

Desalination of a sedimentary rock aquifer system invaded by Pleistocene Champlain Sea water and processes controlling groundwater geochemistry

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Abstract The objective of this study was to identify geochemical processes and Quaternary geological events responsible for the variations in groundwater geochemistry observed in a sedimentary rock aquifer system, including brackish to saline groundwater. Inorganic constituents and environmental isotopes were analyzed for 146 groundwater samples. Dissolution of carbonates dominates in recharge areas, resulting in Ca-, Mg-HCO₃ groundwater. Further along flow paths, under confined conditions, Ca²⁺–Na⁺ ion exchange causes groundwater evolution to Na-HCO₃ type. Na-Cl groundwater is also found and it falls on a seawater mixing line. Using conservative tracers, Cl[–] and Br[–], the original Champlain Sea water is shown to have been, in the region, a mixture of about 34% seawater and 66% fresh-water, a composition still retained by some groundwater. Na-Cl groundwater thus results from mixing with former Champlain Sea water and also from solute diffusion from

overlying marine clay. The system is thus found to be at different stages of desalinization, from the original Champlain Sea water still present in hydraulically stagnant areas of the aquifer to fully flushed conditions in parts, where more flow occurs, especially in recharge zones. The geochemical processes are integrated within the hydro-geological context to produce a conceptual geochemical evolution model for groundwater of the aquifer system.

Keywords Hydrogeochemistry · Salinity · Groundwater · Champlain Sea · Canada

Introduction

The Basses–Laurentides aquifer system is located on the north shore of the St. Lawrence River, northwest of Montreal in Canada (Fig. 1). It covers approximately 1,500 km² in the physiographic region of the St. Lawrence Lowlands. The study area is within the limits of the postglacial Champlain Sea (Fig. 1). Groundwater hydrogeochemistry of this sedimentary rock aquifer system was studied as part of a regional hydrogeological assessment. Nastev et al. (2004, 2005, 2006) investigated the hydraulic properties of the rock aquifer, developed a numerical groundwater flow model for this aquifer and determined the conditions required for its sustainable exploitation. Ross et al. (2004, 2005) developed a 3D geological model of the overlying Quaternary units and assessed the rock aquifer vulnerability on the basis of downward advective time.

The Basses–Laurentides aquifer system has complex flow patterns, with a widely varying groundwater geochemistry including brackish to saline groundwater. The regional rock aquifer system contains buried valleys covered by a thick layer of marine clays that create confined

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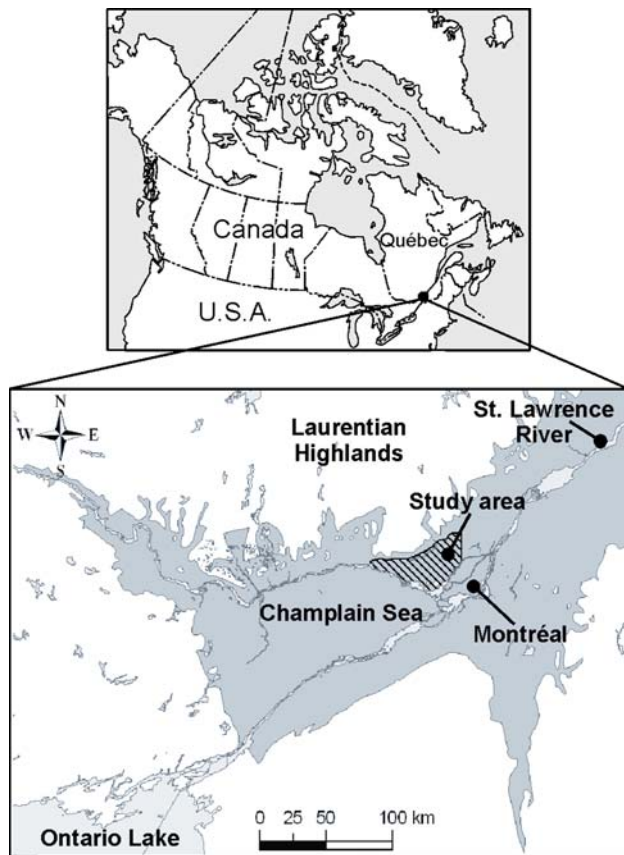


Fig. 1 Location of the study area with the extent of the marine limits of the Champlain Sea (adopted from Parent and Occhietti 1988 and Occhietti 1989). The study area is within the St. Lawrence Lowlands that are underlined by Paleozoic fractured sedimentary rocks

conditions, as well as ridges overlain by thin reworked glacial tills that allow preferential groundwater recharge under unconfined conditions (Nastev et al. 2005). Cloutier et al. (2006) characterized the regional groundwater hydrogeochemistry and established the relationship between groundwater types and hydrogeological settings, with the specific objective of identifying the origin of groundwater in the study area. Cloutier et al. (2008) used multivariate statistics to analyze the geochemical data to better identify the processes controlling the geochemical evolution of groundwater in the aquifer system. A very interesting aspect of the work of Cloutier et al. (2006) is the identification, in the aquifer system under confined conditions, of brackish to saline water of Na-Cl groundwater type. The occurrence of groundwater with high salinity in the study area was also identified in previous studies (Simard 1978; Soucy 1998). For local municipalities that rely on groundwater for their water supply, groundwater with high salinity poses a problem for the provision of potable water.

The objective pursued in this paper is to identify the ongoing geochemical processes as well as Quaternary geological events that have influenced groundwater

geochemistry in this aquifer system. The understanding of geochemical processes controlling current groundwater geochemistry is required for the sound management of groundwater resources in the region. Emphasis is on explaining the presence of brackish to saline groundwater and this paper presents a first quantitative explanation for the occurrence of Na-Cl groundwater in the aquifer system using the conservative elements Cl^- and Br^- , as well as $\delta^{18}\text{O}$. Although the study focuses on a relatively local system, it provides an example of general interest for the potentially long-term effect of a major perturbation on the geochemical evolution of an aquifer system. The study also shows the interrelation between steady state hydraulic conditions and transient geochemical conditions that are still evolving after a major perturbation.

Description of the study area

Geological and hydrogeological setting

The area has generally a flat topography, with the exception of the Monteregian Oka and St. André Hills related to Cretaceous alkaline intrusions (Fig. 2a). The Laurentian Highlands, part of the Grenville Province of the Canadian Shield, border the study area to the north. The study area is bounded to the southwest, south, and southeast by the Outaouais River, the Deux Montagnes Lake, and the Mille Îles River, respectively. The watershed of the Mascouche River forms the eastern limit of the study area.

The Basses-Laurentides aquifer system is part of the geological Province of the St. Lawrence Platform and consists of nearly horizontal Cambrian–Ordovician sedimentary formations lying unconformably on the crystalline basement of the Precambrian Grenville Province (Fig. 2a). Precambrian rocks, such as quartzite, crystallized limestone, gneiss, and anorthosite, form a window through the Paleozoic sequence with the Cretaceous intrusions (Gold 1972; Lewis 1971).

The geological map shows the Cambrian–Ordovician sedimentary sequence covering most of the study area (Fig. 2a). The Cambrian Potsdam Group comprises the Covey Hill Formation (a reddish feldspathic sandstone, locally conglomeratic and poorly cemented) and the Cairnside Formation (a well-cemented, pure, quartz arenite sandstone) (Globensky 1987). The Ordovician Beekmantown Group includes the Theresa Formation (dolomitic sandstone and sandy dolostone), the Beauharnois Formation (sandy to pure, massive, dolostone) and the Carillon Formation (pure dolostone with limestone near its summit) (Salad Hersi et al. 2003). The Chazy Group (sandstone, limestone and shale), Black River Group (dolostone, shale and limestone) and Trenton Group (limestone and shale)

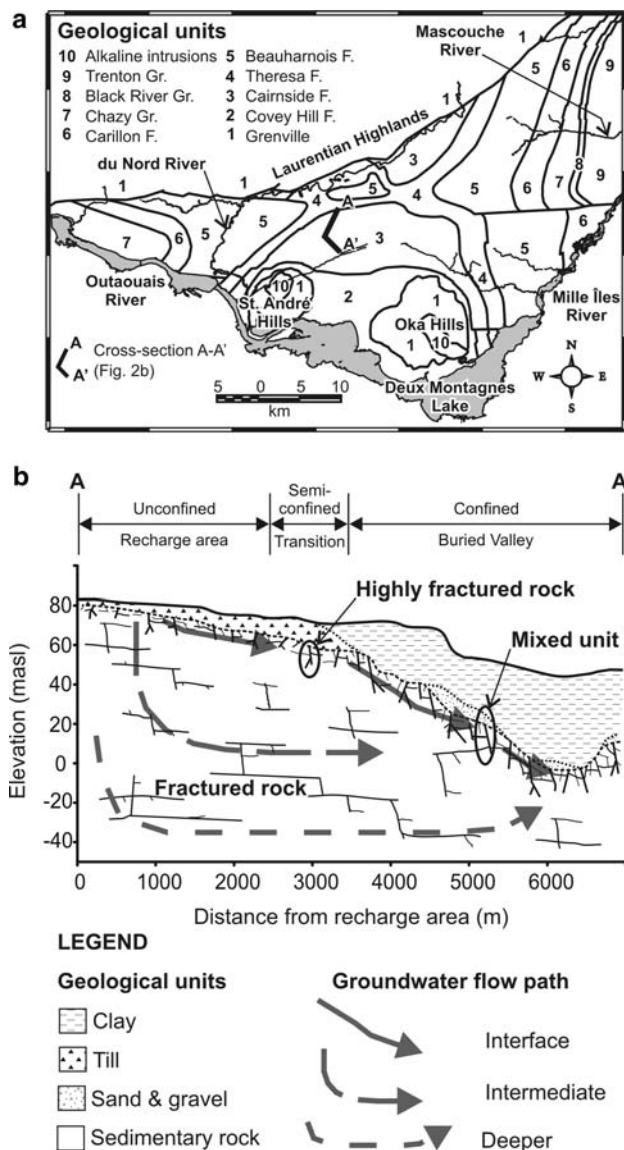


Fig. 2 Geological and hydrogeological contexts. **a** Geology of the Basses–Laurentides sedimentary rock aquifer system, where Precambrian Grenville rocks and alkaline intrusions pierce through slightly dipping Paleozoic formations (map modified from Rocher et al. 2009). **b** Cross-section A–A' illustrating the main hydrostratigraphic units and the groundwater flow conceptual model (modified from Cloutier et al. 2006). Preferential groundwater recharge occurs on crests, where conditions are unconfined. From there, groundwater flows towards the centre of confining buried valleys, preferentially through the “interface flow path” in the highly fractured upper part of sedimentary rocks, sometimes in contact with sand and gravel lenses (together referred to as the “mixed unit”)

complete the sequence (Globensky 1987). More details on the lithology and mineralogy of the sedimentary formations are provided by Cloutier (2004).

