Scenarios of groundwater chemical evolution in a region of the Canadian Shield based on multivariate statistical analysis

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A R T I C L E   I N F O

A B S T R A C T

Study region: The study of groundwater chemistry of the Charlevoix/Haute-Côte-Nord (CHCN) region in the province of Quebec in Canada is part of a regional hydrogeological characterization project.

Study focus: Groundwater was sampled in 113 wells over the 4500 km^2 study area and analyzed for 39 parameters including major, minor, trace and inorganic constituents, plus stable isotopes 2H and 18O. Two multivariate statistical methods, hierarchical cluster analysis (HCA) and R-mode factor analysis (RFA) were combined with graphic methods to classify the samples according to plausible levels of groundwater evolution in that region.

New hydrological insights for the region: Four sample clusters were identified. Cluster 1 is composed of low-salinity Ca-HCO$_3$ groundwater corresponding to recently infiltrated water in surface granular aquifers in recharge areas. Cluster 4 Na-(HCO$_3$-Cl) groundwater is more saline and corresponds to more evolved groundwater probably from confined bedrock aquifers. Cluster 2 and Cluster 3 (Ca-Na)-HCO$_3$ and Ca-HCO$_3$ groundwater, respectively, correspond to mixed or intermediate water between Cluster 1 and Cluster 4 from possibly interconnected granular and bedrock aquifers. This study identifies groundwater recharge, water–rock interactions, ion exchange, solute diffusion from marine clay aquitards, saltwater intrusion and also hydraulic connections between the Canadian Shield and the granular deposits, as the main processes affecting the hydrogeochemical evolution of groundwater in the CHCN region.

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1. Introduction

The chemistry of groundwater in the Canadian Shield and its evolution with depth or with distance along a flowpath have been investigated by numerous authors, namely Gascoyne and Kamineni (1994). Recent and shallow groundwater chemistry is controlled by the composition of the local rock, where dissolution reactions dominate, while its isotopic composition reflects the precipitation. In contrast, the chemistry of deeper groundwater is the result of extensive, long-term interactions with the bedrock (Frape et al., 1984). A number of studies (e.g. Melloul and Collin, 1992; Güler and Thyne, 2004; Silva-Filho et al., 2009) have shown that the hydrogeological context, combined with hydrogeochemical and isotopic characterization of an aquifer can help to identify different types of groundwater ($Ca-HCO_3$, $Na-HCO_3$ and $Na-Cl$ types) as well as the main factors that influence the chemical composition of groundwater. Other studies (Cloutier et al., 2008; Beaudry, 2013; Montcoudiol et al., 2014) have demonstrated a significant correlation between the hydrogeological context and the groundwater chemistry in regions of the Canadian Shield. Characterizing the hydrogeological context in parallel with the hydrogeochemical and isotopic study of groundwater allows a better characterization of groundwater flow and of the evolution of its chemical composition.

Güler et al. (2002) showed that the combination of graphical and multivariate statistical techniques provides a consistent and objective means of classifying large numbers of samples while still preserving the ease of classic graphical representations. Cloutier et al. (2008), Yidana (2010) and Montcoudiol et al. (2014) used multivariate statistical analysis to supplement graphical representations such as Schoeller, Stiff, Durov and Piper diagrams. Using a statistical approach, they successfully identified major groundwater groups and factors affecting the groundwater chemistry in an aquifer.

The main objective of this research is to characterize groundwater chemistry and to identify the relationships between the hydrogeological context and groundwater chemistry in the Charlevoix/Haute-Côte-Nord (CHCN) region by using a combination of multivariate statistical analysis, graphical representations and maps. "Hierarchical cluster analysis" (HCA) and "R-mode factor analysis" (RFA) are combined with graphical analysis using Durov and Stiff diagrams to develop a better understanding of the groundwater chemistry and its evolution in the CHCN aquifer system located in the Canadian Shield.

2. Study area

In 2008, the Government of Quebec implemented the Programme d'acquisition de connaissances sur les eaux souterraines (PACES; Groundwater Knowledge Acquisition Programme) under the MDDEFP (Ministère du Développement Durable, de l'Environnement, de la Forêt et des Parcs), in order to improve knowledge of this resource (Government of Quebec, 2015a,b). This programme consists of a number of regional hydrogeological characterization projects aiming to acquire knowledge on groundwater resources in the southern, more densely inhabited parts of the Province of Quebec, with the objectives of protecting groundwater and ensuring the sustainability of its supply (Chesnaux et al., 2011).

A regional hydrogeological characterization project, conducted by the *Centre d'études sur les ressources minérales* (CERM) at *Université du Québec à Chicoutimi* (UQAC), started in 2012 in the CHCN region as part of the PACES programme. Even though ongoing industrial and agricultural development presents a risk for groundwater contamination in this region, no regional hydrogeological characterization project had yet been carried out. This situation calls for a proper characterization of the natural geochemical properties of groundwater and a better understanding of the natural geochemical processes that affect the groundwater chemistry during its evolution in the aquifer systems.

The CHCN region is located on the north shore of the Saint-Lawrence River to the northeast of Quebec city (Fig. 1). The study region forms an NE elongated stretch of land extending over 236 km, approximately 20 km wide, for a total area of 4500 km^2. The climate of the region is characterized by long and cold winters, followed by short, warm and humid summers. Precipitation is well distributed throughout the year, mostly in snow from November to April, and totalling around 900 mm per year (Government of Quebec, 2015a,b). The vegetation is mainly composed of deciduous and mixed tree stands. Most of the territory is forested; parts of it are exploited by the forestry industry.
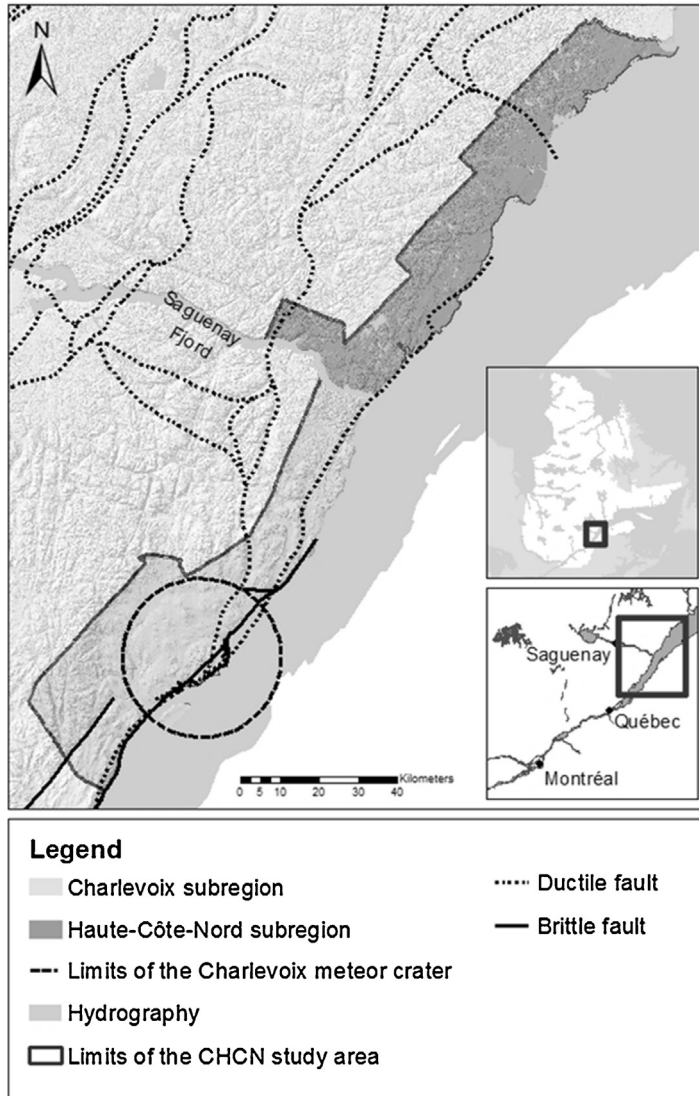
Fig. 1. Location and principal structural features of the CHCN region, Quebec, Canada.

An important physiographic feature is the WNW-trending Saguenay Fjord that separates the study area in two parts: the Charlevoix subregion to the south-west and the Haute-Côte-Nord subregion to the north-east (Cousineau et al., 2014). The topography of the Charlevoix subregion is characterized by a meteoric impact crater dated at 372–335 Ma, called the "Charlevoix meteor crater" (Rondot, 1968). The Mont des Éboulements central uplift, related to the meteor crater, is bounded by normal faults and surrounded by annular lifts and depressions, such as the valleys of Baie St. Paul and La Malbaie, where the topography flattens and elevations decrease to sea level (Rondot, 1998). The Charlevoix subregion lies along the St. Lawrence rift system and is a seismically active zone. The CHCN region is marked by numerous normal faults which were initiated or reactivated during various tectonic events. Many of these normal faults are considered to be still active (Fig. 1).

3. Geological and hydrogeological features

The CHCN region is located at the boundary between three geological provinces of eastern Canada; it is constituted of: (i) crystalline rocks of the Grenville Province of the Canadian Shield, (ii) a lower Paleozoic sedimentary succession of the St. Lawrence Platform, and (iii) units of deformed and transported rocks of the Appalachian orogen to the southeast. The basement is comprised of Proterozoic rocks such as intrusive igneous rocks and high-grade metamorphic rocks. The Grenvillian rocks of the Charlevoix area are mainly composed of high-grade orthogneisses and paragneisses, charnockites, and anorthositic and granitic intrusions (Lemieux et al., 2003). In the Haute-Côte-Nord, Grenvillian rocks include migmatite and gabbro. The Grenville basement is overlain by Lower Paleozoic siliciclastic rocks of the St. Lawrence Platform juxtaposed against accreted units of the Appalachian orogene (Lemieux et al., 2000).

