
Sr ²⁺	1.567	0.445	0.005	29	3.777	4.7
F ⁻	0.54	0.32	0.04	3.2	0.60	2.3
Ba ²⁺	0.187	0.13	0.001	1.1	0.192	2.5
HS ⁻	0.14	0.02	0.02	4.7	0.57	6.6

Results of multivariate statistical analysis

Hierarchical cluster analysis (HCA)

The HCA is a data classification technique. There are different clustering techniques, but the hierarchical clustering is the one most widely applied in Earth sciences (Davis, 1986), and often used in the classification of hydrogeochemical data (Steinhorst and Williams, 1985; Schot and van der Wal, 1992; Ribeiro and Macedo, 1995; Güler et al., 2002).

The main result of the HCA performed on the 144 groundwater samples is the dendrogram (Fig. 4). For this project, the Euclidean distance was chosen as the distance measure, or similarity measurement, between sampling sites. The sampling sites with the larger similarity are first grouped. Next, groups of samples are joined with a linkage rule, and the steps are repeated until all observations have been classified. With this geochemical dataset, Ward's method was more successful to form clusters that are more or less homogenous and geochemically distinct from other clusters, compared to other methods such as the weighted pair-group average. Ward's method is distinct from other linkage rules because it uses an analysis of variance approach to evaluate the distances between clusters (StatSoft Inc., 2004). Other studies used Ward's method as linkage rule in their cluster analysis (Adar et al., 1992; Schot and van der Wal, 1992). Güler et al. (2002) also found that using the Euclidean distance as a distance measure and Ward's method as a linkage rule produced the most distinctive groups.

The classification of the samples into clusters is based on a visual observation of the dendrogram. In our study, the phenon line was drawn across the dendrogram at a linkage distance of about 19 (Fig. 4). Thus, samples with a linkage distance lower than 19 are grouped into the same cluster. This position of the phenon line allows a division of the dendrogram into seven clusters of groundwater samples, named C1–C7. As mentioned by Güler et al. (2002), fewer or greater number of clusters could be defined by moving the position of the phenon line up or down on the dendrogram. This subjective evaluation made HCA a semi-objective method. In this study, the grouping into seven clusters gave the most satisfactory results at forming geochemically distinct clusters,

thus fulfilling the objectives of the classification method.

Observation of the dendrogram reveals some indications of the level of similarity between the seven clusters (Fig. 4). Samples from C1 and C2 are linked to the other clusters at an elevated distance, indicating that these samples are geochemically distinct from the ones of the other five clusters. Among these five clusters, C3 is the less similar as it has a high linkage distance to clusters C4–C7. C4 and C5 have the lower linkage distance between the defined clusters, and thus, have the greater similarity among all clusters. It can thus be expected that the geochemistry of C4 samples would have similarities with the ones of C5. Similarities between the geochemistry of C6 and C7 samples are also expected as both clusters are also linked at a low distance.

To describe the characteristics of each cluster of samples, Table 2 presents the median values of geochemical and physical data, including the 14 chemical parameters used in the HCA, the TDS, the total hardness, and the casing depth of the wells. For these sampling sites, the casing depth generally represents the thickness of surface sediments as boreholes are generally open to the rock aquifer. Thus, an elevated median value of casing depth generally indicates the presence of thick low permeability Champlain Sea clays, suggesting that a majority of the samples of the cluster are under confined conditions. On the other hand, low median values of casing depth indicate a majority of samples under unconfined recharge areas. The median values of the major ions were used to determine a median groundwater type for each cluster using the classification approach presented by Cloutier (2004), and are represented on Stiff diagrams (Fig. 4). Minor and trace constituents with elevated median concentrations are also indicated on Fig. 4, and these are important characteristics of the clusters.

The descriptive statistics and the Stiff diagrams indicate that the seven clusters are geochemically distinct groups of samples (Fig. 4 and Table 2). Samples from C1 have Na–HCO₃ groundwater, are characterized by elevated concentrations in F⁻, Ba²⁺ and HS⁻ and by the lowest total hardness of all clusters. Samples from C2 have Na–Cl groundwater, are characterized by elevated concentrations in Br⁻, and the highest TDS of all clusters. Samples from C3 have Ca–

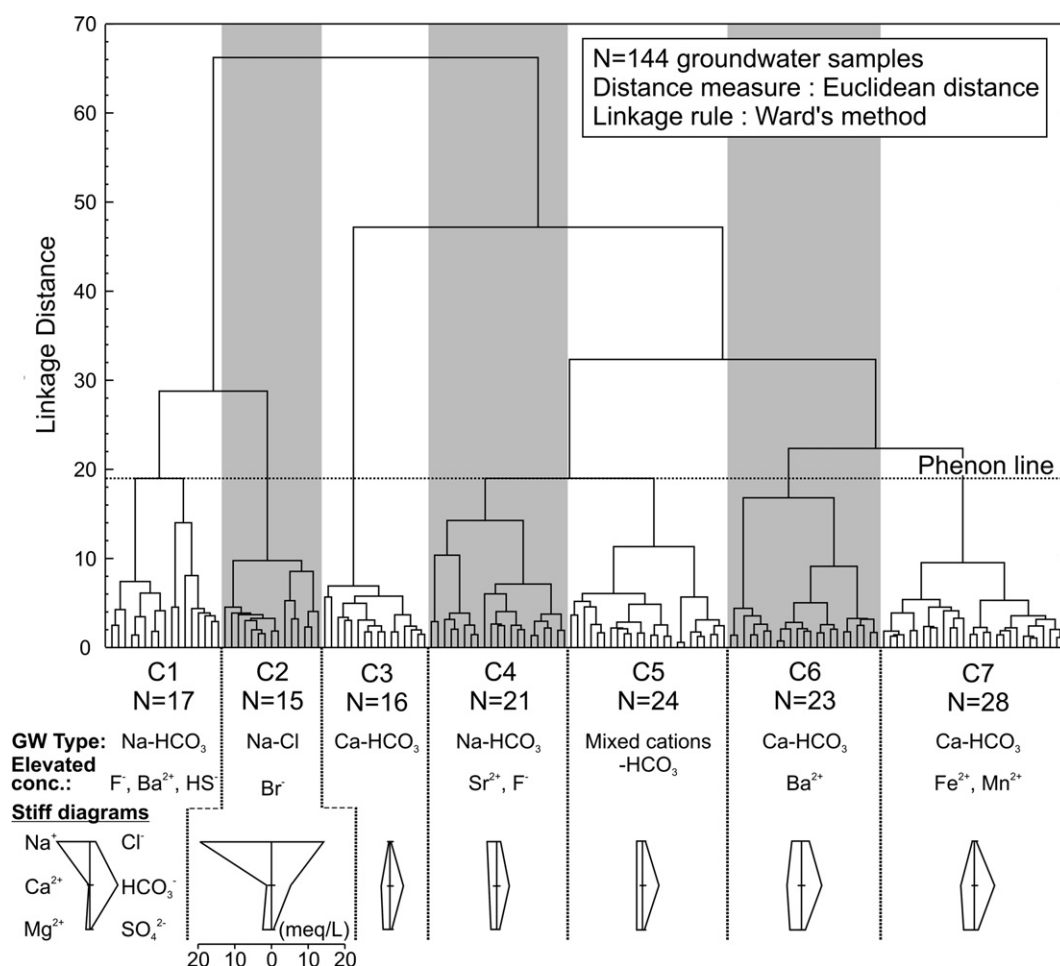


Figure 4 Dendrogram for the groundwater samples, showing the division into seven clusters and the median concentration Stiff diagram of each cluster (GW: groundwater; conc.: concentrations).

HCO₃ groundwater, and have the lowest concentrations for Na⁺ and Cl⁻, as well as for all minor and trace constituents. Samples from C4 and C5 have Na-HCO₃ and mixed cations-HCO₃ groundwater, respectively. The main differences between these two clusters are that C4 has higher Na⁺ concentrations than C5, as well as elevated concentrations in Sr²⁺ and F⁻. C5 has the particularity of having the lowest TDS of all clusters. Samples from C6 and C7, both Ca-HCO₃ groundwaters, have elevated total hardness and elevated SO₄²⁻ concentrations. C6 has elevated Na⁺ and Cl⁻ concentrations relative to C7, as well as elevated concentrations in Ba²⁺. C7 is distinct from C6 by its elevated concentrations in Fe²⁺ and Mn²⁺. The median values of casing depth is above 20 m for C1, C2 and C5, suggesting that a majority of the samples of these cluster are under confined conditions. The clusters C3, C4, C6 and C7 have median values of casing depth below 15 m indicating a majority of samples under unconfined recharge areas.

