Mapping the Interface Between the Intermediate Sulphur Water Regime and Deep Brine in the Paleozoic Bedrock of Southwestern Ontario

Oil, Gas and Salt Resources Library, Open File Data Release 2018-2 Terry R. Carter*, Liz Sutherland**

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Introduction and Purpose

Groundwater contained in Paleozoic bedrock formations and the overlying unconsolidated sediments ("drift") in southern Ontario exhibits increasing salinity with depth (Carter et al, 2014). There is a downdip transition from fresh water at or near the surface in the drift and shallow bedrock, to brackish to saline sulphur water at intermediate depths, to dense brines in the deepest bedrock (Carter et al, 2015a, 2015b, Carter et al, 2014, Sharpe et al, 2014) (Fig.1). The base of the fresh water regime, i.e. the depth at which the water is no longer potable, has been previously mapped by Carter and Clark (2018) in southwestern Ontario. This study attempts to map regional variations in the depth of the interface between the sulphur water regime and the deep brine regime.

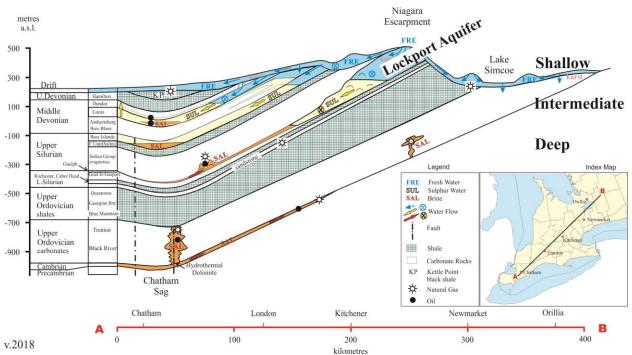


Figure 1: Conceptual model showing hydrochemical subsurface groundwater regimes in southern Ontario: shallow fresh water regime, intermediate brackish to saline sulphur water regime, and deep brine regime. Also shown is the Lockport Aquifer. Modified from Carter et al (2014).

The study area comprises that portion of the province of Ontario, underlain by Paleozoic sedimentary rocks, occurring south and west of the Niagara Escarpment (Fig.2). The study provides, in map form and at regional scale, an approximation of the subsurface interface between the brackish to saline sulphur water at intermediate depths and the brine that occurs in the deepest Paleozoic rocks of southwestern Ontario. The results can be used as a constraint in numeric modeling of the flow of groundwater in the subsurface bedrock formations of southwestern Ontario.

In this report, description of water salinity uses the terminology of Carpenter (1978) and Freeze and Cherry (1979) as adopted by Hiscock and Bense (2014):

Water type	mg/l TDS		
Fresh	0-1,000		
Brackish	1,000-10,000		
Saline	10,000-100,000		
Brine	> 100,000		

Geological and Hydrogeological Setting

Southern Ontario is underlain by marine sedimentary rocks of the Appalachian Basin and Michigan Basin (Fig.2). These Paleozoic sedimentary strata unconformably overlie crystalline metamorphic and igneous rocks of the Canadian Shield, and are covered by a thin veneer of unconsolidated Quaternary and Recent sediments in most of the area. Paleozoic bedrock strata consist of an interlayered succession of sandstones, carbonates, evaporites, mudstones, and siltstones (Fig.3). The bedrock formations dip shallowly to the southwest at 3 to 6 m/km along the crest of the Algonquin Arch, and at 3.5 to 12 m/km down the flanks of the arch westward into the Michigan Basin and southward into the Appalachian Basin (Armstrong and Carter, 2010).

The unconsolidated sediments are variably porous and permeable and water-saturated and are utilized as a source of potable water by most of the water wells drilled in southwestern Ontario (Sharpe et al, 2014). Aquifers in these sediments are complex and discontinuous. The contact with the underlying bedrock is a low-relief angular unconformity resulting from subaerial exposure and erosion of the slightly inclined Paleozoic strata over an extended period of geologic time. The interface between the fresh water-dominated overburden and the relatively less permeable and less porous sedimentary bedrock forms a regional water-bearing interval. This "contact aquifer"is the most widespread potable water aquifer in southern Ontario (Husain, Cherry and Frape 2004; Brunton 2009a, 2009b; Carter, 2012).

Extensive karstic dissolution of the shallow bedrock has occurred in areas of thin overburden where carbonate rocks form the uppermost bedrock layer (Brunton, Priebe and Yeung 2016; Brunton and Dodge 2008; Golder Associates and Ontario Geological Survey, 2008) resulting in greatly enhanced porosity and permeability. These karstic strata form a system of potable water that extends below the drift/bedrock contact. Fresh water occurs up to 130 metres below the top of the bedrock within areas of inferred karst (Carter and Clark, 2018) as determined from GIS queries and quality assurance/quality control (QA/QC) editing of water well records maintained by the Ministry of Environment, Conservation and Parks (MECP) (Fig.4). The potable water regime in the shallow bedrock is the subject of ongoing investigations by the Ontario Geological Survey (OGS) as part of its groundwater mapping program (Brunton, 2009a, 2009b; Brunton, Priebe and Yeung 2016; Priebe and Brunton, 2016; Priebe et al, 2017).

Paleokarst occurs at subsurface unconformities in the Paleozoic sedimentary strata where carbonate rock has been exposed to prolonged periods of weathering in the geologic past (Fig.3). The porous and

permeable rock associated with these paleokarst horizons form the principal regional aquifers in the subsurface bedrock formations. Each of these aquifers are recharged by fresh meteoric water at their outcrop and subcrop edges. This water then flows down-dip and is interpreted to have previously flushed out or diluted the original pore water at shallow to intermediate depths. The depth of penetration depends on the permeability of the formation, past and present hydraulic gradients, and the counteracting buoyancy effects caused by elevated salinity of the intermediate and deep groundwaters. Each subcropping aquifer exhibits a downdip transition from fresh water at shallow depths, to brackish to saline sulphur water at intermediate depths, to highly saline deep brines (Carter et al, 2015a). Sulphur water is also locally reported by water well drillers within the drift (Singer et al, 2003). Cambrian formations do not subcrop in southwestern Ontario and only contain brine.

