

Elucidating the sources and distribution of chlorine in shallow aquifers of the Barlow-Ojibway Clay Belt in northwestern Quebec, Canada

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Summary

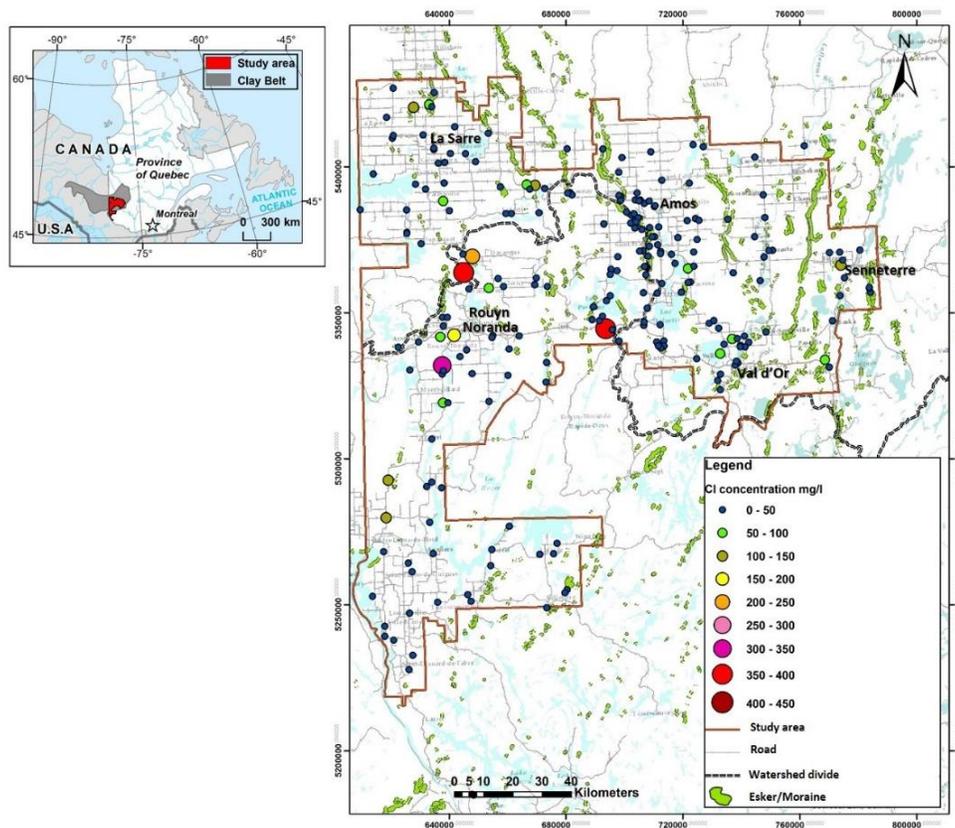
This study aims at elucidating the geogenic and human sources of chloride in the shallow aquifers of the Barlow-Ojibway Clay Belt in northwestern Quebec, Canada. The data from two main databases (PACES-AT and BADGEQ) are jointly interpreted, allowing for a total of 4 027 samples analyzed for [Cl⁻], major ions and trace elements over a 20 000 km² region. The PACES-AT database further includes > 400 analyses of the stable isotopes of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) and 23 analyses of chlorine isotopes ($\delta^{37}\text{Cl}$). GIS-based, graphical and statistical approaches are currently being applied to the datasets in order to identify the sources of Cl in groundwater. Ultimately, this study will provide tools for evaluating the relative contribution of human vs geogenic sources of Cl in the Canadian Shield.