The sedimentary rock units of the study area are rarely exposed because of the Quaternary sediments that overlay them. Quaternary surface sediments mainly consist of a till layer, but glaciomarine, glaciofluvial, lacustrine and alluvial sediments are also present. Till deposits can reach a thickness of 10 m and lie unconformably on rock. In the Haute-Côte-Nord, there is a larger proportion of coastal glaciomarine sediments than in Charlevoix, due to the large coastal area and the great extent of the deltaic systems. Thin glaciomarine sediments such as silty and clay-rich deposits can reach more than 100 m in thickness, while coastal and deltaic silty-sand or sand deposits vary from 1 to 20 m in thickness (Cousineau et al., 2014).

Bedrock aquifers provide most of the drinking water in the Charlevoix subregion, while the resource is mostly pumped from superficial granular aquifers in the Haute-Côte-Nord subregion. A predominance of unconfined aquifers can be identified in the Charlevoix subregion. The Champlain Sea invasion that occurred 10,000 years ago in the southeastern part of the Canadian Shield is still affecting groundwater quality in aquifers located in areas that were covered by that sea (Cloutier et al., 2008; Walter, 2010; Beaudry, 2013; Montcoudiol et al., 2014). Silicate weathering, carbonate dissolution, Ca/Na cation exchange and mixing have been identified as the main processes controlling the chemical evolution of groundwater in this area (Cloutier et al., 2008; Walter, 2010; Beaudry, 2013; Montcoudiol et al., 2014).

4. Methodology

4.1. Hydrogeochemical dataset

A total of 113 wells (Fig. 2), distributed over the entire studied area and at a maximum depth of approximately 170 m, were sampled using a sampling protocol described in CERM-PACES (2013). The type of aquifer intersected by each sampled well, i.e., either bedrock ($n=60$) or Quaternary deposits ($n=53$), and the well depth were determined using data from drilling reports. In situ field measurements were conducted for several parameters such as temperature (T), pH, redox potential (Eh), dissolved oxygen (DO) and total dissolved solids (TDS). Groundwater samples were analyzed for 39 parameters (Table 1) including major, minor, some trace and inorganic constituents, plus the stable isotopes deuterium ^2H and ^{18}O. The ion-balance error was calculated in order to verify the electroneutrality of the samples. Based on this data, 105 samples out of the 113 samples collected were selected for statistical analysis (8 samples were rejected as they presented an ion-balance error above $\pm 10\%$).

4.2. Graphical analysis

Two graphical methods are used to sort groundwater geochemistry samples into groups: the Durov diagram (Durov, 1948) and the Stiff diagram (Stiff, 1951), using the software Aquachem 5.0 (Waterloo Hydrogeologic Inc., 2005).

The Durov diagram displays the relative concentrations of the major cations and anions on two separate trilinear plots together with a central square plot where the points from the two trilinear
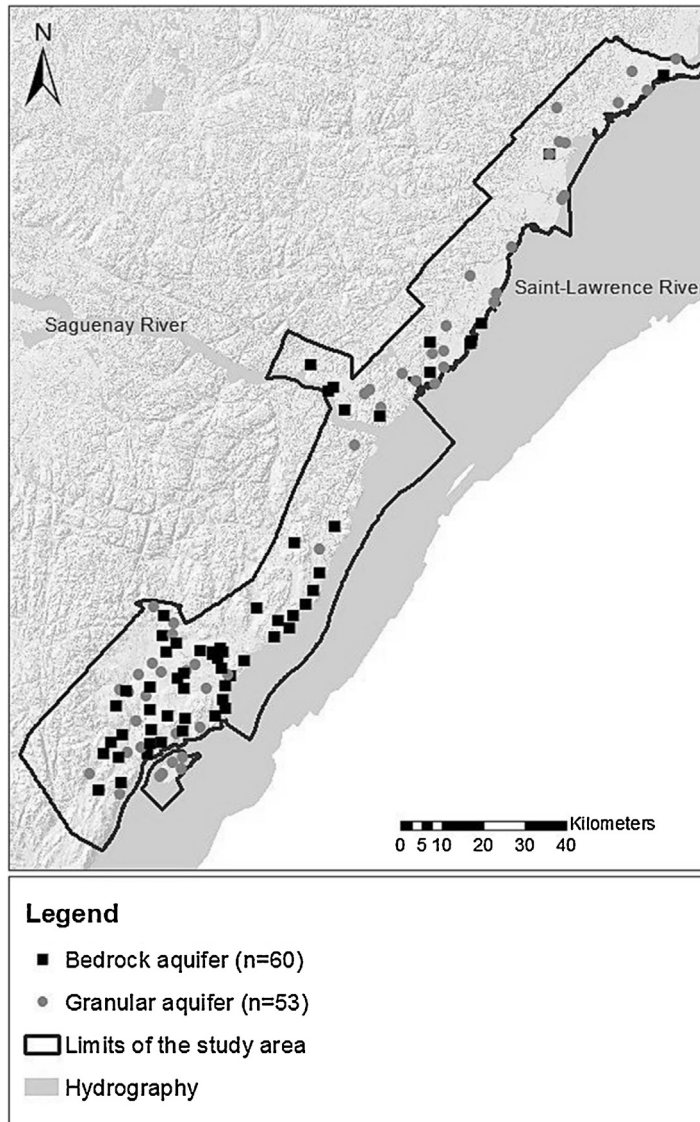
Fig. 2. Location of the sampling sites indicating the aquifer type intersected by the sampled wells.

plots are projected. Most of the 105 groundwater samples (Fig. 3; Table 2) are Ca-HCO$_3$ water type ($n = 80$). The remaining groundwater samples are Na-HCO$_3$ ($n = 13$), Na-Cl ($n = 11$) and Ca-Cl ($n = 1$) water types.

The Stiff diagram is a polygon created from three parallel horizontal axes extending on either side of a vertical zero axis. Cations are plotted to the left of the axis and anions to the right, in units of milliequivalents per litre (meq/L) (Güler et al., 2002). The Stiff diagram allows a visual comparison of waters with different characteristics. Since the pattern tends to maintain its shape upon concentration or dilution, the Stiff diagram also allows the tracing of flowpaths (Güler et al., 2002). The Stiff diagram is particularly useful for comparing results from many samples in combination with a multivariate statistical analysis, as presented below.

Table 1
Chemical parameters analyzed in the laboratory.

Isotopes	$\delta^2 H$	$\delta^{18} O$
	Aluminium (Al)	Magnesium (Mg)
	Antimony (Sb)	Manganese (Mn)
	Silver (Ag)	Molybdenum (Mo)
	Arsenic (As)	Nickel (Ni)
	Barium (Ba)	Lead (Pb)
	Beryllium (Be)	Potassium (K)
	Bismuth (Bi)	Selenium (Se)
Dissolved metals	Boron (B)	Silicon (Si)
	Cadmium (Cd)	Strontium (Sr)
	Calcium (Ca)	Sodium (Na)
	Chromium (Cr)	Uranium (U)
	Cobalt (Co)	Tin (Sn)
	Copper (Cu)	Titanium (Ti)
	Iron (Fe)	Vanadium (V)
	Lithium (Li)	Zinc (Zn)
	Bromine (Br)	Nitrites and nitrates (N)
Anions	Chlorine (Cl)	Sulphate (SO_4)
	Ammoniacal nitrogen ($N-NH_3$)	Sulphur (S)
Others	Inorganic phosphorus	Total alkalinity
	Fluorine (F)	
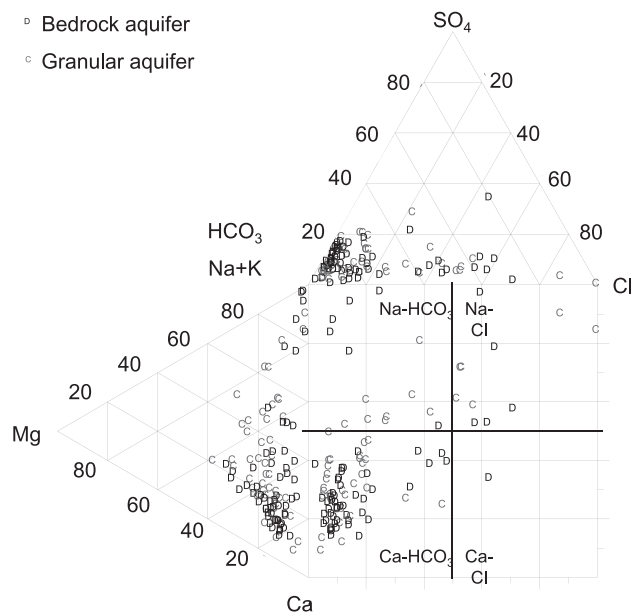
Fig. 3. Durov diagram of the 105 groundwater samples labelled according to the aquifer type. The central square plot of the Durov diagram is divided into four squares to identify the main groundwater types.

Table 2
Number of groundwater samples from bedrock aquifers and from granular aquifers for each water type.