The relation between chemical elements is studied by performing the HCA for the 14 chemical parameters. The lowest linkage distances in the dendrogram of the 14 chemical parameters are for Na⁺, Br⁻ and Cl⁻ (Cloutier, 2004). Other chemical elements linked at low distance include Fe²⁺ and Mn²⁺, Ca²⁺ and Mg²⁺, as well as Sr²⁺ and F⁻.

Principal components analysis (PCA)

The PCA is a data transformation technique that attempts to reveal a simple underlying structure that is assumed to exist within a multivariate dataset (Davis, 1986). From the standardized geochemical dataset, principal components were extracted on the symmetrical correlation matrix computed for the 14 variables. This method, which is concerned with interrelations between variables, is referred to by Davis (1986) as the R-mode technique.

The number of components to keep was based on the Kaiser criterion, for which only the components with eigenvalues greater than 1 are retained (StatSoft Inc., 2004). As a result, all components that contain a greater variance than the original standardized variables are kept (Davis, 1986). The first five components extracted have eigenvalues greater than 1, and account for 78.3% of the total variance in the dataset. To maximize the variance of the first five principal axes, the Varimax normalized rotation was applied (Usunoff and Guzmán-Guzmán, 1989; Melloul and Collin, 1992; Schot and van der Wal, 1992; Jayakumar and Siraz, 1997; Adams et al., 2001; Aiuppa et al., 2003).

Table 3 presents the principal component loadings for these five components, as well as their respective explained

Table 2 Geochemical and physical characteristics of each cluster (median concentrations in mg/L)

Parameters	C1	C2	C3	C4	C5	C6	C7
N:	17	15	16	21	24	23	28
Ca ²⁺	<u>7.9</u>	25.0	48.5	42.0	35.5	78.0	75.0
Mg ²⁺	<u>14.0</u>	29.0	22.0	17.2	19.8	39.0	35.0
Na ⁺	210.0	450.0	<u>6.5</u>	59.0	40.5	57.0	13.4
K ⁺	14.10	15.00	<u>1.25</u>	4.50	4.80	10.00	4.15
HCO ₃ ⁻	460.0	321.3	226.9	<u>215.4</u>	274.6	346.4	332.8
Cl ⁻	48.0	510.0	<u>8.1</u>	35.0	21.5	73.0	15.0
SO ₄ ²⁻	<u>9.0</u>	22.0	18.5	34.0	15.0	58.0	49.0
Fe ²⁺	0.0190	0.2800	<u>0.0060</u>	0.0290	0.1550	0.1200	0.5400
Mn ²⁺	0.0010	0.0580	<u>0.0003</u>	0.0110	0.0490	0.0150	0.0885
Br ⁻	0.130	2.300	<u>0.010</u>	0.050	0.065	0.034	<u>0.010</u>
Sr ²⁺	0.656	1.100	<u>0.095</u>	2.000	0.330	1.260	0.336
F ⁻	0.99	0.48	<u>0.11</u>	1.00	0.31	0.34	0.16
Ba ²⁺	0.220	0.120	<u>0.075</u>	0.100	0.140	0.210	0.140
HS ⁻	0.20	0.04	<u>0.02</u>	<u>0.02</u>	<u>0.02</u>	<u>0.02</u>	<u>0.02</u>
TDS ^a	368	1131	276	310	<u>239</u>	509	383
Total hardness ^a	<u>72</u>	196	211	158	164	355	336
Casing depth (m)	21	34	10	14	27	15	<u>9</u>

N: Number of samples; bold values: highest values; underlined values: lowest values.

^a Calculated (total hardness as CaCO₃).

Table 3 Principal component loadings and explained variance for the five components with Varimax normalized rotation

Parameters	Component 1	Component 2	Component 3	Component 4	Component 5
Ca ²⁺	-0.287	0.839	0.190	0.019	0.097
Mg ²⁺	0.121	0.851	0.184	0.281	-0.151
Na ⁺	0.927	-0.185	0.040	0.095	0.159
K ⁺	0.600	0.058	0.203	0.425	0.373
HCO ₃ ⁻	0.371	0.013	-0.122	0.696	-0.256
Cl ⁻	0.886	0.212	0.012	0.046	0.038
SO ₄ ²⁻	0.059	0.778	0.030	-0.334	0.116
Fe ²⁺	0.097	0.116	0.876	0.077	0.064
Mn ²⁺	0.046	0.176	0.904	-0.013	-0.083
Br ⁻	0.830	-0.167	0.083	0.115	0.232
Sr ²⁺	0.173	0.241	0.039	0.121	0.850
F ⁻	0.463	-0.303	-0.104	-0.014	0.701
Ba ²⁺	-0.034	0.028	0.226	0.742	0.267
HS ⁻	0.184	-0.362	-0.241	0.473	0.356
Explained variance	3.222	2.471	1.842	1.676	1.754
Explained variance (%)	23.0	17.6	13.2	12.0	12.5
Cumulative % of variance	23.0	40.6	53.8	65.8	78.3

Bold values: loadings > 0.7.

variance. Loadings, that represent the importance of the variables for the components, are in bold for values greater than 0.7 (Table 3). Each component is characterized by a few high loadings, and many near-zero loadings, fulfilling the objectives of the rotation. As mentioned by Davis (1986), maximizing the variance implies maximizing the range of the loadings, which tends to produce either extreme, positive or negative, or near-zero loadings. The first two com-

ponents explain 23% and 17.6% of the variance, respectively, and thus, account for the majority of the variance in the original dataset. Components 3–5 are not as important, and each of these three components explains about the same amount of variance, between 12% and 13.2%.

Component 1 explains the greatest amount of the variance, and is characterized by highly positive loadings in Na⁺, Cl⁻ and Br⁻ (Table 3). Component 2 is characterized by

highly positive loadings in Ca^{2+} and Mg^{2+} and the loading is also high for SO_4^{2-} (Table 3). Fig. 5 summarizes this information by showing the position of the loadings of chemical parameters in the plane defined by the axes of components 1 and 2. A descriptive term is defined for each of the first two components based on their characteristic loadings (Fig. 5). Because of the association of Na^+ and Cl^- , component 1 is defined as the "salinity" component in reference to the salt NaCl. Component 2 is defined as the "hardness" component because of its highly positive loadings in Ca^{2+} and Mg^{2+} , the two ions generally used to calculate hardness. Processes responsible for these highly positive loadings are discussed in the section 'Geochemical interpretation and discussion'.

Each of the last three components explains about 12.5% of variance, indicating that these components are related to more local effects than the first two components. Component 3 is clearly characterized by highly positive loadings in Fe^{2+} and Mn^{2+} , indicating a similar geochemical behavior for both elements (Table 3). Component 4 is characterized by highly positive loadings in Ba^{2+} and loadings are also relatively high for HCO_3^- and HS^- as well (Table 3). Finally, component 5 is characterized by highly positive loadings in Sr^{2+} and F^- (Table 3).

Geochemical interpretation and discussion

Groundwater clusters and groups

The Piper diagram of Fig. 6 presents the groundwater samples labeled according to their respective cluster. To allow

a comparison with the groups defined by Cloutier et al. (2006), envelopes of the groundwater group are reported on the Piper diagram (Fig. 6). Groundwater samples are distributed in the various zones of the diamond-shaped field, mainly the Ca–Mg– HCO_3 , Na– HCO_3 and Na–Cl zones. Higher TDS values characterize samples with Na–Cl groundwater (G3).

For each of the seven groundwater clusters, Fig. 7 documents the distribution of samples into the four groundwater groups. The majority of the samples from C1 belongs to G2 (Na– HCO_3) and C2 to G3 (Na–Cl) (Fig. 7), and occupies the extreme lower and the right zones, respectively, of the diamond-shaped field in the Piper diagram (Fig. 6). Samples from C1 have elevated Na^+ concentrations coupled to low Ca^{2+} concentrations, suggesting that Ca^{2+} – Na^+ ion exchange is an important geochemical process for samples of C1. Low SO_4^{2-} concentrations coupled to elevated HS^- concentrations suggest that sulfate reduction is also an important geochemical process for this cluster (Table 2). Samples from C2 have a Na–Cl groundwater type, associated to elevated concentrations in Br^- (Fig. 4 and Table 2). These characteristic samples were interpreted by Cloutier et al. (2006) to result from groundwater mixing with Pleistocene Champlain Sea water or from solutes diffusion from the marine clay aquitard.