The term "sulphur water" is used by drillers of water wells and petroleum wells to describe any water containing dissolved H₂S. The H₂S imparts a distinctive "rotten egg" smell to the water that is readily identifiable with little or no training and can be detected by humans at very low concentrations. In this report sulphur water is used in a slightly more restricted sense to refer to brackish to saline water containing dissolved H₂S at intermediate depths and does not include brines associated with deep sour gas reservoirs in southwestern Ontario. The sulphur water in the intermediate regime also contains elevated concentrations of dissolved sulphate. Sulphur isotopic signatures indicate that this sulphate is derived from dissolution of marine sulphates (Skuce, 2014), principally anhydrite, which is abundant in many of the Devonian and Silurian strata of southwestern Ontario, in particular in the evaporitic Lucas Formation and the Salina Group.

In areas of thicker overburden in southwestern Ontario, where karst is not well-developed (Golder Associates and OGS, 2008), and in areas underlain by shaly bedrock formations, wells that penetrate the bedrock more than a few metres encounter groundwater that contains dissolved H₂S and is increasingly saline. Conceptual modelling based on petroleum well data and geochemical and isotopic analyses has documented an intermediate to deep system of thick regional aquitards and thin confined aquifers containing brackish to highly saline water within the bedrock (Nuclear Waste Management Organization 2011; Hobbs et al. 2011; Carter et al. 2016; Carter 2012; Carter and Fortner 2012; Carter et al. 2014; Sharpe et al. 2014; Skuce 2015; Skuce et al. 2015; Skuce, Potter and Longstaffe 2015). Brackish to saline water containing variable amounts of dissolved H₂S generally occurs at intermediate depths, overlapping with a deep brine regime that contains brine with no dissolved H₂S. Depth of this transition is the subject of this study.

In deep continental bedrock aquifer systems similar to southern Ontario it is a common phenomenon that the concentration of dissolved salts increases with depth, with dense brines occupying the deep bedrock. There is likely little or no movement in these deep brine systems, even on a geologic time scale (Hiscock and Bense, 2014).

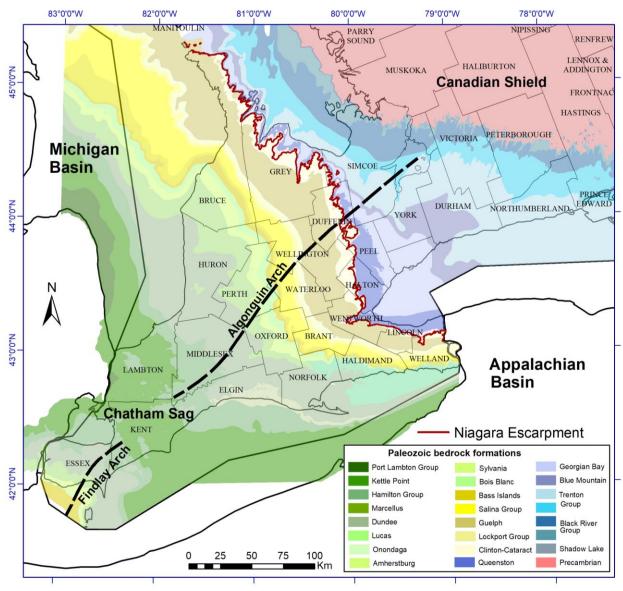


Figure 2. Bedrock geology of southern Ontario, from Somers and Fortner (2017).

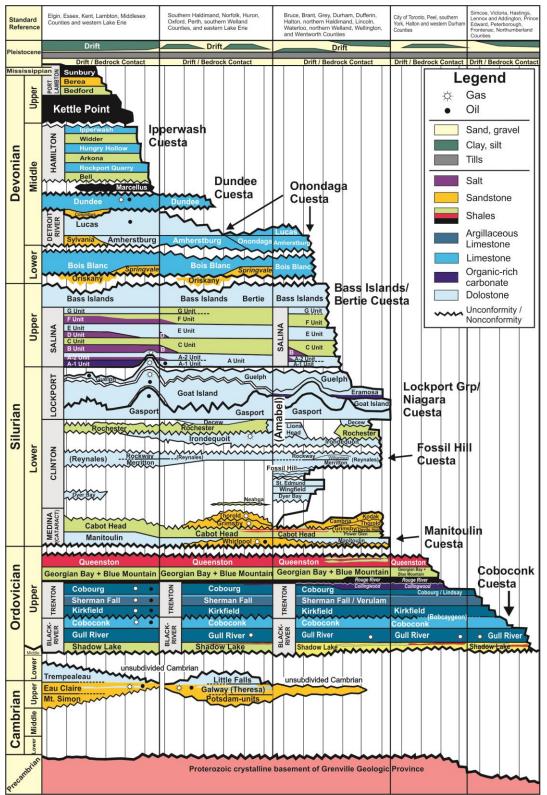


Figure 3. Lithostratigraphy of southern Ontario, from Carter et al (2018), showing regional unconformities representing past periods of exposure, erosion, and/or karstification. Karst intervals in the carbonate strata greatly enhance porosity and permeability and are the main geological control on regional aquifers in the bedrock strata of southwestern Ontario.

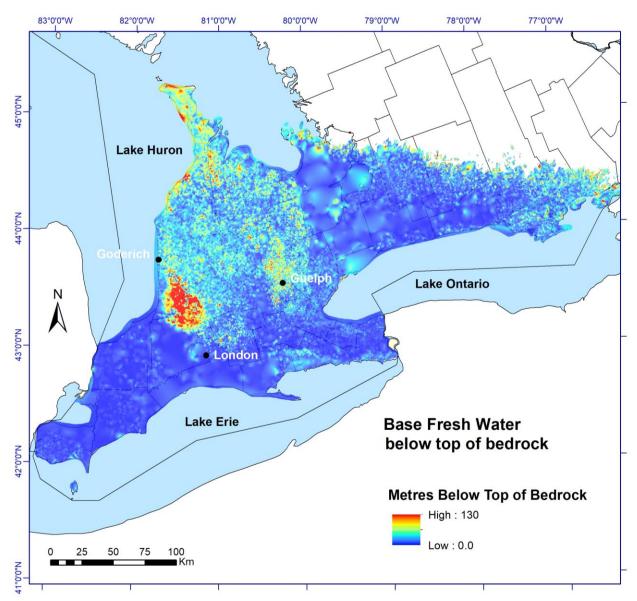


Figure 4. Base of fresh water, metres below top of bedrock, based on water well data maintained by the MOECC (Carter and Clark, 2018). Areas in blue identify the extent of the contact aquifer. Areas in green, yellow and red indicate deep occurrences of fresh water in areas of inferred karst. The large red feature between Goderich and London corresponds to the breathing well aquifer identified by Freckelton (2013).