	Ca-HCO$_3$	Na-HCO$_3$	Ca-Cl	Na-Cl
R	48	8	1	5
G	32	5	0	6

R, bedrock aquifer; G, granular aquifer.

Table 3
Parameters excluded for the multivariate statistical analysis.

Parameters excluded	Reason for the exclusion
EC, TDS, pH, Eh	Parameters with additive characteristics
Temperature	Physical parameter
DO, δ^2H, δ^{18}O	Parameters with low regional variations
Total alkalinity	Parameter linked to HCO_3^- concentration
Al, Sb, Ag, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Sn, Fe, Li, Mn, Mo, Ni, Pb, Se, U, Ti, V, Zn, N-NH$_3$, Br, F, N, P	Parameters with more than 15% of the samples below the detection limit

Table 4
Descriptive statistics for the 105 groundwater samples (concentrations in mg/L).

Parameter	Mean (x)	Median	Minimum	Maximum	Standard deviation (s)	Skewness
Ca^{2+}	18.673	16.000	1.700	110.000	17.276	2.712
Mg^{2+}	3.165	2.100	0.200	25.000	3.698	3.839
K^+	1.676	0.850	0.055	13.000	2.074	2.916
Si^{4+}	6.494	5.900	0.220	16.000	2.446	1.188
Sr^{2+}	0.190	0.095	0.013	2.600	0.383	5.076
Na^+	23.815	5.200	1.000	540.000	63.322	5.961
HCO_3^-	81.786	62.220	3.660	634.400	85.622	3.712
Cl^-	25.418	2.700	0.300	550.000	73.658	4.887
SO_4^-	8.037	5.000	0.275	150.000	15.322	7.925

4.3. Data preparation for the multivariate statistical analysis

The multivariate statistical analysis is an approach to groundwater classification that allows the definition of distinct groups of groundwater samples, as well as correlations between chemical parameters and groundwater samples (Cloutier et al., 2008). The hierarchical cluster analysis (HCA) and the R-mode factor analysis in principal components (RFA) are applied here using the software Statistica version 12 (Statsoft Inc., 2013). The data preparation for multivariate statistical analysis is based on the approach used by Cloutier et al. (2008); several parameters were excluded for the analysis, as explained in Table 3 (Sanford et al., 1993). The multivariate statistical analysis is thus applied to a subgroup of the complete hydrogeochemical dataset. The dataset used in this analysis constitutes a data matrix of 105 sampling sites (observations) by nine chemical parameters (variables). The nine selected parameters include the major constituents Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} and the minor constituents Sr^{2+} and Si^{4+}. For the multivariate statistical analysis, concentration values lower than the detection limit were set at 0.55 times the detection limit (Güler et al., 2002).

All the parameters except Si^{4+} are highly positively skewed and their frequency distribution in mg/L does not follow a normal distribution (Table 4). Thus, each chemical parameter was log-transformed except Si^{4+}. All the variables were then standardized to their standard scores Zi as follows:

$$Z_i = \frac{(x_i - x)}{s} \qquad (1)$$

where Z = standard score of the sample i, x_i = value of sample i, x = mean and s = standard deviation (Davis, 1986). The standardization is applied to ensure that each variable has equal weight in the statistical analyses.

4.4. Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is the most widely applied clustering technique in Earth Sciences and is often used for the classification of hydrogeochemical data (Cloutier et al., 2008). The

agglomerative procedure starts with as many clusters as objects (or individuals). The clusters are then successively merged, according to their similarity, until only one remains (Templ et al., 2008). This agglomerative procedure allows to classify large amounts of hydrogeochemical data into several groups based on specific characteristics (Lambrakis et al., 2004). In this study, the Euclidean distance was chosen as the distance or similarity measure between sampling sites, in combination with Ward's method (Ward, 1963) as the linkage rule, which merges clusters with a minimum information loss criteria based on sums of squares (Templ et al., 2008). Güler et al. (2002) have suggested that using Euclidean distance as the similarity measure, together with Ward's method as the linkage rule, produces the most distinctive groups. A number of other studies have also used Ward's method as the linkage rule (Lambrakis et al., 2004; Cloutier et al., 2008; Templ et al., 2008). The levels of similarity at which observations are joined are used to construct a tree diagram, or a dendrogram (Davis, 1986). A visual observation of the dendrogram allows the grouping of samples into clusters. The characteristics of each cluster can be determined using descriptive statistics and graphical methods. The relations between the clusters can be interpreted in correlation with the hydrogeological and geological contexts.

The HCA was carried out using the cluster analysis module in the Multivariate Exploratory Techniques of the Statistica software version 12.0. The input file contains the raw data consisting of 105 rows (samples) by 9 columns (chemical parameters). The clustering of cases (rows) was selected to cluster the samples, while the clustering of variables (columns) was used to cluster chemical parameters. Joining (tree clustering) was selected as the clustering method.

4.5. R-mode factor analysis (RFA)

The R-mode factor analysis (RFA) is a multivariate statistical technique used for data reduction and for deciphering patterns within large sets of data (Farnham et al., 2003). Once the pattern of the dataset is determined, it may be compressed by reducing the number of dimensions, without losing significant information. With RFA, the data matrix is reduced to factor scores and loadings. A correlation matrix is generally used so that each variable is normalized to unit variance and therefore contributes equally to the factor analysis (Farnham et al., 2003; Chen et al., 2007).

The extraction of factors was conducted on a symmetrical correlation matrix computed for the nine variables. This is the R-mode technique, used to infer relationships between variables (Davis, 1986). Factors are thus calculated so that they take into account the correlations present in the original data, but are uncorrelated to one another. The first factor explains the largest portion of the variance of the original data, and each subsequent factor explains progressively less (Farnham et al., 2003). The data can be reduced to two or three factors explaining the majority of the variance within the original dataset (Farnham et al., 2003; Chen et al., 2007), and a rotation factor can be applied to maximize the variance of the retained factors. In this study, the number of factors to be kept was based on the Kaiser criterion, which selects only the factors with eigenvalues greater than 1 (Cloutier et al., 2008). The method used was the Varimax normalized rotation, as in the analyses conducted by Melloul and Collin (1992), Cloutier et al. (2008) and Montcoudiol et al. (2014). The loadings were then evaluated to identify the elements that are responsible for these correlations. Elements with the greatest positive and negative loadings make the largest contribution. The loadings can therefore be examined to provide further insight into the processes that are responsible for the variation in groundwater geochemistry (Farnham et al., 2003). The factor scores for each groundwater sample can also be plotted and the plots inspected for similarities (Chen et al., 2007).

The RFA was carried out using the Factor Analysis module in the Multivariate Exploratory Techniques of Statistica version 12.0. The input file dataset is the same as for the HCA. The principal components are selected based on the extraction method and the minimum eigenvalue is set to 1, according to the Kaiser criterion. Varimax normalized is finally selected as the rotation factor.
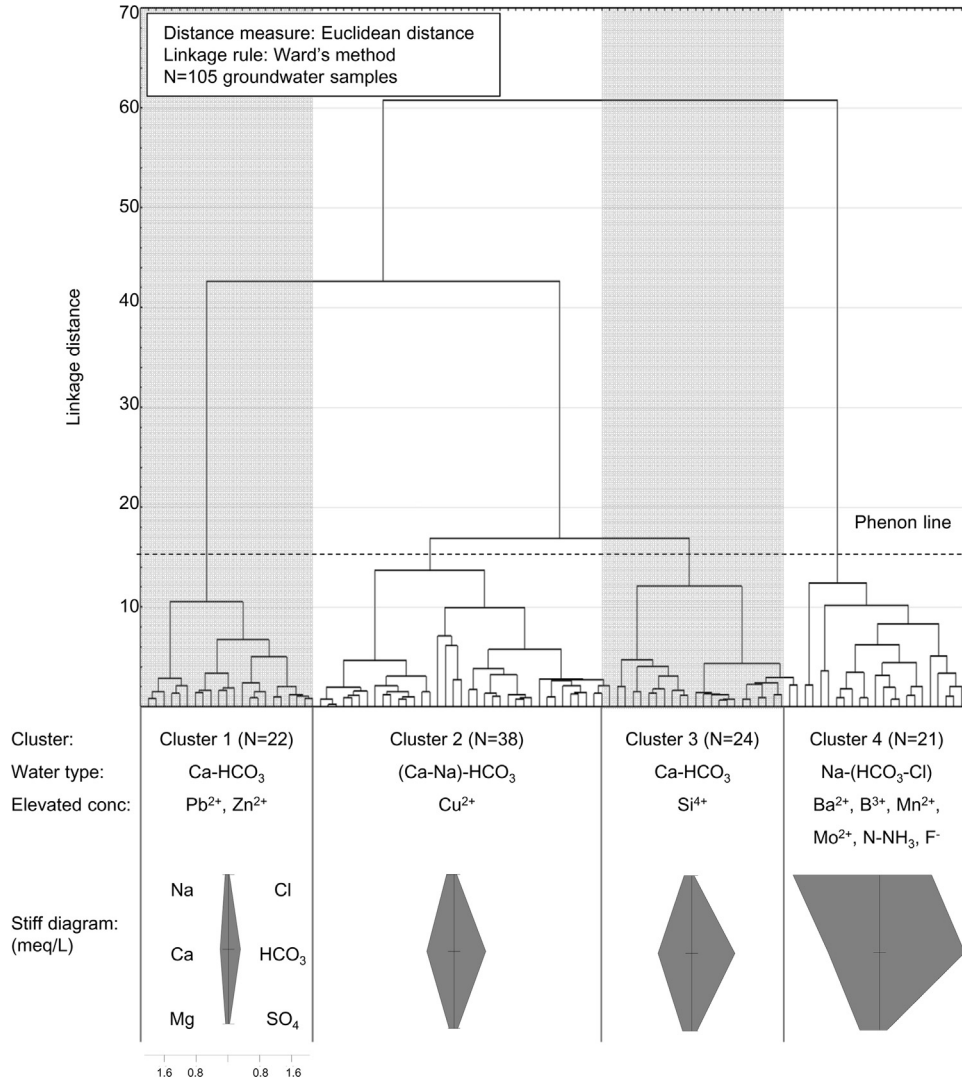
Fig. 4. Dendrogram and Stiff diagrams resulting from the HCA for the 105 groundwater samples, showing the distribution of these samples into four clusters, each having its own characteristic water type. For each cluster are also shown at the "Elevated conc." line those minor and trace constituents for which there was the highest measured concentration. Stiff diagrams are constructed based on the median values calculated for each cluster.

