Characterization of Bedrock Topography, Overburden Thickness and Groundwater Geochemistry in Eastern Ontario

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Abstract

Across eastern Ontario areas of poor water quality have been identified through several groundwater studies completed as part of the Ontario Geological Surveys Ambient Groundwater Geochemistry Program in partnership with local municipalities and conservation authorities. This study focuses on a subset of data collected between 2012 and 2017 between east Ottawa and Champlain Township along the south shore of the Ottawa River. A high degree of variability is observed in groundwater chemistry and geochemical processes which closely relate to major geologic features across the study area (~1600km^2). Over 9000 borehole records were evaluated and used to produce updated bedrock topographic and drift thickness models to better constrain geologic features in the region. These models in conjunction with geochemical results from 369 domestic well water samples highlight the significant implications that stagnant groundwater flow and preferential recharge areas have on groundwater quality across the study area.

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1 Introduction

1.1 Background

Increased development pressure across eastern Ontario has prompted several groundwater studies to be carried out between 2012 to 2017 as part of Ontario's Ambient Groundwater Geochemistry Program (OAGGP) organized by the Ontario Geological Survey with local municipalities and conservation authorities (Hamilton, 2021; Di Iorio et al., 2015, 2017). The objective of these studies was to improve the understanding of groundwater resources across the region as several anomalous geochemical signatures have been identified. This includes elevated levels of halogens (iodide > 10,000 ppb and fluoride > 4 ppm) and methane (> 60 mg/L), in addition to pockets of fossil Champlain seawater (Lemieux et al, 2018b). These exceedances pose a threat to the health and well being of residents who are located outside of areas with municipal water services that rely on private wells to meet their water needs.

The OAGGP has collected and published geochemical data for 3933 groundwater samples across the province following a standardized sampling procedure to produce maps of expected groundwater chemistry at the regional scale (Hamilton, 2021). This dataset serves to: provide baseline conditions, identify anomalous chemical signatures in residential wells, flag possible anthropogenic contamination, and to provide an understanding of the primary geologic controls on groundwater. The east Ottawa and Champlain township groundwater study in 2017 has updated the OAGGP database in eastern Ontario with geochemical results from 369 shallow domestic well water samples (Hamilton, 2021).

The study area was chosen due to the availability of samples and the high degree of variability in groundwater chemistry which has implications for water quality across the region. Similar studies have been completed in southern Ontario at a lower sampling density to map out area's of poor water quality (Hamilton, 2021). A total of 369 groundwater samples are described in this research, all of which are from interface aquifers across the region.

The geological and hydrogeological context of eastern Ontario forms the basis for interpreting these extensive datasets, but establishing this context relies on information derived from well logs resident in Ministry of Natural Resources databases. Although, considerable vetting of well records is required to produce a reliable subset of coherent well logs from which regional geology, bedrock elevations and overburden thickness can be established. The aim of this thesis is to create the geological context required for the interpretation of geochemical facies, processes and anomalies observed within the extensive geochemical dataset collected for Eastern Ontario.

1.1.1 Thesis objectives

The main objectives for this thesis are to:

i. Develop an improved understanding of drift thickness and bedrock surface elevations in an area along the south shore of the Ottawa River, from Ottawa to Hawkesbury in eastern Ontario, by creating a refined borehole dataset to identify the extent of major buried bedrock depressions filled with glaciomarine deposits.

ii. Characterize the distribution of groundwater types, components, and anomalous geochemical signatures to determine how these relate to major buried bedrock depressions.

iii. Investigate the principle geochemical processes responsible for producing the observed results.

iv. Develop a conceptual model of groundwater flow and hydrogeologic environments to illuminate major spatial trends of groundwater chemistry and geologic conditions.

This thesis has been divided into 4 chapters: Chapter one covers the essential background information, the geologic history of the study area and the sampling methodology. Chapter two focuses on the first objective (i) and describes the methodology used for the development of a refined borehole dataset and the mapping results which outline major buried bedrock depressions across the study area. Chapter three focuses on the second objective and characterizes the distribution of groundwater types, components, and geochemical signatures and how these relate to the drift thickness. Chapter four concentrates on the third and fourth objectives and outlines the principle geochemical processes responsible for producing the observed geochemical results in addition to conclusions and suggestions for future work.

1.1.2 Affiliations

A subset of groundwater samples used in this thesis was collected by this author during the 2017 east Ottawa and Champlain township groundwater study, which was a collaborative project with the City of Ottawa and the Ontario Geological Survey with assistance from the South Nation Conservation Authority. These collaborative efforts have produced some of the highest sampling densities within the Ontario Geological Survey's Ambient Groundwater Geochemistry database compared to the rest of the province (Hamilton, 2021).

1.2 Study area

The studied area covers approximately 1600 km^2 in the St. Lawrence lowlands (Figure 1.1). It is located along the south shore of the Ottawa river between east Ottawa and Hawkesbury and is generally bound to the south by highway 417. Across the region most of the land is used for agriculture, with the City of Ottawa and Hawkesbury being the largest urban centers. Villages in the study area with public services use treatment plants from water pumped from the Ottawa river. While residents outside these serviced areas rely on groundwater from shallow aquifers.

1.2.1 Bedrock geology

The study area contains Paleozoic sedimentary formations deposited amid the Ottawa Embayment (Late Cambrian – Upper Ordovician periods) which lie uncomformably above metamorphic and igneous crystalline Precambrian basement (Figure 1.2) formed during the Grenville Orogeny (1.3 – 1.0 Ga) (Armstrong and Dodge, 2007). These Precambrian units consist of gneiss and marble with pegmatitic intrusions and are believed to be present in the northeastern region of the study area along the Ottawa river. However, due to extensive and thick Quaternary sediment cover there are very few to no outcrops to support the presence of these Precambrian formations.

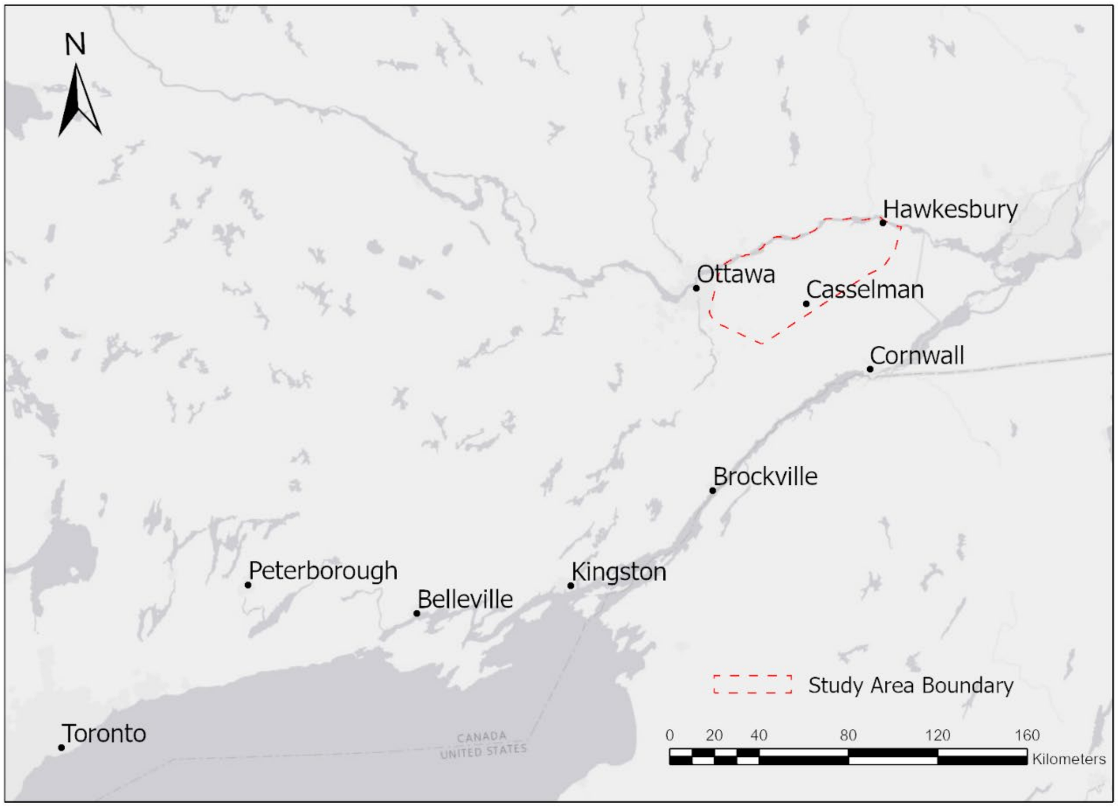

Figure 1.1 Study area boundary

Paleozoic sedimentary formations represent the most common bedrock units across the study and are composed of sandstones and dolostones which are upper Cambrian to Lower Ordovician in age. These units are interbedded with Middle to Upper Ordovician limestone, siltstone, and shales. These Paleozoic sedimentary rocks are believed to reach 1000 meters in thickness (Sanford, 1993), composed in part by the upper Sauk and Lower Tippecanoe sedimentary platform sequences that were deposited as the Iapetus Ocean opened and then closed (Sanford, 1993; Rimando and Benn 2005).

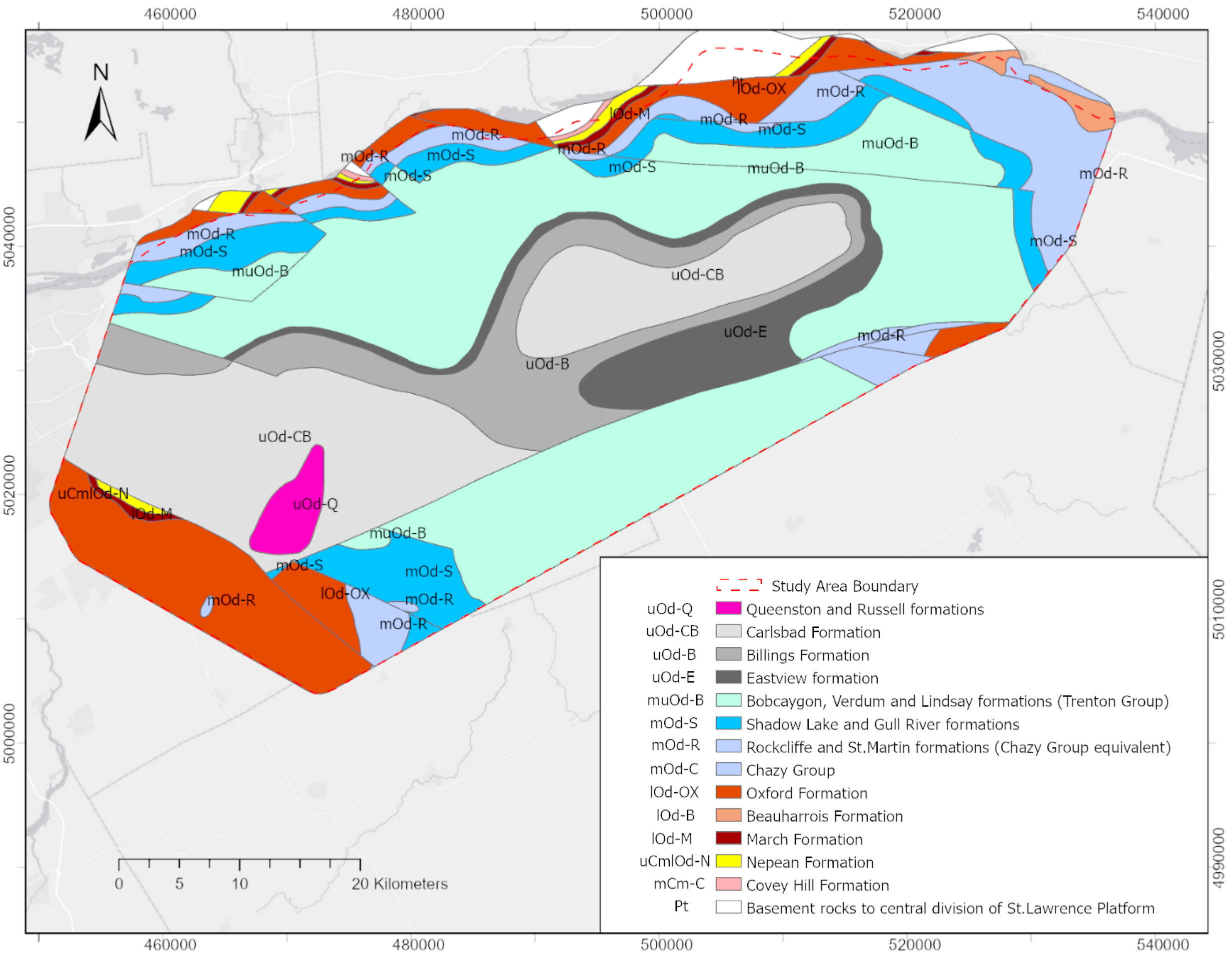

Figure 1.2 Bedrock Geology (Sanford, 2010) of the study area

The oldest Paleozoic units, which are Upper Cambrian in age, compose the Potsdam group that consists of both the Covey Hill and Nepean formations. The Covey Hill formation lies unconformably over the Precambrian basement and displays variable thickness. It is a coarse and clastic unit that grades from an arkosic conglomerate at its base to an orthoquartzpathic sandstone with cross-bedding at the top (Sanford, 1993). This unit is believed to represent a terrestrial alluvial fan with braided fluvial depositions initiated by rifting associated with the opening of the Iapetus Ocean (Wolfe and Dalrymple, 1984, 1985; Rimando and Benn, 2005). The Nepean formation lies uncomfortably above the Covey Hill formation and displays the first evidence of marine deposition while exhibiting indications of terrestrial, subtidal and intertidal environments (Wolfe and Dalrymple, 1984, 1985). This unit consists of mature, orthoquartzitic sandstones with occasional conglomerates, arkose, and shale interbeds at its base.

The Beekmantown group is Lower to Middle Ordovician in age and unconformably overlies the Nepean formation, representative of interior passive margin platform deposition (Williams, 1991; Sloss, 1963). This group consists of the March and Oxford formations which are composed of shallow marine clastic and carbonates rocks exclusive to eastern Ontario. This group is typically dolomitic with minor fossil content, with the exception of stromatolites. Additionally, lenses of gypsum, breccia, mudcracks, and halite clasts are common which highlight the variable lithological and depositional characteristics of the Beekmanton group (Sanford, 1993).