The majority of the samples from C3 belongs to G1 (Ca–Mg– HCO_3), and occupies the extreme left zone of the diamond-shaped field. Groundwater of G1 results from the dissolution of carbonates (Cloutier et al., 2006). Samples from C4 and C5 are found in all groundwater groups, the majority

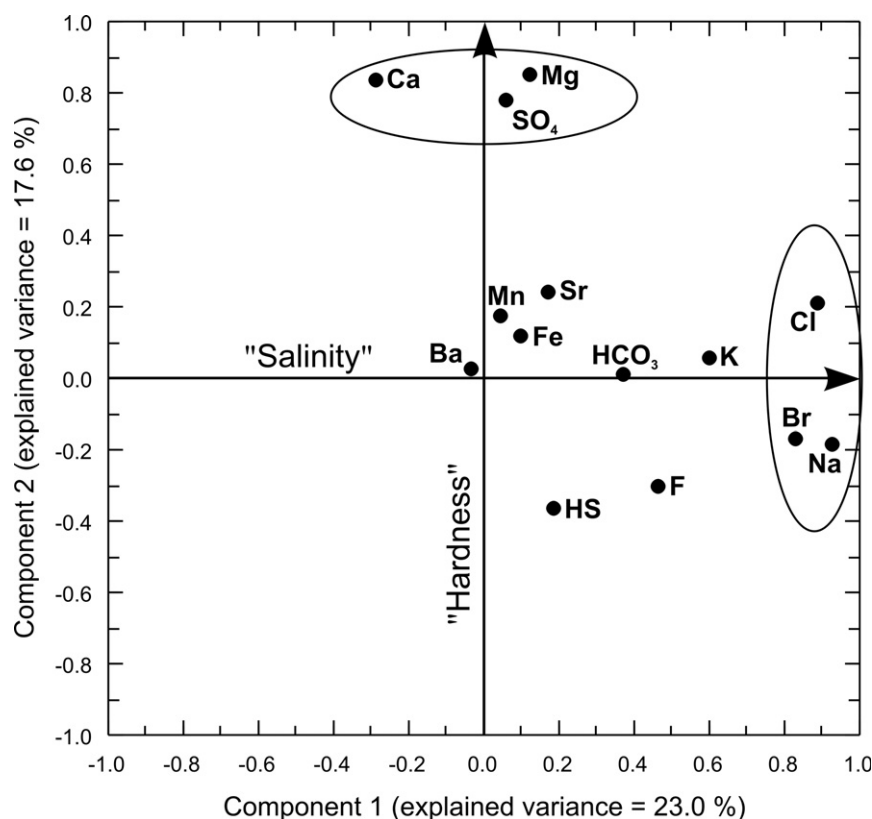


Figure 5 Plot of loadings for the first two components with Varimax normalized rotation.

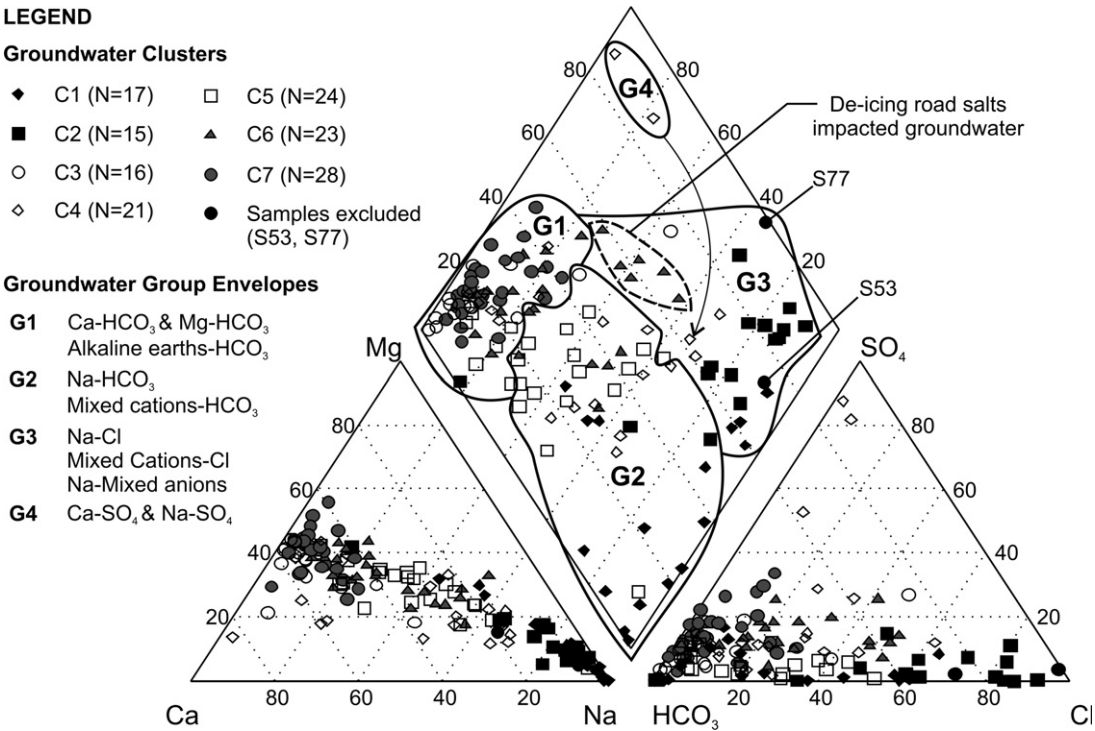


Figure 6 Piper diagram of groundwater samples from the Basses-Laurentides aquifer system labeled according to their groundwater clusters (modified from Cloutier et al., 2006). Groundwater group envelopes are also shown as a reference.

		Groups				N total
		G1	G2	G3	G4	
Clusters	C1	0	13	4	0	17
	C2	1	2	12	0	15
	C3	14	1	1	0	16
	C4	7	9	2	3	21
	C5	8	15	1	0	24
	C6	10	7	6	0	23
	C7	28	0	0	0	28
N total :		68	47	26	3	

Figure 7 Relationship between groundwater clusters and groups (bold numbers indicate the highest values).

of the samples being in G2 and G1, and thus are affected by Ca²⁺–Na⁺ ion exchange and carbonate dissolution. The samples occupy an intermediate zone between the extremes of C3, C1 and C2 (Fig. 6). All samples from C7 belong to G1, and C6 has samples in G1–G3 envelopes. Samples from C6 and C7, both Ca–HCO₃ groundwaters, are thus affected by dissolution of carbonates (Fig. 4). A modern salinity source, de-icing road salts, was identified in samples from a recharge area and could be distinguished by its Cl/Br ratio

(Cloutier, 2004). These Na–Cl groundwater samples, located close to main roads, all belong to C6, thus explaining the elevated Na⁺ and Cl[–] concentrations of C6 relative to C7 (Fig. 6 and Table 2).

This section shows the close link that exists between the groundwater clusters identified here and the groups defined by Cloutier et al. (2006). Considering that major ions are included in the HCA, this link is consistent as the classification in groundwater groups indicated a major ion chemistry controlled mainly by the hydrogeological conditions (Cloutier et al., 2006). As will be discussed below, the presence of minor and trace elements is an advantage for the HCA because it enables the recognition of the distinct minor element signature related to various geological formations.

