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A Regional Chemical Characterization and Analysis of Groundwater in Eastern Ontario

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Abstract

This study utilizes 234 samples to provide a regional characterization and analysis of groundwater chemistry in eastern Ontario, Canada, where elevated TDS, Na and halogens occur in shallow groundwater. Water-types, PCA and mapping are used to investigate the processes and features controlling the chemistry. The chemical patterns are associated with glaciomarine deposits (extent, thickness) and bedrock topography, which modulate residence time and flow-path of groundwater. These determine the relative effects of recharge, ion exchange, salinization and organic breakdown on groundwater chemistry. Anomalous chemistry east of Ottawa (brackish-to-saline TDS; elevated water $\delta^{18}O$; elevated Na, Cl, I, CH_4, pH, F) coincides with a major buried bedrock depression. Here, groundwater stagnation allows build-up of organic decomposition products and sustained residence of Pleistocene Champlain seawater with TDS up to 10400 ppm. This ambient baseline and identified natural and anthropogenic water quality threats and potential groundwater quantity issues will help support effective groundwater resource management.

Keywords

Groundwater, hydrogeology, hydrogeochemistry, geology, regional groundwater, water quality, salinity, Champlain Sea, halogens, chloride, iodine, sodium, principal component analysis (PCA)

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Chapter 1

1 Introduction

1.1 Context

Eastern Ontario (sometimes referred to as "southeastern Ontario") is a region in Southern Ontario, Canada with a significant population. It is a wedge-shaped region (Figure 1.1) between the Ottawa and St. Lawrence Rivers, bordered north and east by Québec and in the south by New York State. The largest urban center in eastern Ontario is Canada's capital city Ottawa. Groundwater is an important resource in eastern Ontario, being depended upon for municipal, industrial and private use. Characterizing and understanding groundwater resources is imperative to protect public health and for sustainable management of the resource.

The Ontario Geological Survey (OGS) is a branch of the Ministry of Northern Development and Mines (MNDM) and serves to document and map Ontario's geological resources. The Ambient Groundwater Geochemistry (AGG) program is an OGS initiative to map groundwater chemistry in Ontario at a relatively high regional sampling density. The AGG program has been operating for a decade and to date has covered all of southern Ontario and the Sudbury area with over 2500 sampling stations. The dataset serves as a baseline and with this information in hand, regional-scale patterns of groundwater chemistry can be investigated. One objective of such studies is to provide understanding of geological controls on groundwater composition. Anthropogenic activities also impact groundwater and can be investigated using this dataset. The AGG dataset contains a wealth of information, which provides a starting point for the understanding of localized groundwater conditions in more detailed, thematic investigations.

In 2012, groundwater in eastern Ontario was sampled through the AGG program (Figure 1.1) and again in 2013 and 2014 to fill sampling gaps or increase sampling density where unusual chemistry was observed. Water at one station (12-AG-202) had an onsite electrical conductivity reading of 3.1 x 10^4 μS/cm and the water was very salty to the taste. These characteristics exist despite this sample's origin from a relatively shallow interface well that is located more than 100 km from the nearest tidewater. Eastern Ontario groundwater commonly exhibits high concentrations of halogens and TDS (total dissolved solids), and spatial patterns of chemistry do not align with geologic units (Colgrove et al. 2014). Bedrock lithological control, therefore, cannot account for groundwater chemistry in eastern Ontario. The investigation comprising this thesis was initiated to determine the dominant controls on groundwater geochemistry in eastern Ontario.

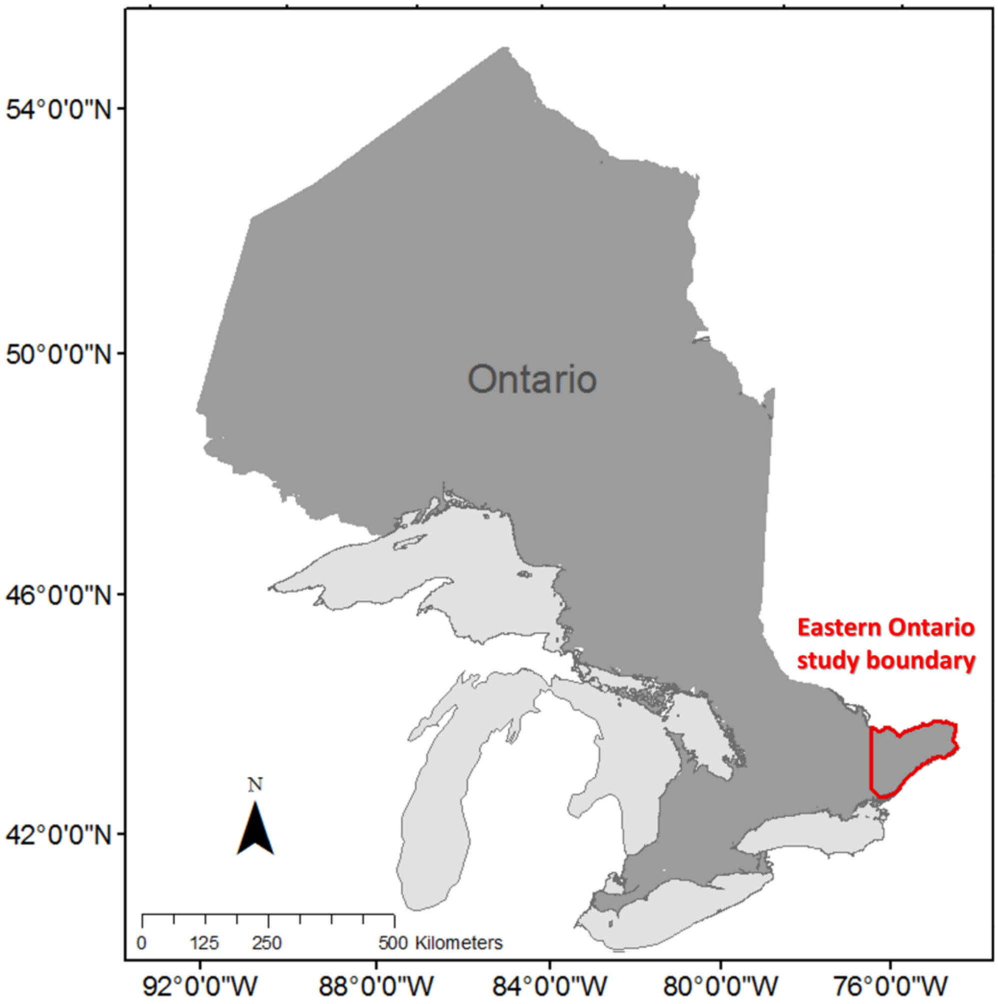

Figure 1.1. Location of the study area (eastern Ontario) in Ontario, Canada.

1.2 Research Overview

A subset of the AGG dataset[1] for an area encompassing all of eastern Ontario was used in this study. It includes hydrogeochemical data from 234 drilled wells with 130 database fields including dissolved chemical constituents (major, minor, trace), isotopes ($\delta^{18}O$, $\delta^{2}H$, ^{3}H), dissolved gases (O_2, CO_2, CH_4), bacteria counts (total, fecal), other water characteristics (pH, ORP, temperature, conductivity, appearance, smell) and station/well attributes.

The objective of this study was to interrogate the AGG database for eastern Ontario to understand the controls on groundwater geochemistry. The approach followed was to:

1) explore the dataset, display regional spatial patterns and determine parameters of greatest interest;

2) identify the physical/geological controls affecting the geochemical baseline conditions, and

3) account for the observed groundwater chemistry in terms of geochemical processes.

Determination of water types (facies) and principal components (from PCA) was combined with spatial concentration trends for many groundwater constituents to determine the chemical processes operating at a regional scale. Spatial relationships among water types, principal components, individual parameters and the physical/geological features of the study area are used to postulate controls on chemistry.

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[1] Available at http://www.mndm.gov.on.ca/en/mines-and-minerals/applications/ogsearth/ambient-groundwater-geochemistry

The focus of this thesis is on regional scale patterns, processes and controls. Some samples may be influenced by more local flow systems and processes, and hence provide local exceptions to regional trends. The entire dataset contains many chemical parameters that are not discussed in this study. For this thesis, a smaller subset of parameters has been used, which includes the most common constituents and others of particular interest for identifying geochemical processes, and/or having concentrations exceeding Ontario Drinking Water Standards (ODWS).

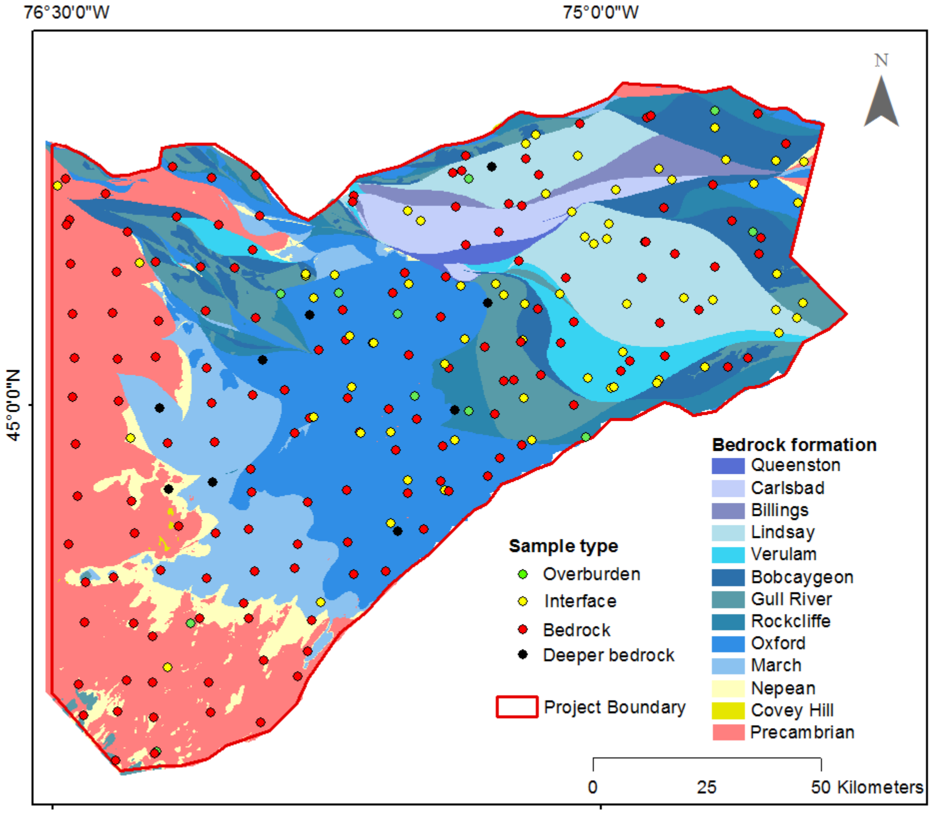

Figure 1.2. Sample locations and type across eastern Ontario. Interface wells are completed within 5m above or below the overburden-bedrock contact. Deeper bedrock wells are those drilled through the subcropping formation to the one below. Paleozoic geology by Armstrong and Dodge (2007).

1.3 Thesis structure

The thesis is structured using the monographic format. The six chapters are Introduction (1 – current chapter), Background Information (2), Methods (3), Results (4), Discussion (5) and Conclusion (6). Chapter 2 describes the geological and hydrogeological characteristics and history of the study area, and the findings of similar hydrogeochemical studies conducted in western Québec. Chapter 3 describes the AGG program protocol (sampling, laboratory analysis and quality control procedures) and data analysis methods (water types, saturation indices, statistics, geospatial analysis). Chapter 4 provides a basic reporting of parameter levels and patterns, as well as results derived from these data to obtain water types, saturation indices, and PCA. Chapter 5 discusses the major chemical processes affecting water chemistry and then the physical controls on these processes. Chapter 6 summarizes the main findings, briefly discusses the implications of this study and provides suggestions for future work.

Chapter 2

2 Background Information

This chapter provides context and background information to support the current study of groundwater chemistry in eastern Ontario. The study area is described in terms of structure, bedrock lithology and overburden geology. Special focus is given to the Quaternary geological history and deposits of the Champlain Sea as they are critical for the study. Previously described hydrogeology is also discussed, first in terms of physical and chemical information for eastern Ontario and then in terms of similar groundwater studies in Québec.

2.1 Site description

The eastern Ontario study area encompasses ~15 500 km^2 extending east from the Frontenac Arch to the Québec border. The region is bounded to the north and south by the Ottawa and Saint Lawrence Rivers, respectively. The land use is largely agricultural, with several urban centers including Ottawa, Cornwall and Brockville. The topography is relatively flat, though the Precambrian Shield in the west and the Glengarry Till Plain near Maxville in the southeast create regional topographic highs (Figure 2.1). A major structural graben and incised valleys in the northeast create a regional topographic low east of Ottawa.

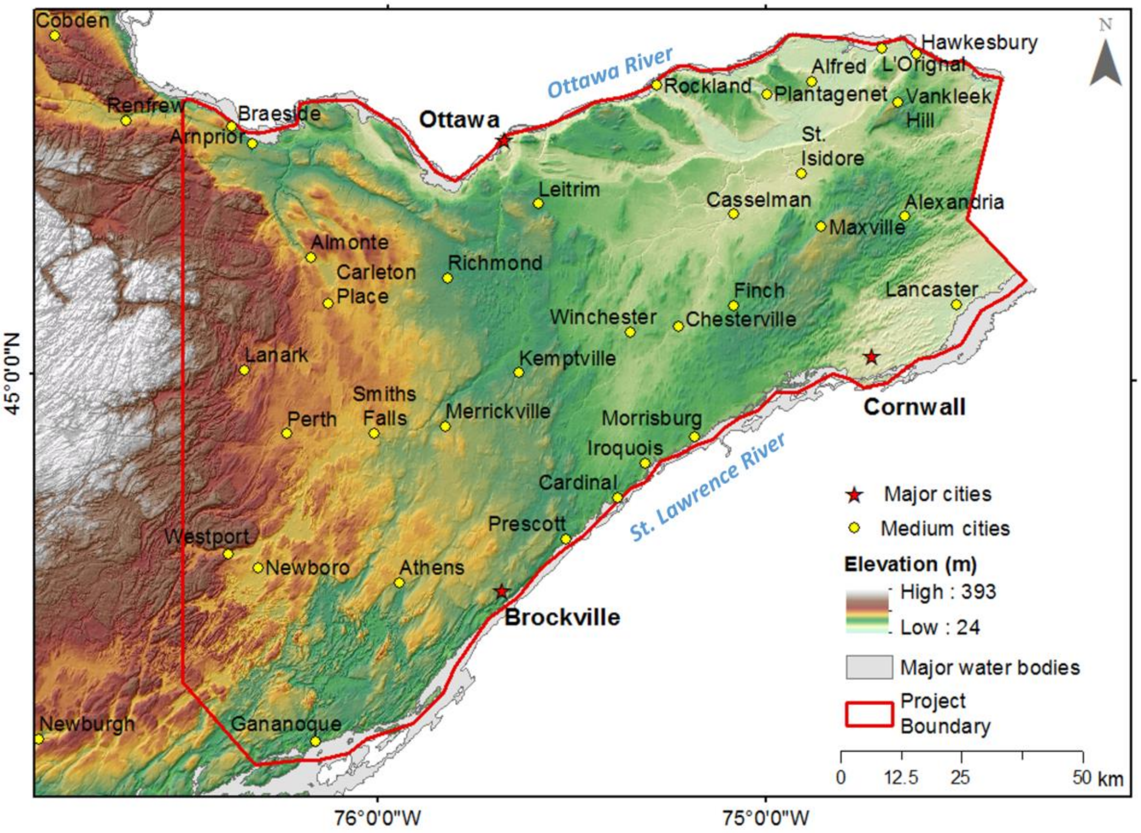

Figure 2.1 Eastern Ontario site map, including medium and major cities and towns, major water bodies and the landscape topography (DEM[2]).

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[2] Digital elevation model

2.2 Geology

2.2.1 Regional overview and structure

The geology of eastern Ontario comprises crystalline Precambrian basement rocks that crop out in the west and are overlain in the rest of eastern Ontario by gently dipping Paleozoic sedimentary rocks (Figure 2.2). The Sauk and lower Tippecanoe sedimentary sequences recorded in eastern Ontario’s Paleozoic rocks. The Sauk is a sequence of passive margin interior sediments recorded in the Beekmantown Group. The lower Tippecanoe is a platform sequence which involved foundering of a foreland-basin carbonate platform, as recorded in the Chazy and Ottawa Groups. The upper Ordovician synorogenic mudrocks (Billings, Carlsbad, Queenston formations) indicate platform foundering (Rimando and Benn 2005 and references therein). Quaternary tills and glaciofluvial and glaciomarine deposits overlie bedrock sparsely in the west and thicken to the east. The thickness of Quaternary deposits is related to the bedrock topography, which is elevated in the west and decreases to the northeast where there is a major (~50 km wide) bedrock depression east of Ottawa (referred to as northeast bedrock depression) (Figure 2.3).

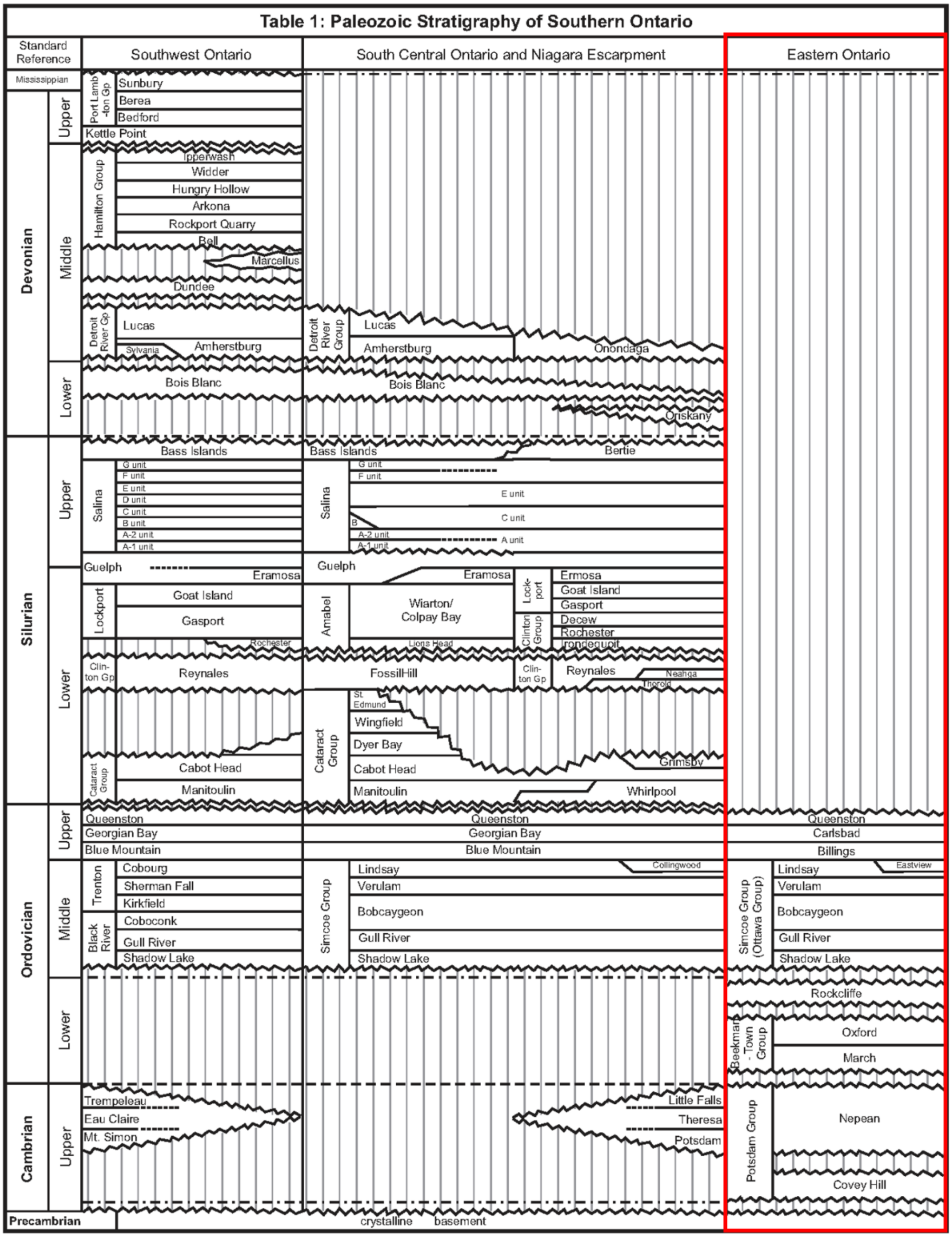

Figure 2.2 Paleozoic stratigraphy of Southern Ontario, modified from Armstrong and Dodge (2007). The eastern Ontario sequence is outlined in red.

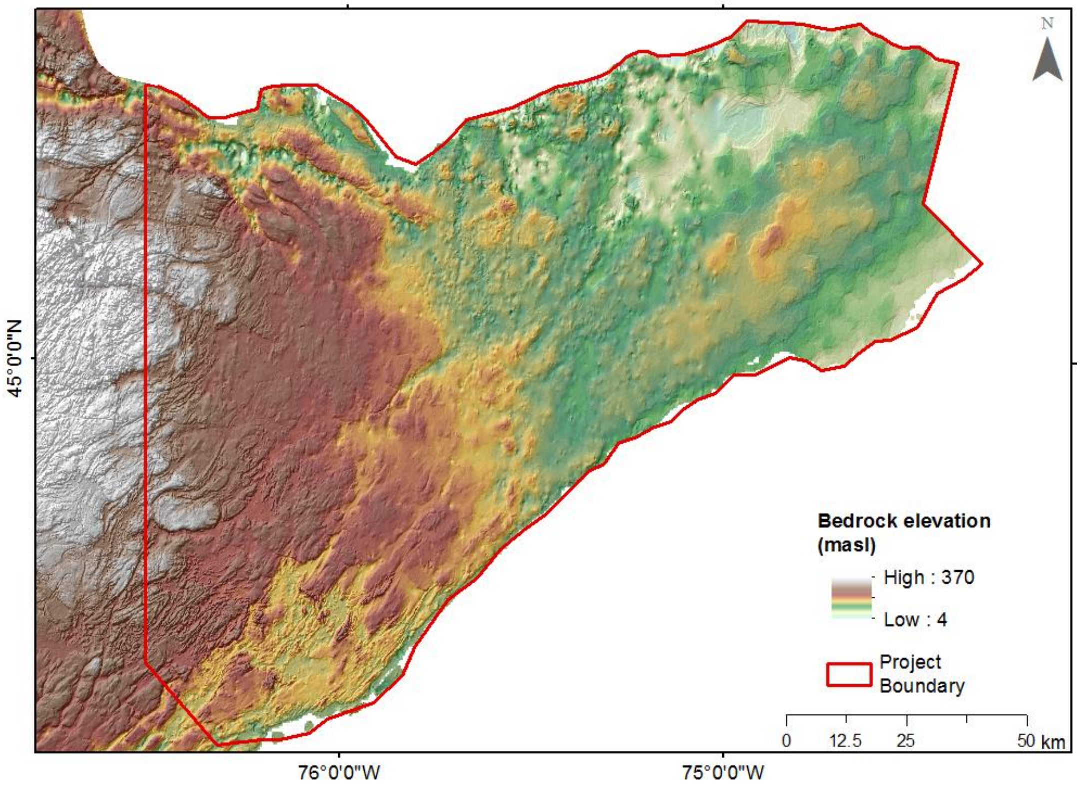

Figure 2.3 Bedrock topography of eastern Ontario. Warmer colours (*i.e.*, yellow, brown) correspond to elevated regions whereas cooler colours (*i.e.*, blue) correspond to bedrock depressions (Gao et al. 2006).

Eastern Ontario comprises the Ottawa Embayment, a sedimentary basin distinct from the Appalachian and Michigan Basins that contain the Paleozoic rocks in the rest of southern Ontario (Figure 2.4). The embayment is an extension of the Québec foreland basin bounded in the west by the Frontenac Arch (Sanford 1993). The Frontenac Arch is a NW-SE-trending basement relief feature, which has been reactivated at various points in time (Sanford 1993). Uplift of the Frontenac Arch is linked to the Taconian post-Ordovician uplift of the Beauharnois Arch, which defined the eastern extent of the Ottawa Embayment and caused it to be a distinct structural depression from the Québec foreland basin (Sanford 1993). The embayment is also confined by the Laurentian Mountains to the north and the Adirondack Mountains to the south.

The large topographic depression of the Ottawa Valley is the result of another major structural feature: the 55 km-wide Ottawa-Bonnechère Graben (OBG) (Kay 1942).

The OBG is thought to have formed during the breakup of Rodinia (late Precambrian to early Paleozoic) as part of a failed triple junction in the St. Lawrence rift system (Burke and Dewey 1973; Rankin 1976; Kumarapeli 1978, 1985). The Ottawa-Bonnechère Graben was likely reactivated during the breakup of Pangea causing extensive block faulting. The near-vertical normal faults have up to 1000 m of displacement (Johnson et al. 1992) and are responsible for the area's complex stratigraphy. The area is still tectonically active, falling within the Western Québec Seismic Zone. Reactivation of faults has caused numerous earthquakes in the study area, including an event near Ottawa of 5.0 magnitude in 2010 (Russell et al. 2011; Rimando and Benn 2005).

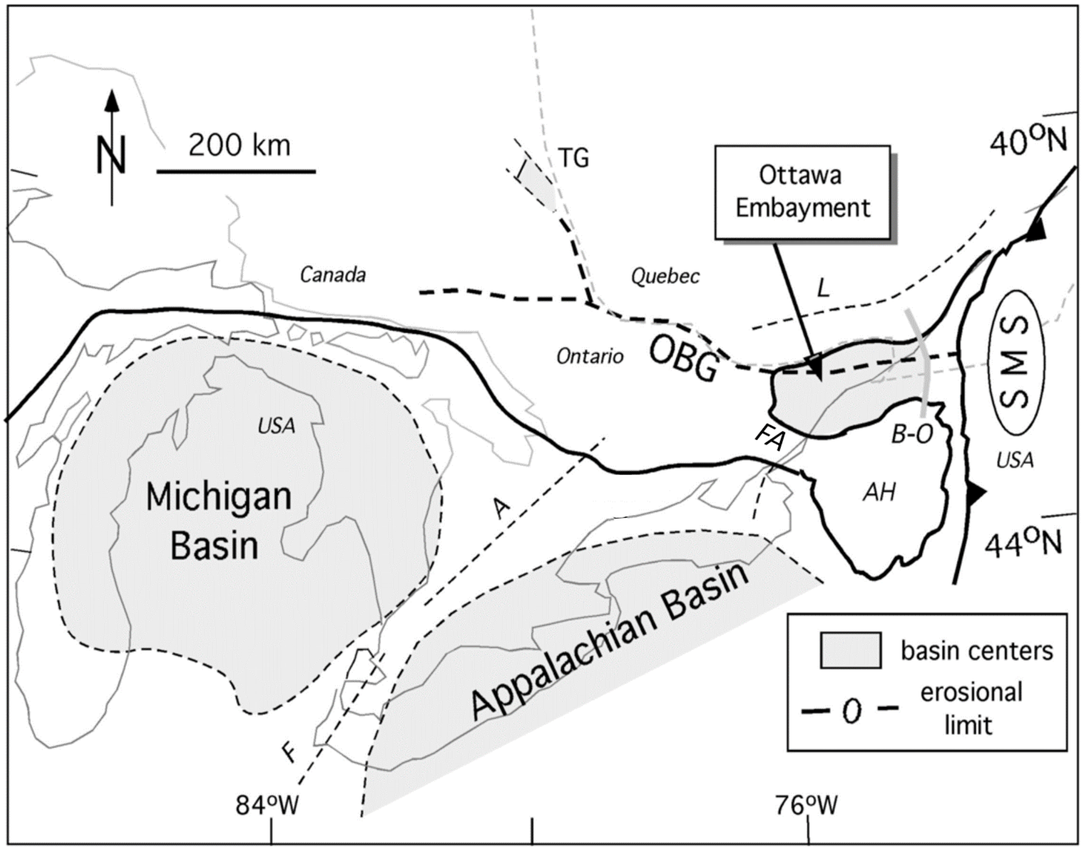

Figure 2.4 Structural features. Eastern Ontario is encompassed by the Ottawa Embayment, distinct from the Michigan and Appalachian Basins. Abbreviations: F=Findlay Arch, A=Algonquin Arch, L=Laurentian Arch, OBG=Ottawa-Bonnechère graben, TG=Timiskaming graben, AH=Adirondack Highlands, B-O=Beauharnois-Oka arch, FA=Frontenac Arch (modified from Gbadeyan and Dix 2013)

2.2.2 Bedrock properties

2.2.2.1 Formation descriptions

Precambrian

The Precambrian Canadian Shield rocks are the oldest in eastern Ontario, and comprise the Laurentian Highlands in the west. They also form the crystalline basement upon which all younger rocks are deposited throughout Southern Ontario. In eastern Ontario, they belong to the middle-Proterozoic, central metasedimentary belt, which is the youngest province accreted during the Grenvillian Orogeny (Cullota et al. 1990). The crystalline metasedimentary and metavolcanic rocks are both highly deformed from multiple mountain-building phases and intruded by felsic to mafic plutons and dykes (Hewitt 1964; Williams et al. 1992) (Figure 2.5).

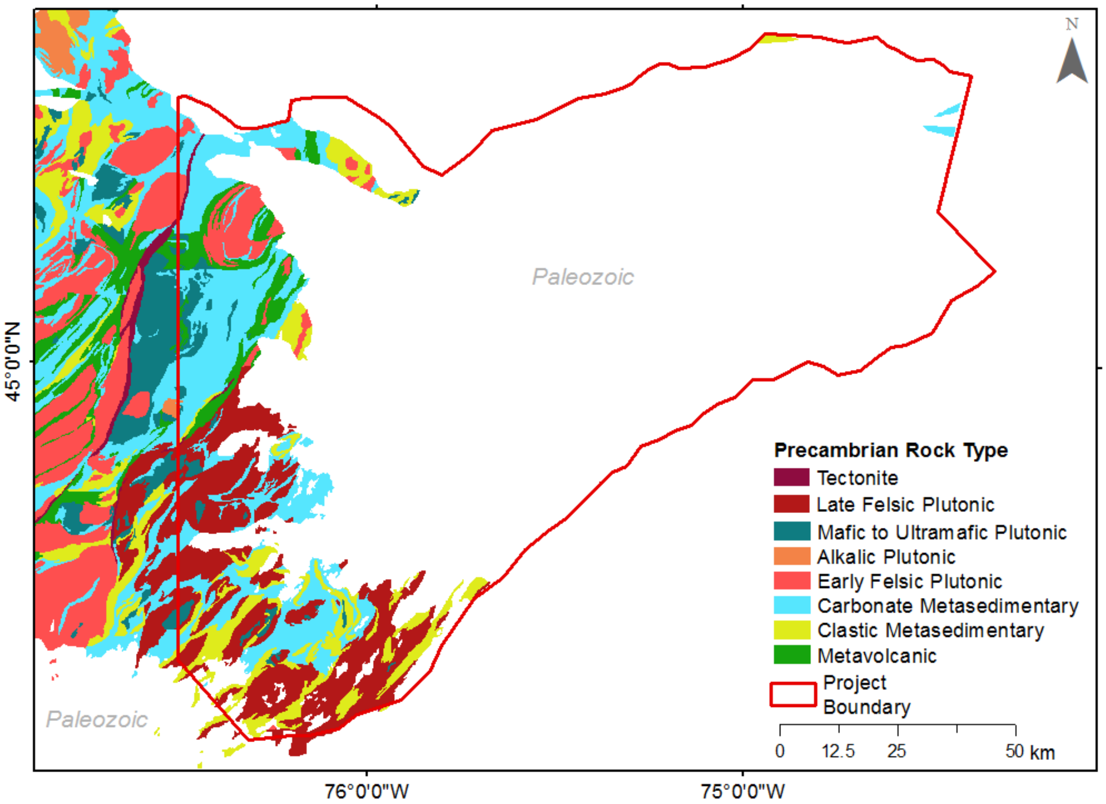

Figure 2.5 Precambrian geology of eastern Ontario with undifferentiated Paleozoic cover (Ontario Geological Survey 2011).

Paleozoic

Paleozoic rocks overlie the Precambrian basement and record upper Sauk and Lower Tippecanoe sedimentary platform sequences, deposited during the opening and closing of the Iapetus Ocean (Sanford 1993; Rimando and Benn 2005). The Paleozoic sedimentary platform has a maximum thickness of 1000 m in the Ottawa Embayment (Sanford 1993).

Potsdam Group (Upper Cambrian)

The oldest Paleozoic rocks of eastern Ontario are upper Cambrian to early Ordovician and belong to the Potsdam Group**,** which comprises the Covey Hill and Nepean formations. The Covey Hill formation unconformably overlies the Precambrian basement with highly variable thickness. It is a coarse, clastic unit that grades from arkosic conglomerate at the base to pink, white and red orthoquartzitic sandstone with cross-bedding at the top (Sanford 1993). This unit likely represents terrestrial alluvial fan and braided fluvial deposition, instigated by rifting at the opening of the Iapetus Ocean (Wolfe and Dalrymple 1984, 1985; Rimando and Benn 2005). The clastic Nepean Formation unconformably overlies the Covey Hill Formation and records the earliest Paleozoic marine deposition, reflecting both terrestrial and subtidal to intertidal environments (Wolfe and Dalrymple 1984, 1985). The Nepean Formation contains mature, orthoquartzitic sandstone of white, grey and yellowish-orange colour, and with conglomerate, arkose and shale interbeds common at the base. The sedimentary rocks of the Potsdam Group were derived from the uplifted Frontenac Arch (Sanford 1993). In eastern Ontario, the Potsdam Group crops out in the southwest (Figure 2.6).

Beekmantown Group (Lower-Middle Ordovician)

The Lower to Middle Ordovician Beekmantown Group unconformably overlies the Nepean Formation and records deposition in an interior passive margin platform (Williams 1991; Sloss 1963). These shallow marine clastic and carbonate rocks make up the March and Oxford formations, which have no equivalent lower Ordovician unit in other parts of Southern Ontario. The Beekmantown Group is typically dolomitic with minimal fossil content, except stromatolites. Additional characteristics include lenses of gypsum, halite casts, breccia and mudcracks. The lithological characteristics suggest a wide range of depositional environments (Sanford 1993). The March Formation (equivalent to Theresa Formation in Québec) increases in thickness from 10 to 60 m toward the center of the Ottawa Embayment (Sanford 1993) and is suggested to have formed in a supratidal to subtidal environment (Williams 1991). The March Formation comprises white and grey, interbedded, orthoquartzitic sandstone and dolomite, with the dominance of dolomite increasing upwards in the section (Sanford 1993). The Oxford Formation (equivalent to the Beauharnois Formation in Québec) overlies the March Formation, thickening east to ~125 m, and is defined by the disappearance of sandstone (Sanford 1993). The Oxford Formation grades from greyish-brown, stromatolitic dolostone to darker, micritic dolostone interbedded with limestone and shale moving basinward (Sanford 1993). This unit was deposited in a supratidal, hypersaline environment (Williams 1991). The equivalent Beauharnois Formation in Québec is reported to host paleokarst, postulated to have formed by interaction with basin-derived fluids (Dix et al. 1998). The Oxford Formation's lower contact with the March Formation is conformable and gradational and is defined by the beginning of the lowest dolomitic bed; the upper contact with the Rockcliffe Formation is abrupt and disconformable.

Chazy Group (Middle Ordovician)

The Chazy Group (containing only the Rockcliffe Formation in eastern Ontario) signifies the beginning of the establishment of a foreland basin carbonate platform in the Tippecanoe Sequence (Dix et al. 1998). It was deposited unconformably on the Oxford Formation in a supratidal to subtidal shelf environment with periodic subareal exposure. It is primarily composed of interbedded quartz sandstone, shale and limestone. The lower member comprises quartz sandstone with shale beds, whereas the upper member has greater shale content and contains shaley, bioclastic limestone and silty dolostone (Johnson et al. 1992; Williams 1991). Ripple marks, cut-and-fill structures and desiccation cracks are found in the sandstone of the unit (Sanford 1993). In its eastern extents, the Rockcliffe Formation contains cross-bedded, crinoidal grainstones and sandstone beds intercalated with calcarenites, which are relicts of the St. Martin Member of the Québec Basin, with which the Rockcliffe was once continuous (Johnson et al. 1992; Williams 1991; Sanford 1993).

Middle-Upper Ordovician (Ottawa Group)

The Ottawa Group disconformably overlies the Chazy Group. A middle to late Ordovician marine transgression from peritidal to open shelf/ramp environments is recorded in the Shadow Lake, Gull River, Bobcaygeon, Verulam and Lindsay formations (Sanford 1993; Salad Hersi and Dix 1999; Sharma et al. 2003). The basal Shadow Lake deposit is composed of cratonic clastic sediments and impure carbonates deposited in a nearshore environment. The Shadow Lake Formation does not crop out in eastern Ontario. The remaining formations of the Ottawa Group are commonly difficult to distinguish due to repeating beds and continuous deposition in a deepening basin (Johnson et al. 1992). The limestone Gull River Formation conformably overlies the Shadow Lake Formation and is marked by the first appearance of a significant carbonate bed (Johnson et al. 1992). The Gull River Formation is composed primarily of fine-grained, grey-brown limestone with variable fossil content, although at its base, the unit contains argillaceous to silty dolostone (Armstrong and Dodge 2007). It was deposited in a supratidal to intertidal flat environment (Johnson et al. 1992). The overlying fossiliferous Bobcaygeon Formation limestone was deposited in a shallow subtidal environment (Johnson et al. 1992). The formation varies vertically, with grainstones and nodular structures at its base and increasing shale content with calcarenitic storm beds towards the top (Armstrong and Dodge 2007). The overlying Verulam Formation is distinguished by further increased shale content deposited in an open marine shelf or ramp with shoal conditions at the top and bottom (Johnson et al. 1992). It is a bioclastic to very fine-grained limestone interbedded with calcareous shale and, at its top, is characterized by coarse-grained calcarenite (Armstrong and Dodge 2007). The Ottawa Group is capped by the middle to upper Ordovician Lindsay Formation. The lower, fossiliferous, argillaceous, coarse-grained limestone unit and the upper, organic-rich and petroliferous, very-fine-grained argillaceous limestone unit (Eastview Member) were both deposited in a deep shelf setting (Armstrong and Dodge 2007; Johnson et al. 1992).

Billings, Carlsbad, Queenston (Upper Ordovician)

The Ottawa Group is conformably overlain by an upper Ordovician sequence of deep to shallow water, basinal siliclastic formations (Sanford 1993). These sediments only outcrop in the northeast and trend ENE-WSW. Following subsidence and faulting, the Billings Formation was deposited in a deep-water environment as a low-organic shale with interbeds of limestone and calcareous siltstone (Johnson et al. 1992; Sharma et al. 2003; Armstrong and Dodge 2007). The Billings Formation was followed conformably by shallowing deposition of the Carlsbad grey shale with interbeds of calcareous fossiliferous siltstone and bioclastic limestone (Armstrong and Dodge 2007; Johnson et al. 1992; Sharma et al., 2003). The youngest unit in eastern Ontario is the Queenston Formation and is described as mostly red shale with siltstone, interbedded with minor sandstone and limestone (Johnson et al. 1992; Sharma et al. 2003 and references therein; Armstrong and Dodge 2007). The 185m of Carlsbad shale and 13m of Queenston shale are only preserved in down-faulted blocks of the Ottawa-Bonnechère Graben (Sanford 1993).

