Hydrogeochemistry and groundwater origin of the Basses-Laurentides sedimentary rock aquifer system, St. Lawrence Lowlands, Québec, Canada

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Abstract A comprehensive hydrogeochemical study was carried out in the Paleozoic Basses-Laurentides sedimentary rock aquifer system in Québec over a 1500 km^2 study area. Groundwater samples were collected at 153 sites, characterizing all geological and hydrogeological units to a maximum depth of 140 m. Groundwater was analyzed for major, minor and trace inorganic constituents, stable isotopes $\delta\,^{2}$H, $\delta\,^{18}$O, and $\delta\,^{13}$C of dissolved inorganic carbon (DIC), and some samples were analyzed for ^{3}H, and ^{14}C of DIC. The regional distribution of groundwater types shows that the hydrogeological conditions exert a dominant control on the major ions chemistry of groundwater. Preferential recharge areas are characterized by tritiated Ca-Mg-HCO_3 groundwater, and confined conditions by submodern Na-HCO_3 and Na-Cl groundwater types. Two groundwater end-members are identified in the aquifer system, modern meteoric water and Pleistocene Champlain Sea water. The region displays significant variations of groundwater geochemistry and quality controlled by glaciation, Champlain Sea invasion, lithological rock diversity, and flow system scales. This situation leads to varied groundwater types and origins within a restricted area.

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Résumé Une étude hydrogéochimique détaillée a été réalisée sur le système aquifère de roche sédimentaire Paléozoïque des Basses-Laurentides, au Québec, sur une région d'étude de 1500 km^2. Des échantillons d'eau souterraine ont été prélevés à 153 sites, caractérisant l'ensemble des unités géologiques et hydrogéologiques jusqu'à une profondeur de 140 m. L'eau souterraine a été analysée pour les constituants inorganiques majeurs, mineurs et traces, les isotopes stables $\delta\,^{2}$H, $\delta\,^{18}$O et δ^{13}C du carbone inorganique dissous (CID), et certains échantillons ont été analysés pour ^{3}H et ^{14}C du CID. La distribution régionale des types d'eau a montré le contrôle des conditions hydrogéologiques sur la chimie des éléments majeurs des eaux souterraines. Les zones préférentielles de recharge sont caractérisées par une eau souterraine enrichie en tritium de type Ca-Mg-HCO_3, et les zones confinées par des eaux souterraines submodernes de types Na-HCO_3 et Na-Cl. Deux sources d'eau souterraine sont identifiées dans le système aquifère, l'eau météorique moderne et l'eau Pléistocène de la Mer de Champlain. La région est caractérisée par des variations significatives de la géochimie et de la qualité des eaux souterraines, contrôlées par les glaciations, l'invasion de la Mer de Champlain, la diversité lithologique des roches, et l'échelle des systèmes d'écoulement. Cette situation engendre donc une grande variété de types et d'origines d'eau souterraine à l'intérieur d'une région restreinte.

Resumen Se llevó a cabo un estudio hidrogeoquímico completo en el sistema acuífero de roca sedimentaria Paleozoico Basses-Laurentides en Québec en un área de 1,500 km^2. Se tomaron muestras de agua subterránea en 153 sitios caracterizando todas las unidades geológicas e hidrogeológicas en una profundidad máxima de 140 m. Se analizó el agua subterránea por constituyentes inorgánicos mayores, menores y traza, isótopos estables δ^{2}H, δ^{18}O, y δ^{13}C de carbono inorgánico disuelto (CID), y algunas muestras se analizaron por ^{3}H y ^{14}C de CID. La distribución

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regional de los diferentes tipos de agua subterránea muestra que las condiciones hidrogeológicas ejercen un control dominante en los iones mayores de química del agua subterránea. Las áreas principales de recarga se caracterizan por agua subterránea tritiada en Ca-Mg-HCO_3, y condiciones confinadas por tipos de agua submodernas Na-HCO_3 y Na-Cl. Se identificaron en el sistema acuífero dos miembros extremos de agua subterránea, agua meteórica moderna, y agua Pleistocena del mar Champlain. La región muestra variaciones significativas de calidad y geoquímica de agua subterránea controlada por glaciación, invasión del mar Champlain, diversidad litológica rocosa, y escalas de sistema de flujo.

Keywords Hydrogeochemistry · Stable isotopes · Groundwater characterisation · Sedimentary rock · Canada

Introduction

Groundwaters of the Basses-Laurentides sedimentary rock aquifer system are a very important supply of freshwater for the region. With a population of about 250 000 inhabitants, approximately 23% depend on groundwater for their water supply. From this 23%, about 62% have their own wells and 38% are served by municipal well fields (MENV 2000). Groundwater also plays an important role in a variety of other sectors, such as agriculture for irrigation of crops and animal watering, groundwater-dependant industries (freshwater bottling, fish farming), rock quarries, or golf course irrigation (Nastev et al. in press a).

In the emerging context of sustainable development, and in the presence of different conflicts between groundwater users in the study area, a regional hydrogeological characterization project was initiated by the regional, provincial and federal governments. The general objective of this large project was to gain a better knowledge and understanding of the groundwater resources (quantity and quality) of the area in order to support their management and protection. Thus, the overall program covers both the hydrodynamics and hydrogeochemistry of the aquifer system. A second objective of this study was to develop a methodology to characterize, at the regional scale, fractured sedimentary rock aquifers (Savard et al. in press). As part of this project, Nastev et al. (2004, in press b) investigated the hydraulic properties and presented a numerical model of the groundwater flow for the regional aquifer, and Hamel et al. (2001) studied groundwater recharge in the sedimentary rock aquifer.

The hydrogeochemical characterization reported here specifically aimed at assessing groundwater quality at the regional scale, determining the groundwater origin, identifying the processes controlling groundwater geochemistry and understanding the geochemical evolution of groundwater in space and time. This report focuses on a complete description of the results of the geochemical characterization program, on the relationship between groundwater types and the geological and hydrogeological conditions, and on identification of the origin of groundwater in the area. Other papers using results from this investigation focus on the geochemical processes and on a multivariate statistical analysis of regional hydrogeochemistry data (Cloutier 2004).

The hydrogeochemical characterization program involved: (1) regional groundwater sampling from the recharge areas along groundwater flow paths to depths of about 140 m, (2) the geochemical characterization of all hydrogeological units, including the different rock formations, the till sediments and the clay aquitard, (3) the combined use of inorganic and isotopic geochemistry, and (4) the isotopic characterization of local precipitation. The complete geochemical dataset and the physical characteristics of the sampling sites are available in a table as Electronic Supplementary Material (ESM). The geochemical dataset establishes the natural geochemical composition of the groundwater in the region. That database can be used to follow the evolution of the water quality, identify areas vulnerable to contamination (Ross et al. 2004), and elaborate management strategies for the groundwater resource (Nastev et al. in press a). The Basses-Laurentides region has a highly variable groundwater geochemistry that made it a very interesting scientific case study. As it will be shown, that variability is largely due to the hydrogeological and geological conditions, and the Quaternary paleohydrogeology of the region.

Regional hydrogeochemical studies have been shown to be valuable to, among other applications, the management of regional aquifers (Gosselin et al. 2001), understanding groundwater evolution (Hendry and Schwartz 1990; Hiscock et al. 1996), tracing groundwater flow (Panno et al. 1994; Clark et al. 1998; Stimson et al. 2001), and salinization of groundwater (Vengosh et al. 2002). These integrated hydrogeochemical studies combine a variety of tools, including major and minor ions, isotope geochemistry, and hydrogeochemical modeling, with physical geological data and geophysics, to understand fluid flow and mass transport in complex aquifer systems. By its comprehensive characterization program, the hydrogeochemical study of the Basses-Laurentides aquifer system presented here is an integrated study, as it uses the knowledge of the geological and hydrogeological setting to support the geochemical interpretation.

Context of the study area

The study area is located on the north shore of the St. Lawrence River, northwest of Montréal as shown in Fig. 1. It covers approximately 1500 km^2, in a geographical region named the Basses-Laurentides. The Basses-Laurentides belong to the physiographic region of the St. Lawrence Lowlands, which has a generally flat topography, with the exception of the Monteregian Hills that are related to Cretaceous intrusions. There are two such intrusions in the Basses-Laurentides, the Oka Hills with a maximum elevation of about 250 m above mean sea level (masl), and the St. André Hills with an elevation of about 130 masl. The Laurentian Highlands, part of the Grenville Province

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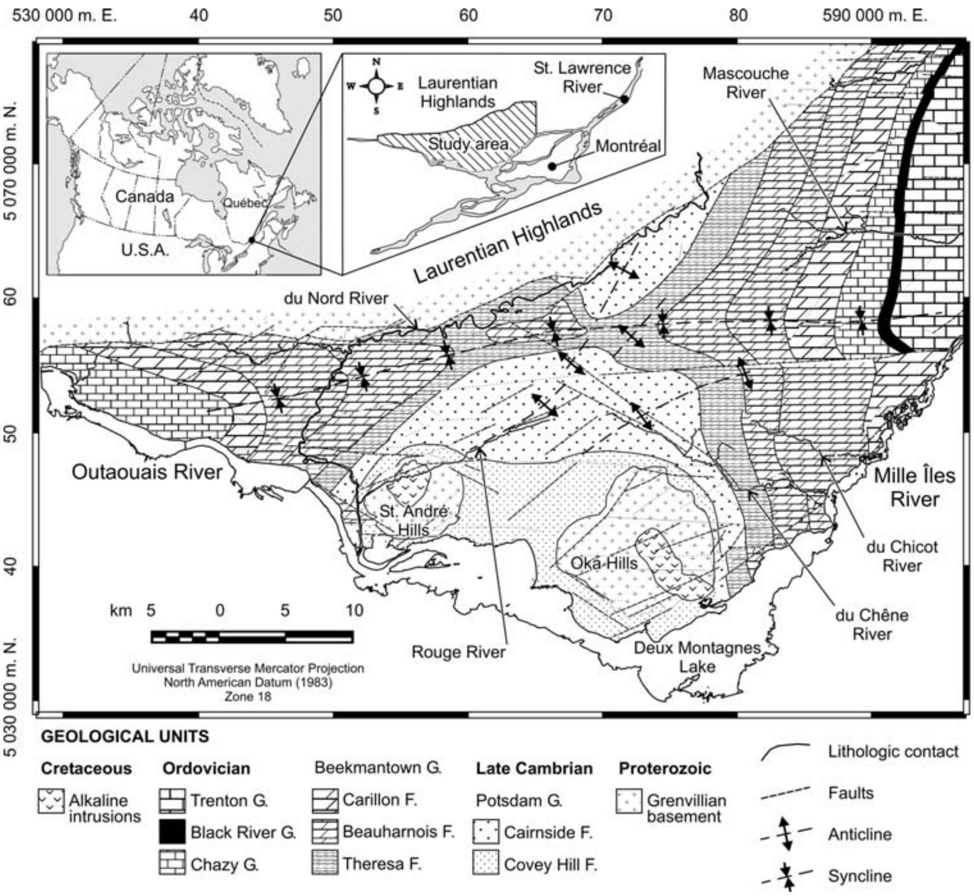

Fig. 1 Location and geology of the Basses-Laurentides sedimentary rock aquifer system (geological map modified from Rocher et al. in press)

of the Canadian Shield, border the study area to the north. The southwest, south, and southeast borders of the study area are surface water boundaries, namely the Outaouais River, the Deux Montagnes Lake, with an elevation of about 23 masl, and the Mille Îles River. To the east, the study area ends in the watershed of the Mascouche River. Many rivers and small streams drain the study area, the main ones being the du Nord River, Rouge River, du Chêne River, du Chicot River, and Mascouche River (Fig. 1).