Hydrogeological context

Fig. 8 presents plots of the principal component scores for the first two components. The scores represent the influence of the component on the groundwater samples. In Fig. 8a, the samples are labeled with the known hydrogeological conditions for the sampling sites. Grouping of samples is possible into this plane defined by the axes of components 1, the “salinity”, and component 2, the “hardness”. Samples from unconfined and semi-confined areas, as well as from surface sediments and springs, dominate in the upper-left quadrant of the diagram. Thus, these are characterized by elevated hardness and lower salinity. On the other hand, samples from confined areas dominate in the lower-right quadrant of the diagram, and thus are characterized by elevated salinity and lower hardness. The scores of the samples indicate that both first components,

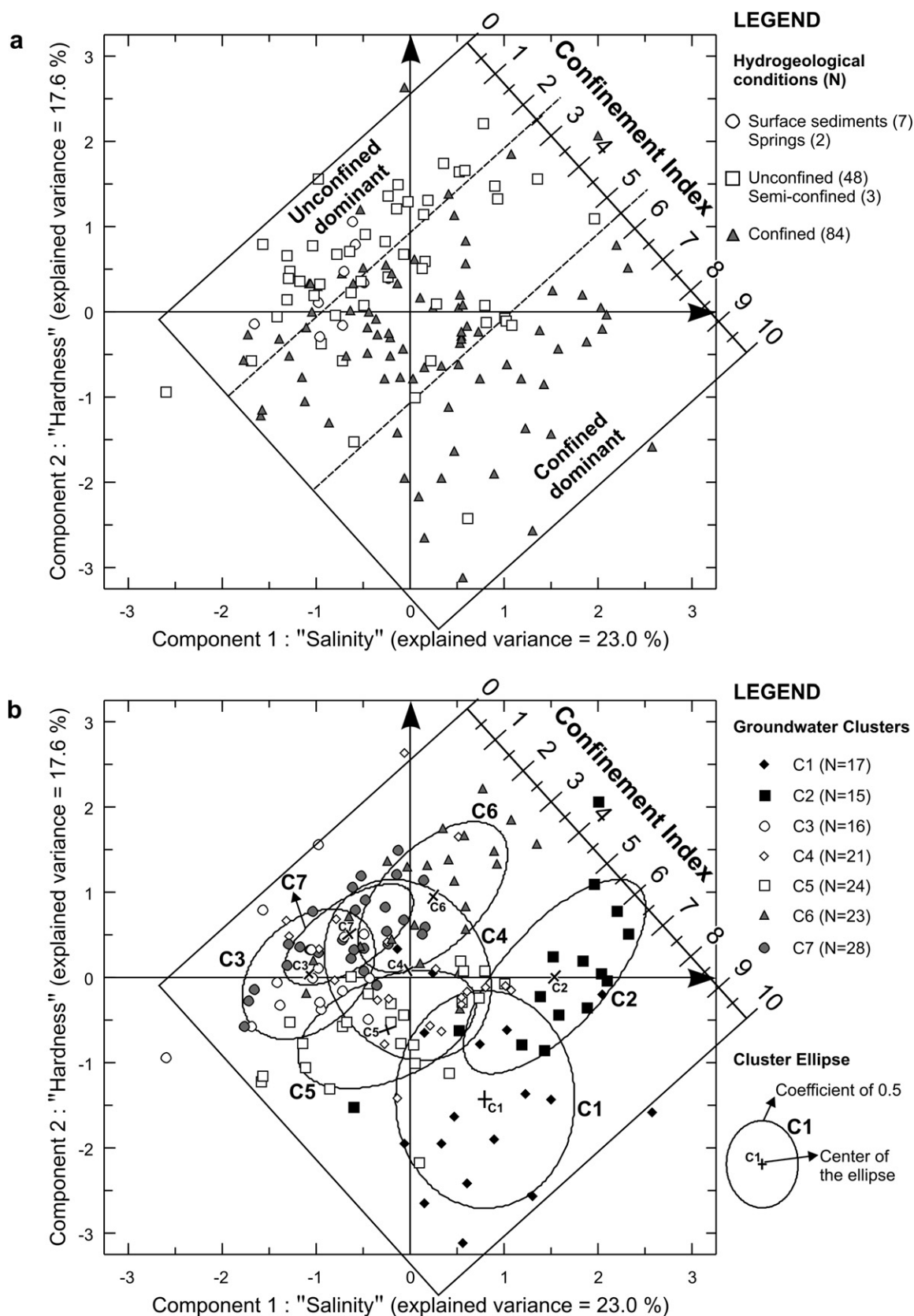


Figure 8 Plot of principal component scores for the first two components for the water samples labeled with (a) the hydrogeological conditions, with the definition of the Confinement Index, and (b) the groundwater clusters, with ellipses at a coefficient of 0.5 for each cluster.

the “salinity” and the “hardness”, are to some extent dependant, or related to, the hydrogeological context.

A Confinement Index (CI), based on the distribution of the scores of components 1 and 2, is defined to integrate both components into a unique parameter (Fig. 8a). We developed this novel, site-specific, index to interpret the PCA and HCA results within the hydrogeological setting. CI ranges from unconfined conditions, at CI = 0, to confined conditions, at CI = 10. The index gives an “apparent” level of confinement for each sampling site. Confinement was chosen to relate components 1 and 2 as it is a parameter based on field knowledge of each sampling site. The “apparent” unconfined conditions dominate at a CI lower than 2.5, and the “apparent” confined conditions dominate at a CI above 5.5. From a CI of 2.5 to 5.5, the sampling sites are defined as “apparent” semi-confined.

Fig. 8b presents the same data as Fig. 8a, the groundwater samples being labeled this time with their respective cluster defined previously. Ellipses were drawn for each groundwater cluster at a coefficient of 0.5. The CI, defined in Fig. 8a, is reported on Fig. 8b to calculate the CI of each cluster ellipse. Table 4 presents the CI of the minimum, maximum, as well as center of the ellipses. Fig. 8b is efficient at separating the various clusters in the plane defined by the axes of components 1 and 2, associated to “salinity” and “hardness”, respectively. This diagram also provides a good visualization of the various groundwater types found in the Basses-Laurentides, as well as insight into the geochemical processes responsible for these variations.

Samples from C1 are in the lower-right quadrant of the diagram, and thus are associated to moderately elevated salinity coupled to low hardness (Fig. 8b). Samples from C2 are in upper-right and lower-right quadrant of the diagram, associated mainly to elevated salinity. Samples from C3 are all left of the component 1 zero line, on both side and relatively close to the component 2 zero line. These are associated mainly to low salinity. Samples from C4 are to the left and right of the component 1 zero line, on both side and relatively close to the component 2 zero line. Most of the samples from C5 are in the lower-left quadrant of the diagram, and are associated to low salinity as well as low hardness. Samples from C6 are above the component 1 zero line, on both side of the component 2 zero line. These samples are associated to elevated hardness, and some have moderately elevated salinity. Finally, samples from C7 are in the upper-left quadrant of the diagram, and thus are associated to elevated hardness coupled to low salinity.

Table 4 Confinement Index for the cluster ellipses shown on Fig. 8b

Cluster	Minimum	Center	Maximum
C1	5	7.25	9.5
C2	5	6.25	7.5
C3	1	2.25	3.5
C4	1.5	3.75	6
C5	3	4.5	6
C6	1.5	2.75	4
C7	1.5	2.25	3

Areal distribution and zoning

The relation between components and the hydrogeological and geological contexts is better seen on the distribution maps of scores (Fig. 9). Elevated scores for component 1 are associated to the aquifer system under confined conditions, as for the buried valleys (Fig. 9a). Numerous sites with moderately positive scores are found in the eastern confined area of the region, and in the unconfined area of St. Janvier. Moderately to highly negative scores are found in the main recharge zones of the study area (Fig. 9a). As demonstrated previously, component 1 is defined by highly positive loadings in Na^+ , Cl^- and Br^- (Table 3). This association of chemical parameters is related to groundwater mixing with Champlain Sea water and solutes diffusion from the marine clay aquitard. Ca^{2+} – Na^+ ion exchange and local anthropogenic contamination are other processes that could be related to component 1. The negative loading of Ca^{2+} , in opposition to the positive loadings in Na^+ , is consistent with the occurrence of ion exchange (Table 3). Other regional hydrochemical studies have also produced a first component with high loadings of elements associated to different salinization processes, such as ion-filtration processes (Usunoff and Guzmán-Guzmán, 1989), infiltration of saline surface water (Adams et al., 2001) and seawater intrusion or infiltration from salts manufacture (Wang et al., 2007).

The distribution map of the scores of component 2 illustrates the relation between the hardness and the geological units (Fig. 9b). Highly positive scores are associated with the unconfined dolostone of Theresa and Beauharnois formations. Moderately to highly positive scores are also found in the dolostone and limestone formations of the Carillon Formation and Chazy Group in the western extremity of the study area. Moderately to highly negative scores are found under confined conditions in the eastern extremity of the study area and in the buried valleys. Component 2 is defined by highly positive loadings in Ca^{2+} and Mg^{2+} , as well as SO_4^{2-} (Table 3). Geochemical processes important for component 2 could include dissolution of carbonate and sulfate minerals, and oxidation of pyrite. Cloutier et al. (2006) presented data suggesting the occurrence of carbonate and sulfate dissolution based on the mineralogy of geological units and mineral saturation indices. The oxidation of pyrite is a hypothesis not yet supported by independent data. The negative scores in the limestone of the eastern extremity are consistent with ion exchange.