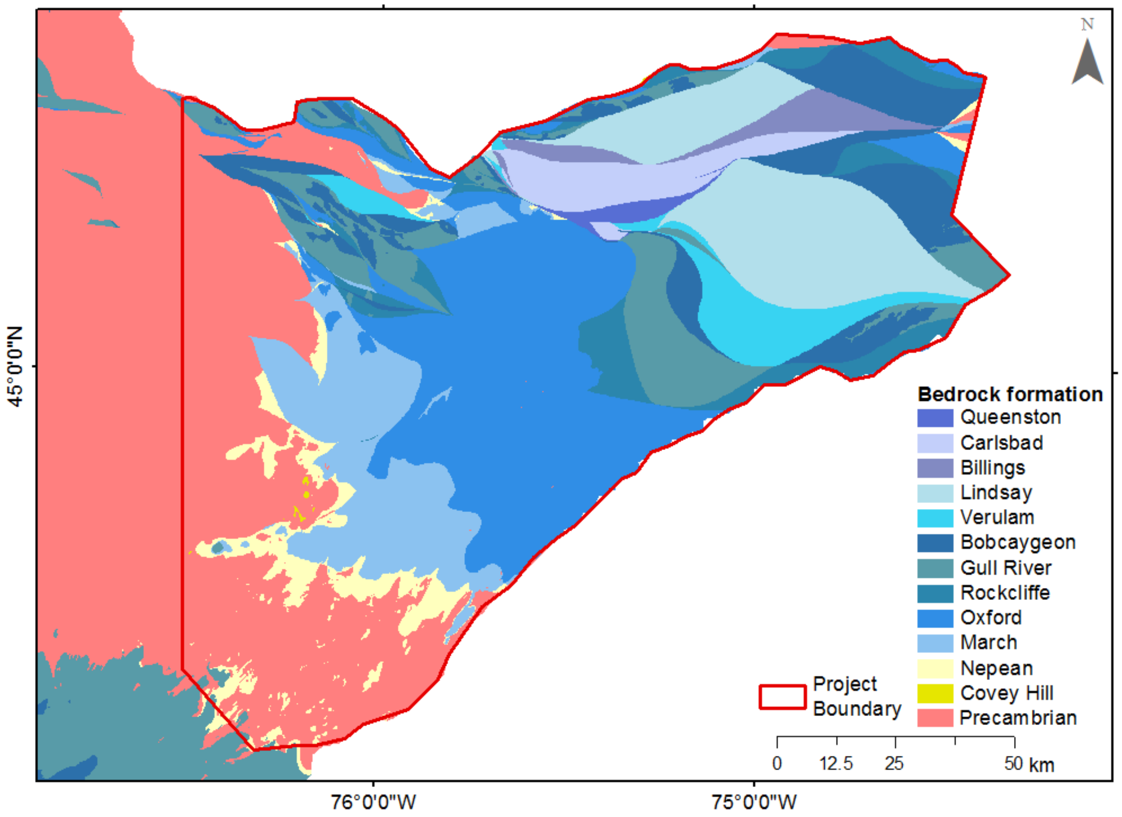

Figure 2.6 Bedrock geology of eastern Ontario, with differentiated Paleozoic formations and undifferentiated Precambrian rocks (Armstrong and Dodge 2007).

2.2.2.2 Karst

Karst refers to the landscape created by chemical weathering and physical erosion of soluble rocks by water. This is an important factor for groundwater science because karst formation greatly increases the porosity, hydraulic conductivity and storage capacity of a geologic unit (Schwartz and Zhang 2003). Karstic features have been identified as “known”, “inferred” or “potential” in parts of eastern Ontario (Brunton and Dodge 2008) (Figure 2.7). “Known karst” refers to areas where karst features have been directly observed, whereas “inferred karst” and “potential karst” highlight regions where direct observation hasn’t been made, but has been extrapolated from known karst (inferred) or identified as susceptible to karstification (potential). Overburden cover in much of the study area prevents direct observation and documentation of karst. In eastern Ontario, there has been direct observation of karst in the Gull River Formation in the northwestern region of the study area. Inferred and potential karstification is assigned to the rest of the Gull River and Bobcaygeon formations, which predominantly subcrop in ribbons across the north and east of eastern Ontario.

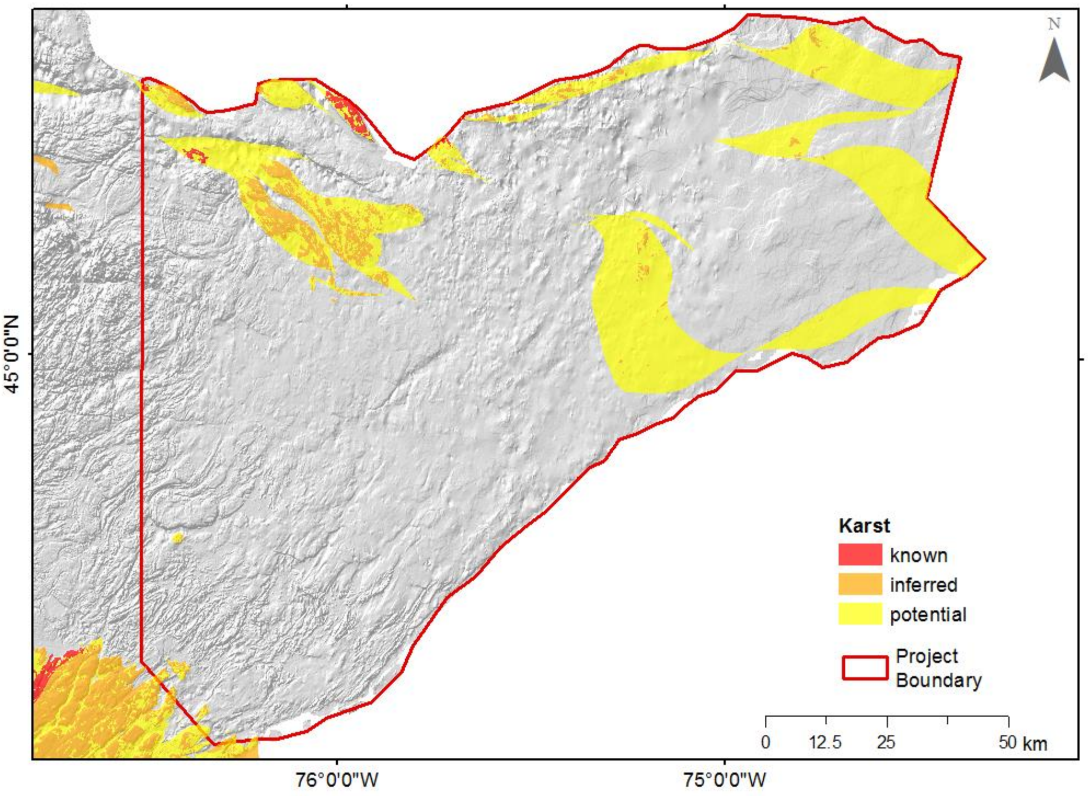

Figure 2.7 Karst map of eastern Ontario (Brunton and Dodge 2008). Known karst has been observed in sections of the Gull River Formation, whereas inferred and potential karst may be found in the Bobcaygeon Formation and the remainder of the Gull River Formation.

2.2.2.3 Hydrothermal deposits

The extensive fault system in eastern Ontario hosts mineralized veins that signify historic fault-controlled circulation of lower temperature hydrothermal fluids (Carignan et al. 1997). There are three recorded stages of hydrothermal mineral deposition in the Ottawa Embayment, which infilled paleoporosity in bedrock units during the Paleozoic and Mesozoic (Dix and Robinson 2003). The first stage of mineralization infilled paleokarst voids of centimeter-scale calcite nodules in the Beekmantown dolostone, up to decimeter scale void-fill in the Oxford Formation (referred to as the Beauharnois Formation in that study) and micrometer-scale dissolutional paleokarst in upper Ottawa

Group limestone (Dix and Robinson 2003). The first two stages of mineralization filled the paleokarst cavities with quartz, calcite, saddle dolomite and sulphates (barite, celestine), sulphides (pyrite, marcasite) and bitumen (Dix and Robinson 2003). Paleofractures were infilled after the karst, creating mostly sub-vertical veins in Precambrian and lower Paleozoic bedrock. There are also horizontal gypsum-filled veins in Beekmantown Formation. The veins in the Precambrian host rock contain calcite, sulphides (galena, sphalerite, pyrite, marcasite, chalcopyrite), barite, fluorite and celestine. The mineralogy is the same in veins hosted by Paleozoic rocks, plus strontianite or comprises an assemblage similar to the paleokarst (Dix and Robinson 2003). Carignan et al. (1997) reported that calcite veins in the Ottawa-Bonnechère Graben also contain abundant galena, sphalerite, barite and fluorite, and more rarely, barite, pyrite, chalcopyrite and celestite. Based on C, O, S and Sr isotopic data, Dix and Robinson (2003) suggested four end-member fluids had mixed in the hydrothermal system: meteoric water, calcium sulphate brines from Ordovician evaporite, Precambrian brines and sedimentary basin brines. In addition, evidence of hydrothermal dolomitization in the Ottawa Group was identified in Paleozoic outliers northeast of Ottawa. It was interpreted to have resulted from migration of basin-derived Ca-Mg-Cl brines along fault and fracture systems (Nurkhanuly 2012).

2.2.3 Overburden

2.2.3.1 Overview

During the Wisconsin glaciation, eastern Ontario was covered by the thick ice of the Laurentide Ice Sheet. Glacial till was deposited over the bedrock in the early Wisconsin and was reworked through multiple advances and retreats and through ensuing marine and fluvial stages (McCormack and Therrien 2014). Meltwater from the retreating Laurentide Ice Sheet is thought to have caused formation of a number of north-south trending eskers and subaqueous fans in eastern Ontario, which are mostly buried under glaciomarine deposits (Russell et al. 2011). The retreat of the Laurentide Ice Sheet allowed invasion of an arm of the Atlantic Ocean through the St. Lawrence Gulf, which existed until approximately 10 ka BP (^{14}C years; Parent and Occhietti 1988). The marine body, known as the Champlain Sea, occupied the isostatically-depressed St. Lawrence Lowlands. The Champlain Sea deposited thick silty clays and some thin marine sands in eastern Ontario. During isostatic rebound, the lowlands were uplifted, causing the Champlain Sea to drain to the east and alluvial conditions to take over. The shift from marine to modern fluvial conditions is recorded by erosional down-cutting into the marine deposits and associated deposition of terraced deltaic fluvial sands, which can be observed to the north and east of Ottawa (McCormack and Therrien 2014).

The Quaternary geology, drift thickness and resulting physiographic regions in the study area are presented in figures 2.8 – 2.10. Drift[3] is discontinuous and thin in the western reaches of the study area across the Smith Falls Limestone Plain and Precambrian Shield. Thickening drift in the east coincides with decreasing bedrock elevation. Till discontinuously crops out throughout the study area (*e.g.*, North Gower Drumlin Field). It is more extensive in the southeast where it comprises the elevated Glengarry Till Plains. Coarse-grained glaciomarine and glaciofluvial deposits dominate the surficial deposits in the center of eastern Ontario (Edwardsburgh Sand Plain) and in the northeast where sand-filled, abandoned, incised channels make up the Russell and

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[3] Drift refers to all unconsolidated sediment overlying the bedrock.

Prescott Sand Plains. Fine-grained glaciomarine deposits make up a significant proportion of the surficial deposits. These are found in a south-pointing wedge that extends from thick packages in the northeast, westward to infilled valleys up the Ottawa Valley to the south-central part of the study area on the north shore of the St. Lawrence River. The fine-grained glaciomarine deposits create the Ottawa Valley and Winchester Clay Plains and part of the Lancaster Flats. Glaciolacustrine clays from Lake Ontario's predecessor glacial Lake Iroquois lie between knobs of Precambrian rock in the southwest, making up the Leeds Knobs and Flats.

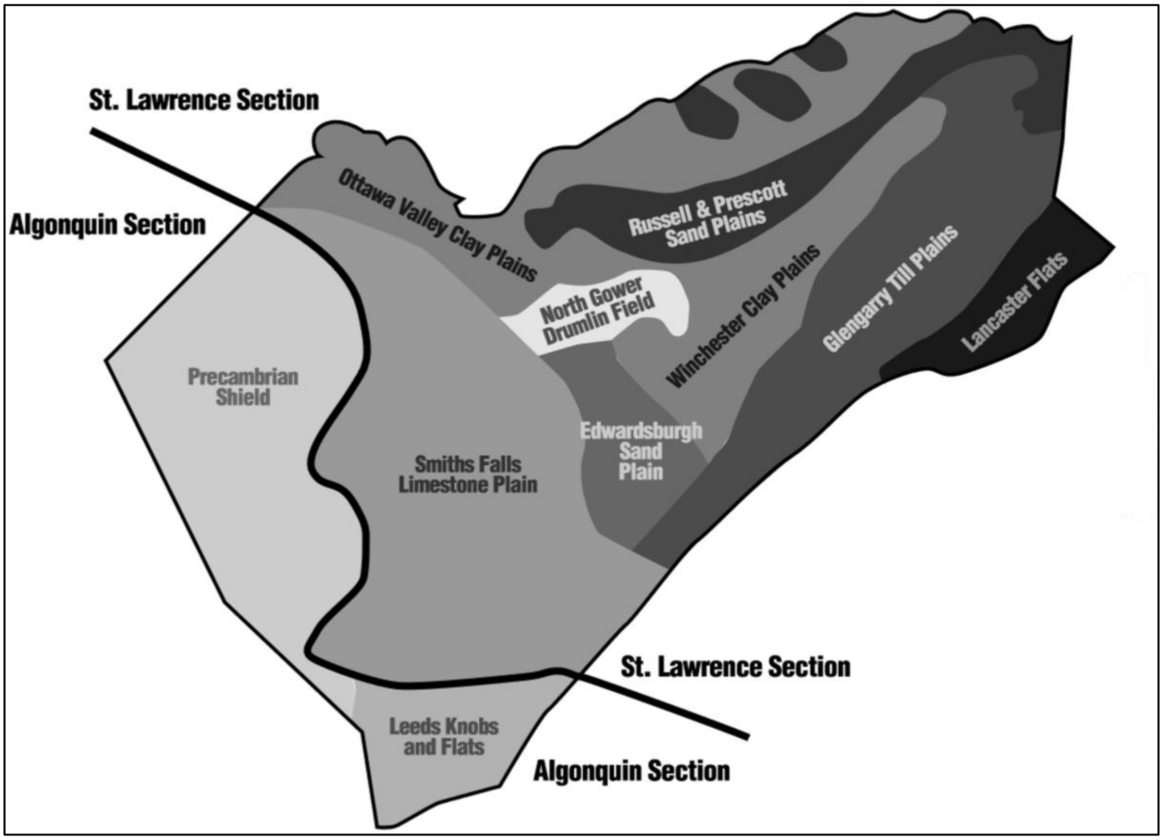

Figure 2.8 Physiographic regions (Chapman and Putnam 1984) in eastern Ontario (reproduced from LandOwner Resource Centre 1997).

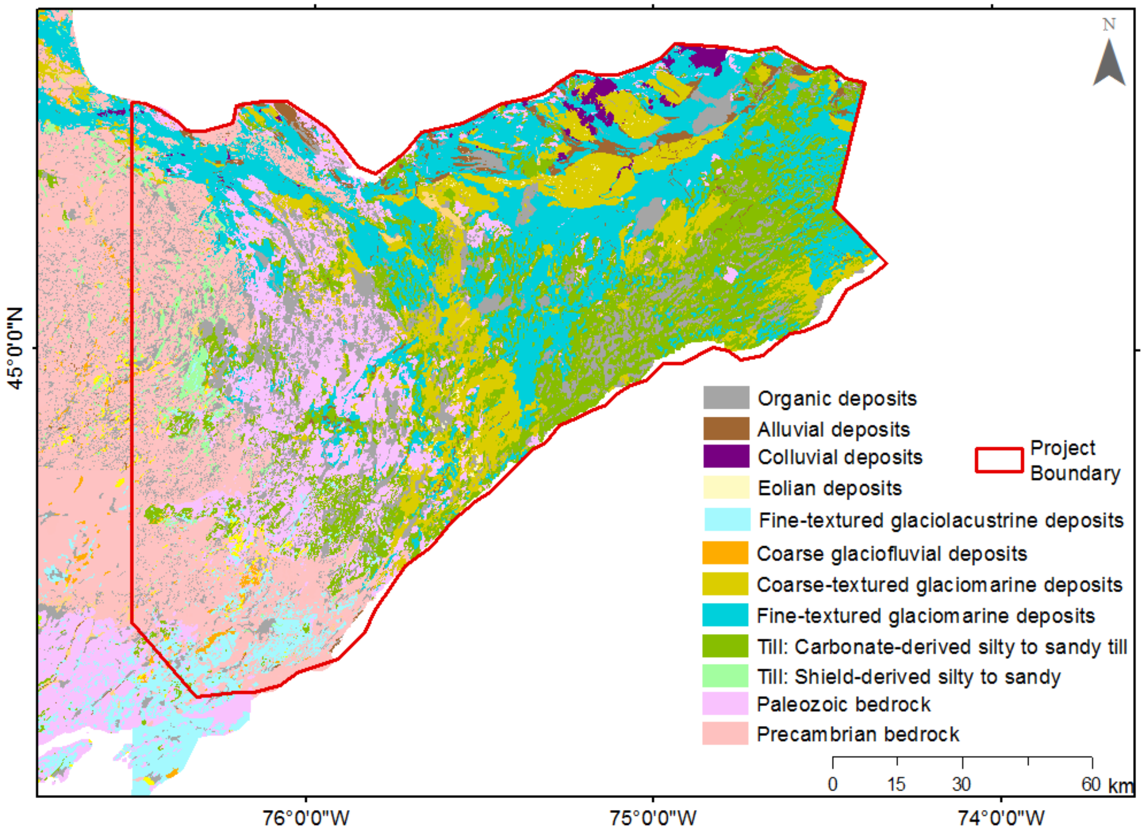

Figure 2.9 Quaternary geology of eastern Ontario (Ontario Geological Survey 2010).

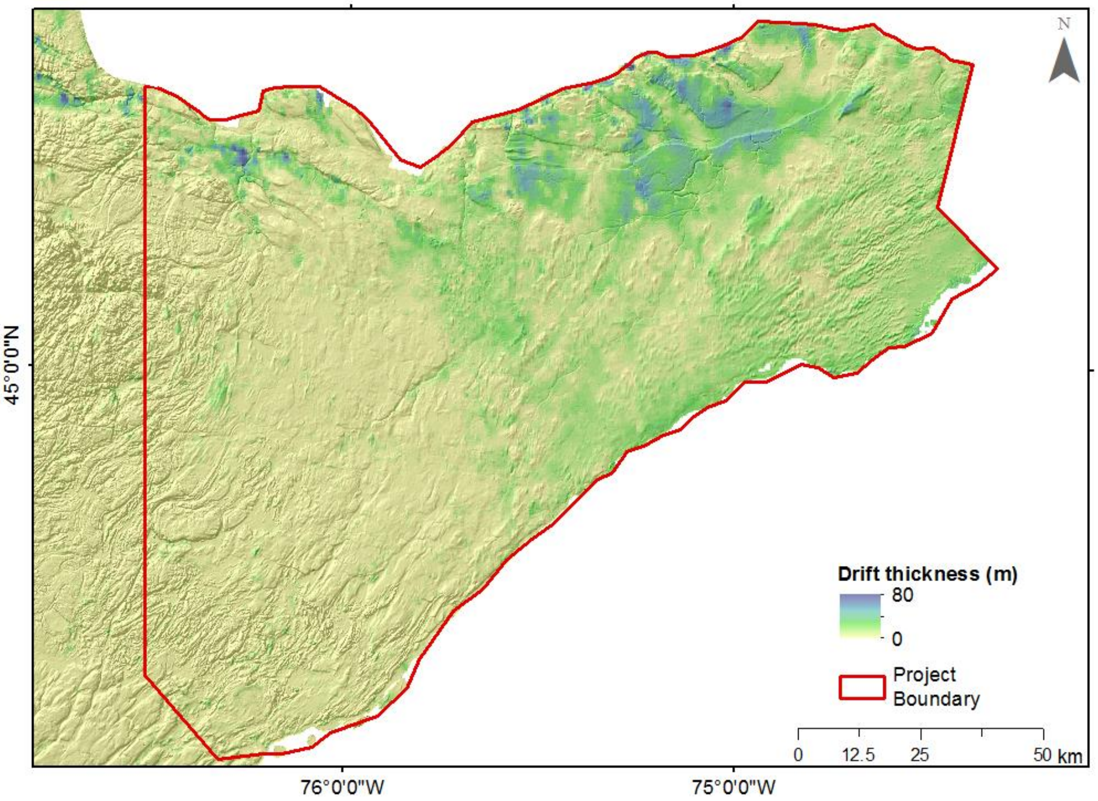

Figure 2.10 Drift thickness in eastern Ontario (Gao et al. 2006).

2.2.3.2 Stratigraphy

The overburden in the Champlain Sea basin can be divided into 6 idealized stratigraphic units (Gadd 1986). The deepest unit (0 -5 m) is compact basal till, reported to be permeable owing to high sand and gravel content. Above this the second unit (1.5 – 9 m) comprises coarse-to-fine silt and silty clay, soft, grey varves. It was thought to have been deposited in freshwater from glacial ponding prior to marine invasion. The third unit (3 – 30 m) appears gradationally above the varves as fossiliferous prodeltaic sediments of light grey silt and silty-clay with black bands. The fourth (3 – 30 m) unit is interpreted as a stratified delta front composed of interbanded, light grey silt and clay, dark-grey clay and red clay. Unit 5 (3 – 15 m) comprises the delta top, containing beds of silty clay to sand, with sand content increasing upward. Units 3, 4 and 5 were gradationally deposited by different stages of the Champlain Sea. The uppermost Unit 6 is commonly eroded and comprises sand and silt-clay strata in abandoned channels and fluvial terraces of the proto-Ottawa River (Gadd 1986; Woodley 1996).

2.2.3.3 Champlain Sea and deposits

2.2.3.3.1 Occurrence

One of the last major depositional events to affect the study area was the incursion of the Champlain Sea. According to Parent and Occhietti (1988), the Champlain Sea was fully established by 12 ka BP (^{14}C years) and remained for about 2 ka in eastern Ontario. The Champlain Sea did not fully inundate the study area; the western portion remained above sea level (Figure 2.11).

Several studies have been conducted to reconstruct the temperature, salinity and chemical composition of the Champlain Sea. Based on porewater concentrations of conservative ions, the Champlain Sea is generally accepted to have been about 33% marine water from the St. Lawrence Gulf and 67% freshwater from rain, snow and glacial meltwater (Cloutier et al. 2010; Desaulniers and Cherry 1989). Hillaire-Marcel and Page (1983) estimated that the freshwater component had a $\delta^{18}O$ of –16 ‰ based on calcite concretions from Lake Deschaillons, which was an ice-contact glacial lake present in the St. Lawrence Lowlands prior to the Champlain Sea. According to Broecker (1974) Pleistocene north Atlantic seawater had a $\delta^{18}O$ of 0±1 ‰. Considering the 2:1 freshwater:seawater mixing model, Champlain Sea clay porewater $\delta^{18}O$ (–10.5 to –9.5 ‰) is within the predicted range near Montreal. Unfortunately, oxygen isotopes alone cannot be relied on to identify Pleistocene water from the Champlain Sea because it falls within the range of modern meteoric water in the region (–12 to –8 ‰) (Desaulniers and Cherry 1989). Other studies highlight the changing nature of the Champlain Sea through its existence. Based on benthic foraminifera, Corliss et al. (1982) used changes in dominating species and varying $\delta^{18}O$ to suggest nearly marine conditions at the initial phase of the Champlain Sea, followed by decreasing salinity and increasing temperature through its evolution.

The 2:1 freshwater:seawater mixing model provides some insight into the nature of the Champlain Sea. However, the Champlain Sea salinity would have varied geographically, vertically within the water column and temporally; therefore description using a single ratio is acknowledged as an oversimplification.

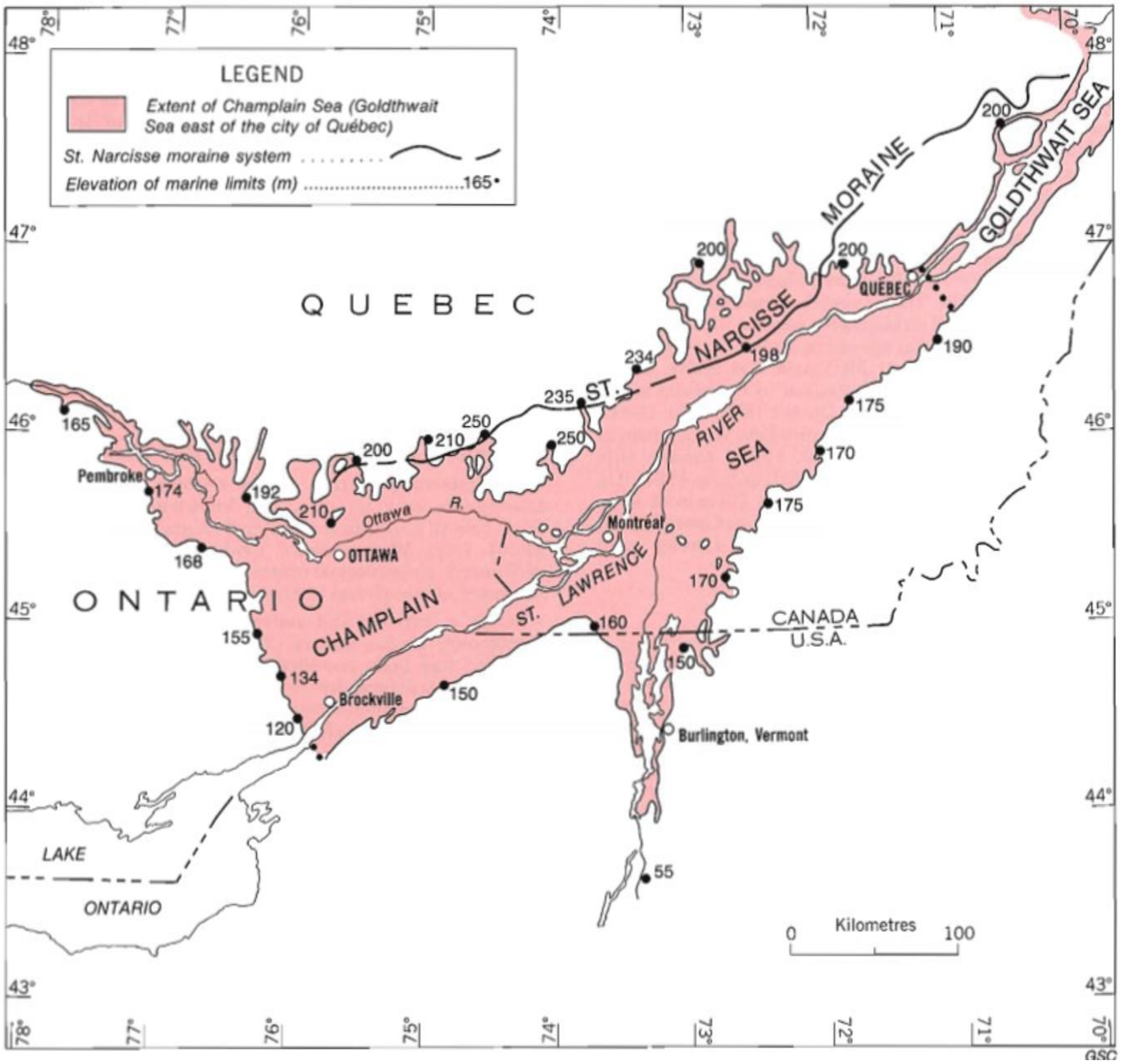

Figure 2.11 Maximum extent of the Champlain Sea (from Sanford 1993 based on Occhietti 1989). The marine incursion did not reach the western portion of eastern Ontario.

2.2.3.3.2 Composition of Champlain Sea clay

The Champlain Sea deposited glaciomarine clays[4] up to 65 m thick (average 30 m) (Karrow 1972). These clays play an important role in the hydrology and hydrogeology of eastern Ontario. Champlain Sea clays are massive silty clays that vary in colour from grey to brown with some black patches and seams of silt and sand (Quigley et al. 1983). Mineralogically, there is some dispute on the relative proportions of clay and non-clay minerals. According to some sources (Quigley et al. 1981; Gillott 1971; Yong et al. 1979), the Champlain Sea clays consist of about half clay minerals, which are dominantly illite and chlorite, with smaller amounts of smectite and vermiculite. Other sources (Bentley and Smalley 1979; Torrance 1990) report a smaller proportion of clay minerals, as low as 13%, although the minerals present are the same. The non-clay fraction is mostly composed of quartz and feldspar, with smaller amounts of carbonate (0 to 12%) and amphiboles, and trace amounts of oxides and amorphous minerals (Torrance 1988, 1990, 1995; Quigley et al. 1983). Quartz and feldspar tend to be the most abundant fraction in silty materials and carbonate content varies depending on location and extent of weathering, decreasing upwards as leaching increased (Quigley et al. 1983; Torrance 1988). The Champlain Sea clays exhibit high cation exchange capacity for divalent cations on the solid phase, with Mg^{2+} and Ca^{2+} ranging from 1.85 to 7.90 meq and 19.3 to 47.4 meq per 100 g of dry clay respectively. By contrast, monovalent Na^{+} exhibits a much lower exchange capacity (0.58 to 0.80 meq per 100 g of dry clay) (O’Shaughnessy and Garga 1994a). The Champlain Sea clays contain abundant organic carbon (0.4 to 1%) (Laventure and Warkentin 1965; Donovan and Lajoie 1979). A study of subsurface Champlain Sea clays at two sites in Québec found the functional groups on this organic matter to mainly be hydroxyls, carboxyls, amines, and phenolic and aromatic hydroxyls. The organic matter, though decreasing in abundance with depth, was deemed to be significant enough to influence sediment properties such that surface functionality is comparable to that of the topsoils (Yong and Mourato 1988 and references therein).

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[4] These deposits are herein described interchangeably as “Champlain Sea clays” or “glaciomarine clays.”

2.2.3.3.3 Physical and transport properties of the Champlain Sea clays

The glaciomarine clays in the St. Lawrence Lowlands are often referred to as the "Champlain Sea clays" or the "Leda clays" and are known for their "sensitivity." Large-scale retrogressive flowslides can occur due to reduction in remoulded shear strength from decreasing porewater salinity (Torrance 1979). The clays have a high moisture content that is explained by their flocculated structure arising from deposition in a saline environment (Torrance 1983; Woodley 1996).

The hydraulic properties of the Champlain Sea clays are of great importance in the present study; these clays likely act as a major aquitard affecting the recharge and flow of underlying aquifers. The hydraulic properties of the clays vary drastically with depth as a result of weathering. The weathered, fractured zone present at the surface ("active zone") extends to different depths depending on location (O'Shaughnessy and Garga 1994a); various studies have reported the active zone to extend down from 3 m (Desaulniers and Cherry 1989) to 10 m (O'Shaughnessy and Garga 1994a). The hydraulic conductivity of the upper, active zone is reported to be 1 to 4 orders of magnitude higher than the underlying unweathered clay (Table 2.1) and controlled by a fracture network as opposed to intergranular pore space (O'Shaughnessy and Garga 1994). O'Shaughnessy and Garga (1994a) concluded that groundwater velocity in the fractured clays ranges from 0.03 to 6.4 m/day, while intergranular flow in the unweathered clays would occur at velocities of 1.11×10^{-6} and $1.11 \text{ X } 10^{-4}$ m/day. In the weathered zone, flow is likely active but lateral, following local variations in topography and discharging to local surface water (Desaulniers and Cherry 1989).

Below the active, weathered zone at a location northeast of Montreal, Desaulniers and Cherry (1989) found that hydraulic head gradually decreased with depth, which could indicate underdraining by a more permeable unit and a downward flow rate of 13 cm/year. The chemical profiles at this location, however, could not be matched using an advection model, whereas a much closer fit was possible using a molecular diffusion model. Desaulniers and Cherry (1989) concluded that the hydraulic gradient is not large enough to reach the threshold of flow in the unweathered clay, suggesting the transport mechanism to be diffusion-, rather than advection-dominated.

Table 2.1 Comparison of hydraulic conductivity[5] values for weathered and unweathered glaciomarine clay, deposited by the Champlain Sea.

	Unweathered clay	**Weathered clay**
Desaulniers and Cherry (1989)	Range: 7.5 x $10^{-''}$ to 4.9 x $l0^{-10}$ m/s Geometric mean: 3.4 x $l0^{-10}$ m/s.	1.4 x 10^{-8} (to 1.2 m depth) 4.8 x 10^{-9} at (1.7 m depth)
O'Shaughnessy and Garga (1994a)	8.2 x 10^{-10} to 1.4 x 10^{-9} m/s	1.85 x 10^{-8} to 2.05 x 10^{-5} m/s

2.2.3.3.4 Porewater composition

The glaciomarine clays were deposited in saline water that is reported to still remain in the porewater in modern time (Torrance 1979; Quigley et al. 1983; Desaulniers and Cherry 1989; O'Shaughnessy and Garga 1994a; Woodley 1996; Cloutier 2004). Where reported, maximum salinities were 15 g/L in Hawkesbury, ON (located northeast in the study area), ~10 g/L at Mer Bleu (east of Ottawa in the study area), 21 g/L north of Plantagenet (ON) and 12.3 g/L near Varennes (northeast of Montreal, Québec) (respectively: Quigley et al. 1983; Woodley 1996; Torrance 1979; Desaulniers and Cherry 1989). Where salinity-depth profiles were obtained, the porewater composition varies vertically. Typically, salinity is lowest in the upper clays and increases with depth, where it may reach a maximum at the bottom of the clay. The main ions in solution are Na^+ and Cl^-, but the proportions of major ions varies with depth (O'Shaughnessy and Garga 1994a). The water types in a core at Mer Bleu changed from Na-Ca-Mg-HCO_3 to

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[5] Hvorslev slug test method used for determination of hydraulic conductivity in unweathered clay and in weathered clay by O'Shaughnessy and Garga (1994a). Desaulniers and Cherry (1989) used a reaming permeameter to determine hydraulic conductivity in weathered clay. See both references for details.

Na-HCO_3 to Na-Cl with depth (Woodley 1996). At Varennes, Na^+, Cl^-, HCO_3^-, Mg^{2+} and K^+ increased in concentration with depth in the unweathered CS clay, while Ca^{2+} and SO_4^{2-} decreased or remained relatively constant (Desaulniers and Cherry 1989); Ca^{2+} and Mg^{2+} were dominant in the upper, weathered clay (O'Shaughnessy and Garga 1994a). The $\delta^{18}O$ of porewater showed little depth variation, ranging from –10 to –8 ‰, –10.9 ‰, and –10.5 to –9.5 ‰ (respectively: Woodley 1996; Cloutier et al. 2006; Desaulniers and Cherry 1989). The changes in salinity encountered in Champlain Sea clay porewater have been attributed to leaching through downward displacement of saline porewater by infiltrating meteoric water (Torrance 1979) and to diffusion in response to lower-salinity groundwater at the surface (Desaulniers and Cherry 1989; Quigley et al. 1983) and in the bedrock (Cloutier et al. 2010). The concentrations of SO_4^{2-}, HCO_3^- and Ca^{2+} are modified in the porewater by biochemical and geochemical processes. Relative to seawater proportions, sulphate and bicarbonate contents are the most altered as a result of sulphate reduction during oxidation of the organic matter in sediments. The resulting HS^- can react with iron-hydroxides causing precipitation of pyrite and marcasite, which cause "black mottling" in the Champlain Sea clays (Donovan and Lajoie 1979). Conversely, sulphate in the porewater associated with weathered clay can be attributed to the oxidation of iron sulphides or sulphur-bearing organic matter (O'Shaughnessy and Garga 1994a; Desaulniers and Cherry 1989).

2.3 Hydrogeology

2.3.1 Regional hydrogeology of eastern Ontario

Information on groundwater flow at the regional scale in southern Ontario has been compiled in Source Water Protection documents and in the MOE "Hydrogeology of Southern Ontario" by Singer et al. (2003). These reports each rely heavily on the MOE water well database, in which thousands of static water levels and pump tests recorded by drillers are the main sources of information about hydrogeological properties. Mississippi-Rideau, Cataraqui and Raisin-South Nation are designated as the "Source Protection Regions" (SPR) in eastern Ontario. Source Protection Regions are partnerships between Conservation Authorities (Figure 2.12) created under the Clean Water Act (Bill 43); the associated Source Protection Committees were charged with creating a protection strategy for drinking water in their region.

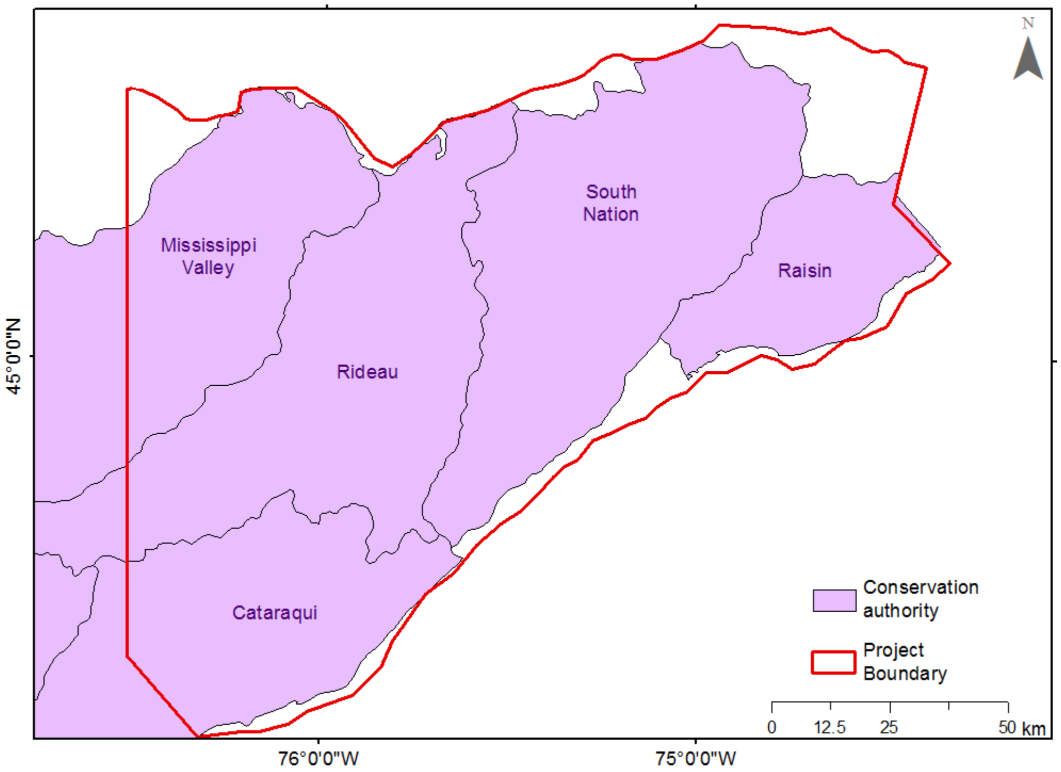


Figure 2.12 Conservation Authorities in eastern Ontario. The Mississippi-Rideau and Raisin-South Nation Source Protection Regions are from the partnership between Conservation Authorities. The Cataraqui Source Protection Region encompasses the Cataraqui Region Conservation Authority.

2.3.1.1 Recharge

In Southern Ontario, recharge to groundwater occurs to the greatest extent during the spring melt (mid-March through April and early May) and, to a lesser extent, during the fall (October to December). During the summer, recharge is limited by evapotranspiration and during winter by frozen ground and precipitation locked up in snow and ice (Singer et al. 2003). Recharge of precipitation to aquifers can also be limited by overland flow and by the agricultural practice of tiling, which both cause direct transport to surface water (RRCA 2012).

In the Raisin-South Nation SPR, most infiltration that recharges the shallow, unconfined aquifers enters at local topographic highs and discharges to local surface water, though the process can be short-circuited by tile drains (RRCA 2012). Only a small amount of recharge moves through confining layers to recharge the deeper overburden and contact aquifers.