Geological setting and history

Paleozoic and cretaceous geology

The Basses-Laurentides aquifer system, which is the focus of this study, is part of the St. Lawrence Platform geological Province (Fig. 1), which consists of nearly horizontal Cambrian-Ordovician autochthonous sedimentary formations lying in unconformity on crystalline basement of the Precambrian Grenville Province (Clark 1972; Globensky 1987). Sedimentary formations rarely crop out in the study area as they are generally covered by Quaternary sediments.

The Cambrian siliciclastic rocks of the Potsdam Group, at the base of the sedimentary sequence, is divided into two formations, the Covey Hill and the Cairnside (Globensky 1987). The Covey Hill is made of a reddish feldspathic sandstone, locally conglomeratic and poorly cemented. The Cairnside is a well-cemented, pure, quartz arenite sandstone. Salad Hersi et al. (2003) subdivide the Ordovician Beekmantown Group into three formations. The first two formations are the dolomitic sandstone and sandy dolostone of the Theresa, and the sandy to pure, massive, dolostone of the Beauharnois. The third formation is the Carillon, a pure dolostone with limestone near the top. The dissolution porosity of the dolostone units of the Beekmantown were cemented mostly by quartz and calcite (Chi et al. 2000). Above these 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). Organic matter is found in the carbonates of the Cambrian-Ordovician sequence as zooclasts and solid bitumen (Héroux and Bertrand 1991). Within the limits of the Montréal area, this sedimentary sequence is at least 1200 m thick (Clark 1972).

Precambrian rocks, such as quartzite, crystallized limestone, gneiss, and anorthosite, crop out north of the study area in the Grenville Province, and also form a window around the alkaline intrusions of Oka and St. André Hills. The Cretaceous intrusions are made of a variety of rocks, such as carbonatites, okaïte, lamprophyre, as well as metasomatic alteration of surrounding rocks (Gold 1972). Ultramafic sills, associated with the intrusions emplacement, are present in the Potsdam Group (Lewis 1971). The main structural features are the normal fault systems to the north along the contact with the Grenville Province, and

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the northeast-southwest anticlines in the center of the region, which expose the Ordovician units on both sides of the Cambrian sandstone.

Quaternary geology

The last Quaternary glaciation covered the Paleozoic and Grenvillian units with Upper Wisconsinan sediments, such as glacial till, and glaciofluvial sand and gravel (Bolduc and Ross 2001). During 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 marine invasion from the St. Lawrence Gulf. This marine invasion, which created the Champlain Sea, established its main basin at about 12 000 BP (Parent and Occhietti 1988) and submerged the study area for about 2000 years (Lévesque 1982). This 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).

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 overlies till or glaciofluvial sand and gravel units of variable thickness. The till is also found at the surface, above the rock sequence, in elevated topographic areas. The Champlain Sea reworked the upper part of this till unit. The till is highly variable in composition and texture depending on the underlying rock units; its composition relates mainly to the glacial erosion of Paleozoic sedimentary formations, such as sandstone, dolostone, and limestone, and, to a lesser extent, Precambrian rocks.

Hydrogeological setting

Hamel et al. (2001) have published a map of the hydrogeological conditions of the study area and a simplified version is presented in Fig. 2a. The map distinguishes the regions of the study area under unconfined or semi-confined conditions, as opposed to confined conditions. Unconfined or semi-confined conditions are generally found in areas

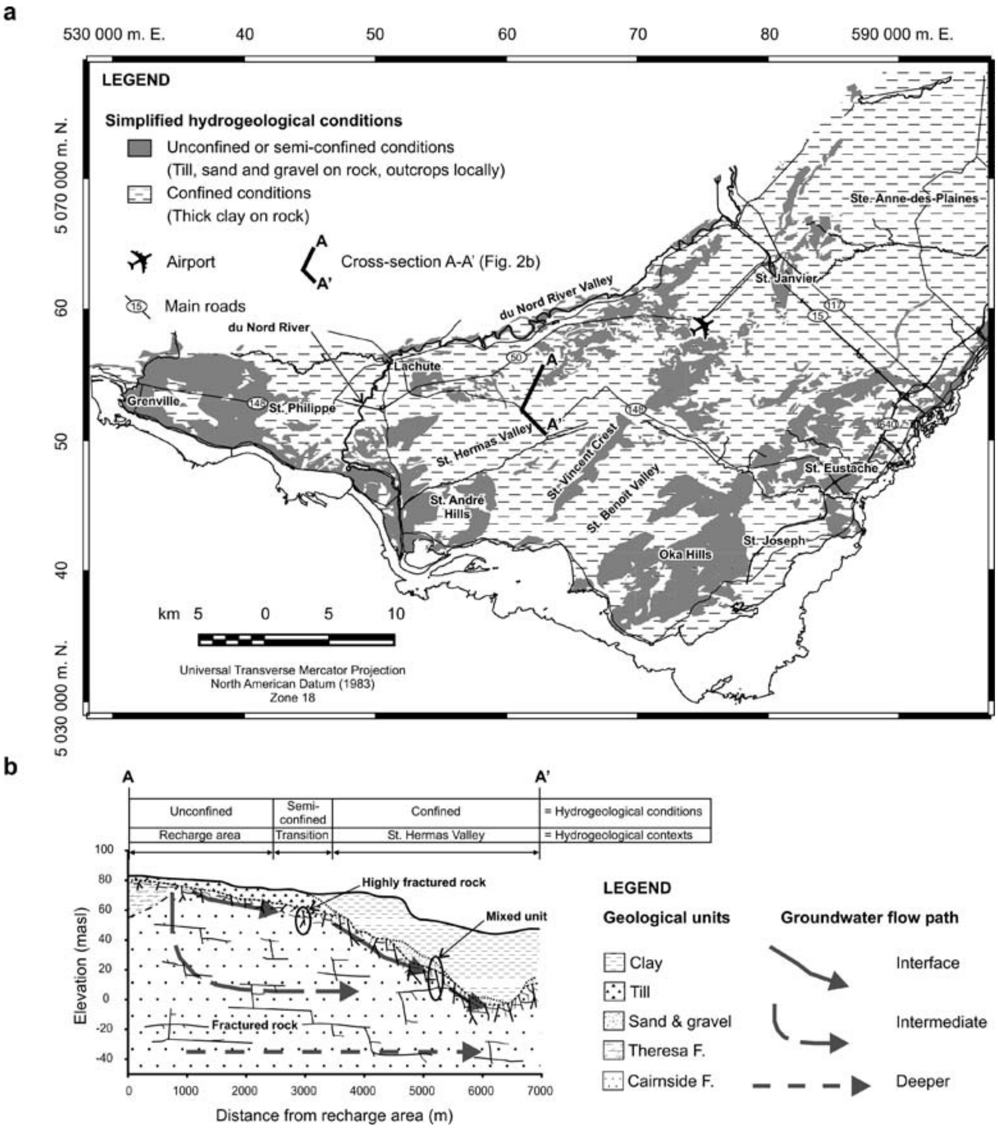

Fig. 2 (**a**) Simplified hydrogeological conditions (modified from Hamel et al. 2001), and (**b**) cross-section A-A′ illustrating the groundwater flow conceptual model and the main hydrostratigraphic units

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of elevated topography, either in bedrock or permeable surficial sediments. These sediments are generally till, but can also be alluvial sand and gravel. This hydrogeological condition is very important, as it characterizes areas of preferential groundwater recharge. The main recharge for the Basses-Laurentides sedimentary rock aquifer system is along a southwest-northeast axis, from Lachute to St. Janvier (Fig. 2a). This axis has an elevation between 70 masl and more than 80 masl. The other recharge zones are the Oka and St. André Hills, the region from the airport to St. Eustache, and the region from Grenville to St. Philippe, west of du Nord River. The last zone is the St. Vincent Crest, northwest of Oka Hills. This southwest-northeast Crest, with an elevation of about 60 masl, is a local recharge zone for the rock aquifer system.

For the remainder of the region, the rock aquifer system is confined by thick, low permeability Champlain Sea clays. These confined conditions prevail in three southwest-northeast trending buried valleys: (1) du Nord River Valley, bordering the Laurentian Highlands, (2) St. Hermas Valley, north of St. André Hills and St. Vincent Crest, and (3) St. Benoît Valley, between St. Vincent Crest and Oka Hills, where the clay thickness can reach more then 90 m. Flowing artesian wells are found in these three buried valleys. The surface elevation is about 60 masl in du Nord Valley, and 50 masl in St. Hermas and St. Benoît valleys. Bedrock depressions, filled with marine clay, are also found along the north-south segment of du Nord River, and at St. Joseph, east of Oka Hills. Finally, the clay reaches a thickness of more than 30 m in the eastern region of Ste. Anne-des-Plaines.