The March formation, or the Theresa formation in Quebec, is believed to have formed in supratidal to subtidal environments and increases from 10 – 60 meters in thickness towards the center of the Ottawa embayment (Williams, 1991). This formation is composed of interbedded orthoquartzitic sandstone and dolostone, with dolomite increasing in abundance in the upper sections (Sanford, 1993). Unconfromably overlying the March formation is the Oxford formation, otherwise known as the Beauharnios formation in Quebec, and is characterized by the disappearance of sandstone and thickens up to 125 meters to the east (Sanford, 1993). Towards the basin's center, the Oxford formation changes from a stromatalitic dolostone to a micritic dolostone that is interbedded with limestone and shale (Sanford, 1993). Deposition of this unit is believed to have occurred in a hypersaline, supratidal environment with an upward decrease in grain size indicating progressive sea level rise during its deposition. Regular fluctuation in sea level during this period is believed to be responsible for the erosion and removal of Early Ordovician units which are not present (Bélanger, 2008).

The Rockcliffe formation is the only member of the Chazy Group in eastern Ontario and unconformably overlies the Oxford formation. The deposition of this formation is associated with renewed transgression in the Middle Ordovician and marks the beginning of the development of a foreland basin carbonate platform (Dix et al., 1998). It is mainly composed of interbedded quartz sandstone, shale, and limestone where the lower sequence consists of quartz sandstone with shale beds and the upper sections display more abundant shale, with shaley bioclastic limestone and silty dolostone (Johnson et al., 1992; Williams, 1991). Characteristics of this formation include ripple-marks, cut-and-fill structures, and desiccation cracks within sandstone components (Sanford, 1993). Eastern sections contain relics of the St. Martin member a of the Quebec Basin which used to be continuous with the Rockcliffe formation and include cross-bedding, crinoidal grainstone, and sandstone beds that are intercalated with calcarenites (Johnson et al., 1992; William, 1991; Sanford, 1993).

The Ottawa Group disconformably overlies the Chazy Group and is a product of deposition which occurred in the middle to late Ordovician during a period of continuous sea level rise marked by marine transgression from peritidal to open shelf environments. This group includes the Shadow Lake, Gull River, Bobcaygeon, Verulam, and Lindsay formations. This group is composed of low-energy and highly fossiliferous interbedded limestone and shale units which implies continuous deposition on a regularly deepening shelf (Johnson et al., 1992).

Upper Ordovician deposits, such as the Billings, Carlsbad, and Queenston formations are indicative of continuously deepening marine environments and are mainly composed of shales and siltstones with interbeds of fine-grained limestone (Johnson et al., 1993). The Billings formation was deposited in a deep-water environment consisting of organic rich shales, similar to the Linsday formation, with 3 to 7 percent of its weight being total organic carbon (NRCAN, 2017). The Carlsbad shale lies conformably over the Billings formation and consists of calcareous fossiliferous siltstone and limestone that indicate shallowing depositional environments (Armstrong and Dodge, 2007; Johnson et al., 1992; Sharma et al., 2003). The Queenston formation represents the youngest bedrock unit in eastern Ontario and is unique in its appearance as it is composed mostly of red shale with siltstone and interbedded with minor amounts of sandstone and limestone (Johnson et al., 1992; Sharma et al., 2003).

1.2.2 Overburden geology and the Champlain Sea Sediments

The overburden described throughout this section refers to the sediments and deposits located between the ground surface and the top of underlying bedrock units. Across the region, both the surficial geology (Figure 1.3) and underlying overburden were emplaced and re-worked by Quaternary processes. During the most recent Wisconsin glaciation, eastern Ontario was overlaid by thick ice cover as part of the Laurentide Ice Sheet which resulted in the deposition of Glacial tills over bedrock units. These sandy tills were derived from the erosion of carbonate bedrock units which were abundant. Reworking of this material occurred through several iterations of glacial advance and retreat prior to the influence of marine and fluvial processes (McCormack and Therrien, 2014). Several North-South trending eskers and subaqueous fans are present under glaciomarine deposits within the study area and are believed to have formed from extensive meltwater transport associated with the Laurentide Ice Sheet retreat which began around 14 ka BP following the most recent glacial maximum (23 ka BP). The resulting inland sea, known as the Champlain Sea, was at its maximum extent around 12.5 ka BP and submerged much of eastern Ontario for approximately 2 ka before isostatic rebound of the continental landmass resulted in the sea draining back out the St. Lawrence seaway into the Atlantic. The Champlain sea was mixture of seawater, glacial meltwater, and Pleistocene meteoric water (Cloutier et al., 2010). The Champlain Sea depositional sequences consist of older basal rhythmites to younger massive muds and red-and-grey stratified muds (Gadd, 1986). These muds overlay subaqueous meltwater outwash sand and gravel deposits which are capped by nearshore sands. The entire mud sequence has been interpreted as a product of deltaic offlap resulting from the regressive phase towards the end of the Champlain Sea. Massive muds are the most abundant component in this sequence with an average thickness of 10 meters but are observed up to 90 meters in thickness (Charron, 1975) with 0.4 – 1% weight percent of organic material (Laventure and Warkentin, 1965).

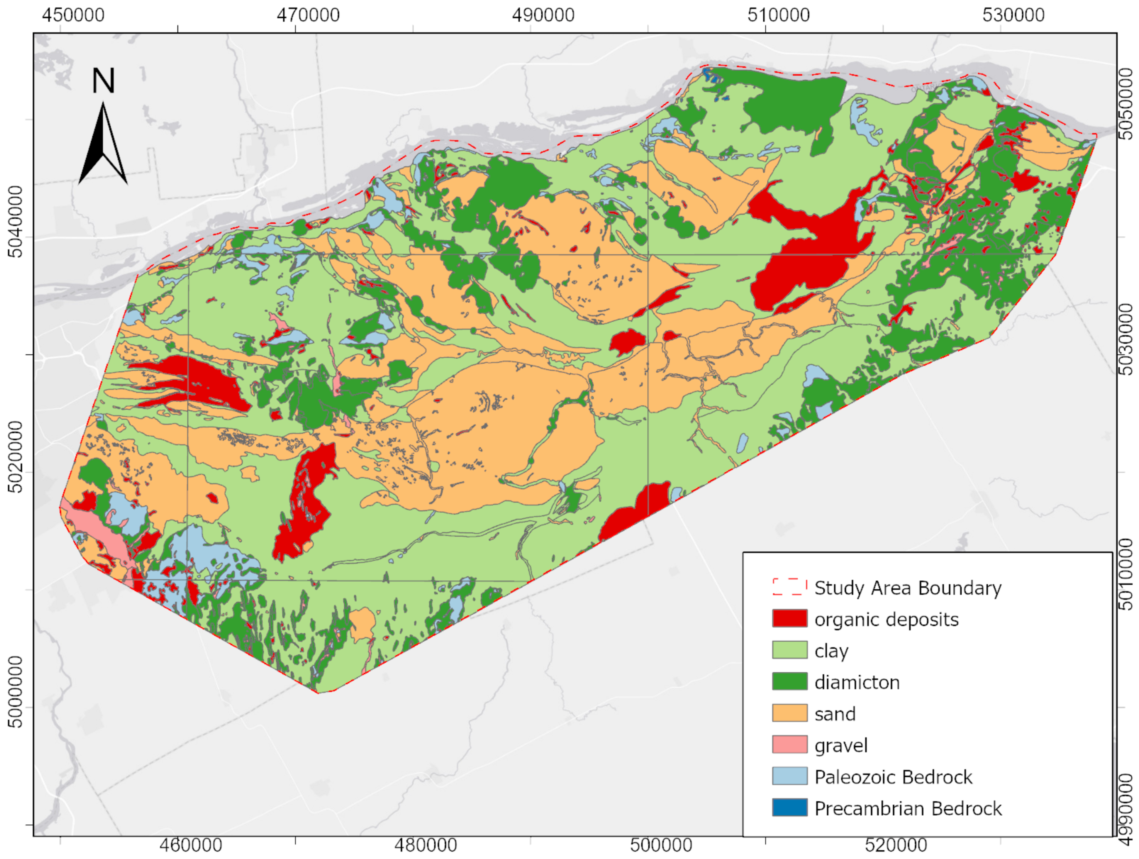

Figure 1.3 Surficial sediments and bedrock outcrops (OGS, 2010) across the study area

The regression of the Champlain Sea corresponds with the evolution of the complex channel systems of the Proto-Ottawa river, due to high flow rates from the melting of ice margins, Lake Agassiz, and the upper great lakes (Fulton, 1987). During this phase (10-4.7 ka BP) unconsolidated sediments were reworked, and as flow rates decreased, abandoned channels and poorly drained glaciomarine muds resulted in the development of peat deposits and wetlands (Fulton, 1987).

1.2.3 Hydrogeology

The main aquifer relied upon by residents across eastern Ontario is analogous with the interface aquifer described by Cloutier et al. (2010), some 100 km east of the current study area. Due to its high yield and relatively shallow accessibility it is the principal target for drillers and homeowners seeking domestic water sources. This interface aquifer is characterized by a layer of permeable tills and outwash sands which are found over highly fractured bedrock, all of which is covered by massive lenses of glaciomarine deposits emplaced during the Champlain Sea episode. Charron (1978) concluded that bedrock topography controls groundwater flow paths at the regional scale in eastern Ontario because it is along this sediment-rock interface that the greatest permeability is found. The interface aquifer flow paths possess similar hydraulic conductivity values to that of the Basse-Laurentide sedimentary aquifer in western Quebec (Cloutier et al., 2010) on the order of 7.8×10^{-4} m/s compared to intermediate and deeper flow path ranges between 10^{-8} to 10^{-4} m/s depending on the Paleozoic sedimentary rocks (Nastev et al., 2004). In contrast, the overlying muds possess much lower hydraulic conductivity ranges, between 10^{-10} to 10^{-8} m/s. Recharge of meteoric water occurs in topographically high areas with little to no glaciomarine sediment cover where it then preferentially flows through the upper layers of bedrock underneath the less permeable massive glaciomarine deposits via the interface aquifer to topographically lower areas. The lowest regions within the study area are major depressions in the bedrock surface that are confined by some of the thickest sediment cover in eastern Ontario. Within these depressions, Cloutier et al., (2010) have identified fossil Champlain seawaters that represent the oldest stage of groundwater flow within the regional interface aquifer. This system is divided into three main components which are displayed in Cloutier's conceptual model shown in Figure 1.4: the hydraulically unconfined recharge area, a transitional area that is semi-confined, and the confined bedrock depressions.

Potentiometric maps have been produced in the Mississippi-Rideau and Rasin-South Nation source water protection reports (RRCA and SNC, 2008) using static water levels contained with the Ontario Water Well Information System (OWWIS), also know as the Ontario Water Well Database (OWWD) and can be seen in Figure 1.5. This highlights the interrelationships between groundwater flow and topography as it moves from higher potentiometric areas to lows and surface waterbodies. Stagnant flow zones are identified by low potentiometric surface elevations which are common in areas where thick sequences of glaciomarine deposits occupy bedrock surface depressions. Flow regimes across the study area are predominately horizontal along the interface aquifer, however vertical solute diffusion within low permeability glaciomarine deposits has been demonstrated to have significant implications on groundwater geochemistry (Cloutier et al., 2006). Massive Champlain Sea clays across the St. Lawrence lowlands have been shown by Chapuis and Saucier (2013) to drain via leaky aquifers which collect small amounts of vertically percolating groundwater over large aerial extents.

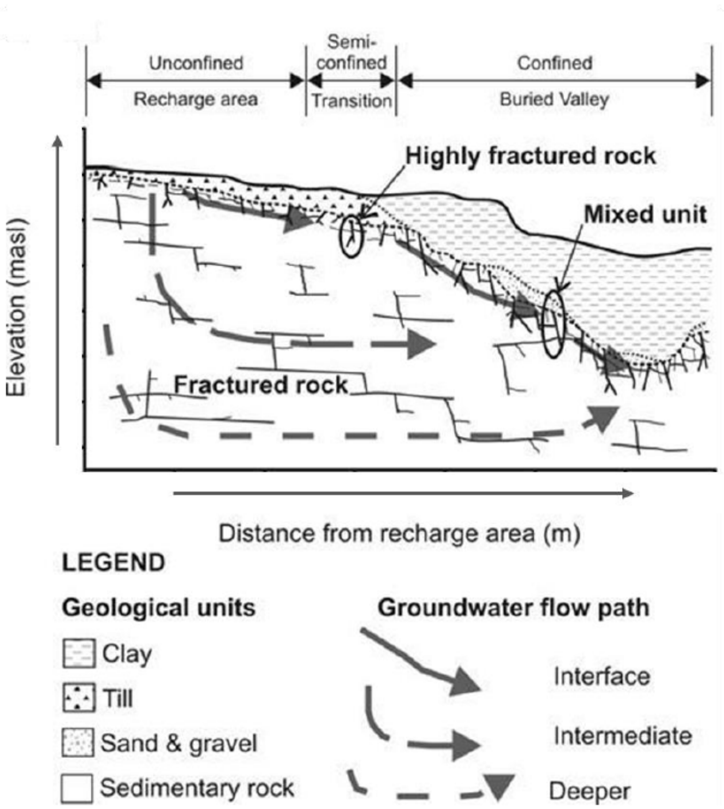

Figure 1.4 Conceptual hydrogeologic model for the Basse-Laurentide sedimentary aquifer system. Modified by Cloutier et al. (2010)

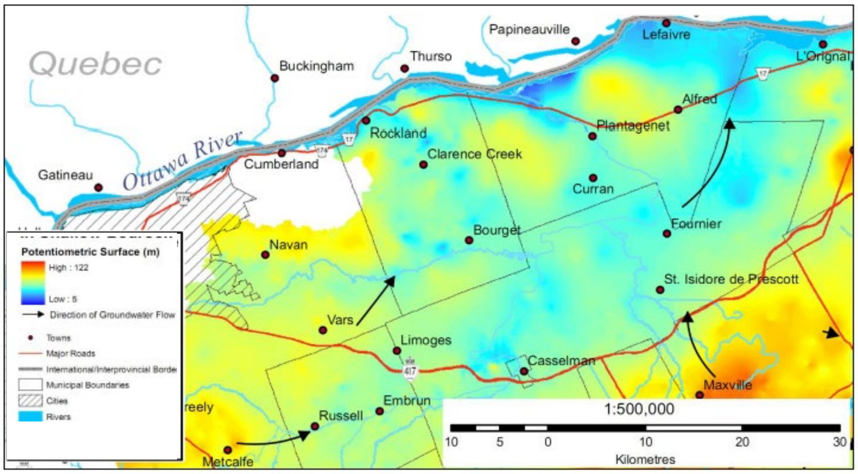

Figure 1.5 Potentiometric surface and groundwater flow map for the interface aquifer in eastern Ontario. (RRCA and SNC, 2008)

1.3 Methods

1.3.1 Ontario Ambient Groundwater Geochemistry Program (OAGGP) and the East Ottawa and Champlain Groundwater Study

Of the total 369 samples used within this study, 170 were collected by this author during the summer of 2017, with the remaining 199 obtained during the summers between 2012 and 2016. All of the samples collected were analyzed following the same methodology established for the OGS's Ambient Groundwater Geochemistry Program, which is responsible for producing detailed geochemical results for 3933 well water samples across Ontario. This program's objective has focused on improving the understanding of regional trends in groundwater chemistry for major aquifers which are relied upon by residents across the province. Anomalous trends in groundwaters in eastern Ontario (e.g., elevated iodide, fluoride, and methane) were first recognized in 2012 when the Ontario Ambient Groundwater Geochemsitry Program (OAGGP) first sampled the area. These findings prompted additional studies which used higher sampling densities across the region through collaborative projects organized by local municipalities (City of Ottawa and the United Counties of Prescott and Russel), and the South Nation Conservation Authority in conjunction with the Ontario Geological Survey (OGS).