The significance of the last three components, in terms of regional processes, is not as important as that of the first two components as they explain a lower percentage of the variance. Additional data, including detailed mineralogy and geochemistry, would be needed to better understand the geochemical processes associated to the components. On the other hand, the distribution map of scores provides an hypothesis for explaining these components. The distribution map of the scores of component 3, related to concentrations in Fe^{2+} and Mn^{2+} , is highly variable and is presented in Cloutier (2004). Highly positive scores are associated to both sandstone and dolostone, under confined and unconfined conditions. Highly positive loadings for both Fe^{2+} and Mn^{2+} indicate a similar geochemical behaviour for these parameters (Table 3). The sources for these elements could be the dissolution of Fe-oxides, Mn-oxides and the oxidation

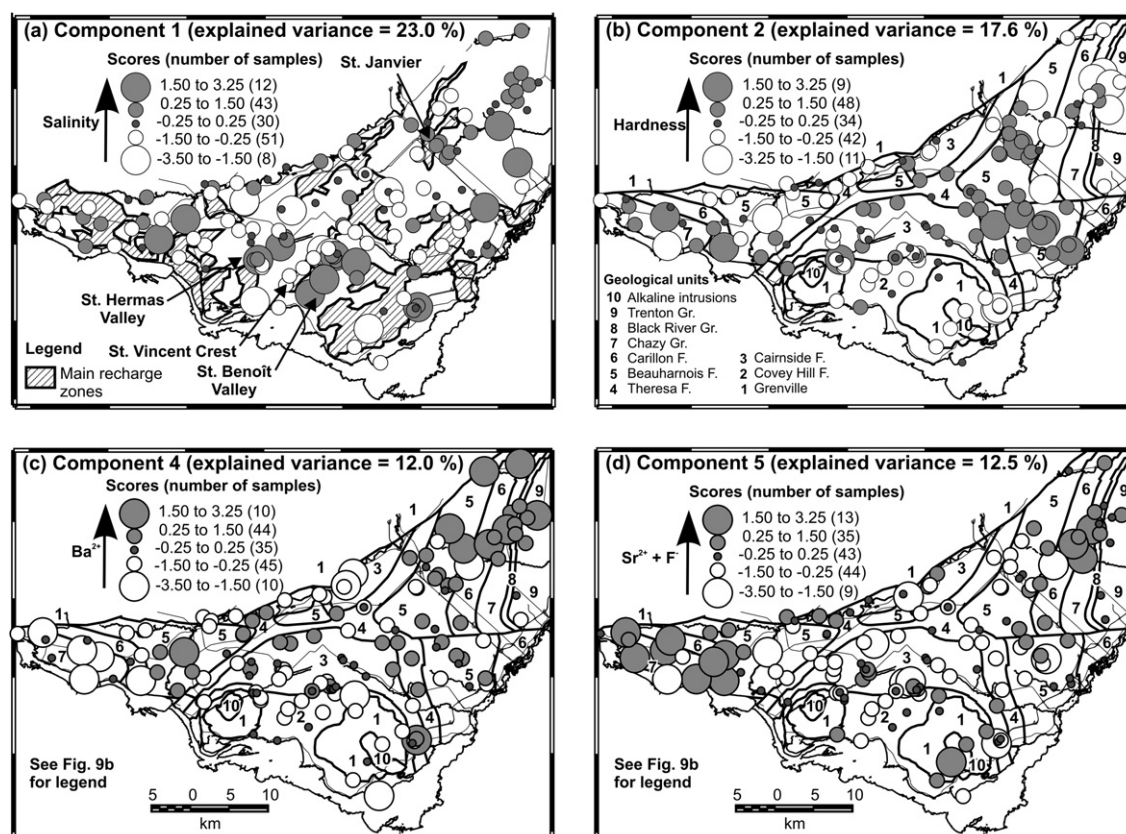


Figure 9 Regional distribution of principal component scores of water samples for (a) component 1 with the recharge zones shown in background (main recharge zones to the rock aquifer modified from Paradis, *in press*), (b) component 2, (c) component 4 and (d) component 5 with the geology shown in background.

of sulfide minerals. The majority of the elevated scores for component 4 are associated to the dolostone and limestone formations in confined area of the eastern extremity (Fig. 9c). Component 4 is related to concentrations in Ba^{2+} , indicating the interaction with Ba-bearing minerals. Loadings are also relatively high for HCO_3^- and HS^- as well (Table 3). The positive loading for HS^- is associated to a negative loading for SO_4^{2-} , and could indicate the occurrence of sulfate reduction. The distribution map of the scores of component 5, associated to concentrations in Sr^{2+} and F^- , is clearly related to the geological units, and indicates the interaction with Sr-bearing and F-bearing minerals. Highly positive scores are associated to the dolostone and limestone formations at both West and East extremities of the study area, respectively, under unconfined and confined conditions (Fig. 9d). Regarding the possible sources for components 4 and 5, Globensky (1987) mentioned that the presence of Ba and F was observed in the sedimentary formations of the St. Lawrence Platform.

Fig. 10 shows the distribution map of the groundwater clusters for the 144 samples, and their relationships with the general hydrogeological conditions introduced previously. Geographical grouping is possible for the majority of the groundwater clusters. This geographical distribution of groundwater clusters was used by Cloutier et al. (*in press*) as a key information to divide the territory into seven groundwater quality zones, with the relative quality decreasing from water quality zones (WQZ) A–G. The water

quality zones were defined by combining the information from this multivariate statistical analysis, with the hydrogeological conditions and the surficial formations thickness maps (Savard et al., *in press*), and by comparing geochemical parameters to guidelines for Canadian drinking water quality of Health Canada (2003).

Clusters C1, C2 and C5 characterize the aquifer system under confined conditions, coherent with their elevated median values of casing depth (Table 2). Samples from C1 dominate in the confined dolostone and limestone in WQZ F. Samples from C2 characterize the buried valley of WQZ G. Finally, samples from C5 are found mainly in the other buried valleys of WQZ A and B.

The preferential groundwater recharge areas are characterized by clusters C3, C4, C6 and C7 (Fig. 10). Samples from C4 are dominant in the limestone and dolostone of the area of WQZ E. The low linkage distance between C4 and C5 explains why two samples of C4 are found in the dominated C5 buried valley of St. Hermas (Fig. 4). Samples from C4 found in confined areas of the du Nord River Valley and in Oka Hills are related to geological factors as elevated concentrations in F^- (Cloutier et al., 2006). Samples from C3 and C7 characterize the main southwest–northeast recharge area as well as the local recharge zone of WQZ C. The main distinction between these two clusters is the elevated concentrations in Fe^{2+} and Mn^{2+} , and elevated total hardness, in C7 relative to C3 (Table 2). Samples from C3 are also found in the buried valley of du Nord River with samples of C5.