The transition from unconfined to confined conditions in the area, as well as the main hydrostratigraphic units adapted from Savard et al. (in press), are illustrated on the cross-section of the groundwater flow conceptual model (Fig. 2b). Infiltration of precipitation recharges the aquifer mainly through the till unit in the unconfined area. The till unit has a Km (geometric mean hydraulic conductivity) of 3×10^{-7} m/s (Hamel et al. 2001). The clay aquitard unit confines the aquifer downgradient of the recharge area. Based on hydrogeological and geological properties, the aquifer system can be divided into two distinct units: the highly fractured and the fractured rocks. The highly fractured rock consists of the first few meters of the sedimentary units that are more weathered, with fractures more inter-connected, than the underlying rock. Simard (1977) also observed this highly fractured unit in a hydrogeological study of the same aquifer. A mixed unit, consisting of highly fractured rock in hydraulic connection with sand and gravel, is also observed in the buried valleys and has a Km of 7.8×10^{-4} m/s (Nastev et al. 2001). These sand and gravel units can be glaciofluvial sediments or till deposited above the sedimentary rocks, below the clay aquitard. Below the highly fractured rock is the fractured rock unit of the aquifer system. As the sedimentary rocks are well cemented by quartz or calcite, the primary porosity is very low. Thus, groundwater flows through secondary porosity, such as fractures, bedding planes, alteration zones, or dissolution cavities. Hydraulic tests on the fractured rock unit provide a value of Km of 2.6×10^{-5} m/s (Nastev et al. 2004). Groundwater flow through the highly fractured rock is more important than in the deeper fractured rock unit, due to a higher hydraulic conductivity.

Figure 3 shows the potentiometric surface of the regional rock aquifer, with arrows showing the general direction of groundwater flow. The main groundwater flow paths are generally from north to south. The potentiometric surface follows the rock or surface topography, and is higher in the preferential groundwater recharge areas identified previously. The groundwater divides are observed in the main recharge areas, such as from Lachute to St. Janvier, and in the local groundwater flow system of the St. Vincent Crest.

Methods

The approach used to study this fractured rock aquifer system was to determine the hydrogeochemistry of groundwater for all hydrogeologic units, starting from the groundwater recharge areas, and following the regional flow paths. The study also involves the recognition of all hydrogeochemical sources that could influence the composition of groundwater, such as rain and snow melt in recharge zones, and clay pore water in the buried valleys. The complete hydrogeochemical characterization program is described by Cloutier (2004).

Groundwater sampling

The regional characterization of groundwater hydrogeochemistry, carried out in 1999 and 2000, consisted of groundwater sampling of private, municipal and observation wells. The private wells in the area are generally 15.24 cm diameter boreholes, with steel casing to bedrock and open to the rock aquifer from there to the bottom of the well. Thus, pumping draws groundwater from the whole open interval in bedrock. The private wells sampled were wells with known construction details, and known stratigraphy as much as possible. For the private and municipal wells, sampling was done using the production pumps, while bypassing water treatment units, if present. Observation wells belong mainly to two series of wells. The first series sampled are 15.24 cm boreholes installed by the Ministry of Natural Resources, Québec, in 1973 (Simard 1978). The second series was installed for the project of the Geological Survey of Canada (Savard et al. in press) in 1999 and 2000. They consist of 7.62 cm and 15.24 cm open boreholes in sedimentary rocks, as well as PVC screened piezometers installed in the surface sediments or mixed units. Sampling of the observation wells was done using either submersible or inertial pumps. Sampling and analytical protocols are detailed in the Appendix.

Regional groundwater samples were collected at 153 sites, to a maximum depth of about 140 m. Thus, the hydrogeochemical study covers the upper portion of the aquifer system, which is used for industrial, agricultural, and drinking water supplies. Figure 3 shows the location of the 146 groundwater sampling sites retained for the geochemical interpretation based on their electro-neutrality

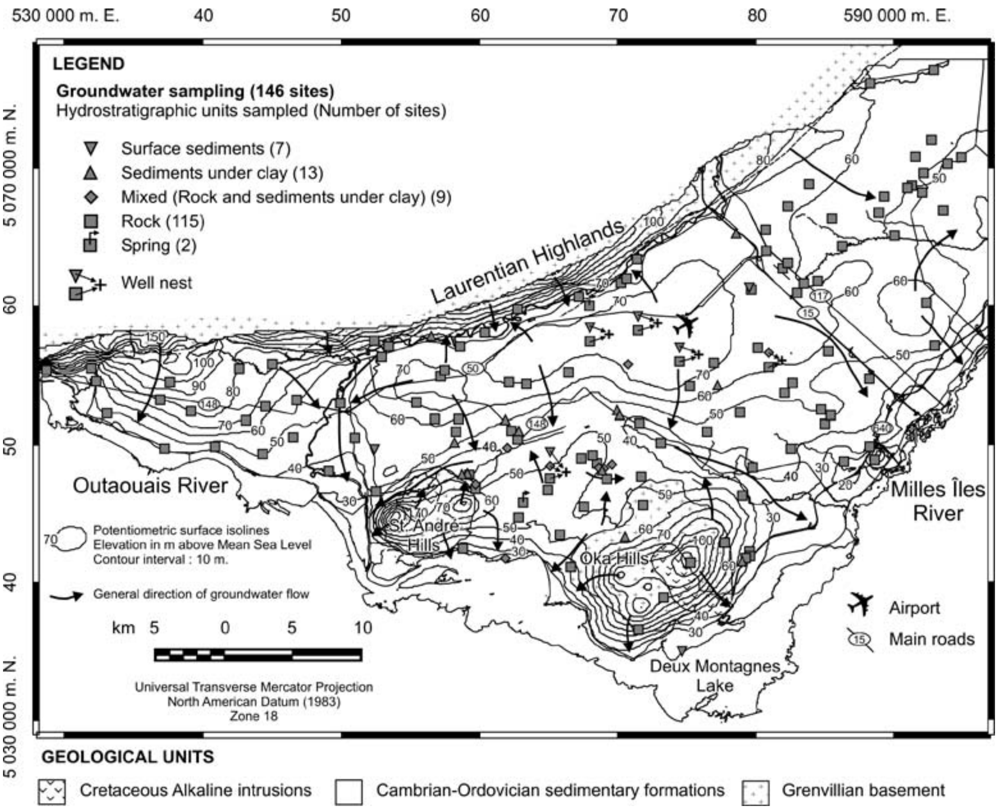

Fig. 3 Potentiometric surface of the rock aquifer in the study area, with the location of the groundwater sampling sites (potentiometric surface map modified from Paradis in press)

(see Appendix). The sampled sites cover all permeable hydrostratigraphic units (Fig. 3): 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 unit. The sampling sites are distributed over the whole region, characterizing the aquifer under unconfined and confined conditions, and for all geological formations. Figure 3 also shows the sampling sites relative to the general direction of groundwater flow. Most wells intercept only one geological formation, as the geological units are flat lying and the wells open interval is short relative to the formation thickness.

In 2000, 17 observation wells out of the 153 sites were sampled with a multilevel system. This system uses groundwater sampling of discrete permeable zones isolated by packers in boreholes open to bedrock, which allows the characterization of vertical trends in groundwater geochemistry. A double packer system, with a screened interval of 3.80 m length, was used to isolate the intervals. Cloutier (2004) provides details on the characterization methodology, including the sampling protocol for the multilevel system.

Results and interpretation of the regional hydrogeochemistry

Hydrogeochemical dataset

The complete geochemical dataset of the 146 samples having an electro-neutrality below 8% is available in Table ESM-1 (Electronic Supplementary Material). The dataset includes *in situ* field measurements, dissolved inorganic constituents, isotopic data, and geochemical modeling results. The dataset also includes physical and hydrogeological characteristics of the sampling sites. As a synthesis of the geochemical dataset, Table 1 presents selected descriptive statistics for the 146 samples. For calculation of the descriptive statistics, the elements with concentrations lower than the detection limit were replaced by the value of the limit.

Major and minor ions groundwater geochemistry

Figure 4 shows the composition of the groundwater samples, labeled according to their hydrogeological conditions, on a Piper diagram (Piper 1944). The 137 samples come from the rock, mixed, and sediments under clay hydrostratigraphic units. An ellipse was drawn to identify the field occupied by the seven groundwater samples from surface sediments and the two spring samples that are believed to discharge from surface sediments. The Piper diagram illustrates that the Basses-Laurentides aquifer system has a highly variable major ion chemistry. The surface sediments ellipse is in the Ca-Mg-HCO_3 zone, characterizing the recharge water in the Quaternary sediments, mainly till. The unconfined and semi-confined sampling sites are concentrated mainly in the Ca-Mg-HCO_3 zone of the diamond-shaped field indicating that it originates mainly from infiltration through the till in the preferential recharge area. In contrast, the confined samples are found in the Ca-Mg-HCO_3, Na-HCO_3, and Na-Cl zones. Samples in the Na-Cl zone are characterized by higher TDS. Sample S77, a

Table 1 Descriptive statistics of selected measured and calculated parameters (concentrations in mg/L unless noted)

Parameters	*N*	Mean	Min	Max	St. dev
pH	146	7.62	6.30	9.26	0.50
EC[a]	146	1077	265	18530	1706
DO[b]	129	2.99	0.12	11.48	2.60
Eh (mV)	123	+202	−6	+413	101
Ca	146	57.3	0.2	790	78
Mg	146	28.8	0.04	390	33
Na	146	135.7	1.6	3100	312
K	146	7.67	0.13	34	6.45
Cl	146	174	0.1	6500	591
SO_4	144	56.2	0.5	1200	119
Tot. Alk.[c]	142	266	33	810	99
DIC	130	65	14.4	180	23
Fe	143	0.487	0.0007	15	1.456
Mn	146	0.0812	0.0003	0.93	0.1477
Br	144	0.78	0.002	23	2.69
Sr	145	1.72	0.005	29	4.15
F	142	0.54	0.04	3.2	0.6
Ba	146	0.19	0.001	1.1	0.19
HS (as S)	142	0.14	0.02	4.7	0.58
SiO_2	146	12.9	5.5	24	3.6
B	145	0.15	0.002	1.4	0.21
NO_3 (as N)	144	0.40	0.02	11.7	1.49
NH_4 (as N)	144	0.33	0.02	7	0.69
PO_4 (as P)	144	0.16	0.01	2.1	0.40
DOC[d]	143	2.4	0.2	16.2	2.9
TDS[e]	146	610	138	11337	1025
HCO_3[f]	146	310.1	40.0	922.0	113.3
δ^2H (‰)	146	−76	−97	−56	5
$\delta^{18}O$ (‰)	146	−11.3	−14.0	−8.5	0.6
$\delta^{13}C_{DIC}$ (‰)	105	−14.3	−20.2	−4.7	2.4

N: Number of samples, Min.: Minimum, Max.: Maximum, St. dev.: Standard deviation

[a] Electrical conductivity corrected to 25°C (µS/cm)

[b] Dissolved oxygen

[c] Total alkalinity as $CaCO_3$

[d] Dissolved organic carbon

[e] Calculated total dissolved solids

[f] Geochemical calculations with PHREEQC 2.6 (Parkhurst and Appelo 1999)

sample from St. Benoît Valley, has the highest TDS of all the wells sampled in the course of this project (calculated TDS=11 337 mg/L). In the transition from Ca-Mg-HCO_3 to Na-HCO_3 and Na-Cl zones of the diamond-shaped field, the unconfined samples are less abundant relative to the confined samples. The Na-HCO_3 and Na-Cl zones are dominated by samples under confined conditions. No such grouping is observed when samples are divided by geological formations (Cloutier 2004). Thus, the Piper diagram indicates that the major ion chemistry is controlled more by the hydrogeological conditions than by the geology of the aquifer.