1.3.2 Site Selection

Site selection for the OAGGP aimed to acquire a homogeneous spatial distribution of samples which included one "bedrock water sample" acquired from a bedrock well and one "overburden water sample" from an overburden well per 10 x 10 km grid. Samplers used the OWWIS to prioritize well targets contingent on the availability of well records that could be verified based on location (drillers sketch) and matching details with homeowners' comments (i.e. year of installation and depth). Subsequent programs, which took place between 2013 and

2016 used similar techniques but at a higher sampling density (2 x 2 km grid overlay) to better capture regional variability. During 2017 the City of Ottawa adopted a new strategy which focused on prebooking sampling locations, using advertisements via multiple media outlets to inform residents in the study area, and set up appointments with interested homeowners who were able to provide well records and fit into the desired sample distribution plan. This strategy was a major success with far more interested homeowners than was required to meet the desired sample distribution. Inherit bias in the sampling population is present however, due to several factors; 1) land use where few wells exist due to underdevelopment, 2) areas of known poor water quality where residents prefer dug/bored wells rather than drilled wells that reach bedrock, and 3) developed areas where municipal water services are available resulting in an absence of wells. Additional information on sampling bias can be found in Hamilton and Lee (2012).

1.3.3 Sampling procedures

Homeowner interviews were completed upon arrival at the sampling station to identify water quality/quantity concerns, and to confirm well information matches the corresponding well record. Afterwards, a visual inspection of the well was completed, GPS coordinates were obtained, and well stick-up and static water level was recorded. Subsequently a pre-sampling inspection was completed to verify that the sampling point bypassed any water treatment processes that homeowners may have installed. This was done by checking the pressure tank, the well intake and where possible following the line to the access point. For locations where this was not possible, a hook up was completed at the pressure tank. For cases where existing infrastructure was not available, a portable submersible pump was attached to polyethylene tubing that connected to the sampling manifold. The sampling manifold connected to the untreated access point via a 1.6 cm-inside diameter, nylon braided, clear polyvinyl chloride

(PVC) tubing. This manifold then connected to two 0.95-cm diameter silicon tubes with flow control valves, one of which attached to a flow-through cell that was fitted with a YSI multiparameter instrument while the other was used to fill sample bottles. Furthermore, a discharge line was connected to the manifold consisting of another 1.6 cm inside diameter nylon braided, clear polyvinyl chloride (PVC) tubing which ran to a 120L purging bin to allow for the calculation of the total volume purged before sampling.

Prior to sample collection, water was purged via the discharge line continuously at a high flow rate until stable readings were reached on the YSI multiparameter (EXO-1) instrument. This instrument measured the following in real-time: temperature, conductivity, pH, dissolved oxygen, and oxidization-reduction potential (ORP). All of which were used to verify stable readings. Prior to each sampling day the YSI was calibrated using a three-point pH calibration (4, 7 and 10) and a two-point dissolved oxygen calibration (100% and 0%). Additionally, electrical conductivity was checked each day (1413 us/cm solution) and ORP was checked weekly using ZoBells solution (+240 mV). Once stable readings were achieved, water was collected in 14 separate bottles that would be analyzed for: metals (60 mL), anions (60 mL), mercury (60 mL), I/Br (60 mL) , stable isotopes (^{18}O and ^{2}H; 125 mL), tritium (250 mL), dissolved organic and inorganic carbon (DIC and DOC; 2 x 40 mL), total Kjeldahl nitrogen + ammonia and ammonium (45 mL), nitrate and nitrite (45 mL), bacteria (250 mL), colour (45 mL), dissolved gases (CH_4, CO_2; 1.2 L and filled to 600 mL), and a spare bottle (250 mL). Prior to filling the bottles for the metal, anions, and mercury analyses, water was first pressure filtered using a 0.45 um Millipore^{Tm} Durapore (Polyvinylide fluoride (PVDF) via a rubber free polypropylene syringe. Care was taken when taking samples to minimize the headspace and prevent chemical reactions from occurring after filling. Additional steps were taken prior to collection to preserve samples including TNK and ammonia with 1:1 sulfuric acid, I/Br with 0.2 nickel acetate, mercury with 1% HNO3 and 2% HCL.

1.3.4 On-site measurements and analysis

A YSI EXO 1 multiparameter data logging instrument was used to continuously record measurements of temperature, electrical conductivity, pH, ORP, and dissolved oxygen at each sampling site. Alkalinity was measured on site by titrating 1.6 M H_2SO_4 into 100 mL of sample that had an indicator packet of bromocresol green added. Titrated volumes were recorded at three endpoints, blue grey, violet grey, and pink. Hydrogen sulphide levels were measured at sites where the characteristic “rotten egg” smell was identified, dissolved oxygen was absent, and ORP was negative. This was completed using a HACH model 2238-01 test kit (upper limit of 11.25 ppm) by preparing a blank of de-ionized water to be compared with the prepared sample via a colour wheel. Dissolved CH_4 and CO_2 samples were stored upside down and in a shaded room before they were measured in the morning of the following day after collection using an RKI Eagle 2 Portable Multi-Gas Meter; this meter possesses two CH_4 sensors (low level <25,000 ppm and high level up to 50% CH_4). The Eagle 2 was calibrated daily for low level methane (25,000 ppm) and CO_2 (2.50 % CO_2), and weekly for high level methane (50% by volume). Before measurements were taken, the temperature of each sample was checked and recorded using a handheld thermometer. The concentrations of gases within the headspace were used to estimate their aqueous concentration using Henry’s law and are explained in greater detail in McIntosh et al. (2014). Iodide concentrations, as iodine were measured within five days of collection to minimize errors due to volatilization using an Iodide Ion Selective Electrode (Arion model 9453BN) connected to an Orion Five-Star (A324) meter. The instrument was calibrated prior to measurement, using 10 ppb and 1000 ppb standards. Once the calibration was complete, the headspace (~2 mL) of each sample was discarded and 1 mL of ionic strength adjuster was added with a magnetic stir bar. The sample was then placed on a magnetic stirring plate and a measurement was taken after 15 minutes had passed and stable readings were acquired. Samples with greater than 1000 ppb were set aside and remeasured afterwards once the iodide meter was recalibrated using 1000 ppb and 10 000 ppb standards.

Major and minor cations and anions were analyzed at Geoscience Laboratories (GeoLabs) in Sudbury. Nitrate and Nitrite, ammonia/ammonium, and total Kjeldhal nitrogen were analyzed by SGS analytical laboratories in Lakefield, ON. Tritium content was analyzed by Isotope Tracers Technologies (IT^2) in Waterloo, ON. Further information on laboratory techniques can be found in the Support Document as part of the OGS data release (Hamilton, 2021).

1.3.5 Data Quality Assurance and Control

Throughout the multiple groundwater sampling projects that comprise the dataset used in this thesis, a series of known standards, duplicates, and blanks were added throughout the field seasons at random to verify laboratory results. Furthermore, many parameters were analyzed using two methods which could be used to identify any errors that may have occurred in the laboratory's analysis process (Hamilton, 2015). Charge balance errors (CBE) were also calculated to test the dataset and flag any analytical errors contained within. CBE compared the positive and negative charges in solution; they should be electronically neutral in natural waters. This is done by:

$$\% \text{ CBE } = [\Sigma Cations - \Sigma Anions] / [\Sigma Cations + \Sigma Anions] * 100$$

Additional details concerning the accuracy and precision of these samples are available within the supporting documentation as part of the OAGGP data release (Hamilton, 2021).

2. Bedrock topography and drift thickness mapping

2.1 Introduction

The geospatial mapping of bedrock topography and overburden thickness outlined in this chapter was completed in eastern Ontario between Ottawa and Hawkesbury on the south shore of the Ottawa River. Invaded by the Champlain Sea, circa 10-12 ka, groundwater located within bedrock surface depressions in this area retains a component of fossil seawater (Lemieux, 2018a) and exhibits several anomalous geochemical patterns including elevated concentrations of methane (>50 mg/L) and halogens, including iodide (> 10,000 µg/L). The effect of high iodide concentrations in well water was observed by Rogerson (2018) who found strong correlations between bulk iodine concentrations in dairy milk and elevated iodide levels in groundwater. Understanding the relationships between these patterns in groundwater and bedrock topography and drift thickness is essential for future evaluations of regional groundwater quality. Later chapters discuss, in greater detail, these chemical patterns and their relationships with bedrock elevation. However, before this could be assessed, improvements to bedrock topographic and overburden thickness maps were required. Existing published maps of these parameters by the Ontario Geological Survey (OGS) relied heavily on water well records to determine bedrock elevations. Due to many problems with the OWWD, discussed further in section 2.2.2, much care was required in selecting wells to be used for determining bedrock elevations (Gao et al., 2007). This chapter will discuss the improvements made to a regional well and bedrock outcrop dataset that was used to map regional bedrock depressions and drift thickness. In addition, geospatial mapping techniques used throughout the modelling process are elaborated upon. Finally, the results of bedrock topography and drift thickness mapping are shown with the interpretation of key geologic features.

2.2 Methodology

The methods used in the development of bedrock topographic and overburden thickness maps outlined in Figure 2.1 involved two major tasks. The first was gathering and filtering data from several sources and the use of 3D visualization and geospatial analyst tools in ESRI's ArcPro to evaluate and correct well information in the study area, where necessary. The second was using the cleaned and filtered dataset to generate the drift thickness and bedrock topographic maps in ArcPro. Each stage of work is outlined and elaborated upon in detail throughout this section.

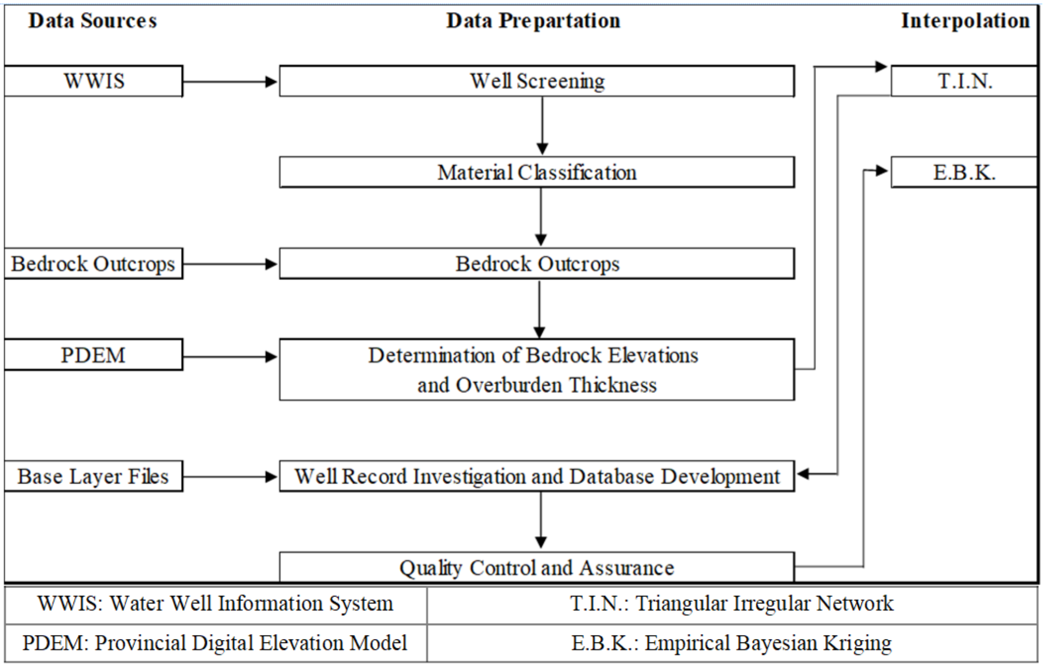

Figure 2.1 Workflow outlining main tasks completed as part of bedrock topography and overburden thickness mapping

2.2.1 Data Sources

Data files were downloaded from the Ontario GeoHub, Scholars GeoPortal, and the Ministry of Energy, Northern Development and Mines, and data features within the study area were extracted. Corrections and refinements were then carried out to improve the reliability of well records in the provincial database, discussed in Section 2.2.2.

The Ontario Water Well Information System (WWIS), also known as the Ontario Water Well Database (OWWD) was developed by the Ministry of the Environment (MOECC, 2018) and contains over half a million well/borehole installation records across Ontario (Gao et al., 2007). It is the largest open access database of subsurface materials in Ontario today, with over 19,000 records in the designated study area in eastern Ontario (Figure 2.2). The database contains a large amount of water well information including construction techniques, downhole material descriptions, and GIS location methods and more.