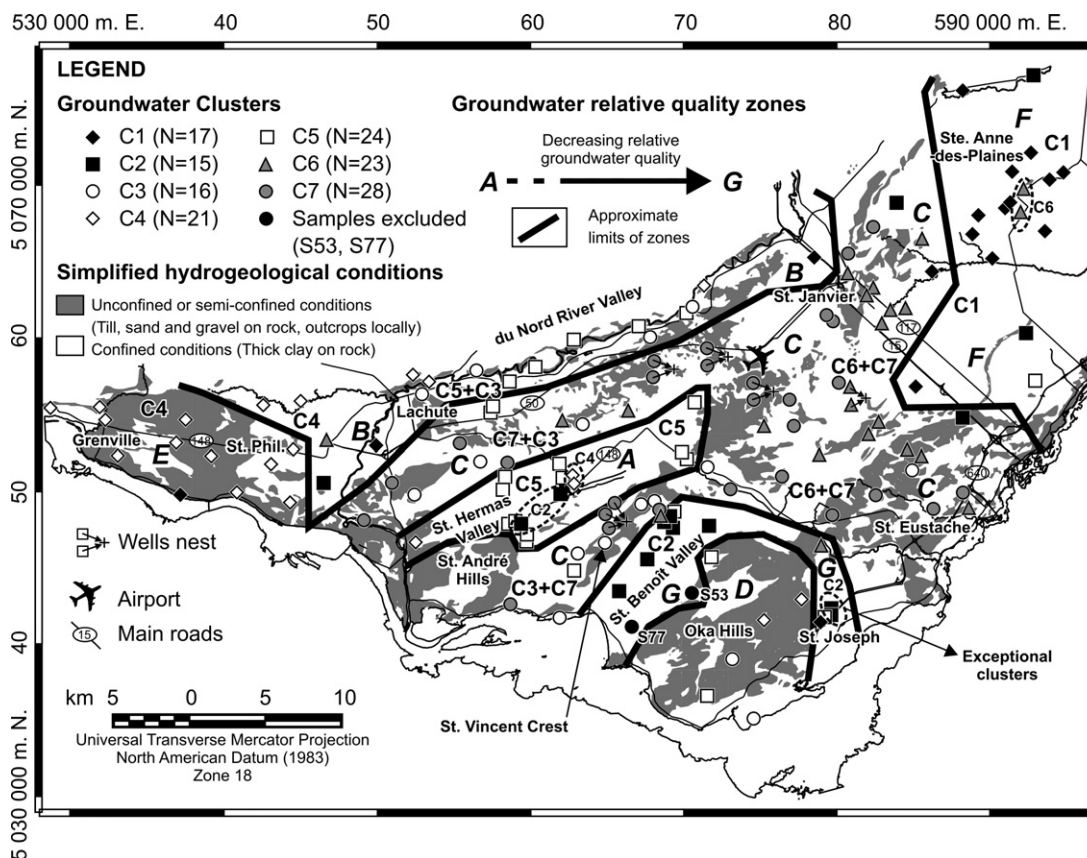


Figure 10 Zoning of groundwater quality: regional distribution of groundwater clusters, and their relation to the groundwater relative quality zones and to the hydrogeological conditions (modified from Cloutier et al., 2006). Areas with exceptional clusters are circled with dashed lines.

The last area is the unconfined dolostone are dominated by clusters C6 and C7 (WQZ C). The elevated median values for Na^+ and Cl^- in C6 is due to samples contaminated by de-icing road salts along main roads. The other difference between both clusters is the elevated concentrations in Fe^{2+} and Mn^{2+} in C7 relative to C6 (Table 2).

Hydrogeochemical evolution

From the areal distribution of principal component scores and groundwater clusters (see section 'Areal distribution and zoning'), it becomes apparent that the region can be divided into four main geochemical areas (Fig. 11a): (1) the Western End, (2) the Central Crests and Valleys, (3) the Eastern Area and (4) the Far Eastern End. This division is used for the interpretation of the hydrogeochemical evolution of groundwater of the Basses-Laurentides aquifer system.

Fig. 11 presents relationships between the groundwater clusters, the main groundwater groups, and the Confinement Index (CI) obtained from components 1 and 2 (Fig. 8), and this, for the four main geochemical areas. The groundwater clusters are positioned according to their relative importance within each geochemical area. The CI of cluster ellipses calculated from Fig. 8b (Table 4) and the "apparent" level of confinement defined in Fig. 8a are integrated in Fig. 11a. The figure also indicates the num-

ber of unconfined and confined sampling sites for each cluster according to field knowledge. In this case, the unconfined condition includes the semi-confined, as well as the surface sediments and spring samples.

Fig. 11b shows the relationship between the clusters and the main groundwater groups, and allows the classification of the clusters into levels of groundwater evolution. Median concentrations of selected elements from the clusters are also reported to facilitate the link between the groundwater evolution and geochemical processes presented by Cloutier et al. (2006). As a complement to Fig. 11, Table 5 presents the main geochemical areas, geological and hydrogeological contexts with their respective groundwater clusters as well as the main geochemical processes inferred responsible for the hydrogeochemical evolution of groundwater.

The Western End

The Western End area, dominated by samples of cluster C4, is generally an unconfined region, with a strong hydraulic gradient, and consists of dolostone and limestone formations (Fig. 2). C4 is characterized mainly by Ca-Mg-HCO_3 groundwater (G1) and Na-HCO_3 groundwater (G2), thus modern recharge and evolved groundwater, respectively (Fig. 11b). Its CI varies from 1.5 to 6, indicating "apparent" hydrogeological conditions from unconfined to confined (Fig. 11a). This "apparent" confined condition is coherent with the presence of nine sites under confined conditions

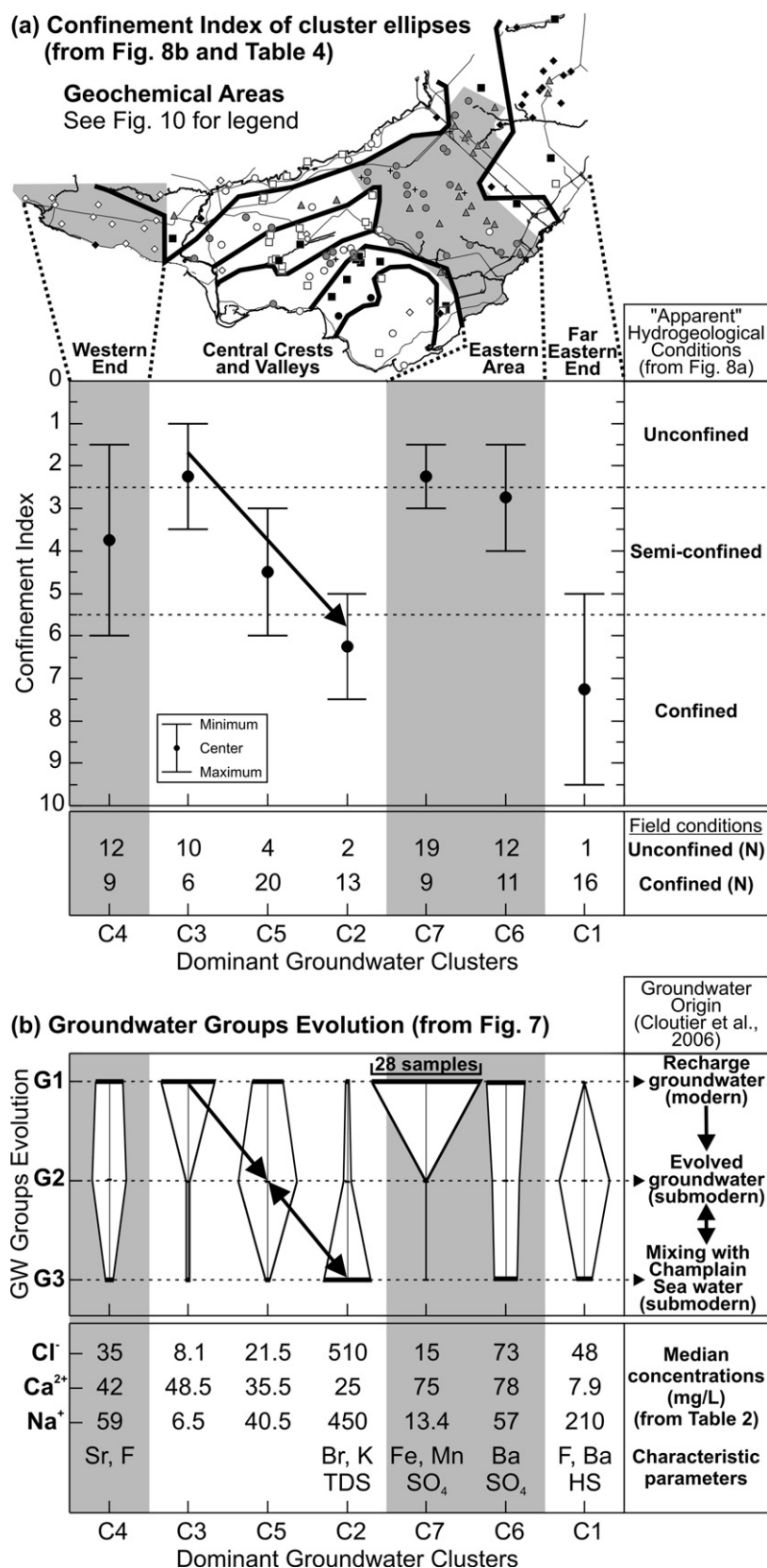


Figure 11 Evolution of groundwater geochemistry. The main geochemical areas are shown above the graph of (a). Clusters specific to these areas are presented in the same order as they appear in these areas in the two graphs: (a) range plot of the Confinement Index (Fig. 8a) for the cluster ellipses related to the main geochemical areas, and (b) plot showing the relationship between the clusters and the groundwater groups evolution within the main geochemical areas (see Fig. 6 for definition of groundwater groups).