Surficial geology has a significant impact on the recharge rate in a given area. Both the Cataraqui and Mississippi-Rideau SPR reports stress the impact on hydrogeology of the extensive bare bedrock and thin overburden in their regions (CRCA 2008; MVCA 2011). Limited overburden may allow rapid infiltration, preventing filtering of contaminants and pathogens. Extensive vertical fracturing in eastern Ontario provides high-velocity conduits to aquifers, allowing significant recharge and vulnerability to contamination in the Smith Falls Limestone Plain (CRCA 2008). The composition of drift and bedrock also has a major impact on recharge. Surficial sand and gravel deposits, eskers and the Nepean Formation are reported to be significant recharge areas in the Mississippi-Rideau SPR. Most (89%) of this SPR is designated as highly vulnerable aquifer (MVCA 2011). In the Raisin-South Nation SPR, the Edwardsburgh Sand Plain, isolated areas at the edge of the Prescott-Russell Sand Plains and, to a lesser extent, the Winchester Clay Plain, have areas of thin drift that may allow deeper recharge (Barnes 2009). In particular, the Edwardsburgh Sand Plain may be a significant area of recharge to overburden and bedrock aquifer systems because permeable, coarse-grained glaciomarine deposits overlie the Oxford limestone there. Charron (1978) found recharge areas in a portion of eastern Ontario (corresponding approximately with the Raisin-South

Nation) to comprise exposed bedrock ridges and the till ridge (Glengarry Till Plain). Till in eastern Ontario has a wide range of vertical hydraulic conductivity from 1×10^{-3} to 1×10^{-10} m/s (average: 1.0×10^{-8} m/s) similar to some reports for the glaciomarine clay (8.8×10^{-8} m/s) (WESA 2006).

2.3.1.2 Groundwater flow direction

Mississippi-Rideau and Raisin-South Nation SPR reports contain potentiometric maps (*i.e.*, display the energy available for groundwater to move at any given point) created from the static levels in MOE drilling records which delineate groundwater flow paths (figures 2.13, 2.14). In these SPRs, groundwater flow generally followed topography, flowing from higher potential elevated areas to lower potential depressions and surface water bodies. This is also stated to be the case in the Cataraqui SPR (CRCA 2008). In the Mississippi-Rideau SPR, the flow is generally from south-west to north-east. In the South Nation Conservation Authority, regional groundwater flow is generally towards the South Nation River. The exception seems to be in the northeast in bedrock valleys; there was insufficient data to conclude whether or not bedrock valleys are significant in the regional flow system (Barnes 2009). In the RRCA, flow is generally from the northwest towards the St. Lawrence River, except in the far northeast where flow may move across the Québec border. In the Raisin-South Nation SPR, flow in the bedrock is dominantly horizontal (RRCA 2012).

Charron (1978) used groundwater chemistry to delineate groundwater flow patterns based on anion-dominance and total dissolved solids (TDS). It was determined that discharge areas coincide with the major bogs and that linear bedrock ridges prevent groundwater in the discharge area from moving to the Ottawa River, creating the sizeable wetlands. Charron (1978) concluded that groundwater flow is controlled by bedrock topography through the entire flow path because the greatest permeability is found at the sediment-rock interface.

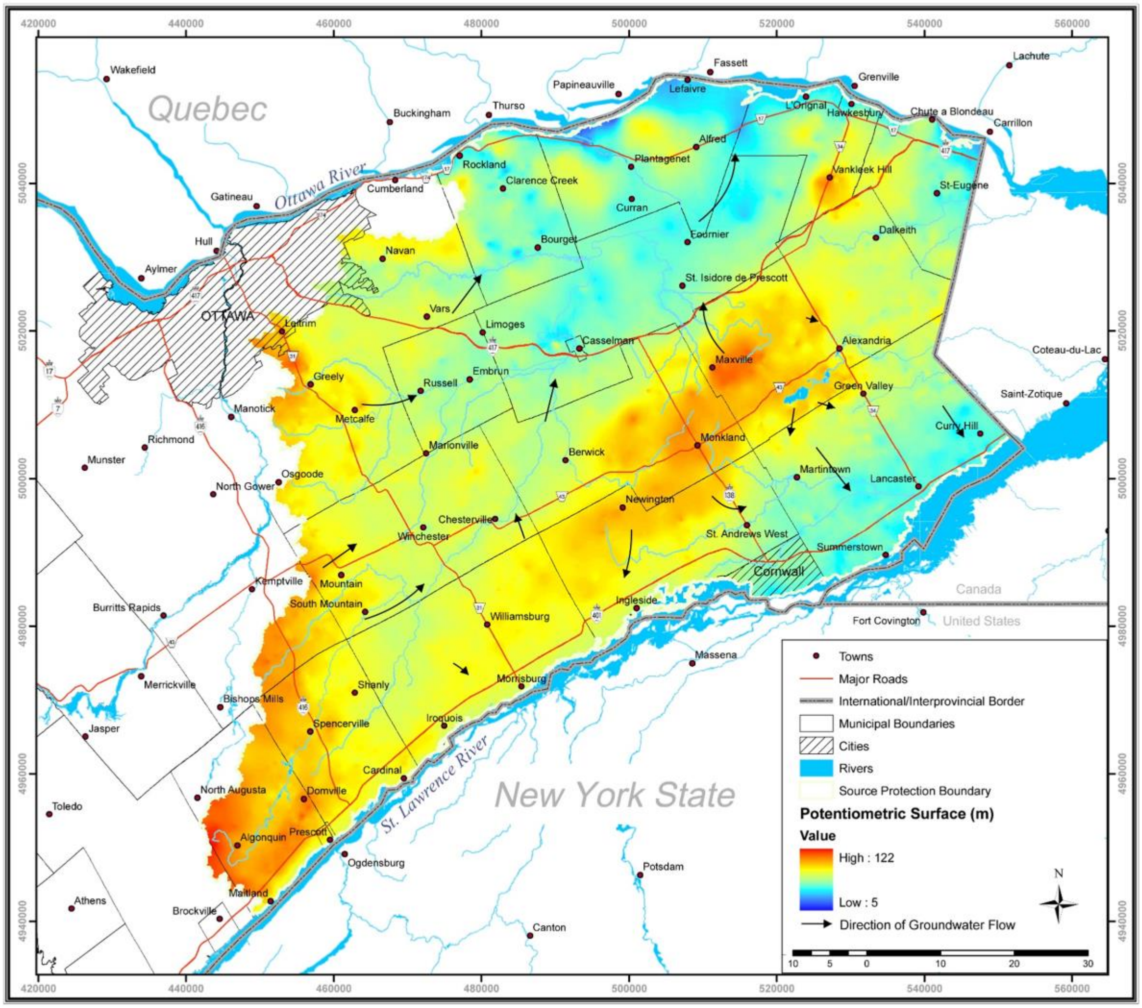
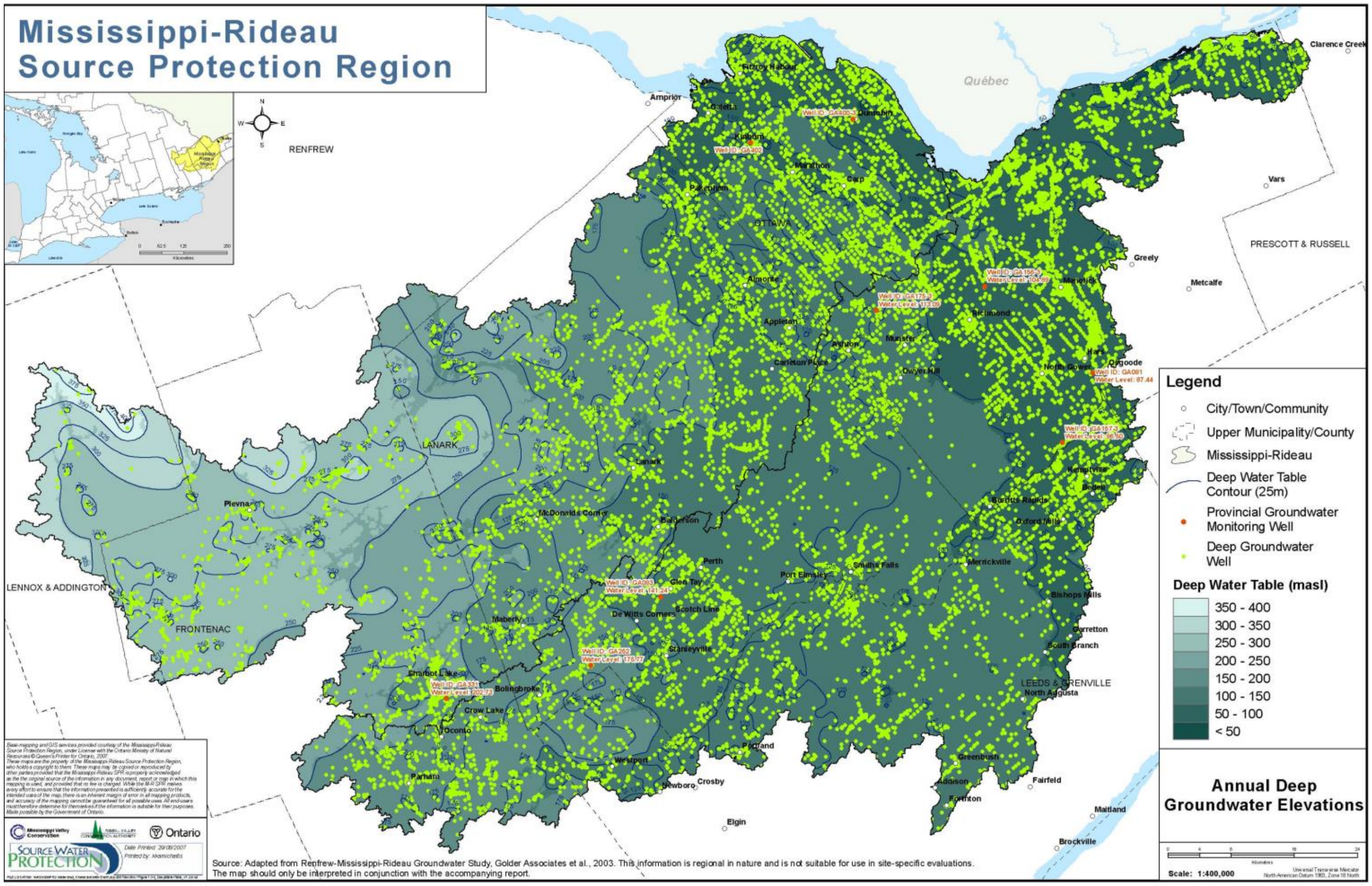


Figure 2.13 Potentiometric map of groundwater in the shallow bedrock of the Raisin-South Nation SPR (modified from SNCA 2012; Reproduced by permission of Phil Barnes).



Source: Adapted from Renfrew-Mississippi-Rideau Groundwater Study, Golder Associates et al., 2003. This information is regional in nature and is not suitable for use in site-specific evaluations. The map should only be interpreted in conjunction with the accompanying report.

Figure 2.14 Potentiometric map of the deep groundwater in Mississippi-Rideau SPR (from MVCA 2011; Reproduced by permission of Brian Stratton).

2.3.1.3 Bedrock parameters

The “interface” or “contact” aquifer is heavily exploited in Southern Ontario. It comprises the upper few meters of fractured and weathered bedrock and the basal, hydraulically conductive till overlying it. They create a hydrologically-connected unit with enhanced permeability compared to many other units (Singer et al. 2003; McIntosh et al. 2014). Many wells in the St. Lawrence Platform and in areas covered by thick, fine grained drift exploit the interface aquifer.

In Precambrian shield areas or regions with thin drift bedrock wells are commonly completed deeper into the bedrock. Primary porosity in the Precambrian Shield is very low, except where weathering has occurred (Trainer 1988). Therefore, domestic wells drilled into crystalline shield rocks rely on fracture permeability to supply groundwater at a reasonable rate. Research performed at Precambrian Shield mine and disposal sites suggest that fractures can be meters to tens-of-meters long (*e.g.,* Raven 1986; Raven and Gale 1986; Stevenson et al. 1996). Interconnected fracture networks allow groundwater circulation. A study near Chalk River found complex fracture networks in Grenville Province crystalline rocks to reach depths of up to 100 m and vertical hydraulic conductivity to be 100 times greater than radial hydraulic conductivity (Raven 1986). Flow properties along a single fault can also vary at similar depths because of stress variability (Raven and Gale 1986). Metamorphosed Precambrian Shield carbonate rocks (marble) can also develop highly permeable karst, creating a distinct hydrogeologic unit (Roy et al. 2006). Because of its thin, discontinuous soil cover and variable fractures, the Precambrian Shield tends to have more localized recharge and discharge zones than more porous aquifers (Gleeson and Novakowski 2009; Rouleau et al. 2014).

Singer et al. (2003) compiled hydrogeological data for geological units across Southern Ontario, including eastern Ontario. The carbonate platform has generally “good” yield in drilled wells, while the shale-rich Billings-Carlsbad-Queenston hydrogeological group had “fair” yield and the Precambrian Shield scored “poor.” A more detailed summary of the hydraulic parameters of the bedrock units is compiled in Table 2.2.

Table 2.2 Some hydraulic parameters of bedrock units in eastern Ontario.

Hydro-geologic Unit[6]	**Transmissivities (m^2/day)**[6]				**Typical K**[7] **(Based on primary lithology) (m/s)**
	10th [8]	**90th** [8]	**Geometric mean**	**Description**	
Precambrian (N=7875)	0.4	43	4	Poor but highly variable	Igneous and metamorphic: Fractured: $8x10^{-9}$ to $3x10^{-4}$ Unfractured: 3×10^{-14} to $2x10^{-10}$
Nepean-March-Oxford (N=7418)	0.5	121	20	Good	Sandstone: $3x10^{-10}$ to $6x10^{-6}$ Dolomite: $1x10^{-9}$ to $6x10^{-6}$
Rockcliffe (N=1771)	2	104	16	Good	Sandstone and Shale: $1x10^{-13}$ to $6x10^{-6}$
Ottawa Group (N=7251)	1	71	12	Good	Limestone: $1x10^{-9}$ to $6x10^{-6}$ Karst and reef limestone: $1x10^{-6}$ to $2x10^{-2}$
Billings-Carlsbad-Queenston (N=969)	1	52	6	Fair	Shale: $1x10^{-13}$ to $2x10^{-9}$

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[6] As defined by Singer et al. (2003); transmissivity values are rounded

[7] General values of hydraulic conductivity (K) for rock types from Schwartz and Zhang (2003)

[8] Percentile

2.3.1.4 Groundwater chemistry

2.3.1.4.1 Shallow groundwater

A regional study of groundwater chemistry in a portion of eastern Ontario was conducted almost 40 years ago (Charron 1978). Based on high-density sampling, Charron (1978) used spatial chemical variation as a way to determine groundwater flow patterns, assuming recharge water carries a bicarbonate signature and evolves along the flow path to discharge as a chloride-type water. Recharge chemistry was identified in the Glengarry Till Plain and exposed bedrock ridges, whereas a discharge signature was found in wetlands in the northwest. Magnesium, sodium, potassium, chloride and bicarbonate were more concentrated in discharge than recharge areas, whereas calcium showed the opposite trend. Nitrate displayed a more random, point-source pattern, reflecting local contamination. Though bedrock lithology was not a focus of the study, Charron (1978) concluded that hardness, silica content and sulphate concentration were a result of water-rock interaction. High silica content seemed to reflect interaction with granitic rocks. Sulphate was high where shales, such as those present in the Rockcliffe Formation, were encountered, and low where granite and sandstone existed or where sulphate reduction had occurred. Charron (1978) argued that soft water could be explained by interaction with granite and sandstone, except in the north-central part of the study area where water softness was attributed to ion exchange.

Some water quality data obtained through wells from Ontario’s Provincial Groundwater Monitoring Network (PGMN) and other sources were compiled in the Source Water Protection documents for each SPR. Some health-related and non-health related water quality parameters that typically exceed Ontario Drinking Water Standards (ODWS) have been reported by two SPRs. In the Cataraqui SPR, these most commonly included hardness and reactive silica, while sodium, conductivity, iron, manganese, chloride, sulphate, sulphide, organic nitrogen, nitrate and TDS were also found to be in excess in a number of wells (Trow Associates Inc. 2007; Dillon Consulting Ltd. 2001). Almost all wells tested through the PGMN network in the Raisin Region – South Nation SPR exceeded the standards for at least one of aluminum, chloride, iron, manganese or hardness. One PGMN well at Alfred Bog showed an average chloride concentration of

4880 mg/L (SNCA 2012; RRCA 2012). The Ontario Drinking Water Standards are also exceeded for one or more parameters in the Mississippi-Rideau SPR, but those occurrences are not a focus in that report (MVCA 2011). In the Mississippi-Rideau SPR, Golder et al. (2003) characterized the groundwater associated with different lithologies. Limestone and shale were sodium-dominated, while dolostone, sandstone and Precambrian Shield rocks were calcium-dominated. In the Cataraqui Region, water quality was found to be strongly influenced by carbonate dissolution and agricultural practices (CRCA 2008).

Singer et al. (2003) compiled MOE well water records and chemical analyses to characterize the groundwater chemistry in bedrock units across southern Ontario (Table 2.3). It is difficult to compare results between bedrock units as the sample sizes are quite different; it remains notable nonetheless that the Billings-Carlsbad-Queenston shale hydrogeological group has particularly high TDS, sodium and chloride water and was described as having “generally poor” water quality (Singer et al. 2003). Singer et al. (2003) also compiled quality data for overburden units. Those results are not included here, however, because the sampling is difficult to ascribe to a particular sediment type, and the well may not have been completed in the same unit exposed at the ground surface.

Table 2.3 Groundwater chemistry (as water quality) for different bedrock units (grouped by hydrogeological unit) (Singer et al. 2003).

	Water type	**Driller description**	**TDS (mg/L)**	**Hardness**	**PDWO[9] exceedances (% of samples)**
Precambrian	Ca-HCO_3 HCO_3 (N=3)	Most Fresh Small amount with “salty”, “sulphurous” and “mineral”	412.33 mean (N=8)	Ranges from acceptable to unacceptable	Fe 43 % SO_4 25 %
Nepean March Oxford	HCO_3 Ca-HCO_3 (N=28)	Fresh (N=17164) Sulphur (N=193) Salt (N=33)	486.28 – 1380.00 (N=33)	Ranges from optimal to unacceptable	TDS 28 % NO_3 some
Rockcliffe	HCO_3 (N=1)	Fresh (N=2026) Sulphur (N=42) Salt (N=21)	304.00 (N=1)	Tolerable	N/A (1 sample)
Ottawa Group	Ca-HCO_3 HCO_3 Na-K-HCO_3 (N=32)	Fresh (N=9144) Sulphur (N=502) Salty&Mineral (N=402)	732.90 mean (N=29)	Ranges from optimal to unacceptable	TDS: 62 % Fe: 45 % Na: 21 % Cl: 10 % SO_4: 3 % NO_3 (several)
Billings Carlsbad Queenston	Na-K-Cl Na-K-HCO_3 HCO_3 (N=10)	Fresh (N=846) Sulphur (N=148) Salty&Mineral (N=64)	947.10 mean (N=10)	Ranges from optimal to unacceptable	TDS: 70 % Na: 50 % Cl: 30 % Fe: 33 %

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[9] Provincial drinking water standards

2.3.1.4.2 Deep groundwater

Shallow groundwater is generally accepted to be meteoric in origin. However, there are deep-residing ancient brines in both the Canadian Shield and the St. Lawrence platform that should also be considered as potential mixing sources in the study area.

Pinti et al. (2011) analyzed eight deep brine samples taken from depths of 900 to 1400 m in the St. Lawrence Platform near Trois-Rivières, Québec (Figure 2.15). They found them to be of Na-Ca-Cl type and to have Cl/Br ratios between 25 000 and 45 000. The low bromide content suggests the source of these brines may be halite dissolution, with long residency time allowing excess calcium to accumulate. The average TDS of these samples was ~196 g/L, with the maximum value at ~315 g/L.

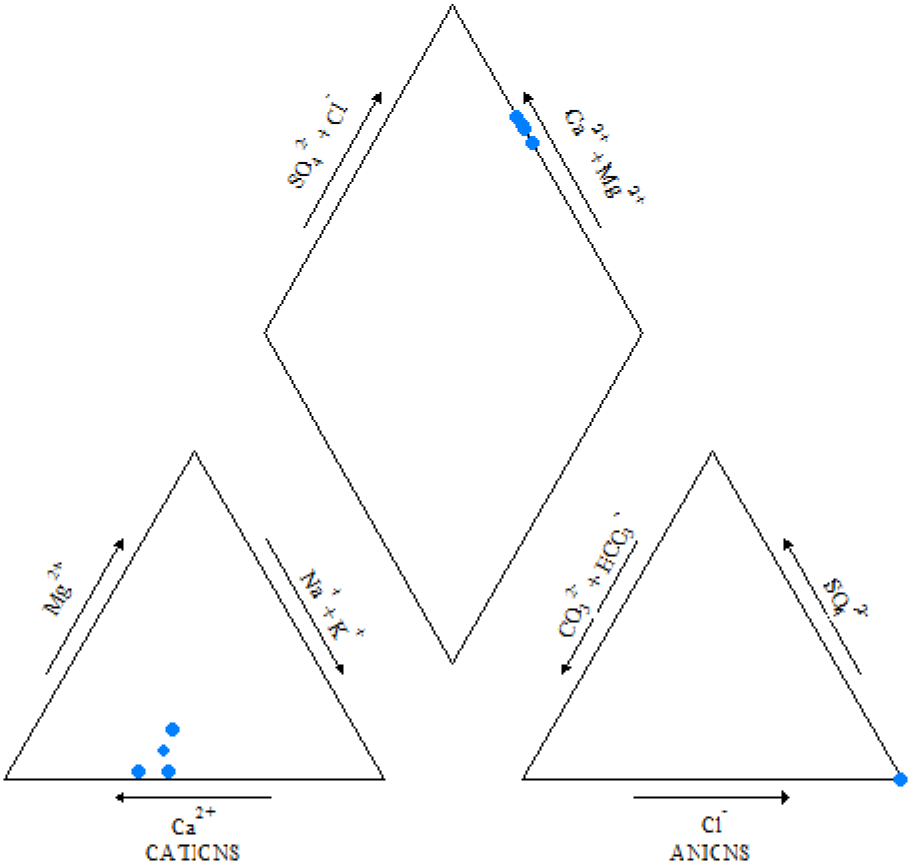

Figure 2.15 Piper diagram showing the major ion proportions of four St. Lawrence Platform brines for which a full suite of chemical data were available. Cations are

dominated by sodium and calcium while the anions are dominantly chloride. The resulting water type is Na-Ca-Cl (Pinti et al. 2011).

Three water sources are possible within the Canadian Shield: modern recharge, glacial meltwater and brine. Studies at Atomic Energy of Canada Ltd. (AECL) research sites report that, in recharge zones, groundwater up to 200-300 m depth is typically fresh, modern recharge. Chemical constituents are derived from the dissolution of silicates, amounting to characteristic Ca-HCO_3 water type and TDS values up to 500 mg/L. Na-HCO_3 waters may also derive from ion exchange on clay surfaces in fractures. At 200-300 m depth, the freshwater transitions from modern recharge to glacial meltwater. These have similar TDS concentrations as modern waters but have been identified isotopically as meltwater-sourced. Subglacial meltwater infiltrated the aquifers during glacier ablation in the late Pleistocene, likely enhanced by high hydraulic gradients in melting glaciers (McIntosh and Walter 2006). Below glacial meltwater are Precambrian Shield brines. These are postulated to have infiltrated during the early Paleozoic or, alternately, to have been forced by high pressure, lateral flow into the Precambrian rock by adjacent basinal sediments. Waters resulting from the first of these mechanisms are characterized by a (Ca-Na)-Cl water type and TDS up to 300 g/L. Those derived from the latter mechanism typically have a (Na-Ca)-Cl water type and TDS less than 100 g/L. In regional discharge areas, the upward flow of water along fractures and faults can exhibit brackish, Na-Cl type water (paragraph sourced from Rouleau et al. 2014, with references there in; Gascoyne 2004). Rouleau et al. (2014) compiled chemical analyses for a number of Canadian Shield-representative groundwaters. Figure 2.16 displays the major ion composition of shallow sample TW3 from a Grenville Province gneiss at Perth, ON and two “Reference” groundwaters representing the average chemical compositions at AECL research sites across the Canadian Shield. CS-50 represents the average chemical composition up to 100 m deep, and CS-750, 500 to 1000 m depth.

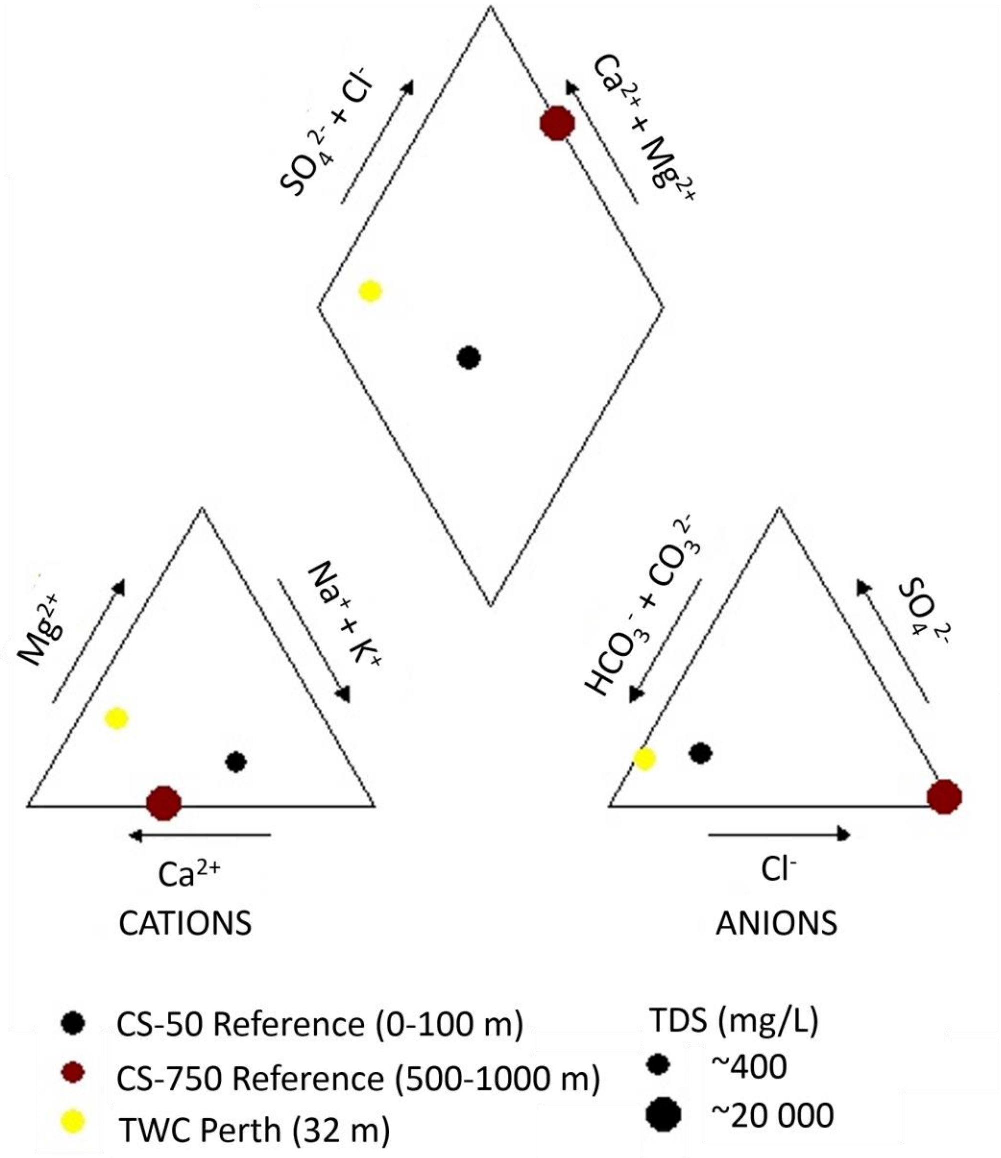

Figure 2.16 Piper diagram of three Canadian Shield waters. The size of the symbol is proportional to the TDS (mg/L). The deep groundwater (CS-750) is brine-influenced, showing a Ca-Na-Cl water type, distinct from the shallower samples showing more of a Ca-HCO_3 or Na-Ca-HCO_3 type (Rouleau et al. 2014 and references therein).

2.3.2 Champlain Sea effect on aquifer chemistry (Québec)

Numerous hydrogeochemical studies in Québec (Cloutier 2004; Cloutier et al. 2006; 2008; 2010; Blanchette et al. 2013; Larocque et al. 2013; LeBlanc et al. 2013; Montcoudiol et al. 2015; Talbot Poulin et al. 2013) have investigated the regional controls on groundwater chemistry in relation to the Champlain Sea event. The investigations generally use major-ion water types, multivariate statistics (HCA, PCA, FA *etc.*), saturation indices and other tools to relate aquifer chemistry to geologic and hydrogeologic conditions. The overarching finding is that the Champlain Sea invasion at ~10 ka BP (^{14}C years) still affects the chemistry of groundwater in the St. Lawrence Lowlands in Québec. The marine incursion deposited extensive glaciomarine clays and it saturated the bedrock aquifers with saline water, both of which profoundly influence hydrochemistry today. The groundwater chemistry is controlled by the "hydrogeologic condition" or the level of confinement, which is largely a function of the extent of the Champlain Sea clay aquitard in relation to bedrock topography (Cloutier et al. 2010).

In elevated, unconfined regions, recharge occurs and the Ca-HCO_3 water type is created through the dissolution of (a) carbonate minerals present in the St. Lawrence Platform and till matrix (Cloutier et al. 2010; Montcoudiol et al. 2015), and (b) silicates, particularly plagioclase (Ca) feldspar, in Precambrian Shield areas (Montcoudiol et al. 2015). The Ca-SO_4, Na-SO_4, Mg-HCO_3 and Ca-Mg-HCO_3 water types have also been attributed to processes affecting modern recharge waters (Cloutier et al. 2010). Under increasingly confined conditions, Ca-Na ion exchange occurs at exchange sites on clay minerals that were saturated with sodium by the Champlain Sea. This process has been deemed responsible for the Na-HCO_3 and Mx-HCO_3 (Mx = mixed cations) water types (Cloutier et al. 2010; Blanchette et al. 2013; Montcoudiol et al. 2015). Conditions of confinement and slow, converging flow have allowed stagnation of remnant Champlain Sea water in the bedrock aquifer, particularly in buried bedrock valleys (Cloutier et al. 2010). The Na-Cl type is attributed to mixing with Champlain Sea water and, in unconfined regions, contamination by de-icing road salts, animal and human waste, and halite dissolution (Blanchette et al. 2013; Montcoudiol et al. 2015). Conceptual models for groundwater evolution have been developed in several studies for their respective

Champlain Sea-affected areas; the model by Cloutier et al. (2010) is shown here as an example (Figure 2.17).

Cloutier et al. (2010) compared porewater extracted from a thick sequence of glaciomarine clay to bedrock groundwater (TDS = ~11 g/L) sampled from the underlying confined bedrock valley. Using conservative tracers (Cl, Br, δ^{18}O and Cl/Br ratio), they concluded that the similarities suggest a similar solute source, *i.e.* the Champlain Sea. Comparing chloride and bromide concentrations with those of seawater, Cloutier et al. (2010) found that both porewater and bedrock water were 34% seawater, “typical” of the Champlain Sea, as determined by Desaulniers and Cherry (1989). Cloutier et al. (2010) concluded that the saline sample extracted from the bedrock valley represented a mixing end-member, and that the aquifer system was at different stages of desalination, with many samples falling along freshwater-seawater dilution lines on Cl^- versus Br^- and Cl^- versus Cl/Br plots.

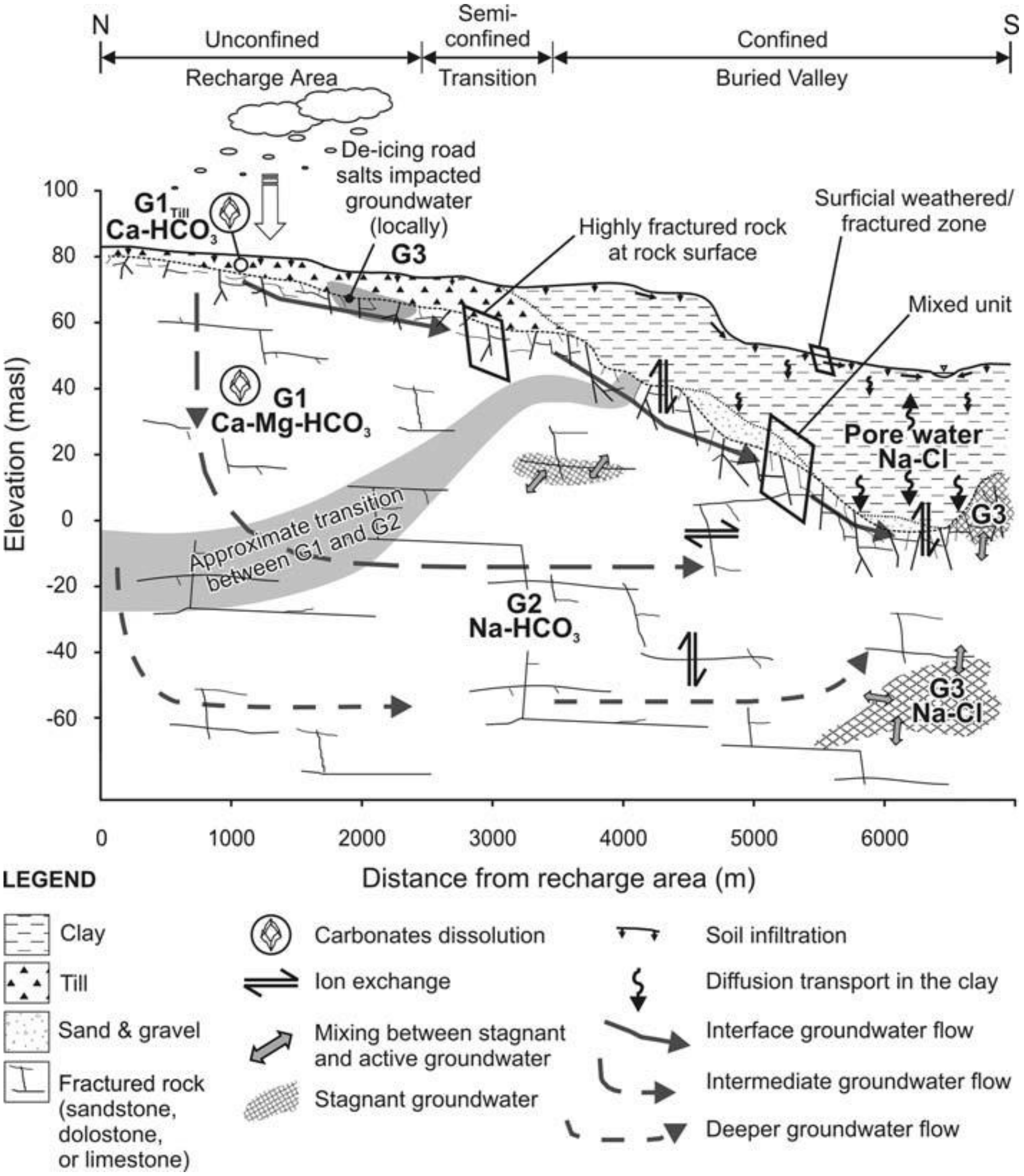

Figure 2.17 Conceptual model of groundwater evolution in the Basses-Laurentides aquifer system (Cloutier et al. 2010; Permission received from Springer for reproduction). Recharging water (G1, Ca-HCO3 type) enters the system at elevated, unconfined areas. The recharging water evolves under greater confinement through ion exchange (G2, Na-HCO3 type) in the bedrock or at the interface. In confined, bedrock valleys, converging flow causes stagnation and mixing with remnant Champlain Sea water or diffusion of solutes from the marine clays (G3, Na-Cl type).

Chapter 3

3 Methods and Dataset

3.1 Ambient Groundwater Geochemistry (AGG) program sample collection

3.1.1 Sampling points

A uniform grid of 10 km by 10 km was placed on a map of the study area to define sampling density. For each square, an effort was made to collect both a "bedrock water sample" from a well completed in the bedrock and an "overburden water sample" from a well completed in the overlying glacial drift. The 234 samples collected were accessed through pre-existing private (domestic, agricultural) and monitoring wells, which were initially located using the Ministry of Environment (MOE) well record database. Utilization of existing private wells has many advantages, but it results in inherent biases in sampling population. In areas with either (1) few residences and no monitoring wells, (2) very thick drift, (3) thin or discontinuous drift, (4) poor water quality, and/or (5) widespread distributed water systems, it was commonly impossible to obtain a bedrock water sample, an overburden water sample or either, despite best efforts. More detailed information on sampling biases can be found in Hamilton and Lee (2012).

3.1.2 Sampling groundwater

Once the sampling point had been established, a representative water sample was obtained from the well. Depending on the nature of the well (*e.g.*, diameter) and existing infrastructure (*i.e.*, pump, treatment system, plumbing), sampling equipment was attached in different ways. In most cases the well-owner's pump and plumbing was used to transport water from the well to the sampling equipment and the connection to the plumbing was always made before any water treatment system. In the absence of domestic plumbing infrastructure, a portable submersible pump or, exclusively in the case of shallow bored or dug wells without existing infrastructure, a manual foot-valve pump attached to polyethylene tubing was used. The standard sampling apparatus included a sampling manifold connected to the water supply tap. The manifold and supply hose were made from a 1.6 cm-inside-diameter, nylon-braided, clear polyvinyl chloride (PVC) tubing. Attached to the manifold were a discharge outlet and two 0.95 cm-diameter silicon tubes with stopcocks, one to fill sample bottles and the other to supply the flow-through cell (a chamber in the line) of a multiparameter instrument. During the purging and sampling stages, water was allowed to flow at a high rate continuously out the discharge line to waste via a garden-hose. Water flowed through the flow cell for the duration of purging and sampling. High-flow purging was used until the real-time readings of temperature, conductivity and oxidation-reduction potential (ORP) had stabilized, after which sampling began. These parameters were measured using a YSI® sonde (Model 600LXM), attached to the flow-through cell, and plotted in real-time using HydroPlusCE® logging software and a hand-held Archer® field computer.

3.1.3 Sample collection

Following purging of the well, separate sample bottles were filled for chemical analyses as follows: cations, anions, mercury (Hg), iodide (I^-), stable isotopes ($\delta^{18}O$ and $\delta^{2}H$), tritium (^{3}H), dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), ammonia (NH_3) and ammonium (NH_4), nitrate (NO_3) and nitrite (NO_2), total Kjeldahl nitrogen (TKN), bacteria and dissolved gases (CO_2, CH_4). Water added to the cation, anion and mercury sampling bottles was pressure-filtered using 0.45 μm Millipore™ Durapore® (polyvinylidene fluoride (PVDF)) membrane filters attached to rubber-free polypropylene syringes. Water samples were collected in 60 mL polyethylene bottles (cations, anions, mercury, iodide, NO_3^-+NO_2^-, NH_3+NH_4^+, TKN, DIC+DOC), 120 mL polyethylene bottles (stable isotopes), 250 mL polyethylene bottles (tritium), 250 mL sterile HDPE bottles (bacteria) and 1.2 L borosilicate glass graduated storage bottles filled to 600 mL (dissolved gases). Care was taken to minimize the headspace in the sampling bottles in order to minimize chemical reactions, with the exceptions of the bacteria and dissolved gas bottles which both required a headspace. All bottles except bacteria were filled through the silicon sampling tube on the manifold. The bacteria bottle was filled directly from the tap after disinfection using antibacterial wipes for at least 20 seconds and flushing for a further 10 seconds.

3.2 AGG chemical analysis

3.2.1 On-site determinations

Several time-sensitive (HS^-, alkalinity) and probe-determined (pH, temperature, ORP, conductivity, dissolved oxygen (DO)) parameters were measured at the sampling site. The YSI® sonde, connected in a flow-through cell, has probes for pH, temperature, electrical conductivity and ORP. Upon observing stable readings, the sampler would record the values for each and continuous digital logs were also kept. DO was measured in the field using three different methods, depending on the year of the program. The earlier approach was to use a HANNA® HI 769828-1 multiparameter instrument, which was employed only in the absence of any smell of hydrogen sulphide (H_2S), which damages the instrument's sensitive membrane. Upon detecting H_2S by smell, a value of 0 was assigned to DO as it is incompatible in solution with dissolved H_2S. The second approach (used in 2013 and 2014) employed a stand-alone YSI®ODO (optical DO meter) with logging software and an optical sensor that could be utilized in the presence of H_2S. In a few cases where a DO probe failed, DO was determined using an azide modification of the Winkler Method 8215 (Hach Company 2006). Alkalinity was determined by titration with a HACH® 16900-01 digital titrator to 3 pH points using a bromocresol green-methyl red indicator. The on-site measurement of alkalinity was ultimately used to determine bicarbonate (HCO_3) concentration through linear conversion, in the assumption that HCO_3 was the sole source of alkalinity in the water. There are other sources of alkalinity in groundwater, but their concentrations are insignificant compared to bicarbonate within the pH range of eastern Ontario groundwater. Finally, if it was detected by smell, dissolved hydrogen sulphide (HS^-) was analyzed using the methylene-blue method using a HACH® model 2238-01 test kit. The smell test was employed because experience showed that if it was undetectable by scent, the measured concentration was invariable below the detection limit of 0.01 mg/L.