Context and objectives

Chlorine (Cl) is an element of the halogen group of the periodic table. It has an atomic mass of 35,4527 amu, two stable isotopes (³⁵Cl, ³⁷Cl) and one naturally occurring cosmogenic radioactive isotope (³⁶Cl). Chlorine has different oxidation states (from Cl⁻¹ to Cl⁺⁷) but the chloride ion (Cl⁻) is the only significant form in shallow natural waters. It is recognized as the element presenting the highest mobility during weathering and transport processes (Gaillardet et al., 2005). This is explained by the geochemical behavior of Cl, the latter not being significantly involved in redox and sorption reactions and not being included as a major component of the structure of highly soluble minerals (Hem, 1985). In simple terms, once released into groundwater, Cl⁻ is likely to remain in solution through the entire groundwater flow system. This gives Cl⁻ a great potential for tracing hydrological processes along groundwater flow systems. While chlorine can be found in evaporites, marine sedimentary rocks and marine sediments, it only occurs as a trace constituent in most igneous and metamorphic rocks. In shield areas dominated by crystalline rocks, the main natural sources of Cl⁻ are therefore (1) the atmosphere and (2) shield brines. Human sources such as de-icing salts (NaCl and CaCl₂) and sewage can strongly affect Cl⁻ concentrations in surface- and groundwater. Several studies have indeed revealed increasing trends of chloride in groundwater, suggesting a recent human driven degradation of groundwater quality (Pollok and Toler, 1973; Howard and Haynes, 1993; Perera et al., 2013; Trenouth et al., 2015; Marques et al., 2019). Nevertheless, deciphering the relative contribution of natural vs anthropic sources of Cl⁻ in groundwater remains challenging because advection-dispersion-diffusion and mixing processes occurring in groundwater flow systems over various timescales can complicate the identification of local sources. Fitting in the pre-established context, this study aims at elucidating the sources of Cl⁻ in shallow aquifers (1.8 m to 182 m) of the Barlow-Ojibway Clay Belt in northwestern Quebec, Canada (Figure 1). The study area is of particular interest because more than 70% of the local population depends on groundwater for their drinking water supply (Cloutier et al., 2016). Most of the aquifers in this area are dominated by Ca-Mg-HCO₃ water type (Cloutier et al., 2016).

Nevertheless, previous studies revealed high Cl^- concentrations in some areas where a $\text{Ca-Na-HCO}_3\text{-Cl}$ water type was identified (Bondu et al., 2017; Rey, 2020). Since the region is found outside the limits defined by the marine transgressions associated with the last deglaciation, the main source of Cl^- is either anthropogenic pollution or ancient brines from the Canadian Shield. Chemical data including major and trace elements along with isotopic analyses ($\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$ - $\delta^2\text{H}$, ^3H) are used here to document the sources of Cl^- in the study area.

Figure 1 Study area and dissolved $[\text{Cl}^-]$ concentrations available in the PACES-AT database



Methods and data sources

Two main databases are available for documenting dissolved Cl^- in the study area. The BADGEQ database (Lalonde et Pelletier, 1983; Lalonde et al., 1980) includes geochemical data from more than 5 300 groundwater samples collected between 1974 and 1979 by the Quebec Ministry of Energy and Resources (MERQ). Among these, 3 562 samples were analyzed for Cl^- . The PACES-AT database (Cloutier et al., 2016) includes geochemical data from more than 400 groundwater samples collected between 2006 and 2014 by the UQAT. Most of the available samples were collected from private wells, while some were collected in boreholes and groundwater springs. Both databases include measurements of physicochemical parameters (pH, conductivity, temperature) and major ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^-), among others. The PACES-AT database further provides dissolved Br^- concentrations and analyses of the stable isotopes of water ($\delta^{18}\text{O}$ - $\delta^2\text{H}$). Twenty-three of these samples were also analyzed for chlorine isotopes $\delta^{37}\text{Cl}$. The ^3H content was also analyzed for 98 water samples included in the PACES-AT database.

Elemental concentration ratios and isotopic compositions are used here for elucidating the sources of Cl^- in groundwater of the study region. Regional maps illustrating Cl^- concentrations in groundwater are also constructed in order to assess potential human influences on water quality. Although Cl/Br vs Na/Br molar ratios and the Cl/Br ratio vs Cl^- are commonly used to identify salinity sources (Walter et al., 1993; Kloppmann et al., 2001; Alcalá and Custodio, 2008), these measurements could not be used here since Br concentrations were below detection limits for most samples.