Table 5 Main geochemical areas, geological and hydrogeological contexts related to groundwater clusters

Properties of the geochemical areas:	Geochemical area (see Fig. 11a)			
	Western End	Central Crests and Valleys	Eastern Area	Far Eastern End
Main groundwater clusters	C4	C3, C5, C2	C7, C6	C1
Geological context	– Dolostone – Limestone	– Sandstone – Dolostone	Dolostone	– Dolostone – Limestone
Hydrogeological conditions	Mainly unconfined	From unconfined to confined	Mainly unconfined	Confined
Relative hydraulic gradient	Strong	Strong to moderate	Small	Small
<i>GW Evolution:GW Group</i>				
Recharge GW: G1	C4 (unconfined)	C3 (unconfined)	C7/C6 (unconfined)	C1 (confined)
Evolved GW: G2	C4 (confined)	C5 (confined)	C6 (confined)	
Ancient Champlain Sea water: G3		C2 (confined)	C6 (contaminated)	
Confinement Index (CI)	1.5–6	1–3.5 (C3) 3–6 (C5) 5–7.5 (C2)	1.5–3 (C7) 1.5–4 (C6)	5–9.5
High principal components scores	Component 5	Component 1 in buried valleys	Component 2	Components 4 and 5
Characteristic parameters	Sr, F	Br, K, TDS (C2)	SO ₄ (C7/C6) Fe, Mn (C7) Ba (C6)	F, Ba, HS
Main geochemical processes	– Dissolution of carbonates – Dissolution of Sr-bearing and F-bearing minerals	– Dissolution of carbonates (C3) – Ion exchange (C5) – Groundwater mixing (C2) – Solute diffusion from marine clays (C2)	– Dissolution of carbonates and sulfates (C7/C6) – Dissolution of Fe-oxides, Mn-oxides and oxidation of sulfide minerals (C7) – Anthropogenic NaCl (C6)	– Ion exchange – Sulfate reduction – Dissolution of F-bearing and Ba-bearing minerals

The main geochemical processes inferred responsible for the evolution of groundwater geochemistry are also indicated.

in C4. On the other hand, most of these confined sites are in the Central Crests and Valleys area and Na–HCO₃ groundwater (G2). C4 has a strong geological signature on its water composition, as revealed by elevated concentrations in Sr²⁺ and F[–].

The Central Crests and Valleys

The Central Crests and Valleys area, dominated by samples of cluster C3, C5 and C2, has alternating confined buried valleys and unconfined crests, and consists of sandstone and dolostone formations. C3 is characterized by Ca–Mg–HCO₃ modern recharge groundwater (G1) (Fig. 11b). With a CI from 1 to 3.5, C3 is under “apparent” unconfined to semi-confined condition (Fig. 11a). Samples of C3 are generally located on unconfined crests, in preferential groundwater recharge areas, which are affected by strong topographic gravity driven hydraulic gradient. With its low Cl[–] and Na⁺ concentrations, C3 is clearly recharge groundwater. This groundwater composition results from dissolution of carbonates, calcite and dolomite, in the till and rock formations (Cloutier et al., 2006).

C5 is characterized by Ca–Mg–HCO₃ groundwater (G1) and mostly Na–HCO₃ groundwater (G2), representing the evolution of modern recharge to evolved groundwater (Fig. 11b). With a CI from 3 to 6, C5 is under “apparent” semi-confined to confined condition (Fig. 11a). In fact, field conditions confirm that most of the sites are under confined conditions. Samples of C5 are located in the buried valleys, mainly St. Hermas Valley, and in intermediate locations between recharge zones and “stagnant” valley centers. Hydrochemical data presented by Cloutier et al. (2006) suggested that the evolved Na–HCO₃ groundwater (G2) is mostly affected by Ca²⁺–Na⁺ ion exchange. This is consistent with the Na⁺ concentration of C5 larger than its Ca²⁺ and Cl[–] concentrations.

C2 is dominated by Na–Cl evolved and ancient groundwater (G3) (Fig. 11b). C2 has a CI from 5 to 7.5, indicating “apparent” semi-confined to confined condition, and has most of its sites under field confined conditions. Samples of C2 are located in the buried valleys, mainly St. Benoît Valley, and in the central “stagnant” part of St. Hermas Valley and of St. Joseph. Groundwater mixing with Pleisto-

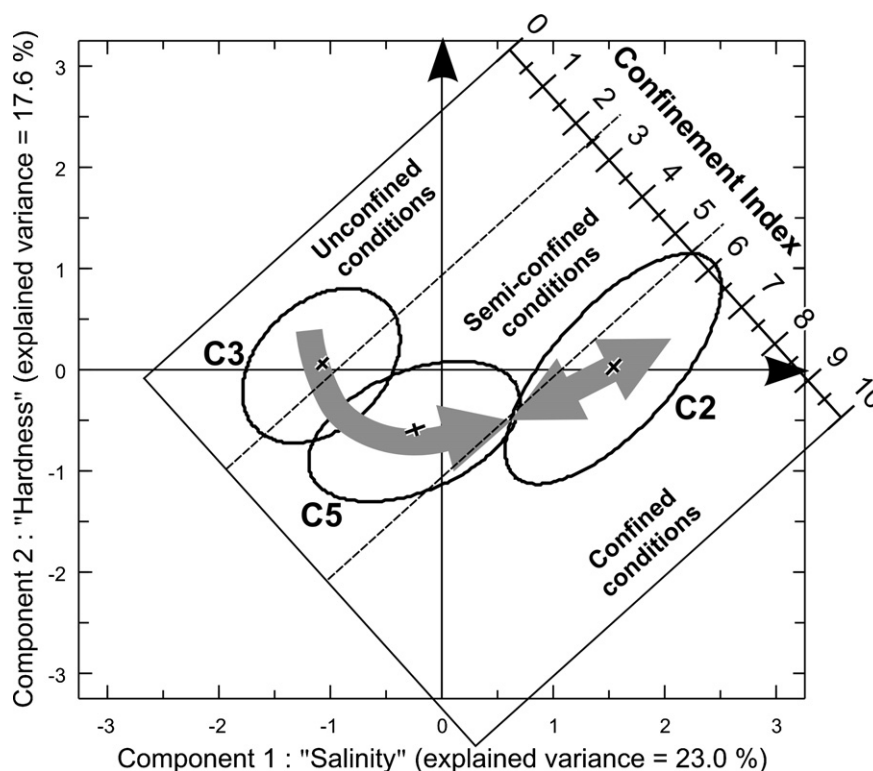


Figure 12 Hydrogeochemical evolution of groundwater of the Central Crests and Valleys area, where clusters C3, C5 and C2 are present, into the plane of principal components 1 and 2 (Confinement Index and “apparent” level of confinement from Fig. 8a; cluster ellipses from Fig. 8b). Groundwater belonging to C3 is present in preferential recharge areas and evolves along its flow path by ion exchange into groundwater of C5. Mixing of C5 groundwater with former Champlain Sea water produces groundwater belonging to C2.

cene Champlain Sea water as well as solutes diffusion from the marine clay aquitard are the main processes affecting the evolution of the evolved and ancient Na–Cl groundwater (G3) (Cloutier et al., 2006). This is consistent with the elevated Cl^- , Na^+ , Br^- and K^+ concentrations, as well as elevated TDS, of C2. The lowest linkage distances in the dendrogram are for Na^+ , Br^- and Cl^- , confirming the importance of the Pleistocene Champlain Sea water end-member in the Basses-Laurentides aquifer system (Cloutier, 2004).

The Eastern Area

The Eastern Area, dominated by samples of clusters C7 and C6, is generally an unconfined plateau, with small hydraulic gradients, and consists mainly of dolostone of the Theresa and Beauharnois formations (Fig. 2). C7 is characterized exclusively by the Ca–Mg– HCO_3 recharge groundwater (G1) (Fig. 11b). Its CI varies from 1.5 to 3, indicating “apparent” hydrogeological conditions from unconfined to semi-confined (Fig. 11a). Actually, field data indicate that the majority of the sites are under unconfined conditions. The recharge groundwater of C7 is distinct from the one of C3 by its elevated concentrations in Fe^{2+} and Mn^{2+} , as well as its elevated concentrations in Ca^{2+} , Mg^{2+} and SO_4^{2-} , showing the influence of lithology on groundwater composition.