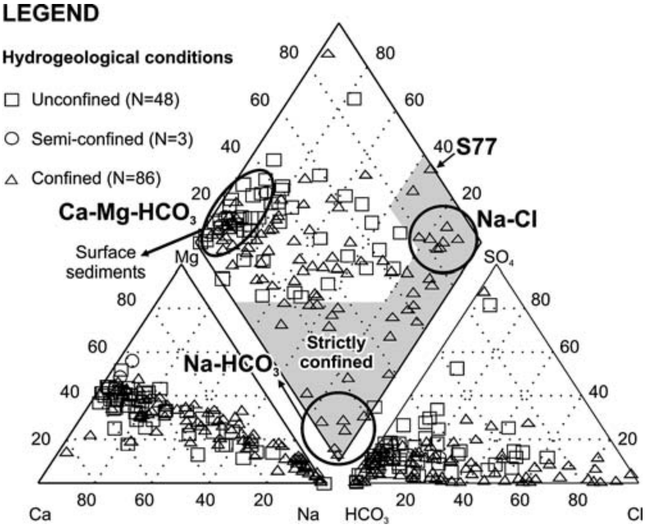

Fig. 4 Piper diagram illustrating the major ion chemistry of the groundwater samples labeled with the hydrogeological conditions

To facilitate the description and understanding of the regional groundwater hydrogeochemistry, geographical representations of some major and minor elements are used in Fig. 5. The chemical parameters chosen show regional variations, and can be used to identify and understand the processes controlling the groundwater geochemistry and the geochemical evolution of groundwater. Samples plotted in the geological maps are from the rock units, including the mixed unit and the sediments under clay unit. Thus, the regional distribution maps do not include samples from the surface sediments. Each map has a box plot diagram of the parameter to present the statistical results of surface sediments, unconfined and confined conditions. Descriptive statistics of the samples, in relation to the hydrogeological conditions and the geological units, are presented in Table ESM-2 and ESM-3 (Electronic Supplementary Material).

Box plots of field parameters show an increasing pH and a decreasing Eh from the surface sediments, to the unconfined, and confined samples (Fig. 5b). Values of pH greater than 8 are associated with the confined limestone of Ste. Anne-des-Plaines, and are found as well in St. Hermas and du Nord River valleys, and St. Joseph. Values of pH less than 8 characterize the preferential recharge areas. The recharge areas are generally characterized by higher Eh values than confined areas. DO has a behavior similar to Eh, with DO values decreasing from the surface sediments, to the unconfined, and confined samples (Table ESM-2).

The distribution of Ca^{2+} (Fig. 5c) is similar to that of Mg^{2+}. In the box plots, Ca^{2+} concentrations are more or less similar in the surface sediments and unconfined samples. The concentrations decrease in the confined areas of Ste. Anne-des-Plaines and buried valleys. The decrease is more important for Ca^{2+} than Mg^{2+}, with a median concentration of 62 mg/L in the unconfined, to 32.5 mg/L in the confined samples (Table ESM-2). The dolostone unit has the highest median concentrations for both ions (Table ESM-3). The distribution of Na^+ (Fig. 5d) has some similarities with that of Cl^-. Concentrations are higher in

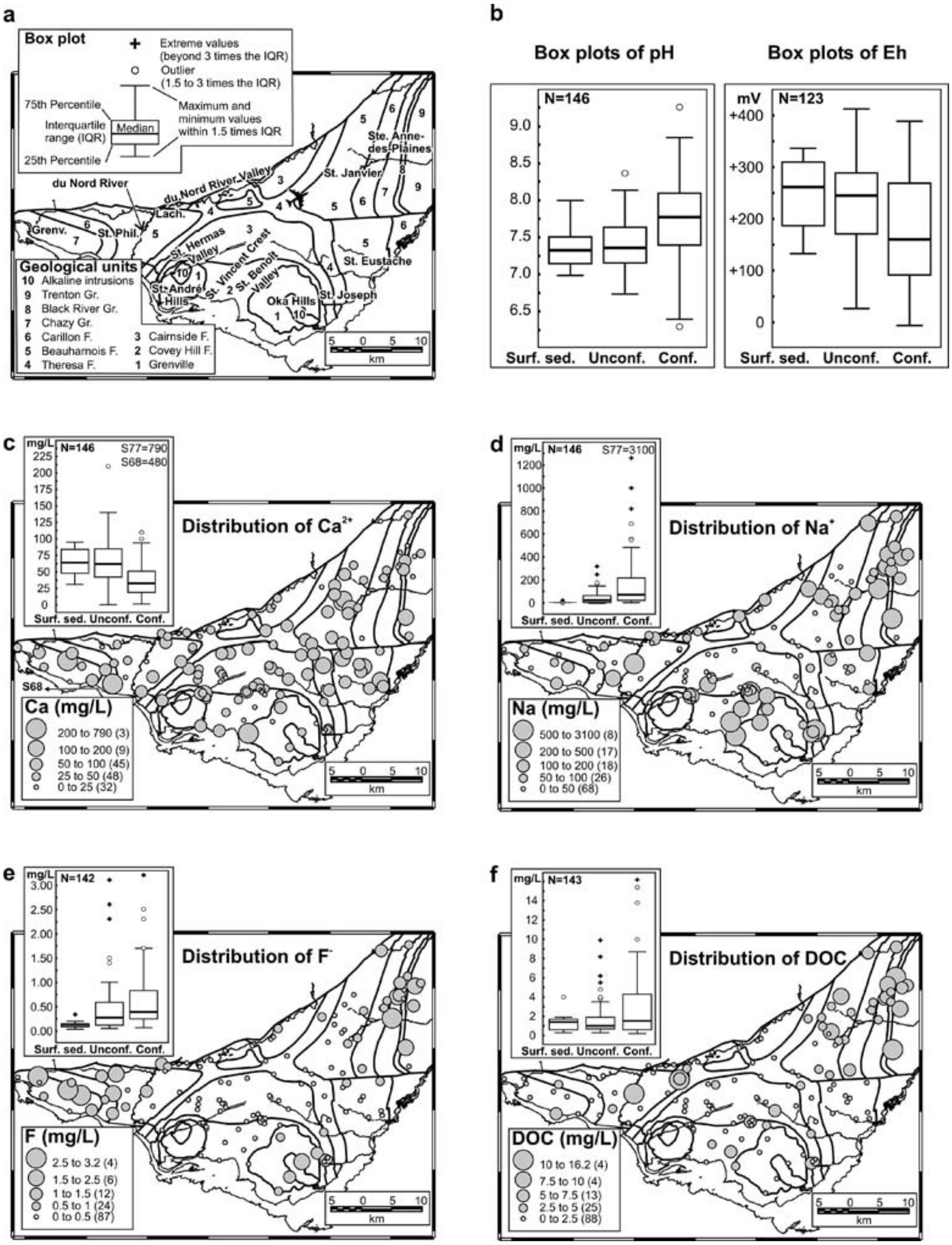

Fig. 5 (**a**) Legend for Fig. 5b to 5f (Gren. : Grenville, St. Phil. : St-Philippe, Lach. : Lachute), (**b**) box plots of the Basses-Laurentides aquifer system for the hydrogeological conditions of pH and Eh,(**c**) box plots of the Basses-Laurentides aquifer system for the hydrogeological conditions and regional distribution maps for the rock, mixed, and sediments under clay samples of Ca^{2+}, (**d**) Na^{+}, (**e**) F^{-}, and **f** DOC (Surf. Sed.: Surface sediments and springs, Unconf.: Unconfined and semi-confined, Conf.: Confined)

the buried valleys, particularly in St. Benoît Valley, and at St. Joseph. High values of both ions are also found in the unconfined area close to St. Janvier, along the main roads 15 and 117 (see Fig. 2a for roads location). On the other hand, the Na^{+} increase in the confined limestone of Ste. Anne-des-Plaines is not coupled to a Cl^{-} increase. Box plots show very low values of Na^{+} in the surface sediments. An important increase in concentration is observed from the unconfined to confined areas, characterized by elevated outliers and extreme values. The distribution of Br^{-} is very similar to Cl^{-} and thus Na^{+}, with an increase from the unconfined to confined conditions (Table ESM-2). An important observation is that Br^{-} values, unlike Cl^{-} and Na^{+}, do not increase in the unconfined area close to St. Janvier. The distribution of major ions Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, and minor ions Br^{-} is thus greatly influenced by the hydrogeological conditions. Cloutier (2004) showed that the distribution of SO_4^{2-}, HS^{-}, and NO_3^{-}, is also influenced by the hydrogeological conditions.

The distribution of F^{-} shows similar patterns for unconfined and confined conditions, with elevated numbers of outliers and extreme values (Fig. 5e). Concentrations in the surface sediments are much lower. High F^{-} concentrations dominate in the dolostone and limestone of the Carillon Formation, and in the limestone of the Chazy, Black River and Trenton groups. Thus, elevated concentrations are found in the eastern region of Ste. Anne-des-Plaines, and in the western region of Grenville to St. Philippe. F^{-}

in higher concentrations is also present in the Precambrian rocks of Oka Hills. As for F^-, Cloutier (2004) showed that the distribution of the minor ions Fe^{2+}, Mn^{2+}, Sr^{2+} and Ba^{2+}, is highly influenced by the geology.