5. Results

5.1. Hierarchical cluster analysis (HCA)

The classification of the samples into clusters is based on a visual inspection of the dendrogram (Fig. 4). By moving the position of the phenon-line up or down on the dendrogram, one can define a greater or a lesser number of clusters (Güler et al., 2002). In this study, the phenon-line was drawn across the dendrogram at a linkage distance of 15. Samples with a linkage distance lower than 15 are thus grouped into the same cluster. This allows a division of the dendrogram into four clusters of groundwater samples.

Table 5

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

Parameters N	Cluster 1 $N = 22$	Cluster 2 $N = 38$	Cluster 3 $N = 24$	Cluster 4 $N = 21$
Chemical parameters used in the HCA				
Ca^{2+}	4.90	15.50	19.00	**29.00**
Mg^{2+}	1.05	1.75	3.15	**6.80**
Na^+	2.20	4.85	4.95	**56.00**
K^+	0.60	0.60	1.35	**3.20**
HCO_3^-	21.35	54.90	73.81	**146.40**
Cl^-	0.90	2.55	2.35	**52.00**
SO_4^{2-}	1.65	5.00	7.00	**10.00**
Si^{4+}	6.15	5.25	**7.15**	6.50
Sr^{2+}	0.03	0.09	0.16	**0.24**
Other chemical parameters				
Ba^{2+}	0.00	0.00	0.00	**0.02**
B^{3+}	0.01	0.01	0.01	**0.05**
Cu^{2+}	0.00	**0.00**	0.00	0.00
Mn^{2+}	0.00	0.00	0.00	**0.02**
Mo^{2+}	0.00	0.00	0.00	**0.00**
Pb^{2+}	**0.00**	0.00	0.00	0.00
Zn^{2+}	0.01	0.00	0.01	0.01
Total alkalinity	17.50	45.00	60.50	**120.00**
$N-NH_3$	0.01	0.02	0.03	**0.06**
F^-	0.06	0.20	0.10	**0.40**
Stable isotopes				
δ^2H (VSMOW)	−84.17	−87.24	**−90.13**	−86.29
$\delta^{18}O$ (VSMOW)	−12.01	−12.35	**−12.77**	−12.25
Physical parameters				
Temperature (°C)	**8.94**	7.68	**7.35**	7.63
pH	6.19	**7.63**	7.26	7.61
Dissolved O_2	**8.31**	3.65	0.63	0.00
TDS	24.50	61.00	71.50	**215.00**
Well depth (m)	2.75	**65.00**	45.50	54.00

N, number of samples; bold values: highest values; underlined values: lowest values.

The dendrogram inspection provides some indication of the level of similarity between the four clusters (Fig. 4). The linkage distance between Cluster 4 and the three other clusters is elevated (61), which indicates that groundwater samples in Cluster 4 are clearly and geochemically distinct from the groundwater samples of the three other clusters. Among these three clusters, Cluster 1 is the least similar with a high linkage distance (43) to Cluster 2 and Cluster 3. Cluster 2 and Cluster 3 have the lowest linkage distance (16) of the four clusters and have the greatest similarity among all clusters. It can therefore be expected that the geochemistry of the groundwater samples of Cluster 2 and Cluster 3 would present some similarity.

To evaluate the characteristics of each cluster of groundwater samples, Table 5 presents the median values of geochemical and physical data, including the 9 chemical parameters used in the HCA, as well as 10 minor and trace constituents, stable isotopes δ^2H and $\delta^{18}O$, temperature, pH, dissolved oxygen, TDS and well depth. Only 10 of the 30 other minor and trace constituents analyzed in the laboratory are included in this table because the median concentrations of the remaining constituents are identical for each cluster of samples and, therefore, appear irrelevant to our study. Minor and trace constituents with elevated median concentrations are indicated in Fig. 4. Stiff diagrams for each cluster based on the median values calculated for each cluster are also presented in Fig. 4. Stiff diagrams for Cluster 1, Cluster 2 and Cluster 3 have a similar shape with Ca^{2+} and HCO_3^- as the dominant ions, whereas the Stiff diagram for Cluster 4 shows a distinctive shape, with Na^+, HCO_3^- and Cl^- as the dominant ions. Table 6 presents the number of Ca-HCO_3, Na-HCO_3, Ca-Cl and Na-Cl water type samples from bedrock aquifers and from granular aquifers for each cluster, based on the previous inspection of the Durov diagram.

Table 6

Number of groundwater samples in each cluster of Ca-HCO$_3$, Na-HCO$_3$, Ca-Cl, and Na-Cl water types, from bedrock aquifers and from granular aquifers.

	Cluster 1		Cluster 2		Cluster 3		Cluster 4	
	R	G	R	G	R	G	R	G
Ca-HCO$_3$	1	16	22	8	16	7	9	1
Na-HCO$_3$	0	3	3	2	0	1	2	2
Ca-Cl	0	0	1	0	0	0	0	0
Na-Cl	0	2	0	2	0	0	5	2
Total	**1**	**21**	**26**	**12**	**16**	**8**	**16**	**5**

R, bedrock aquifer; G, granular aquifer.

Table 7

Factor loadings and explained variance for the three factors with Varimax normalized rotation.

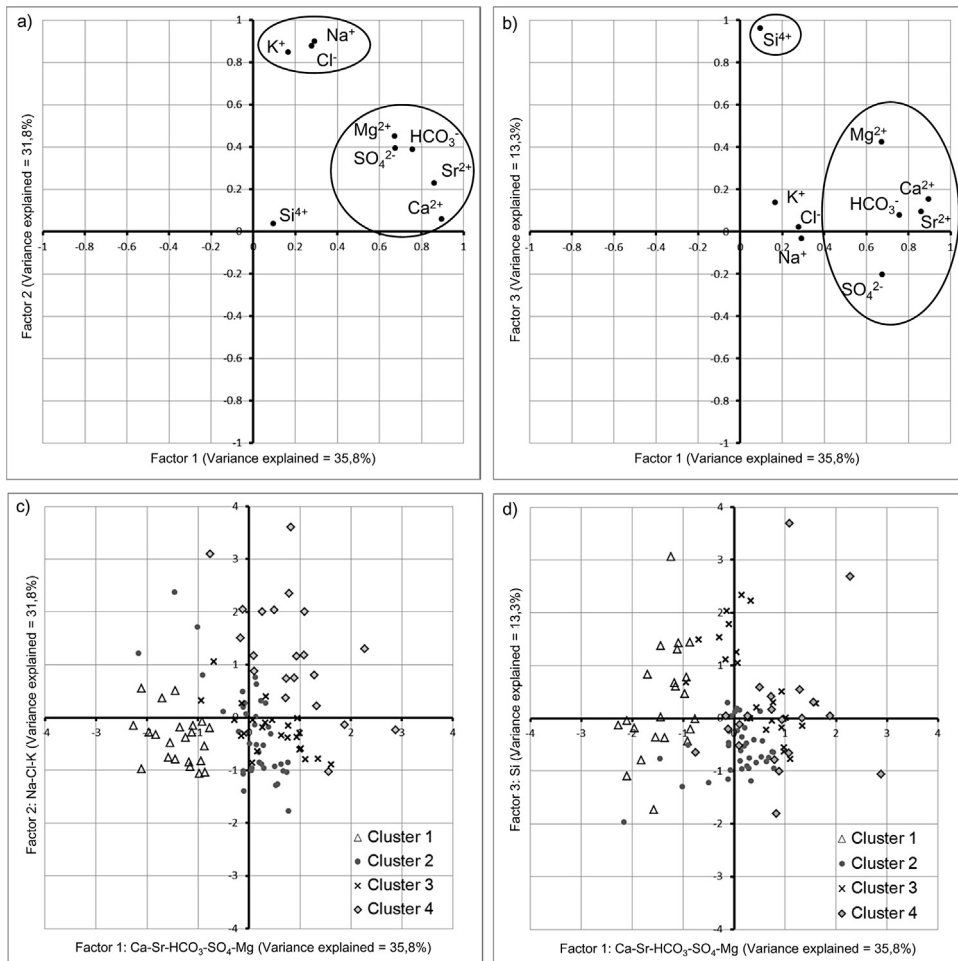| Parameters	Factor 1	Factor 2	Factor 3
Ca^{2+}	**0.90**	0.06	0.15
Mg^{2+}	**0.67**	0.45	0.42
K$^+$	0.17	**0.85**	0.14
Si^{4+}	0.10	0.04	**0.96**
Sr^{2+}	**0.86**	0.23	0.09
Na$^+$	0.29	**0.90**	-0.03
HCO$_3$$^-$	**0.76**	0.39	0.08
Cl$^-$	0.28	**0.88**	0.02
SO$_4$$^{2-}$	**0.68**	0.39	-0.20
Explained variance	3.23	2.86	1.20
Explained variance (%)	0.36	0.32	0.13
Cumulative % of variance	0.36	0.68	0.81

Bold values: loadings >0.67.