C6 is characterized by groundwater of the three main groups, particularly Ca–Mg– HCO_3 (G1). Thus, this could

indicate the evolution of recharge to evolved and ancient groundwater (Fig. 11b). With a CI from 1.5 to 4, C6 is in “apparent” unconfined to semi-confined condition (Fig. 11a). Actually, field conditions indicate that about half of the samples of C6 are under confined conditions. The presence of Na–Cl groundwater (G3) is actually the result of a modern salinity source, and not of the mixing with ancient Champlain Sea water. As mentioned previously, the samples defined by Cloutier (2004) as being impacted by de-icing road salts all belong to C6. This explains the presence of Na–Cl groundwater of C6 in unconfined conditions, as well as its elevated Na^+ and Cl^- concentrations relative to C7. As C7, C6 has elevated concentrations in Ca^{2+} , Mg^{2+} and SO_4^{2-} related to the geological context.

The Far Eastern End

The Far Eastern End area, dominated by samples of cluster C1, is generally a confined region, with a relatively low hydraulic gradient, and consists of dolostone and limestone formations (Fig. 2). C1 is characterized mainly by the Na– HCO_3 evolved groundwater (G2), with some Na–Cl ancient groundwater (G3) (Fig. 11b). Its CI varies from 5 to 9.5, indicating that “apparent” confined conditions dominate the Far Eastern End area, in agreement with the field knowledge (Fig. 11a). For samples of C1, elevated concentrations in Na^+ , relative to Ca^{2+} and Cl^- concentrations, is consistent with ion exchange (Fig. 11b). C1 has also a strong geological signature on its water composition, as revealed by elevated

concentrations in F^- and Ba^{2+} . Elevated HS^- concentrations, consistent with sulfate reduction, are also evidence of confined anoxic conditions.

Long-term system evolution

Fig. 11 and Table 5 indicate that the complete hydrogeochemical evolution of groundwater of this aquifer system, from modern recharge to evolved and ancient groundwater, is only found in the Central Crests and Valleys area. Fig. 12 presents this complete hydrogeochemical evolution path using the cluster ellipses into the plane of principal components 1 and 2. The arrow from the center of the ellipse C3 to C5 is the inferred ion exchange path from Ca–Mg– HCO_3 modern recharge groundwater (G1) in “apparent” unconfined condition to Na– HCO_3 evolved groundwater (G2) in “apparent” semi-confined condition. The double arrow between ellipses C5 and C2 represents the mixing of Na– HCO_3 evolved groundwater (G2) with Na–Cl Champlain Sea water (G3) under “apparent” confined conditions. The fact that the hydrogeochemical evolution of groundwater can be represented in the plane of components 1 and 2 confirms the importance of these first two components, defined as the “salinity” and the “hardness” components, in the hydrogeochemistry of the Basses-Laurentides aquifer system.

A great challenge in hydrogeology is the forecasting of the long-term evolution of hydrogeological systems. By studying the paleo-hydrogeology of an active groundwater system, and by showing that this system is still influenced by a major Quaternary geological event (the Champlain Sea episode), our study presents an example of the long-term evolution of hydrogeological systems, and of the importance of groundwater as a geological agent. Tóth (1999) demonstrated the role of groundwater as a geological agent in a regional, gravity-driven flow system. The present study identifies several processes discussed by Tóth (1999) and that contribute to the evolution of groundwater, from the preferential recharge areas and along the flow system. A distinctive feature of the Basses-Laurentides aquifer system is that it was affected by a major geological event, rather than following a steady and continuous evolution. The Champlain Sea water invaded the aquifer system, thus imposing new hydrogeological and hydrogeochemical conditions to the system about 10,000 years ago. We have demonstrated here and in Cloutier et al. (2006) that these conditions are still present in some hydraulically stagnant parts of the system in the center of buried valleys, as well as in the marine clay pore water. These saline waters will continue to influence the geochemistry of the underlying aquifer system for a long time.

Conclusions

The interpretation of the geochemical evolution of groundwater in the study area takes into account previous work that identified the origin of groundwater (Cloutier et al., 2006), and recognized the on-going geochemical processes as well as the Quaternary geological events that influenced groundwater geochemistry in this aquifer system (Cloutier, 2004). To further refine our geochemical interpretation, we applied well-proven multivariate statistical methods

(HCA and PCA), which are well-suited here because of highly variable groundwater geochemistry influenced by a variety of geological and hydrogeological factors.

The HCA classified the 144 groundwater samples into seven geochemically distinct clusters (C1–C7). Samples from clusters C3, C4, C6 and C7 are mostly located in preferential recharge areas. The majority of these samples have Ca–Mg– HCO_3 recharge groundwater (C3, C6, C7) and Na– HCO_3 evolved groundwater (C4). Samples that belong to the other three clusters (C1, C2, C5) characterize samples from the aquifer system under confined conditions. The majority of these samples have Na– HCO_3 evolved groundwater (C1, C5) and Na–Cl ancient groundwater that exhibits elevated concentrations in Br^- (C2). In addition to recognizing the importance of hydrogeological conditions on groundwater geochemistry, the distribution of clusters also showed the significant influence of the geological formations on minor and trace elements, such as Fe^{2+} , Mn^{2+} , Sr^{2+} , F^- and Ba^{2+} . Thus, HCA is more accurate than conventional qualitative methods regarding the geographical zoning of samples and it allows the recognition of the distinct minor element signature related to various geological formations.

The first five components of the PCA account for 78.3% of the total variance in the dataset. Component 1, characterized by highly positive loadings in Na^+ , Cl^- and Br^- , is related to groundwater mixing with Champlain Sea water and solute diffusion from the marine clay aquitard and is defined as the “salinity” component. With high positive loadings in Ca^{2+} and Mg^{2+} , component 2 suggests the importance of dissolution of carbonate rocks in this aquifer system and is defined as the “hardness” component. The scores of the samples calculated in the PCA indicated that first components, the “salinity” and the “hardness”, are to some extent both dependant, or related to, the hydrogeological context. A novel site-specific indicator, called the Confinement Index (CI), was defined to integrate both components into a unique parameter. Scores of samples labeled with their clusters were represented in the plane defined by the axes of components 1 and 2, and the CI was calculated for each cluster ellipse. The CI could relate the combined principal components to the global hydrogeological context, thus to the level of confinement of groundwater, which is also an indication of its “evolution level”.

Multivariate statistical methods also allowed to define the spatial geochemical zonation of the aquifer system that takes into account both the effects of lithologies and hydrogeological contexts. The distribution map of score for component 1 indicates that elevated scores are associated to the aquifer system under confined conditions, as for buried valleys. Highly positive scores for component 2 are associated with the dolostone of Theresa and Beauharnois formations, illustrating the relation between the hardness and the geological units. The distribution of components 3–5 are related to more local effects and suggest the influence of lithology, such as the interaction with Sr-bearing, F-bearing and Ba-bearing minerals. Thus, the PCA much better explains the distinct roles of lithologies and hydrogeology on the groundwater geochemical signature.

The integration of all classification methods within the geological and hydrogeological contexts allowed the division of the region into four main geochemical areas, and these were used to refine our interpretation of the hydrog-

eochemical evolution of groundwater of the Basses-Laurentides aquifer system (Fig. 11 and Table 5). Every geochemical area can be distinguished by the geological formations, hydrogeological contexts, hydraulic gradients, groundwater groups and clusters, CI, as well as main geochemical processes. Thus, the following factors were recognized as influencing the evolution of groundwater identified in every geochemical area: (1) geological characteristics including sedimentary rock type and till mineralogy; (2) hydrogeological characteristics represented by the level of confinement and the hydraulic gradient; and (3) geological history by the latest glaciation as well as Champlain Sea invasion. The main geochemical processes identified for this aquifer system are all apparent in the Central Crests and Valleys area. This hydrogeochemical evolution includes carbonate dissolution in recharge areas, to ion exchange in the confined areas, as well as groundwater mixing with Champlain Sea water, and solute diffusion from the marine clay aquitard in the deepest portions of the aquifer system.

Within this study, different levels of groundwater evolution were identified as part of global desalination following Champlain Sea water intrusion in the aquifer system about 10,000 years ago. This aquifer system thus shows how much longer it may take for similar systems to attain a geochemical "steady state" compared to a fluid flow steady state. This hydrogeochemical study brings independent and new pieces of information that improved our understanding of the aquifer system dynamic. Thus, a better understanding of the groundwater flow system and the geochemical processes could emerge from the interaction between hydraulic and geochemical modeling. The regional understanding of the Basses-Laurentides aquifer system can be used to follow the evolution of water quality due to human activities, identify areas vulnerable to contamination (Ross et al., 2004), elaborate management strategies for the resource (Nastev et al., 2006), and evaluate the impact of future development on the groundwater resource.

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