3.2.2 Sample preservation for laboratory analysis

Samples that were retained for later analysis, in some cases, required sample preservation and treatment techniques to be employed. All bottles, except the 1.2 L dissolved gases bottle, were immediately refrigerated after collection to slow biological activity and inorganic reactions. NH_3+NH_4^+ and TKN were preserved using approximately 1 mL of sulphuric acid (H_2SO_4). Bacteria were preserved using approximately 1 g sodium thiosulfate pentahydrate ($Na_2S_2O_3 \bullet 5H_2O$). Cations were acidified (to pH<2) with 0.7 mL of J.T. Baker® Ultrapure nitric acid (HNO_3) to achieve an acid concentration of approximately 1%; mercury was acidified with 1.5 mL of 2 % (vol.) Fisher Chemical Optima grade hydrochloric acid (HCl) to achieve an acid concentration of approximately 2%. Other bottles were unpreserved apart from refrigeration.

3.2.3 Laboratory analytical methods

Analysis of dissolved gases (CO_2 and CH_4) and iodide (I^-) was performed shortly after sampling at a temporary field laboratory. For CO_2 and CH_4, the half-filled 1.2 L dissolved gas bottle was allowed to equilibrate to laboratory temperature overnight and the headspace analyzed the following day using a RKI® Eagle portable multi-gas detector. Each morning, prior to analyzing the previous day's samples, the instrument was calibrated using three methane standards (50%, 1% and fresh air as 0%) and two CO_2 standards (2.50% and air as 0.00%, *i.e.* the ~0.04% in air was zeroed-out). The equilibration temperature was recorded and used with the headspace gas composition to calculate dissolved gas concentrations using Henry's Law ($C=kP_{gas}$) and the Ideal Gas Law ($PV=nRT$).

Iodide was measured in the field laboratory using an Orion™ 9453BN iodide ion-selective electrode (ISE) connected to Orion™ 4-Star portable pH/ISE meter. From the time of sample collection, the iodide samples were treated with 2 mL of a saturated solution of nickel acetate to precipitate any dissolved sulphide (S^{2-}) that could interfere with the iodide ISE. The iodide ISE was calibrated before each day of analysis using two iodide standards of concentrations 10^{-5} M (1267 ppb) and 10^{-7} M (12.67 ppb), respectively.

Analysis of time-sensitive parameters was performed at SGS Analytical Laboratories (Lakefield, Ontario, Canada), including dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), nitrogen compounds (NO_3^-, NO_2^-, NH_3, NH_4^+, TKN and organic nitrogen) and bacteria (total and fecal coliform). DIC and DOC were analyzed with a SKALAR® segmented flow autoanalyzer (SGS method MTH-EWL-39). All nitrogen compounds were reported as N, with NO_3^- and NO_2^- being analyzed using a Dionex Ion Chromatograph (SGS reference method MTH-CHR-1), while NH_3+NH_4^+ and TKN were analyzed using a SKALAR® segmented flow autoanalyzer (SGS reference methods MTH-EWL-37 (NH_3 +NH_4) and MTH-EWL-32 (TKN)). The methods used for nitrogen parameters and fecal coliform followed the protocol of the United States Environmental Protection Agency (EPA) (Hautman and Munch 1997) and American Public Health Association (Eaton 2005). Total coliform bacteria counts per 100 mL were made using membrane filtration as suggested by the Ontario Ministry of the Environment and Energy (SGS reference method MTH-MICRO-1; MICROMF-E3407A procedure). Fecal coliform bacterial counts per 100 mL were also determined by membrane filtration in accordance with the American Public Health Association (Eaton 2005) (SGS reference method MTHMICRO-4: 9222 D Fecal Coliform Filter Procedure).

The majority of parameters (major, minor and trace cations and anions) were analyzed at the Ontario Geological Survey’s Geoscience Laboratories (GeoLabs) in Sudbury, Ontario, Canada. The precision and accuracy of analytical results from the Geoscience Laboratories are better than ±10% (2σ) (Richardson and Morrison 1995). Cation concentrations were determined by Inductively Coupled Plasma–Mass Spectroscopy (ICP–MS) using a Perkin Elmer ELAN® DRCII (GeoLabs method reference codes: IMX-CUS, IMW-100 and IMC-100) or Inductively Coupled Plasma-Atomic Emission Spectroscopy using a Teledyne Leeman Laboratories Prodigy, Dual View (ICP–AES) (GeoLabs reference method IAW-200), with many parameters having redundant analysis through both methods. Mercury content was analyzed by Atomic Fluorescence Spectrometry (AFS) using a PS Analytical Millennium Merlin with an overnight digestion using bromine monochloride (BrCl) (GeoLabs reference method HGW-100) (Pamer 2008). The analytical determination of mercury concentration was adapted from EPA protocol (Telliard 2002; 2005). Ion Chromatography (IC) was used to determine anion concentrations, using a Dionex™ (Model ICS-3000) dual-pump system ion chromatograph (GeoLabs reference method ICW-100 or ICW-CUS). Carbonate eluent, potassium hydroxide eluent and dual analysis were the methods used for the IC analyses (Pamer 2011).

The stable isotopes of water (δ^{18}O and δ^{2}H) were analyzed at the Laboratory for Stable Isotope Science (LSIS) at the University of Western Ontario, London, Ontario, Canada in 2012, and at Isotope Tracer Technologies in Waterloo, Ontario, Canada in 2013 and 2014. The stable isotopic results are reported in parts-per-thousand (‰) relative to Vienna Standard Mean Ocean Water (VSMOW) using the normal δ-notation. LSIS used a Picarro® L1102-I δ^{2}H and δ^{18}O Water Isotope Analyzer, and reported precision of better than ±0.2‰ for δ^{18}O and ±2.5 ‰ for δ^{2}H, based on replicate analyses of samples. Accuracy was tested regularly in each analytical session using two standards of quite different δ^{2}H and δ^{18}O values, which were independent of the calibration curve that relates raw δ-values to the internationally accepted VSMOW-SLAP calibrated results (Coplen 1994; 1996). Results for these standards were within 0.1‰ and 1‰ of their accepted values for δ^{18}O and δ^{2}H, respectively. Isotope Tracer Technologies used a Picarro® CRDS Isotopic Water Analyzer (Model L1102-I) with typical precision reported at ±0.1‰ for δ^{18}O and ±0.6‰ for δ^{2}H. Accuracy was ensured as the batches of 10 samples were bracketed before and after with a set of 3-4 in-house standards with a large range of isotopic composition.

Tritium (^{3}H) was also analyzed at Isotope Tracer Technologies in Waterloo. The method employed was liquid scintillation counting after enrichment. The reported concentrations of tritium were given in tritium units (TU), with a detection limit (LLD) of 0.8 TU. At low levels, the 1 sigma error was 0.5 TU and each batch of analyses included 3 backgrounds, 1 spike, 1 repeat and 1 “check” known sample.

3.3 AGG quality control

Samples were submitted to the various laboratories in batches that contained blind duplicates, blanks and standards. A field duplicate was performed randomly once in every 20 samples, which included duplicating on-site determinations of alkalinity and hydrogen sulphide contents. A standard was also included in every 20 samples sent to a laboratory for chemical analysis, which was a certified reference material (SLRS-5), a spiked in-house standard (BLK-1) and non-spiked in-house standards (BLK-1 and BLK-2). The standards were optimized in order to ensure that all elements were present above detection in at least one of the standards and usually two or more, therefore ensuring accuracy could be assessed at different concentration levels (Burnham et al. 2012). Blank samples were filled with ultrapure distilled, deionized water that was treated with the same preservation chemicals as regular samples. Many parameters were analyzed by two methods, which could be used to identify any laboratory mix-ups, instrument and calibration errors and sequencing problems (Hamilton 2015). Charge balance error (CBE) provided another test of analytical error for the major ion chemistry. CBE compares the positive and negative charges in solution, as they should be equal (electrically-neutral) in natural waters. CBE is calculated as:

$$\mathbf{\%\ CBE = [\Sigma cations - \Sigma anions] / [\Sigma cations + \Sigma anions] \times 100} \qquad \textbf{Equation 3.1}$$

Two hundred twenty-seven (227) samples had CBE < ± 10%, while the remaining 7 samples displayed an excess of anions (up to 32%). More details concerning the precision and accuracy for samples analyzed a as part of the AGG are available with the MRD-283 database (Hamilton 2015).

In addition to the 234 samples utilized for the chemical analysis of eastern Ontario, 30 large-diameter bored/dug wells were also sampled within the study area as part of the AGG program. The large-diameter nature of these wells leads to water stagnation and storage effects that make it difficult to obtain a representative sample of the aquifer. Therefore, these samples were excluded from further consideration in this study, but still serve to inform other investigations of the AGG dataset.

3.4 Derivative methods

3.4.1 Water facies

“Water types” were assigned to each sample as a way to group similar samples and to assess the geochemical history of the water. In order to effectively represent water types graphically and geographically, the classification scheme was made simple enough to include only a small number of categories. The classification method of Cloutier

(2004) was used, in which water types are named based on the dominant major cation (Ca, Mg, Na, or K) and dominant major anion (HCO_3, Cl^-, or SO_4^{2-}). The name combines the cation and anion ion with the highest meq/L concentration (*e.g.*, $Ca\text{-}HCO_3$), unless all are below 20% meq, in which case a mixed (Mx) label is used (*e.g.*, $Mx\text{-}HCO_3$). This classification scheme does not consider minor and trace constituents, physical or other bulk parameters or isotopic characteristics. Those additional characteristics are addressed separately in the interpretation of the water chemistry across the study area (Chapter 5).

3.4.2 Geochemical saturation indices

Saturation indices (SI) describe the extent of equilibrium between a mineral and a solution, and are defined as the log of the ratio of the ion-activity product (IAP) to the solubility product (K_{SP}):

$$\mathbf{SI = \log(IAP/K_{SP})} \qquad \textbf{Equation 3.2}$$

A negative SI means that the solution is undersaturated with respect to the mineral, leading to dissolution if in contact with the mineral. A positive SI means that the solution is oversaturated with respect to the mineral in question, leading to mineral precipitation. An SI of 0 means that the solution is in equilibrium with the mineral and therefore it should not dissolve or precipitate.

Values of SI were calculated for the entire AGG dataset using the geochemical modelling software PHREEQC (PH, REdox, EQulibrium, in C programming language; Parkhurst and Appelo 1999) and the user-friendly AQUACHEM® (software for handling groundwater quality data) interface. The minerals included in the calculations were calcite, dolomite, gypsum, anhydrite and halite, because of their prevalence in Southern Ontario. Modelling with this software provides superior results to hand calculation of SI values; the modeling program takes into account the effects of salinity on pCO_2 and pH, H^+ activity and temperature on equilibrium constants.

3.4.3 Statistical analysis

Descriptive statistics (count, minimum, maximum, arithmetic mean, median, standard deviation) were performed on the dataset as a way of briefly summarizing the results for all parameters. Within the dataset and particularly for the trace elements, many values were reported to be below the detection limit of the laboratory instrument. In these cases, the data entry was replaced with a value of one-half of the detection limit for statistical treatments. The percentage of samples with a censored (below detection limit) value is listed in the summary statistics table (Appendix B).

Principal Component Analysis (PCA) was also performed on the dataset. PCA is a multivariate statistical technique that reduces the dimensionality in a dataset of many, interrelated variables. It works by transforming the many parameters into a fewer number of uncorrelated "principal components" (PCs), ordered by the amount of variability they account for within the dataset (Jolliffe 2002). In effect, the components will group parameters that vary together, either positively or inversely, allowing for deeper interpretation of processes occurring in eastern Ontario.

SPSS (Statistical Package for the Social Science) was used to perform PCA on 23 parameters of 231 samples. Three outliers (samples 12-AG-202, 12-AG-208, 13-AG-718) were excluded from analysis because their total dissolved solids (TDS) fall far in the positive skew of the distribution of values (~10.4, 7.2, and 8.0 g/L). Outliers can have disproportionate effects on the outcome of PCA (Jolliffe 2002). Too few samples would be retained if samples were removed based on the distribution of each parameter, therefore TDS was used to establish outlying samples. The selection of parameters used in the PCA was based on several criteria. First, there was a condition of a 10:1 sample to parameter ratio. Also, additive parameters (*e.g.*, TDS), redundant parameters (*e.g.*, DIC to HCO_3), parameters having more than 40% left-censored (below detection limit) or 0 data (*e.g.*, Cd, CH_4, respectively), and parameters with a direct relationship to another (*e.g.*, δ^2H to δ^{18}O) were excluded from analysis. Finally, in order to maintain the desired ratio of samples to parameters, parameters that provided little information to PCA were also excluded. These were determined from multiple trial runs of PCA using different combinations of parameters and parameters with loadings consistently near zero were removed. The remaining variables selected for PCA were pH, CO_2, δ^{18}O, Ca, Mg, Na, K, HCO_3, SO_4^{2-}, Cl^-, Br^-, F^-, Fe, Sr, Si, DOC, NH_3+NH_4^+, B, Ba, I^-, Li, Mn and Se.

Some assumptions in PCA rely on normality of data, but most of the geochemical constituents display positively skewed distributions. To minimize this issue, all parameters, except normally-distributed pH and Si, were log-transformed to achieve or increase normality. Jolliffe (2002) noted that it is not necessary to assume a particular distribution for many purposes of PCA, particularly in descriptive rather than inferential uses, which is the application in the present study. Therefore the non-normality of some of the parameters that remained after the transformations was accepted and noted during interpretation of the PCA results.

The extraction of principal components from a dataset is accomplished by decomposition of a covariance or correlation matrix. In this dataset, a correlation matrix was used because of the need to standardize the variety of units of measurement (*i.e.*, mg/L, μg/L, pH units, ‰) and the intended descriptive application (Jolliffe 2002). A Varimax orthogonal rotation with Kaiser Normalization (Kaiser 1958) was applied to the factor axes to simplify the structure of the output. The rotation polarizes loadings towards 1 or 0, clarifying what is “important” to simplify interpretation of the principal components (Jolliffe 2002). The extraction was originally performed by selecting PCs based that have eigenvalues (a matrix algebraic function that measures PC significance) greater than 1. However, upon examining the Scree plot (PC versus eigenvalue as in Figure 4.13), 4 principal components were retained based on the position of the “elbow”. This is the point at which the slope in the Scree plot becomes more flat, indicating the point at which the components account for much less variability.

3.4.4 Geo-spatial / geo-statistical methods

Spatial analysis of various parameters was conducted to determine patterns of groundwater chemistry and relationships to geological features. It awas done using Esri® ArcGIS® mapping software and shapefiles (GIS map layers of different features (*e.g.*, bedrock geology, cities, rivers *etc.*)) provided by the Ontario Geological Survey. Spatial variation in the sample constituents are represented by either graduated symbols or kriged surfaces (continuous colour scheme of values interpolated throughout entire study area). Graduated symbols were created using the Jenks Natural Breaks clustering method (Jenks 1967), which maximizes the variance between classes, while minimizing in-class variance. Natural breaks were often manually adjusted based on the researcher’s judgement in order to create more meaningful classes. In some cases (*e.g.*, pH, ORP), classification was entirely manual to capture the magnitudes relative to two opposing endmembers (*e.g.*, acidic/basic, reducing/oxidizing). In some cases, kriging was found to highlight a phenomenon in a more effective way or was used to create a surface upon which to combine visualization with point symbols. The technical kriging options were as follows: ordinary, spherical-semivariogram (a measure of spatial autocorrelation or statistical dependence) using an 8 point, variable search radius with 20 000 m maximum distance and a 10 000 m output grid with stretched colour ramp display (*i.e.*, a continuous hot to cold colour-scheme).

Chapter 4

4 Results

Results are presented in two sections: primary and derivative. Primary results summarize the main findings directly derived from laboratory and field measurements. Statistical and other manipulations performed upon the primary dataset are reported as ‘derivative results’ and used to support the interpretations of the data presented in Chapter 5.

4.1 Primary results

Primary results are summarized for all parameters[10] as descriptive statistics (Appendix B) and elaborated on for parameters that are key to watch quality or interpretation. These include master variables (pH, oxidation-reduction potential (ORP)), total dissolved solids (TDS), halogens (Cl^-, Br^-, I^-), major ions (*e.g.*, Na, HCO_3, SO_4^{2-}) and isotopes ($\delta^{18}O$, δ^2H, ^3H).

4.1.1 Master variables

The “master variables” in groundwater chemistry are the pH and redox state, because they control the composition through redox and acid-base reactions.

4.1.1.1 pH

Eastern Ontario exhibits variable pH, ranging from 5.71 to 9.05. The mean and median pH values are slightly basic at 7.18 and 7.12, respectively. Groundwater pH tends to increase towards the east and the north, with more acidic groundwater grouping in the southwest and more basic groundwater regionally dominating in the east and northwest (Figure 4.1).

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[10] Valency is not specified unless analysis was ion specific.

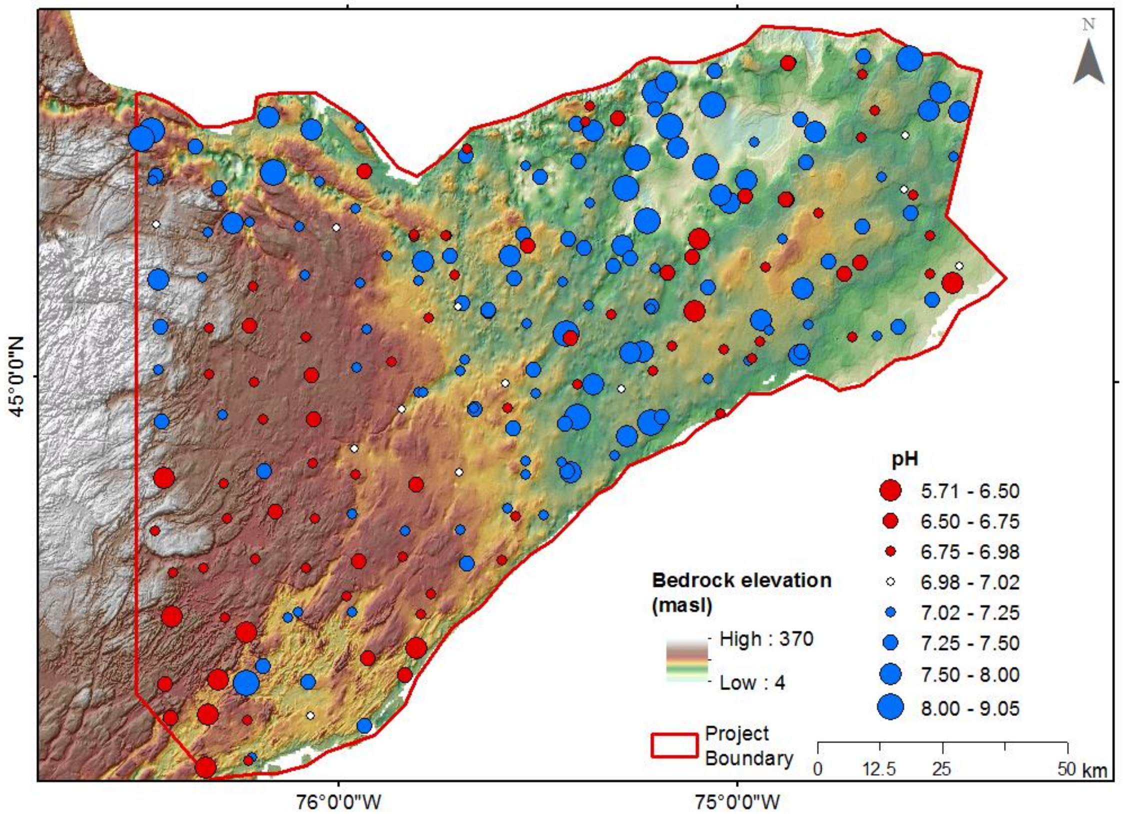

Figure 4.1 Spatial distribution of groundwater pH in eastern Ontario. Red, white and blue symbols represent acidic, neutral, and basic pH classes, respectively.

4.1.1.2 ORP

The oxidation-reduction potential of samples ranges from -350 mV to +260 mV, with the mean and median showing a predominance of reducing conditions at -68 mV and -100 mV, respectively. Oxidizing conditions prevail in the west, while reducing conditions dominate in the east and north. Dissolved oxygen (DO), hydrogen sulphide (H_2S) and methane (CH_4) are all useful indicators of redox conditions. Dissolved oxygen is present in 54 samples, which are largely situated in the west and southwest of the study area. Hydrogen sulphide was detected by smell in 131 wells, which have an average of 0.16 mg/L S^{2-}. Hydrogen sulphide is nearly absent in the west and quite common in the east. Methane occurred in concentrations up to 99 mg/L. The presence of methane is common in the east and very elevated methane concentrations mainly cluster in one area in the northeast (east of Ottawa). DO, H_2S and CH_4 each dominate in different regions, though there is some overlap between H_2S and CH_4.

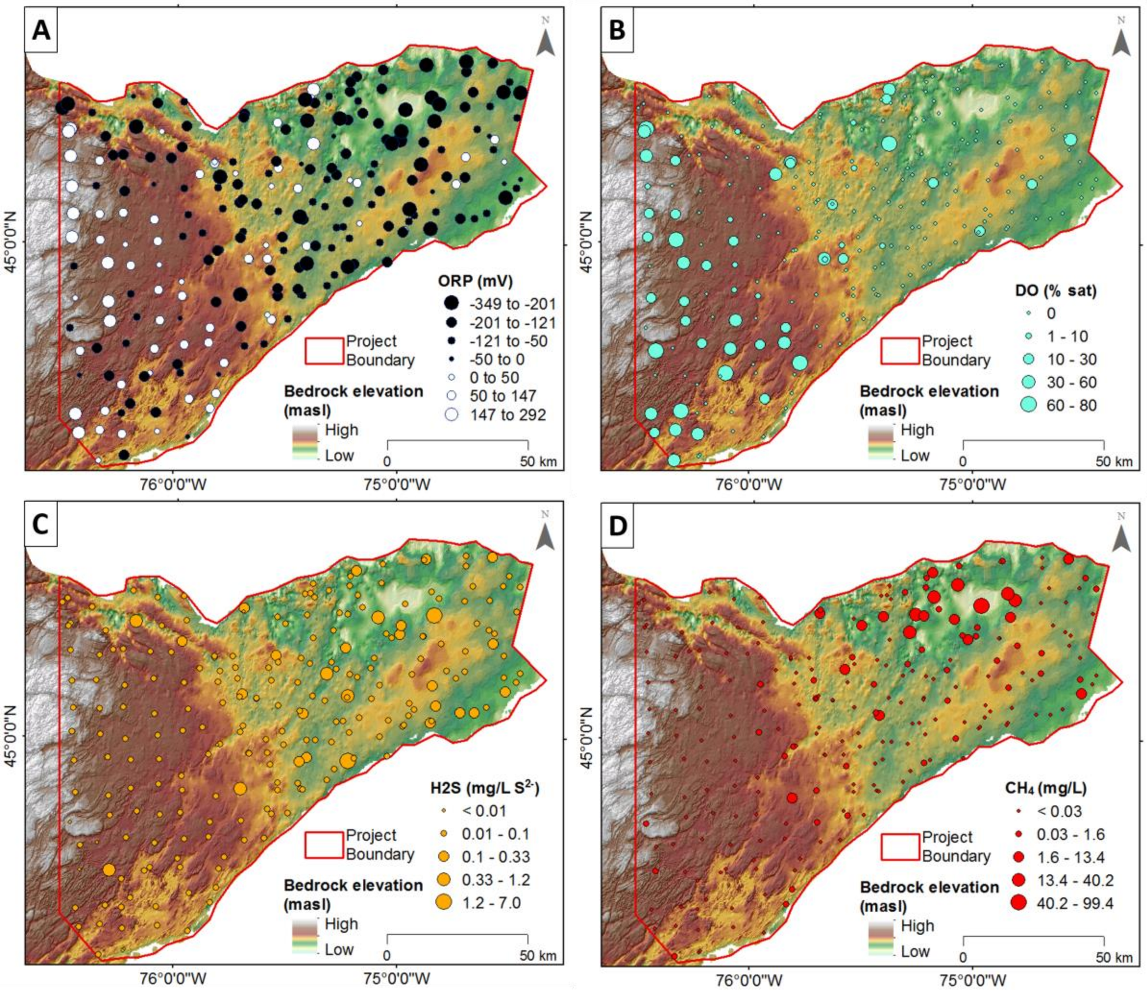

Figure 4.2 Spatial variation in (A) oxidation-reduction potential (ORP), (B) dissolved oxygen (DO; percent saturation), (C) dissolved hydrogen sulphide (HS^-), and (D) methane (CH_4).

4.1.2 Total dissolved solids (TDS)

The groundwater of eastern Ontario has median and mean TDS values of 560 mg/L and 810 mg/L, respectively. The higher mean than median value reflects a positive skew in the data towards high TDS (Figure 4.3A). According to the salinity scheme by Davis (1964), 198 (85%) samples classify as “fresh” water because their TDS is below 1000 mg/L, however the 111 samples in the range of 500 – 1000 mg/L have somewhat elevated TDS according to some sources (ODWS 2006). At the higher TDS, 35 samples between 1000 and 10 000 mg/L and 1 sample at ~10 400 mg/L are considered “brackish” and “saline” (Davis 1964). Spatially, groundwater TDS increases moving towards the northeast, though a few mineralized samples cluster in the southwest (near Westport, Newboro, Gananoque).

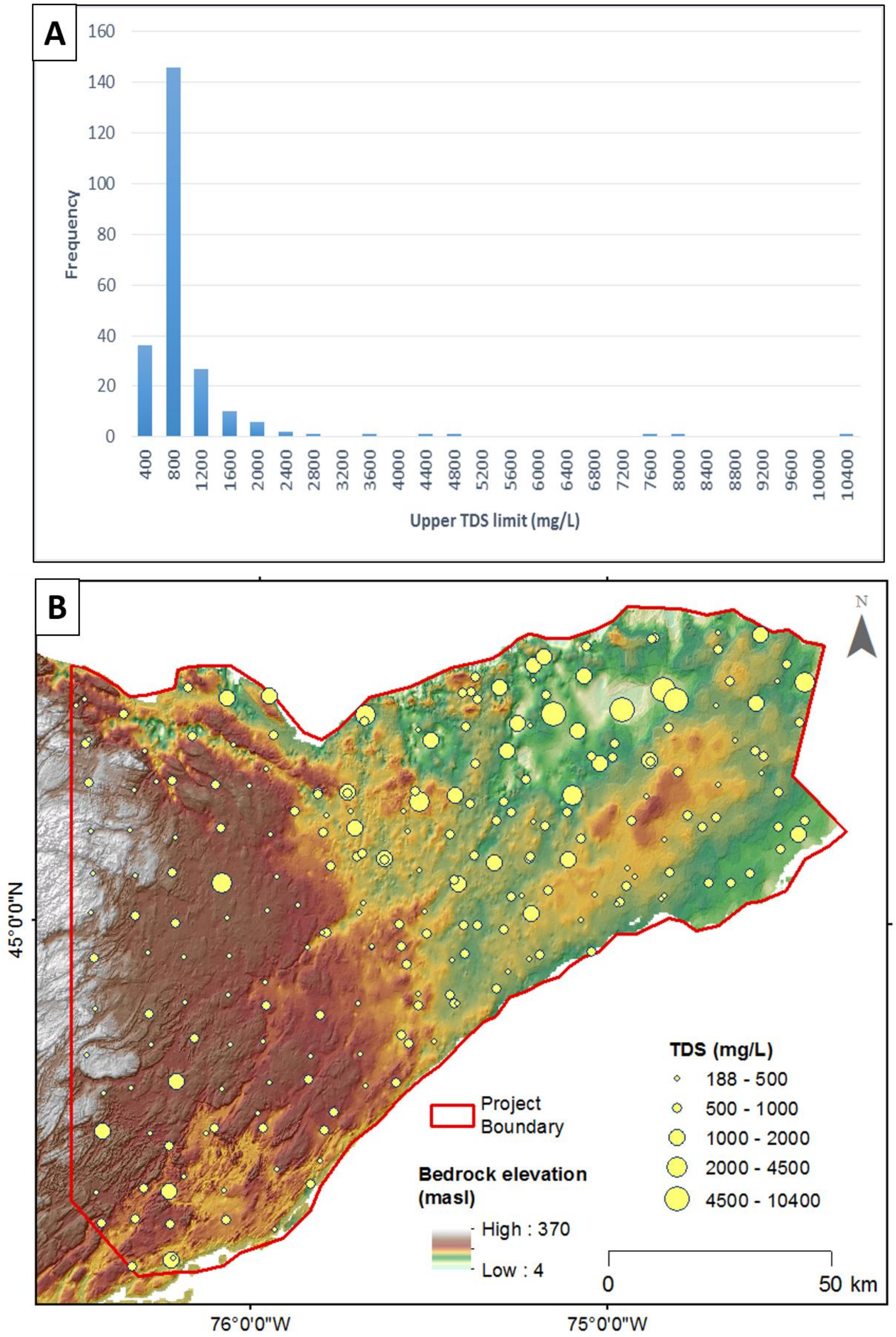

Figure 4.3 Total dissolved solids (TDS) in eastern Ontario groundwater. (A) Frequency histogram of TDS revealing a strong positive skew in the distribution. (B) Spatial distribution of TDS in eastern Ontario.

4.1.3 Halogens

Groundwater in eastern Ontario contains high levels of chloride (Cl^-), bromide (Br^-) and iodide (I^-). Chloride is the most abundant halogen and is considered one of the major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}) in groundwater chemistry. The median and mean chloride concentrations are 41 mg/L and 177 mg/L, respectively, and the maximum concentration reaches up to ~5800 mg/L in the highest TDS sample (12-AG-202). Bromide, a minor ion in groundwater chemistry, is less abundant than chloride, with median and mean concentration of 0.07 mg/L and 0.59 mg/L respectively. Iodide, a trace element, is by far the least abundant of the halogens. Iodide concentrations are highly elevated in the shallow groundwater of eastern Ontario relative to the rest of Southern Ontario (Figure 4.5) with median, mean and maximum concentrations of 130 μg/L, 100 μg/L and 6650 μg/L, respectively. All three halogens have maximum concentrations in the northeastern parts of the study area. Chloride and bromide concentrations are also elevated in the southwest, though not necessarily in the same samples. Chloride is concentrated in the central-north part of the study area immediately south of the urban part of the City of Ottawa, unlike bromide and iodide.

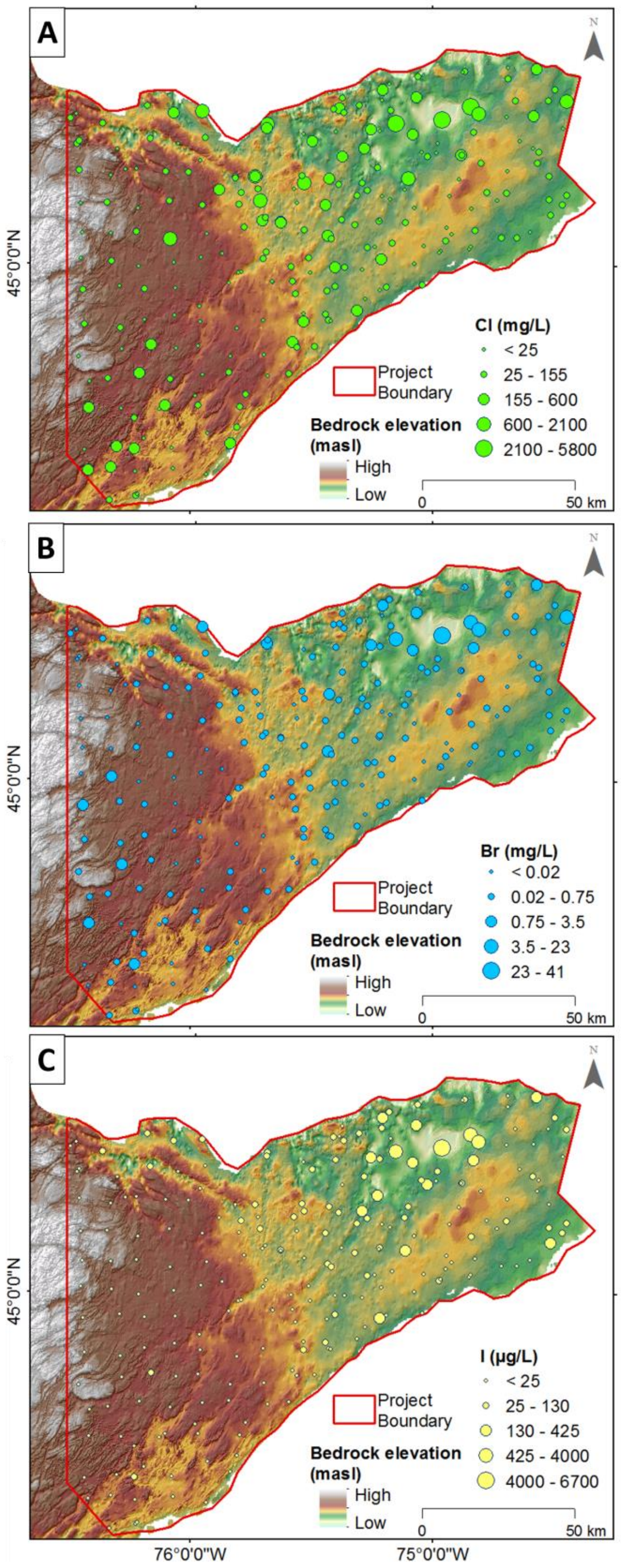

Figure 4.4 Spatial patterns of the halogens (A) chloride, (B) bromide and (C) iodide in eastern Ontario.

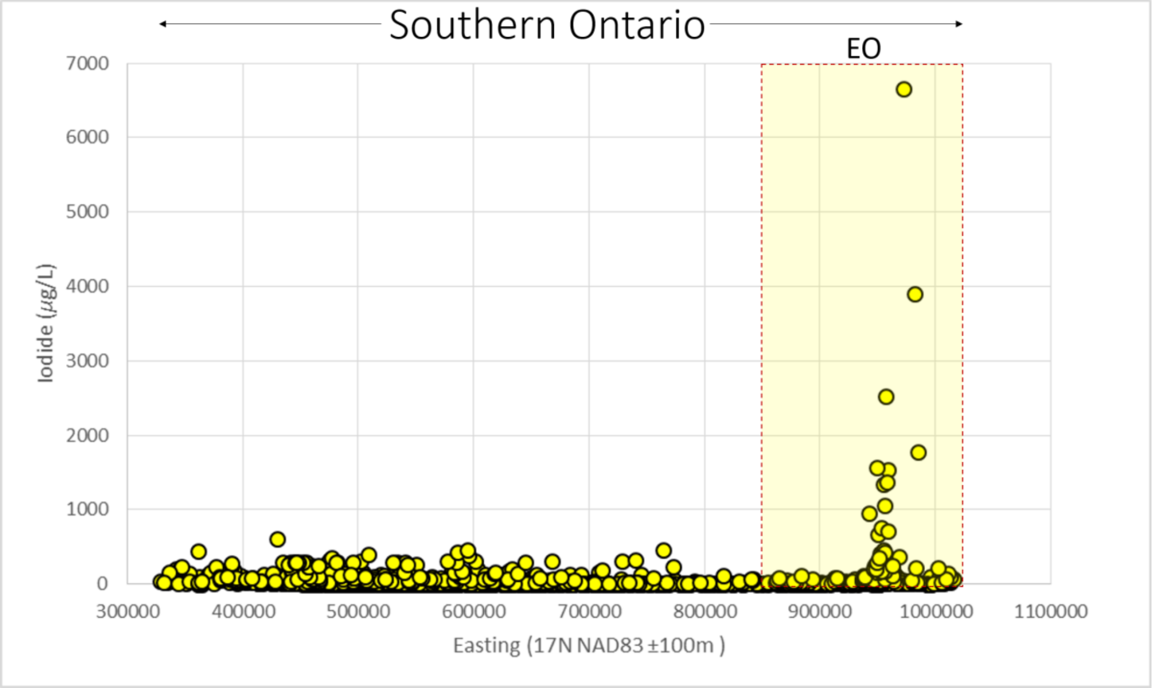

Figure 4.5 Iodide concentrations of all AGG samples across Southern Ontario (no bored or dug wells) from west (left) to east (right). Eastern Ontario (EO) has comparatively high levels of iodide (Hamilton 2015).

4.1.4 Major ions

Sodium (Na) and bicarbonate (HCO_3) are also elevated in eastern Ontario relative to the provincial average. The median, mean and maximum values for sodium are 36 mg/L, 114 mg/L and 2850 mg/L, respectively. Sodium is concentrated in the north and northeast (east of Ottawa), similar to some halogens. Bicarbonate concentrations are less positively skewed (closer to a normal distribution) than those of TDS, halogens and sodium, and have a median and mean of ~300 mg/L and 350 mg/L, respectively. The nature of the distribution of HCO_3 (less skewed) causes its spatial variation to be less distinct than TDS, halogens and Na. The highest concentrations occur in the northeast, as with all other parameters discussed so far. Sulphate (SO_4^{2-}) has mean, median and maximum concentrations of 53 mg/L, 37 mg/L and 610 mg/L, respectively. Sulphate is particularly elevated in several samples from the southwest (between Westport and Gananoque), though the western part of the study area generally has low concentrations. The eastern part of the study area has generally higher sulphate concentrations (particularly near Winchester, Chesterville, Finch), although very low concentrations are conspicuous in the northeast, centered on an area east of Ottawa, where halogens, Na, TDS and HCO_3 concentrations are highest.

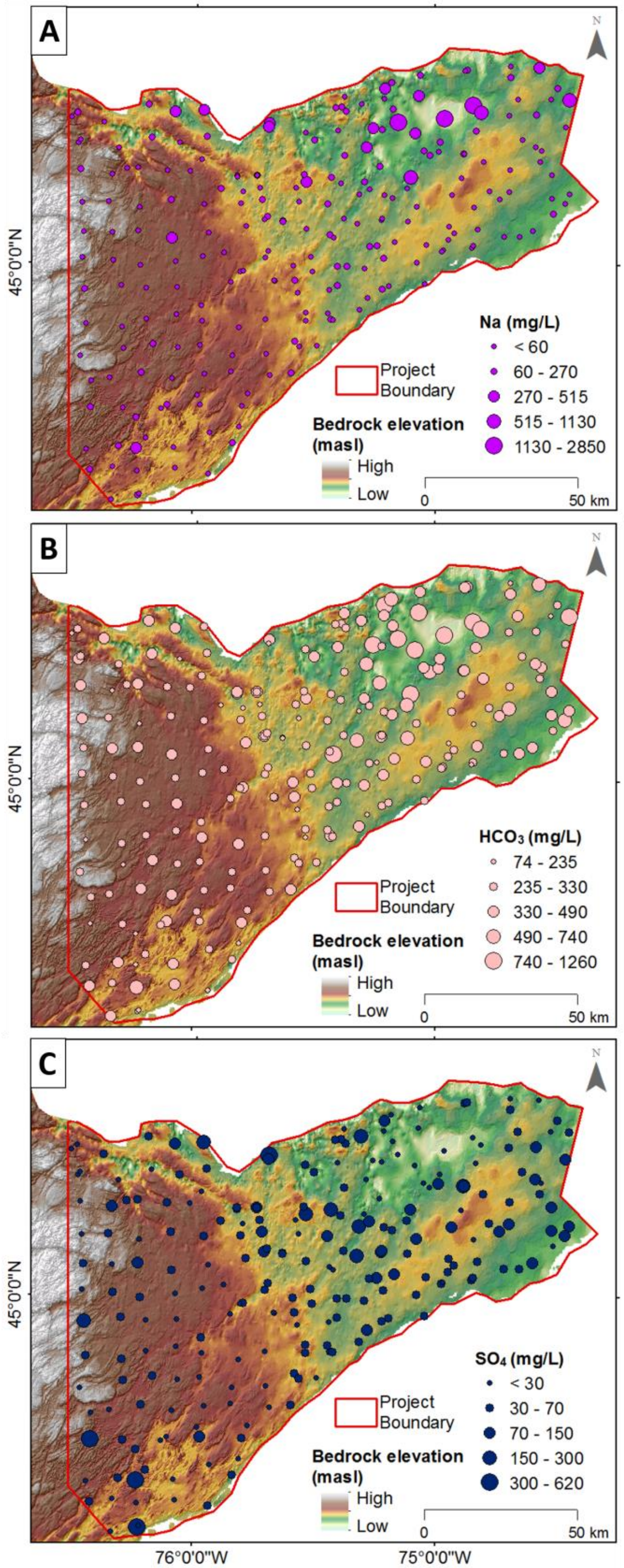

Figure 4.6 Spatial distributions of (A) sodium, (B) bicarbonate and (C) sulphate.