The last Quaternary glaciation covered the rock units with Upper Wisconsinan sediments, such as glacial till and glacio-fluvial sand and gravel (Bolduc and Ross 2001). During deglaciation, the Laurentide Ice Sheet was retreated

from the St. Lawrence Valley. The combined depression of the continent, due to the glaciation, and the retreat of the Laurentide Ice Sheet led to marine invasion from the St. Lawrence Gulf, which created the Champlain Sea (Fig. 1). The main basin of the Champlain Sea was established around 12,000 BP (Parent and Occhietti 1988) and submerged the study area for about 2,000 years (Lévesque 1982). The Champlain Sea water was a mixture of continental waters, including meltwater from the Laurentide Ice Sheet and local precipitation, and salt water from the St. Lawrence Gulf (Hillaire-Marcel 1988). The Champlain Sea episode led to the deposition of marine sediments, mainly clayey-silts to silty-clays that can reach a thickness of more than 80 m in the study area (Bolduc and Ross 2001).

A cross-section of the conceptual groundwater flow model shows the transition from unconfined to confined conditions from topographic highs to buried valleys (Fig. 2b). The unconfined conditions, characterizing areas of preferential groundwater recharge, are generally areas of elevated topography, sometimes with rock outcrops or with thin to thick permeable surface sediments, generally till that can be reworked. Thus, precipitation recharges the aquifer mainly by infiltration through the till unit. Away from the recharge zone, the clay aquitard unit consisting of thick low permeability Champlain Sea silts and clays confines the rock aquifer, especially in buried valleys, where the aquitard is thicker (Fig. 2b). Based on its hydrogeological and geological properties, the rock aquifer system can be divided into two distinct units: (1) the highly fractured rock, generally limited to the upper 10 m of the rock sequence, and (2) the underlying fractured rock. A mixed unit, consisting of highly fractured rock in hydraulic connection with sand and gravel, is also observed in the buried valleys. More details on hydrostratigraphic units are provided by Cloutier et al. (2006).

Due to its higher permeability, more groundwater flow occurs in the highly fractured rock at the interface with overlying surficial sediments (Fig. 2b). Intermediate and deeper flow paths also occur in the underlying fractured rock (Fig. 2b). Most of the groundwater flow paths are directed towards the center of buried valleys. The central part of the study area presents alternating ridges (crests) and buried valleys generally oriented east–west. This leads to converging groundwater flow from crests towards valleys, and then diverging flow from the central part of valleys to their eastern and western ends (Fig. 3). Hydrogeological contexts and flow patterns influence hydrogeochemical conditions, as will be explained next.

Regional hydrogeochemical context

The Basses–Laurentides aquifer system has a highly variable groundwater geochemistry. The following description

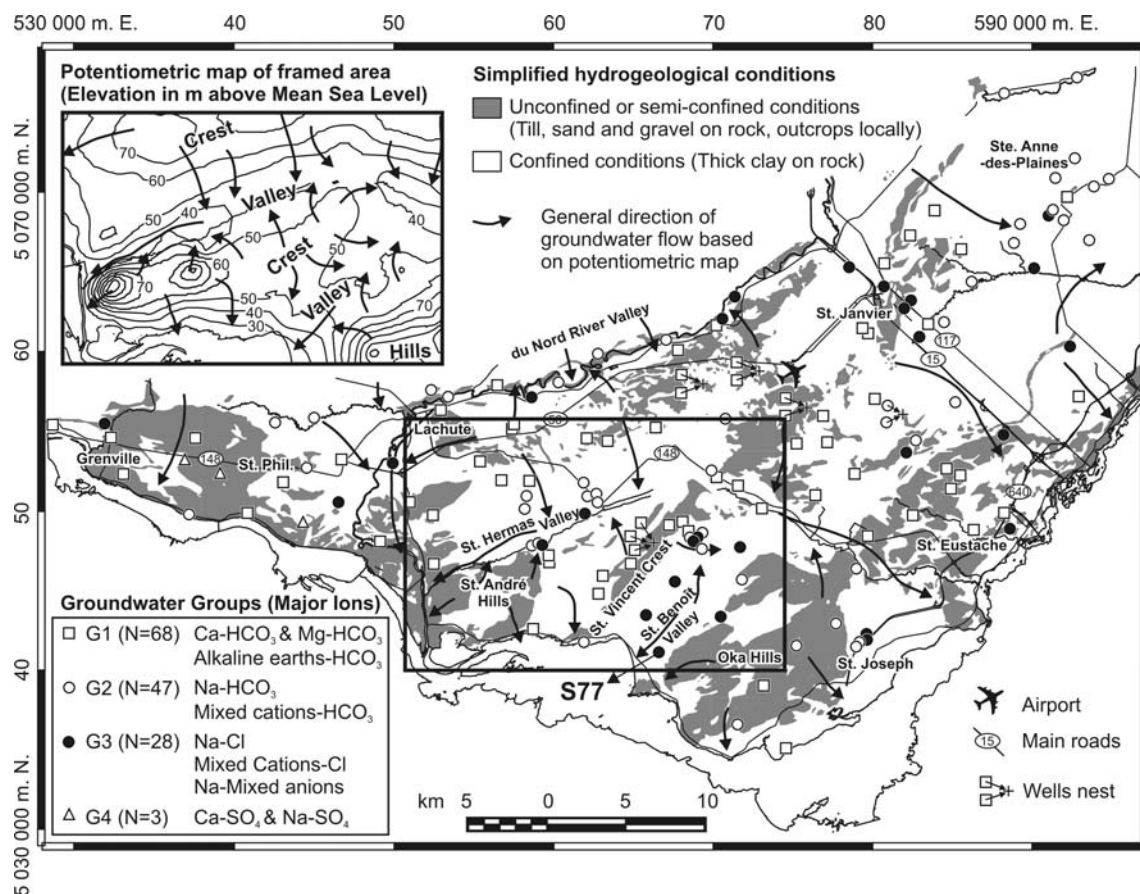


Fig. 3 Map of groundwater groups and their relation to hydrogeological conditions and general directions of groundwater flow (modified from Cloutier et al. 2006). Group G1 is found mostly, where unconfined recharge areas occur, whereas Group G2 is present

mostly under confined conditions. Group G3 is restricted mainly to the center of valleys, where convergent and divergent flow patterns occur as shown on the potentiometric map

of the regional hydrogeochemical context uses the groundwater classification approach of dominant and mixed groundwater types presented by Cloutier (2004). This approach, based on major ions concentrations, classifies the Basses-Laurentides groundwater samples into six dominant and four mixed groundwater types (Table 1). Cloutier et al. (2006) classified these ten groundwater types into four main groundwater groups, Ca-, Mg- HCO_3 (G1), Na- HCO_3 (G2), Na-Cl (G3) as well as Ca- SO_4 and Na- SO_4 (G4).

Figure 3 shows the spatial distribution of groundwater groups for the 146 samples, and their relationships with aquifer conditions, classified as areas of (1) unconfined or semi-confined conditions, and (2) confined conditions, based on mapped aquitard thickness. The general groundwater flow direction in the regional rock aquifer is from north to south (Nastev et al. 2005). However, as mentioned before, the potentiometric surface also follows the bedrock or surface topography and is higher in the preferential groundwater recharge areas found on crests. Confining conditions prevail in three southwest–northeast trending

buried valleys found in the central part of the study area: du Nord River Valley, St. Hermas Valley, and St. Benoît Valley, where clay thickness can reach more than 90 m. The clay reaches a thickness of more than 30 m in the eastern part of the region, around Ste. Anne-des-Plaines, leading to generally confined conditions.

The spatial distribution of groundwater groups (Fig. 3) shows that hydrogeological conditions exert an important control on hydrogeochemistry. Qualitative interpretation of ^3H data shows that preferential recharge areas, characterized by Ca-, Mg- HCO_3 water (G1) as well as Ca- SO_4 and Na- SO_4 (G4), have modern, tritiated groundwaters, and that the confined aquifer, characterized by Na- HCO_3 (G2) and Na-Cl (G3) water, have submodern groundwaters. Groundwater, G2 results from the evolution of G1, and groundwater G3 from the mixing of G2 with Pleistocene Champlain Sea water (Cloutier et al. 2006; Table 1). Higher total dissolved solids (TDS) characterize samples of the Na-Cl groundwater G3. Sample S77, located in the buried valley of St. Benoît (Fig. 3), has the highest TDS of the wells sampled in the course of this project (calculated

Table 1 Groundwater groups and types determined by Cloutier et al. (2006)

Groundwater group (<i>N</i>)	Dominant water type (<i>N</i>)	Mixed water type (<i>N</i>)	Hydrogeological Conditions	Groundwater origin ^a
G1 (68)	Ca-HCO ₃ (59) Mg-HCO ₃ (4)	Alkaline earth-HCO ₃ (5)	Unconfined Semi-confined	Modern meteoric water
G2 (47)	Na-HCO ₃ (35)	Mixed cations-HCO ₃ (12)	Confined	Evolved G1 (submodern)
G3 (28)	Na-Cl (25)	Mixed cations-Cl (2) Na-Mixed anions (1)	Confined	Mixing of G2 with Pleistocene Champlain Sea water (submodern) ^b
G4 (3)	Ca-SO ₄ (2) Na-SO ₄ (1)		Unconfined Semi-confined	Modern meteoric water

N number of samples

^a The division in modern and submodern waters, i.e. recharged prior to 1952, is a qualitative interpretation of the ³H data (Clark and Fritz 1997)

^b Except the samples located in the recharge zone, principally at St. Janvier along the main roads 15 and 117, contaminated by de-icing road salts (see Fig. 3 for road locations)

TDS = 11,337 mg/L). Although they are located in, or close to, unconfined areas, some samples collected along the main highways 15 and 117, particularly around St. Janvier, have Na-Cl groundwater (Fig. 3). For these samples, it was shown that groundwater is contaminated by de-icing road salts, which gives its Na-Cl characteristics, without the high Br[−] found in marine water (Cloutier et al. 2006).