The Cluster 1 samples ($n = 22$) are mainly of the Ca-HCO$_3$ water type and are characterized by elevated concentrations of Pb^{2+}, Zn^{2+} and dissolved oxygen. The Cluster 1 samples also have the lowest pH and the lowest TDS values of all clusters. The Cluster 2 samples ($n = 38$) are mainly of the (Ca-Na)-HCO$_3$ water type and are characterized by elevated concentrations of Cu^{2+}, and by the lowest concentrations of Si^{4+} of all clusters. The Cluster 3 samples ($n = 24$) are of the Ca-HCO$_3$ water type and are characterized by the highest concentrations of Si^{4+} of all the clusters. The Cluster 2 and Cluster 3 samples show a number of similarities, including the TDS median value, but the Cluster 3 samples have higher concentrations of Mg^{2+}, K$^+$, HCO$_3$$^{2-}$, and Sr^{2-} than Cluster 2 samples. The Cluster 4 samples ($n = 21$) are of the Na-(HCO$_3$-Cl) water type and are characterized by elevated concentrations of Ba^{2+}, B^{3+}, Mn^{2+}, Mo^{2+}, N-NH$_3$ and F$^-$, as well as the lowest concentrations of Cu^{2+} and dissolved oxygen of all clusters, and the highest TDS values of all clusters. Ninety-five percent of Cluster 1 groundwater samples are from shallow granular aquifers, whereas 76% of Cluster 4 groundwater samples are from deeper bedrock aquifers. The Cluster 2 and Cluster 3 samples contain groundwater from both shallow and deep, granular and bedrock aquifers.

5.2. R-mode factor analysis (RFA)

The RFA allowed the extraction of nine factors. Only the first three factors have eigenvalues greater than 1; a Varimax normalized factor rotation was applied in order to maximize the variance. The first three factors account for 81% of the total variance in the dataset. The factor loadings for the first three factors and their respective explained variance are presented in Table 7. The first two factors, respectively, explain 35.9% and 31.8% of the variance, and therefore explain most of the variance in the dataset, while factor 3 explains 13.3% of the variance in the dataset.
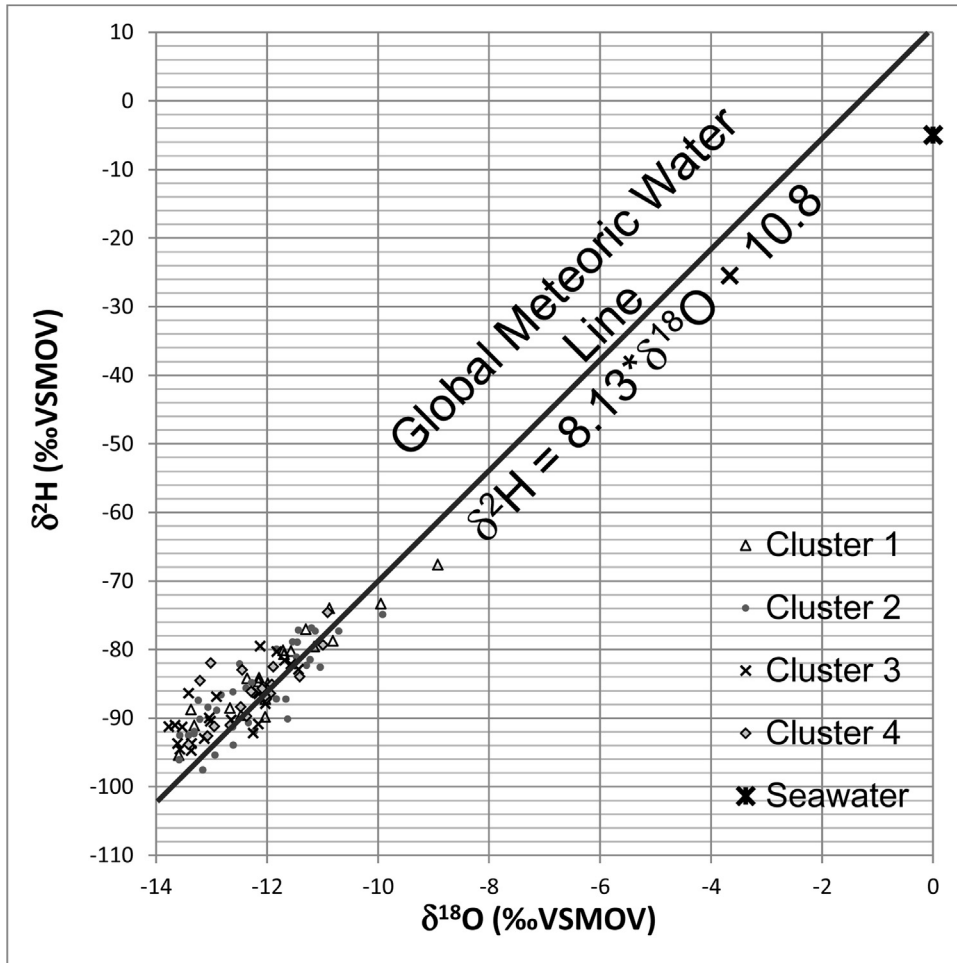
Fig. 5 shows the position of the loadings of chemical parameters in a plane defined by the axes of Factors 1 and 2 (a), and in a plane defined by the axes of Factors 1 and 3 (b). These plots help to identify which chemical parameters are associated with each factor. Factor 1 explains the greatest amount of

Fig. 5. Plot of the loadings for Factor 1 and Factor 2 (a) and for Factor 1 and Factor 3 (b) with Varimax normalized rotation. Plot of the factor scores for Factor 1 and Factor 2 (c) and for Factor 1 and Factor 3 (d) with the groundwater samples labelled according to their respective clusters.

the variance, and is characterized by highly positive loadings in Ca^{2+}, Sr^{2+} and HCO_3^-. The loading is also high for SO_4^{2-} and Mg^{2+} (Fig. 5a). Because of the association of Ca^{2+} and Mg^{2+}, Factor 1 is defined as the «hardness» factor (Cloutier et al., 2008). Factor 2 is characterized by highly positive loadings in Na^+, Cl^- and K^+ (Fig. 5a). Factor 2 is thus defined as the «salinity» factor. Factor 3 is characterized by a very highly positive loading in Si^{4+} (Fig. 5b).

RFA results are consistent with the HCA results, as illustrated in Fig. 5. The factor scores represent the influence of the factor on the groundwater samples (Cloutier et al., 2008). The distinction between clusters of samples is clear when plotting scores for Factor 1 versus Factor 2 (Fig. 5c). Cluster 1 samples are located on the middle-left side of the plot, whereas Cluster 4 samples are located on the upper right side. Cluster 2 and Cluster 3 samples are located in the middle of the plot and cannot be differentiated according to these factors. The distinction of Cluster 2 and Cluster 3 samples is however possible when plotting scores for Factor 1 versus Factor 3 (Fig. 5d). Cluster 1 samples are characterized by medium to high negative scores for Factor 1, low negative scores for Factor 2, and medium negative to high positive scores for Factor 3. Most Cluster 2 samples are characterized by low positive scores for

Fig. 6. Plot of $\delta^{18}O$ VSMOW versus δ^2H VSMOW, with the groundwater samples labelled according to their respective cluster. The Global Meteoric Water Line and the isotopic composition of seawater are indicated.

Factor 1, medium negative to low positive scores for Factor 2 and negative scores for Factor 3. Some end-members of Cluster 2 have high negative scores for Factor 1 in contrast to high positive scores for Factor 2. Cluster 3 samples have positive scores for Factor 1 and low negative scores for Factor 2 and low negative to high positive scores for Factor 3. Most of Cluster 4 samples have medium to high positive scores for Factor 1 and Factor 2, and medium negative to high positive scores for Factor 3.

5.3. Stable isotopes δ^2H and $\delta^{18}O$

The distribution of the samples in Fig. 6 follows the Global Meteoric Water Line, as calculated by Craig (1961), towards seawater isotopic composition ($\delta^2H = -5‰$ and $\delta^{18}O = 0‰$). This reflects mixing between seawater and meteoric water (Walter, 2010), and indicates that groundwater was not affected by evaporation processes. No distinction of isotopic composition can be observed based on the clusterization of the samples. Because of this alignment, we can state that all groundwater sampled for this study has a common origin, i.e., it is recharge water commonly found in temperate
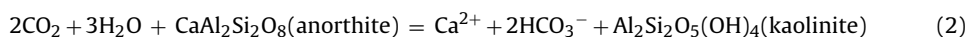
to cold climates. The calculation of the median values for stable isotopes (Table 5), however, allows a distinction since the Cluster 3 samples are slightly enriched in δ^2H.