The regional distribution of DOC (Fig. 5f) is not that different from the ones of $PO_4{}^{2-}$ and $NH_4{}^+$. These three parameters have higher interquartile ranges, outliers and extreme values, in the confined conditions. Even though there is some local variability, the larger grouping of elevated concentrations is found in the confined limestone of Ste. Anne-des-Plaines. The limestone unit has the highest median value for all three parameters (Table ESM-3). The distribution of $PO_4{}^{2-}$, $NH_4{}^+$, and DOC, could be influenced by both the hydrogeological conditions and geology.

Groundwater types and groups based on major ions

Various approaches have been taken to classify groundwater (Piper 1944; UNESCO 1975; Hem 1985) and they have been applied to regional studies (Back 1966; Ophori and Tóth 1989; Panno et al. 1994; Hiscock et al. 1996; Eberts and George 2000; Gosselin et al. 2001). Major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions ($HCO_3{}^-$, Cl^-, $SO_4{}^{2-}$) are most often used to determine the groundwater type of a sample. The approach of dominant and mixed groundwater types used for this study is described by Cloutier (2004).

Figure 6 shows the distribution map of the groundwater types for the 146 samples, and their relationships with the hydrogeological conditions. The ten water types are associated with four main groups, G1 to G4. Table 2 summarizes the information regarding each group, including the geology, the percentage of samples in the study area, the hydrogeological conditions where these types of water are more likely to be found, the main and secondary geographical areas where they are found, as well as the median values for the major elements. To help visualize the geographical grouping of water types, the groundwater relative quality zones are mapped (Fig. 6). The limits of the water quality zones were based on the distribution of groundwater groups. The relative groundwater quality, from zone A to G, were defined from the comparison of parameters to drinking water quality guidelines (Cloutier et al. in press). The main features of Fig. 6 and Table 2 are that samples located in the unconfined or semi-confined areas are characterized by groundwater belonging to Group 1 (G1) and Group 4 (G4), particularly by the dominant groundwater type Ca-HCO_3. Group 2 (G2) and Group 3 (G3) characterize the confined aquifers, dominated by the groundwater types Na-HCO_3 and Na-Cl respectively. Thus, the distribution map of groundwater types shows that the major ion chemistry of the groundwater is strongly related to the hydrogeological conditions.

The groundwater G1, representing 47% of the samples, is mainly found under unconfined and semi-confined conditions (Fig. 6 and Table 2). These samples are prevalent in the preferential groundwater recharge areas, namely from Lachute to St. Janvier, from the airport to St. Eustache, the St. Vincent Crest, as well as from Grenville to St. Philippe. The seven groundwater samples from the surface sediments, as well as the two springs, have a Ca-HCO_3 water type, and thus, belong to G1. As groundwater in the surface sediments is at the beginning of the flow system, the origin of groundwater G1 is modern meteoric water. The majority of samples from G1 have undersaturated to near equilibrium calcite and dolomite saturation indexes, suggesting that dissolution of carbonates is active in the recharge areas (Cloutier 2004).

Groundwater G4, representing only 2% of the samples, is a minor group (Fig. 6 and Table 2). The G4 samples are present in the dolostone and limestone on the west side of the territory, in the recharge area of Grenville to St-Philippe. Their elevated $SO_4{}^{2-}$ and Ca^{2+} concentrations relative to G1 result from local geochemical processes. The two samples with Ca-SO_4 water type have gypsum saturation indexes of −0.13 and −0.57 (Table ESM-1). Their near equilibrium values are evidence that gypsum dissolution is occurring at these sites.

The groundwater G2, representing 32% of the samples, characterizes areas mainly under confined conditions (Fig. 6 and Table 2). These samples are prevalent in the clay plain of Ste. Anne-des-Plaines, in the buried valleys of St. Hermas and du Nord River, as well as Oka Hills. Some geochemical characteristics of sites from these areas were illustrated previously, such as elevated Na^+ (Fig. 5d), low Ca^{2+} concentrations (Fig. 5c), and elevated pH. Table 2 shows that, from G1 to G2, the median value of Ca^{2+} decreases and that of Na^+ increases. Cl^- increases as well, but not as much as Na^+. The increase in Na^+ and pH, combined with a decrease in Ca^{2+}, suggests that Ca^{2+}-Na^+ ion exchange (where Ca^{2+}_{water} exchanges with $Na^{+}_{mineral}$) could be responsible for the evolution of groundwater from Ca-Mg-HCO_3 to Na-HCO_3 water (Thorstenson et al. 1979 ; Henderson 1985). Table 2 also shows that the median value of $SO_4{}^{2-}$ decreases from G1 to G2. This decrease is observed mainly in Ste. Anne-des-Plaines, where HS^- increases and low Eh suggest the occurrence of sulfate reduction (Cloutier 2004).

The groundwater G3, representing 19% of the samples, is prevalent under confined conditions (Fig. 6 and Table 2). These samples are characteristic of the buried valley of St. Benoît, but can be found sporadically in the buried valleys of St. Hermas and du Nord River, at St. Joseph, and Ste. Anne-des-Plaines as well. Some sites along the main roads 15 and 117, particularly around St. Janvier, have Na-Cl or mixed cations-Cl groundwater types even though they are located in unconfined areas. Table 2 shows that, from G1 to G3, the median values of Na^+ and Cl^- increase significantly. From the knowledge of the geological history, the source for Na^+ and Cl^- could be Champlain Sea water.

In order to understand the origin of the Na-Cl water, pore water was extracted from the clay aquitard at five sites and analyzed for major elements, as well as for Br^-, Sr^{2+}, δ^2H and $\delta^{18}O$. There are similarities in elements concentration between the groundwater S77, the most saline groundwater located in St. Benoît Valley, and the clay pore water sample C85-14. Groundwater S77 has a Cl^- concentration of 6500 mg/L, and a Br^- concentration of 23 mg/L. S77, a

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Table 2 Characteristics of groundwater types and groups

	Group 1 (G1)	Group 2 (G2)	Group 3 (G3)	Group 4 (G4)
Dominant Water Type (*N*)	Ca-HCO_3 (59) Mg-HCO_3 (4)	Na-HCO_3 (35)	Na-Cl (25)	Ca-SO_4 (2) Na-SO_4 (1)
Mixed Water Type (*N*)	Alkaline earth-HCO_3 (5)	Mixed cations-HCO_3 (12)	Mixed cations-Cl (2); Na-Mixed anions (1)	
Geology				
Surface sed	9	0	0	0
Sed. under clay	3	7	3	0
Limestone	6	8	4	2
Dolostone	28	18	10	1
Sandstone	21	9	11	0
Grenvillian	1	5	0	0
Total	68	47	28	3
%	47	32	19	2
Hydrogeological conditions	Unconfined Semi-confined	Confined	Confined	Unconfined Semi-confined
Main locations	Lachute to St. Janvier; Airport to St. Eustache; St. Vincent Crest; Grenville to St. Philippe	Ste. Anne-des-Plaines; St. Hermas Valley; du Nord River Valley; Oka Hills	St. Benoît Valley	Grenville to St. Philippe
Secondary locations	Around St. André Hills; du Nord River Valley; Oka Hills	St. Benoît Valley; St. Joseph	St. Joseph; St. Hermas Valley; du Nord River Valley; Ste. Anne-des-Plaines; St. Janvier (along main roads)	
Median concentration (mg/L)				
Ca^{2+}	61	28	24.5	210
Mg^{2+}	29	21	29	38
Na^{+}	13.6	77	305	90
K^{+}	3.7	7.8	15	5.3
HCO_3^{-}	291	297	332	181
Cl^{-}	11.5	47	390	33
SO_4^{2-}	34	24	48.5	660

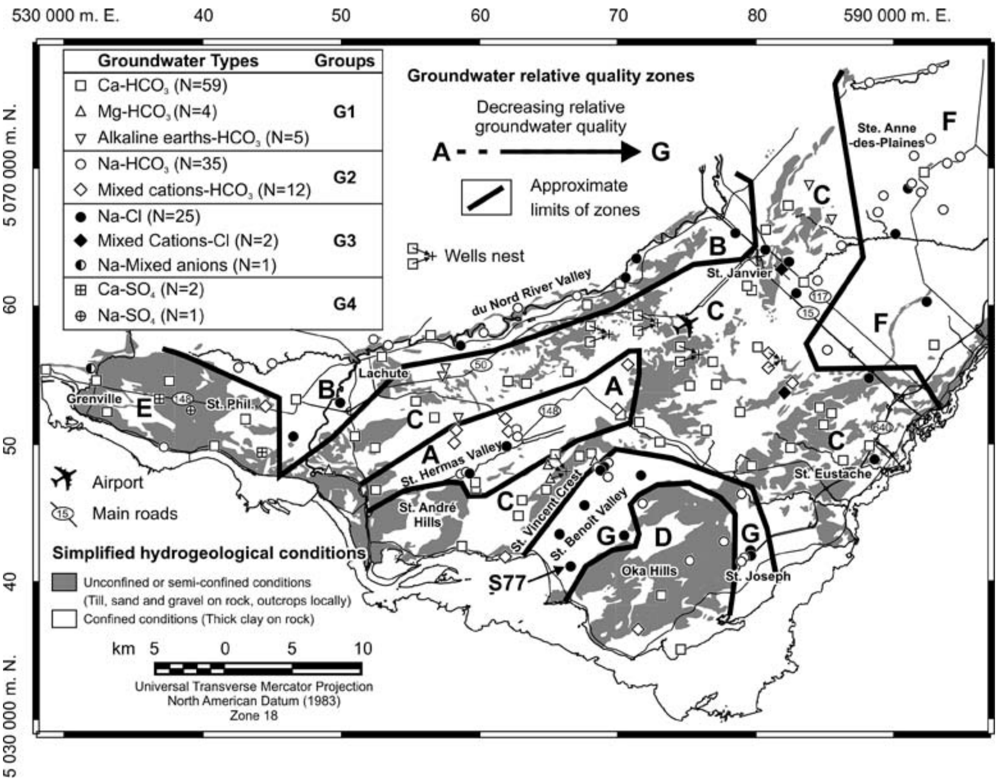


Fig. 6 Regional distribution map of groundwater types and groups, and their relation to the hydrogeological conditions (groundwater relative quality zones from Cloutier and Bourque in press)

private well, is a 15.24 cm diameter boreholes with steel casing to bedrock. The clay thickness reaches about 70 m, and the well is open from about 70–140 m in sandstone (Covey Hill Formation). The well S77 was also sampled with the multilevel system, with five levels sampled between 71 and 101 m. The concentrations in Cl$^-$ vary from 6300 to 6600 mg/L, indicating the presence of saline groundwater for at least the first 30 m of the aquifer in the area. The pore water sample is from site S85, in St. Hermas Valley, where the clay thickness reaches 46 m. Sample C85-14, from a depth of 14.1 m, has the highest Cl$^-$ concentration in this profile, 6900 mg/L, and a Br$^-$ concentration of 18 mg/L.