Methods of investigation

The approach used for this study was to determine the hydrogeochemistry of groundwater for all hydrogeologic units of the Basses-Laurentides aquifer system, starting from the groundwater recharge areas along the regional flow direction. The study also characterized the hydrogeochemistry of all sources that could influence the composition of groundwater, such as rain and snow in recharge zones, and clay pore water in the buried valleys. The regional characterization of groundwater hydrogeochemistry, performed in 1999 and 2000, consisted of groundwater sampling of private, municipal and observation wells. Regional groundwater samples were collected at 153 sites, to a maximum depth of about 140 m. Sampling sites are evenly distributed over the region and cover the following permeable hydrostratigraphic units: surface sediments, such as till, sediments under clay deposits, the mixed unit consisting of highly fractured rock and sediments under clay deposits, and fractured rock units.

In situ field measurements were made on water samples for temperature, pH, electrical conductivity, dissolved oxygen, and redox potential. Groundwater samples were analyzed for major, minor and trace inorganic constituents for a total of 36 parameters, stable isotopes $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), and some

samples were analyzed for ³H and ¹⁴C of DIC. The sampling and analytical protocols, as well as the complete hydrogeochemical dataset, are presented in Cloutier et al. (2006). For the 153 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 their analyses were generally missing major ions. The remaining 146 groundwater samples with electro-neutrality below 8% are retained for the following interpretation of the main geochemical processes.

Results and interpretation of main geochemical processes

This section documents the interpretation of the main geochemical processes that are controlling the evolution of groundwater in the aquifer system. The description starts from the process found to be dominant in recharge areas, carbonate dissolution, to processes prevalent under confined conditions, being ion exchange and groundwater mixing.

Dissolution of carbonates

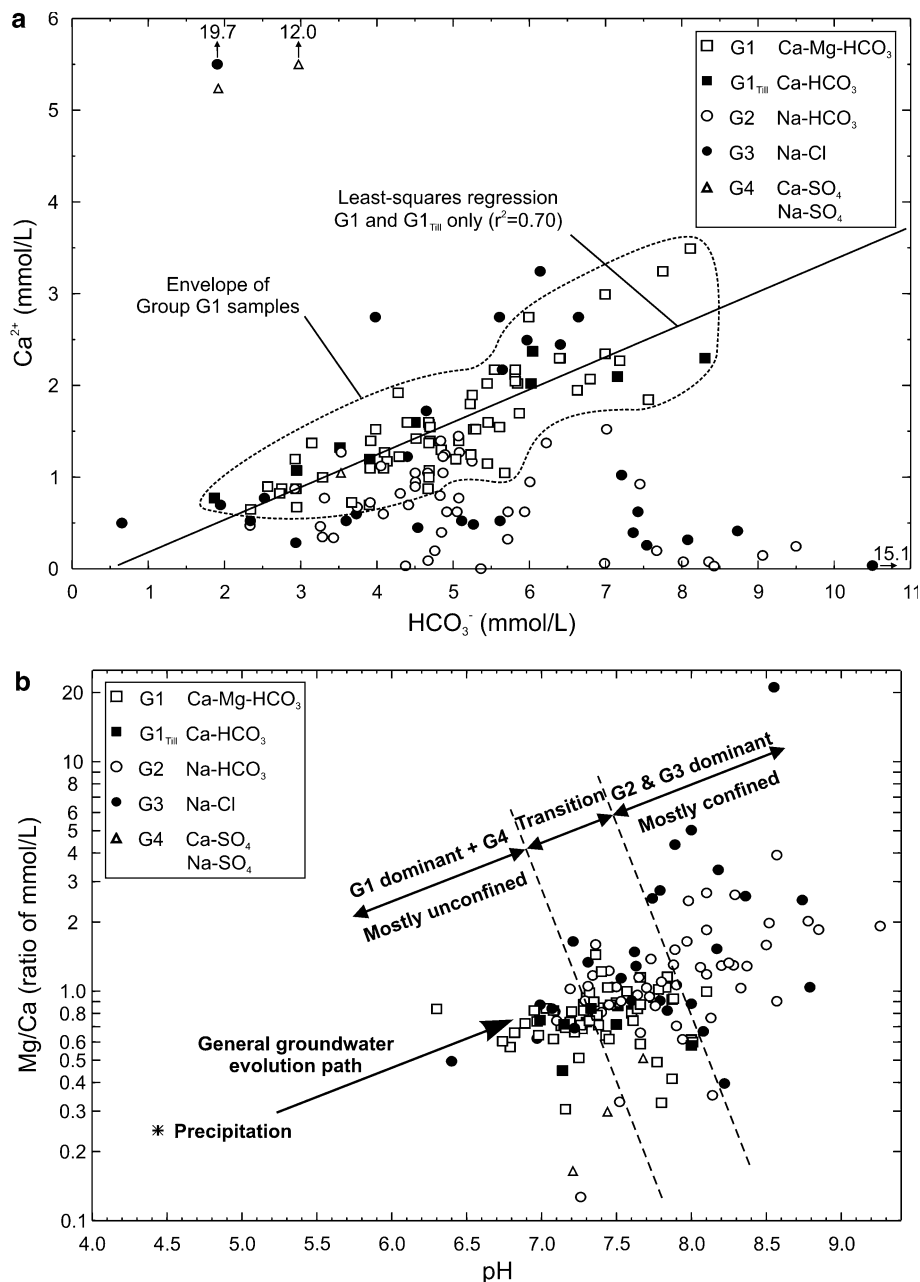
Figure 4a shows the relationship between Ca²⁺ and HCO₃[−] for the groundwater groups. Groundwater samples from the surface sediments, G1_{Till}, were given a different symbol to show their relative position compared to the other G1 samples. Groundwaters of G1_{Till} plot in the same field as groundwaters from the rock aquifer belonging to G1, suggesting that similar processes affect them. Figure 4a shows a linear relation ($r^2 = 0.70$) of increasing concentration between Ca²⁺ and HCO₃[−] for samples of G1 (Ca-, Mg-HCO₃) and G1_{Till} (Ca-HCO₃), which could be explained by dissolution of calcite that can be written as

$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$ (Appelo and Postma 2005). Samples of G2 (Na- HCO_3) and G3 (Na-Cl) show more spread on the diagram. For HCO_3^- above 7 mmol/L, Ca^{2+} concentrations for both groups G2 and G3 decrease to values lower than 0.5 mmol/L (Fig. 4a).

A clear trend of increasing Mg/Ca with increasing pH is observed, from precipitation to groundwaters of G1 and G4 in preferential recharge areas, to groundwaters of G2 and G3 under confined conditions (Fig. 4b). Again, groundwaters from the surface sediments, G1_{Till}, plot in the same field as groundwaters from the rock aquifer belonging to G1. The majority of Ca-, Mg- HCO_3 (G1) samples have a pH between 6.8 and 8.0, and a Mg/Ca ratio between 0.6 and 0.9. These

Mg/Ca ratios for G1 are close to the expected value of 0.8 for groundwater in equilibrium with calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$] (Appelo and Postma 2005). Thus, the relationship between Ca^{2+} and HCO_3^- and that between the Mg/Ca ratio and pH indicate dissolution of calcite during infiltration, as well as dissolution of dolomite that can be written as $\text{CaMg}(\text{CO}_3)_2 \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$ (Appelo and Postma 2005). Occurrence of marine carbonate dissolution has been shown by Cloutier et al. (2006) from stable carbon isotopes on DIC in the till groundwater, and is consistent with the presence of calcite and dolomite in the till matrix as described in previous work (Lévesque 1982). Groundwaters of G2 and G3 dominate at elevated pH and at

Fig. 4 Evidences of carbonates dissolution. **a** The relationship between Ca^{2+} and HCO_3^- concentrations for Group G1 samples could be explained by dissolution of calcite. **b** There is a relation between Mg/Ca and pH and the Mg/Ca ratio for G1 is typical of groundwater in equilibrium with calcite and dolomite (precipitation calculated by averaging monthly data from the Department of the Environment, Québec, 1994–1996)