4.1.5 Isotopes

4.1.5.1 Stable isotopes

The oxygen and hydrogen isotopic compositions of groundwater (δ^{18}O and δ^{2}H) reflect the recharge source, as well as any other processes that have affected the isotopic system since recharge (Clark and Fritz 1997). Figure 4.7 displays the δ^{18}O and δ^{2}H relationship obtained for 234 groundwater samples analyzed in this study, relative to two local meteoric water lines (LMWL) known for the study area. The LMWLs were calculated based on isotopic data for monthly accumulations of precipitation collected at Ottawa from 1993 to 2007 (IAEA/WMO 2016) and a research station at Point Petre between 1996 and 2011 (unpublished data from FJ Longstaffe in 2014), without consideration of differences in precipitation amounts from month to month. The groundwater data mostly plot above the LMWLs, with 5 samples falling on the LMWLs at higher isotopic compositions. The equation of line of best fit for the groundwater data is $\boldsymbol{\delta^{2}H}=6.8\boldsymbol{\delta^{18}O} + 1.5$. The δ^{18}O displays a 4.6‰ range (from –13.1 to –8.5‰), while δ^{2}H displays a 32 ‰ range (from –88 to –55‰). The sample (14-AG-076) with the highest δ^{2}H and δ^{18}O stands alone on Figure 4.7. This urban sample from Ottawa could not be properly purged, and therefore it is not isotopically representative of aquifer chemistry and was not used in calculation of the regression line or the kriged maps (Figure 4.8).

The krig map of δ^{18}O reveals that the extreme west and southwest of the study area has more ^{18}O-enriched groundwater (mostly ranging from –11 to –10‰) than to the immediate east. A very sudden isotopic depletion of 1 to 2‰ is apparent in groundwater from this western area moving 10 – 20 km east (Figure 4.8A), across a line that roughly corresponds to the Precambrian-Paleozoic contact. From approximately this contact eastward in a NW-SE - trending area is a central region with depleted ^{18}O groundwater ranging mostly from –13 to –12‰. East of this ^{18}O is more enriched, particularly in a wedge-shaped region in the northeast that ranges in δ^{18}O mostly from –11 to –10‰.

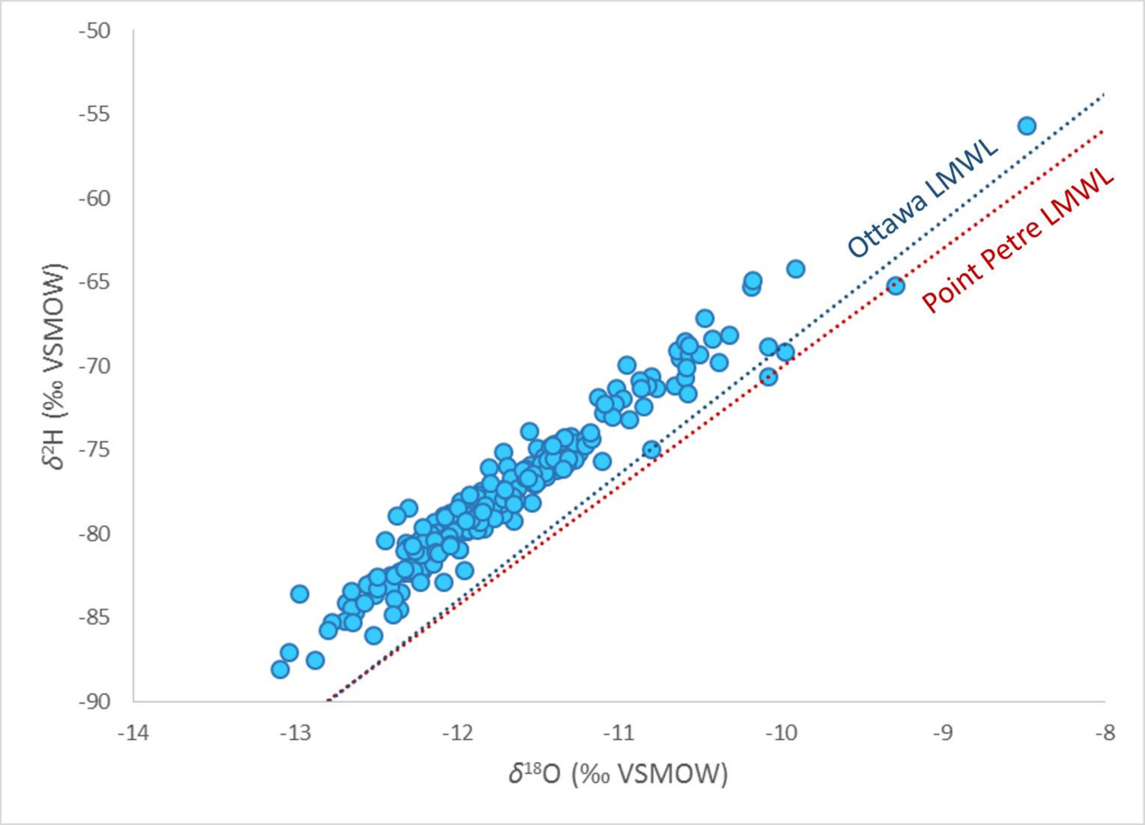

Figure 4.7 Relationship between the stable isotopes of water (δ^{18}O and δ^2H) for the eastern Ontario groundwater samples (blue points). The groundwater data fall above the Ottawa Local Meteoric Water Line (LMWL) (IAEA/WMO 2016) and Point Petre LMWL (unpublished data from FJ Longstaffe in 2014).

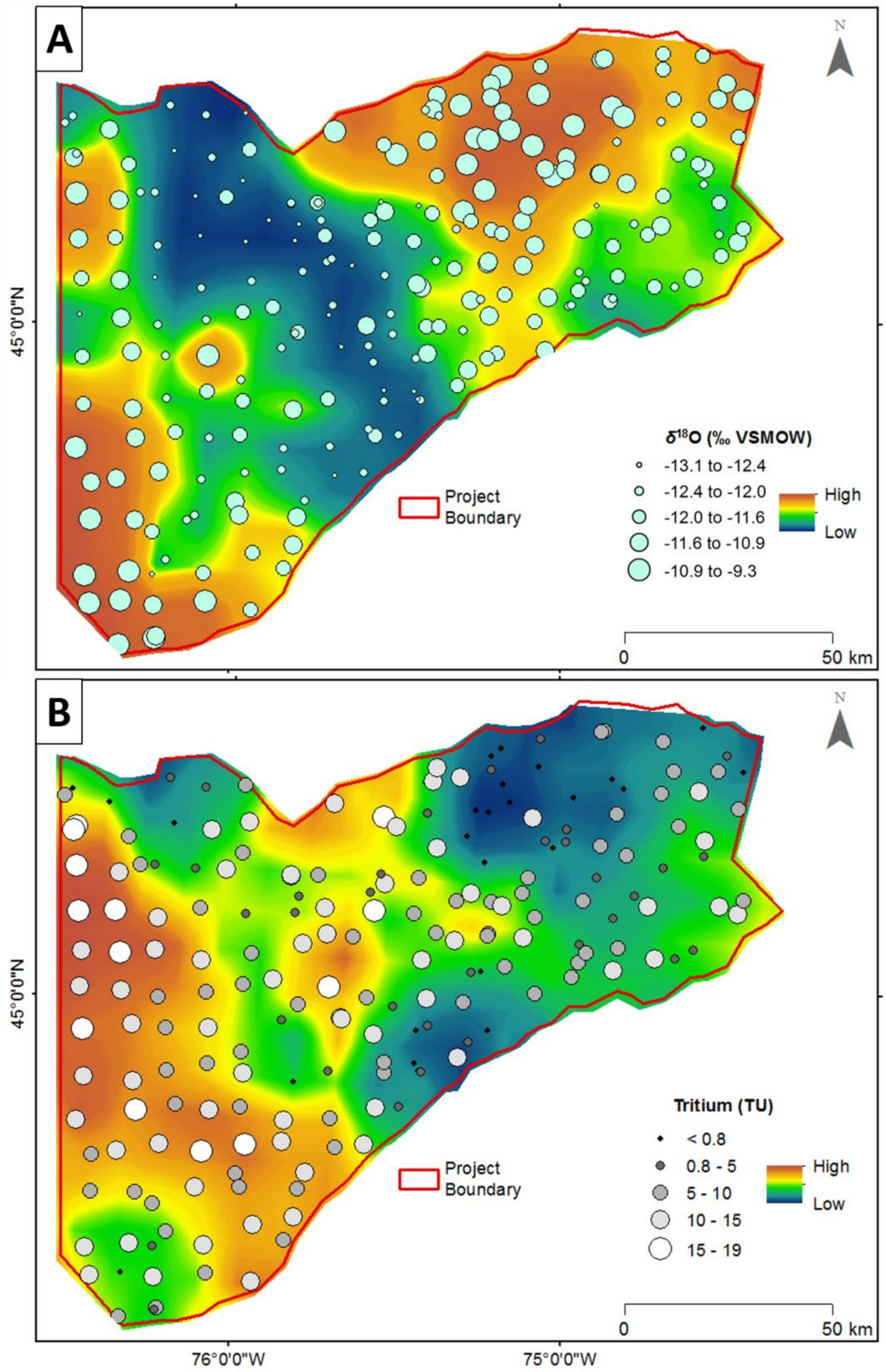

Figure 4.8 Discrete sample compositions and continuous kriged surfaces of (A) δ^{18}O and (B) tritium, showing spatial variation in eastern Ontario.

4.1.5.2 Tritium

The semi-quantitative use of tritium is to differentiate pre-1952 water from younger groundwater. The levels of tritium prior to nuclear testing in the 1950s and early 1960s were less than 5 TU. With a half-life of 12.26 y, water recharged before 1952 would have a modern-day tritium concentration close to or below the detection limit (0.8 TU) (Domenico and Schwartz 1990). Within the sample set, 231 of the 234 have data for tritium. Due to reasons stated above, sample 14-AG-076 has been removed, leaving 230 analyses. The mean and median concentrations are 7.8 TU and 8.1 TU respectively. Twenty-seven (27) samples lacked detectable tritium (detection limit = 0.8 TU), while the maximum concentration observed was 19.1 TU (Figure 4.9). The mean concentration in shallow bored and dug wells (N=30) sampled in eastern Ontario as part of the AGG program is 15.8 TU, which provides an estimate of the expected concentration of very recently infiltrated groundwater. The point concentrations and continuous kriged surface convey that there is higher tritium content in the west than in the east. Three regions have clusters of samples that lack detectable tritium: the northeast (east of Ottawa), the northwest (east of Arnprior), and the southcentral (between Winchester and Iroquois). The mid- to north-central portions of eastern Ontario show more local variation in tritium (between approximately Ottawa, Kemptville and Finch) (Figure 4.8B).

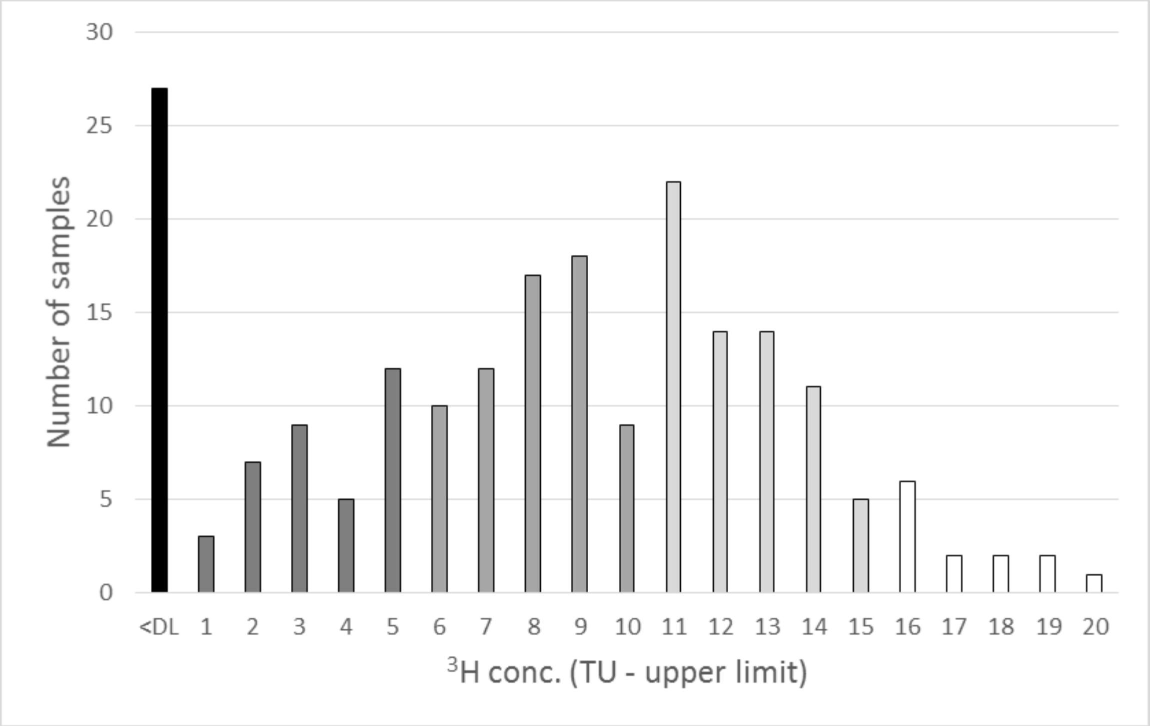

Figure 4.9 Frequency histogram of tritium concentration in eastern Ontario groundwater samples. The shades of the bars correspond to the symbols in Figure 4.8B.

4.2 Derivative results

4.2.1 Major ion chemistry

Piper (1944) provided a way of visualizing major ion chemistry using the relative proportions of the major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-}) within a water sample. The Piper diagram for eastern Ontario reveals a wide range of major ion chemistry and a diverse set of water facies (Figure 4.10). There is a general cation dominance of calcium and an anion dominance of bicarbonate in most samples. There is little sulphate compared to chloride and bicarbonate.

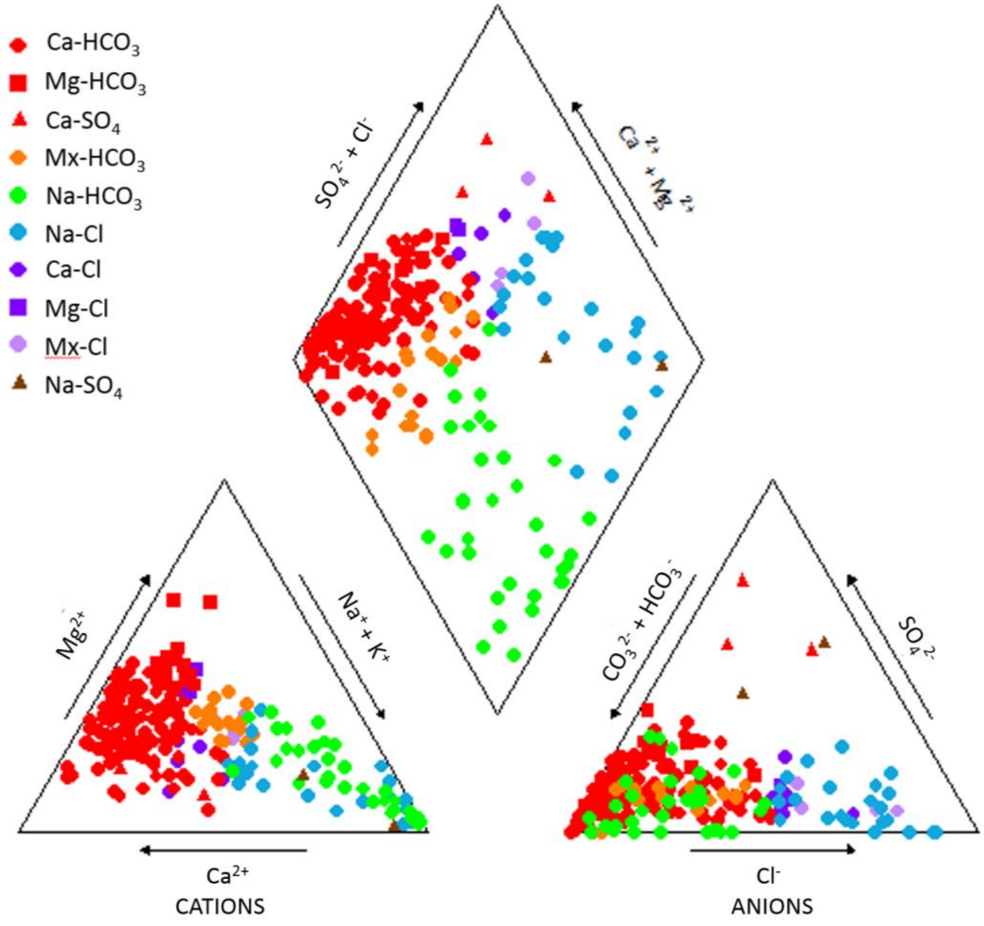

Figure 4.10 Piper plot showing the relative proportions of the major cations (left ternary plot), major anions (right ternary plot) and major ions (diamond plot). The diagram reveals diverse major ion chemistry in eastern Ontario. The symbols express the water type for each sample.

The Piper plot (Figure 4.10) can be used to visualize the relative proportions of major ions, but it does not define discrete categories. Therefore, the analytical results for the major ions were used to assign a “water type” to each sample in the dataset (Figure 4.10 symbols). Water types capture the nature of the major ion chemistry, which can then sometimes be associated with different origins and/or geochemical processes. Having discrete categories is also useful for graphical analysis and spatial mapping during analysis. The most predominant water type in eastern Ontario is Ca-HCO_3, comprising ~55% of the samples. It occurs in all parts of the study area, but is particularly dominant in the west and southeast. The next most common water type is Na-HCO_3, comprising ~15% of the samples. This water type is predominant in the northeast and also in two pockets in the northwest near Arnprior and in the southcentral region between Winchester and Cardinal. The third most common water type is Na-Cl, making up ~10% of the population. The Na-Cl water type is widely spread across eastern Ontario, but it is particularly pronounced in the northcentral and northeast. Eighteen (18) and 13 samples respectively make up the Mx-HCO_3 (Mx = mixed cations) and Mg-HCO_3 groups, which both occur in the eastern half of the study area (Figure 4.11). Ca-Cl, Ca-SO_4, Mg-Cl, Mx-Cl, and Na-SO_4 water types also occur in eastern Ontario, but each make up < 5% of the dataset (Table 4.1).

Table 4.1 Water-type frequency in eastern Ontario

Water Type	**N**	**%**
Ca-Cl	6	3
Ca-HCO_3	129	55
Ca-SO_4	3	1
Mg-Cl	2	1
Mg-HCO_3	13	6
Mx-Cl	4	2
Mx-HCO_3	18	8
Na-Cl	23	10
Na-HCO_3	34	15
Na-SO_4	2	1

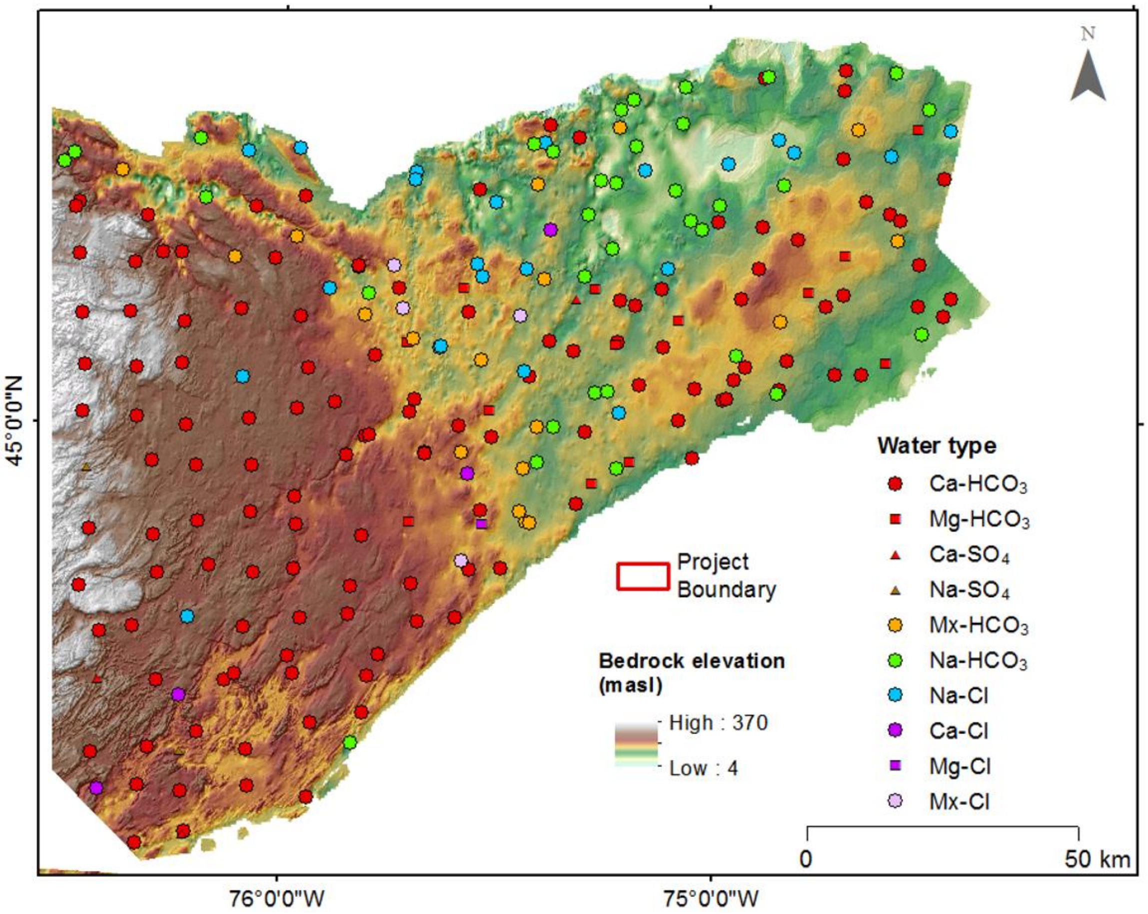

Figure 4.11 Spatial distribution of water types in eastern Ontario.

4.2.2 Saturation indices (SI)

All 234 samples are undersaturated with respect to anhydrite, gypsum and halite (Figure 4.12). Gypsum and anhydrite are most undersaturated in the northeast. Halite is most undersaturated in the west and the southeast, and closest to saturation in the northeast. Two-hundred and eighteen (218) samples are undersaturated with respect to calcite, with the greatest undersaturation occurring in the west and southwest of the study area. SI values for calcite become less negative in the east and the 16 oversaturated samples occur mostly in the northwest and scattered in the east. Two-hundred and thirteen (213) samples were undersaturated with respect to dolomite, with the lowest SI values occurring in the southwest. Dolomite SI values get closer to equilibrium towards the east and the 21 oversaturated samples cluster in the northwest and northeast of the study area.

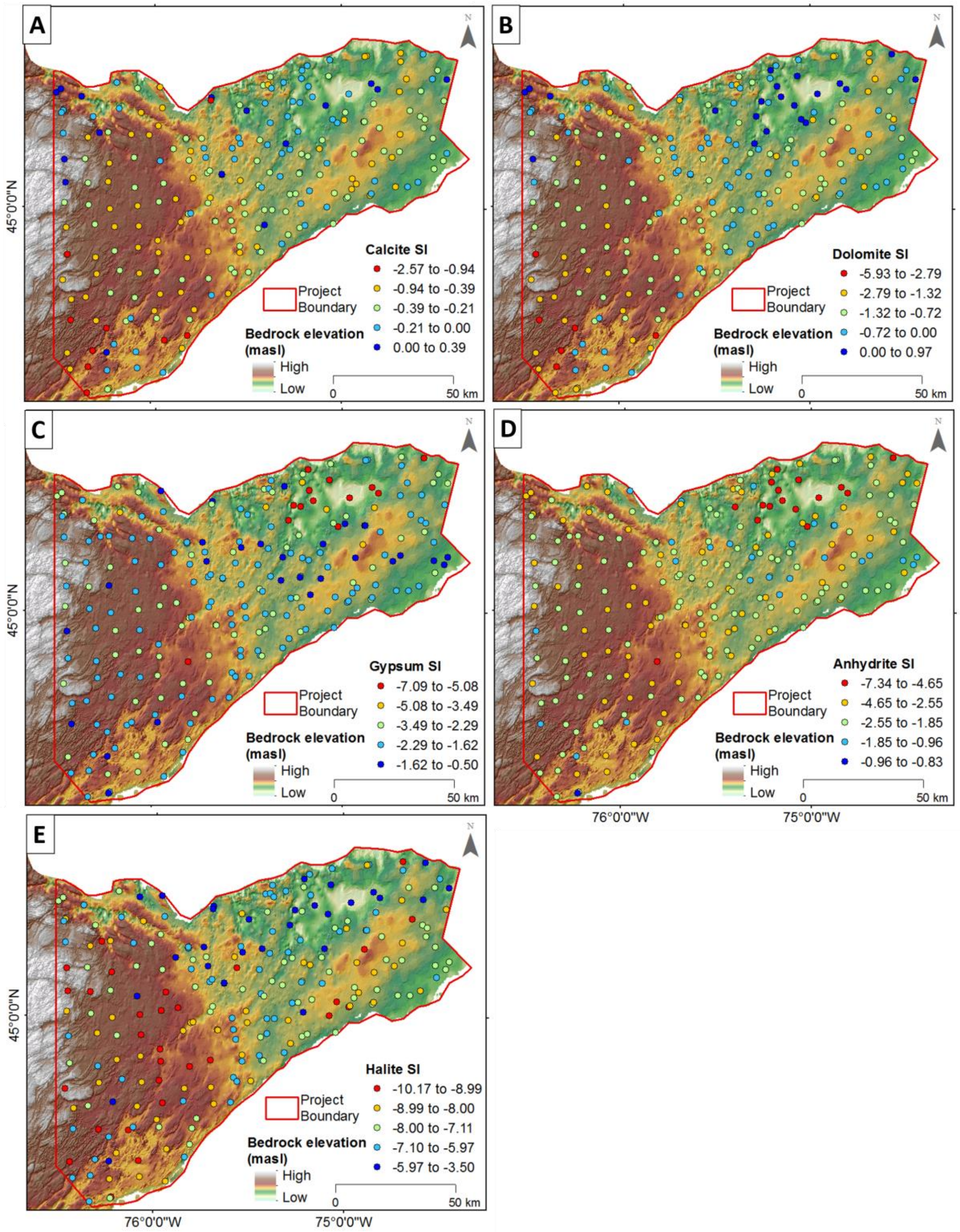

Figure 4.12 Spatial distribution of saturation indices (SI) for common minerals in southern Ontario: (A) calcite, (B) dolomite, (C) gypsum, (D) anhydrite, (E) halite.

4.2.3 Principal component analysis (PCA)

The first four principal components account for ~62% of variance within the data applied for PCA, with PC1, PC2, PC3 and PC4 accounting for 19 %, 17 %, 14% and 12% of variance, respectively. PC1 shows significant positive loadings (> 0.7) for Ca, CO_2 and Mg, and significant negative loadings (< -0.7) for pH and F^- (Figure 4.14). Positive PC1 scores are strong in some samples in the southwest, south-central and southeast. Samples with strong negative scores mostly cluster in three groups along the north of the study area from west to east near Arnprior/Dunrobin, Rockland/Casselman and Hawkesbury; and one in the southcentral portion of the study area between Winchester and Cardinal. Positive and negative scores for PC1 are often found in the same areas. PC2 shows significant positive loadings for Se, Br^-, Cl^- and Na. Samples with positive scores for PC2 mostly exist in a triangular wedge in the east (from Pontiac to Prescott to L’Original), and in a smaller region in the west/southwest. Strong negative scores for PC2 are regionally dominant in the west (outside the positive zone mentioned) and in the southeast (near Vankleek Hill, Maxville and south of Finch). PC3 has significant positive loadings for HCO_3, NH_3+NH_4^+, DOC and Ba. Samples with strongly positive scores for PC3 cluster in the northeast (between Winchester, St. Isidore and Rockland), while more negative scores exist just south, east and west of that area and in the southwest. Apart from the southwest, the west tends to show neutrality (scores close to zero) with respect to PC3. PC4 has significant positive loadings for Sr and Li. Samples with positive PC4 scores are regionally prevalent in the east, whereas strongly negative scores cluster in the west, particularly around Smith’s Falls-Athens (Figure 4.15).

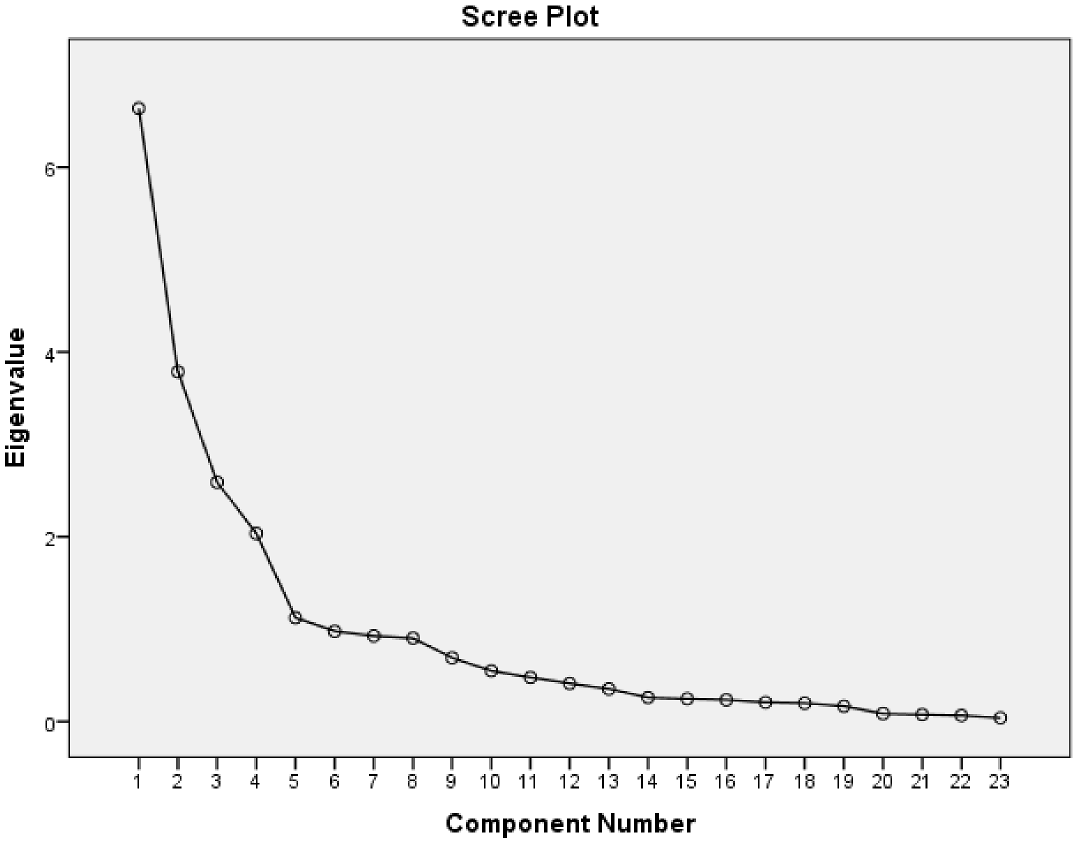

Figure 4.13 Scree plot displaying the eigenvalues versus principal component scores. Using the Cattell method (Cattell 1966), the first 4 components are retained as significant, since the slope changes drastically at component 5, showing that at that point, components account for less variability and are therefore less significant.

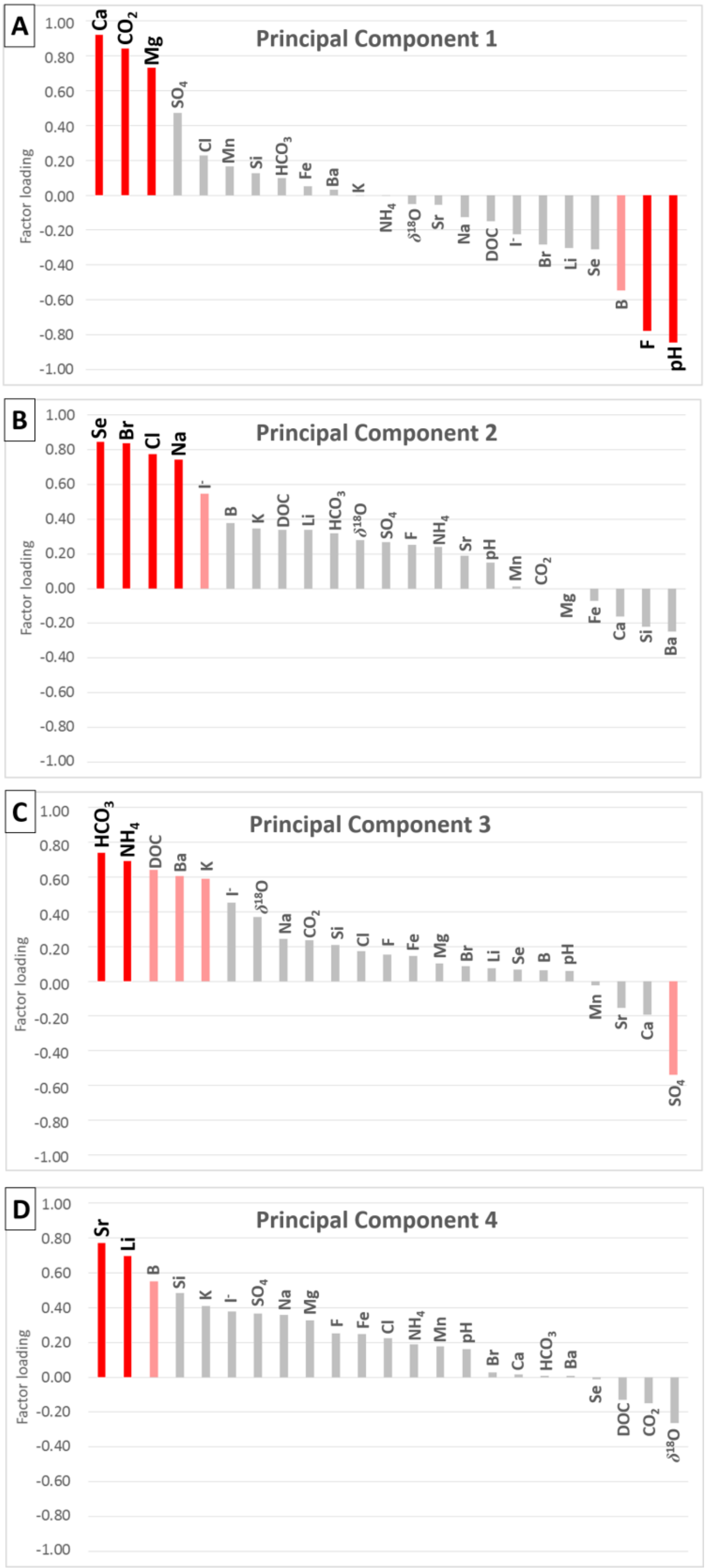

Figure 4.14 Factor loadings for PC (A)1, (B)2, (C)3, (D)4. Bright red signifies strong loadings (>|0.7|), softer red signifies moderate loadings (|0.5 -0.7|), grey are <|0.5|.

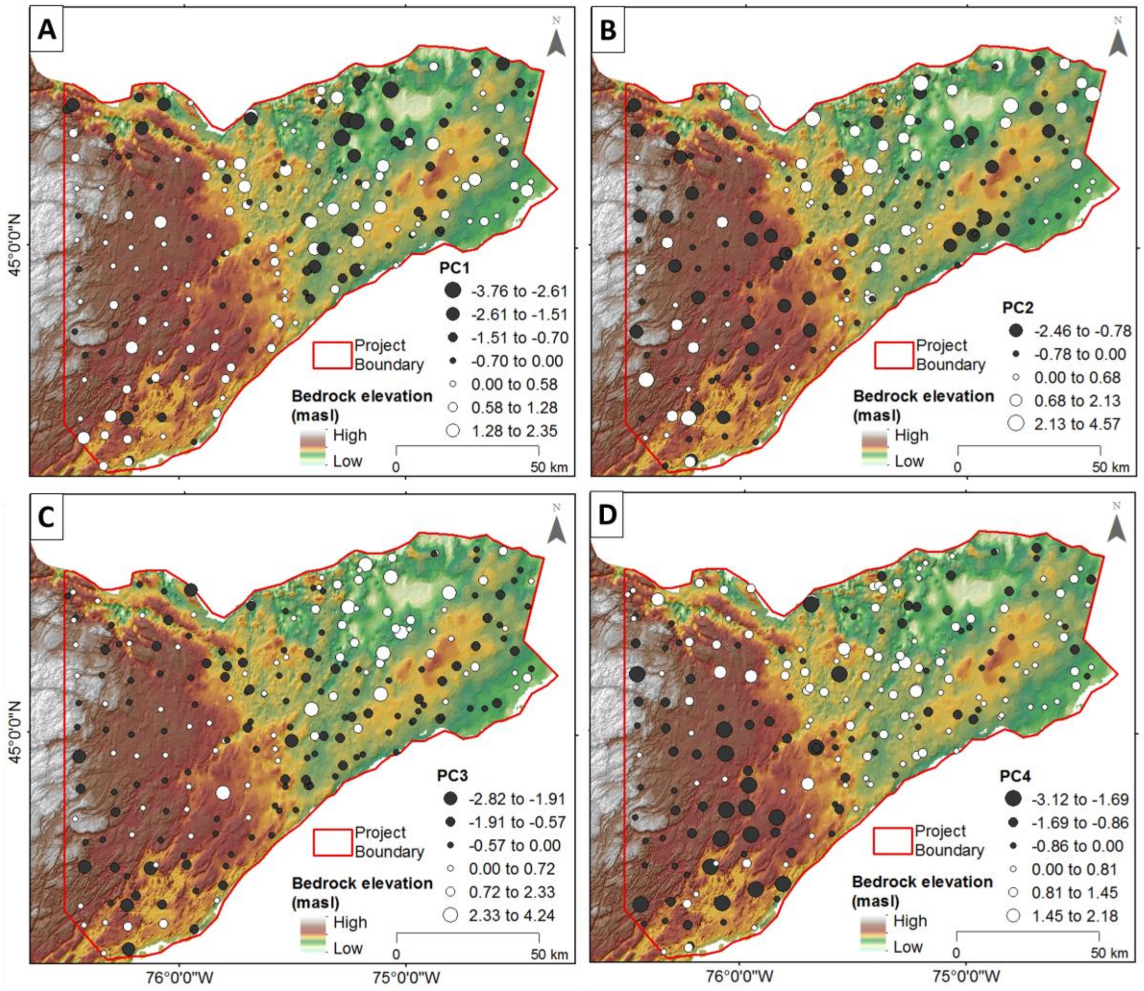

Figure 4.15 Principal Component scores for (A) PC1, (B) PC2,(C) PC3, (D) PC4. Black symbols represent negative scores for the PC, whereas white symbols represent positive scores. Symbol size indicates the relative magnitude of positive or negative loading for each PC.