Preliminary results and discussions

The data reveal $[\text{Cl}^-]$ ranging between $1,41 \times 10^{-6}$ mol/l and 0,011 mol/l with an average of $3,3 \times 10^{-4}$ mol/l. Chloride concentrations exceeding $2,82 \times 10^{-5}$ mol/l are measured in 103 samples (24% of total samples) while 10% have $[\text{Cl}^-]$ exceeding 0,0028 mol/l. Figure 1 shows the spatial distribution of $[\text{Cl}^-]$ data from the PACES-AT database. It reveals that high $[\text{Cl}^-]$ are not systematically associated with the urban areas (e.g.: Rouyn-Noranda, Val-d'Or, La Sarre, Amos, Senneterre). Overall, there is a greater proportion of $[\text{Cl}^-] > 50$ mg/L in the western part of the study area, although there is currently no documented rocks or sediments containing Cl^- in this area. This could indicate a greater influence of anthropic sources of Cl^- in the western part of the region. Nevertheless, the first observations of the median $[\text{Cl}^-]$ from PACES-AT database is not significantly higher than that of BADGEQ database, despite the fact that BADGEQ samples were collected between 1974 and 1979 while the PACES-AT were collected between 2006 and 2014. This could suggest that the anthropic impact is not the only cause of the higher chlorine concentrations observed in groundwater of the Abitibi-Témiscamingue region since $[\text{Cl}^-]$ is at steady state for more than 30 years. Such question further highlight the need to better identify the sources of Cl within groundwater in the study area.

Figure 2A and 2B show the $[\text{Cl}^-]$ reported against $[\text{Na}]$ and $[\text{Ca}]$, respectively. The halite (NaCl) and calcium chloride (CaCl_2) dissolution lines are also shown therein. Groundwater with salinity originates from the dissolution of NaCl and CaCl_2 would lie along the dissolution lines of both salts. However few samples plot close to the aforementioned lines. The latter most likely reflect the dissolution of salts used for roads de-icing. The vast majority of samples plot below the NaCl and CaCl_2 dissolution lines, even when $[\text{Cl}^-]$ is plotted against the sum of $[\text{Na}^+]$ and $[\text{Ca}^{2+}]$ (Figure 3), suggesting the importance of processes as water/rock interaction on $[\text{Na}^+]$ and $[\text{Ca}^{2+}]$ in groundwater of these shallow aquifers. The data shown in Figure 3 reveal that the influence of NaCl and CaCl_2 on dissolved ions concentrations is likely limited. This suggests that other sources of Cl^- should be responsible for the high chloride values.

The available data with respect to brines of the Canadian shield reveals that the latter generally present Na/Cl molar ratios ranging between 0,47 mol/l and 0,64 mol/l and Ca/Cl molar ratios ranging between 0,095 mol/l and 0,23 mol/l (Frape et al., 1984). The plot of samples of both databases in Na/Cl ratios against Ca/Cl ratios diagram (Figure 4) reflect a mixing of different sources of Cl^- in groundwater of the region such as the mixing with brines, saline and brackish deep groundwater of the Canadian shield. The isotopic composition of Cl ($\delta^{37}\text{Cl}$) can be used to determine the origin chlorine. Generally, $\delta^{37}\text{Cl}$ values rang from -0.50 to $+0.69$ ‰ in groundwater, from -0.60 to $+1.20$ ‰ for halite and -2.06 to $+1.01$ ‰ for salt lake brine (Kaufmann et al., 1988). The $\delta^{37}\text{Cl}$ values measured in samples from the study region show a broad range, between -0.37 ‰ and $+1.8$ ‰ (SMOC), suggesting also the mixing of Cl^- from different sources.

Figure 2 Dissolved [Cl] plotted against dissolved [Na] (A) and [Ca] (B)