Open File List

- **1.** Sulphur Water and Brine Report.pdf: This document contains a brief explanation of the data, the maps, mapping and quality control methods, and a discussion of the results.
- 2. Figures: A folder with 8 maps in .jpg format, showing the occurrence of sulphur water, saline water, and brine in the subsurface Paleozoic bedrock of southern Ontario, corresponding to figures 6 to 13 in the report.

3. GIS Maps: A folder with data inputs used to generate the Nearest Neighbor surfaces and help simplify usage. The folder contains shapefiles (.shp) and raster (.grd or .tif) files. Files were created in and compatible with ArcMap 10.1. Also included are the water data points in Excel (.xlsx) format. *This folder is only accessible by members of the Oil, Gas and Salt Resources Library*.

Sources of Information

Petroleum Well Records

The Ministry of Natural Resources and Forestry (MNRF) regulates the drilling, operation and eventual decommissioning of petroleum wells in the province of Ontario under the authority of the Oil, Gas and Salt Resources Act and its regulations and standards. MNRF collects and manages data from petroleum wells, including production of oil, natural gas and formation water. Source records for petroleum wells drilled in Ontario are maintained at the Petroleum Operations Section of the MNRF in London, Ontario, with public access via the Oil, Gas and Salt Resources Library (Library). Source records for this information are paper reports stored in conventional hard-copy well files. There is a separate well file for each unique petroleum well.

The earliest petroleum well records on file with the Ministry of Natural Resources and Forestry date to 1860, but systematic publication of well data by the Ontario government only began in 1915 when the Ontario Bureau of Mines included a summary of well drilling activity in its annual report (Beards, 1967).

Petroleum Well Database

Digital petroleum well records are maintained on the Ontario Petroleum Data System (OPDS). OPDS is an Oracle relational database with a custom Powerbuilder interface designed and maintained by the Petroleum Operations Section of the MNRF. Data management and quality assurance is a shared responsibility of MNRF and the Library. Public access to petroleum well data is managed by the Library.

OPDS contains information for all wells drilled under the authority of the Oil, Gas and Salt Resources Act and Ontario Regulation 245/97. Within the act, a well is legally defined as "a hole in the ground, whether completely drilled or in the process of being drilled, for the purpose of,

(a) the production of oil, gas or formation water, including the production of coal bed methane but excluding the production of fresh water,

(b) the injection, storage and withdrawal of oil, gas, other hydrocarbons or other approved substances in an underground geological formation,

(b.1) a compressed air energy storage project that is prescribed, or any part or portion of such a project as may be prescribed,

- (c) the disposal of oil field fluid in an underground geological formation,
- (d) solution mining, or
- (e) geological evaluation or testing rocks of Cambrian or more recent age

OPDS records provide geological, drilling and engineering information on approximately 27,000 petroleum and related wells drilled in Ontario since 1858. Stored data includes well location, status, depths, geological formation tops, well construction, oil/gas/water intervals, logged and cored intervals, and storage location of drill cuttings from bedrock formations penetrated by the well. Water interval data includes depth, static level, water type and host geological formation. Every single paper record in the MNRF petroleum well files is associated with a digital well record in OPDS. However, it is important to note that petroleum well records contain very little information about unconsolidated sediments that overlie the bedrock.

Basic data for petroleum wells in southern Ontario is available for public viewing at <u>www.ogsrlibrary.com</u>. Oil, gas and water interval data and formation top depths are value-added data available only to registered Library members or by purchase of select datasets.

Water Interval Records

OPDS contains over 35,000 records of water-bearing intervals encountered during the drilling of petroleum wells in Ontario (Carter et al, 2015a). Most of these records are obtained from wells drilled by the cable tool method.

In the cable tool drilling method, the borehole is created by percussion without the use of hydraulic pressure. Any water encountered while drilling will immediately enter the well bore. The depth interval at which this occurs is recorded by the driller. It is usually only possible to accurately record the top of the interval, as water will continue to enter the well bore until the interval is sealed by a casing. The drilling process is sufficiently slow that the resulting water column stabilizes, and the driller can record the depth to the top of the column of water as the static level. Almost all of the water interval data in OPDS was acquired in this way. The static level and water type for the water intervals is required to be reported by the operator to MNRF (Fig.5). The observed results are summarized on the drilling and completion reports in the well files and transcribed to OPDS.

Wells drilled with rotary drilling rigs use drilling muds under hydraulic pressure to prevent the uncontrolled entry of any formation fluids into the well bore, and consequently do not usually provide any information on water-bearing intervals. Examples of exceptions are detection of a sulphur smell from the drilling mud, recorded at a specific drilling depth, or record of the depth of a lost circulation zone.

Drillers record a description of the water type from each of the water-bearing intervals they encounter using terminology similar to that used by water well drillers. Water type descriptions provide a subjective judgement of water quality and provide field evidence of microbial activity where identification of sulphur water implies the presence of sulphate-reducing bacteria. Sulphur water is water containing dissolved H₂S and is readily identified by drillers by its distinctive "rotten egg" smell. Water types recordable in OPDS are:

BLK – Black BRA – Brackish FRE – Fresh LOS – Loss of circulation MIN – Mineral SAL – Salt (saline water and/or brine) SUL – Sulphur (dissolved H₂S, identified by rotten egg smell)

The geological formation within which the water occurs has been interpreted by MNRF or Library staff by comparison of the water interval depths to the formation top depths recorded for the wells. The terminology used to identify formations in the database is consistent with Armstrong and Carter (2010) (Fig.3). The coding of the geological formation in the data record makes it possible to map aquifers and aquitards in the Paleozoic bedrock as the occurrence of water, by type, in each geological formation (Sharpe et al, 2014, Carter et al, 2014a, Carter et al, 2015a). It is also possible to construct static level maps for these aquifers (Carter et al, 2015b).

INITIAL WATER INTERVAL	STATIC LEVEL	TYPE	Anal	Analysis Formation
141 -	36.00	Sulphur	N	Lucas
20 -	11.00	Fresh	N	Kettle Point

Figure 5. Screenshot of water interval data for a petroleum well as entered in OPDS from the Form 7 (Well Completion Report). Interval and static level depths are recorded in metres below rig floor.