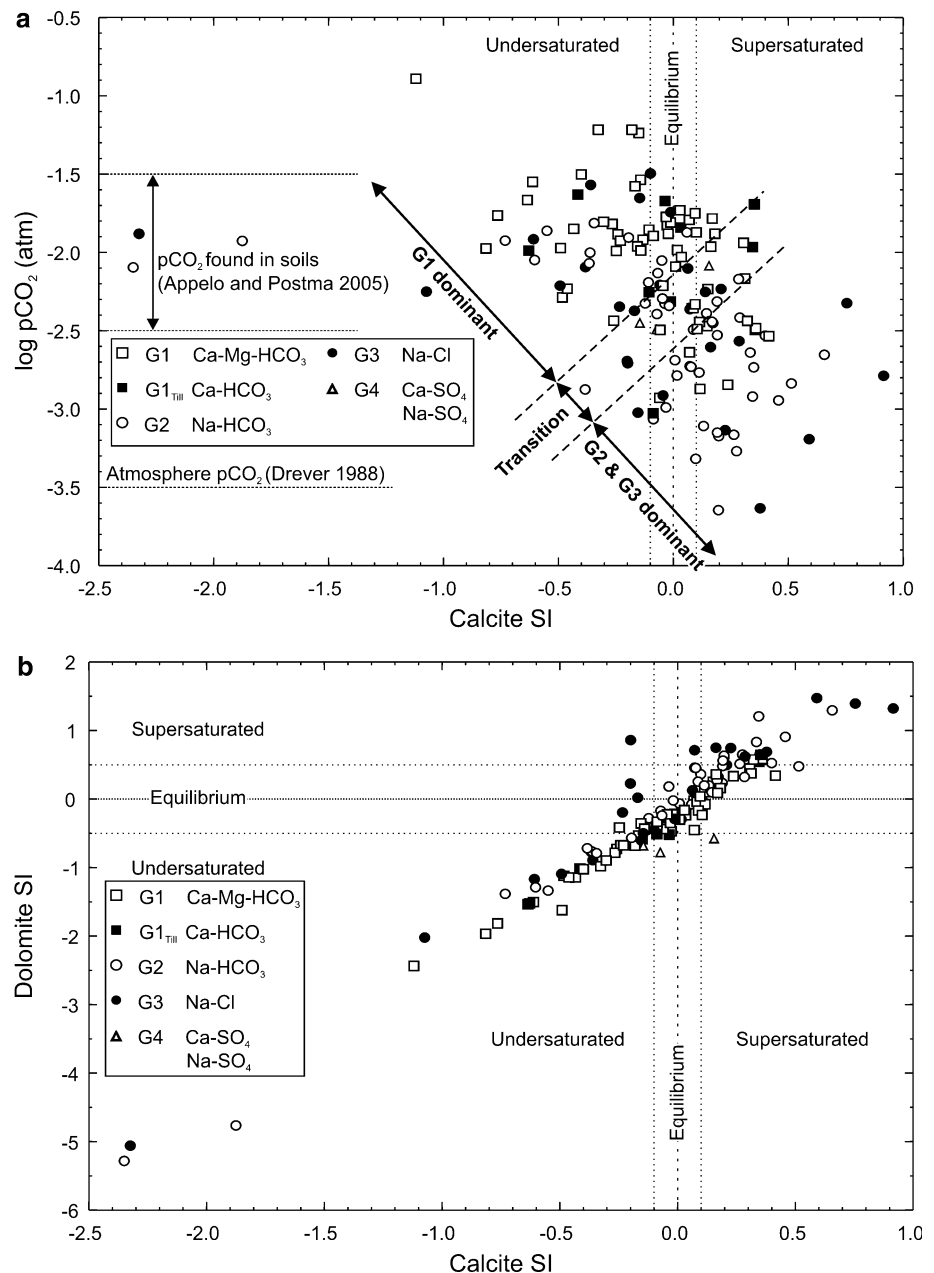


Mg/Ca above 1 (Fig. 4b), and other processes that contribute to the increase in pH, as well as Mg/Ca ratios, must affect these two groups.

Carbonate dissolution is caused partly by processes occurring in surface soils. Respiration and decay of organic matter increase CO_2 partial pressure ($p\text{CO}_2$) in soil gases relative to the atmosphere, which has a $p\text{CO}_2$ of $10^{-3.5}$ atm (Drever 1988). Appelo and Postma (2005) mention that $p\text{CO}_2$ values of $10^{-1.5}$ – $10^{-2.5}$ atm are commonly found in soils. This elevated $p\text{CO}_2$ for soil water has a major impact on the interaction with carbonate minerals present in surface sediments. Geochemical modeling was performed with PHREEQC 2.6 (Parkhurst and Appelo 1999) to

evaluate the likelihood of carbonate dissolution during infiltration through soil and surface sediments. Figure 5a indicates that the majority of samples from G1 (Ca-, Mg- HCO_3), including G1_{Till}, and G4 (Ca- SO_4 , Na- SO_4), have a $p\text{CO}_2$ of $10^{-1.5}$ – $10^{-2.5}$ atm, and a calcite saturation index (SI) undersaturated or near equilibrium, with an uncertainty of ± 0.1 units (Langmuir 1971). Samples from G2 (Na- HCO_3) and G3 (Na-Cl), under confined conditions, are showing a trend of lower $p\text{CO}_2$, with a calcite SI evolving from undersaturated to near equilibrium and supersaturated. These results indicate that samples in preferential groundwater recharge areas (G1 and G4) are dissolving calcite in an open system with respect to CO_2 . As calcite

Fig. 5 Evidences of carbonates dissolution. **a** For Groups G1 and G4 samples under unconfined conditions, ranges of log $p\text{CO}_2$ and calcite saturation index (SI) are indicative of dissolving calcite in an open system with respect to CO_2 . **b** Dolomite SI versus calcite SI for the groundwater groups indicate that conditions in recharge areas could allow the dissolution of both dolomite and calcite



dissolution consumes H^+ , pH buffering must be observed in the infiltrated water. The pH of precipitations is low, with a monthly average of 4.4, but it is buffered to a median pH of 7.3 in surface sediments (Fig. 4b).

A linear relation exists between dolomite and calcite SI (Fig. 5b). As for calcite, the majority of samples from G1, including G1_{Till}, and G4, have a dolomite SI undersaturated or near equilibrium, with an uncertainty of ± 0.5 units (Plummer et al. 1990). Samples from G2 and G3, under confined conditions, have a dolomite SI evolving from undersaturated to near equilibrium and supersaturated. Therefore, samples in groundwater recharge areas have the potential to dissolve dolomite as well as calcite. The increase of Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations in surface sediments is the main characteristic of all groundwater samples from G1 (Ca-, Mg- HCO_3). The dissolution of carbonates, initiated in surface sediments, is active in the sedimentary rock aquifer system as well, and is mainly the result of water–rock interaction with the dolostone and limestone formations.

Ion exchange

Hydrogeochemical data suggest that Ca^{2+} – Na^+ ion exchange, where Ca_{water}^{2+} exchanges with $Na_{mineral}^+$, could be the main geochemical process involved in the evolution of groundwater from Ca-, Mg- HCO_3 (G1) to Na- HCO_3 (G2) water types (Cloutier et al. 2006). The ion exchange reaction is written as $1/2 Ca^{2+} + Na-X \rightarrow 1/2 Ca-X_2 + Na^+$, where X indicates the mineral exchanger (Appelo and Postma 2005). Conditions required in the aquifer system for ionic exchange to operate are a recharged groundwater with elevated Ca^{2+} concentrations, and the presence of minerals with both high cation exchange capacities (CEC) and Na^+ on their exchange sites.

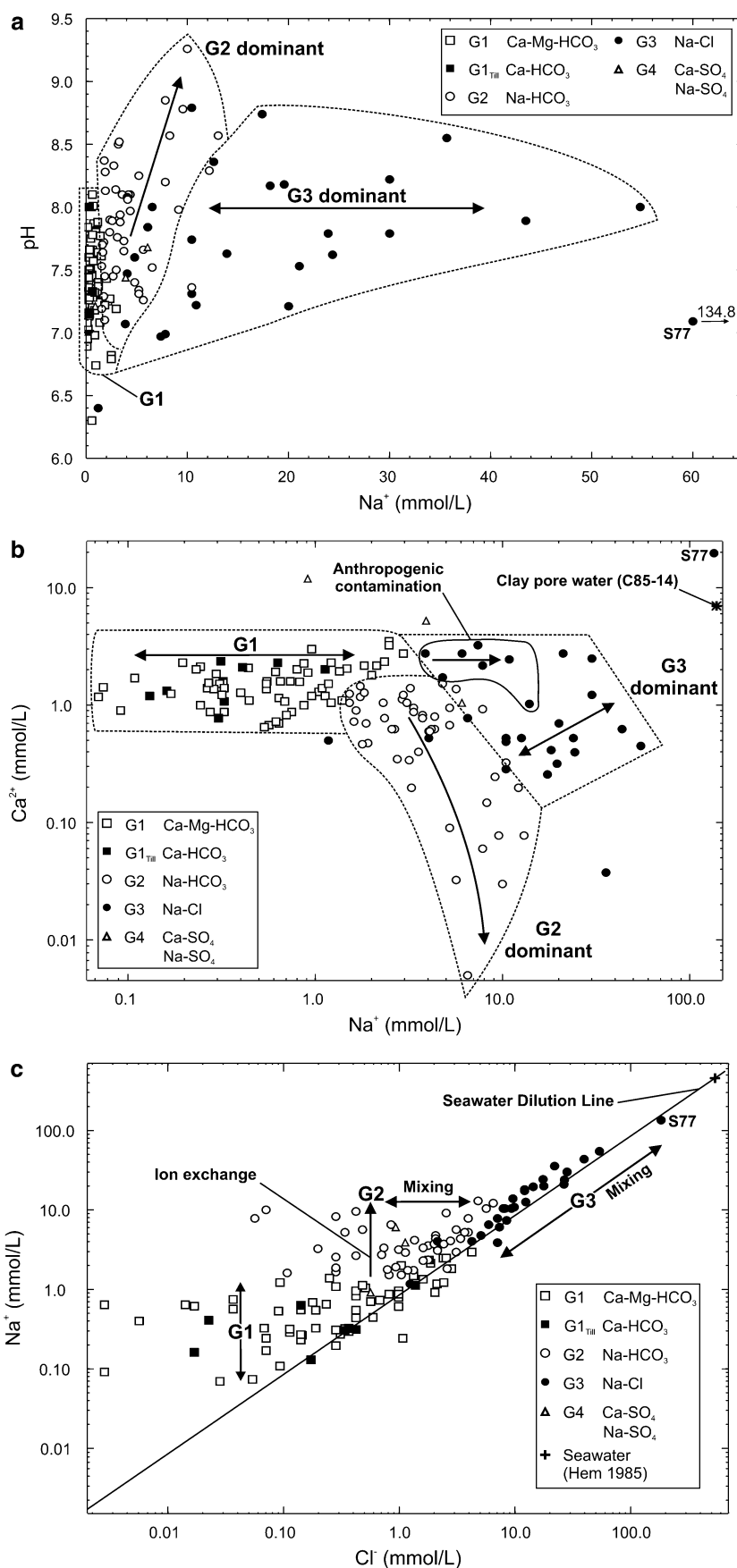
The first condition was demonstrated in the previous section on carbonate dissolution, which showed that recharged water dissolves carbonates in the till, and thus increases its Ca^{2+} concentration. The limestone has clay minerals, and shale beds, that could act as mineral exchangers (Globensky 1987). Globensky (1987) indicates that the dolostones have some clay minerals and iron oxides that could act as mineral exchangers, but it is unknown if they are abundant enough to account for the amount of Ca^{2+} – Na^+ exchange. This is also the case in St. Hermas Valley, where the pure quartz sandstone has some traces of micas and iron oxides. When clay minerals and iron oxides are not present in sufficient quantity to account for ion exchange, other sources for the exchange must be found. A possible source in the sandstone of the Potsdam Group are the minerals of the ultramafic sills observed in the rock cores retrieved from a well in St.