Chapter 5

5 Discussion

The following discussion aims to identify the main geochemical processes that have produced the chemical results presented in Chapter 4. The geochemical processes are assessed along with the physical components of the environment in order to determine the ultimate *controls* on groundwater chemistry in eastern Ontario at the regional scale. Many more local-scale processes affecting groundwater are not discussed, as this work is based on a *regional-scale* sampling program.

5.1 Principal Components

Principal Components Analysis (PCA) components 1, 2 and 3 were given descriptive names according to interpretation of their strongly loading parameters. Components 4 and 5 have proven to be less useful for interpretation and therefore remain unnamed. **Component 1** loads strongly and positively for calcium (Ca), dissolved carbon dioxide (CO_2) and magnesium (Mg), and strongly and negatively for pH and fluoride (F^-). It also loads negatively for boron (B) (-0.55). Cloutier et al. (2008) reported a similar component, which they described as “Hardness”. In eastern Ontario, this is an appropriate name for PC1 because of the strong positive loadings for Ca and Mg, which control hardness, and because of the strong negative loadings for F^-, which is most elevated in Ca-depleted, soft water (Ozsvath 2009) and lowest in hard water due to depressed fluorite solubility. Positive CO_2 and negative pH can be attributed to acidic recharge, which dissolves Ca- and Mg-containing minerals and will be discussed further later.

Component 2 has only strong positive loadings, with some minor negative loadings. The positive loadings (>0.6) are selenium (Se), bromide (Br^-), chloride (Cl^-) and sodium (Na), with I^- also elevated (0.55). Na, Cl^- and Br^- occur in significant concentrations in seawater and the spatial patterns of PC2 (Figure 4.15B) align well with patterns of total dissolved solids (TDS) (Figure 4.3B). PC2 is therefore named “Salinity.” Cloutier et al. (2008) had strong loadings of Na and Cl^- for their PC1, which they also named “salinity”; Se was not analyzed in their study. Selenium loads strongly because it correlates well in the dataset with the other high-loading parameters including Br^-, Cl^-, Na, and I^-.

Component 3 has strong positive loadings (>0.6) that correspond to bicarbonate (HCO_3), ammonium (NH_4), dissolved organic carbon (DOC) and barium (Ba), while potassium is also positively related (0.59). This component is named "Organics" since DOC is one of the parameters and HCO_3 and NH_3 can be products of organic decay. Ba is related to sulphate reduction, and is discussed later. The strongest negative loading is SO_4^{2-} (-0.54), which is also consistent with sulphate reduction.

Component 4 has strong positive loadings for strontium (Sr) and lithium (Li), with boron (B) elevated as well (0.55), but does not show distinct patterns related to geology or physiography and is not considered further here.

Table 5.1 Important characteristics of principal component scores

	PC1	**PC2**	**PC3**
Descriptive name	Hardness	Salinity	Organics
Positive loadings, >0.6	Ca, CO_2, Mg	Se, Br^-, Cl^-, Na	HCO_3, NH_3, DOC, Ba
Negative loadings, <-0.6	pH, F^-	None	None

5.2 Regional Processes

The “regional processes” discussed in this section were identified by combining PCA, water facies, individual chemical parameters and related geological features to interpret large-scale patterns. The most significant processes recognized are recharge, ion exchange, salinization and organic degradation.

5.2.1 Process 1: Recharge

Preferential groundwater recharge in geographically discreet areas influences groundwater chemistry in eastern Ontario at the regional scale. These are areas of high potentiometric elevations and appear to have relatively high rates of infiltration owing to the hydraulic properties of the surficial material. The characteristic geochemical response indicative of recharge includes prevalence of the Ca-HCO_3 water-type, relatively acidic pH, low TDS and negative loadings for Salinity (PC2). Elevated tritium and oxidation-reduction potential of the groundwater are additional indicators of recharge.

5.2.1.1 Ca-HCO_3 water

The Ca-HCO_3 water type makes up 55% of the dataset. In similar groundwater studies, it commonly comprises fresh, modern, meteoric water, and usually dominates unconfined recharge areas (*e.g.,* Cloutier et al. 2010; Blanchette et al. 2013; Montcoudiol et al. 2015). In eastern Ontario, the Ca-HCO_3 water type occurs across the study area except in the northeastern bedrock depression. There are two areas where this water type is particularly prominent (Figure 5.1).

The first Ca-HCO_3 zone covers a large elevated region in the west part of the study area, which approximately corresponds to the Smith Falls Limestone Plain and Precambrian Highlands where drift cover is thin and discontinuous. The Cataraqui and Mississippi-Rideau source protection reports have noted that rapid recharge and aquifer vulnerability occur in the bare limestone plain (CRCA 2011; MVCA 2011). Ca-HCO_3 is largely dominant in the very southwest of the study area, but Ca-Cl and Na-SO_4 water types also contribute to the geochemical signal.

The second Ca-HCO_3 region occurs over a smaller, elevated area in the east, which encompasses a variety of geologic environments. This region includes part of the Glengarry Till Plain and, in the west, an area where till and Paleozoic bedrock knobs crop out of the glaciomarine clay aquitard. The portion corresponding to the Glengarry Till Plain is elevated in both surface and bedrock topography. However the western edge of the Ca-HCO_3 region shows only elevated topography and/or bedrock topography at the till and bedrock knobs. The Glengarry till ridge has been identified as an important recharge zone because of its large areal extent and higher permeability relative to the surrounding low-permeability glaciomarine clays (Charron 1978). Similarly, gaps in the presence of glaciomarine clay in the western area may allow local scale recharge to the interface aquifer that extends into surrounding areas overlain by the clay aquitard (Charron 1978). Groundwater movement, both generally and in the study area, mimics topography, flowing from higher elevation to lower elevation (Schwartz and Zhang 2003; SNCA 2012; CRCA 2011; MVCA 2011); therefore elevated regions of Ca-HCO_3-dominance likely correspond to recharge areas.

Conversely, where glaciomarine deposits exist, the Ca-HCO_3 water type is comparatively uncommon. Such deposits exist at lower surface and bedrock elevation and act as aquitards, confining the bedrock aquifer. The Edwardsburgh (marine) sand plain was stated (Barnes 2009) to be a recharge region, but the bedrock aquifer does not show a particular dominance of Ca-HCO_3 or elevated tritium contents, suggesting it may not allow recharge to the regional system.

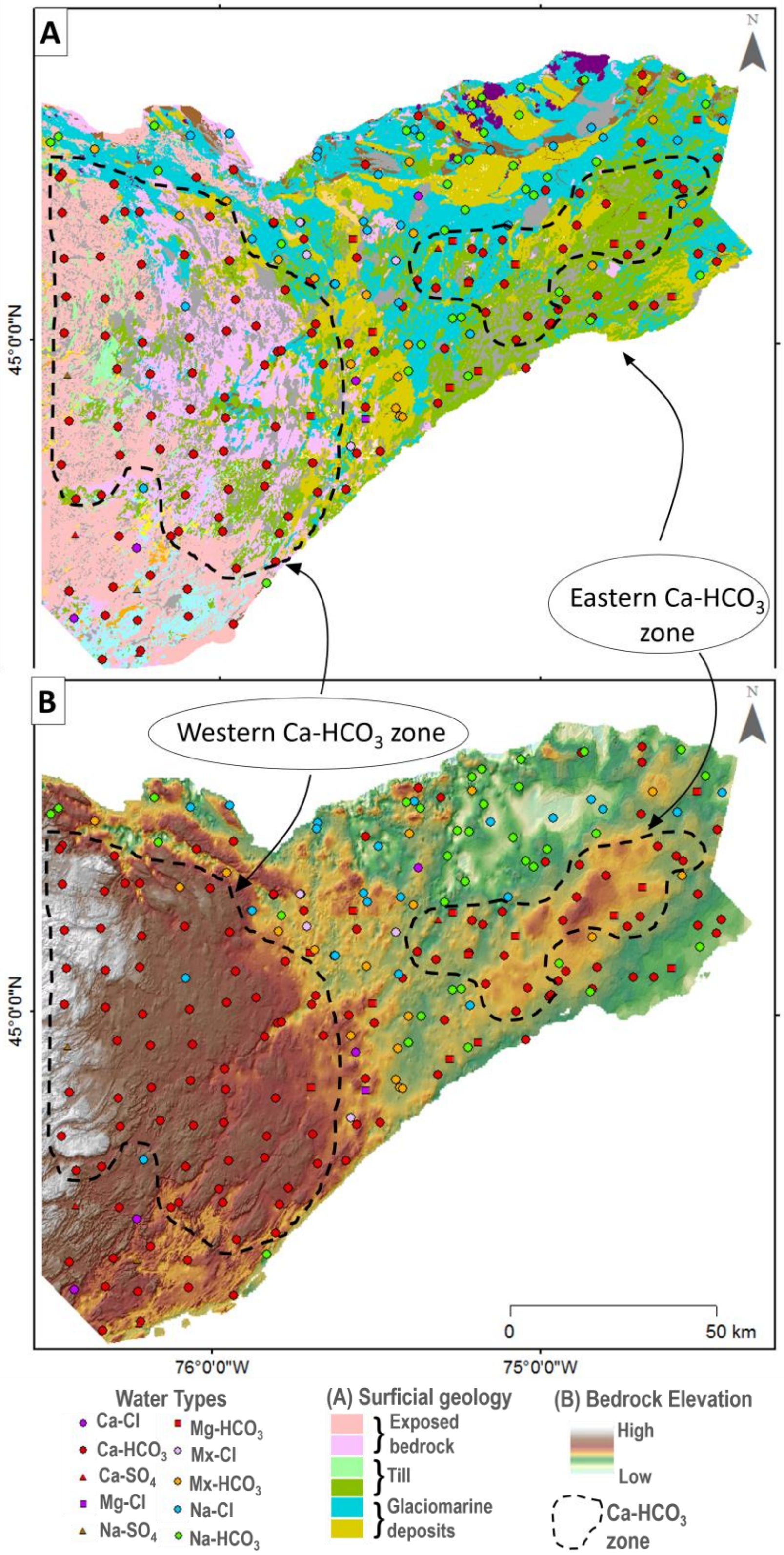

Figure 5.1 Ca-HCO$_3$ dominance is related to (A) surficial geology and (B) bedrock topography. A more detailed legend for surficial geology can be found in Figure 2.9.

5.2.1.2 Tritium

The tritium concentration in groundwater can be used to confirm modern recharge in the Ca-HCO_3 zones. High tritium is common in the west of the study area, coincident with elevated topography. The western Ca-HCO_3 zone correlates mostly with this high tritium area, supporting the idea that modern recharge controls water chemistry (Figure 5.2). The average detectable tritium concentration is 10.7 TU and was below detection in one sample. There is less tritium in the eastern Ca-HCO_3 zone, averaging at 8.4 TU indicating an older groundwater age, likely due to the presence of expansive overburden. Though not pronounced in kriged surface (Figure 5.2), this zone has more tritium than groundwater in surrounding areas, indicating preferential recharge. At the western edge of the eastern Ca-HCO_3 zone are a group of Ca-HCO_3, Mg-HCO_3 and Ca-SO_4 samples that have more elevated tritium contents compared to surroundings. These fall in the center of the South Nation watershed and have high sulphate contents compared to surrounding regions (Figure 4.6C). As discussed, enhanced infiltration occurs in this area via exposed till and bedrock knobs, which allow recharge beneath the glaciomarine clays. Buried eskers, fans and grounding-line moraine may also contribute to enhanced infiltration in this area (Cummings et al. 2011).

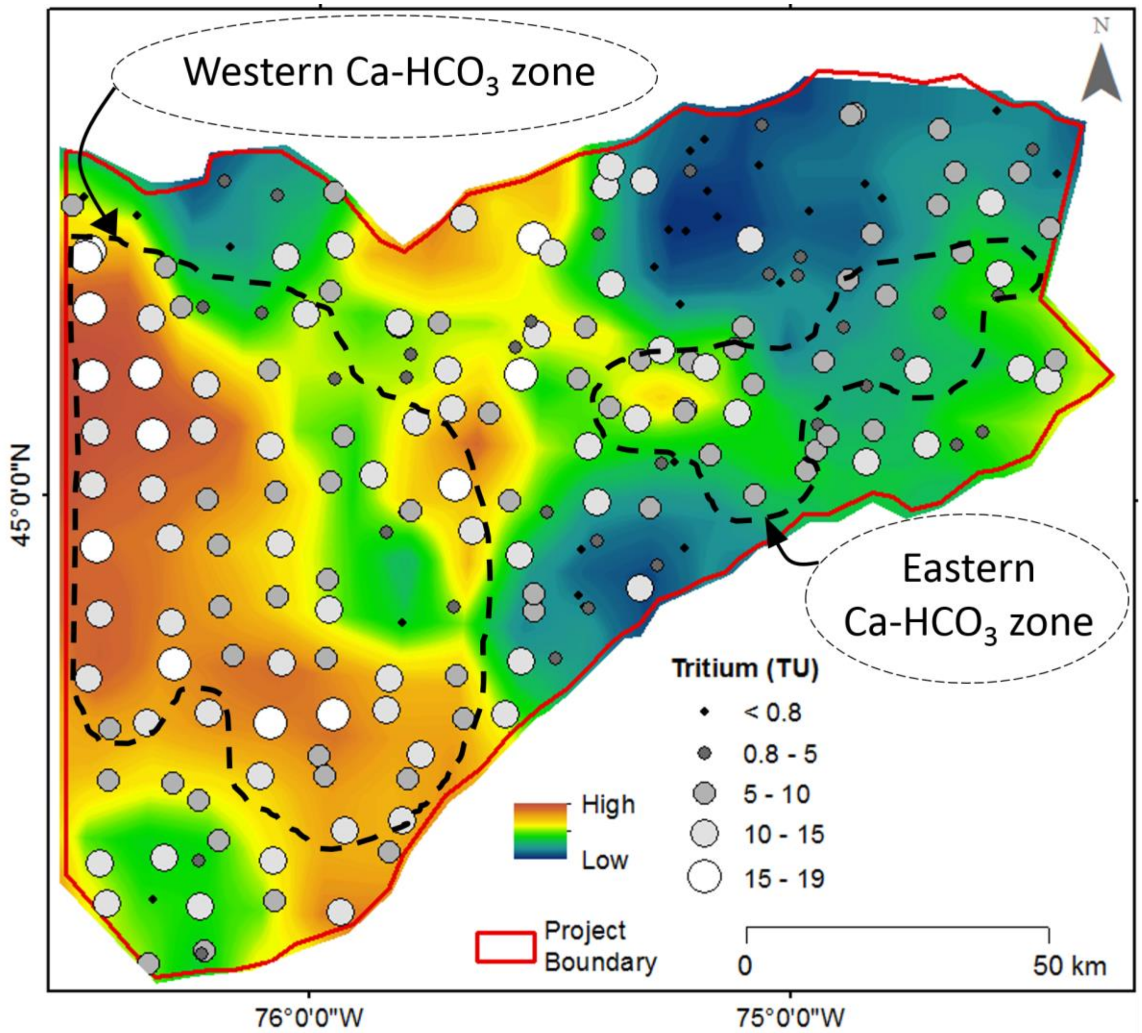

Figure 5.2 Ca-HCO$_3$ zones (black dashed outlines) relate to tritium levels. The western Ca-HCO$_3$ zone aligns with regionally high tritium.

5.2.1.3 Recharge geochemistry

The dominance of Ca and HCO$_3$ in these groundwaters can be explained by the dissolution of Ca-rich minerals. In the western Ca-HCO$_3$ zone, calcite and dolomite (CaCO$_3$ and CaMg(CO$_3$)$_2$) are common in the Smith Falls Limestone Plain and metacarbonates of the Canadian Shield. The Ca-bearing Precambrian silicates may include pyroxene, amphibole and calcic plagioclase (*e.g.,* anorthite). Apart from the carbonate minerals, Montcoudiol et al. (2015) found only anorthite (CaAl$_2$Si$_2$O$_8$) to be significant in their study of groundwater evolution in a Precambrian setting. This was attributed to relatively high solubility of anorthite; therefore it is considered another potential Ca source in the west of eastern Ontario where the Shield crops out. In the eastern Ca-HCO_3 zone, the bedrock units and overlying till are also carbonate-rich (Cummings et al. 2011).

Rainwater dissolves CO_2, creating carbonic acid and a slightly acidic pH, which drives mineral dissolution during infiltration in recharge areas. Additionally, respiration in soils increases the partial pressure of carbon dioxide (pCO_2) which further drives dissolution. Dissolution of calcite, dolomite and anorthite occurs in the following reactions (equations 5.1, 5.2, 5.3 respectively):

$$\mathbf{CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3} \qquad \textbf{Equation 5.1}$$

$$\mathbf{CaMg(CO_3)_2 + 2H_2O + 2CO_{2(g)} \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-} \qquad \textbf{Equation 5.2}$$

$$\mathbf{2CO_2 + 3H_2O + CaAl_2Si_2O_8 \rightarrow Ca^{2+} + 2HCO_3^- + SiAl_2O_5(OH)_4} \qquad \textbf{Equation 5.3}$$

The pH in the Ca-HCO_3 regions is low compared to areas of eastern Ontario where other water types are common. The dissolution reactions consume H^+, which buffers the acidity of infiltrating meteoric water.

Modelling of saturation indices in PHREEQC showed that almost all groundwater samples from the two Ca-HCO_3-dominant regions are undersaturated with respect to calcite and dolomite (Figure 4.12). Cloutier et al. (2006) analyzed δ^{13}C of DIC in the nearby Basses-Laurentides aquifer (southwest Québec) and found that, in recharge areas, dissolution of marine carbonates was adding bicarbonate to the groundwater. The majority of groundwater samples in eastern Ontario, however, are undersaturated with respect to calcite and dolomite and are exposed to these phases, without Ca-HCO_3 being the dominant water type. Therefore, dissolution of Ca-rich minerals cannot alone dictate the water type. The low Salinity (PC2) and TDS in the Ca-HCO_3 regions, suggest that other processes overprint Ca-rich mineral dissolution under different geologic conditions and over longer residency. The Ca-HCO_3 zones have a low proportion of glaciomarine clays, which can cause evolution of the water types through ion exchange and diffusion/expulsion (see section 5.2.3) and through attenuating recharge of fresh water.

Negative loadings for Salinity (*i.e.*, positive “freshness”), low TDS, elevated tritium contents and elevated ORP in the western Ca-HCO_3 zone all confirm active recharge, facilitated by the thin and discontinuous nature of the drift. In the eastern Ca-HCO_3 zone the reducing conditions and lower tritium contents indicate infiltration rates are slower. Thicker drift and recharge through till likely impedes the rate but the results are still consistent with regional recharge.

5.2.2 Process 2: Ion exchange

Natural water softening is an important chemical process affecting regional groundwater chemistry in eastern Ontario. Softening is the removal of divalent and trivalent cations from solution, and their replacement by monovalent species, thus reducing the *hardness* of a solution. Hardness is defined as the sum of dissolved calcium and magnesium in a solution (USGS 2016).

Softening occurs through the process of ion exchange. In eastern Ontario, ion exchange appears to occur through removal of Ca^{2+} and its replacement by Na^+. The reaction can be modelled as:

$$\mathbf{Ca^{2+} + 2Na_{ad} \rightarrow Ca_{ad} + 2Na^{+}} \qquad \textbf{Equation 5.4}$$

Two moles of Na^+ adsorbed (ad) onto a negatively charged surface are replaced by one mole of dissolved Ca^{2+}, causing the sodium to desorb into solution. Because of their divalent charge, Ca^{2+} and Mg^{2+} have a higher affinity for adsorption than monovalent Na^+ and K^+ (Drever 1988). This, along with concentration differences, works to remove Ca^{2+} and Mg^{2+} from groundwater and replace them with Na^+, thereby causing groundwater evolution from Ca-HCO_3 (and Mg-HCO_3) water type to Na-HCO_3 water type. In much of eastern Ontario, the Champlain Sea incursion is a potential source of Na on sorption surfaces.

Evidence for ion exchange in eastern Ontario is apparent in the PC1 (Hardness) where certain areas show strong negative scoring. Strong negative affinity for *hardness* can be thought of as *softness*. The negative scores result from low Ca and Mg concentrations, high F^- concentration, low CO_2, and/or elevated pH. Spatial representation of PC1 scoring and the water types reveal that negative scores for PC1 cluster strongly in the same three zones where the Na-HCO$_3$ water type predominates (Figure 5.3). It is commonly concluded that the Na-HCO$_3$ water type evolves from the Ca-HCO$_3$ water type by ion exchange (*e.g.*, Cloutier et al. 2010; Blanchette et al. 2013; Montcoudiol et al. 2015).

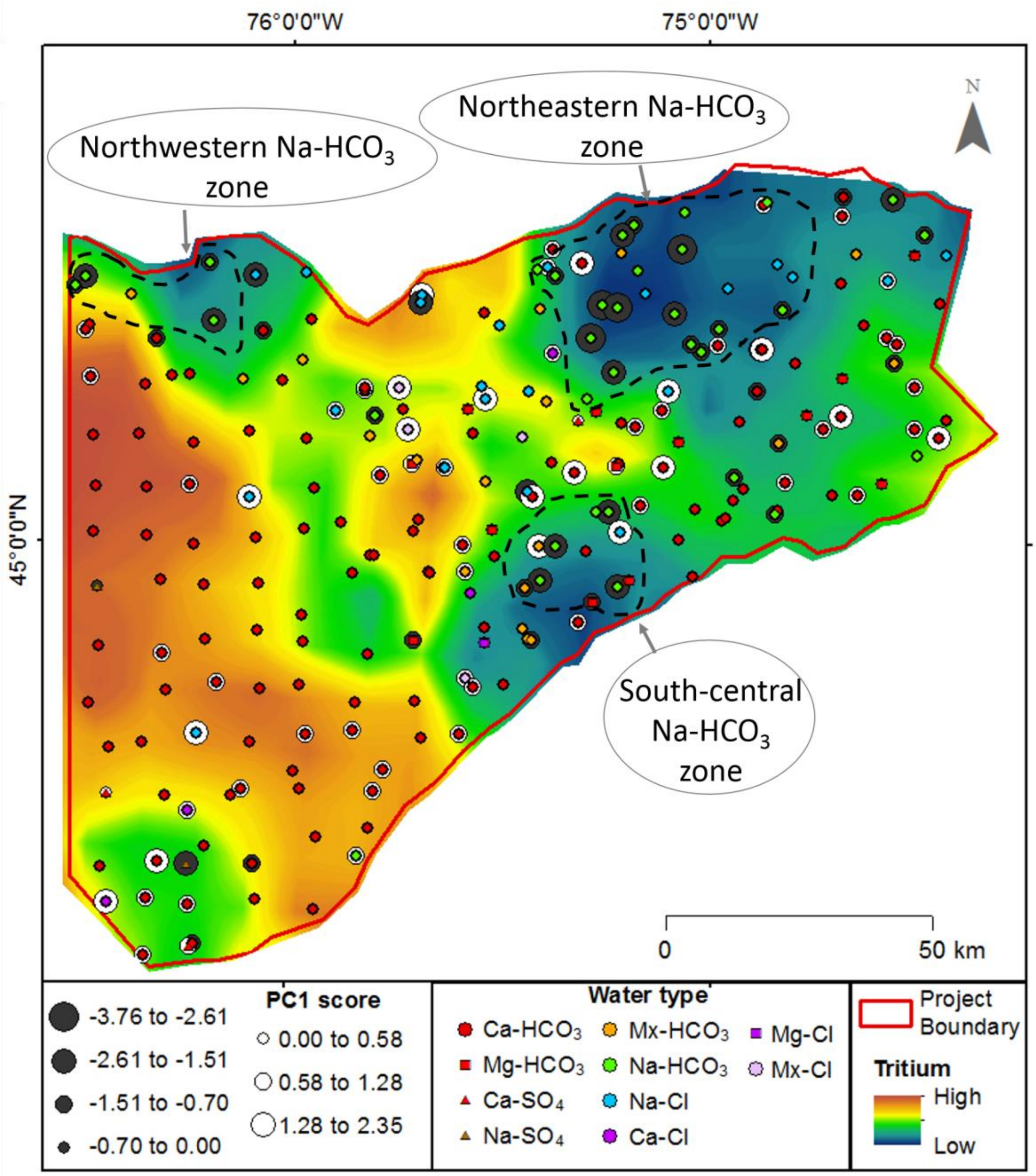

Figure 5.3 The Na-HCO$_3$ water type dominates in 3 areas (circled, labelled). These areas also exhibit strong negative scores for Hardness (PC1) and low tritium.

In addition to PC1 and the presence of Na-HCO_3 water, the inverse relationship between Na and Ca in the Na-HCO_3 water type (Figure 5.4A) is characteristic of waters affected by the ion exchange reaction. This affects the carbonate system, which is the governing control on pH in most natural waters (Drever 1988). Combining equation 5.1 and 5.4:

$$\mathbf{CaCO_3 + 2Na_{ad} + CO_2 + H_2O \rightarrow 2Na + 2HCO_3^- + Ca_{ad}} \qquad \textbf{Equation 5.5}$$

$NaHCO_3$ has a far higher solubility than $CaCO_3$ and therefore bicarbonate increases as this reaction progresses; and because the bicarbonate anion is a weak base, pH also rises. With the further input of HCO_3 by calcite dissolution, or additional input from organic breakdown, the pH continually rises. This lowers the solubility of calcite still further and puts additional downward influence on the concentration of calcium in equilibrium with calcite. The Na-HCO_3 water type has an average pH of 7.94, which is the highest measured for all of the water types (Figure 5.4B).

Softening increases the solubility of fluorite (CaF_2) as follows:

$$\mathbf{CaF_2 \rightarrow Ca^{2+} + 2F^-} \qquad \textbf{Equation 5.6}$$

And combining equation 5.1 and 5.6 yields:

$$\mathbf{CaF_2 + 2Na_{ad} \rightarrow 2Na^+ + 2F^- + Ca_{ad}} \qquad \textbf{Equation 5.7}$$

NaF is far more soluble than fluorite and therefore as the reaction (Equation 5.7) progresses, the result is increased fluorite dissolution. This is demonstrated, in eastern Ontario, by the negative relationship between Ca and F^- concentrations (PC1; Figure 5.4C). Fluorite has been identified in calcite veins in the Ottawa-Bonnechère Graben (Carignan et al. 1997) and may also derive from fluoroapatite ($Ca_5(PO_4)_3F$) in phosphate minerals. Phosphate lags have been reported in the uppermost Lindsay Formation (Johnson et al. 1992). Additionally, fluoride retention on charged surfaces is pH-dependent, with displacement occurring at elevated pH due to electrostatic forces and displacement by OH^- (Cronin et al. 2000). The Na-HCO_3 group exhibits the highest average F^- concentration of all the water types (1.2 mg/L). Nine samples exceed the Ontario Drinking Water Standards (ODWS) health standard of 1.5 mg/L.

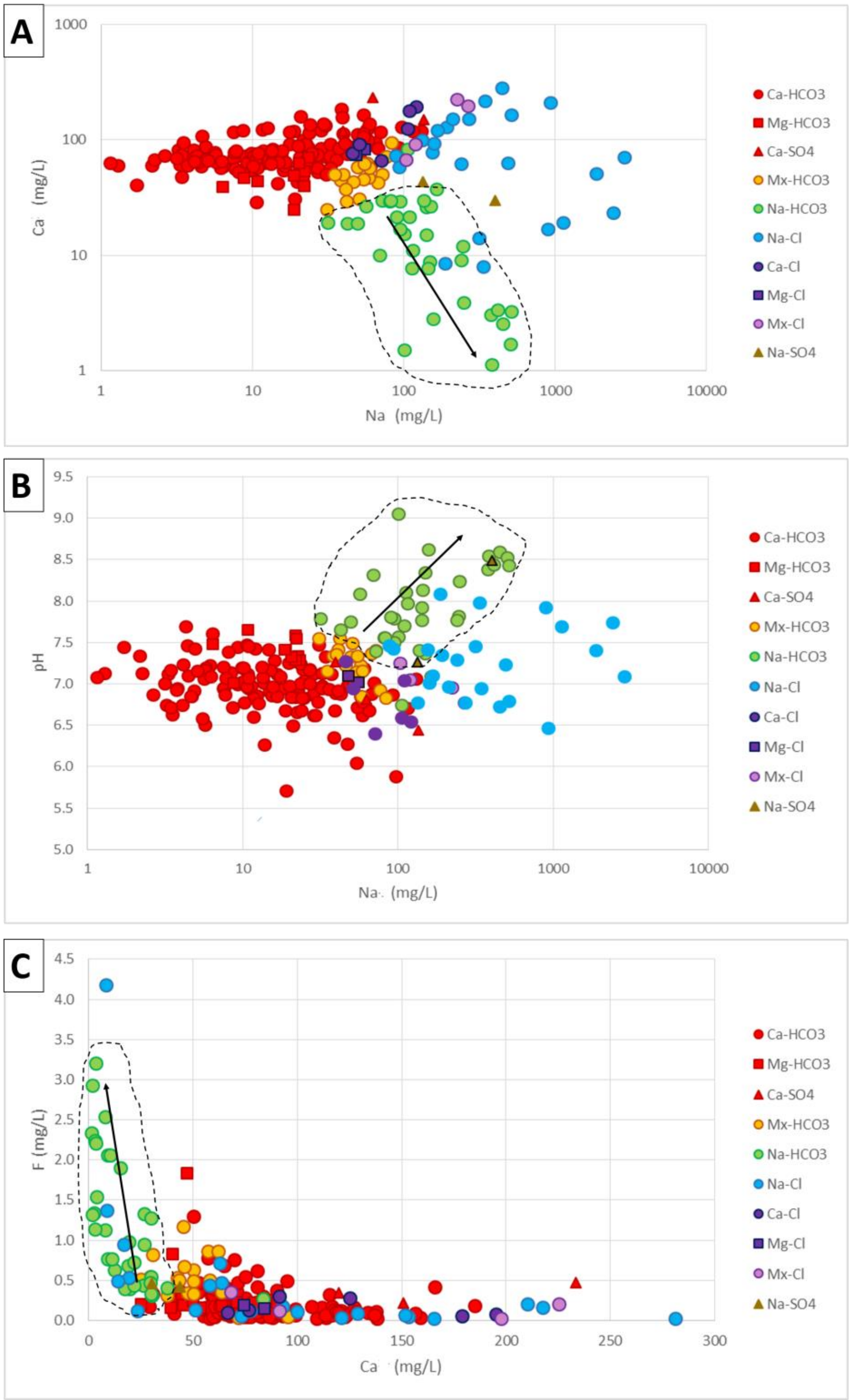

Figure 5.4 Evidence that ion exchange is the source of Na-HCO$_3$ water: (A) negative relationship between Ca and Na, (B) positive relationship between Na and pH, and (C) negative relationship between Ca and F$^-$.

$Na\text{-}HCO_3$ water is dominant in three areas of eastern Ontario (Figure 5.3). The samples exist primarily in the wedge of glaciomarine deposits and are particularly common where thick drift has infilled bedrock valleys and depressions. There is no strong relationship with this water type and bedrock lithology. The relationship of the $Na\text{-}HCO_3$ water type with glaciomarine deposits, thick drift and bedrock depressions indicates that confinement and restricted flow is an important factor driving ion exchange in the study area. Of the 33 $Na\text{-}HCO_3$ samples tested for tritium, 15 had contents below detection, indicating lack of recharge since the 1950s, and probably much earlier. The preponderance of low tritium in eastern Ontario groundwaters occurs in the same areas as $Na\text{-}HCO_3$ water type and negative PC1 (Hardness) loadings (Figure 5.3).

5.2.3 Process 3: Salinization

Examination of the regional groundwater chemistry in eastern Ontario shows that salinization is an important geochemical process operating at the regional scale.

5.2.3.1 Salinity in eastern Ontario

Salinity can be described by the concentration of dissolved solids (TDS). According to the salinity classification scheme of Davis (1964), 198 samples in the dataset are considered to be “fresh” water, falling below 1000 mg/L TDS. Of the remaining 36 samples, 35 are classified as “brackish” (TDS between 1000 and 10000 mg/L) and 1 sample is classified as saline at ~10400 mg/L TDS. TDS increases toward the northeast, suggesting a regional control on groundwater salinization.

The patterns of Salinity (PC2) are similar to those of TDS (figures 4.15B and 4.3B). PC2 is an important component, accounting for 17% of variability in the PCA dataset, indicating that salinization is an important process in eastern Ontario. The salinity component is comprised largely of positive loadings for Se, Br^-, Na and Cl^-. This is reflected in the prevalence of sodium- and chloride-type waters with high TDS and high PC2 scores. The Na-Cl and Mx-Cl types have the highest average TDS of the water types at ~2600 mg/L and ~1300 mg/L respectively.

Na-Cl-type and high TDS groundwater samples have commonly been associated with long-residing, evolved groundwater (*e.g.* Charron 1978; Cloutier et al. 2010). Salinization, however, can result from multiple processes, including prolonged water-rock interaction, dissolution of evaporite minerals, mixing of fresh and formational waters, seawater intrusion, solute diffusion from an aquitard and anthropogenic contamination (Cloutier et al. 2010; Hem 1985; Appelo and Postma 2005; Richter and Kreitler 1993). Distinguishing specific sources of salinity in eastern Ontario is important for understanding regional groundwater evolution and for water resource management and is considered next.

5.2.3.2 Distinguishing sources of salinity

The ratio of chloride to bromide (Cl/Br), the relationship between chloride concentration (Cl^-) and the stable oxygen isotope of water ($\delta^{18}O$) are used to gather information on the nature and number of Cl^- sources. Principal components, tritium (^3H) and other parameters are used to further constrain possible salinity sources.

5.2.3.2.1 Tools

Cl^-, Br^- and δ^2H and $\delta^{18}O$ of water are “conservative tracers” in groundwater. A parameter is considered “conservative” if its concentration in groundwater is not significantly affected by geochemical cycles. Conservative tracers can have distinct concentrations and ratios in different groundwater salinity sources, which are maintained through time. As Cl^- and Br^- are not abundant in rock-forming minerals (apart from evaporites), significant concentrations in groundwater can usually be attributed to processes other than mineral dissolution along the flowpath. In groundwater, Cl^- and Br^- can be found in high concentrations as a result of seawater intrusion, brine mixing, diffusion or expulsion from clays, recrystallization of minerals, or anthropogenic sources (Davis et al. 1998 and references therein). The Cl/Br ratio is largely conservative and is useful to determine sources of salinity in groundwater. The $\delta^{18}O$ (and δ^2H) value of groundwater is a property intrinsic to the water itself, and can reflect its source(s), secondary processes such as evaporation, and in medium to high temperature hydrochemical systems, the nature and extent of water-rock interaction (Clark and Fritz

1997). Tritium (^3H) is a non-conservative tracer and can provide information on the age of water, which can be used to rule out potential salinity sources that are time-period specific (recent, submodern, *etc*.).

5.2.3.2.2 Plots

Three types of bivariate plots (Cl^--Cl/Br; Cl-$\delta^{18}O$; PC1-PC2) were created to investigate different sources of elevated Cl^- in eastern Ontario:

1. The Cl^--Cl/Br relationship (Figure 5.5) in the groundwater samples is symbolized by both water type (with emphasis on chloride-types) and tritium level. The chloride-type samples (*i.e.*, Na-Cl, Ca-Cl, Mg-Cl, Mx-Cl water types) display a wide range of Cl/Br and two end-member trends emerge. The first involves ~6 high-Cl^-, low Cl/Br (< ~300) samples that trend along the seawater-dilute groundwater mixing line. Lower tritium content is seen at lower Cl/Br, with the 5 highest-Cl^- samples in the first trend lacking detectable tritium. The majority of remaining chloride-type samples have elevated Cl/Br (>1000) with a weak positive relationship between Cl^- and Cl/Br. These samples have detectable tritium that is often high (>10 TU).

2. On the Cl^--$\delta^{18}O$ plot (Figure 5.6), it is apparent that most chloride-type samples increase in tritium content with enriched ^{18}O. However, five high-Cl^- samples have no detectable tritium at a relatively enriched, narrow $\delta^{18}O$ range of –11 to –10 ‰ (VSMOW). These five samples correspond to those referred to above on the Cl^--Cl/Br plot following the seawater-groundwater mixing line (referred to as Group A from here on).

3. For Hardness (PC1) versus Salinity (PC2) (Figure 5.7), the three samples removed as outliers for PCA analysis were the highest-Cl^- Na-Cl samples from Group A. The two remaining Group A samples show elevated salinity with slightly negative hardness. Those chloride-type samples with high Cl/Br (>500) and detectable tritium (figures 5.5, 5.6) (Group B from here on) share similar space with the Ca-HCO_3 water type, and trend from 0 hardness-negative salinity to high hardness-moderate salinity. Five samples (Group C from here on) plot outside these two groups but three plot with the Na-HCO_3 type. Group C has characteristics between Groups A and B.

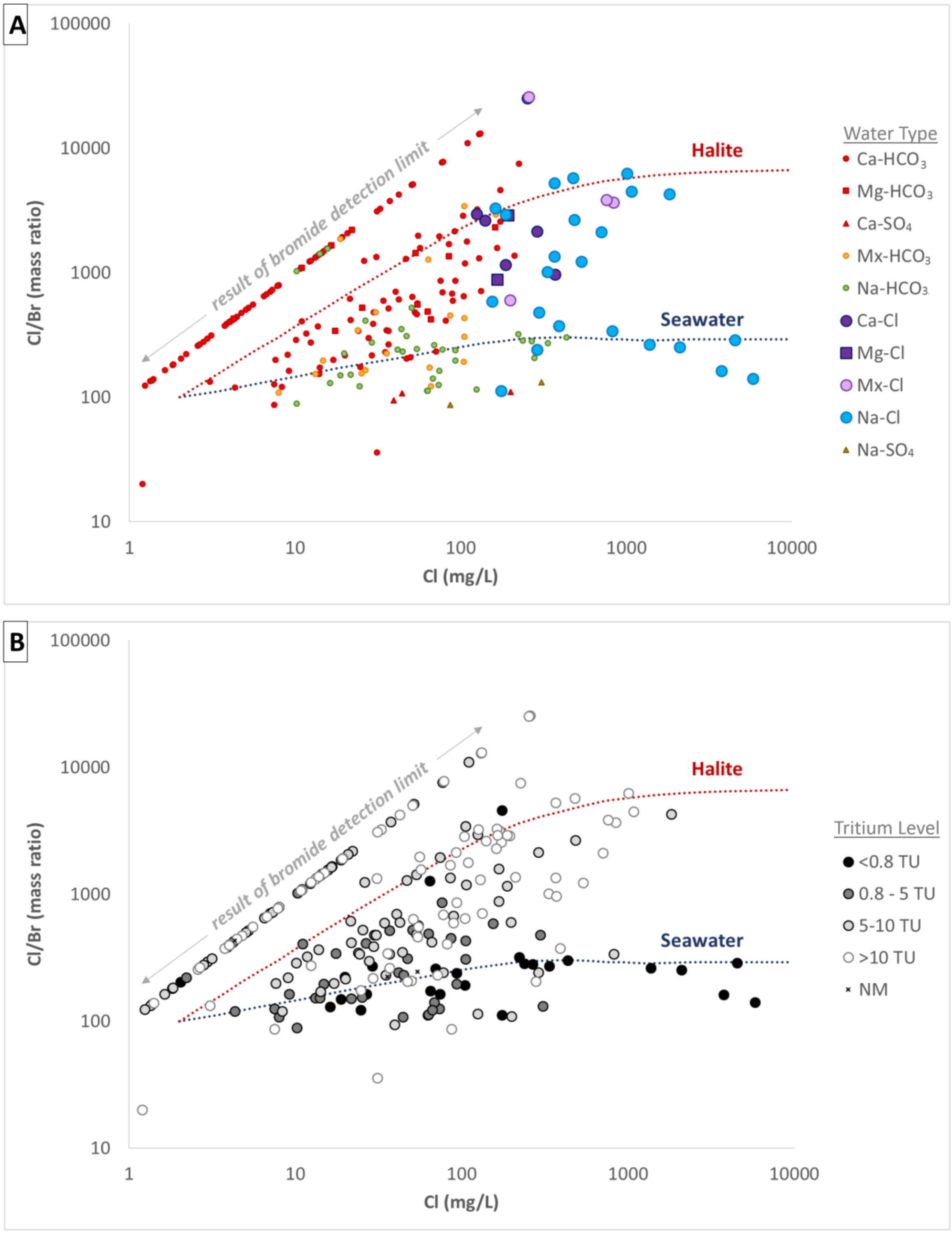

Figure 5.5 Log-log graph of chloride concentration (mg/L) versus the Cl/Br mass ratio, symbolized by (A) water type, (B) tritium concentration. Some samples were not analyzed for tritium (NM). Binary mixing lines between dilute groundwater and seawater and dissolved halite are reproduced after Katz et al. (2011).