The concentrations of the conservative elements Cl$^-$ and Br$^-$, that can be used as tracers to identify the origin of groundwater salinity (Vengosh et al. 2002), are in the same range for S77 and C85-14. This similarity in Cl$^-$ and Br$^-$ suggests a unique and common origin for both samples. As the clay was deposited in the Champlain Sea, it is supposed that sample C85-14, the most saline sample at that site, represents the original Champlain Sea water for this area. As mentioned previously, Champlain Sea water was composed of a mixture of Pleistocene meteoric water and glacial meltwater from the Laurentide Ice Sheet, and seawater from the Gulf. Thus, the groundwater sample S77 is believed to belong to a stagnant part of the aquifer system, and is interpreted as the original Champlain Sea end-member for the study area. Similarity between the two samples is also observed in their δ^{18}O, the clay pore water having a δ^{18}O of −10.9‰, and S77 of −11.0‰. The other samples from G3 would be the result of groundwater mixing between residual Champlain Sea water, and water infiltrating the aquifers following deglaciation. For the St. Janvier samples, the low Br$^-$ concentrations indicate a different source. Located in a recharge area, and close to main roads, de-icing salts are the most plausible source of Na$^+$ and Cl$^-$ for these samples. The mixing model for the origin of groundwater salinity, based on the comparison to seawater, Cl/Br ratio, and δ^{18}O, is more developed in Cloutier (2004).

Groundwater isotopic signatures

δ^{18}O and δ^2H values

Through infiltration in the preferential groundwater recharge areas, precipitation is the main source of groundwater renewal to the Basses-Laurentides aquifer system. The δ^2H and δ^{18}O values of precipitation samples were used to establish the local meteoric water line, the Basses-Laurentides Meteoric Water Line (BLMWL) (Cloutier 2004). Figure 7 shows that the groundwater samples are distributed around the BLMWL, and indicates no significant isotopic modifications by evaporation. The Basses-Laurentides Groundwater Line (BLGWL), calculated by least-squares regression of the 146 groundwater samples, is not far from the BLMWL. Cloutier (2004) showed that there is no preferential grouping of samples related to geology. The meteoric water line for Ottawa (Rozanski et al. 1993) is at the lower limit of the groundwater samples, more or less parallel to the BLMWL. The Ottawa station is located about 120 km west of the study area, in the continuation of the St. Lawrence Lowlands.

The mean δ^{18}O for all groundwater samples is −11.3‰, with a standard deviation of 0.6 (Table 1). The δ^{18}O values

Fig. 7 δ^2H and $\delta^{18}O$ for groundwater of the Basses-Laurentides sedimentary rock aquifer system

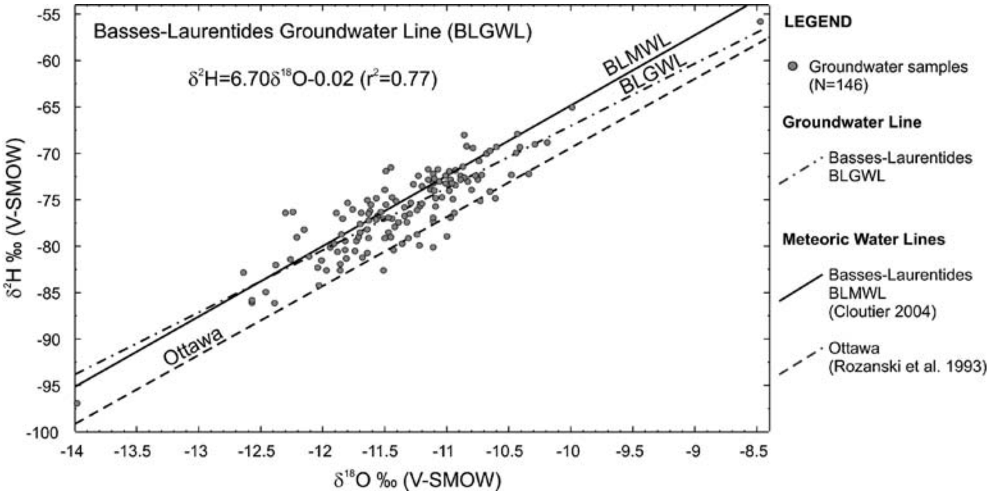
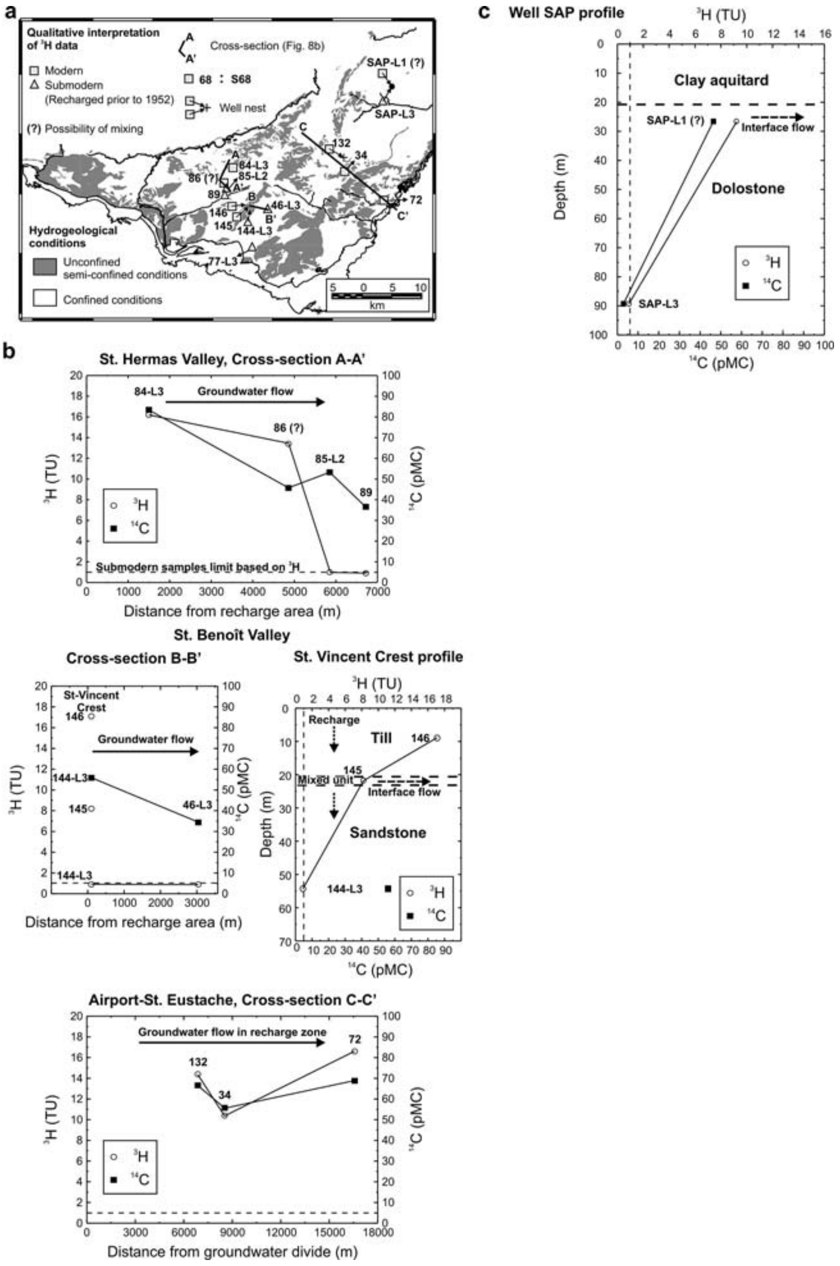


Fig. 8 (**a**) Qualitative interpretation of ^3H data, and location of cross-sections, (**b**) ^3H and ^{14}C of DIC along the 3 cross-sections, and (**c**) vertical distribution of ^3H and ^{14}C results at well SAP, Ste. Anne-des-Plaines



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have a relatively small range, with about 83% of the samples between −12.0‰ and −10.5‰. Groundwater under unconfined and semi-confined conditions has a normal distribution, with a mean $\delta^{18}O$ of −11.4‰ and a standard deviation of 0.5. This mean value, representing the recharged groundwater to the Basses-Laurentides aquifer system, is very similar to the $\delta^{18}O$ weighted annual mean of −11.21‰ for Ottawa precipitation (IAEA 2001). An interesting observation is that no significant variations are found in $\delta^{18}O$ between groundwater from unconfined and confined conditions. The normal distribution is relatively similar, and the mean $\delta^{18}O$ of confined groundwater is −11.3‰ with a standard deviation of 0.6. This uniformity in $\delta^{18}O$ between unconfined and confined conditions could indicate a common origin for both groundwaters, namely modern precipitation, or well mixed groundwater sources in the confined aquifers. The discrimination between these possibilities is discussed in a paper which describes geochemical processes in greater details (Cloutier 2004).

Carbon-13 on DIC

Stable carbon isotopes on DIC are useful as tracers of dissolved inorganic carbon sources and carbonate evolution in groundwaters (Chapelle and Knobel 1985; Clark and Fritz 1997; Cane and Clark 1998). Study of $\delta^{13}C_{DIC}$ is particularly relevant in the groundwater of the Basses-Laurentides aquifer system as it comprises carbonate formations, and the till in recharge areas is made in part of carbonate minerals. $\delta^{13}C_{DIC}$ were analyzed for 105 out of the 146 groundwater samples. The $\delta^{13}C_{DIC}$ values are highly variable, and range from −20.2‰ to −4.7‰. The mean $\delta^{13}C_{DIC}$ for the samples is −14.3‰, with a standard deviation of 2.4 (Table 1). About 70% of the groundwater samples have a $\delta^{13}C_{DIC}$ between −16.0‰ to −12.0‰, which indicates that dissolution of marine carbonates could be an important process in this aquifer system.