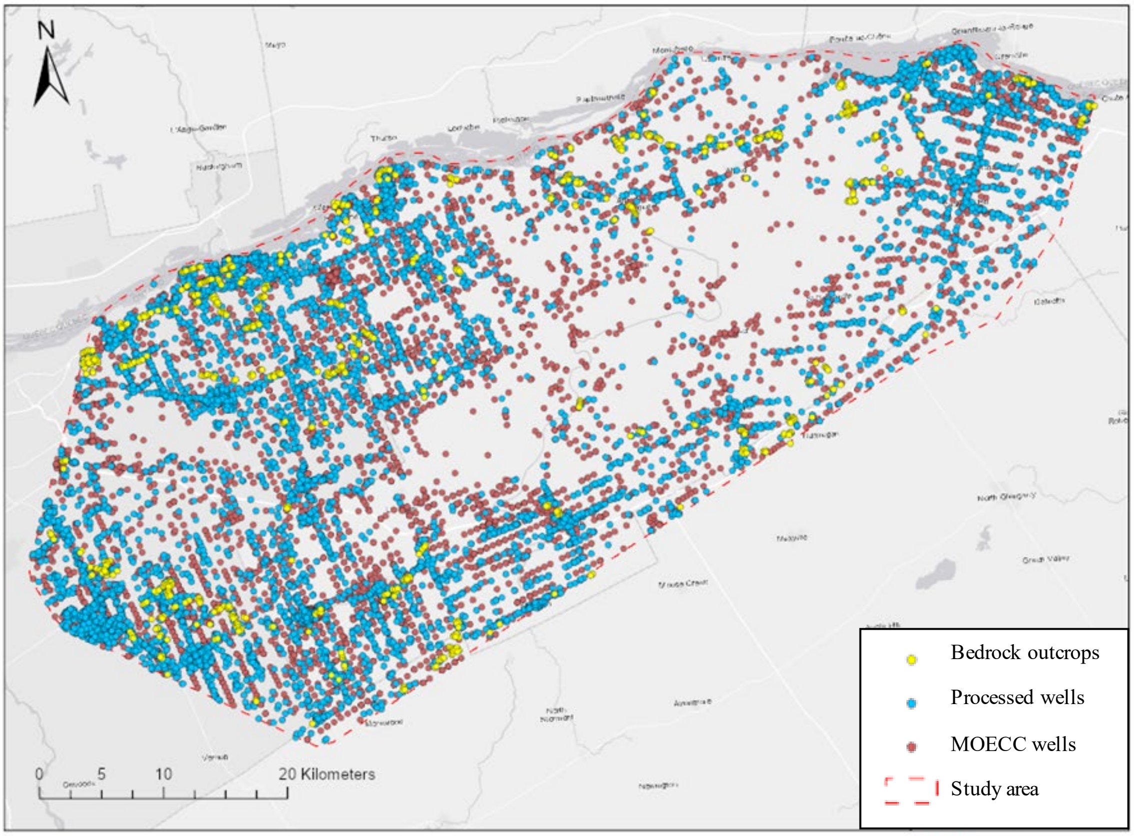

Figure 2.2 Distribution of bedrock outcrops (MRD 216), well records (MOECC, 2018) and processed well records.

Inconsistencies in data quality within the OWWD require extensive quality control protocols to reduce the influence of incorrect locations and material descriptions. Unreliable locations can result from: georeferencing errors, incorrect drillers notes, data entry errors, and ambiguity in well locations as a result of the confusing survey fabric in eastern Ontario (Gao et al., 2007). Similarities in lot and concession survey fabrics in the region occur in several areas (e.g., "Clarence Twp." and "Clarence Twp. OS", where "OS" means Old Survey) and have contributed to confusion and subsequent errors in recording and/or geolocating of many wells, especially ones that are located solely by lot and concession. In addition to location errors, material (i.e., lithology) description errors exist including null data fields. Unstandardized or incorrect geological material descriptions and additional data entry errors had to be identified and mitigated.

Geographical reference files were used to evaluate the locations of well features by comparing their positions to well record information (drillers sketches, lot and concession numbers or addresses). These files include: the Ontario Hydro Network (Ministry of Natural Resources and Forestry, Provincial Mapping Unit, 2017a), the Ontario Railway Network (Ministry of Natural Resources and Forestry, Provincial Mapping Unit, 2017b), the Ontario Road Network (Ministry of Natural Resources and Forestry, Provincial Mapping Unit, (2017c), the improved lot fabric (Ministry of Natural Resources, 2017) and the Digital Raster Acquisition Project Eastern Ontario (Ministry of Natural Resources and Forestry, Provincial Mapping Unit, 2014). Additional information is available on Ontario's GeoHub (https://geohub.lio.gov.on.ca/).

A digital elevation model (DEM) is an interpolated raster elevation dataset that provides a measure of ground surface elevations in meters above mean sea level. It provides a 3D representation of the ground surface and is visualized by a grid of regularly placed cells or pixels to which elevation values are referenced (Ministry of Natural Resources and Forestry, Provincial Mapping Unit, (2017d).). The Provincial Digital Elevation Model (PDEM) was used to assign surface and water well strata elevations which were in turn used as the basis of determining overburden thickness and bedrock elevations. This provincial DEM has 5 m resolution and is based on three source datasets: the Ontario Radar DSM, OBM, DTM points and contours, and the 2002 GTA ortho contours.

Geological known bedrock outcrops and quarries in Eastern Ontario was extracted from OGS miscellaneous release – data (MRD) 207 (Gao et al., 2007) (Figure 2.2). Outcrop and quarries within this data release are in the form of shapefiles or vector features and contain classification codes that differentiate features as outcrops or quarries. Outcrops, by definition, occur in areas of zero drift thickness and therefore are used in this study to identify points where ground surface elevation is equal to bedrock elevation. Quarries occur in areas of thin drift and therefore surface elevation was also set to equal bedrock elevation. The bedrock geology map by the Geological Survey of Canada (Stanford, 2005) was used as the geological base for this study.

2.2.2 Data Preparation

Approximately 19,000 well records are included in the subset of the OWWD that encompasses the study area. Not all of these are useful because of location, borehole logging, and data entry errors. After several iterations of data filtering, ~8000 (~40%) wells were retained for further well evaluation. This phase of work was essential in cleaning up the working dataset to allow further investigations and corrections using the well data by removing wells that added ambiguity to the interpolation dataset. Shallow dug and bored wells encompass 3% of the total wells in the dataset and were removed as these contain no relevant information on extracting bedrock elevation and drift thickness. Construction material codes were used to identify shallow dug and bored wells, and well features that contained null information fields. Following the initial filtering phase, 868 wells were removed from the dataset, 244 shallow wells and 624 wells with null construction method codes. Following this, additional queries were run to isolate and remove wells that were located based on the lot centered method. Due to the simplistic nature of this technique, an abundance of errors were identified. Wells located using this method were positioned exclusively by placing wells in the center of their lots based on lot/concession and township information. Extensive errors in well locations was due to incorrect lot identification due to similarities between different lot fabric surveys across eastern Ontario from overlapping surveys and the amalgamation of lower tier townships. Even where the lot and concession numbers are correctly reported, the position of the wells are only known to within the boundaries of the surveyed lots, which in Ontario are typically 604 x 1409 meters (3/8 x 7/8 of a mile). Following the second phase of filtering, 382 wells were removed, resulting in 6750 wells that were retained for the next phase of clean up.

Following the initial well-data filtering procedures, material description information within the formation table in the OWWD was generalized to facilitate the interpretation of bedrock surface elevations. This generalization was essential as it allowed for drift thickness and the top of the bedrock to be determined. Materials codes within the primary material field, or "MAT1" (Table 2.1), were classified as representing either bedrock or overburden material types. This method is known as the First-Attribute-Method and has been used by several hydrogeologists (e.g., Beckers and Frind, 1997; Holysh and Kassenaar, 1997) and was evaluated by Russell et al. (2009). Wells with material codes that couldn't be used to determine bedrock elevations or overburden thickness were removed. These codes included those denoting previously drilled or dug wells, null data, and unknown and other materials fields. The remaining wells were divided into two groups, the first was used to determine minimum depth to bedrock values for well logs containing bedrock units (limestone, shale, sandstone, and others). This information formed the basis for determining initial bedrock elevations within the study area. The second was used to determine drift thickness and contained all the retained wells. This information would be used to constrain areas of thick drift with few wells reaching the bedrock surface and serve to provide a quality control check for wells with both a minimum depth to bedrock and overburden thickness values.

Bedrock elevations and overburden thickness values were determined for all wells retained from the previous stages of work. Accomplished by assigning minimum depth to bedrock based on the top depth of the first bedrock material recorded. Bedrock elevations were generated from subtracting minimum depth to bedrock values by surface elevations and assigned to each bedrock well.

Limitations in data coverage in areas of thick overburden where few wells reach bedrock because of known poor water quality at depth or expensive drilling costs created uncertainty and required additional constraints in these scenarios, such as the calculation of minimum depth to bedrock values where bedrock wells are absent. Overburden thickness was calculated by summing the individual overburden material layers for each well. This method helped flag wells with overburden recorded below bedrock materials.

Due to the many issues within the OWWD including georeferencing, data entry, and driller errors, additional processing was required before interpolation could take place. Manual investigation of well records in low density areas, integration of known bedrock outcrops, resolutions to contrasting data signatures and null data fields was completed to improve data quality.

Additional data validation protocols focused on justifying well features with the highest interpolation weights in the dataset which are located in low-density areas with few nearby values that are available to predict bedrock elevations. Using kernel density kringing in ArcPro, feature densities were generated across the study area and zones with less than 3 wells per 1 km^2 were defined as low-density. These zones were delineated with polygons providing visual aid in the assessment of well distributions. From here wells were extruded in 3D based on bedrock elevations and a triangular irregular network (T.I.N.) was created to aid in identifying peaks and troughs corresponding to wells with contrasting signals. Anomalous wells were checked, confirmed, corrected, or rejected by investigating well record pdfs to verify locations and bedrock elevations. Lot and concession information, and well driller sketches and notes were used in conjunction with municipal lot fabrics, and google maps and aerial imagery with GIS measuring tools to verify and correct well locations where possible. If a well was determined to be incorrectly located without a possible resolution, the well was removed from the dataset.

Known bedrock outcrops provided by the OGS (Gao et al., 2007) supplied an enhanced dataset to further contain zones of thin overburden. A total of 728 outcrops and quarries were added to the dataset and bedrock elevations for these features were set to equal ground surface elevations (Figure 2.2).

Contrasting information between wells that share the same locations but have different well ids created uncertainty because of contrasting depths to bedrock. ArcPro's find identical geospatial tool was used to create grouping codes for wells at the same well locations. These codes were then used to create statistical comparisons of mean and standard deviation of bedrock elevations for wells that shared the same locations using a script created for R. Wells with less than 2 m difference used mean values to extract bedrock elevations, those with greater than 2 m difference in low density areas were investigated and corrected where possible or removed. In high density areas, these wells were removed from the dataset.

Quality assurance and control protocols focused on null data fields within the formation table in well records which created issues when determining bedrock elevations and overburden thickness assignments. A comparison was completed between minimum depth to bedrock and overburden thickness values. Bedrock wells with discrepancies between the two values were flagged. In low density areas these flagged wells were manually investigated and were verified, corrected, or removed using the above-mentioned technique, in high density areas wells were removed from the dataset.

2.2.3 Interpolation

A TIN was used to help identify inconsistencies in well bedrock elevations derived. A TIN represents a surface as sets of non-overlapping continuous triangular facets of irregular sizes and shapes. This method is advantageous because of the efficiency of the data storage and simple data structure for accommodating irregularly spaced elevation data. Advantages have also been found when TIN models are used for inter-visibility analysis on topographic surfaces (Lee, 1989), and extraction of hydrological terrain features (de Floriani et al., 1986).

This final phase of work involved the interpolation of bedrock topographic and overburden thickness maps with the improved well and bedrock outcrop dataset. Empirical bayesian kriging (EBK) was chosen as the best means to capture local variability and regional scale patterns while providing statistical details on the modelling procedure. This process relies on semivariograms, which are graphs that describes the expected difference in value between pairs of samples with a given relative orientation (Clark, 2001). EBK varies from classical kriging methods by accounting for the error introduced by the semivariogram model. This is achieved by simulating many semivariogram models and predicting a new value for each of the input data locations. New semivariogram models are then created from each new value and weights are assigned using Bayes rule (Krivoruchko, 2012). Modelling parameters were compared to determine the lowest possible root-mean-squared (RMS) (Babish, 2002). These RMS values were generated by the geostatistical wizard in ArcPro with results visible in Table A.1, Table A.2, and Table A.3 in Appendix A.

2.3 Mapping results

Comparisons of RMS values for the unmodified and the processed datasets are 11.2 and 8.05 respectively which highlights a 32.7% increase in data consistency between calculated and interpolated values based on the dataset refinements discussed in this chapter. Greater detail on interpolation parameter settings can be viewed in Appendix A. Eastern Ontario is characterized by overburden reaching 152 meters in thickness (Figure 2.3) and bedrock elevations ranging between 102 meters below sea level (m.b.s.l.) and 118 meters above sea level (m.a.s.l.) (Figure 2.4). Similarities are observed between the bedrock surface and ground surface elevations with major bedrock depressions being located around major bogs (Mer Bleue and Alfred) in the region. Paleochannels observed in DEM data are consistent with bedrock lows including the larger W-E trending regional paleochannel and smaller NW-SE trending channels.

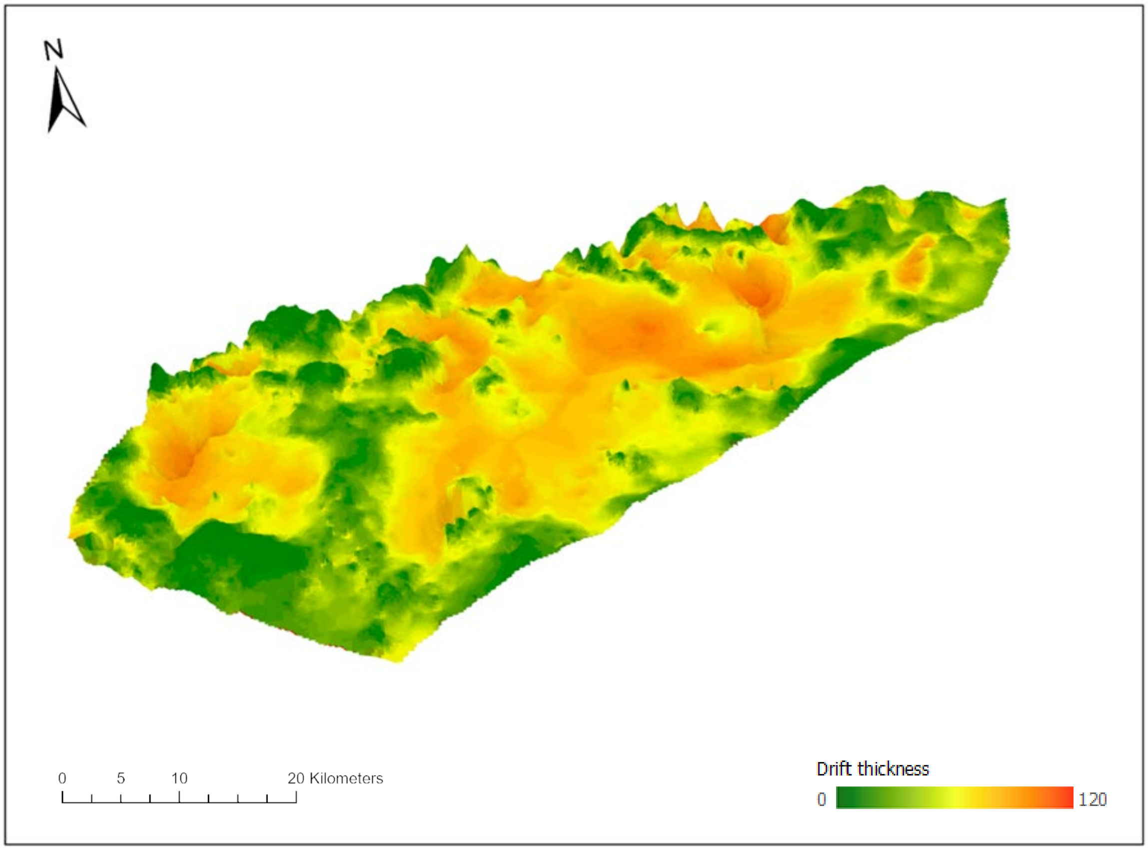

Figure 2.3 Drift thickness plotted with bedrock topography (this study) in 3D showcasing the relationship between bedrock uplands with limited drift cover (green) and bedrock depressions with thick drift cover (orange).