6. Interpretation and discussion

HCA allows grouping the 105 groundwater samples into four clusters. The TDS values increase from Cluster 1 to Cluster 4 (Table 5) and the opposite is observed regarding the concentration in dissolved oxygen. The Cluster 1 groundwater samples have a more acidic pH than the groundwater samples of the three other clusters, and their temperature is the highest. Table 6 indicates that the Cluster 1 samples are mainly Ca-HCO$_3$ water type and come from shallow granular aquifers (95%). The Cluster 2 samples are mainly (Ca-Na)-HCO$_3$ water type and come from both shallow and deep, granular (31.6%) and bedrock aquifers (68.4%). The Cluster 3 samples are Ca-HCO$_3$ water type and also come from both shallow and deep, granular (33.3%) and bedrock aquifers (66.7%). The Cluster 4 samples are Na-(HCO$_3$-Cl) water type and come from deeper bedrock aquifers (76.2%). These observations indicate that the four clusters are geochemically distinct groups of groundwater samples, which were collected from different hydrogeological contexts, suggesting a relationship between groundwater chemistry and the hydrogeological context.

A Gibbs diagram (Gibbs, 1970) is presented in Fig. 7, plotting the TDS concentration as a function of the ratio between Cl and Cl + HCO$_3$ with the samples labelled according to their respective cluster. Since the TDS concentration increases from Cluster 1 to Cluster 4, the four clusters are easily distinguishable. All the groundwater samples mainly fall in the domain influenced by the geology. The Cluster 1 samples fall closer to rainwater than the samples in the other clusters, which is consistent with the previous observations (Table 5). The groundwater samples of Cluster 1 could thus correspond to low-salinity and recently infiltrated waters in recharge areas (Frape et al., 1984; Gascoyne and Kamineni, 1994). Elevated concentrations in Pb^{2+} and Zn^{2+} for Cluster 1 samples compared to the three other clusters are unexplained. The Cluster 2 and Cluster 3 samples are more influenced by the water–rock interactions and freshening has affected some of the Cluster 2 samples. These samples could correspond to mixed or intermediate water types from granular and bedrock aquifers (Frape et al., 1984; Rajmohan and Elango, 2004; Subramani et al., 2010). This last observation highlights the possibility of hydraulic connections between the Canadian Shield bedrock and the granular deposits as recently demonstrated by Chesnaux et al. (2012) and Richard et al. (2014). The Cluster 4 samples would therefore correspond to more saline and probably more mature water from bedrock aquifers (Frape et al., 1984; Gascoyne and Kamineni, 1994). These samples can be divided into two subgroups: one subgroup of samples influenced by the water–rock interactions and one subgroup of samples corresponding to mixtures between seawater and water undergoing some freshening (Fig. 7). These last samples mainly correspond to Na-Cl groundwater type, which could be the result of the natural evolution of groundwater along its flowpath and corresponding to ancient groundwater (Frape et al., 1984; Gascoyne and Kamineni, 1994). This groundwater type could also result from numerous groundwater salinization processes such as solute diffusion from a marine clay aquitard or saltwater intrusion (Cloutier et al., 2008; Beaudry, 2013; Montcoudiol et al., 2014).

Fig. 8a shows HCO$_3^-$ and Ca^{2+} enrichment from Cluster 1 to Cluster 4 by plotting HCO$_3^-$ concentration versus Ca^{2+} concentration with the groundwater samples labelled according to their respective clusters. Cluster 1 samples are characterized by the lowest HCO$_3^-$ and Ca^{2+} concentrations. Cluster 2, Cluster 3 and Cluster 4 samples are characterized by enrichment in Ca^{2+} and HCO$_3^-$. The distribution of the Cluster 2 and Cluster 3 samples follows the theoretical line of calcite and anorthite dissolution (Montcoudiol et al., 2014). Ca-rich mineral dissolution can thus be proposed as the primary process of Ca^{2+} and HCO$_3^{2-}$ enrichment for Cluster 2 and Cluster 3 samples (Rajmohan and Elango, 2004; Subramani et al., 2010; Montcoudiol et al., 2014). The weathering of Ca-rich silicates and the calcite dissolution (Eqs. (2) and (3); Appelo and Postma, 2005) are presented as a consistent process of Ca^{2+} and HCO$_3^-$ enrichment of the groundwater, since the basement of the study area is made up of charnockitic gneiss, granite and anorthosite, but also limestone in the area surrounding the meteor crater (Lemieux et al., 2003).
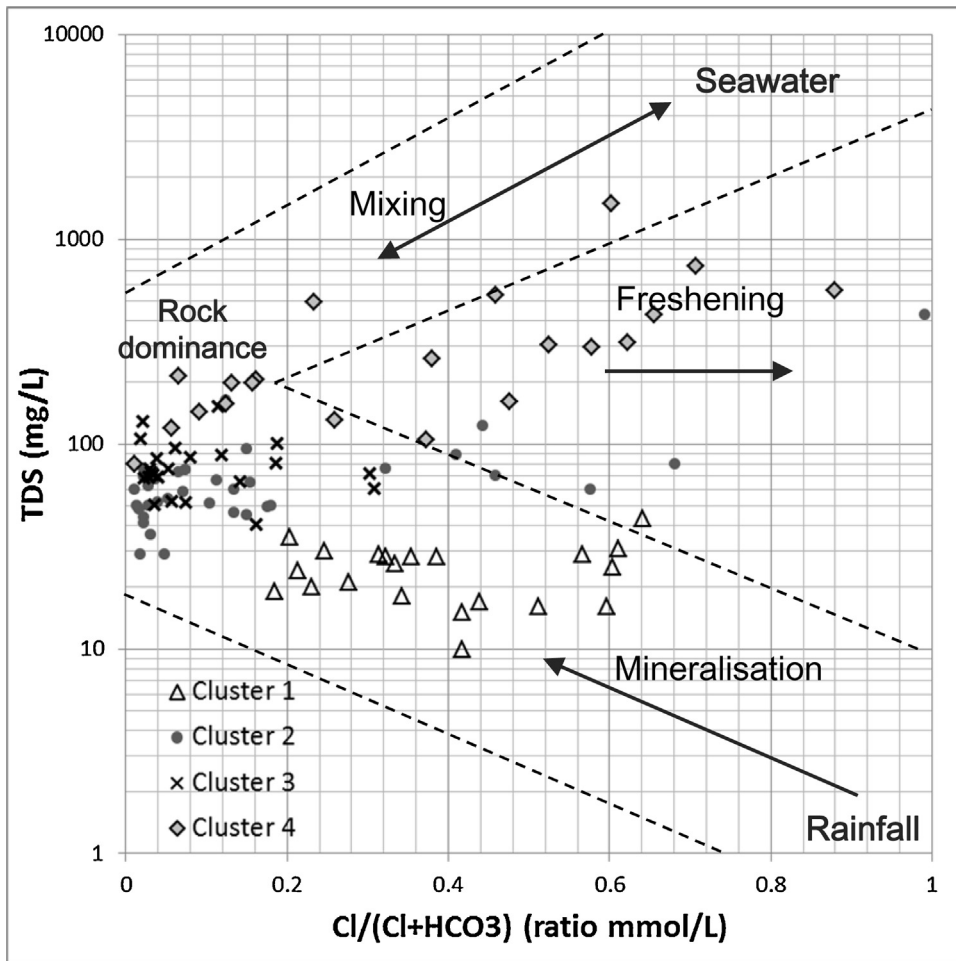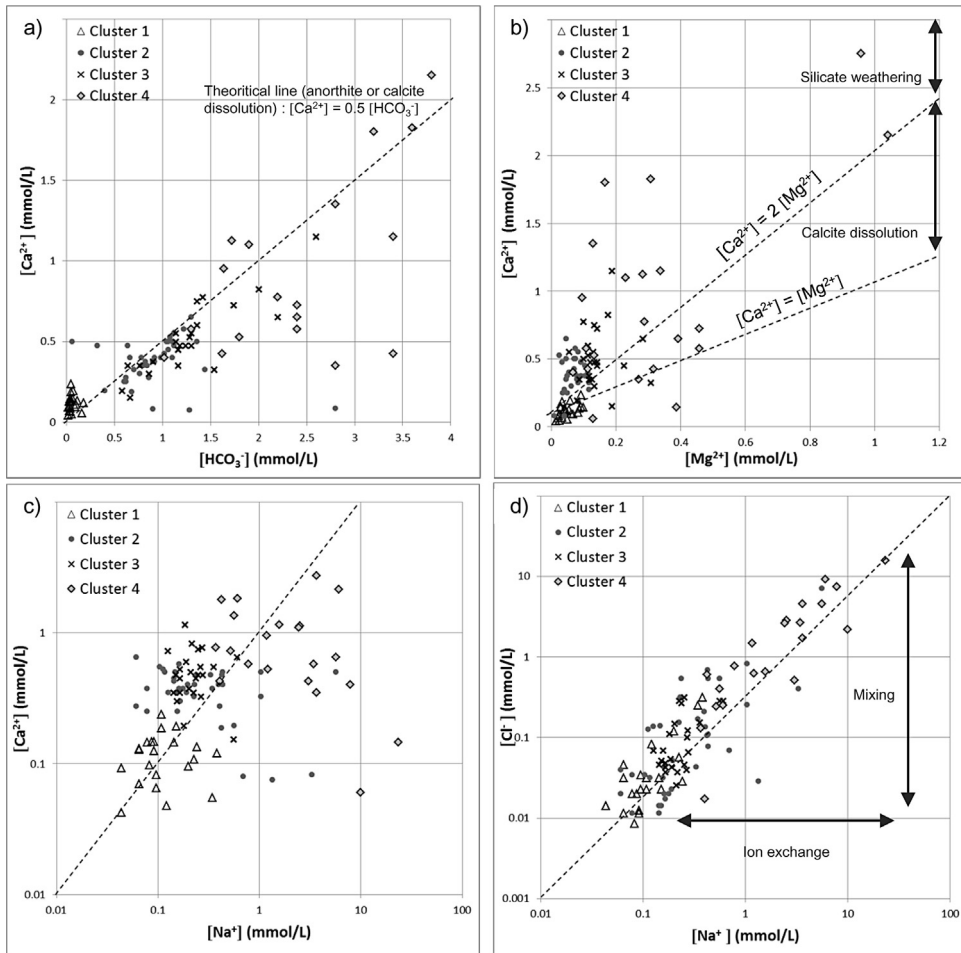
$$2CO_2 + 3H_2O + CaAl_2Si_2O_8(\text{anorthite}) = Ca^{2+} + 2HCO_3^- + Al_2Si_2O_5(OH)_4(\text{kaolinite}) \tag{2}$$