Water Analyses

Chemical analyses of water samples from selected subsurface bedrock formations of southern Ontario were acquired by the MNRF in 2011-2013 in partnership with the University of Western Ontario. The complete set of data and description of sampling methods are available in Skuce (2014).

Chemical analyses are also available for water samples collected by the operators of licensed petroleum wells. During the drilling of a petroleum well, the well operator may take a sample of water that has been encountered during drilling and submit it for chemical analysis by a commercial laboratory. A copy of the analytical results is required to be submitted to the MNRF. This data becomes part of the public record after the expiry of a 1 year confidentiality period. The water analyses are measurements of the concentration of a limited suite of dissolved elements and compounds, including Na, Ca, Mg, Cl, SO₄, HCO₃, and total dissolved solids, as well as pH, density, and resistivity. The water analysis data from these reports has been compiled in an Excel data file by the Library.

Data Quality Issues

Water Interval Records

There are numerous possible sources of error for the water interval data, considering the large number of well drillers involved and the informal data collection protocol. The accuracy of individual records cannot be guaranteed and should be used with caution. Nonetheless, when used as a dataset at a regional mapping scale, the compiled data provide valuable information about the occurrence and types of water in the bedrock of southern Ontario (see Carter et al. 2015a, 2015b).

A number of quality assurance issues were identified during review of the data. Corrective edits were applied to several hundred records where it was possible to reliably determine a resolution. If a corrective edit could not be identified, the unreliable records were omitted from the mapping process. Data quality issues are listed below.

- 1. Incomplete reporting: There is no corrective fix for this issue.
- 2. Inaccurate well location.
- 3. Typographic data entry errors: These were identified by comparison with source records and corrected during the anomaly editing exercise.
- 4. Lack of well casing to separate shallow and intermediate water intervals from deeper water intervals, resulting in mixing. Identification of water type in these cases is considered unreliable.
- 5. Identification of brines as sulphur water by drillers, especially for wells drilled into sour gas and oil reservoirs in the Guelph Formation and the A-1 and A-2 units beneath western Lake Erie and in Kent and Essex counties. The water encountered in these areas has a sulphurous smell as correctly reported by the drillers, but the water has salinities exceeding 100,000 mg/l total dissolved solids, ranging from 250,000 to 400,000 mg/l, as confirmed by chemical analyses in this report. These waters have been reclassified as brines in this study.

- 6. Lack of data for the base of water intervals. This creates uncertainty in the precision of mapping of the base of the sulphur water regime.
- 7. Water containing dissolved salt, i.e. water with a salty taste, and which has no sulphur odour, is identified by both water well and petroleum well drillers as "salt water". The salinity is unknown, and consequently cannot be accurately classified as brackish, saline or brine. This is the largest source of error in accurate identification of deep brines vs brackish to saline "sulphur water" of the intermediate regime and makes accurate mapping of the interface between the deep brine and the intermediate groundwater regime problematic.

An iterative process of quality assurance edits was performed. After completion of each round of edits, preliminary versions of the maps were interpolated. All "anomalies" represented by single wells on these maps were reviewed and corrective edits applied. The maps were then regenerated for a further round of anomaly checks and corrective edits.

Water Analyses

Sampling methods and data quality issues for the MNRF analytical data is described in Skuce (2014).

Water analyses reported by the operators of petroleum wells have a range of data quality concerns. Water samples were collected by a wide variety of well operators and were obtained from a variety of sources or collectors, including drill stem test chamber, wellhead valve, flow line, swab, bailer, production tank, and separator, each of which may create issues with data quality. Samples collected during drilling operations may be susceptible to contamination by drilling fluids. Dilution of the very saline deep brines typical of southern Ontario is a possibility. The laboratory analyses were completed by a limited number of different commercial laboratories between 1948 and 2001 with one sample collected and analysed in 1907. These issues create uncertainty about the consistency and precision of individual results. Nonetheless, taken as a group of data, the water analyses provide quantitative values for water salinity which are inherently more precise than the qualitative judgements of well drillers for the water interval data, and provide valuable insights into regional variations in salinity in bedrock groundwaters.

Mapping Methods

Creating geologically meaningful maps from the OPDS data is dependent on the design of GIS data filters and selection methods to derive a subset of wells with the required attributes, and quality assurance editing of this new dataset. For this mapping exercise, the data filtering procedure was designed to select the deepest reported occurrences of sulphur water, and the shallowest reported occurrences of salt water at each well location. If the resulting maps were reliable, the interface between the two maps would approximate the base of the saline to brackish sulphur water regime and the top of the brine regime.

An interim map was prepared for each data set after the initial data filtering exercises. Anomalous data were identified by visually reviewing the maps and editing or deleting individual records contributing to contouring anomalies. This process was repeated four times before a geologically acceptable result was obtained.

Three data interpolation algorithms are supplied with the Spatial Analyst extension of ArcMap 10.1; inverse distance weighted, kriging and natural neighbours. After trial and error, it was determined that the natural neighbours algorithm produced the most geologically meaningful results and was therefore used to create interpolated surface and contour maps of the edited data.

Mapping Results

Total Dissolved Solids - Lockport Group + Salina A-1 and A-2 Units

The Lockport Group, as redefined by Brunton and Brintnell (2011) (Guelph, Eramosa, Goat Island, and Gasport formations), form a regional aquifer extending beneath all of southern Ontario (Fig.1). These formations form a northwest-southeast subcrop-outcrop belt in southwestern Ontario and dip shallowly southwest into the Chatham Sag (Fig.2). In the deepest part of the Chatham Sag the top of the Lockport Group is over 750 metres below the surface and is overlain by thick beds of Salina Group halite (Fig.3). There are a large number of oil and natural gas reservoirs with associated water in the Guelph Formation and the immediately overlying Salina A-1 and A-2 units. For the purposes of this study, analyses of water from all these formations has been compiled and grouped to map regional variations in total dissolved solids.

The water analysis data was queried to select samples from only these formations. After QA/QC filtering, analytical results were available for 139 samples. Of these, 2 are classified as fresh water, 21 as brackish to saline water, and 116 as brine, as per Hiscock and Bense (2014). Eighty percent of the brine samples have values ranging from 230,00 to 410,000 mg/l with a median value of 314,000 mg/l total dissolved solids. The overwhelmingly large proportion of brine vs fresh water samples is a direct result of the preferential sampling of deep formation water from oil and gas reservoirs.