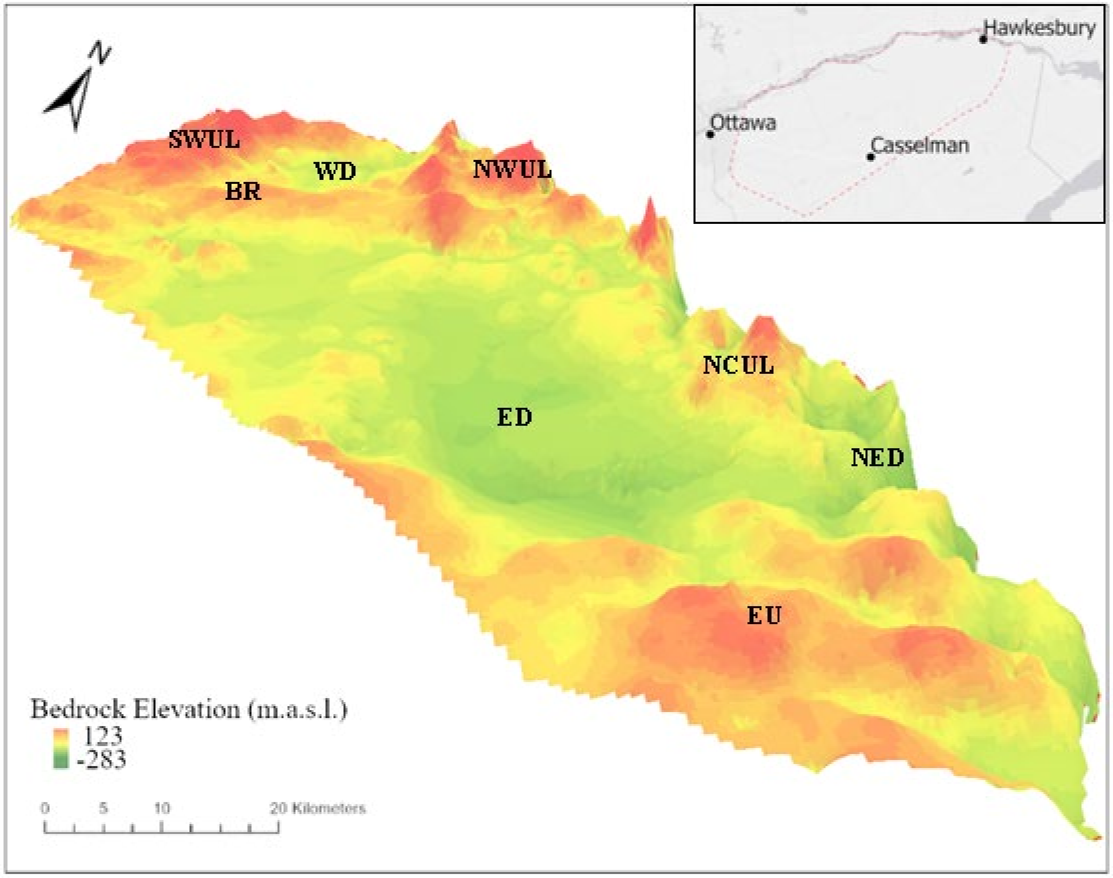

Figure 2.4 Bedrock topographic model of the study area with major features extruded into 3D.

The western depression (WD) is located around the Mer Bleue bog and has an extent of approximately 184 km^2 with the bedrock surface as low as 10 m.a.s.l. with overburden reaching 61 meters in thickness. The WD is bound to the north (NWUL) and south (SWUL) by uplands with a bedrock ridge (BR) along the eastern margin. This bedrock ridge divides the WD from the larger eastern depression (ED) and trends 11° NE over 19 kilometers, truncated along the Gloucester fault. This ridge is unique as southern sections have been mapped by the OGS and GSC as the Queenston formation, characterized by a distinct red shale appearance (Sanford, 2008). Supporting evidence of the Queenston can be found in along this ridge in drillers records that indicate red shale was logged (Figure 2.5A and B).

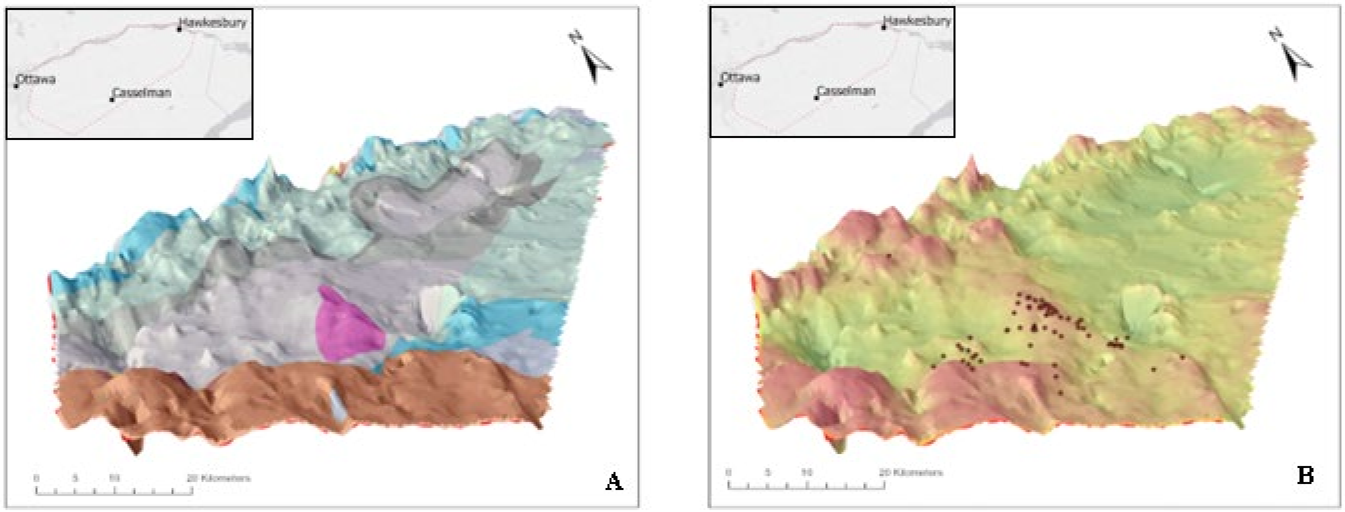

Figure 2.5 Bedrock topography in 3D with A.) bedrock geology (Sanford, 2008) displaying relationships between the bedrock ridge (BR), the Queenston formation (pink) and B.) well records within processed WWIS records containing 'red shale' in material codes.

East of this ridge is the larger eastern depression which has an approximate extent of 410 km^2 with bedrock elevations as low as 11 m.b.s.l. and overburden thickness depths up to 82 meters which contain the Alfred bog. Along the northern margin of the ED, the North Central Uplands (NCUL) are separated by bedrock lows consistent with paleochannels observed in surficial DEM data. These features can be found to the north-west of Alfred and contain numerous known bedrock outcrops. These uplands separate the ED from the Northeastern Depression (NED) which is characterized by a narrow conduit approximately 3-6 km in width that connects to the ED. This conduit is connected to a larger depression along the Ottawa river that contains the deepest recording of bedrock in eastern Ontario at 102 m.b.s.l. with 150 meters of overburden.

3 Groundwater geochemistry results

This chapter outlines in-field and laboratory results for the 369 groundwater samples collected between 2012 and 2017 in eastern Ontario from interface aquifers. Descriptive statistics can be viewed in Table B.1 in appendix B. Key and anomalous parameters unique to eastern Ontario (i.e., pH, redox indicators, major ions, minor ions, and isotopic parameters) are elaborated upon and investigated using multivariant statistical analysis. Mineral saturation indices were also plotted to aid with the interpretation of geochemical processes discussed in chapter four.

3.1 pH and redox

Variable pH trends are observed with values ranging between 6.41 to 9.31. Regionally, pH signatures are slightly basic with an average pH of 7.7. Slightly acidic to neutral pH conditions prevail in bedrock upland settings with basic conditions dominating in transitional zones between uplands and major depressions (Figure 3.1).

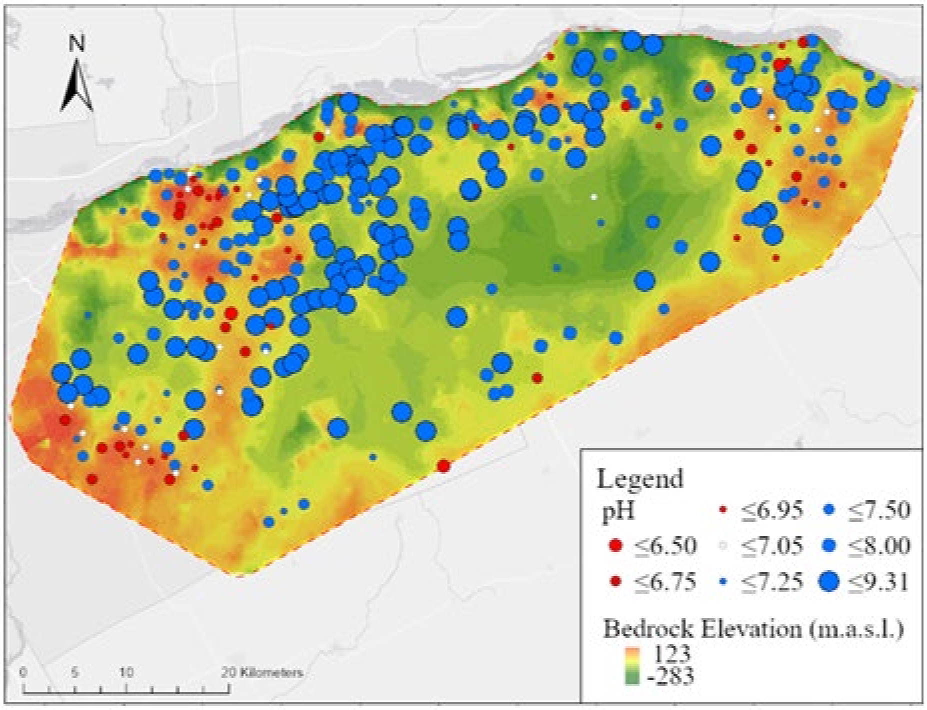

Figure 3.1 Spatial distribution of pH measurements plotted with bedrock elevation from this study.

Parameters such as dissolved oxygen (D.O.), hydrogen sulphide (H_2S) and methane (CH_4) are key indicators of redox reactions. Mapping of these parameters reveals important trends (Figure 3.2A-C) across the study area that correspond to bedrock elevation and overburden thickness. Detectable amounts of DO were found in 57 samples (Figure 3.2A) primarily obtained from bedrock upland locations where glaciomarine deposits are absent. Hydrogen sulphide was detected in 179 wells (Figure 3.2B) by smell tests. However, the highest measured levels of H_2S were found in transition zones located between bedrock uplands and bedrock depressions with thick sequences of glaciomarine deposits. Methane was detected in 211 samples (Figure 3.2C), with the highest measured concentrations located in bedrock depressions characterized by low bedrock elevations and thick drift.

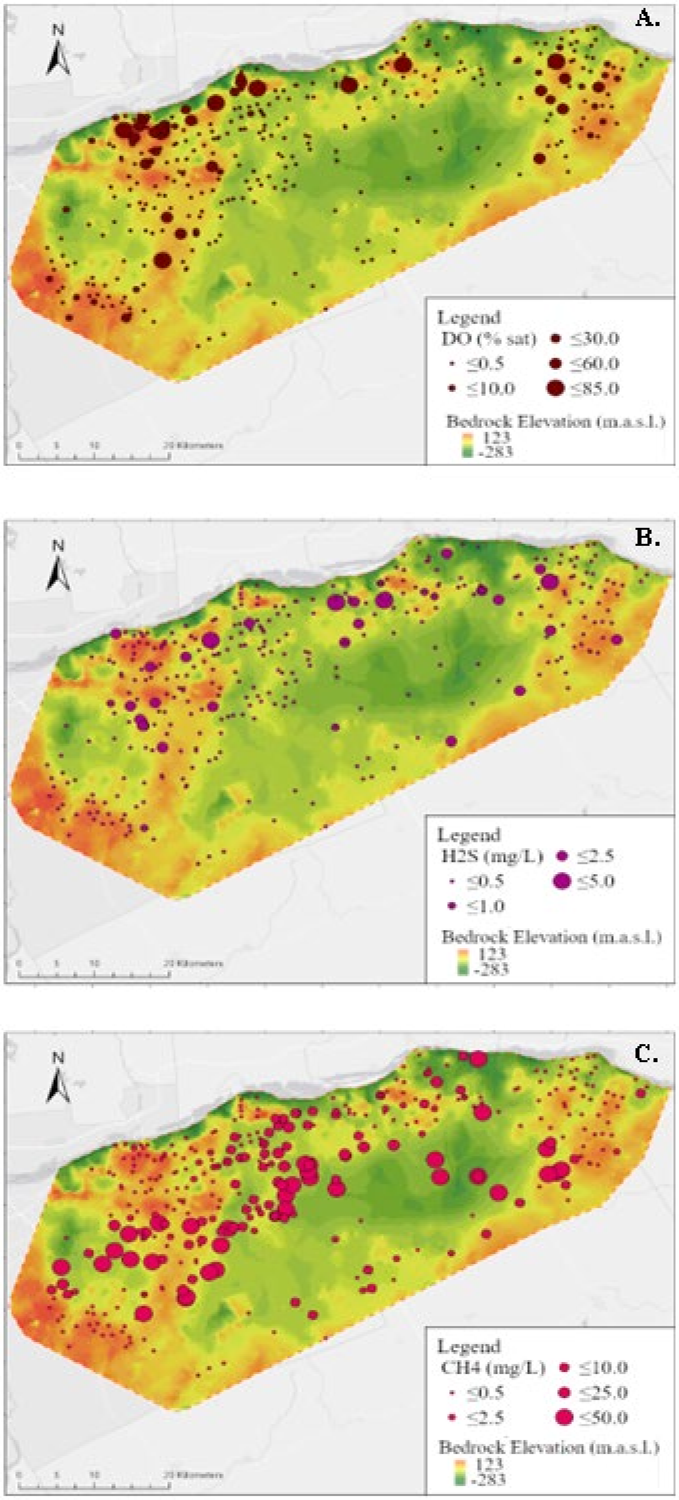

Figure 3.2 Spatial variation of A) dissolved oxygen (D.O.), B) hydrogen sulphide and C) methane plotted with bedrock elevation from this study.