Fig. 7. Gibbs diagram plotting the TDS concentration as a function of the ratio between Cl and Cl + HCO₃ with the samples labelled according to their respective clusters. The main processes affecting each cluster of groundwater samples are determined according to the Cl and HCO₃ ratio.

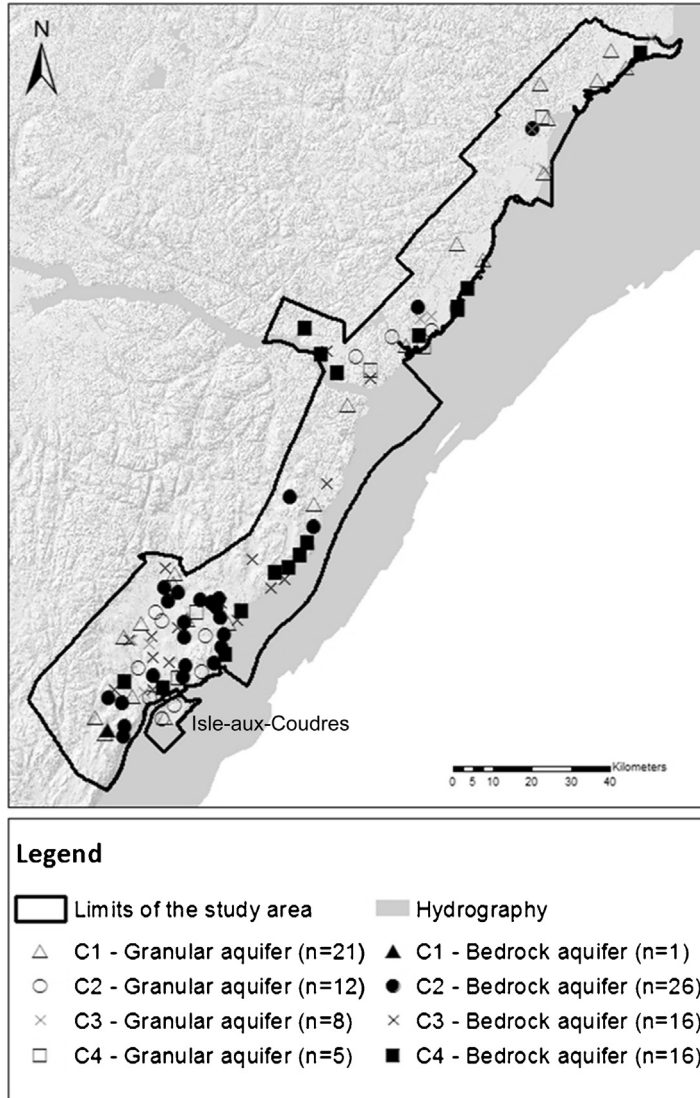$$CO_2 + H_2O + CaCO_3(\text{calcite}) = Ca^{2+} + 2HCO_3^- \tag{3}$$

These chemical reactions (Eqs. (2) and (3)) are consistent with the RFA results which show a high loading for silica on the third factor, further suggesting the importance of silicate weathering. This is also consistent with the Cluster 2 and Cluster 3 samples influenced by the water–rock interactions based on the Gibbs diagrams. In this study, the dissolution of anorthite is presented as the primary process of Ca^{2+} and HCO_3^- enrichment because this silicate mineral is easily dissolved (Montcoudiol et al., 2014). In Fig. 8b, most of the groundwater samples plot above the $[Ca^{2+}] = 2 [Mg^{2+}]$ line, indicating that silicate weathering dominates over carbonate dissolution (Rajmohan and Elango, 2004). However, some of the Cluster 3 and Cluster 4 samples plot below this line, indicating that the dissolution of calcite could also be a process of Ca^{2+} and HCO_3^- enrichment for some of these cluster samples (Rajmohan and Elango, 2004; Subramani et al., 2010; Montcoudiol et al., 2014).

In Fig. 8c, the samples from Cluster 1 to Cluster 4 mainly show an enrichment in Ca^{2+} and Na^+ concentrations which could be explained by silicate weathering (not only Ca-rich minerals) and calcite dissolution (Montcoudiol et al., 2014). Some of the Cluster 2 and Cluster 4 samples show high Na^+

Fig. 8. Plot of HCO_3^- concentration versus Ca^{2+} concentration (a), Mg^{2+} concentration versus Ca^{2+} concentration (b), Na^+ concentration versus Ca^{2+} concentration (c) and Na^+ concentration versus Cl^- concentration (d), with the groundwater samples labelled according to their respective clusters. The linear relationship between Ca^{2+} and HCO_3^- (a) and the comparison between Ca^{2+} and Mg^{2+} (b) are evidence of Ca-silicate weathering and calcite dissolution. Indications of Ca^{2+}/Na^+ ion exchange are provided by a decrease in Ca^{2+} concentration (c) or to constant Cl^- concentrations and enrichment in Na^+ (d) mainly for the Cluster 2 and Cluster 4 samples compared to the other samples. Enrichment in Cl^- and constant Na^+ concentrations suggest a mixing process (d).

concentrations associated with a lower Ca^{2+} concentration than the other samples. These samples appear to be mixtures influenced by ion exchange (Fig. 8d). The process of ion exchange is known to explain the deficit of calcium versus sodium in groundwater (Appelo and Postma, 2005). Based on the RFA results (Fig. 5), these samples are characterized by negative scores for hardness (Factor 1) in contrast to positive scores for salinity (Factor 2) which is consistent with the occurrence of ion exchange. The Cluster 1, Cluster 3 and Cluster 4 samples mainly follow the seawater dilution line but the Cluster 2 samples are more randomly distributed, reflecting significant ion exchange and mixing (Fig. 8d). The shape of the Stiff diagram for Cluster 4 samples is characterized by higher Na concentrations (Fig. 4). This could be explained by groundwater Na-enrichment (Cloutier et al., 2008;

Fig. 9. Regional distribution of the 105 groundwater samples with the samples labelled according to their respective clusters and the geological context. C1: Cluster 1; C2: Cluster 2; C3: Cluster 3 and C4: Cluster 4.

Walter, 2010; Montcoudiol et al., 2014) related to cation exchange of Na^+ by Ca^{2+} according to Eq. (4) (Gascoyne and Kamineni, 1994):

$$Ca^{2+} + 2Na\text{-}X(s) = 2Na^+ + Ca\text{-}X(s) \tag{4}$$

The Cluster 2 samples are thus influenced by Ca-rich silicate weathering, ion exchange and mixing while the Cluster 3 samples appear to be more affected by Ca-rich silicate weathering and calcite dissolution.