Hermas Valley, which are associated to the intrusions emplacement (Lewis 1971). A second possible source is the ionic exchange with minerals in the till and in the clay aquitard unit above the highly fractured rock unit. This possibility could be the case in Ste. Anne-des-Plaines, where most of the wells have a relatively short opening in the highly fractured rock unit, just below the clay, as well as in St. Hermas Valley, where the majority of the wells are installed in the sediments under the clay unit, or in the mixed unit, in contact with the clay aquitard. Thus, as water flows in the confined aquifer, Ca_{water}^{2+} could exchange with $Na_{mineral}^+$ of the confining aquitard, producing the Na- HCO_3 water type of G2. As mentioned, the mineral exchangers must have Na^+ adsorbed on their exchange sites for the exchange reaction to happen. This issue, related to the origin of salinity in the Basses–Laurentides aquifer system, is discussed in the next section on groundwater mixing and salinity origin.

Figure 6a shows that groundwaters of G1 (Ca-, Mg- HCO_3) have low Na^+ concentrations and pH values ranging from 6.3 to 8.1, characteristic of unconfined conditions. From the recharge areas, groundwater flows through the aquifer system under confined conditions. Samples of G2 (Na- HCO_3) and G3 (Na-Cl), characteristic of these confined conditions, form separate fields on the diagram. Relative to G1, samples of G2 show increasing pH values with increasing Na^+ concentrations, which is consistent with ion exchange operating from G1 to G2 (Fig. 6a). Groundwaters from G3 show a trend of increasing Na^+ concentrations relative to G2 samples, indicating that a second Na^+ source is involved in the evolution from G2 to G3 groundwaters. The increase in Na^+ concentrations for groundwaters of G2 is coupled to a sharp decrease in Ca^{2+} concentrations, confirming the importance of Ca^{2+} – Na^+ ion exchange (Fig. 6b). As illustrated in Fig. 6a, samples from G3 are characterized by an increase in Na^+ concentration compared to G2 (Fig. 6b). This Na^+ concentration increase is towards the clay pore water sample C85-14 and sample S77, which has the highest TDS of the wells sampled in the study area. Seven samples of G3, located in recharge areas, are labelled as anthropogenic contamination (Fig. 6b). These are the samples identified by Cloutier et al. (2006), being contaminated by de-icing road salts. Their position on the diagram indicates that their geochemistry results from the addition of Na^+ to G1 waters.

The increase in Na^+ concentration for groundwaters of G2 (Na- HCO_3) is not really coupled to a Cl^- increase, which constitutes another argument in favor of Ca^{2+} – Na^+ ion exchange for the evolution of G2 (Fig. 6c). On the other hand, G3 (Na-Cl) samples show a linear increase between Na^+ and Cl^- . In addition, groundwaters from G3 plot near, or slightly above, the seawater dilution line.

Fig. 6 Evidences of ion exchange and mixing.
a Increase in pH with Na^+ concentration for Group G2 samples is consistent with ion exchange causing groundwater to evolve from G1 to G2 compositions. **b** A sharp decrease in Ca^{2+} concentration as Na^+ concentration increases for Group G2 samples is confirming the importance of Ca^{2+} – Na^+ ion exchange. **c** The increase in Na^+ concentration not coupled with a similar trend in Cl^- for samples of Group G2 is again compatible with ion exchange. On all the three diagrams, samples from Group G3 depart from trends found in Group G2 samples and G3 samples plotting on the seawater dilution line (c) indicate that mixing is prevalent for these samples



Groundwaters from G2 plot above the seawater dilution line, having a Na^+ surplus relative to Cl^- .

Figure 6a to c indicate that Ca^{2+} – Na^+ ion exchange is the main geochemical process affecting groundwater belonging to G2. The distribution of G2 also indicates the possibility of mixing with groundwater of G3, increasing its Cl^- concentrations relative to Na^+ (Fig. 6c). Groundwaters from G3, which are affected by mixing with G2, must originate from another process to explain their elevated Na^+ as well as Cl^- concentrations. The trend of G3 groundwaters towards seawater suggests that groundwater mixing, with an end-member having a seawater component, is characteristic of G3 groundwaters evolution. This is further discussed next.

Origin of groundwater salinity

Most of the samples of G3 can be categorized as brackish water defined by a TDS between 1,000 and 10,000 mg/L (Freeze and Cherry 1979). These samples exceed the Canadian drinking water quality guideline for Cl^- of 250 mg/L (aesthetic objective of Health Canada 2007). With a calculated TDS of 11,337 mg/L, sample S77 from St. Benoît Valley is the only sample in the saline water class.

Increasing salinity in groundwater may result from different processes, such as water–rock interaction along the flow path, dissolution of evaporite rocks, old or current seawater intrusion, mixing with formation water, solute diffusion from aquitard containing saline pore water, and anthropogenic contamination, such as de-icing road salts or agricultural input (Hem 1985; Appelo and Postma 2005; Richter and Kreitler 1993). In the Basses–Laurentides aquifer system, the increase in salinity is associated with an increase in Na^+ and Cl^- (Fig. 6c). In the geological context of the region, it is unlikely that water–rock interaction could produce the Na–Cl water type of G3 in the upper portion of the sedimentary rock aquifer system. As there are no evaporite formations in the aquifer, and this is not a coastal aquifer, other sources must be examined to explain the origin of salinity. Contamination by de-icing road salts explains the salinity found in some samples in the recharge areas, but not in the valleys, where thick clay deposits provide a good protection to the aquifer system. The geological background of the area gives a limited number of possibilities for the presence of brackish to saline water in the upper portion of the aquifer system.

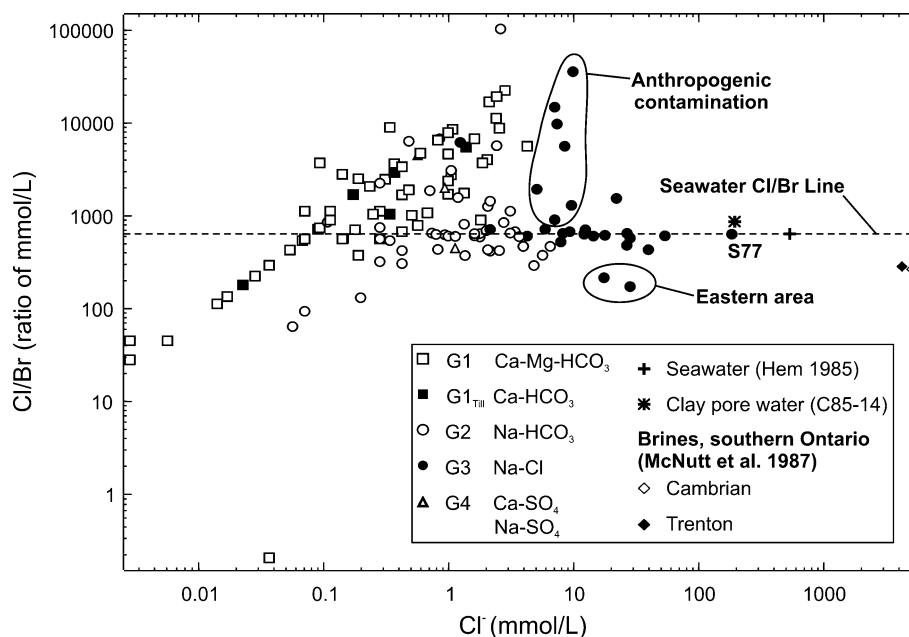
Since the Cambrian–Ordovician sedimentary formations of the St. Lawrence Lowlands represent a complete cycle of marine transgression–regression (Globensky 1987), it is expected that brine formation waters could still be present in those geological units. In fact, Globensky (1972) mentioned that salt water is found in the Trenton and Potsdam

groups, generally in wells deeper than about 150 m, thus, below the studied portion of the aquifer system. The salt water is often associated with presence of oil and natural gas (Globensky 1972). In most recent geological times, a series of glaciations during the Quaternary may have affected the geochemistry of the groundwater, by flushing the upper portion of the aquifer system with glacial meltwater. The last major geological event to affect the study area is the marine invasion from the St. Lawrence Gulf during the last deglaciation. As the Champlain Sea occupied the study area during late Pleistocene, a seawater component could be the source of salinity in the upper portion of the aquifer system. The already shown linear relationship between Cl^- and Na^+ for samples of G3 (Na–Cl) and their location near the seawater dilution line provide initial indications for a marine water source of salinity (Fig. 6c). The Champlain Sea clays, deposited during the marine episode, could also contribute to the salinity of the aquifer system through solute diffusion of its saline pore water.

Cloutier et al. (2006) have shown that sample S77, the most saline of G3 (Na–Cl) groundwater samples found under confined condition in St. Benoît Valley (Fig. 3), has a geochemistry very similar to the pore water in marine clay (sample C85-14). The clay pore water was extracted by squeezing Champlain Sea clay samples from a clay core retrieved at a site in St. Hermas Valley, where the clay has a thickness of 46 m. Sample C85-14, from a depth of 14.1 m, has the highest Cl^- concentration in this profile (6,900 mg/L). Similarities between groundwater sample, S77 and clay pore water were observed for Cl^- and Br^- , two conservative ions that can be used as tracers to identify the origin of groundwater salinity (Richter and Kreitler 1993; Andreasen and Fleck 1997; Vengosh et al. 2002), as well as in $\delta^{18}\text{O}$ values (−10.9‰ for the clay pore water C85-14 and −11.0‰ for the groundwater S77).