3.2 Major ions

Spatial variability of major and minor ions in groundwater displays distinct signatures corresponding to their relative locations with respect to a regional buried bedrock valley. Samples in areas of lower bedrock elevations and thick overburden display elevated sodium (Figure 3.3A), bicarbonate (Figure 3.3D), and sulphate (Figure 3.3C) levels compared to those in bedrock uplands. Sodium averages throughout the study area are 417 mg/L with a maximum concentration of 6807 mg/L. The mean concentration of bicarbonate across all samples was 508 mg/L with a maximum value of 1746 mg/L. Potassium results contain an average of 13 mg/L with a maximum value of 170 mg/L. Samples located in bedrock uplands, where drift thickness is limited and glaciomarine deposits are absent display elevated calcium (Figure 3.3B) levels with mean and maximum values for calcium are observed to be 51 mg/L and 441 mg/L, respectively. Further relationships are observed between samples with elevated calcium concentrations and low pH measurements (Figure 3.4) and is elaborated in greater detail in section 4.2. Sulphate distributions (Figure 3.3C) indicate concentrations occur independent of bedrock topography with elevated signatures dominating in the south-west of the study area, around Greely Ontario. The presence of the Queenston formation in proximity to samples with elevated values indicate a relationship between bedrock geology and elevated SO_4 values. Mean and maximum sulphate values in the study area are 50.4 mg/L and 2552 mg/L respectively. Several samples located in the transition zone between bedrock uplands and the buried bedrock valley demonstrate some of the highest levels of phosphate (Figure 3.5E) in the province. Within the study area, phosphate contains mean and maximum values of 0.87 mg/L and 14.2 mg/L, respectively.

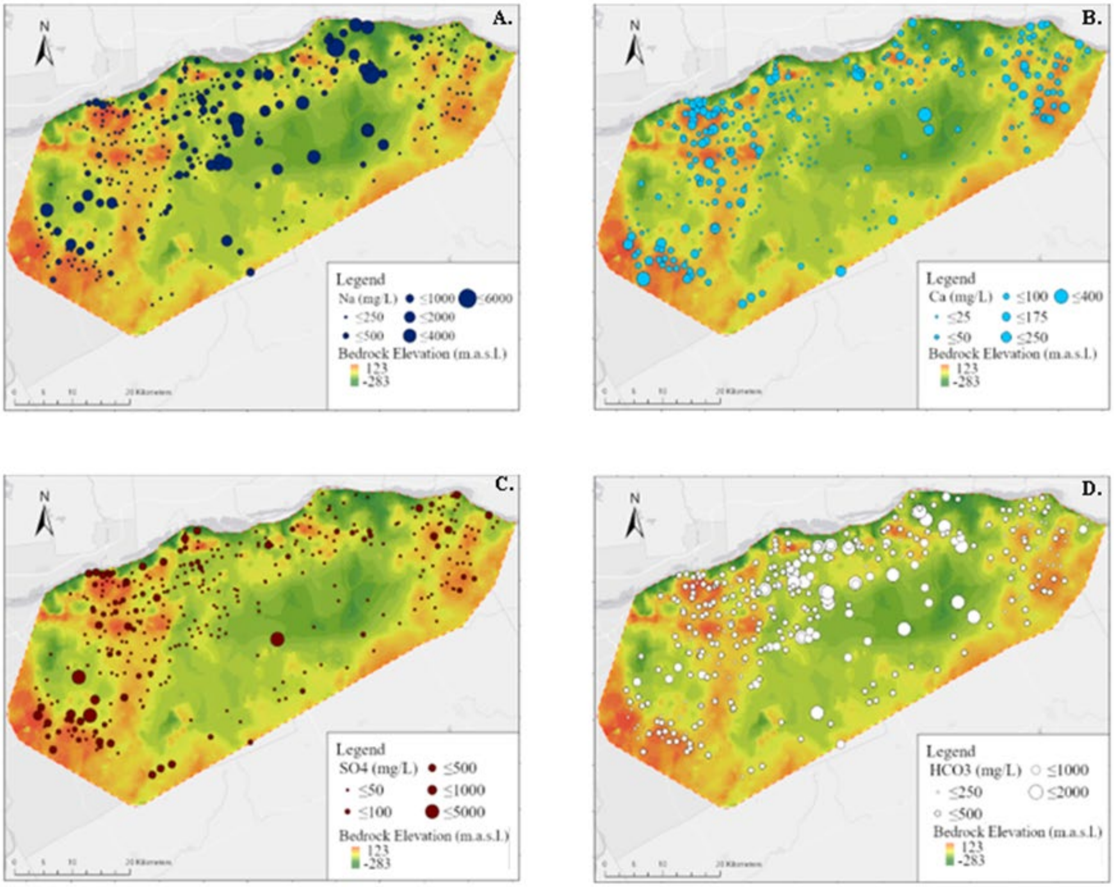

Figure 3.3 Spatial patterns of A) sodium, B) calcium, C) sulphate and D) bicarbonate plotted with bedrock elevation from this study.

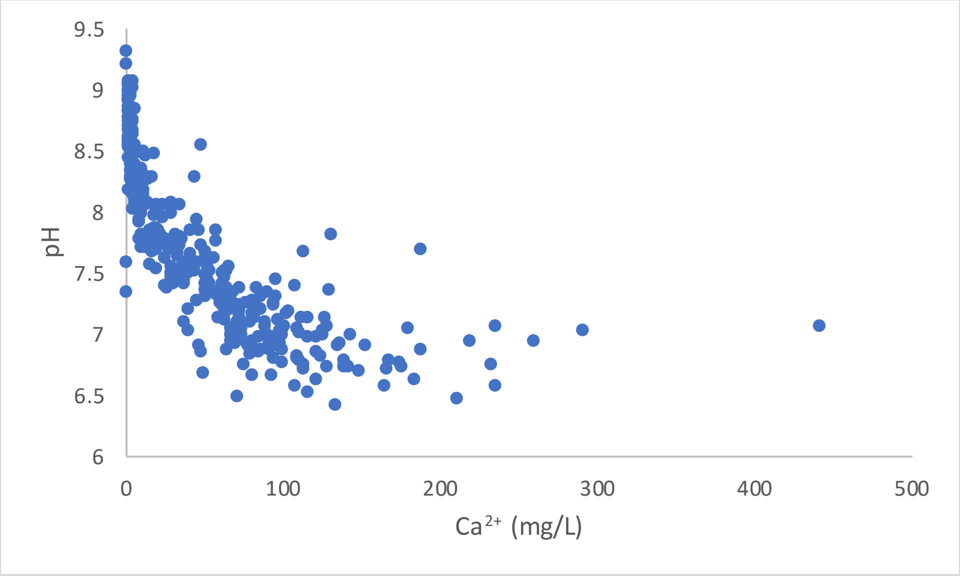

Figure 3.4 pH measurements vs calcium concentrations for interface aquifer groundwater samples.

Eastern Ontario displays some of the highest levels of chloride, bromide, and iodide in the province (Table 3.1). Comparisons of OAGGP data between eastern and southern Ontario is seen below. Similarities in the spatial distribution of these halogens is observed with some variability in samples with elevated fluoride (Figure 3.5C). Chloride is the most abundant with a regional mean of 580 mg/L and a maximum concentration of 13622 mg/L. Elevated chloride signatures are observed in samples obtained from areas associated with a major buried bedrock valley while bromide follows a similar distribution pattern to chloride where the largest concentrations appear to be in areas of thick drift and low bedrock elevations (Figure 3.5B and D). The maximum observed concentration of bromide was 73.5 mg/L, with a regional mean of 2.2 mg/L. Additionally, bedrock depressions are characterized by high concentrations of iodide up to 10812 ug/L, an average of 392 ug/L, and a median of 50 ug/L (Figure 3.5A). Within the study area, samples have a mean fluoride concentration of 0.73 mg/L with a maximum value of

5.14 mg/L. A total of 58 samples exceed the maximum acceptable concentration for fluoride in drinking water (1.5 mg/L; Service Ontario, 2002).

Table 3.1 Statistical comparison of Ambient Groundwater Geochemistry Program data for eastern and southern Ontario. Parameters in study area (E.O.) and Southern Ontario (S.O.) – data extracted from MRD 283 REV-2 (Hamilton, 2021).

Parameter	**Units**	**E.O. Count**	**S.O. Count**	**E.O. Mean**	**S.O. Mean**	**E.O. Median**	**S.O. Median**	**E.O. Max**	**S.O. Max**
Sodium	mg/L	369	1503	417.2	76.7	150.6	28.2	6807.0	2034.0
Chloride	mg/L	369	1503	582.1	92.9	75.3	15.4	13622.0	3800.5
Bromide	mg/L	369	1503	2.17	0.67	0.15	0.05	73.53	42.27
Iodide	µg/L	369	1436	388.7	37.9	48.3	12.0	10812.0	615.0
Phosphate	mg/L	369	1500	**0.86**	**0.08**	0.02	0.02	14.21	45.00

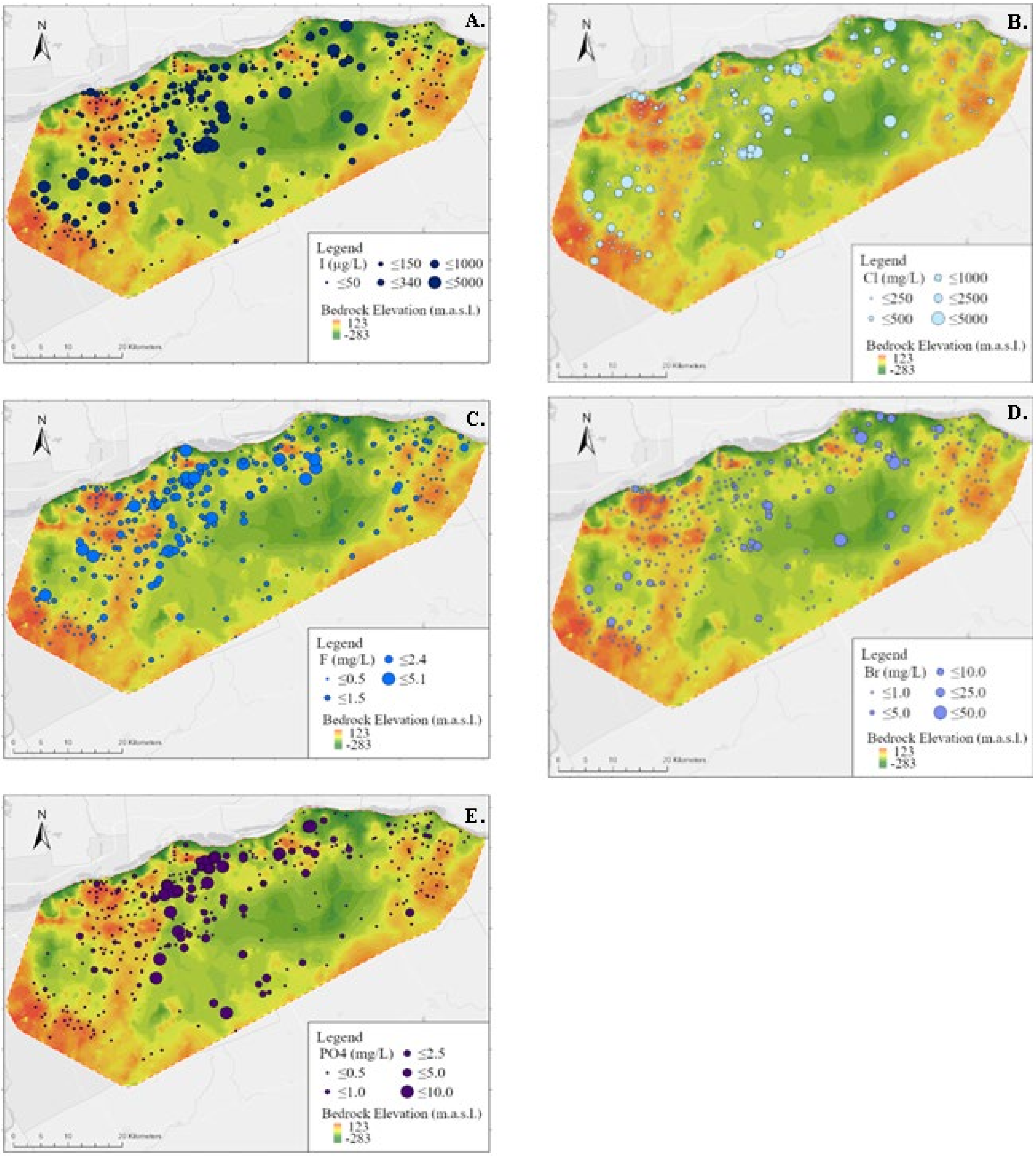

Figure 3.5 Spatial distribution of A) iodide, B) chloride C) fluoride D) bromide and E) phosphate with bedrock topography (this study).

3.3 Saturation indices

Saturation indices for all Ambient Groundwater Geochemistry Program samples were calculated by the Ontario Geological Survey as part of the Miscellaneous Release—Data 283 – Revision 2 (Hamilton, 2021) for the most common mineral phases in Ontario. Within the study area all samples were undersaturated in gypsum, anhydrite, and halite. A total of 239 (64.7%) were undersaturated in calcite, with most oversaturated samples found to occupy areas characterized by low bedrock elevations and thick drift cover (Figure 3.6A). Two-hundred and twelve samples (57.5%) were undersaturated in dolomite, where oversaturated samples found in areas of low bedrock surface elevations and thick drift cover followed similar spatial trends to calcite (Figure 3.6B).