The geographical location of the clusters is presented in Fig. 9. The Cluster 2 samples collected from granular aquifers are located in the Haute-Côte-Nord, and on the island Isle-aux-Coudres, whereas the samples from bedrock aquifers are mainly located in the Charlevoix subregion, in the area surrounding
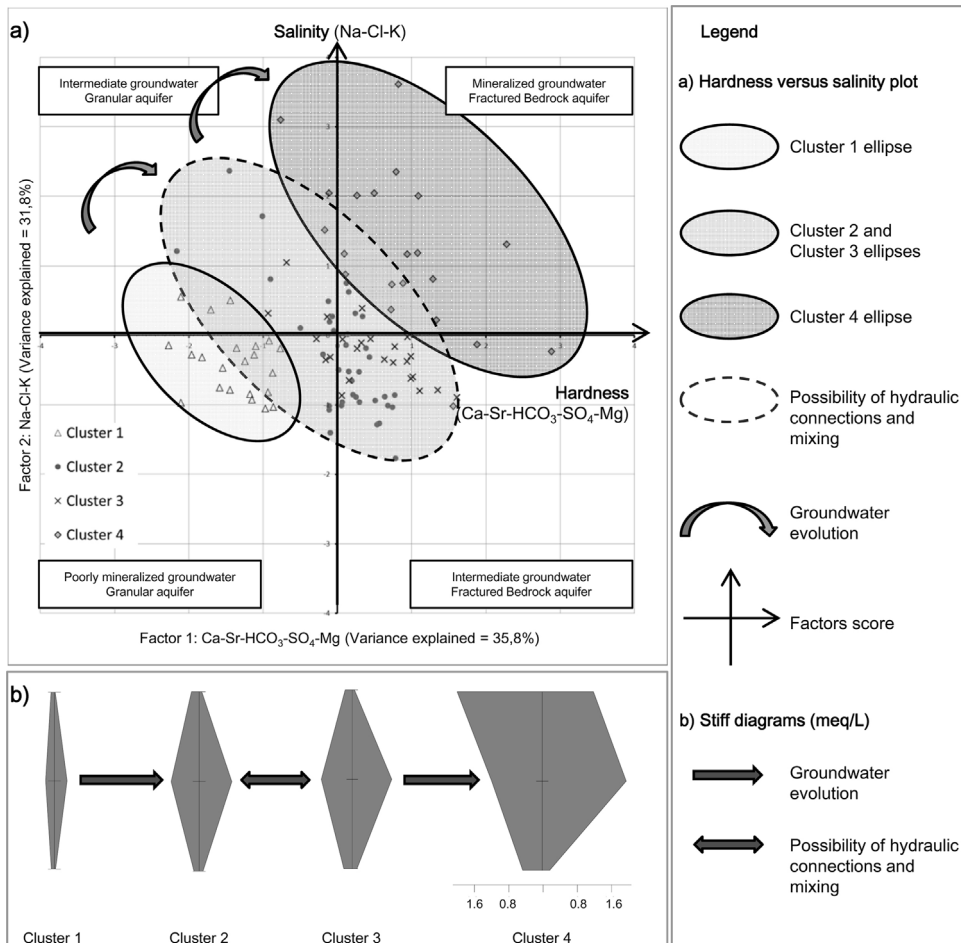
Fig. 10. Evolution of groundwater hydrogeochemistry. Plot of the factor scores for Factor 1 and Factor 2 with the samples labelled according to their respective clusters (a), and Stiff diagrams showing the relationship between the clusters and the groundwater groups' evolution (b). Groundwater of Cluster 1 corresponds to recharge groundwater and evolves along its flow path into Cluster 2 and Cluster 3 affected by possible hydraulic connections. Cluster 2 and Cluster 3 groundwaters then evolve into Cluster 4 groundwater present in discharge areas.

the meteor crater. A similar observation can be made regarding the Cluster 3 samples: the samples from granular aquifers are located in the Haute-Côte-Nord and the samples from bedrock aquifers are mainly located in the Charlevoix subregion. Since the Cluster 4 samples are located along the St. Lawrence River and the Saguenay coast where glaciomarine silty-sands and clays were deposited during the Goldthwait Sea episode 14,000 BP (Cousineau et al., 2014), solute diffusion from marine clay or saltwater intrusion can also be proposed as processes of groundwater salinization (Cloutier et al., 2008; Beaudry, 2013; Montcoudiol et al., 2014). A first Cluster 4 subgroup is thus composed of groundwater influenced by Ca-rich silicate weathering and calcite dissolution while a second Cluster 4 subgroup is composed of a mixture between seawater and water undergoing some freshening influenced by ion exchange. Higher concentrations of Sr^{2+}, Ba^{2+}, B^{3+}, Mn^{2+}, Mo^{2+}, and F^- in the Cluster 4 samples suggest a more intensive alteration of the bedrock minerals.

Finally, Fig. 10 presents a plot of the scores for the first two factors, hardness and salinity, with the samples labelled according to their respective cluster. This plot allows a good visualization of

the various groundwater types found in the region of Charlevoix and Haute-Côte-Nord, as well as insight into the geochemical processes responsible for these variations. The four clusters can be classified into plausible levels of groundwater evolution in the Charlevoix and Haute-Côte-Nord region. Cluster 1 represents low-salinity Ca-HCO$_3$ groundwater that corresponds to recently infiltrated water from surface granular aquifers in recharge areas. Cluster 4 Na-(HCO$_3$-Cl) groundwater is more saline and corresponds to more evolved groundwater. This groundwater plausibly originates from confined bedrock aquifers, since the Cluster 4 samples are distributed along the St. Lawrence River, where glaciomarine and marine sediments were deposited, forming an aquitard. Hardness (Factor 1) and salinity (Factor 2) have a strong positive influence on more saline groundwater samples from fractured rock aquifers of Cluster 4. On the contrary, these two factors have a negative influence on poorly mineralized waters from granular aquifers of Cluster 1. As mentioned previously, hardness (Factor 1) could be associated with the weathering of anorthite or with the dissolution of calcite of the silicate bedrock, but also with the groundwater recharge process. Salinity (Factor 2) could be associated with Na$^+$ enrichment processes such as Ca^{2+}/Na$^+$ ion exchange and with numerous processes of groundwater salinization such as solute diffusion from marine clay aquitards or saltwater intrusion (Cloutier et al., 2008; Beaudry, 2013; Montcoudiol et al., 2014). The Cluster 2 and Cluster 3 intermediate or mixed groundwater samples are less strongly influenced by the two first factors than the other cluster samples. The Cluster 2 and Cluster 3 (Ca-Na)-HCO$_3$ groundwaters could correspond to mixed or intermediate groundwater between Cluster 1 and Cluster 4 from possibly interconnected granular and bedrock aquifers (Chesnaux et al., 2012; Richard et al., 2014). The Cluster 3 samples are more influenced by Factor 3 (Si^{4+}). This third factor could also be associated with silicate weathering, since the study area is underlain by silicate rocks, as mentioned previously. This is consistent with the Cluster 3 samples having the highest concentrations in Si^{4+} of all clusters. The fact that the hydrogeochemical evolution of groundwater can be represented in the plane of Factors 1 and 2 confirms the importance of these two factors defined as the «hardness» and the «salinity» in the hydrogeochemistry of the Charlevoix/Haute-Côte-Nord aquifer system.

7. Conclusion

The groundwater chemistry of the Charlevoix/Haute-Côte-Nord region was studied as part of a regional hydrogeological characterization project. Groundwater samples were collected at 113 sites distributed over the whole study area, either in the bedrock (60 sites) or in the surficial deposits (53 sites). An ion-balance calculation led to the selection of 105 samples for the analysis.

The analysis of the stable isotopes δ^2H and δ^{18}O suggests that sampled groundwater has a common origin: recharge waters in a temperate to cold climate. This shows that there is mixing between seawater and meteoric water. The hierarchical cluster analysis allowed the sorting of the 105 samples into four clusters and to define a spatial geochemical zonation of the aquifer system. The four clusters are geochemically distinct groups of groundwater samples, and there appears to be a relationship between the groundwater clusters and the hydrogeological context. The R-mode factor analysis allowed the extraction of nine factors. The three first factors account for 81% of the total variance in the dataset. Factor 1 explains 35.9% of the variance and is characterized by highly positive loadings in Ca^{2+}, Sr^{2+}, HCO$_3{}^-$, SO$_4{}^{2-}$, and Mg^{2+}. Factor 2 explains 31.8% of the variance and is characterized by highly positive loadings in Na$^+$, Cl$^-$ and K$^+$. Factors 1 and 2 were defined as "hardness" and "salinity" factors, respectively. Hardness (Factor 1) could be associated with the weathering of Ca-rich silicates or the dissolution of calcite contained in the silicate bedrock. Salinity (Factor 2) could be associated with Ca^{2+}/Na$^+$ ion exchange and with numerous processes of groundwater salinization such as solute diffusion from marine clay aquitards or saltwater intrusion. Factor 3 explains 13.3% of the variance and is characterized by a very highly positive loading in Si^{4+} and could also be associated with the Ca-rich silicate weathering.

The integration of HCA, RFA and graphical analysis results allowed the classification of the four clusters into plausible levels of groundwater evolution in the Charlevoix and Haute-Côte-Nord region. Cluster 1 low-salinity Ca-HCO$_3$ groundwater corresponds to recently infiltrated water from surface granular aquifers in recharge areas. Cluster 4 Na-(HCO$_3$-Cl) groundwater is more saline and corresponds to more evolved groundwater. This groundwater plausibly comes from confined bedrock

aquifers. Cluster 2 and Cluster 3 (Ca-Na)-HCO$_3$ groundwater could correspond to mixed or intermediate groundwater between Cluster 1 and Cluster 4, from possibly interconnected granular and bedrock aquifers.

This study identified the main processes affecting the hydrogeochemical evolution of groundwater in the CHCN region as the following: groundwater recharge, water–rock interactions, ion exchange, solute diffusion from marine clay aquitards or saltwater intrusion, but also hydraulic connections between the Canadian Shield and the granular deposits.

These results are consistent with other studies carried out in other regions of the Canadian Shield, where geological and hydrogeological characteristics and geological history, including the latest glaciation and sea water invasion, were found to be the primary factors influencing the evolution of groundwater geochemistry (Cloutier et al., 2008; Beaudry, 2013; Montcoudiol et al., 2014). However, a better knowledge of the hydrogeological conditions would allow a better characterization of groundwater chemistry in relation to the hydrogeological context and a better identification of the geochemical processes influencing the evolution of groundwater chemistry. Further investigations, including more detailed studies of the lithology of the stratigraphic units of the CHCN aquifer system and the interpretation of pumping tests in order to identify hydraulic connections, could support the relationships between groundwater chemistry and the hydrogeological context discussed in this study. A local investigation and a greater amount of geochemical and hydrogeological data could allow a mapping of groundwater recharge areas.

Conflict of interest

The authors declare that there is no conflict of interest.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ejrh.2015.06.004.

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