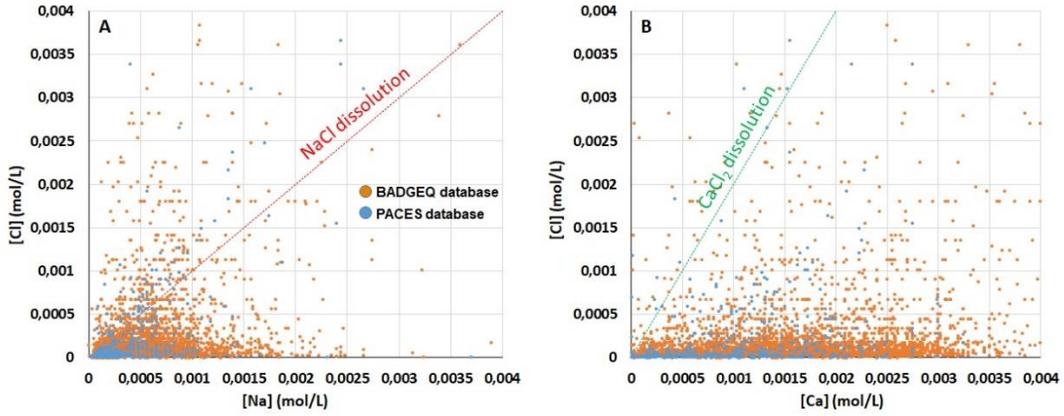


Figure 3 Dissolved [Cl] plotted against the sum of dissolved [Na] and [Ca]

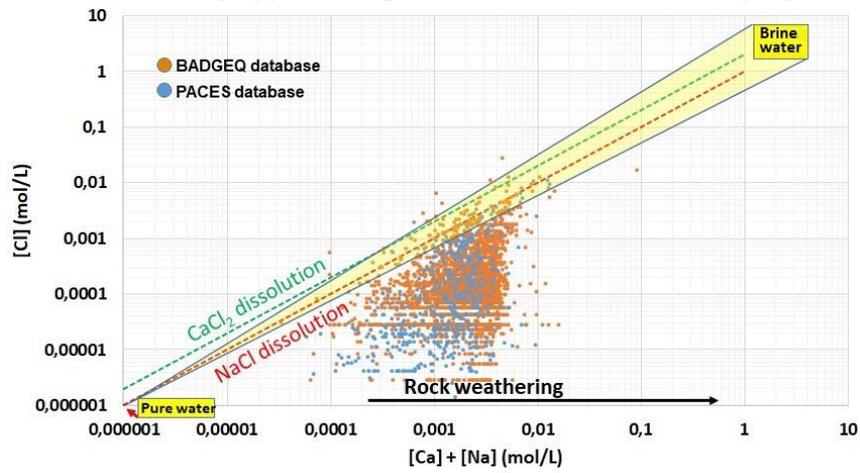
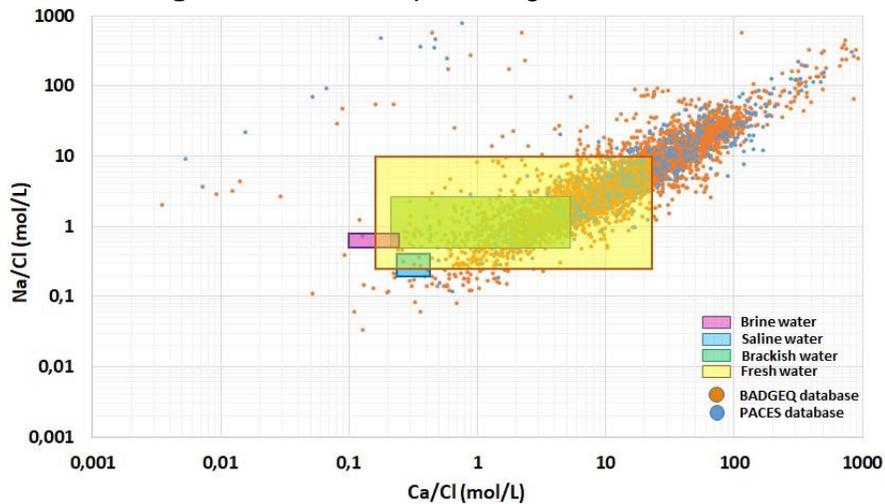


Figure 4 Na/Cl ratio plotted against Ca/Cl ratio



Opening remarks

The results of the study provide information aimed at elucidating the sources of chloride in the shallow aquifers of the Barlow-Ojibway Clay Belt. The preliminary interpretation of Cl^- , Na^+ , Ca^{2+} , and $\delta^{37}\text{Cl}$ suggests the mixing of Cl^- from different sources, as de-icing salts and brines. Next steps will include GIS-based and statistical approaches to interpret the data considering the sampling sites hydrogeological contexts. A comprehensive understanding of the sources of chloride is mandatory to assure sound management of these shallow aquifers.

Acknowledgements

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