Figure 7 shows the relationship between Cl/Br ratio and Cl^- for the groundwater groups, as well as for possible end-members, including the clay pore water sample C85-14, seawater, and brine samples. The brine samples have representative compositions of formation waters for the Cambrian and Trenton formations of southern Ontario presented by McNutt et al. (1987). Sample S77, the groundwater sample with the highest salinity (TDS expressed as salinity of 11.3 g/L), plots on the seawater Cl/Br line, suggesting that seawater is a component of this sample (Fig. 7). The other samples from G3 (Na–Cl), as well as some samples from G2 (Na– HCO_3), plot on or near the seawater Cl/Br line. The clay pore water sample, C85-14, plots slightly above the seawater Cl/Br line, and has a similar Cl^- concentration as S77. The compositions of the two brines have a Cl/Br lower than seawater, showing enrichment in Br^- relative to seawater. Two samples from

Fig. 7 Evidence of mixing. Diagram of Cl^-/Br^- versus Cl^- for the groundwater groups and possible end-member samples. Most samples from Group G3 fall on the seawater Cl^-/Br^- ratio line, indicating the importance of mixing. G3 samples with large Cl^-/Br^- ratios are related to contamination by de-icing salt



the limestone in the eastern area of St. Anne-des-Plaines have a Cl^-/Br^- lower than seawater that could result from solute diffusion from the shale beds of the Chazy and Trenton groups (Globensky 1987). Figure 7 is also helpful in distinguishing the samples from G3 that are affected by anthropogenic contamination. The samples plot above the seawater Cl^-/Br^- line, indicating that the Cl^- increase is not coupled to a Br^- increase. This group of groundwater includes the samples in the preferential recharge areas along main highways 15 and 117 (Fig. 3). High Cl^-/Br^- ratio may be produced by dissolution of de-icing road salts or agricultural chemicals, such as fertilizers (Davis et al. 2001). The trend in the samples from G1 characterizes groundwater in unconfined conditions affected by an increase in Cl^- concentrations, when Br^- concentrations are still at low background level (Fig. 7). Andreassen and Fleck (1997) used a similar trend to show the effect of Cl^- contamination from an anthropogenic source that does not contain Br^- . In the Basses-Laurentides, the Cl^- concentrations for the G1 samples that are part of the trend are low, generally below 1 mmol/L. The sources of this relatively slight contamination, when compared to samples from G3 affected by anthropogenic contamination, could be many and include de-icing road salts or fertilizers.

Since the clay was deposited in the Champlain Sea environment, Cloutier et al. (2006) assumed that the clay pore water sample C85-14, the most saline sample at that site, represents the original Pleistocene Champlain Sea water for the Basses-Laurentides aquifer system. As mentioned previously, the Champlain Sea did not have a typical seawater composition. It was diluted seawater resulting from the mixture between continental waters, including meltwater from the Laurentide Ice Sheet and

local precipitation, and salt water from the St. Lawrence Gulf (Hillaire-Marcel 1988). The similarity between the clay pore water and the groundwater S77, in their conservative ions ratio and concentrations, as well as in their $\delta^{18}\text{O}$, suggests that both samples have the same water origin. Thus, it could be assumed that the groundwater from S77 is close to the original saline end-member of the area. Conservative tracers Cl^- and Br^- can be used to determine the percentage of seawater present in the original Champlain Sea water. Table 2 compares concentrations of Cl^- and Br^- , in mmol/L, for groundwater S77 and seawater. For that sample, the ratios to seawater for both conservative ions are 0.34. Thus, the original Champlain Sea water in the Basses-Laurentides was likely a mixture of about 34% “normal” seawater and 66% freshwater. In a study of Champlain Sea clay near Varennes, northeast of Montréal, Desaulniers and Cherry (1989) calculated a very similar mixture of 33% seawater and 67% freshwater at a depth of 27 m in the clay deposit.

Groundwater mixing model

Figure 8 uses Br^- and Cl^- diagrams to explain the model proposed for the origin of salinity in the area. Step 1

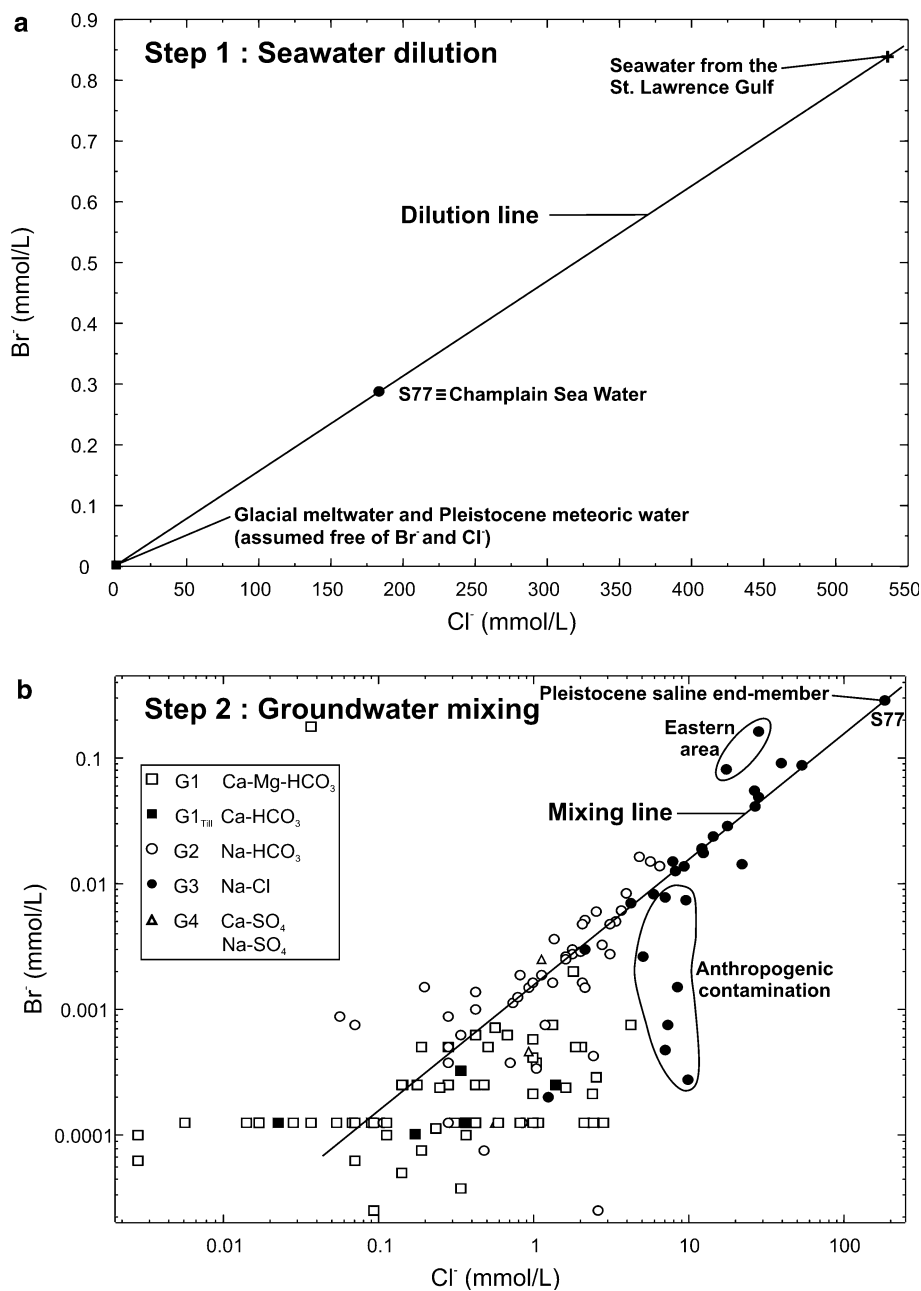
Table 2 Comparison of Cl^- and Br^- (mmol/L) between the groundwater sample S77 and seawater

Ions	S77	Seawater ^a	S77/Seawater
Cl^-	183.34	535.92	0.34
Br^-	0.2878	0.8385	0.34

^a Hem (1985)

Fig. 8 Model for the origin of salinity in groundwater using diagrams of Br^- versus Cl^- .

a Step 1 involved seawater dilution with fresh water to produce the Champlain Sea water (sample S77 retains the original composition). **b** Step 2 involved groundwater mixing with Champlain Sea water that had originally invaded the aquifer system. Samples from Group G3 are closer to the original saline end-member and show a strong mixing signature. Some of the G2 samples also fall on the dilution line



(Fig. 8a) presents the dilution line between a saline end-member, the seawater invading the study area during late Pleistocene, and a freshwater end-member, the glacial meltwater from the Laurentide Ice Sheet and Pleistocene meteoric water. This freshwater end-member is assumed to be free of Cl^- and Br^- . Groundwater sample S77 exactly falls on the line joining the seawater and freshwater end-members (Fig. 8a). This supports the conclusion that dilution is responsible for the level of salinity found in groundwater sample S77, representing the composition of the original Champlain Sea water for the study area. Thus, sample S77 is assumed to represent the Pleistocene saline

water end-member for the Basses-Laurentides aquifer system.

Step 2 illustrates the mixing of the Pleistocene water source, S77, with modern meteoric water (Fig. 8b). In this figure, log scales are used for better visualization. The mixing line of Fig. 8b has the same equation as the dilution line of Fig. 8a, which assumes that modern meteoric water is free of Cl^- and Br^- . Most samples from G3 (Na-Cl) and G2 (Na- HCO_3) plot along the mixing line, indicating that mixing occurred between “evolved” G2 and G3 groundwaters and former Champlain Sea water. The contaminated samples identified in Fig. 7 plot below the mixing line,

confirming the different origin for their salinity (de-icing road salts).