The data was plotted and contoured to show the regional variation in total dissolved solids (Fig. 6). Salinity increases downdip from approximately 200 mg/l total dissolved solids in the outcrop belt to a maximum reported value of over 600,000 mg/l in the deep subsurface. The interface between brackish and saline water of the intermediate sulphur water regime and deep brine occurs approximately 35 to 65 km downdip from the subcrop exposure of these formations. This correlates to a depth of approximately 250 to 300 metres below the top of bedrock.

Base of Sulphur Water

Depth values from the water interval data set, where water type was recorded as sulphur water by the driller, were used to generate a map showing the deepest recorded intervals of sulphur water. Nearly 9000 data points were utilized (Fig. 7). Two maps have been created: the base of sulphur water measured in metres below the top of bedrock and the base of sulphur water measured in metres subsea, but only the first is shown here (Fig.8). No water analysis data was incorporated. It should be noted that there is an inherent inaccuracy in these maps as only the top of the water interval is recorded in the data set. But as the bedrock aquifers are at most a few metres or tens of metres thick, the maps provide a reasonable approximation of the base of the sulphur water regime in the bedrock of southern Ontario.

Comparison to the base of fresh water mapping of Carter and Clark (2018) identified isolated areas where the interpolated sulphur water raster surface extended above the fresh water raster surface, which is inconsistent with the observed regional hydrochemical zonation. Within these areas a raster calculation was used from the Spatial Analyst extension of ArcGIS 10.1 to reassign the base-of-sulphur-water pixels to equal the value from the base-of-fresh-water raster.

QA/QC review of this qualitative data included a comparison to the water analysis data for samples from the Lockport Group + Salina A-1 Unit + Salina A-2 Unit (see Fig.6). This comparison identified a large number of wells where the driller identification of sulphur water, based on a rotten egg odour of the water, coincided with areas where the analytical data documents the presence of dense brines. In westcentral Lake Erie, between Norfolk County and Essex County, the analytical data indicates the presence of dense brines with total dissolved solids content ranging from 250,000 to over 400,000 mg/l (Fig.6). Within this area all data points identified as sulphur water by the driller were reclassified as brine. Outside this area, at scattered locations, there are a number of wells with sulphur water reported in these formations which cannot be verified, but this data has been retained in the data set.

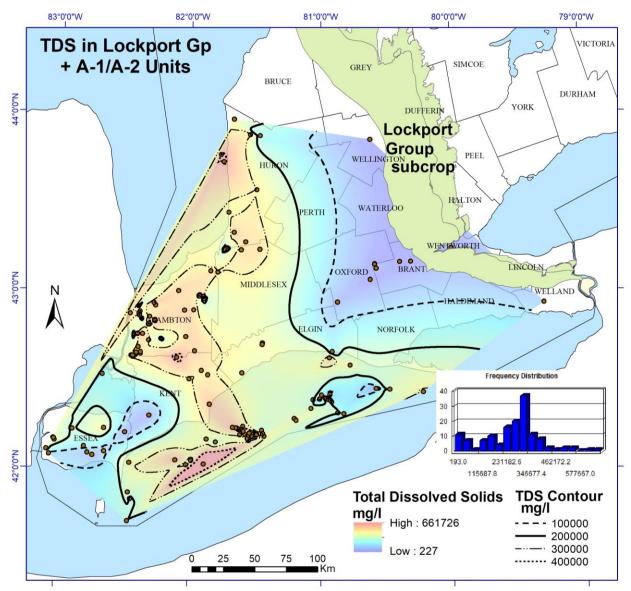


Figure 6. Raster surface and contour map of total dissolved solids in the Lockport Group + Salina A-1 Unit and Salina A-2 Unit in the subsurface of southern Ontario downdip from the subcrop belt of these formations. Subcrop-outcrop belt of Lockport Group shown in green. Circles show location of data points.

The map shows *regional* occurrence of sulphur water at depths ranging from the top of bedrock to approximately 200 metres below the top of bedrock (Fig.8). This water is largely confined to the Dundee, Lucas, Amherstburg and Onondaga formations, and to a lesser extent in the Bois Blanc and other formations stratigraphically above the Salina Group (Fig.9). Sulphur water is also widely reported in the overlying unconsolidated sediments within the water well records maintained by MECP (Singer et al, 2003). Within this regional distribution, there are a number of widely scattered, isolated, anomalously deeper occurrences of sulphur water within the Lockport Group, principally with the Guelph Formation.

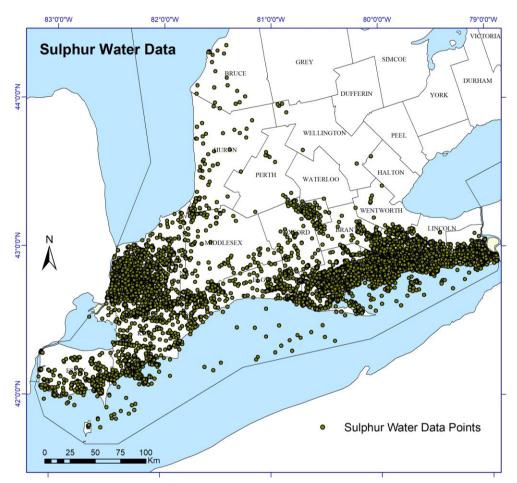


Figure 7. Map showing location of approximately 9000 petroleum wells for which sulphur water depth data was utilized in this study.

There are two distinctive areas of deeper occurrence of sulphur water. In Huron and southern Bruce counties is a distinctive NNW-SSE trending zone confined to the A-1 Carbonate Unit, at depths of 300 to 350 metres below the bedrock surface (Fig.10). This "Huron-Bruce Anomaly" occurs 25 to 50 km southwest and downdip from the A-1 Carbonate subcrop belt. The second is a large zone beneath Lake Erie where sulphur water occurs at depths from 200 to 285 metres below the top of bedrock. This water is largely confined to the Bass Islands/Bertie Formation (Fig.11).