In the recharge area, the infiltrated water is in equilibrium with the soil CO_2 which has, for natural vegetation in temperate regions (C_3 vegetation), a $\delta^{13}C$ of about −23‰ V-PDB (reference defined by the IAEA in Vienna to report $\delta^{13}C$ measurements) (Clark and Fritz 1997). Dissolution of carbonate minerals in recharge areas adds HCO_3^- to the DIC of groundwater. As most marine carbonates have $\delta^{13}C$ of −2 to 0‰ V-PDB (Mazor 1991), their dissolution, and the addition of enriched HCO_3^-, contribute to the enrichment of groundwater $\delta^{13}C_{DIC}$ relative to $\delta^{13}C$ of soil CO_2. In a study of groundwater recharge to Paleozoic carbonate aquifer located in the St. Lawrence Lowlands southwest of this present study, Cane and Clark (1998) calculated the $\delta^{13}C_{DIC}$ of groundwater resulting from infiltration through C_3 vegetation ($\delta^{13}C_{CO_2} = -23‰$) following the dissolution of carbonate ($\delta^{13}C=0‰$). The final $\delta^{13}C_{DIC}$ calculated is −14‰ for open system, and −11.5‰ for closed system conditions. Sample S146, a groundwater from the till at St. Vincent Crest recharge area, has $\delta^{13}C_{DIC}$ of −15.0‰, very close to the calculated value of Cane and Clark (1998) for carbonate dissolution in an open system condition. Thus, the variation in $\delta^{13}C_{DIC}$ of samples from depleted to enriched values would be caused by carbonate dissolution operating in open, to semi-open, and finally under closed conditions.

Tritium and radiocarbon dating

To evaluate the mean residence time of groundwater and, by extension, the activity of the flow system, fourteen samples were analyzed for enriched ^3H, and twelve for radiocarbon analysis of DIC. The samples were chosen to represent the different hydrogeological settings of the aquifer system. Figure 8a presents the distribution of the sampling sites. Of the fourteen samples, seven were collected using the multilevel sampling system (S46-L3, S77-L3, S84-L3, S85-L2, S144-L3, SAP-L1, SAP-L3). The left part of the label represents the observation well ID, as S46, that was also sampled by conventional sampling. The right part (L3) is the level sampled which represents the third level sampled in well S46. Samples SAP-L1 and SAP-L3 were collected at well SAP, an observation well that does not appear in the geochemical dataset of the 146 samples because its conventional sample was rejected due to analytical problems. The ^3H data were corrected for the elapsed time between sampling and analysis, in order to determine the ^3H concentrations at the time of sampling. These calculations were made using the ^3H decay equation, and tritium's half-life, $t_{1/2}$ of 12.43 years (Clark and Fritz 1997). Measured and corrected ^3H data are presented in the Table ESM-1 dataset.

The qualitative interpretation of the ^3H data (Fig. 8a) is based on the presence of tritium in groundwater, and allows division into modern and submodern waters, i.e. recharged prior to 1952 (Clark and Fritz 1997). A quantitative interpretation of the ^{14}C data will be presented in a subsequent paper. The qualitative interpretation of the mean residence time of groundwater is generally consistent with the hydrogeological map (Fig. 8a). Six samples with modern tritiated water characterize groundwater in the preferential recharge areas, under unconfined or semi-confined conditions. Two samples, S86 and SAP-L1, are confined and have modern tritiated water. These sites could have been affected by groundwater mixing, modifying their ^3H and ^{14}C values. Finally, six samples are submodern water, and characterize groundwater in the confined aquifers such as the buried valleys.

Figure 8b shows ^3H and ^{14}C variations along three cross-sections. Four samples were analyzed in St. Hermas Valley cross-section A-A′, from S84-L3 in the recharge area, to S89 in the confined aquifer downgradient. With a ^3H value of 16.2 TU and a ^{14}C of 83.5 pMC, S84-L3 is clearly a modern, recently recharged groundwater. The first well downgradient in the valley, S86, with a ^3H of 13.4 TU, also has a value that could indicate the presence of recently recharged groundwater. On the other hand, its much lower ^{14}C, 45.7 pMC, suggests older water. This apparent contradiction in age could result from mixing of old groundwater with modern water infiltrating along the well casing. The last two sites, S85-L2 and S89, having 1 and <0.9 TU respectively and low ^{14}C, are classified as submodern groundwater. Thus, the St. Hermas Valley cross-section A-A′ shows an evolution from modern groundwater in the recharge area, to submodern groundwater in the buried valley.

Five samples were analyzed in the St. Benoît Valley. Four of these sites are on the cross-section B-B′. Sites S146, S145 and S144-L3 are part of a well nest located in the local recharge zone of St. Vincent Crest, and are illustrated in Fig. 8b. The first two samples, from the till and mixed unit, were analyzed for ^{3}H only. Their values of 17.1 TU in the till, and 8.2 TU in the mixed unit, clearly show that groundwater recharges the aquifer through the till. The rock sample S144-L3 has no detectable ^{3}H, indicating that the recent recharge likely flows preferentially in the upper, highly fractured rock unit. The sample downgradient in the valley, S46-L3, has no detectable ^{3}H, and a ^{14}C lower than S144-L3. The last sample from St. Benoît Valley, S77-L3, has no detectable ^{3}H, and a very low ^{14}C of 10.9 pMC. The St. Benoît Valley cross-section B-B′ thus indicates that precipitation recharges the aquifer through the till, and that groundwater flows preferentially in the interface zone. In the fractured rock aquifer, ^{14}C decreases from St. Vincent Crest to the buried valley downgradient.

The next three sites are from the cross-section C-C′, in the unconfined to semi-confined area from the airport to St. Eustache. S132, S34 and S72, have all ^{3}H above 10 TU, indicative of modern groundwater, and their ^{14}C vary from 55.7 to 68.8 pMC. Groundwater recharge thus probably occurs along the entire flow path in this area. Even though the main recharge area for cross-section C-C′ is in the north part of the section, the hydrogeological conditions of the area allow infiltration of precipitation all along the section. Dissolution of ^{14}C-free marine carbonate under closed conditions could explain that these three sites have significant tritium and a ^{14}C activity less than modern values, in agreement with the $\delta^{13}C_{DIC}$ data.

Finally, the profile of well SAP shows the results of two samples collected with the multilevel system (Fig. 8c). Sample SAP-L1, below the clay aquitard, has 9.2 TU and a ^{14}C of 46.5 pMC. The deepest sample, SAP-L3, has no detectable ^{3}H, and a very low ^{14}C of 3.0 pMC. As for the St. Vincent Crest profile, the presence of tritium below the aquitard suggests that groundwater flows preferentially in the highly fractured rock at the interface zone. The source for this modern water would be the recharge zone, located about 5 km northwest of well SAP (Karanta et al. 2001). It is possible that mixing in the well, prior to sampling, has contributed to lower the tritium and ^{14}C values of SAP-L1 by mixing modern groundwater with deeper, much older, groundwater.

Discussion

This discussion integrates the main observations to develop a conceptual model for the origin and evolution of groundwater geochemistry in this regional sedimentary rock aquifer. The geochemical processes involved in this evolution are described in more detail in Cloutier (2004).

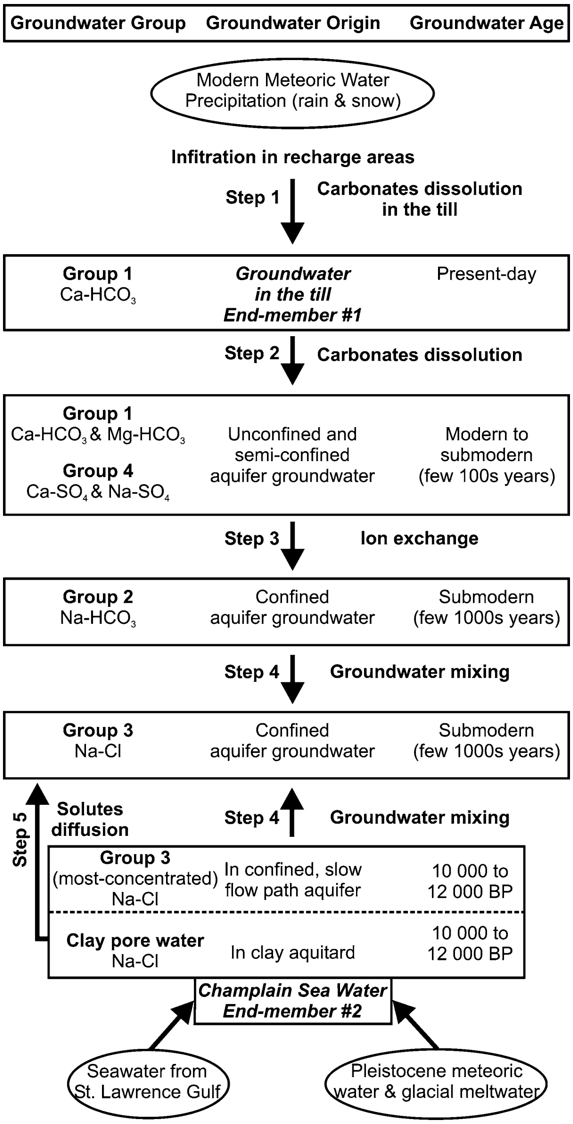

Fig. 9 Conceptual model of groundwater origin and relationships between groundwater end-members

Figure 9 shows the interpretation of the relationships between the geological history and geochemical evolution of groundwater as well as their relative qualitative isotopic age. The relationships among the groundwater groups and the overall groundwater geochemical evolution represented here constitute the conceptual hydrogeochemical model for the Basses-Laurentides aquifer system.