Isotopic data also support the interpretation of groundwater salinity by mixing with Champlain Sea water. Figure 9 shows a diagram of $\delta^{18}\text{O}$ versus salinity. The two end-members of this mixing system are seawater from the St. Lawrence Gulf and the freshwater component defined as glacial meltwater from the Laurentide Ice Sheet and Pleistocene meteoric water. The ratios of the conservative tracers of Table 2 can be used to evaluate the $\delta^{18}\text{O}$ and salinity of the Champlain Sea water in the study area. Thus, by mixing both end-members in a proportion of 34% seawater with 66% freshwater, an estimate is obtained for the original Champlain Sea water with a $\delta^{18}\text{O}$ of -10.6‰ and a salinity of 11.9 g/L. This is close to groundwater sample S77, which has a $\delta^{18}\text{O}$ of -11.0‰ and a salinity of 11.3 g/L. The dilution and mixing models shown in Figs. 8 and 9 demonstrate that groundwater S77 has for origin the Champlain Sea water, and can be defined as the Pleistocene water end-member for the study area. The $\delta^{18}\text{O}$ value of the Pleistocene water is similar to the local modern meteoric water. As an example, the $\delta^{18}\text{O}$ weighted annual means for precipitation in Ottawa, 120 km west of the study area, is -11.21‰ (IAEA 2001). This similarity prevents the discrimination of Pleistocene water on the basis of $\delta^{18}\text{O}$ only, and thus, is responsible for this uniformity in $\delta^{18}\text{O}$ between unconfined and confined conditions identified by Cloutier et al. (2006). This situation is different from southwestern Ontario, where Pleistocene water can be identified based on its depleted $\delta^{18}\text{O}$ relative to modern meteoric water. There, the last glaciation was in a glacio-lacustrine environment, and $\delta^{18}\text{O}$

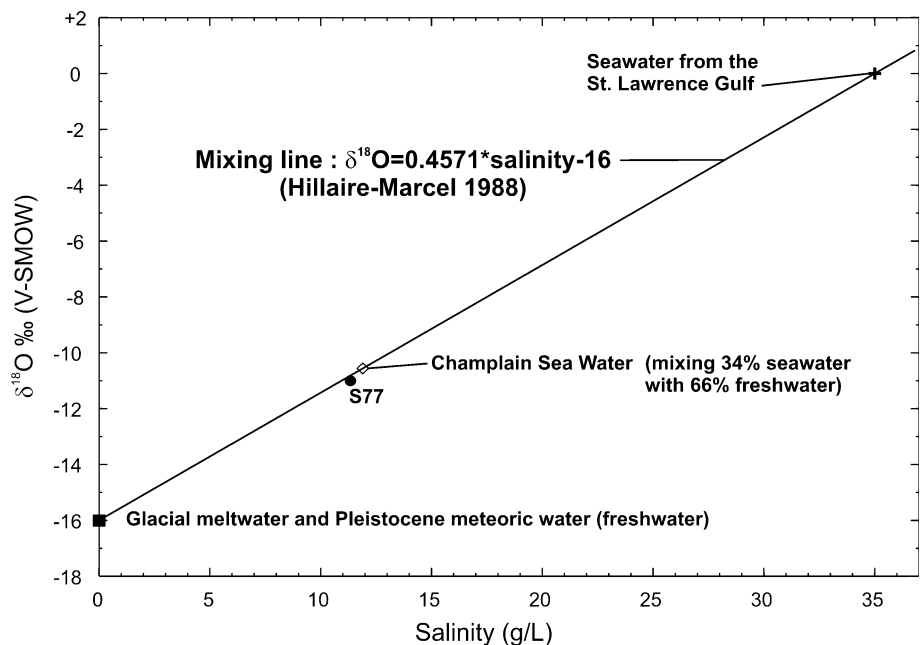
values in the clay pore water, and in the aquifer below the clay, vary from -16.0‰ to -17.5‰ (Desaulniers et al. 1981; Husain et al. 1998). These values for southwestern Ontario Pleistocene water are in the range of the freshwater component $\delta^{18}\text{O}$ value estimated by Hillaire-Marcel (1988), and used in Fig. 9.

Discussion

Salinization and refreshing of the aquifer system

The groundwater mixing model demonstrates the importance of the Champlain Sea episode on the hydrogeochemical evolution of groundwater in the Basses-Laurentides aquifer system. Conservative tracers Cl^- and Br^- , supported by $\delta^{18}\text{O}$ values, allowed an estimation of the percentage of seawater present in the original Champlain Sea water for the study area, a mixture of about 34% seawater and 66% freshwater. Several studies addressed the issue of Champlain Sea salinity variations (Hillaire-Marcel 1988; Rodrigues and Vilks 1994; Brand and McCarthy 2005; Cronin et al. 2008). Paleosalinity changes in the Champlain Sea were studied by Cronin et al. (2008) by combining a variety of tools, including stable isotopes, pollen stratigraphy and micropaleontology of sediment cores from Lake Champlain in Vermont. Their results suggested a sharp decrease in Champlain Sea salinity, most likely caused by rapid freshwater discharge eastward from glacial Lake Algonquin into the Champlain Sea (Cronin et al. 2008). In the Basses-Laurentides, the fossil Champlain Sea water is preserved today in the clay, such as in the clay pore water sample

Fig. 9 Model for the origin of salinity in groundwater using diagrams of $\delta^{18}\text{O}$ versus salinity based on Hillaire-Marcel (1988). Sample S77 is very close in chemical composition and isotopic signature to the inferred original Champlain Sea water



C85-14, and locally in the rock aquifer, such as site S77 in the buried valley of St. Benoît. The Champlain Sea water contributed to the salinization of at least the studied upper portion of the aquifer system (above 140 m depth).

This salinization event is similar to a seawater intrusion process, with the intruding saline water exchanging $\text{Na}^+_{\text{water}}$ with $\text{Ca}^{2+}_{\text{mineral}}$ present in the geological formations, and can be written as $\text{Na}^+ + 1/2 \text{Ca-X}_2 \rightarrow \text{Na-X} + 1/2 \text{Ca}^{2+}$ (Appelo and Postma 2005). The retreat of the Champlain Sea allowed the start of the desalinization process, or the refreshing of the aquifer as described by Appelo and Postma (2005). Flushing of the aquifer system by fresh groundwater recharge leads to Ca^{2+} – Na^+ ion exchange and to the mixing of the recharged water with the Pleistocene saline water end-member. The spatially variable intensity of flushing (equivalent number of pore volumes circulated) and the presence of preferential flow paths and stagnant zones are largely responsible for the present-day geochemistry of groundwater in the rock aquifer system. Thus, the Basses–Laurentides aquifer system can be viewed as being at different stages of desalinization following the Pleistocene invasion of Champlain Sea water in the system.

Groundwater flow patterns are thought to have played a major role in preserving the former Champlain Sea water signature in the aquifer system. Major occurrences of Group G3 Na-Cl groundwater are found at the center of valleys: du Nord River, St. Hermas and especially St. Benoît (Fig. 3). As noted before, groundwater is recharged on the crests found north and south of these valleys and then flows towards the buried valley centers, where flow then diverges towards their eastern and western ends (see potentiometric contours and flow paths in the inset map of Fig. 3). These converging–diverging flow patterns do not lead to important groundwater flow in the central part of these valleys. Considering the physiography of the area, it is likely that these groundwater flow patterns were established soon after the Champlain Sea retreat. Limited groundwater flow at the center of these valleys has likely thus prevented the originally present Champlain Sea water in the rock aquifer from being “flushed”. These flow patterns contribute to preserving the fossil saline groundwater signature and allow mixing to occur with more recent groundwater, especially Group G2 groundwater. In the otherwise quite similar aquifer system found in the Châteauguay River watershed, south across the St. Lawrence River from the study area, brackish to saline water occurrence is much more limited. Even though there are traces of the former presence of Champlain Sea water that covered the watershed, steady and continuous groundwater flow paths from a large main recharge area has allowed the almost total desalination of the Châteauguay aquifer system (Blanchette et al. 2005).

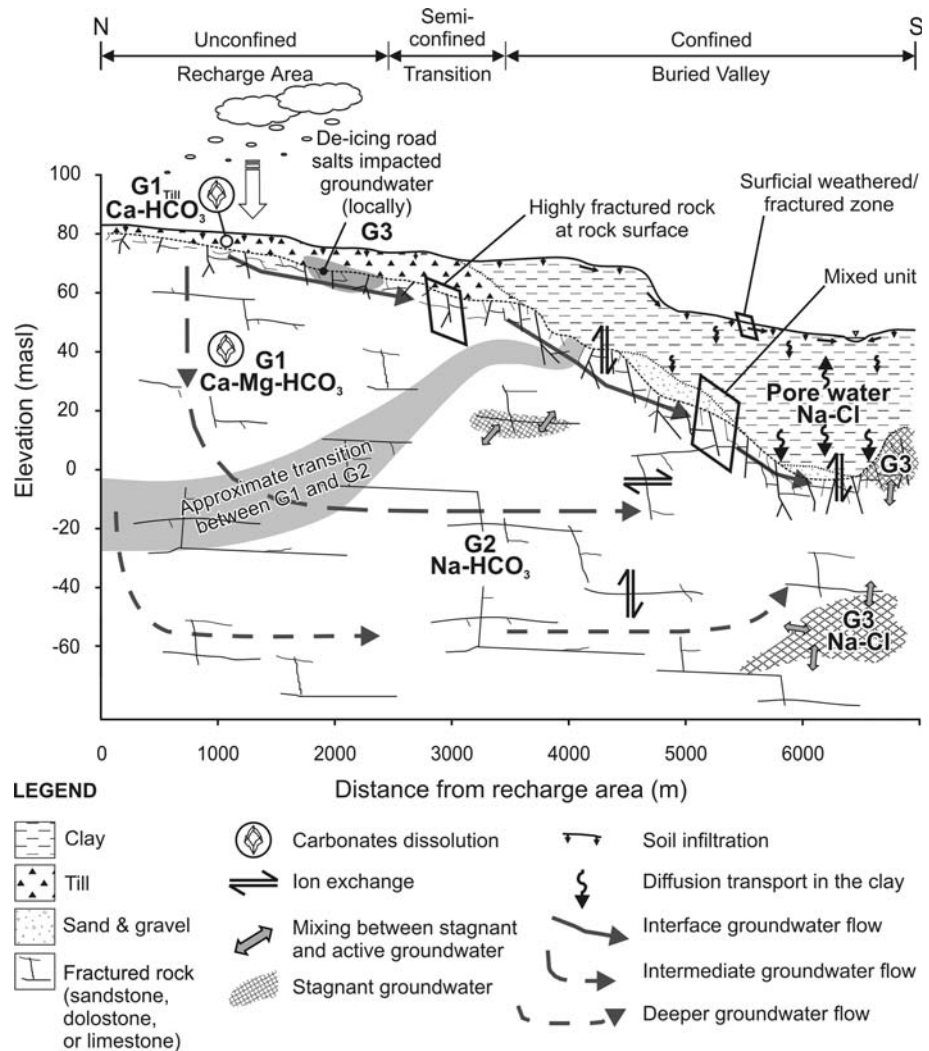
In the St. Benoît Valley, most groundwater samples have Group G3 Na-Cl water and sample S77 has a composition close to the original Champlain Sea water. This valley is at the least advanced stage of the desalinization process. This poorly flushed area could be considered a relatively stagnant part of the aquifer system, where the converging–diverging groundwater flow pattern has led to a stable “singularity” at the valley center, where little flow occurs (Fig. 3). The other two buried valleys in the study area, St. Hermas and du Nord River, as well as the Ste. Anne-des-Plaines area, are in a more advanced stage of desalinization. The sites with Na-Cl groundwater types in these two valleys could be local, stagnant water, or solutes diffusing downward from the clay aquitard. In the two valleys, there is a limited but present flow path in the valley centers as well as local contacts with overlying rivers that could account for some saline water flushing. In the Ste. Anne-des-Plaines area, the flow pattern is relatively linear towards the south, but there is a restricted recharge area to the north that may not provide sufficient groundwater entry to allow efficient desalinization. Still, in these last three areas, a good part of the Cl^- has already been flushed, with Na^{2+} lagging behind on exchange sites. Cationic exchange of $\text{Ca}^{2+}_{\text{water}}$ with $\text{Na}^+_{\text{mineral}}$ gives the Na- HCO_3 groundwater type that dominates in these areas.