There are a number of wells reported to have encountered sulphur water at depths exceeding 300 metres below the bedrock surface at scattered locations in Welland, Lincoln, Haldimand, Norfolk, Wentworth, Oxford, Essex, and western Elgin counties, and eastern Lake Erie. These wells plot within a transition zone between the deep brine and the shallow fresh water regime, in water with a salinity of less than 200,000 mg/l (Fig.12).

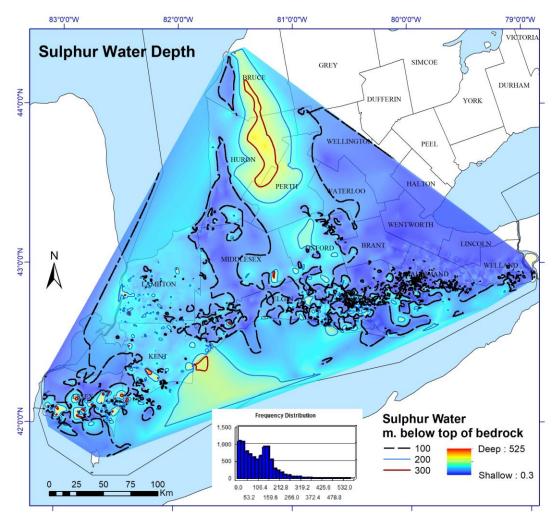


Figure 8. Deepest occurrence of sulphur water recorded in petroleum well records, measured in metres below top of bedrock. The map indicates widespread occurrence of sulphur water at shallow to intermediate depths in bedrock formations stratigraphically above the top of the Salina Group.

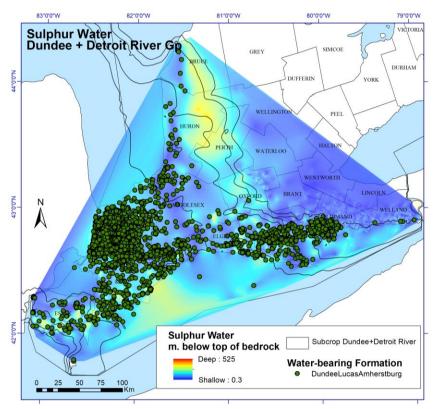


Figure 9. Subcrop belt and sulphur water in the Dundee, Lucas, Amherstburg, and Onondaga formations.

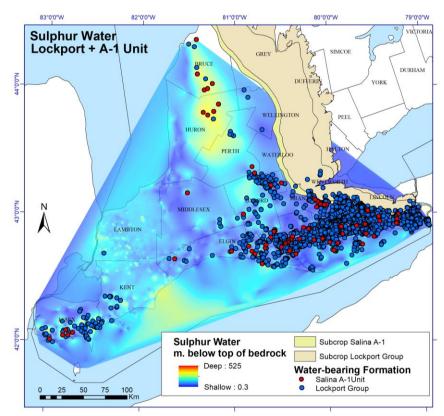


Figure 10. Subcrop belt and sulphur water in the Lockport Group and Salina A-1 Unit.

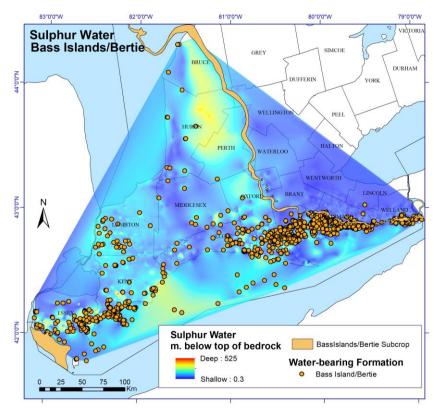


Figure 11. Subcrop belt and sulphur water in the Bass Islands/Bertie formations.

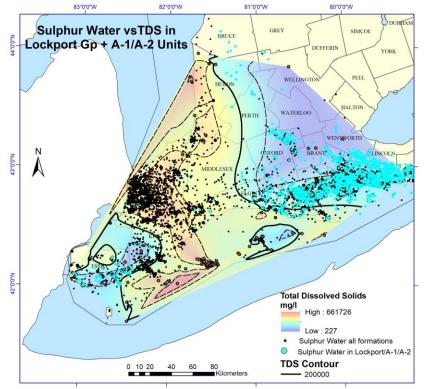


Figure 12. Wells at which sulphur water is reported to occur in the Lockport Group + Salina A-1 Unit and Salina A-2 Unit, shown with blue circles, vs. map of total dissolved solids in the same formations.

Top of "Salt Water"

The OPDS water interval records include a subjective water type identified as "salt water". This water type includes all water containing dissolved salt, regardless of concentration, and which does not have an odour of dissolved H_2S . It includes both saline water and brine, and consequently cannot be used to interpret or map the depth transition from brackish to saline water of the intermediate regime to the dense brine of the deep regime.

Brine can be reliably identified in chemical analyses. The database of industry water analyses was filtered to select analyses where the total dissolved solids exceeds 100,000 mg/l. This discounted nearly half of the available data. Other quality constraints resulting in exclusion were: no recorded depth, and duplicate analyses of the same water sample. Out of the 1024 records in the water analysis database, only 312 analyses were suitable for mapping after QA/QC filtering.

The geographic distribution of brine analyses from the above filtering exercise has been compared to a raster plot of water interval records where the driller recorded a "salt water" interval. At individual wells with more than one recorded salt water interval, only the shallowest depth value was utilized for mapping. In addition, records for formations of Ordovician, Cambrian, or Precambrian age were excluded as these formations always contain brine west of the Niagara Escarpment. In this way only the shallowest occurrences of brine were included in the resulting rasterized data set.

The raster map shows a widespread occurrence of salt water at depths ranging from only a few metres below the top of bedrock, to very deep, 820 metres below the top of bedrock. In contrast the analytical data shows that most brine occurs at depths greater than 200 metres below the top of bedrock, with the shallowest brine recorded at 40 metres below the top of bedrock. Only 14 of 312 available records show brine at depths shallower than 200 metres below the bedrock top. These shallow brine occurrences are scattered and isolated.

The areas of shallow "salt water" in Figure 13 coincide with the occurrence of brackish to saline water lacking dissolved H_2S , within the intermediate groundwater regime (Fig.9,10, 11), and does not reliably indicate the presence of brine. The raster map is not considered to be useful in mapping the depth transition from the intermediate sulphur water regime to the deep brine regime and is presented here for information purposes only.