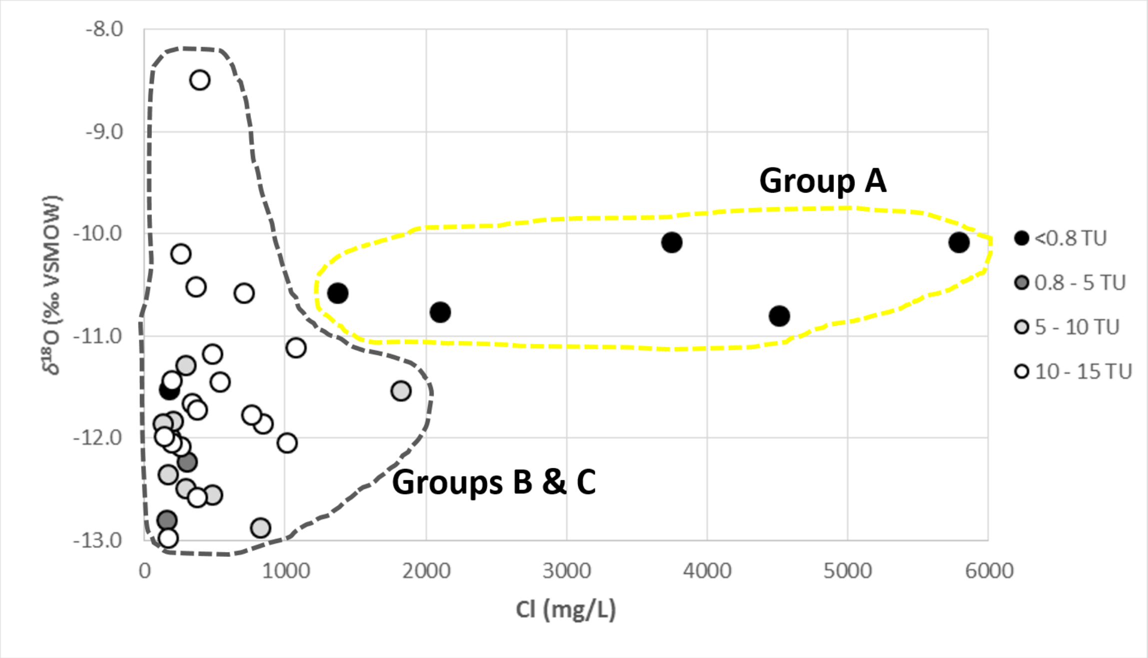

Figure 5.6 Chloride concentration versus δ^{18}O, symbolized by tritium concentration for chloride-water-types.

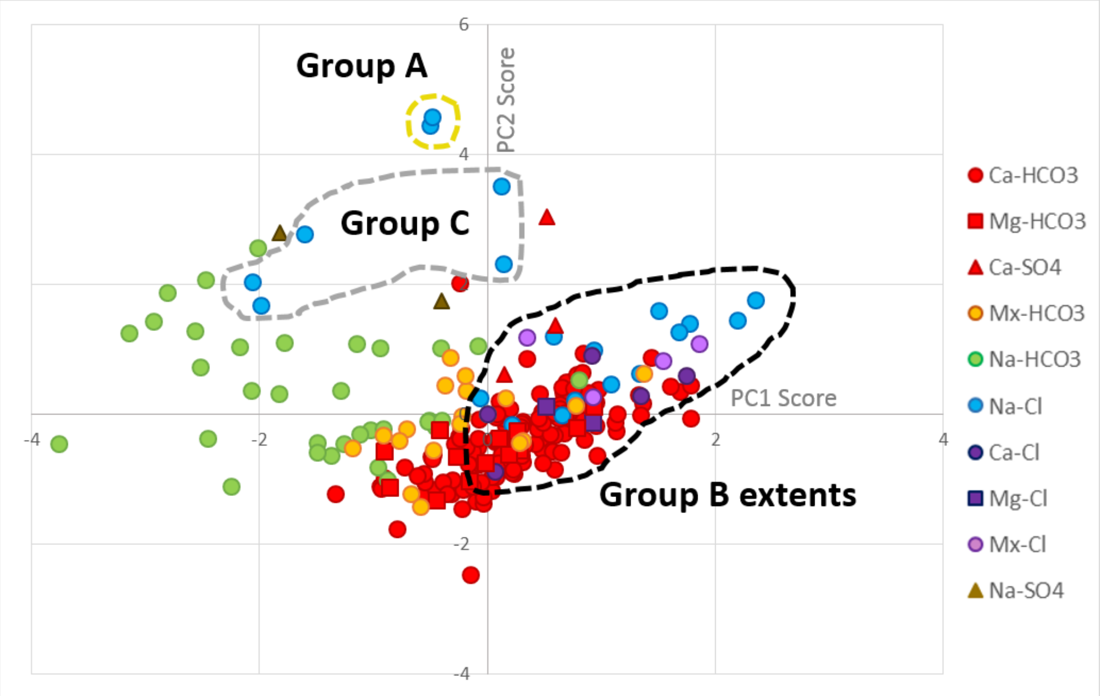

Figure 5.7 Salinity (PC2) versus Hardness (PC1) scores symbolized by water type. Three groups emerge from figures 5.5, 5.6, 5.7. The Group B extents are shown, but the envelope includes other samples, not part of any chloride group.

5.2.3.3 Interpretation

5.2.3.3.1 Group A

Group A is composed of five Na-Cl-type, bedrock-interface samples all of which have high chloride (average = 3500 mg/L). This is evident on the PC1-PC2 plot, where the two Group A samples exhibit the highest Salinity (PC2) scores with relatively neutral scores for Hardness (PC1). The group is characterized here as having no detectable tritium, Cl/Br ratios following the seawater-groundwater mixing line, and δ^{18}O within a relatively narrow range between –11 and –10‰ (VSMOW). Parameters of interest are compared in Appendix C, which shows that TDS, Ca/Na ratio, alkalinity, NO_3^-/NO_2^-, B and Se concentrations are particularly distinctive in Group A. The five Group A samples were collected geographically close to one another within a major bedrock depression in the northeast infilled with thick glaciomarine clays (Figure 5.8). Four of these five samples were taken from wells that were completed at the interface of shale (Billings and Carlsbad Formations), whereas the well for the fifth sample is suspected to be completed at the interface of Bobcaygeon limestone in a separate bedrock depression.

Several studies of groundwater within the limits of the Pleistocene Champlain Sea found that the marine incursion at ~10 ka BP (^{14}C years) still influences groundwater chemistry (Desaulniers and Cherry 1989; Cloutier et al. 2006, 2008, 2010; Blanchette et al. 2013; Montcoudiol et al. 2015). The characteristics of Group A, including elevated TDS, a Na-Cl-type, the narrow range for δ^{18}O (Table 5.2) and close adherence to a seawater-dilute groundwater mixing line (Figure 5.5), suggests Group A originated by mixing of fresh and Champlain Sea water.

The most saline sample (12-AG-202) has a Cl^- concentration that is ~30% of normal seawater concentration, and ~90% of the expected Cl^- concentration of the Champlain Sea, based on a 1/3 seawater concentration model (Desaulniers and Cherry 1989; Cloutier et al. 2010). The four other Group A samples have lower Cl^- concentrations; however their relationships with δ^{18}O and Cl/Br are consistent with a mixing line between fresh water and Champlain Sea water (figures 5.5 and 5.6).

Table 5.2 Conservative tracers in Group A compared to seawater and Champlain Sea (CS) water

Sample	Bedrock unit	Cl^-	Br^-	Cl/Br	$\delta^{18}O$	Seawater% (from Cl^-)	CS% (from Cl^-)
Seawater[11]	-	19000	65	292	0	100	-
CS water[12]	-	6333	22	292	10.7[13]	33	100
12-AG-140	Bobcaygeon	1370	5.2	260	-10.6	7	22
12-AG-202	Carlsbad	5790	40.9	140	-10.1	31	91
12-AG-207	Carlsbad	2100	8.3	250	-10.8	11	33
12-AG-208	Billings	3750	23.0	160	-10.1	20	59
13-AG-718	Billings	4510	15.7	290	-10.8	24	71

Inferring that the salinity and Cl^- content in Group A originates from Champlain Sea water, there are two explanations for its variable seawater proportions: (1) they reflect the original composition and the spatial and temporal variability in the Champlain Sea; (2) the original high (1/3) seawater salinity has been diluted since its original entrapment by more modern meteoric water. If the variability reflected original composition, one would expect to see decreasing Cl^- content paired with decreasing $\delta^{18}O$ arising from greater Pleistocene freshwater content (estimated at –16‰ VSMOW; Hillaire-Marcel and Page 1983). Within Group A, there is only a very weak positive relationship between Cl^- and $\delta^{18}O$. Instead Cl^- content is variable while most $\delta^{18}O$ fluctuates between –11 and –10‰. This pattern supports the second explanation.

Four of the Group A samples cluster together in a major northeastern bedrock depression (Figure 5.8). The fifth is also located in a bedrock depression just east of the other four. The average drift thickness for the five samples is 41 m, with saline sample 12-AG-202 drawn from beneath 62 m of drift. The drift is mainly composed of glaciomarine clay. Samples from the northeast bedrock depression have no detectable

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[11] Goldberg (1963)

[12] Based on 2/3 dilute freshwater, 1/3 ocean water mixing model (Desaulniers and Cherry, 1989; Cloutier et al., 2010).

[13] Based on 2/3 Pleistocene freshwater (–16‰; Hillaire-Marcel and Page 1983) and 1/3 Pleistocene ocean water (0±1‰; Broeker 1974) mixing proportion (Desaulniers and Cherry 1989; Cloutier et al. 2010).

tritium, indicating that confinement by thick clay and convergent, stagnant flow in the bedrock depression are preventing modern recharge.

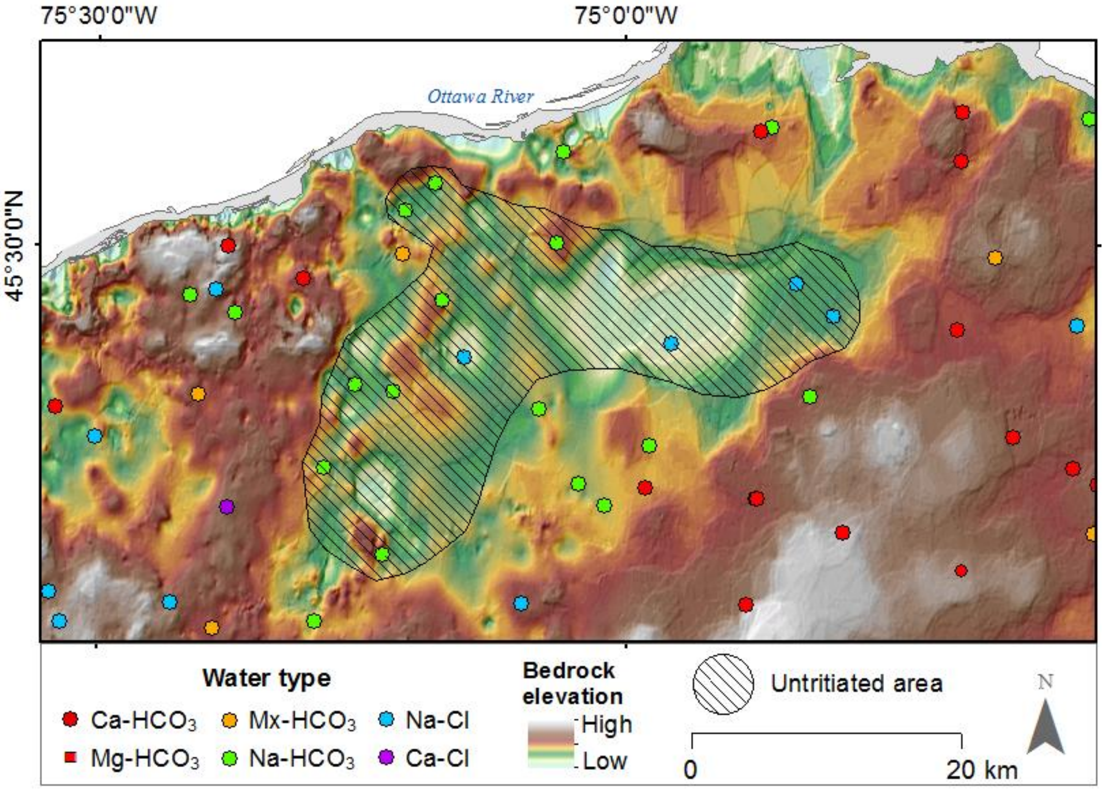

Figure 5.8 Groundwater lacking detectable tritium (untritiated) resides in the northeast bedrock depression as a result of complicated discharge related to bedrock topography. All Na-Cl samples (blue) in the northeast bedrock depression are Group A, attributed to a component of Champlain Sea water.

5.2.3.3.2 Group B

Group B (N=25) differs from Group A by having Cl/Br ratios >500 (average = 4569) and high tritium (average = 10.4 TU) (Figure 5.5). It also has a lower Cl^- concentration (average = 460 mg/L) and variability in $\delta^{18}O$ (range = –13.0 to –10.2‰) (Figure 5.6). In addition, Group B occupies a space on the PC1-PC2 plot (Figure 5.7) distinct from the other chloride-type waters, mostly showing positive Hardness with positive Salinity and overlapping with the $Ca\text{-}HCO_3$ water type. Group B exists across a wide geographic area and diverse geological environments.

Group B has elevated salinity and chloride-type chemistry, but does not display Champlain Sea characteristics. It has Cl/Br ratios that are much higher than seawater and its $\delta^{18}O$ has a greater range than Group A. Its B, Li and Se levels are lower than those of groups A and C. Group B has variable cation dominance with Cl^- dominance, as, shown by the presence of Na-Cl, Ca-Cl, Mg-Cl and Mx-Cl water types. The average Ca/Na ratio of Group B (0.91) is significantly higher than Group A (0.02). Group B shows a distinct positive relationship among Ca, Na and Cl^-, which is reflected in the positive relationship between PC1 and PC2 scores (Figure 5.7).

Three possible explanations for the elevated Cl/Br ratios of Group B are: (1) mixing with Saint Lawrence Platform (SLP) brines, (2) dissolution of naturally occurring halite, and (3) anthropogenic contamination.

1) Mixing of a small amount of SLP brine with fresh groundwater could account for the characteristics of Group B. The SLP brines are a Na-Ca-Cl water type, which could explain the positive relationship among Ca, Na and Cl^- and the presence of Mx-Cl and Ca-Cl water types in Group B. A Piper plot of SLP brine samples and approximate typical recharge in eastern Ontario shows that some Group B samples fall between these two endmembers (Figure 5.9). The elevated Cl/Br ratios in Group B could also arise from mixing with SLP brines (Cl/Br = 25 000 to 45 000). However, most Group B samples are not located near the Ottawa River, where one would expect regional discharge (Figure 5.10). In addition, Group B tends to have elevated tritium contents and many samples are

located in areas of preferential recharge. These factors suggest that mixing with SLP brines is not the main process controlling Group B water chemistry.

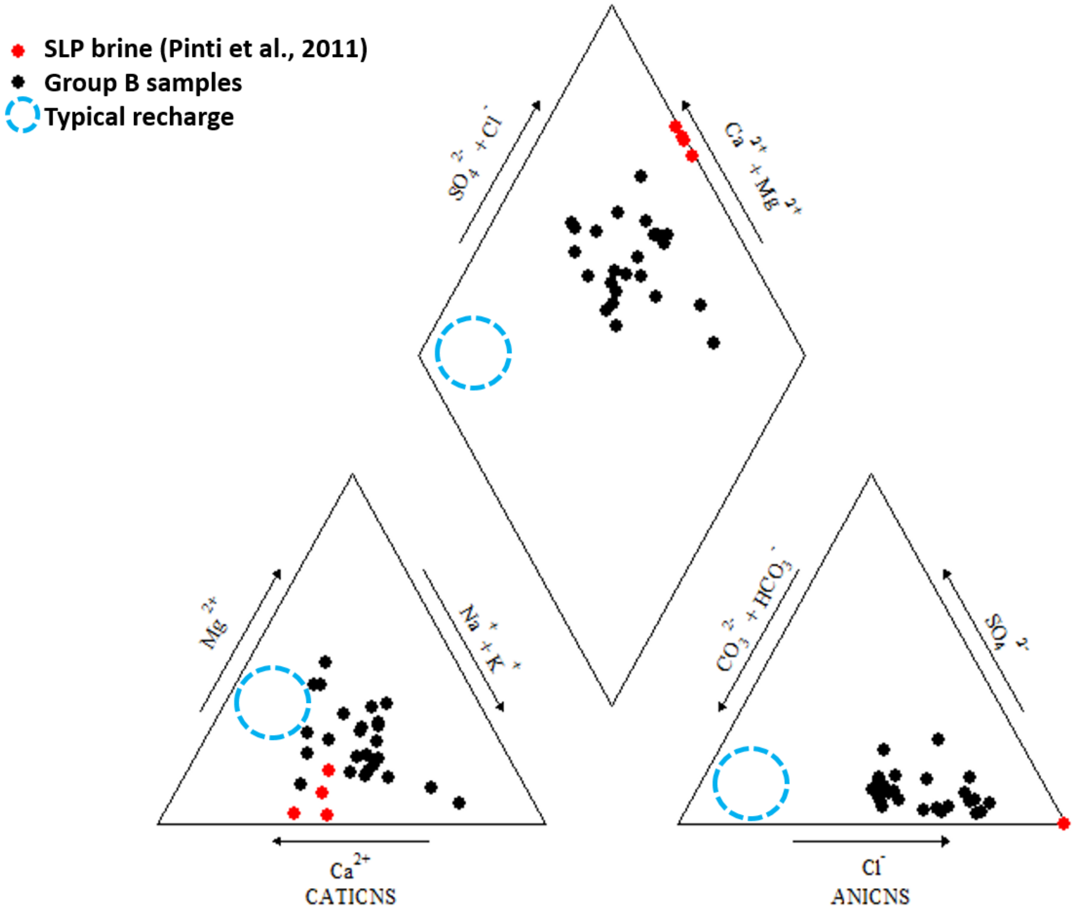

Figure 5.9 Piper plot showing that the composition of some Group B samples (black) could result from mixing of fresh recharge and SLP brines.

2) Dissolution of natural halite could also explain Group B chemistry. Halite casts are known from the Beekmantown Group (Sanford 1993), which is present in eastern Ontario, but the halite may have been dissolved long before modern groundwater recharged the system. The Cl/Br ratios of Group B range from 590 to 25700, with 18 of 25 samples falling within the halite range (1000 to 10 000; Davis et al. 1998). All groundwater samples in eastern Ontario are undersaturated with respect to halite (Figure 4.12E), and therefore halite would be readily dissolved upon contact. In addition, the majority of samples in eastern Ontario have elevated Cl/Br ratios, which could suggest a regional source enriched in Cl$^-$ but depleted of Br$^-$. However, the association of Group B

with elevated tritium is not well explained by dissolution of natural halite. Most samples with no detectable tritium have low Cl/Br ratios. If halite in bedrock was the source of Cl^- in Group B, then one would also expect its presence in older water samples.

3) Anthropogenic contamination is a third potential Cl^- source for Group B. Human-influenced contamination sources that could result in elevated Cl/Br ratios include sewage, septic and animal waste, fertilizers and de-icing road salts (Davis et al. 1998; Panno et al. 2006). Group B samples occur across a wide area in diverse geological environments, associated with no other natural physical parameters, such as topography or drift thickness. Anthropogenic influence is the most plausible of the three explanations and is discussed in detail below.

The Group B samples plot close to the groundwater–halite and halite-septic effluent binary mixing lines on a Cl^--Cl/Br chart (Figure 5.11). There is some chloride-enrichment from the halite-septic effluent line, apparently due to mixing of waters impacted by a halite source with Champlain Sea-influenced waters or with sewage of variable Cl^- and Br^- composition. Both halite and septic effluent are chloride and salinity sources in eastern Ontario. Fourteen of 25 Group B samples (52%) occur within the City of Ottawa, although it accounts for only ~18% of the land area in eastern Ontario. The rural population density increases towards the urban center of Ottawa, hence increasing the density of private septic systems. There is also a spatial association between Group B samples and the major Highways 416, 417 and 15 in eastern Ontario (Figure 5.10). In the nearby Basses-Laurentides aquifer system, Cloutier (2004) attributed elevated Cl/Br in groundwater along a major highway to de-icing road salts. There are no chloride-type samples associated with Highway 401. Proximity to the St. Lawrence River where discharge occurs may limit road salt impacts in the bedrock aquifer.

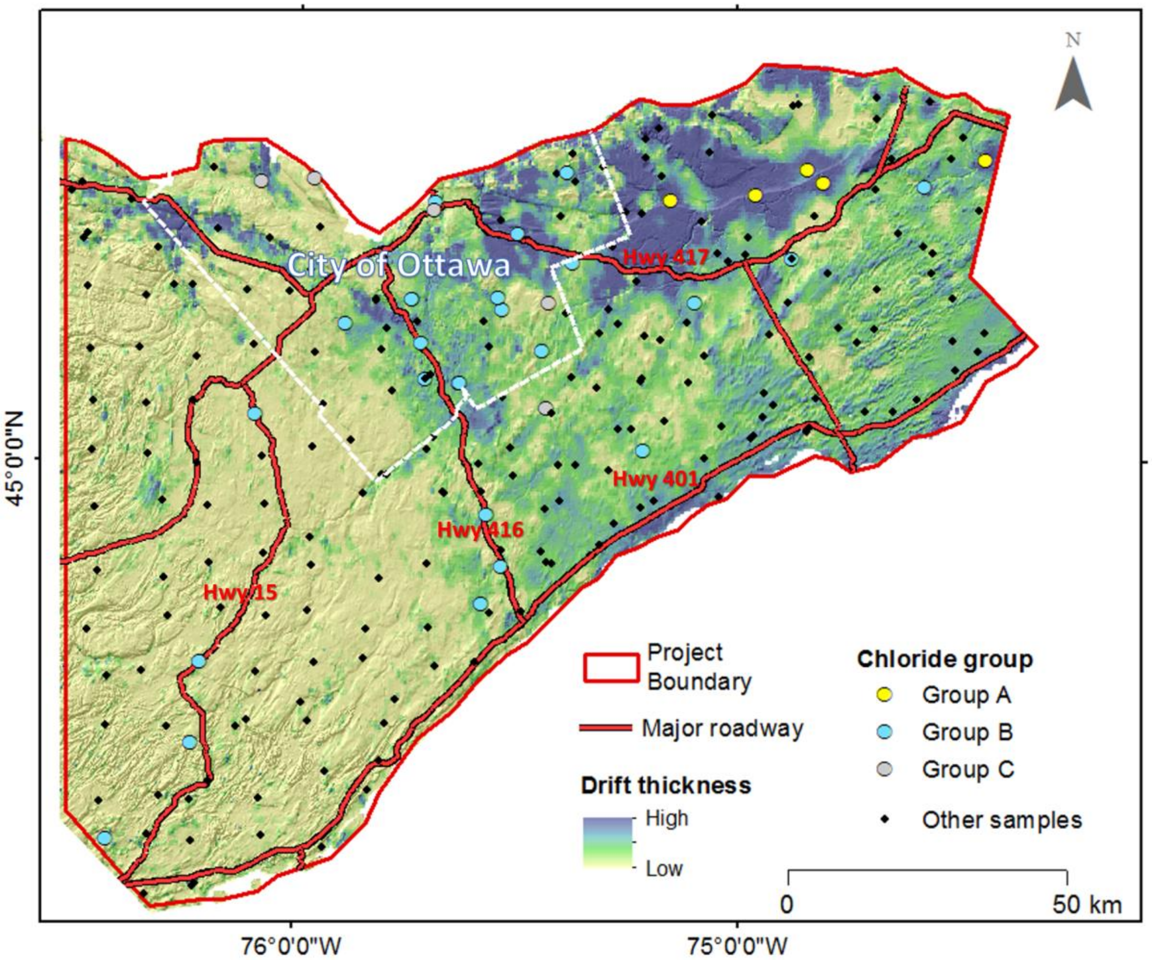

Figure 5.10 Locations of chloride-type samples, divided into groups A, B and C and some anthropogenic salt sources (*i.e.*, Ottawa, highways).

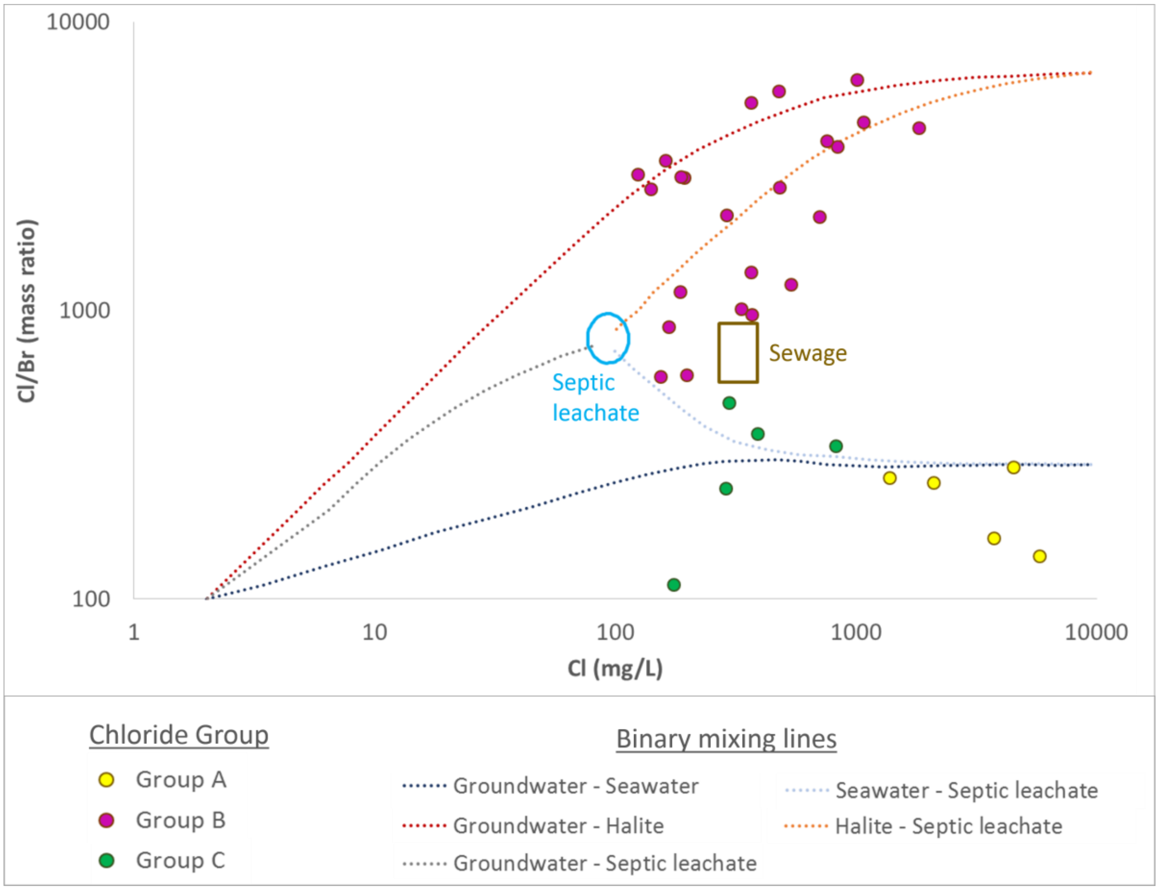

Figure 5.11 Log-log Cl/Br versus Cl$^-$ plot showing the three groups of chloride-type samples and their relationships to binary mixing lines between possible Cl$^-$ sources and dilute groundwater. Sewage (Vengosh and Pankratov 1998) and septic effluent (Panno et al. 2006) are indicated. Figure is after Katz et al. (2011).

The position of a subset of Group B samples along the binary mixing line between septic leachate and halite (Figure 5.11) could be attributed to groundwater affected by both septic effluent and road salt, or alternatively to water affected by septic systems of residences utilizing water softeners. Water softeners are backwashed with a saturated NaCl solution to rejuvenate the resin filter (Thomas 2000). Backwashing, which occurs about once a week, results in a mix of Na-Cl (68%), Ca-Cl (22%) and Mg-Cl (10%) in the backwash water (Weickart 1976). This could account for the positive relationship between Na and Ca in Group B, as well as the Ca-Cl and Mx-Cl water types. This explanation is supported because samples near the septic leachate – halite binary mixing line have particularly high calcium concentrations. However, softeners are common across all of the Southern Ontario area and yet a review of the AGG dataset (Hamilton 2015) indicates that Ca-Cl and Mx-Cl water types cluster only in the Ottawa area. The high density of development in rural parts of the City of Ottawa may result in a greater expression of the softener-effect in eastern Ontario than other parts of the province.

Softener backwash could account for the positive Na-Ca relationship but another explanation could be the use of Ca-Cl road deicers. The City of Ottawa uses a mix of sodium-chloride salt and calcium-chloride brine on their streets (City of Ottawa 2005), which may account for high Ca. A more speculative explanation could be that the concentrated Na from road salt in infiltrating water is causing release of calcium adsorbed on clays (Brown and Misut 2010) in zones of highly active recharge.

5.2.3.3.3 Group C

Group C comprises 5 samples that could not be confidently placed in groups A or B based on the criteria described earlier for each. Group C has Cl^- < 1000 but greater than 100 and Cl/Br < 500 (Figure 5.11) and the origin of these halogens is not consistent within the group.

Three samples (12-AG-087, 12-AG-262, 14-AG-076) have Cl/Br ratios higher than seawater (340, 480, 370) and parallel the seawater – septic effluent binary mixing line. They each have detectable tritium, indicating interaction with modern recharge and are located close to the south shore of the Ottawa River. Some anthropogenic inputs or mixing between different sources can produce such low Cl/Br ratios. In these cases, older, regional discharge to the river or Champlain Sea-influenced water in bedrock valleys may be mixing with a modern, anthropogenic source. Samples 14-AG-076 and 12-AG-087 were taken from urban and karstic areas, respectively, making anthropogenic impacts likely. Sample 12-AG-262 has low tritium (2.5 TU) and plots closely to the Na-HCO_3 water type (Figure 5.7). Here, older, ion-exchange-affected water in a buried valley may be mixing with septic effluent, as suggested by Cl/Br of 480 (Davis et al., 1998).

The remaining two samples (12-AG-144, 12-AG-044) sit below the groundwater-seawater mixing line, similar to Group A (Figure 5.11), with Cl/Br below seawater. Sample 12-AG-144 has some Group A characteristics (*i.e.,* neutral PC1 with elevated PC2 (Figure 5.7), Cl/Br=240), though it has detectable tritium, significant sulphate (162 mg/L) and is positioned on a thinly-covered, bedrock knob. Bacterial counts (total = 10; fecal = 1) and detectable nitrate (0.06 mg/L) suggest potential septic or agricultural influence. The mechanism to mix Champlain Sea water in the environment of a bedrock knob is unclear. The final sample (12-AG-044) has no detectable tritium, suggesting an older water source. It has Group A characteristics, but its δ^{18}O is lower (–11.5‰) and it does not exist in a significant bedrock depression. It may represent mixing of a small amount of Champlain Sea water with a large quantity of old, lower-δ^{18}O, cooler climate meteoric water, which evolved further via ion exchange and diffusion/expulsion of Cl^- and Br^- from overlying glaciomarine clays.

5.2.3.4 Regional Salinization

In addition to high-TDS, chloride-type waters, eastern Ontario has other high TDS water facies. The spatial patterns of TDS, halogens and several other dissolved constituents increase with the appearance and increasing thickness of glaciomarine drift, which is concomitant with decreasing bedrock elevation (*e.g.,* figures 4.3B and 4.4). Salinity (PC2) shows the same spatial pattern, indicating that the influence of Se, Br^-, Na, and Cl^- extends beyond the major northeastern bedrock depression. The presence of relict Champlain Sea water in the bedrock aquifer was postulated to be a function of stagnation and confinement, characterized by the Na-Cl water type having higher δ^{18}O and no detectable tritium. Samples from the area of regional salinization, by comparison, mostly have detectable tritium. This indicates a more active flow system and replacement of water in the bedrock aquifer since the Pleistocene and that connate waters cannot be the sole source of salinity here.

Many studies report continued presence of saline porewater in the Champlain Sea clays across eastern Ontario and Québec (Desaulniers and Cherry 1989; Woodley 1996; Torrance 1979; Quigley et al. 1983; Cloutier 2004). Cloutier et al. (2010) suggested that diffusion of solutes from the Champlain Sea clay porewater could create mineralized, Na-

Cl-type water in the underlying bedrock aquifer. Analysis of porewaters from clays collected in vertical profiles through these glaciomarine clays often reveals lower salinity at the top (*e.g.,* Torrance 1988; Woodley 1996), indicating diffusion. Expulsion of saline porewater from the glaciomarine clays during compaction is another process suggested to move solutes from the aquitard to the bedrock aquifer (Marc Laurencelle pers. comm. 2015; unreferenced). Therefore, it is possible that the glaciomarine clay aquitard is contributing dissolved solids to the underlying bedrock aquifer through diffusion and/or expulsion. Desaulniers and Cherry (1989) ruled out advection as a transport mechanism based on the clay's very low hydraulic gradient and conductivity.

5.2.4 Process 4: Organic Decomposition

Organic decomposition is an important geochemical process operating at a regional scale in eastern Ontario. Evidence of this process, discussed below, is drawn from PC3, ORP, H_2S, CH_4, and I^-.

5.2.4.1 PC3 "Organics"

Principal component 3 was named "Organics" because most of the constituents that load strongly (positive: HCO_3, NH_3+NH_4^+, DOC, Ba) and moderately (positive: K, negative: SO_4^{2-}) are associated with decomposition of organic matter and are the reactants and products of redox reactions potentially related to organic matter. These are discussed, in turn, below.

Groundwater bicarbonate (HCO_3), which loads most strongly and positively, can be produced by dissolution of carbonate minerals, as well as by metabolic respiration reactions associated with microorganisms. In eastern Ontario, however, HCO_3 correlates very poorly with the PC most related to carbonate dissolution (PC1) and instead correlates with products of organic decomposition (DOC and NH_3+NH_4^+). The positive loading of DOC results from elevated concentrations of DOC in these waters that is likely reflective of elevated organic matter in the marine clays. NH_3 and NH_4^+ are the most reduced forms of dissolved N in groundwater and, as a constituent of all proteins, are found in most organic matter. NH_4^+ can become concentrated in groundwater when there is anoxic decay of significant amounts of buried organic matter, thus explaining its relationship with other organic products/reactants (Lingle 2013).

The high positive loading for bicarbonate and moderate negative loading for SO_4^{2-} can be explained by sulphate reduction, represented by the following reaction:

$$\mathbf{2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-} \qquad \textbf{Equation 5.8}$$

During oxidation of organic matter (CH_2O), SO_4^{2-} is reduced to hydrogen sulphide (H_2S) by sulphate-reducing bacteria (SRB), which dissociates to its dissolved form $HS^-_{(aq)}$. Sulphate reduction occurs only under reducing conditions in the redox sequence after O_2, NO_3^-, Fe^{3+} and Mn^{4+} are reduced, which is reflected in the negative ORP of all samples with PC3 scores over +1. The removal of SO_4^{2-} can account for the positive loading of Ba because it promotes barite dissolution:

$$\mathbf{BaSO_4 \rightarrow Ba^{2+} + SO_4^{2-}} \qquad \textbf{Equation 5.9}$$

SO_4^{2-} removal by SRB drives the reaction to the right allowing an increase in barium concentration. Barite has been documented in calcite veins in eastern Ontario (Dix and Robinson 2003; Carignan et al. 1997).

5.2.4.2 Redox indicators

Dissolved oxygen (DO), hydrogen sulphide (H_2S), and methane (CH_4) are key indicators of the nature of redox reactions, but were not included in PCA because of their high proportion of zero-values that prevented normalization through log-transformation. Spatial mapping of these three parameters and ORP readings indicates progressively more reducing conditions from southwest to northeast across the study area (Figure 4.2). DO and oxidizing conditions predominate in the southwest in a pattern that corresponds to the absence of glaciomarine deposits and to the subcrop of the Nepean and March formations and Precambrian basement.

The presence of H_2S predominates to the north and east in the study area, corresponding to thickening drift, and indicates sulphate reduction. CH_4 concentrations are high in the northeast that, in particular, correspond to the large bedrock depressions infilled with thick glaciomarine deposits. The area predictably shows low SO_4^{2-} and H_2S, as SO_4^{2-} has mostly been converted to sulphide, which may have subsequently been precipitated as pyrite and marcasite, through reaction with dissolved or mineralogical iron. This produces black mottling in the glaciomarine clays (Donovan and Lajoie 1979). In the same region, depletion of SO_4^{2-} has caused the groundwater to be particularly undersaturated with respect to gypsum and anhydrite (Figure 4.12).

The presence of biogenic CH_4 indicates organic decomposition under highly reducing conditions. Biogenic CH_4 is produced during methanogenesis by reduction of CO_2 or organic molecules such as acetate (CH_3COOH):

$$\mathbf{CH_3COOH \rightarrow CH_4 + CO_2} \qquad \textbf{Equation 5.10}$$

$$\mathbf{CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O} \qquad \textbf{Equation 5.11}$$

Methanogenesis occurs when other, more efficient terminal electron acceptors (TEA) (*i.e.*, O_2, NO_3^-, Fe^{3+}, Mn^{4+}, SO_4^{2-}) are unavailable. The depletion of alternate TEAs indicates advanced stages of organic decay. The dataset does not contain carbon isotopes for methane, which could be used to conclude a biogenic over thermogenic source of methane (Baldassare and Laughrey 1997). However, the relatively shallow depth of groundwater and spatial association of CH_4 with I^- (section 5.2.4.3) support a biogenic origin to CH_4 in eastern Ontario

5.2.4.3 Iodide

In addition to typical products and reactants of major redox reactions, the trace halogen iodide (I^-) can be linked to organic decomposition and can contribute additional information about processes affecting groundwater chemistry in eastern Ontario. For shallow groundwater, I^- concentrations are very high in the study area, averaging ~100 μg/L. However, the distribution of results is highly skewed, with the majority (N = 171) of samples having more typical groundwater concentrations <~30 μg/L, while a smaller population (N=61) have higher concentrations (up to 6650 μg/L). Earlier (Table 5.2), it was concluded that groundwater in chloride Group A contained up to 31% seawater in areas of stagnation. Seawater has an average iodine concentration of 0.06 mg/L (6 x 10^1 μg/L; Goldberg 1963). Hence, the high I^- concentrations cannot simply be a product of mixing of freshwater with Champlain Sea water (~1/3 seawater). The chloride Group A samples have I^- concentrations that are 1.6 to 110 times the concentration of iodine in seawater and have I/Cl ratios generally much higher than seawater (Table 5.3).

Table 5.3 Comparison of Cl^-, I^- and I/C in seawater and Group A Na-Cl samples.