Finally, the recharge areas are completely flushed of the Champlain Sea water component. It was demonstrated that the Na-Cl water types in these areas result from anthropogenic de-icing salt contamination.

Hydrogeochemical conceptual model

Groundwater groups and water sources are represented in Fig. 10 to show their relative position within the groundwater flow conceptual model to produce a conceptual geochemical model of groundwater evolution. Present-day precipitation infiltrates the soils and the permeable surface sediments, generally till, in the groundwater recharge areas. The starting point for the geochemical evolution of groundwater consists of carbonate dissolution in surface sediments following water infiltration in the soil zone. The linear relation between Ca^{2+} and HCO_3^- , the Mg/Ca ratios between 0.6 and 0.9, the pH increase relative to precipitation, as well as the undersaturated to near equilibrium calcite and dolomite SI, have been presented as evidence of carbonate dissolution operating in the surface sediments. Carbonate dissolution is responsible for the geochemical characteristics of G1_{Till} (Ca- HCO_3) and is consistent with both the $\delta^{13}\text{C}_{\text{DIC}}$ of the till groundwater (Cloutier et al. 2006) and the availability of calcite and dolomite in the till matrix. The geochemistry of G1_{Till} is very important, as it controls to a large extent that of G1 (Ca-, Mg- HCO_3). Groundwater, G1 is the recharged groundwater in the

Fig. 10 Conceptual hydrogeochemical model of groundwater evolution within the Basses-Laurentides sedimentary rock aquifer system. Recharge preferentially occurs in unconfined areas, where carbonate dissolution leads to the initial Group G1 groundwater composition. Further flow away from recharge zones into confined conditions leads to Group G2 composition due to ion exchange. The aquifer is still undergoing an active desalination process by flowing groundwater that mixes with remnants of the original Champlain Sea water that had invaded the aquifer system. Groundwaters of Group G3 retain a clear signature of that original saline water in relatively low flow zones



sedimentary rock aquifer system, following its infiltration through the till. Samples that belong to this group are located in unconfined to semi-confined conditions near recharge areas. Water–rock interaction, as carbonate dissolution, is also active in the sedimentary rock particularly in the dolostone and limestone formations.

From recharge areas, groundwater flows through the active aquifer system under confined conditions, resulting in a geochemical evolution to G2 (Na-HCO_3). This groundwater flow occurs as interface preferential groundwater flow in the highly fractured rock or mixed unit, as well as intermediate to deeper groundwater flow in the fractured sedimentary rock (Fig. 10). Active post Champlain Sea groundwater flow is responsible for the on-going desalinization of the confined aquifer system. The approximate transition front from G1 ($\text{Ca-}, \text{Mg-HCO}_3$) to G2 (Na-HCO_3) is more advanced in the interface zone due to faster groundwater flow (Fig. 10). Being confined by the clay aquitard, the geochemistry of G2 groundwaters is not affected by direct recharge but by the geochemical

processes occurring along the flow path, from the recharge areas to the sampling site. Due to the diversified geological and hydrogeological contexts of the Basses-Laurentides, the geochemical evolution paths and the resulting water types vary accordingly to the sedimentary formations, the depth of groundwater flow, as well as the geographical area. In buried valleys, interface flow occurs below the Champlain Sea clay aquitard that has a Na-Cl pore water geochemistry. The contact with the clays leads to $\text{Ca}^{2+}_{\text{water}} - \text{Na}^{+}_{\text{mineral}}$ ion exchange that results in G2 (Na-HCO_3) groundwater in the confined aquifer system. Evidence of $\text{Ca}^{2+} - \text{Na}^{+}$ ion exchange occurring along the groundwater flow path includes an increasing trend between pH and Na^{+} concentrations coupled to a decrease in Ca^{2+} concentrations, as well as an increase in Na^{+} concentrations not strongly coupled to a Cl^{-} increase. The active intermediate and deeper groundwater flow in the sandstone and dolostone of the buried valleys is also impacted by ion exchange with mineral exchangers of the rock formations, also resulting in G2 groundwaters.

Former Pleistocene Champlain Sea water is still present in the aquifer system, either as the most concentrated stagnant groundwater, in poorly flushed zones of the aquifer system, such as site S77 in St. Benoît Valley, and as pore water of the Champlain Sea marine clay aquitard. Locally, stagnant brackish to saline groundwater mixes with G2 groundwaters to produce areas of G3 (Na-Cl) groundwaters. Conservative tracers Cl^- and Br^- , as well as $\delta^{18}\text{O}$, confirmed that these brackish to saline groundwaters originate from the Champlain Sea water. This mixing is observed at a larger scale for the St. Benoît Valley, where the Pleistocene Champlain Sea water was sampled (site S77), but can be present sporadically in the St. Hermas and the du Nord River valleys as well. Locally, in stagnant parts of the system, downward diffusion of Cl^- and Na^+ from the aquitard could result in groundwater with G3 characteristics. Due to this downward diffusive transfer of solutes, the brackish to saline pore water of the aquitard has major impacts on the geochemistry of groundwater from the interface zone, increasing groundwater salinity in more isolated sections of the aquifer system. Groundwater, G3 is also observed locally in preferential recharge areas, and results in there from a contamination by de-icing road salts. The Cl^- concentrations of these de-icing road salts impacted groundwater is not coupled to a Br^- increase as it is for the samples of G3 located under confined condition, thus confirming their different origin.

Relationships between hydraulic and geochemical conditions

Although focused on a local aquifer system, the data and interpretation from this study provide a generally meaningful illustration of the relationships between hydraulic and geochemical conditions. Confined or unconfined conditions as well as flow patterns were shown to have an important role in the geochemical evolution of groundwater. Such coupling has been observed by numerous previous studies and general conceptual models have integrated the generally expected geochemical evolution of groundwater under “natural equilibrium” (Tóth 1999). An original aspect of the present study is that it illustrates the geochemical evolution of an aquifer system following a major perturbation, namely Champlain Sea water intrusion in the aquifer. Different parts of the aquifer were shown to still be at various stages of a desalinization process. So, although hydraulic conditions are likely to have reached somewhat steady state relatively shortly after the Champlain Sea retreat, still evolving and transient geochemical conditions are prevailing to this day, 10,000 years after the perturbation. The study area thus shows that long-term geochemical recovery may be required by some aquifer

systems after major perturbations, and that locally prevailing hydraulic conditions affect the rate of this recovery.

Summary and conclusions

This paper aimed to identify the main active geochemical processes as well as the Quaternary geological events that have influenced groundwater geochemistry in the Basses–Laurentides. The aquifer system of the Basses–Laurentides consists of Cambrian–Ordovician sedimentary formations (sandstone, dolostone, and limestone) lying on Precambrian crystalline basement. Unconfined conditions characterize the areas of preferential groundwater recharge, where precipitation infiltrates soils and till. The marine clay aquitard confines the rock aquifer, for example in buried valleys. From the recharge areas, groundwater flows through the highly fractured rock and mixed unit at the interface with the overlying clay aquitard, as well as intermediate to deeper groundwater flow in the fractured sedimentary rock unit.

The interpretation of the main geochemical processes presented in this paper relies on the classification of groundwater groups determined by Cloutier et al. (2006). The main geochemical processes that are affecting the evolution of groundwater groups were presented with respect to their relative position in the groundwater system, starting from the recharge and along groundwater flow paths. Dissolution of carbonates, calcite and dolomite, dominates in the preferential recharge areas resulting in Ca-, Mg- HCO_3 (G1) groundwater. Ca^{2+} – Na^+ ion exchange, groundwater mixing with Pleistocene Champlain Sea water as well as solute diffusion from the marine clay aquitard are the main processes under the confined conditions resulting in a Na- HCO_3 (G2) and Na-Cl (G3) groundwater. This interpretation of groundwater groups within the hydrogeological contexts defined the main geochemical processes, thus providing the meaning of these groups in terms of groundwater evolution in the Basses–Laurentides sedimentary rock aquifer system.

The last major geological event to affect the study area is the marine invasion from the St. Lawrence Gulf during the last deglaciation. This paper has further confirmed that the resulting Champlain Sea was a mixture of continental fresh water and seawater from the Gulf. The analysis has also shown that fossil Champlain Sea water is still found in stagnant parts of the aquifer system and in the pore water of thick marine clays left by the Champlain Sea episode. It was demonstrated that the marine invasion that resulted in the Champlain Sea is the cause of the salinization of the aquifer system. Conservative tracers Cl^- and Br^- , supported by $\delta^{18}\text{O}$ values, allowed an estimation of the percentage of seawater present in the original Champlain

Sea water for the Basses–Laurentides, a mixture of about 34% seawater and 66% freshwater. The present geochemistry of groundwater indicates that the aquifer system is at different stages of desalinization, from the fossil Champlain Sea water in stagnant parts to fully flushed sections of the aquifer system in preferential recharge areas. A modern salinity source, de-icing road salts, was identified in recharge areas and could be distinguished by its Cl/Br ratio. This knowledge of the main geochemical processes that are affecting the evolution of groundwater, particularly the distribution and origin of groundwater salinity, is important for the municipalities of the region in their planning and managing of the groundwater resource.

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