Discussion and Interpretation

Isotopic fingerprinting (δ^{18} O and δ^{2} H) of subsurface groundwater in bedrock formations of southwestern Ontario indicates that shallow fresh water has a modern meteoric signature (Skuce, 2014; Skuce et al, 2014). Available samples from the intermediate sulphur water regime have cold-climate isotopic ratios of oxygen and hydrogen indicating the water likely originated as glacial meltwater. The deep brine is interpreted to be modified remnants of highly evaporated seawater (Dollar et al., 1991; Hobbs et al., 2011, Skuce, 2014; Skuce et al, 2015) of Silurian age (Clark et al, 2013) and is inferred to have formed under evaporitic conditions prevailing during deposition of the Salina Group and possibly also the Lucas Formation.

There is a down-dip transition from shallow fresh water, to brackish-to-saline sulphur water at intermediate depths, to highly saline brine in the deep groundwater regime (Hobbs et al, 2011; Carter et al, 2014) (Fig.1). Fresh water is largely confined above the bedrock surface in most of southwestern Ontario, with local exceptions where inferred karst and paleokarst have enabled penetration of fresh water

up to 130 metres below the bedrock surface. Recent studies by the OGS have identified fresh water several tens of metres below the bedrock surface in the outcrop-subcrop belt of the Lockport Group.

The intermediate regime is interpreted to represent downdip penetration of both modern meteoric water and glacial meltwater into the subsurface where bedrock formations outcrop at the surface or subcrop beneath thin overburden. It is inferred to have partially to completely displaced any original pore fluids with consequent dilution of the total dissolved solids content. The present study indicates that this transition occurs relatively abruptly over a distance of approximately 25 to 65 km (Fig.6,10).

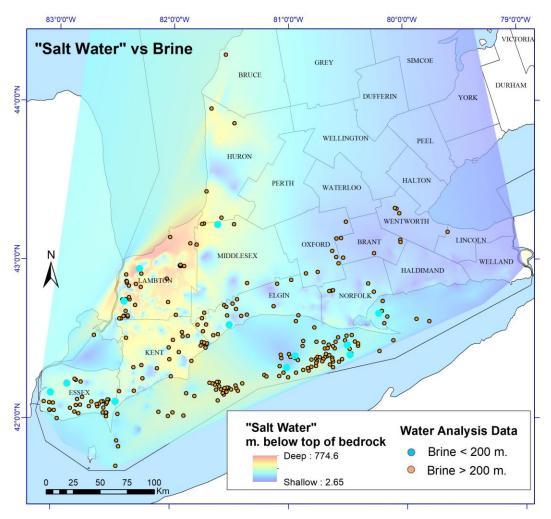


Figure 13. The regional occurrence of "salt water" vs brine in the subsurface of southern Ontario, measured relative to the top of bedrock. The salt water raster surface is derived from water type records in OPDS, where water type is identified as salt water. The water analysis points are petroleum industry water analyses.

The depth of the transition zone between the brines and the overlying groundwater regimes has been estimated to occur at depths between 200 and 450 metres below the bedrock surface in previous regional studies (Skuce, 2014; Skuce et al, 2015; Clark et al, 2010a, 2010b, 2011) and at 169 metres at the proposed Deep Geologic Repository on the shore of Lake Huron in Bruce County (Clark et al, 2013). This study indicates a regional transition from brackish-to-saline water of the intermediate sulphur water regime to deep brine at approximately 200 to 300 metres below the top of bedrock and locally to 350

metres (Fig.8), providing better resolution on the earlier regional work. Modern and ancient meteoric water of the shallow to intermediate regimes is generally stratigraphically confined above the Salina Group. The principal exception is downdip penetration in subcropping/outcropping porous and permeable karstic strata of the Lockport Group, and more specifically the Guelph Formation.

The aquifers of these hydrochemical systems are stratigraphically isolated from each other in the subsurface by low-permeability conditions in the evaporites of the Salina Group, Silurian shales of the Rochester and Cabot Head formations, Ordovician shales of the Queenston, Blue Mountain and Georgian Bay formations. Additional constraints on water movement are: the low topographic gradients in the region; the density contrast between the brine and the shallow to intermediate waters; and a general lack of discharge pathways for the brine (Hobbs et al., 2011; Sharpe et al., 2014; Clark et al, 2013)).

The salt water data in the water type records of the Ontario petroleum well database cannot be used as reliable indicators of the presence of highly saline brine, and thus do not provide an accurate record of the top of the deep brine regime. They do indicate the widespread occurrence of brackish to saline water at relatively shallow depths in much of southwestern Ontario.

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References

Armstrong, D.K., and Carter, T.R. 2010. The subsurface Paleozoic stratigraphy of southern Ontario. Ontario Geological Survey, Special Volume 7, 301 p.

Armstrong, D.K. and Dodge, J.E.P. 2007. Paleozoic geology of southern Ontario; Ontario Geological Survey, Miscellaneous Release—Data 219.

Beards, R.J. 1967. Guide to the subsurface Palaeozoic stratigraphy of southern Ontario; Ontario Department of Energy Resources Management, Paper 67-2, 19p.

Brunton, F.R. 2009a. Karst mapping and groundwater of southern Ontario; in Groundwater and Geology – Foundation for Watershed Planning, Latornell Conference, pre-meeting core workshop, November 17, 2009, p.1-15.

——— 2009b. Update of revisions to the Early Silurian stratigraphy of the Niagara Escarpment: Integration of sequence stratigraphy, sedimentology and hydrogeology to delineate hydrogeologic units; in Summary of Field Work and Other Activities 2009, Ontario Geological Survey, Open File Report 6240, p.25-1 to 25-20.

Brunton, F.R. and Brintnell, C. 2011. Final update of Early Silurian stratigraphy of the Niagara Escarpment and correlation with subsurface units across southwestern Ontario and the Great Lakes Basin; in Summary of Field Work and Other Activities 2011, Ontario Geological Survey, Open File Report 6270, p.30-1 to 30-11.

Brunton, F.R., Brintnell, C., Jin, J. and Bancroft, A.M. 2012. Stratigraphic architecture of the Lockport Group in Ontario and Michigan – A new interpretation of Early Silurian "basin geometries" and "Guelph Pinnacle Reefs"; in 51st Annual Conference – Ontario – New York, Oil & Gas Conference, Oct. 23-25, 2012, Niagara Falls, Ontario, p.1-37.