Modern meteoric water, as rain and snow melt, infiltrates the Basses-Laurentides sedimentary rock aquifer system in the preferential recharge areas (Step 1). These recharge areas generally consist of elevated topographic regions covered by carbonate-rich till sediments. Groundwater in the till, end-member #1, belongs to G1 and is characterized by Ca-HCO$_3$ type water. δ^{18}O and δ^2H values of the groundwater from the surface sediments fall in the range of values obtained for the regional precipitation. Tritium data from the local recharge zone of St. Vincent Crest indicate the presence of modern meteoric water in the till. Also from St. Vincent Crest, the $\delta^{13}C_{DIC}$ value in the till indicates an open system carbonates dissolution, consistent with the characteristic Ca-Mg-HCO_3 groundwater type in recharge areas.

From the surface sediments, groundwater flows in the fractured sedimentary rocks of the unconfined and semi-confined aquifer, in the preferential recharge areas (Step 2). This groundwater is dominated by G1 (Ca-HCO_3 and Mg-HCO_3), with a few samples of G4 (Ca-SO_4 and Na-SO_4) in the carbonates of the western part of the study area (Fig. 6). Their mean $\delta^{18}O$ is very similar to the weighted mean annual $\delta^{18}O$ for Ottawa precipitation. The qualitative interpretation of the tritium data shows that these groundwaters are generally modern. With no tritium detected, the sample (S144-L3) from the fractured rock aquifer at St. Vincent Crest is classified as submodern, even though it belongs to G1. Thus this sample was recharged prior to 1952, and could be a few 100s of years old. $\delta^{13}C_{DIC}$ value and ^{14}C activity in the groundwater indicate the occurrence of closed system carbonates dissolution. Strontium isotopes in the groundwater from the dolostone and limestone of G1 and G4 are also consistent with water-rock interaction of carbonates along the flow system (Cloutier 2004). Carbonate dissolution, supported by the saturation indexes, could occur in contact with carbonate formations or with carbonate minerals on fracture surfaces.

The groundwater flow, from the unconfined to confined aquifer, results in a groundwater evolution to G2 (Na-HCO_3) and G3 (Na-Cl). This evolution is particularly noticeable in St. Hermas Valley, where modern meteoric Ca-Mg-HCO_3 water (G1) in the recharge area evolves to G2 mixed cations-HCO_3 and Na-HCO_3 water (Step 3), to finally G3 Na-Cl water (Step 4/Step 5) in the center of the valley (Fig. 6). Hydrogeochemical data suggest that $Ca^{2+}_{water}-Na^{+}_{mineral}$ ion exchange could be responsible for the evolution of groundwater from G1 to G2 (Cloutier 2004).

Conservative tracers Cl^- and Br^- allow the identification of Champlain Sea water, the Pleistocene end-member #2 for the study aquifer. The Champlain Sea water was a mixture of St. Lawrence Gulf seawater with Pleistocene meteoric water and glacial meltwater. The end-member is found at site S77 in St. Benoît Valley, as well as in the clay pore water. As both samples are interpreted as original Champlain Sea water, their groundwater age is estimated at 10 000 to 12 000 BP. Two possibilities could be invoked for the occurrence of G3 water: First, is the mixing of G2 water with stagnant aquifer zones previously saturated with Champlain Sea water as S77 (Step 4), and second is the diffusion of solutes from low permeable units, particularly the clay aquitard (Step 5). With the exception of the interface sample in Ste. Anne-des-Plaines, and of a sample from St. Hermas Valley that is believed to be affected by mixing with meteoric water, the tritium data indicate submodern groundwater for G2 and G3 waters. As these groundwaters cannot be older than the Champlain Sea water end-member, their groundwater ages are interpreted as being a few 1000s years.

Summary and conclusions

This report presents the results obtained from a comprehensive regional hydrogeochemical study, allowing the determination of groundwater origin, and a first qualitative understanding of the main geochemical processes controlling groundwater geochemistry and its spatial evolution. Piper diagrams, as well as the distribution map of groundwater types and the descriptive statistics, indicate that the major ion chemistry is controlled mainly by the hydrogeological conditions. Groundwater groups G1 (Ca-HCO_3 and Mg-HCO_3) and G4 (Ca-SO_4 and Na-SO_4) are found in preferential groundwater recharge areas, whereas G2 (Na-HCO_3) and G3 (Na-Cl) groundwater are found under confined conditions. On the other hand, the distribution of minor ions, such as F^-, is controlled by the geochemistry of the geological formations. The δ^2H and $\delta^{18}O$ of the groundwater samples are distributed around the local meteoric water line, the BLMWL. The mean $\delta^{18}O$ for the recharged groundwater to the aquifer system is very similar to the weighted annual means $\delta^{18}O$ for the region. Qualitative interpretation of ^3H data shows that zones identified as preferential recharge areas have modern groundwater ages whereas zones under deep buried valleys have submodern ages. Isotopic data in profiles where discrete groundwater samples were obtained show evidence of preferential groundwater flow in the upper part of the bedrock aquifer. $\delta^{13}C_{DIC}$ and ^{14}C also indicate that water-rock interactions occur from recharge areas along groundwater flow paths.

The study shows the importance of the geological history on the hydrogeochemistry of the aquifer system. The till mineralogy, related mainly to the glacial erosion of sedimentary formations, has a large influence on the geochemistry of the modern recharge groundwater end-member. The glaciofluvial deposits, and the highly fractured and weathered upper bedrock, represent a highly permeable zone under the clay deposit. Some hydrogeochemical indications of faster interface flow were observed for this zone. The Pleistocene Champlain sea invasion led to salinization of the aquifer, and a Champlain Sea water end-member is still present in the aquifer. The clay deposits from the Champlain Sea episode act as a contaminant barrier for the aquifer, but also as a long term source of Na^+ and Cl^- to the underlying aquifer. The buried valleys and the Cretaceous intrusions, with their influence on the groundwater flow, could be the cause of stagnant zones of Champlain Sea water, as for site S77 in St. Benoît Valley. The complex geological history, including the latest glaciation and the Champlain Sea invasion, and the variety of geological and hydrogeological conditions, result in variable groundwater chemistry.

The main geochemical processes involved are carbonate dissolution, Ca^{2+}-Na^+ ion exchange, mixing with saline water, and diffusion from the Champlain Sea clay. These processes are farther analyzed by Cloutier (2004). The combined results of these ancient and present hydrogeological and geochemical processes confer to the Basses-Laurentides sedimentary rock aquifer system its present-day, highly variable, groundwater geochemistry. Most of the processes affecting this regional aquifer are analogous to those discussed by Tóth (1999) in his representation of groundwater evolution of a regional, gravity-driven flow system, in a confined aquifer with stagnant zones of saline water of ancient origin. The origin of this saline water indicates that saline and brackish groundwater occurrences can be expected in aquifers of similar settings, as in other areas flooded by the Champlain Sea, or in areas flooded by other post-glacial seas, such as the Laflamme and Goldthwait Sea in eastern Canada.

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Appendix

In situ field measurements were made on water samples for the following parameters: temperature with a glass thermometer, pH (accuracy of ±0.1 pH unit) and electrical conductivity (EC) with a YSI 63 meter, dissolved oxygen (DO) with a YSI 95 meter, and redox potential with a Hanna Instruments ORP HI 98201 meter. The redox measurements were corrected for the difference between the standard potential of the reference electrode being used at the solution temperature and the potential of the standard hydrogen electrode (Cloutier 2004). The field measurements were made using a container large enough to limit sample exposure to the atmosphere. Private wells were purged until stabilization of field measurements before sampling. The observation wells were purged with an approach combining field measurement stabilization, and a minimum of 3–5 well bore volumes.

Samples for major, minor and trace constituents were collected in plastic bottles, kept in coolers, and shipped to the laboratory at the end of the day. Duplicate samples, about 7% of the total, were also submitted to verify data quality and accuracy. The laboratory of the Québec Environment Ministry performed the analyses using standard methods. Table ESM-1 provides the field sampling protocol and the method of analysis. Electro-neutrality was calculated to verify the analyses reliability. An electro-neutrality of ±5% is acceptable (Freeze and Cherry 1979). For the 153 regional groundwater samples, 134 samples have an electro-neutrality below 5%, 12 between 5 and 8%, and 7 above 10%. Samples with an electro-neutrality above 10% were rejected as they were generally missing important ions. The 146 groundwater samples, with electro-neutrality below 8%, are retained for the geochemical interpretation.

Samples for δ^2H and δ^{18}O were collected in 60 ml HDPE bottles. The analyses were performed at the Delta-Lab of GSC-Québec and at the G.G. Hatch Isotope Laboratories of the University of Ottawa. H_2 gas was extracted from water samples using the zinc reduction method (Coleman et al. 1982). An IRM spectrometer (Micromass Prism III) (Delta-Lab) and an automated double collector VG 602E mass spectrometer (G.G. Hatch) were used to analyze the δ^2H ratios. Oxygen of 1 ml water samples was equilibrated with commercial CO_2 at a controlled temperature using an automated system. $\delta^{18}O_{water}$ was subsequently analyzed on the equilibrated CO_2 with a VG-SIRA 12 IRMS. Isotopic results are reported with the standard δ notation as per mil (‰) deviations relative to V-SMOW. Analytical precision is ±0.1‰ for δ^{18}O and ±1.5‰ to ±2‰ for δ^2H. Samples for $\delta^{13}C_{DIC}$ were filtered, collected in 250 ml glass bottles, and preserved with $HgCl_2$ to prevent modifications due to bacteriological reactions. Samples were analyzed by the Delta-Lab within a week following sampling. The $\delta^{13}C_{DIC}$ extractions were made by vacuum line acid stripping using 100% H_3PO_4, converting all dissolved inorganic carbon to CO_2. A VG-SIRA 12 IRMS was used to analyze the extracted CO_2. Isotopic results are reported with the standard δ notation as per mil (‰) deviations relative to NBS-19 (V-PDB), with an analytical precision of ±0.1‰. Some samples collected in 1 L HDPE bottles were analyzed for enriched ^{3}H and ^{14}C of DIC. Fourteen samples were analyzed for enriched ^{3}H at the Environmental Isotope Laboratory (EIL) of the University of Waterloo by liquid scintillation counting. The precision for enriched ^{3}H is ±0.8 TU. From these fourteen samples, twelve were analyzed for radiocarbon analysis of DIC. CO_2 was extracted at the EIL, and analyzed by AMS at the IsoTrace Laboratory of the University of Toronto. The average precision for ^{14}C is ±0.5 pMC.

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