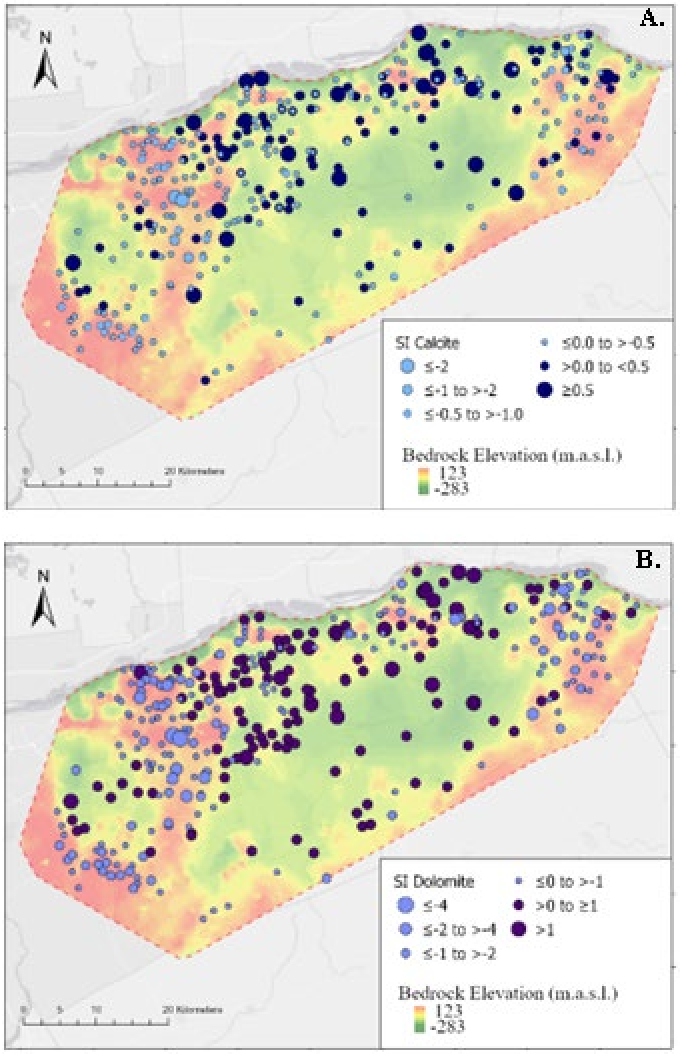

Figure 3.6 Spatial variation of calculated saturation indices for A) calcite and B) dolomite by (Hamilton, 2021) with bedrock topography (this study).

3.4 Isotopes

Oxygen and hydrogen isotopic compositions in groundwater are useful tools in tracing the origin of water and solutes. In addition, geochemical processes also have important implications on isotopic signals through fractionation and distillation. Comparisons between local meteoric water lines and groundwater isotopic signals can be observed in Figure 3.7. The local meteoric water line (LMWL) for the Ottawa area was derived from isotopic data accumulated from monthly precipitation collected in Ottawa (IAEA/WMO, 2020). The line of best fit for groundwater samples is $\delta^2H = 6.5\delta^{18}O - 2.36$, with all but 10 samples plotting above the Ottawa LMWL (Figure 3.6). Across the region $\delta^{18}O$ values range between –15.47% and –7.85% with a mean of –10.84%. and a standard deviation of 0.77.

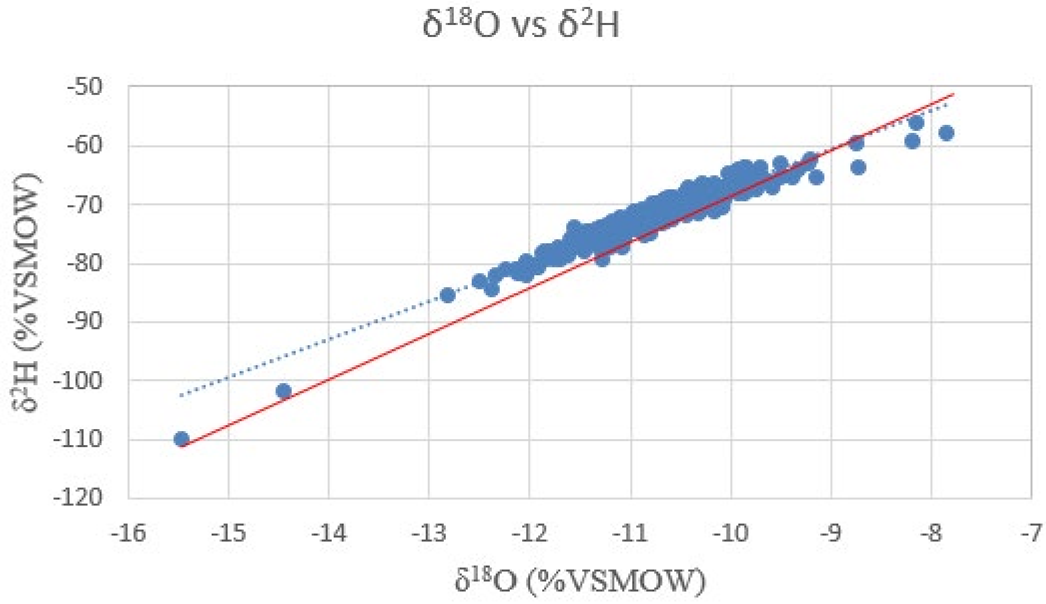

Figure 3.7 δ2H vs δ18O (%VSMOW) plotted against the red Ottawa Local Meteoric Water Line (IAEA/WMO, 2020).

Enriched signatures are observed for $\delta^{18}O$ in bedrock depressions while depleted values trend in upland settings (Figure 3.8B). Similar depletion and enrichment trends can be seen in $\delta^{2}H$ data, which ranges between –110.1% and –56.3% (Figure 3.8C).

Tritium is an important tool for dating modern groundwaters because of its half-life of 12.32 years. Though limited amounts of tritium are still produced today from a variety of sources, increasing atmospheric concentrations generated by the testing of thermonuclear devices resulting the well-known 1963 tritium peak observed in precipitation (Clark, 2015). Water recharged before 1952 would possess modern day tritium concentrations close to or below the detection limit. Tritium was analyzed in 369 samples across eastern Ontario, of which 111 samples did not contain detectable tritium (<0.8 T.U.). The mean and maximum tritium values are 5.4 T.U. and 21.2 T.U., respectively. Spatial patterns (Figure 3.8A) reveal undetectable and low tritium levels in bedrock depressions with elevated tritium signatures present in upland settings. This coincides with $\delta^{18}O$ and $\delta^{2}H$ data where older groundwaters are present in stagnant flow zones in bedrock depressions capped by thick sequences of overburden cover.

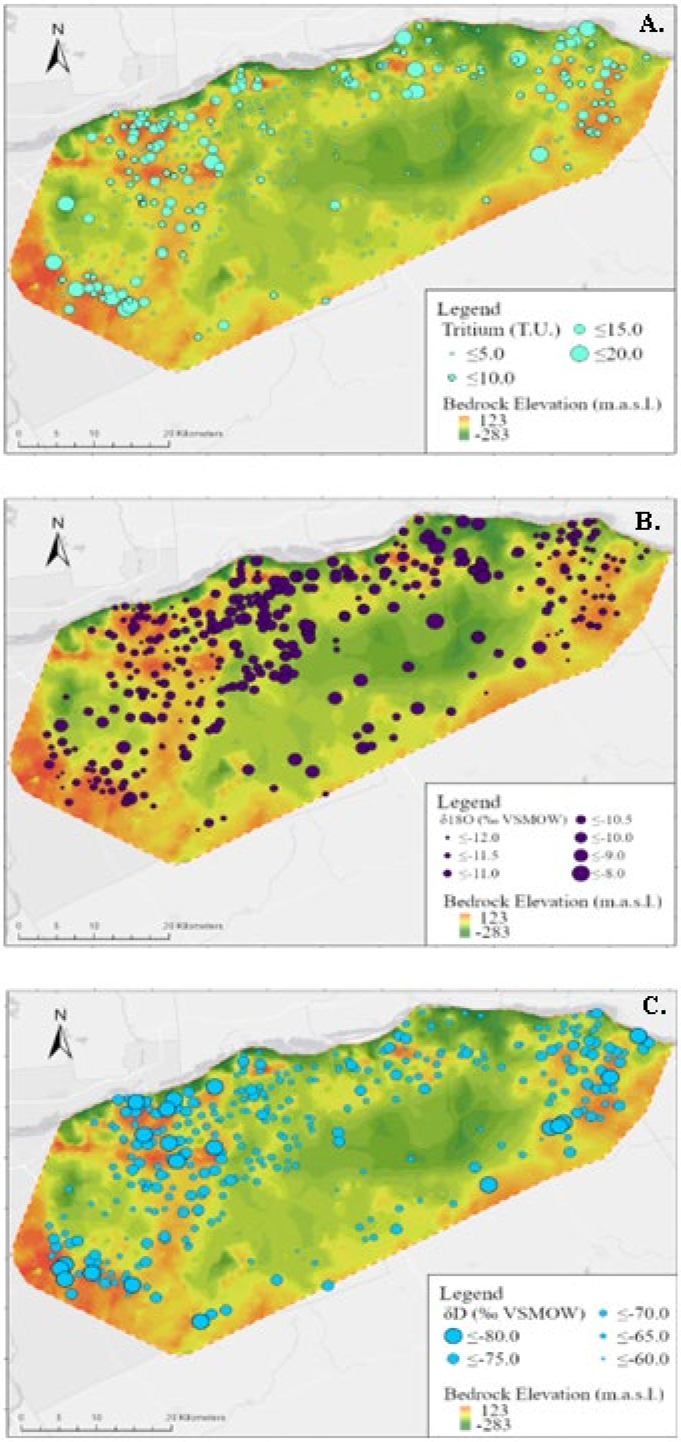

Figure 3.8 Spatial variation of A) tritium, B) oxygen-18 and C) deuterium plotted with bedrock elevation from this study.

3.5 Principal Component Analysis (PCA)

The first five principal components account for 80% of the variance within the dataset determined by PCA with PC1, PC2, PC3, PC4, and PC5 accounting for 43.9%, 18.5%, 8.6%, 5.4%, and 4.1% of the total variance within the dataset. PC1 and PC2 contain more than 10% of the total variance and are investigated in greater detail while PC3, PC4 and PC5 are not discussed further as they are minor components (<10% of total variance). Loading scores for PC1 (Figure 3.9) are characterized by significant (>0.7) positive loading scores for B (0.91), I (0.87), NH_4 (0.86), Na (0.83), CH_4 (0.79), Br (0.77), HCO3 (0.76), pH (0.71) and K (0.7). Moderate (>0.6) positive loading scores are observed for DOC (0.65), PO_4 (0.61), and F (0.60). Inversely, PC1 contains significantly (< –0.7) negative scores for tritium (–0.85), moderately (< –0.6) negative scores for SO4 (–0.68) and Ca (–0.66). Regional trends are observed between PC1 loading scores and bedrock elevations (Figure 3.10A), with negative scores dominating in bedrock uplands and positive scores prevailing in bedrock depressions. Loading scores for PC2 (Figure 3.8) are characterized by significant positive loading scores for Mg (0.87) and CO_2 (0.73), and moderately positive loadings for Ca^{2+} (0.67) and Cl^- (0.65). Conversely, moderately negative loading scores were determined for pH (–0.62), F (–0.57), PO_4 (–0.29), H_2S (–0.14), and CH_4 (–0.10). Negative loading scores are observed in transitional zones between major bedrock depressions and bedrock uplands with positive scores present in bedrock depressions and bedrock uplands (Figure 3.10B).

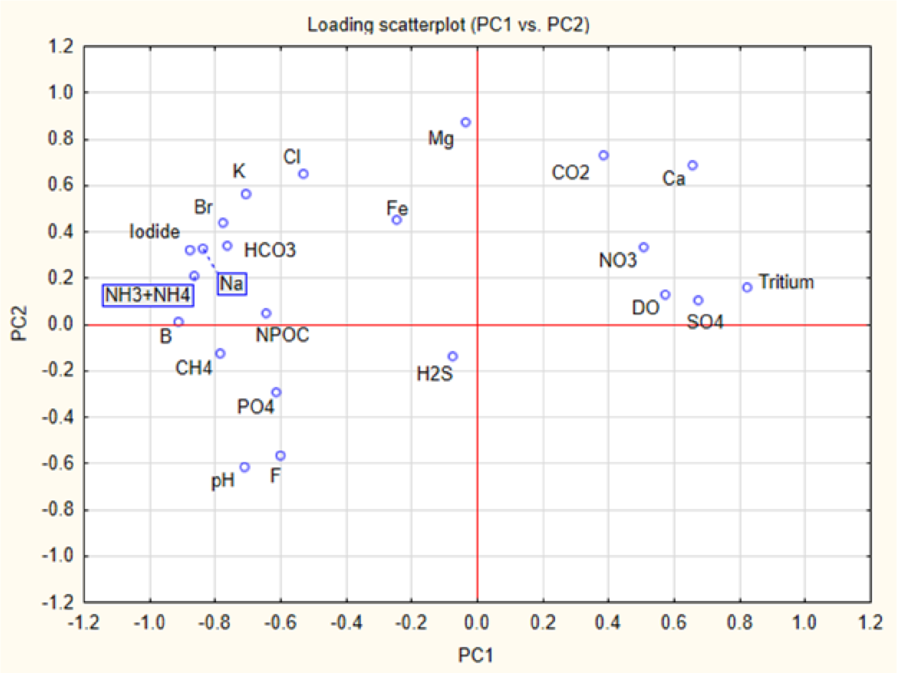

Figure 3.9 Principal Component Analysis loading scores scatterplot for PC1 and PC2.