	Seawater	**12-AG-140**	**12-AG-202**	**12-AG-207**	**12-AG-208**	**13-AG-718**
Cl^- (mg/L)	19000	1370	5790	2100	3750	4510
I^- (μg/L)	60 (iodine)	95	6650	1770	3900	2530
I^- (X Seawater)	1	1.6	110	30	65	42
I/Cl (X Seawater)	1	22	364	267	329	178
Cl^- (% Seawater)	100	7	31	11	20	24

Elevated I^- concentrations have been noted in recent estuarine deposits and attributed to biological uptake by marine organic matter, subsequent burial in sediment and release during anaerobic diagenesis (Lloyd et al. 1982). In eastern Ontario, the glaciomarine clays and some of the younger Paleozoic bedrock formations (*i.e.*, Lindsay, Billings) contain a considerable amount of organic matter (Laventure and Warkentin 1965; Donovan and Lajoie 1979; Dix and Jolicoeur 2011). I^- concentration is spatially linked to the extent of the glaciomarine deposits (Figure 5.12). This pattern suggests that iodide in eastern Ontario groundwater may be a product of extensive anaerobic decomposition of organic matter, in addition to the iodine supplied directly by Champlain Sea water. Further, the glaciomarine clays create a confining aquitard, creating the anoxic conditions that preserve iodine's reduced form (I^-) and inhibit its bioavailability for uptake (Price and Calvert 1977).

If I^- in eastern Ontario is produced by anaerobic decomposition of marine organic matter, one might expect it to load more strongly for Organics (PC3, I = 0.45) than for

Salinity (PC2; I = 0.55). Salinity in eastern Ontario groundwater was produced in fresh groundwater mostly from mixing with Champlain Sea water and diffusion/expulsion of solutes from saline porewater and by anthropogenic contamination. Salinity arising from the first two of these processes is linked to extended residence time in the aquifer, which is an important contributor to high I^- concentrations and high I/Cl ratios in several studies of groundwater in marine sediments (*e.g.*, Maida 1989; Lloyd et al. 1982). Iodide concentration may relate to both the Organics and Salinity components because it is a product of breakdown of marine organic material that has accumulated over extended residence time. The link between residency and I^- concentration is supported by similar spatial patterns to CH_4 (figures 4.2D and 4.4C), which is associated with organic decomposition over prolonged residence time. In trial runs of PCA where I^- and CH_4 were both included, they loaded strongly and positively for the organics component.

The extremely high I^- in groundwater in eastern Ontario suggests anaerobic decomposition of iodine-rich organic matter in the marine clays and/or Paleozoic marine sediments is occurring. The much higher concentrations of I^- in eastern Ontario than the elevated iodine reported in southwestern Ontario in similar Paleozoic strata (Hamilton 2015) suggests Champlain Sea clays are the predominant source of iodine. The very high concentrations of I^- indicate that it is accumulating as a reaction product and not being quickly removed from the system. Glaciomarine clays act to confine the aquifer and this is exacerbated in the northeast bedrock depression that has experienced little groundwater replacement since the Pleistocene (Figure 4.4C).

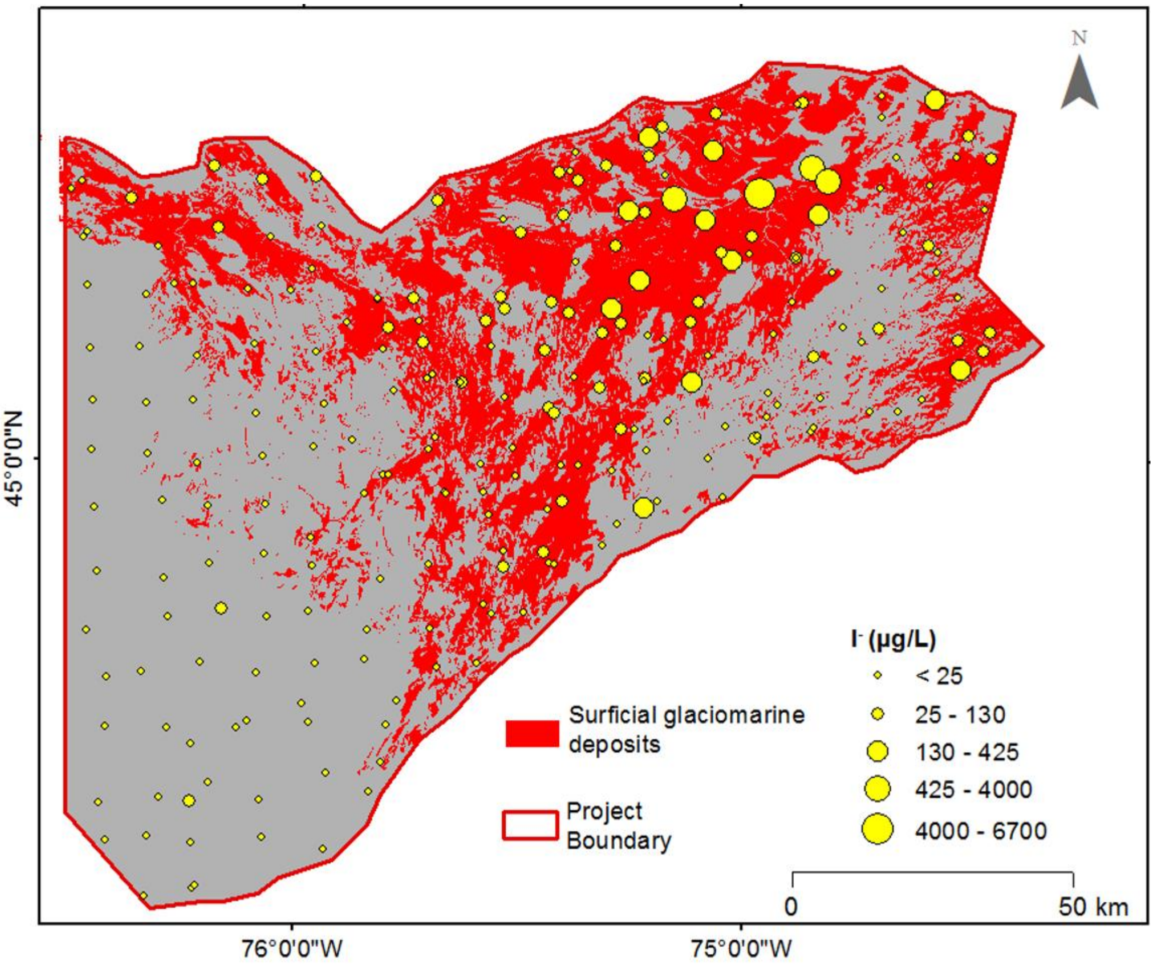

Figure 5.12 I^- concentrations are related to the distribution of glaciomarine deposits.

5.2.4.4 Yellow water

Water colour was recorded during sampling. Many samples had a bright yellow colour, to a degree that is unique to eastern Ontario within the AGG program (2012 pers. comm. with SM Hamilton; unreferenced). Reports of "dark yellow" are associated with positive PC3 (Organics) scores (Figure 5.13). This suggests that organic decomposition products may be causing the colour. The uniqueness of the colour to eastern Ontario groundwater samples, again implicate marine organics in the Champlain Sea glaciomarine clays as a cause of the unique groundwater chemistry in this part of southern Ontario.

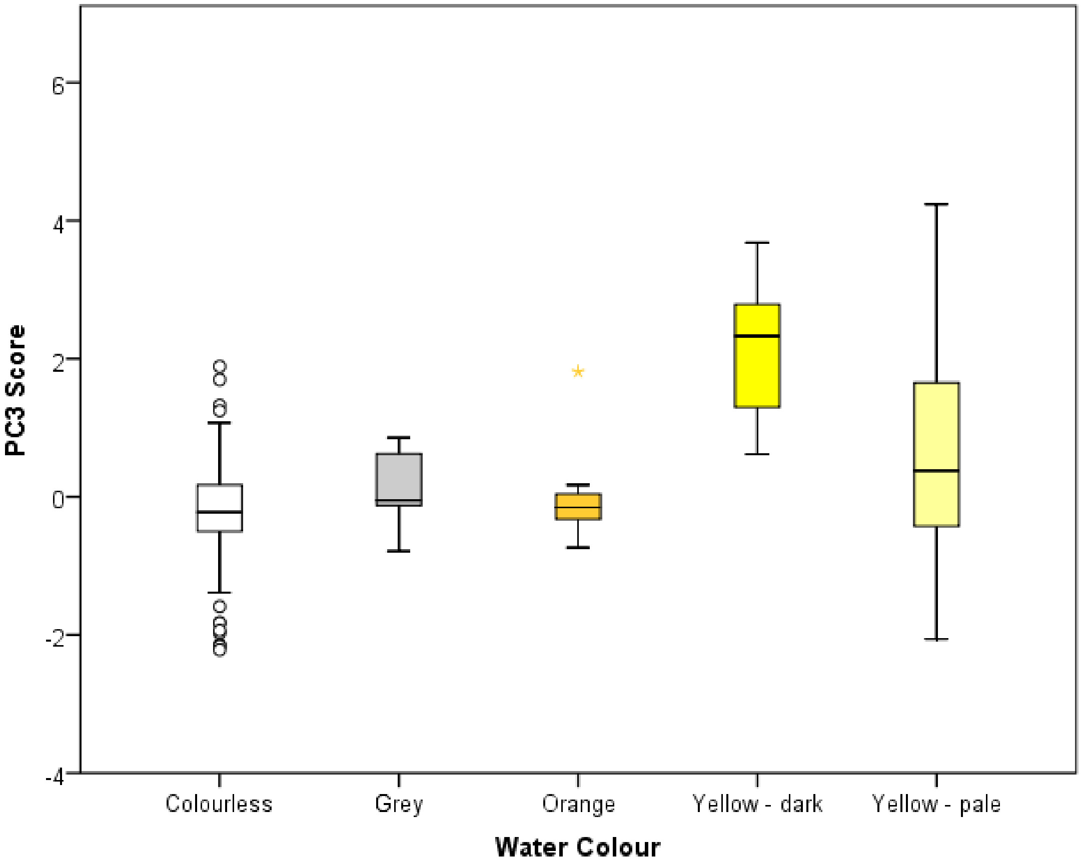

Figure 5.13 PC3 (Organics) by water colour. Yellow, especially dark yellow, is most strongly associated with Organics. The box brackets the middle 50% of the data and the dark horizontal line represents the median concentration. The whiskers at the top and bottom represent the extents of the concentration data, excluding outliers (hollow circles) and extreme values (star).

5.3 Physical Controls

Regionally significant processes relate to two physical features in eastern Ontario: bedrock topography and the glaciomarine deposits (extent and thickness; Figure 5.14). They are inter-related as overburden, including glaciomarine deposits, generally accumulates in bedrock depressions. Each of the main processes relate as follows:

- Recharge occurs at elevated bedrock topography, where glaciomarine deposits are absent or sparse.
- Ion exchange alters groundwater chemistry where glaciomarine deposits accumulate, particularly in bedrock valleys and depressions where they are thick.
- Salinization results from diffusion/expulsion where glaciomarine deposits accumulate and from mixing where they fill a major bedrock depression.
- Advanced organic decomposition occurs most strongly in a major bedrock depression capped by thick glaciomarine clays.

The influence of bedrock topography can be explained by its relation to drift thickness and its control on the flow path of groundwater. In the presence of less permeable, fine-grained, glaciomarine deposits, the weathered, fractured bedrock-sediment interface becomes the zone of preferential flow (Charron 1978; Singer et al. 2003). The glaciomarine deposits play such a prominent role because (1) they facilitate aquifer groundwater evolution through diffusion/expulsion from saline clay porewater and ion exchange, and (2) they act as an aquitard, limiting recharge and inducing preferential flow along the bedrock interface. The two features essentially work together to modulate residence time.

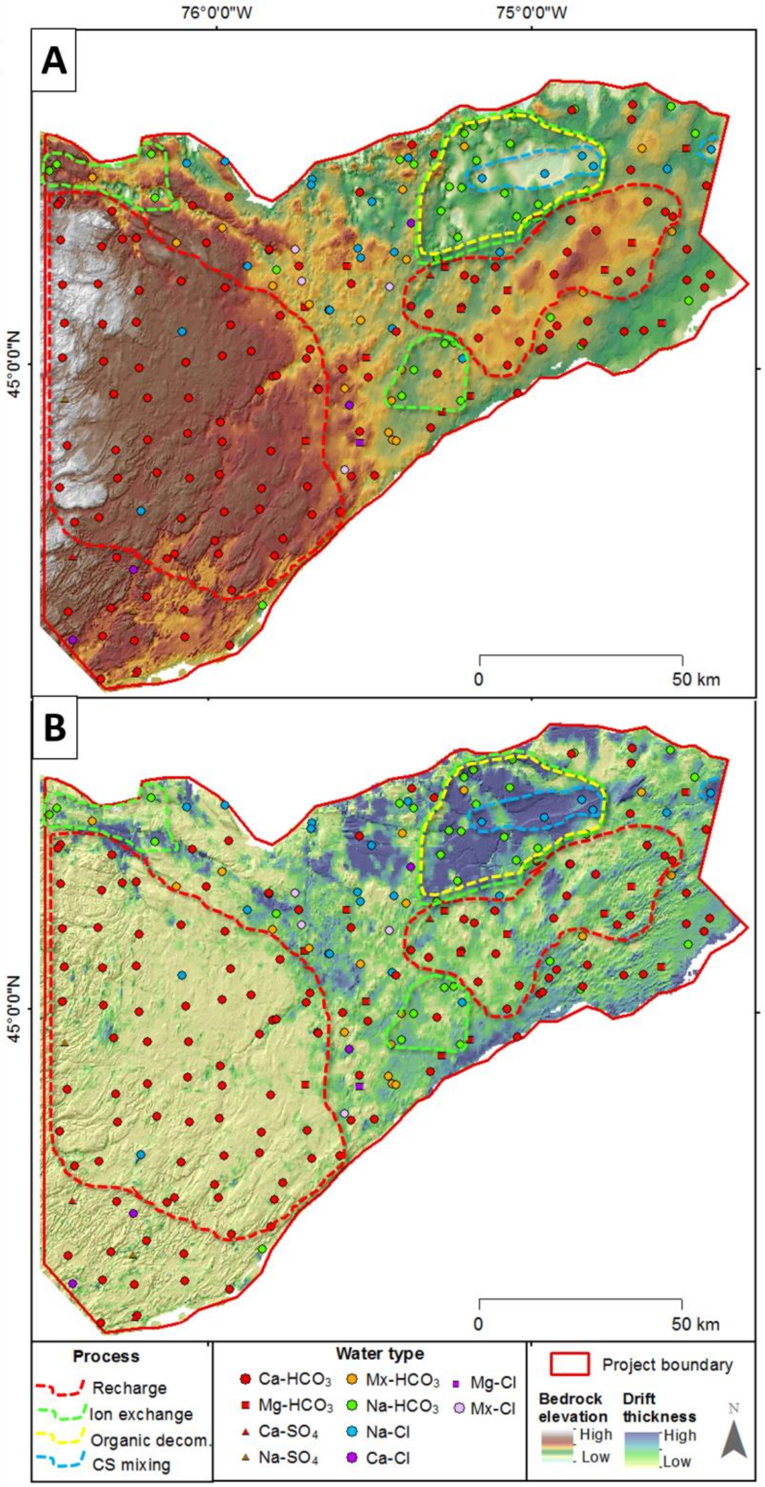

Figure 5.14 Determination of groundwater chemistry by regional processes is driven by (A) bedrock topography and (B) the thickness and extent of glaciomarine deposits. Not all drift is glaciomarine (*e.g.*, most of the southeast; see Figure 2.9). CS stands for Champlain Sea.

The importance of residence time for the chemical character of eastern Ontario groundwater is reflected by the strong relationship between the process zones (Figure 5.14) and tritium content (figures 5.2, 5.3, 5.5, 5.8). The two regional recharge zones have tritium content elevated relative to surroundings, indicating younger water. Ion exchange, organic decomposition and mixing with Champlain Sea water prevail in areas where groundwater is untritiated, signifying no contribution of modern recharge in at least ~60 years.

In addition to hosting untritiated groundwater, the presence of relict Champlain Sea water in the northeast bedrock depression (*i.e.*, Group A Na-Cl samples) means that groundwater age may be up to 10 ka. Here, groundwater in the South Nation Conservation Authority does not easily discharge to the South Nation River or north to the Ottawa River (Figure 2.13; SNCA 2012), because the morphology of the bedrock surface, the capping clays, the extremely low gradients and the higher density of the brackish and saline groundwaters restricts it. Cloutier et al. (2010) reported that Pleistocene seawater lingers in clay-filled bedrock valleys in the Basses-Laurentides bedrock aquifer (southeast Québec) as the result of converging flow and hydraulic stagnation, which is the probable explanation in the northeast bedrock depression (eastern Ontario) as well. The presence of saline water in domestic wells could be enhanced by upconing of deeper, saline groundwater caused by pumping (*e.g.*, Zhou et al. 2005) beneath thick clay (up to 70m) where groundwater replacement is restricted. Extended residence time can explain the anomalous groundwater chemistry in the northeast bedrock depression, as reactions can proceed over a long time, allowing build-up and depletion of associated chemical species (*e.g.*, CH_4, I^-, pH, SO_4^{2-}).

Groundwater $\delta^{18}O$ provides yet more evidence of the nature of groundwater flow. The ^{18}O-enrichment in the northeast of the study area partly corresponds to the northeast bedrock depression and may be explained by mixing with isotopically-enriched Champlain Sea water ($\delta^{18}O = -10.7‰$; Cloutier et al. 2010). However, for such samples that are less saline, the amount of mixing with Champlain Sea water (as indicated by Cl^- concentration) does not correspond to the amount of ^{18}O enrichment. If diffusion were responsible, the discrepancy might be explained by differing diffusion rates between ^{18}O

and dissolved solids. There is also relatively ^{18}O-enriched groundwater in the west and southwest study area (Figure 4.8A), which is outside the maximum extent of the Champlain Sea (Figure 2.11). The pattern aligns with the region of Precambrian bedrock, where infiltration is almost exclusively through fracture flow, thus allowing recharge of a greater proportion of warm-weather, ^{18}O-rich summer precipitation. Fracture flow allows rapid infiltration, thereby limiting the evapotranspiration, which otherwise reduces groundwater recharge by summer precipitation. Fractures in silicate Precambrian bedrock also allow for less groundwater storage than other media and therefore less seasonal mixing. Meanwhile, the spatial association between the isotopic aberration in the east and the depression strongly suggests that residence time and Champlain Sea water are linked to the relative ^{18}O-enrichment by one mechanism or another. Therefore, there are at least two sources of ^{18}O-enrichment in eastern Ontario groundwater, owing to nature of groundwater flow.

Chapter 6

6 Conclusion

This study characterizes and explains the regional groundwater chemistry of eastern Ontario using 234 water samples collected across approximately 15 500 km^2. These data are a subset of the Ambient Groundwater Geochemistry (AGG) Program of the Ontario Geological Survey, which has baseline groundwater data for all of southern Ontario (Hamilton 2015). This MSc project works to provide an understanding of these data for eastern Ontario by identifying chemical trends, water facies and outliers, and explaining these in terms of geochemical processes and the physical controls on groundwater chemistry. The main findings of the study are summarized here, as well as some applications and suggestions for future work.

The chemical results of particular interest are the elevated total dissolved solids (TDS), elevated halogen concentrations (Cl^-, Br^-, I^-) and isotopic aberrations in eastern Ontario groundwater. Ten water types, based on the proportions of major ions, were found, with the $Ca\text{-}HCO_3$, $Na\text{-}HCO_3$ and Na-Cl types being the most prevalent at the regional scale, together accounting for 79% of the total number of samples. Principal Component Analysis (PCA) reveals 3 principal components (PC) that account for many of the chemical trends seen in eastern Ontario. The descriptive labels given to the PCs were based on the dominant geochemical factor that influences them: “Hardness” (PC1), “Salinity” (PC2) and “Organics” (PC3).

Combining results of principal component analysis, major-ion water type and other chemical constituents present pointed to four main processes operating at the regional scale in eastern Ontario.

(1) **Groundwater recharge** was identified and is characterized by the $Ca\text{-}HCO_3$ water type, negative scores for Salinity (PC2) and detectable tritium.

(2) Evidence of **ion exchange** was found in the Na-HCO_3 water type, which is characterized by elevated pH, elevated fluoride and negative Hardness (PC1) scores.

(3) **Salinization** was identified based on elevated TDS, high Salinity (PC2) scores and a chloride water type (Ca-Cl, Mx-Cl, Mg-Cl or Na-Cl), and was attributed to mixing with connate Champlain Sea water, anthropogenic contamination and/or diffusion/expulsion from glaciomarine clays.

(4) **Organic degradation** was found to be important in eastern Ontario based on PC3 (Organics) and elevated CH_4 and I^-.

The geochemical processes are controlled by the interplay between bedrock topography and fine-grained, Pleistocene glaciomarine deposits, where present. The latter are discontinuous or absent where the bedrock surface is elevated and in these areas, groundwater recharge has a dominant influence on the chemistry. As the bedrock topography decreases eastward, glaciomarine deposits appear and thicken. These deposits lengthen residence time and alter the original recharge chemistry through ion exchange and diffusion/expulsion from saline porewater. Where the bedrock surface forms valleys or depressions, the glaciomarine deposits are generally thick, preventing recharge and leading to extended groundwater residence time. Here ion exchange and diffusion are the dominating processes; anthropogenic contributions are limited because of low recharge. Table 6.1 summarizes typical chemistry for groundwater under the different conditions created by bedrock topography and the glaciomarine deposits.

Table 6.1 Summary of groundwater characteristics resulting from bedrock topography and the glaciomarine deposits.

	Champlain Sea clays	Flow regime	Groundwater chemistry
Elevated bedrock	Generally absent or thin/discontinuous	Recharge	**Dominant process:** Carbonate mineral dissolution **Typical chemistry**: Ca-HCO_3 water type; relatively low (circum-neutral) pH; fresh; modern
Intermediate bedrock elevation	Present and generally continuous, but may be weathered	Mid flow path	**Dominant processes**: Ion exchange, diffusion/expulsion anthropogenic mixing* **Typical chemistry**: Variable water types (especially Mx-HCO_3, Cl-types); elevated TDS; elevated pH; elevated Cl^-
Bedrock valley	Thickened and likely unweathered	Slow discharge	**Dominant processes**: Ion exchange **Typical chemistry**: Na-HCO_3 water type; elevated pH; elevated F^-; submodern (often untritiated)
Northeast bedrock depression	Very thick and unweathered	Convergent, stagnant	**Dominant processes:** Mixing with Champlain Sea water, advanced organic breakdown, ion exchange **Typical chemistry:** Na-HCO_3 and Na-Cl water types; alkaline pH; brackish to saline TDS; depleted of SO_4^{2-}; ^{18}O-enriched; High I^- and CH_4; elevated levels of most elements and compounds; untritiated.

*Occurs mostly where high population density coincides with recharge windows/fractured clay.

In the case of the northeastern bedrock depression, discharge is restricted by the morphology of the bedrock surface and presence of thick, fine-grained glaciomarine deposits. Ion exchange and diffusion/expulsion continue to operate, but very prolonged groundwater residence time also allows the accumulation of advanced breakdown products from organic matter contained in glaciomarine and shale deposits. In some areas of the depression where water is nearly stagnant, saline water from the Champlain Sea remains, long after its retreat about 10 ka BP.

Residence time and quality are important for managing groundwater as a resource in eastern Ontario. Recharge zones were identified, one of which has high tritium contents in the middle of the South Nation Conservation Authority, where a number of communities (*e.g.*, Winchester, Chesterville, Marionville) rely on municipal groundwater and has not yet been discussed in Source Protection documents. Anthropogenic influence is apparent in most areas only to a small extent, as indicated by elevated Cl/Br ratios and low levels of NO_3^-. More significant impacts are seen in individual cases (point contamination) and in the City of Ottawa, where population density is high. Contributions from septic effluents and/or road de-icers can be detected in interface and bedrock aquifers despite the presence of significant drift. Where the glaciomarine clays are weathered through their entire profile, rapid infiltration in fractures, desiccation cracks and root casts in the clay may allow enhanced anthropogenic contributions to groundwater in densely populated areas. The slow movement and poor quality of water in infilled bedrock depressions, in particular, should be noted as a potential concern for public health and further development.

There are several areas where more detailed investigations would provide a greater understanding of eastern Ontario groundwater chemistry:

> (1) The specific mechanisms by which fine-grained glaciomarine deposits provide elevated solutes to bedrock groundwater should be determined. The possibilities of diffusion and fracture flow have been briefly investigated, but other processes, such as expulsion of bound water from clays should also be considered. The control that

these various processes exert on Cl/Br ratios is important for differentiating chloride sources in eastern Ontario.

(2) The impact on water and solute transport in eastern Ontario by seismic events in the Western Québec Seismic Zone should be investigated.

(3) In comparison with other parts of southern Ontario, the concentrations of trace metals (*e.g.*, chromium, cesium, niobium, rubidium, thorium, titanium, vanadium, tungsten, zirconium) and rare earth elements are elevated within the eastern Ontario study area; particularly in the northeast and Precambrian Shield parts. As they are potentially deleterious in water supplies and the ecosystem, it may be of interest to further investigate their source.

(4) Selenium represents an important groundwater constituent in eastern Ontario (*i.e.*, PC2) that is not yet well understood. Its significance may relate to sulphides or marine organics (*e.g.*, Matamoros-Veloza et al. 2011), but further investigation is suggested.

In summary, the fine-grained glaciomarine deposits and bedrock topography together control the residence time of groundwater by constraining the flow path and the rate of infiltration, affecting the relative influences of recharge, ion exchange, salinization and organic breakdown on chemistry. Residence time, particularly while in contact with the glaciomarine clays, is the single most profound control on the variability of groundwater chemistry in eastern Ontario.

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Appendices

Appendix A : Sample names utilized in the current study from MRD 283-Revised

Sample ID	Sample ID	Sample ID	Sample ID
12-AG-001	12-AG-036	12-AG-072	12-AG-110
12-AG-002	12-AG-037	12-AG-073	12-AG-111
12-AG-003	12-AG-038	12-AG-074	12-AG-112
12-AG-004	12-AG-040	12-AG-076	12-AG-113
12-AG-006	12-AG-041	12-AG-077	12-AG-114
12-AG-007	12-AG-042	12-AG-078	12-AG-116
12-AG-010	12-AG-043	12-AG-080	12-AG-117
12-AG-011	12-AG-044	12-AG-081	12-AG-118
12-AG-012	12-AG-045	12-AG-083	12-AG-120
12-AG-013	12-AG-046	12-AG-085	12-AG-122
12-AG-014	12-AG-047	12-AG-086	12-AG-124
12-AG-015	12-AG-048	12-AG-087	12-AG-125
12-AG-016	12-AG-050	12-AG-090	12-AG-126
12-AG-017	12-AG-051	12-AG-091	12-AG-127
12-AG-018	12-AG-052	12-AG-092	12-AG-128
12-AG-019	12-AG-053	12-AG-093	12-AG-130
12-AG-020	12-AG-054	12-AG-094	12-AG-131
12-AG-021	12-AG-055	12-AG-095	12-AG-132
12-AG-022	12-AG-057	12-AG-096	12-AG-133
12-AG-023	12-AG-058	12-AG-097	12-AG-134
12-AG-024	12-AG-061	12-AG-098	12-AG-135
12-AG-025	12-AG-062	12-AG-100	12-AG-137
12-AG-026	12-AG-063	12-AG-101	12-AG-138
12-AG-027	12-AG-064	12-AG-102	12-AG-140
12-AG-028	12-AG-065	12-AG-103	12-AG-141
12-AG-030	12-AG-066	12-AG-104	12-AG-143
12-AG-031	12-AG-067	12-AG-105	12-AG-144
12-AG-033	12-AG-070	12-AG-107	12-AG-146
12-AG-034	12-AG-071	12-AG-108	12-AG-150

Sample ID	Sample ID	Sample ID	Sample ID
12-AG-151	12-AG-198	12-AG-240	13-AG-024
12-AG-152	12-AG-200	12-AG-241	13-AG-026
12-AG-153	12-AG-201	12-AG-242	13-AG-027
12-AG-156	12-AG-202	12-AG-243	13-AG-028
12-AG-157	12-AG-204	12-AG-244	13-AG-030
12-AG-160	12-AG-207	12-AG-245	13-AG-046
12-AG-161	12-AG-208	12-AG-246	13-AG-091
12-AG-162	12-AG-213	12-AG-247	13-AG-093
12-AG-163	12-AG-214	12-AG-248	13-AG-697
12-AG-164	12-AG-215	12-AG-250	13-AG-702
12-AG-166	12-AG-216	12-AG-251	13-AG-718
12-AG-168	12-AG-217	12-AG-252	13-AG-747
12-AG-170	12-AG-218	12-AG-253	14-AG-053
12-AG-171	12-AG-220	12-AG-254	14-AG-054
12-AG-172	12-AG-221	12-AG-258	14-AG-055
12-AG-174	12-AG-222	12-AG-261	14-AG-056
12-AG-175	12-AG-223	12-AG-262	14-AG-057
12-AG-176	12-AG-224	12-AG-264	14-AG-058
12-AG-177	12-AG-225	12-AG-265	14-AG-060
12-AG-178	12-AG-227	12-AG-267	14-AG-063
12-AG-180	12-AG-228	13-AG-001	14-AG-064
12-AG-182	12-AG-230	13-AG-002	14-AG-065
12-AG-183	12-AG-231	13-AG-003	14-AG-066
12-AG-184	12-AG-232	13-AG-004	14-AG-067
12-AG-187	12-AG-233	13-AG-006	14-AG-068
12-AG-188	12-AG-234	13-AG-008	14-AG-070
12-AG-190	12-AG-236	13-AG-021	14-AG-071
12-AG-193	12-AG-237	13-AG-022	14-AG-072
12-AG-194	12-AG-238	13-AG-023	14-AG-073

Appendix B: Summary statistics[14]

Parameter	Units	Count	% Censored	Average	Median	Min	Max	Standard Deviation
Field and Aggregate Parameters								
TDS	mg/L calculated	234	0.0	810.7	555.7	187.9	10396.7	1037.4
Conductivity	μS/cm	229	0.0	1274	737	258	31050	2628
pH	pH units	234	0.0	7.18	7.12	5.71	9.05	0.45
ORP	mV $_{Ag\text{-}AgCl}$	232	0.0	-67.7	-99.5	-348.8	256	124.1
Alkalinity	mg/L as $CaCO_3$	234	0.0	289	251	61	1036	142
Temperature	°C corrected	232	0.0	10.04	9.85	7.48	29.24	1.62
Major Ions								
Ca	mg/L	234	0.0	72.538	67.837	1.13	281.204	45.444
Mg	mg/L	234	0.0	30.344	24.794	1.511	358.263	29.748
Na	mg/L	234	0.0	114.149	35.508	1.154	2851.197	299.896
K	mg/L	234	1.7	7.61	3.95	< 0.005	123.7	13.85
HCO_3	mg/L	234	0.0	352	306	74	1263	173
SO_4^{2-}	mg/L	234	2.6	53.92	37.34	< 0.05	613.73	74.43
Cl^-	mg/L	234	0.0	177.20	41.15	0.96	5786	578.37
Nitrogen Parameters								
NO_3^-	mg/L as N	234	59.4	0.83	< 0.013	< 0.006	11.5	1.85
NO_2^-	mg/L as N	234	90.6	0.008	< 0.005	< 0.003	0.3	0.031
$NH_3 + NH_4^+$	mg/L as N	234	23.5	0.56	0.11	< 0.04	18.7	2.07
TKN	mg/L as N	234	17.9	0.76	0.2	< 0.05	23.8	2.49
Organic N	mg/L as N	234	45.3	0.22	0.06	< 0.05	5.89	0.54
Minor Ions								
Br^-	mg/L	234	30.3	0.587	0.068	< 0.02	40.91	3.272
F^-	mg/L	234	0.4	0.409	0.219	< 0.01	4.185	0.569
I^-	μg/L	233	14.6	96.2	12.9	< 5	6650	538.2
PO_4^{3-}	mg/L	234	92.3	0.169	< 0.04	< 0.04	14.206	1.048
DIC	mg/L	234	0.0	80.5	68.4	14	497	50.5
DOC	mg/L	234	15.4	3.7	2.1	< 1	44.6	5.1
B	μg/L	234	0.4	228	80	< 4	3634	402

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[14] Values are reported to the decimal count of the raw data received from the laboratories

Fe	μg/L	234	37.6	397	106	< 15	5762	805
Sr	μg/L	234	0.0	1932	1037	60	18037	2651
Si	μg/L	234	0.0	6346	5768	1931	13432	2384
Bacteriological Parameters								
Total Coliform	Counts/100 mL	233	0.0	4	0	0	128	12
Fecal Coliform	Counts/100 mL	232	0.0	0	0	0	30	2
Trace Constituents								
Ag	μg/L	234	88.5	< 0.005	< 0.005	< 0.005	0.022	0.002
Al	μg/L	234	94.9	< 5	< 5	< 5	283	22
As	μg/L	234	4.7	0.355	0.192	< 0.3	5.853	0.554
Ba	μg/L	234	1.7	219.2	110.6	< 0.02	4940	473.7
Be	μg/L	234	87.6	< 0.01	< 0.01	< 0.01	0.107	0.008
Bi	μg/L	234	100.0	< 0.05	< 0.05	< 0.05	< 0.05	N/A
Cd	μg/L	234	73.1	< 0.01	< 0.01	< 0.01	0.063	0.010
Ce	μg/L	234	36.3	0.0789	0.0036	< 0.002	11.62	0.7674
Co	μg/L	234	41.0	0.127	0.019	< 0.005	3.352	0.341
Cr	μg/L	234	37.6	0.221	0.045	< 0.02	16.527	1.138
Cs	μg/L	234	1.7	0.0518	0.0308	< 0.0005	0.578	0.0797
Cu	μg/L	234	21.4	3.90	0.77	< 0.2	143.56	10.96
Dy	μg/L	234	40.6	0.0150	0.0014	< 0.001	1.565	0.1071
Er	μg/L	234	42.7	0.0121	0.0014	< 0.001	1.199	0.0825
Eu	μg/L	234	92.3	0.0020	< 0.0004	< 0.0004	0.2791	0.0188
Ga	μg/L	234	6.8	0.0072	0.0048	< 0.002	0.0725	0.0090
Gd	μg/L	234	23.5	0.0158	0.0026	< 0.001	1.5	0.1023
Hf	μg/L	234	94.9	< 0.004	< 0.004	< 0.004	0.023	0.002
Hg	ng/L	234	73.9	< 1.5	< 1.5	< 1.5	8.1	1.0
Ho	μg/L	234	17.9	0.00356	0.00034	< 0.0001	0.368	0.02523
La	μg/L	234	6.8	0.0416	0.0047	< 0.001	4.3	0.2881
Li	μg/L	234	1.7	15.32	8.98	< 0.01	124.7	19.08
Lu	μg/L	234	20.9	0.00298	0.00034	< 0.0001	0.2101	0.01517
Mn	μg/L	234	21.4	37	13	< 2	1038	95
Mo	μg/L	234	2.1	1.591	0.842	< 0.01	22.2	2.645
Nb	μg/L	234	64.5	0.0028	< 0.001	< 0.001	0.0924	0.0081
Nd	μg/L	234	29.9	0.0574	0.0062	< 0.003	6.18	0.4124
Ni	μg/L	234	11.5	1.12	0.55	< 0.1	20.01	2.02
Pb	μg/L	234	3.4	0.0795	0.0297	< 0.002	0.8506	0.1266
Pr	μg/L	234	28.2	0.0118	0.00085	< 0.0004	1.369	0.0912
Rb	μg/L	234	1.7	5.009	3.392	< 0.005	89.1	7.856
Sb	μg/L	234	46.6	0.026	0.012	< 0.01	0.513	0.052
Sc	μg/L	234	73.9	0.10	< 0.1	< 0.1	1.44	0.13

Se	μg/L	234	29.5	1.03	0.32	< 0.2	29.02	2.89
Sm	μg/L	234	24.4	0.0132	0.0020	< 0.001	1.36	0.0915
Sn	μg/L	234	74.4	0.019	< 0.01	< 0.01	0.814	0.075
Ta	μg/L	234	88.5	0.00031	< 0.0003	< 0.0003	0.02028	0.00139
Tb	μg/L	234	35.0	0.00227	0.00018	< 0.0001	0.2453	0.01670
Th	μg/L	234	80.3	0.0032	< 0.001	< 0.001	0.2384	0.0176
Ti	μg/L	234	77.4	0.43	< 0.1	< 0.1	15.77	1.52
Tl	μg/L	234	50.0	0.0094	0.0008	< 0.001	0.1825	0.0213
Tm	μg/L	234	26.1	0.00190	0.00026	< 0.0001	0.1774	0.01217
U	μg/L	234	1.7	0.925	0.376	< 0.0002	23.99	2.003
V	μg/L	234	7.3	0.2056	0.0536	< 0.03	2.3773	0.3581
W	μg/L	234	39.7	0.212	0.013	< 0.01	8.794	0.788
Y	μg/L	234	1.7	0.1525	0.0286	< 0.0005	12.13	0.8654
Yb	μg/L	234	41.5	0.0138	0.0015	< 0.001	1.26	0.0863
Zn	μg/L	234	32.5	4.1	1.5	< 1	128.8	10.8
Zr	μg/L	234	84.6	0.10	< 0.1	< 0.1	1.81	0.18
Isotopic Parameters								
Tritium	TU	231	13.0	7.8	8.1	< 0.8	19.1	5.1
$\delta^{18}O$	‰ VSMOW	234	0.0	-11.70	-11.79	-13.09	-8.49	0.67
$\delta^{2}H$	‰ VSMOW	234	0.0	-77.53	-78.12	-88.01	-55.62	4.67
Dissolved Gases								
Dissolved Oxygen	% Saturation	233	0.0	7.4	0	0	89.8	17.6
H_2S	mg/L S^{2-}	153	4.6	0.16	0.01	< 0.01	7	0.77
$CH_{4(aq)}$	mg/L	233	0.0	1.5595	0.0034	0	99.3921	8.2439
$CO_{2(aq)}$	mg/L	233	0.0	5.9823	4.2449	0	42.5282	6.2362

Appendix C: Comparison of characteristics of chloride groups A, B and C.

	Group A	**Group B**	**Group C**
N	5	25	5
Sample Numbers	**12-AG-**140, 202, 207, 208 **13-A**G-718	**12-AG-**001, 003, 006, 020, 047, 057, 058, 065, 074, 102, 103, 104, 107, 125, 126, 133, 162, 170, 214, 231, 232, 248 **13-AG-**024 **14-AG-**060, 074	**12-AG-**044, 087, 144, 262 **14-AG-**076
Water types	Na-Cl	Na-Cl, Ca-Cl, Mg-Cl, Mx-Cl	Na-Cl
Cl^- av. (mg/L)	3500	460	390
Cl/Br range	141 - 287	592 - 25748	112 – 480
Cl/Br av.	220	4570	310
Na/Cl av.	0.54	0.44	0.89
Ca/Na	0.02	0.91	0.10
δ^{18}O range (‰ VSMOW)	–10.8 to –10.1	–13.0 to –10.2	–12.9 to –8.5
δ^{18}O av. (‰VSMOW)	–10.5	–11.7	–11.5
TDS av. (mg/L)	6720	1280	1190
pH av.	7.57	6.97	7.60
Alkalinity av. (mg/L as $CaCO_3$)	910	280	230
Detectable tritium (N)	0 / 5	25 / 25	4 / 5
Detectable tritium av. (TU)	N/A	10.4	7.4 (of 4)
Detectable NO_3^- (top N), NO_2^- (bottom N)	0 / 5 0 / 5	12 / 25 19 / 25	3 / 5 0 / 5
B av. (μg/L)	1370	70	550
Li av. (μg/L)	37	14	53
Se av. (μg/L)	16.0	0.5	4.4
Grouped by:	-High Cl^- with consistent δ^{18}O -low, consistent Cl/Br -Tritium below detection	-Moderate Cl^- with wide range of δ^{18}O - Cl/Br high (>500) and tends to increase with Cl^- -Detectable tritium	-Relatively low Cl^- and Cl/Br (<500) -Some NO_3^- present -Similar to Group A but off on at least one factor

Curriculum Vitae

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Abstracts & Publications:

Colgrove, L.M., Hamilton, S.M., Longstaffe, F.J. 2014. Patterns and Controls of Shallow Groundwater Chemistry in Eastern Ontario *in* Summary of Field Work and Other Activities 2014, Ontario Geological Survey, Open File Report 6300, p. 34-1 to 34-10.

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