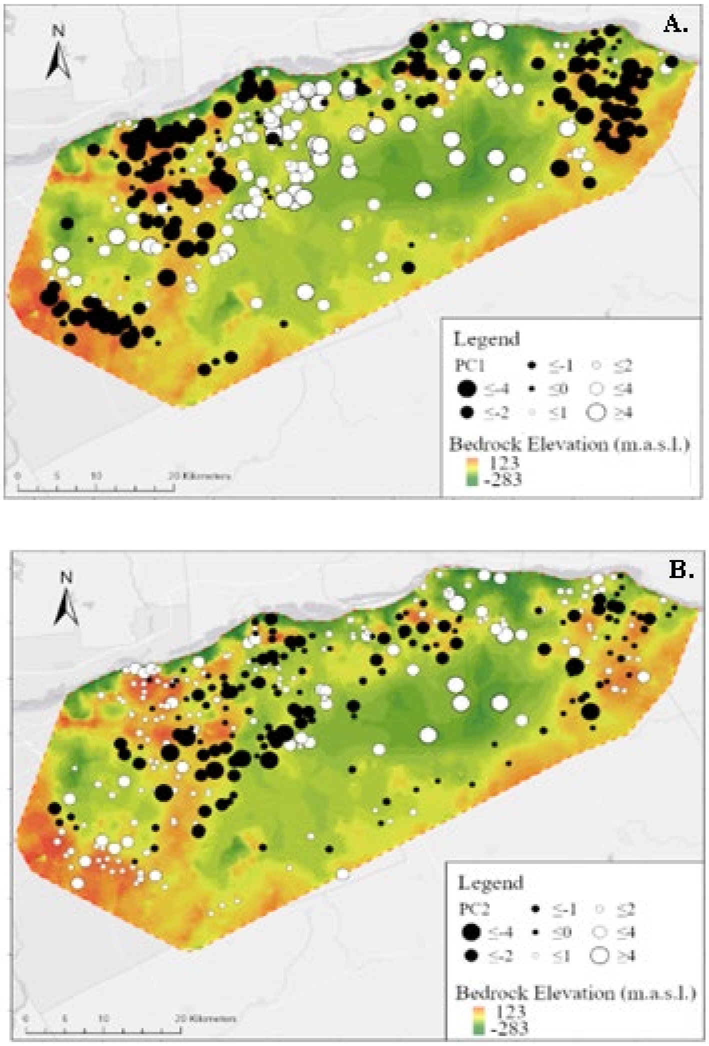

Figure 3.10 Regional trends of principal component scores for A) PC1 and B) PC2 plotted with bedrock topography.

4 Discussion

The variability in groundwater chemistry and geochemical processes closely relate to the major geologic features in eastern Ontario. Stagnant groundwater flow and preferential recharge areas have significant implications on groundwater quality across the study area and are outlined in this section. These respective conditions have been interpreted using geochemical data from 369 well water samples collected from interface aquifers and geologic information from over 9000 borehole records. From Chapter 2, this region is characterized by highly variable drift thickness, largely controlled by the distribution of buried bedrock valleys. The two large depression systems are divided by a bedrock ridge containing red shale of the Queenston formation (Figure 2.5 A and B). These large depressions are constrained by bedrock uplands to the south and east with isolated uplands along the Southern margin of the Ottawa river, and divided by bedrock lows that correspond with paleochannels observed in DEM data. The north-eastern margin of the ED exhibits a bedrock low that displays a linear trend from the ED into the modern Ottawa River.

The geochemical evolution in this system is related to the age of groundwaters. Isotopic indicators (tritium, D, and ^{18}O) have been mapped to outline modern and sub-modern groundwaters across eastern Ontario. Significant portions of the study area display isotopic and chemical evidence of conditions indicative of stagnant groundwater flow. This is confirmed by the spatial distribution of tritium in groundwater, presented in Figure 3.8A. Confined conditions, due to the presence of thick sequences of clays and muds derived from the Champlain Sea, are associated with low to less-than-detectable tritium. Inversely, clear spatial trends are apparent in tritiated samples, predominately located in bedrock uplands with limited drift thickness where glaciomarine deposits are absent. Information from material logs contained within water well records indicate that lenses of massive clays and muds that reach up to several meters in thickness within bedrock surface depressions where wells are drilled into bedrock.

The geochemical processes were identified by linking principal component analysis and geochemical parameters with geological features. The most important processes influencing groundwater chemistry within the region are recharge, ion exchange, salinization, and degradation of organics.

4.1 Recharge Geochemistry

Groundwater recharge represents the earliest phase of regional groundwater flow paths and is characterized by distinct spatial patterns of recharge parameters (tritium in young groundwaters with elevated O_2 and low pH) that coincide with bedrock topographic highs with permeable sediment cover. These elevated O_2 (Figure 3.2A) and tritium (Figure 3.8A) values along with relatively low pH ranges (Figure 3.1) are geospatially related to the bedrock highs where overburden is thin (Figures 2.3 and 2.5). These are associated with a dominance of Ca^{2+} in groundwaters that can be explained by the dissolution of carbonate minerals during recharge with low pH groundwaters, which are abundant both in bedrock units and overlying till (Cummings et al., 2011). Colgrove (2016) showed almost all samples located within Ca dominated groundwater regions in eastern Ontario were undersaturated in calcite and dolomite. Important correlations are observed between slightly acid pH values and elevated Ca^{2+} concentrations in groundwater samples (Figure 3.4). This can be explained by the dissolution of soil CO_2, which creates carbonic acid and slightly acid pH conditions that drive mineral dissolution while infiltration occurs in recharge areas. Furthermore, respiration in soils raises the partial pressure of carbon dioxide also driving dissolution.

Though elevated Ca^{2+} concentrations prevail in recharge zones, bicarbonate levels remain relatively low compared to samples located in bedrock depressions, far from recharge zones because of HCO_3 enrichment due to methanogenesis in buried bedrock depressions.

4.2 Cation Exchange

Beyond the recharge areas along bedrock highs, and towards the peripheries of the deep bedrock basins, groundwater geochemistry evolves from a Ca^{2+} dominated groundwater towards Ca^{2+} depleted facies through natural water softening. This process involves ion exchange, which is responsible for altering the composition of groundwater through exchange reactions between water and sediments in the aquifer. Infiltration of Ca-HCO_3 waters into deeper Na-clays results in the exchange on these negatively charged sediments. The natural water softening process is described as:

$$2Na_{(clay)} + Ca^{2+}_{(aq)} \rightarrow Ca_{(clay)} + 2Na^{+}_{(aq)}$$

As groundwater infiltrates into these deeper settings with abundant Na-rich deposits, the waters are naturally softened by the exchange of Ca^{2+} from solution with Na^{+} from sediments. This, combined with concentration gradients between the two mediums, work to remove calcium and magnesium from groundwater and replacing them with sodium. The result of this is an evolution from calcium dominated to sodium dominated groundwaters across the region. The invasion of the Champlain Sea is a likely source of sodium on sediment sorption sites as seen in western Quebec (Cloutier et. al., 2009).

Furthermore, natural water softening has implications for elevated fluoride concentrations because of the low solubility of fluorite (CaF_2) in most groundwaters due to elevated Ca^{2+}.

$$CaF_2 \rightarrow Ca^{2+} + 2F^{-}$$

As Ca^{2+} is removed from solution by exchange onto clays, fluorite can dissolve, releasing F^{-} into groundwater; evidence of this process is seen in the negative relationship between Ca^{2+} and F^{-}. Figure 3.5C shows the elevated F^{-} concentrations associated with zones adjacent to bedrock highs beyond the recharge areas where Ca^{2+} levels are greatly reduced due to cation exchange with Na^{+} clays.

4.3 Saline groundwater

The relationship between conservative tracers Cl and Br, and tritium levels provide additional insights into our regional understanding of the saline groundwaters observed in this area. Spatial relationships between high Cl^{-} samples (Figure 3.5B) are observed in the wells with low to less-than-detectable tritium (Figure 3.8A). These wells are found within the regions of thick overburden in the deep bedrock valleys, suggesting the occurrence of residual seawater. Saline groundwaters reported across eastern Ontario and

Quebec have been attributed to porewater contained within Champlain Sea clays (Desaulniers and Cherry, 1989; Torrance, 1979; Quigley et al., 1983; Cloutier, 2004). Champlain sea clays, mapped in Chapter 2, have thicknesses reaching 100 meters in areas of low bedrock elevations. The occurrence of remnant Champlain seawater is further suggested by the enrichments in stable isotopes ($\delta^{18}O$ and δD; Figures 3.5 B and C), where values for $\delta^{18}O$ in high Cl^- waters are enriched by as much as 4‰ over values for groundwaters in the recharge areas.

4.4 Redox evolution

The chloride-rich groundwaters, reside as residual Champlain Sea waters observed in the thick assemblages of Champlain Sea sediments are associated with redox indicators of highly reducing conditions. Spatial mapping of such redox indicators (DO for oxidizing conditions, and CH_4 for advanced redox evolution to low electromotive potentials) (Figures 3.2A and C) show the thick overburden areas are zones of high methane. This is further demonstrated by the principal component analysis (Figure 3.9) which shows a strong association between CH_4 and I^-. This is consistent with similar studies that highlight strong correlations between oxidizing and reducing conditions with bedrock topography and drift thickness (Lemieux et al., 2018A). Interestingly, H_2S does not clearly follow this association with deep stagnant zones (Figure 3.2B). However, H_2S is readily sequestered by ferrous iron as FeS in reducing zones of aquifers and so quickly disappears along the groundwater flow path into low redox environments (Clark, 2015). This process may also be responsible for the lack of apparent spatial trends of iron and manganese within the study area.

An important observation associated with the deep saline groundwaters from bedrock lows with low redox conditions is high iodide, I^-. High I^- has been observed in such groundwaters (Lemieux et al., 2018B). Elevated concentrations of iodide in groundwaters contained in sodium dominated areas are observed in bedrock depressions overlaid by thick sequences of glaciomarine sediments. Correlations between elevated iodide levels, salinity, and decomposition of organic material suggests that the saline pore waters are affected by the decomposition of organic matter such as marine phytoplankton contained within massive muds (Lemieux et al, 2018B). These anomalies are associated with methane anomalies where reduction of sedimentary organic carbon during the archaeal methanogenesis of these Champlain Sea sediments released organically-bound iodine into solution.

5 Conclusions

Refinements made to well records across the study area have helped refine bedrock topographic and drift thickness models, in additional to identifying previously undocumented extents of the Queenston formation in eastern Ontario. Furthermore, characterization of groundwater chemistry has highlighted key relationships between groundwater quality and its relative position within regional scale flow systems controlled by bedrock topography throughout the region. Geochemical processes such as cation exchange, organic decomposition, and salinization closely coincide with bedrock depressions overlain with thick drift cover. Recharge geochemistry, characterized by low pH, elevated DO, and tritium is evident in samples collected in bedrock uplands with limited drift cover. Across the region, wells located in areas with depressed bedrock surfaces are more likely to possess elevated levels of sodium, chloride, methane, and iodide. Inversely, wells constructed in locations with raised bedrock surfaces and limited drift cover are more likely to possess hard water (elevated calcium) and nitrate.

Across eastern Ontario there's an abundance of geological material information captured in water well records. Errors within these records limit their reliability by users, however using a standardized approach wells can be filtered for use with relative ease. These records, in combination with information from available datasets such as the Ambient Groundwater Geochemistry Program, can enhance our understanding of complex hydrogeological environments to assist with efficient and informed decision making on land use management in the face ever mounting development pressure.

Future work should focus on standardizing the means in which local municipalities receive hydrogeological information submitted as part of development applications to facilitate the construction of geoscience information databases. These databases can then be used to develop tools to improve the efficiency of reviewers when assessing hydrogeological and geotechnical conditions.

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Appendix A: Kriging Interpolation Parameters

Table A.1 Semivariogram type and transformation parameters with root-mean-squared values used for EBK interpolation.

Semi-variogram Type	**Transformation**	**Subset Size**	**Overlap Factor**	**Number of Simulations**	**RMS**
Power	None	100	1	100	8.237
Linear	None	100	1	100	8.246
Exponential	Empirical	100	1	100	8.087
Exponential Detrended	**Empirical**	**100**	**1**	**100**	**8.053**
Whittle	Empirical	100	1	100	8.128
Whittle Detrended	Empirical	100	1	100	8.062
K-Bessel	Empirical	100	1	100	8.125
K-Bessel Detrended	**Empirical**	**100**	**1**	**100**	**8.059**

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Table A.2 Modelling parameters include; Subset size, overlap factor and number of simulation modelling parameters with RMS values providing a measure how closely the interpolated surface matches the input dataset.

Semi variogram Type	**Transformation**	**Subset Size**	**Overlap Factor**	**Number of Simulations**	**RMS**
Exponential Detrended	Empirical	100	1	100	8.053
Exponential Detrended	Empirical	200	1	100	8.113
Exponential Detrended	Empirical	100	1	500	8.048
Exponential Detrended	Empirical	100	1	5000	8.041
Exponential Detrended	Empirical	100	2	500	8.059
Exponential Detrended	Empirical	100	0.5	500	8.527
Exponential Detrended	**Empirical**	**50**	**1**	**500**	**7.94**
Exponential Detrended	Empirical	50	1	5000	7.943

Table A.3 Comparison of processed and unprocessed dataset RMS values.

Sample Set	**Semi variogram Type**	**Transformation**	**Subset Size**	**Overlap Factor**	**Number of Simulations**	**RMS**
Unverified	Exponential Detrended	Empirical	100	1	100	11.2033
Verified	Exponential Detrended	Empirical	100	1	100	**8.0529**

Appendix B: Groundwater chemistry statistics

Table B.1 Descriptive statistics of the 369 groundwater samples from the OAGGP

Parameter	**Average**	**Standard Deviation**	**Max**	**Min**
pH	7.71	0.67	9.31	6.41
Ca (mg/L)	51.18	57.14	441.10	0.05
DO (%Saturation)	4.66	15.08	89.40	0.05
H2S (mg/L)	0.48	2.32	37.50	0.01
K (mg/L)	13.01	21.30	170.00	0.09
Mg (mg/L)	35.06	80.91	701.13	0.00015
Na (mg/L)	416.25	882.52	6807.01	3.16
Cl (mg/L)	580.62	1688.83	13622.00	0.19
HCO3 (mg/L)	474.07	311.82	1746.00	111.00
SO4 (mg/L)	63.06	300.23	4942.62	0.03
NO3 (mg/L)	0.44	1.64	15.40	0.003
NH3/NH4 (mg/L)	1.22	2.96	20.80	0.01
Br	2.16	7.11	73.53	0.01
F (mg/L)	0.73	0.79	5.14	0.01
B	456.49	496.06	2810.00	6.00
I	389.43	1202.10	10812.00	2.50
PO4	0.86	1.91	14.21	0.02
Fe	465.09	980.52	9811.00	0.47
CO2	16.10	21.17	162.40	0.05
Tritium	5.38	5.03	21.21	0.40
DOC	6.25	6.43	44.60	0.50
CH4	6.35	12.65	93.22	0.05
Well Screen Elevation	143.66	28.43	211.31	38.72