Brunton, F.R. and Dodge, J.E.P. 2008. Karst of southern Ontario and Manitoulin Island; Ontario Geological Survey, Groundwater Resources Study 5.

Brunton, F.R., Priebe, E.H. and Yeung, K.H. 2016. Relating sequence stratigraphic and karstic controls of regional groundwater flow zones and hydrochemistry within the Early Silurian Lockport Group of the Niagara Escarpment, southern Ontario; in Regional-scale Groundwater Geoscience in Southern Ontario: An Ontario Geological Survey and Geological Survey of Canada groundwater geoscience open house, Geological Survey of Canada, Open File 8022, p.4. doi:10.4095/297722.

Carpenter, A.B. 1978. Origin and chemical evolution of brines in sedimentary basins. In Thirteenth annual forum on the geology of industrial minerals, eds. K.A. Johnson and J.A. Russell, Oklahoma Geological Survey, Circular 79, p.60-77.

Carter, T.R., 2012. All is well – Regional groundwater systems in southern Ontario, in Ontario Oil & Gas 2012, Ontario Petroleum Institute, p.44-48.

Carter, T.R., and Clark, J., 2018. Base of fresh water, bedrock karst, and the contact aquifer in southern Ontario, as interpreted from water well records; Oil, Gas and Salt Resources Library, unpublished report.

Carter, T.R., Fortner, L., Skuce, M.E., and Longstaffe, F.J., 2014. Aquifer systems in southern Ontario: hydrogeological considerations for well drilling and plugging, Canadian Society of Petroleum Geologists, Geoconvention 2014, abstract, accessed at:

http://www.geoconvention.org/archives/2014abstracts/298_GC2014_Aquifer_Systems_in_Southern_Ont ario.pdf

Carter, T.R., Wang, D., Castillo, A.C., and Fortner, L., 2015a. Water Type Maps of Deep Groundwater from Petroleum Well Records, Southern Ontario; Oil, Gas and Salt Resources Library, Open File Data Release 2015-1.

Carter, T.R., Wang, D., Castillo, A.C., and Fortner, L., 2015b. Static level maps of deep groundwater from petroleum well records, Southern Ontario; Oil, Gas and Salt Resources Library, Open File Data Release 2015-2.

Clark, I.D., Al, T., Jensen, M., Kennell, L., Mazurek, M., Mohapatra, R., and Raven, K.G., 2013. Paleozoic-aged brine and authigenic helium preserved in an Ordovician shale aquiclude. Geology, vol.41, no.9, p.951-954.

Clark, I., Mohapatra, R., Mohammadzadeh, H., Kotzer, T., 2010a. Porewater and Gas Analyses in DGR-1 and DGR-2 Core. Technical Report TR-07-21, Intera Engineering Ltd., Ottawa.

Clark, I., Liu, I., Mohammadzadeh, H., Mohapatra, R., Zhang, P., Wilk, M., 2010b. Porewater and Gas Analyses in DGR-3 and DGR-4 Core. Technical Report TR-08-19, Intera Engineering Ltd., Ottawa.

Clark, I., Scharf, V., Zuliani, J., Herod, M., 2011. Porewater and Gas Analyses in DGR-3 and DGR-4 Core. Technical Report TR-09-04, Intera Engineering Ltd., Ottawa.

Freckelton, Candace N., 2013. A Physical and Geochemical Characterization of Southwestern Ontario's Breathing Well Region, University of Western Ontario, Electronic Thesis and Dissertation Repository. 1105, https://ir.lib.uwo.ca/etd/1105Freckelton, 242 p.

Freeze, R.A., and Cherry, J.A., 1979. Groundwater. Prentice-Hall Inc, Englewood Cliffs, New Jersey, USA, 603 pp.

Golder Associates Ltd, and Ontario Geological Survey, 2008. 3-D field investigation of Paleozoic bedrock and boreholes in thin-drift limestone-dolostone plains of southern Ontario; Ontario Geological Survey, Supplementary Report to Groundwater Resources Study 5, 53 p.

Hiscock, K.M., and Bense, V.F., 2014. Hydrogeology: Principles and practice, Wiley Blackwell, Oxford, U.K., 518 p.

Hobbs, M.Y., Frape, S.K., Shouakar-Stash, O., and Kennell, L.R., 2011. Regional hydrogeochemistrysouthern Ontario. Nuclear Waste Management Organization, Report NWMO DGR-TR-2011-12, Toronto, Canada, http://www.nwmo.ca/uploads/DGR%20PDF/Geo/Regional-Hydrogeochemistry---Southern-Ontario.pdf, accessed on June 11, 2013.

Husain, M.M., Cherry, J.A. and Frape, S.K. 2004. The persistence of a large stagnation zone in a developed regional aquifer, southwestern Ontario; Canadian Geotechnical Journal, v.41, p.943-958.

Johnson, M.D., Armstrong, D.K., Sanford, B.V., Telford, P.G., and Rutka, M.A., 1992. Paleozoic and Mesozoic geology of Ontario; in Geology of Ontario, Ontario Geological Survey Special Volume 4, Part 2, p.907-1010.

Nuclear Waste Management Organization, 2011b. Geosynthesis; Nuclear Waste Management Report NWMO DGR-TR-2011-11, Toronto, Canada, Accessed June 11, 2013 at: http://www.nwmo.ca/uploads/DGR% 20PDF/Geo/Geosynthesis.pdf

Priebe, E.H. and Brunton, F.R. 2016. Regional-scale groundwater mapping in the early Silurian carbonates of the Niagara Escarpment: Final update; in Summary of Field Work and Other Activities, 2016, Ontario Geological Survey, Open File Report 6323, p.29-1 to 29-10.

Priebe, E.H., Neville, C.J., and Brunton, F.R., 2017. Discrete, high-quality hydraulic conductivity estimates for the Early Silurian carbonates of the Guelph region; Ontario Geological Survey, Groundwater Resources Study 16, 45 p.

Sharpe, D.R., Piggott, A., Carter, T.R., Gerber, R.E., MacRitchie, S.M., de Loe, R., Strynatka, S. and Zwiers, G. 2014. Southern Ontario hydrogeological region, p.444-499, *in* Rivera, A. (editor), Canada's Groundwater Resources, Fitzhenry and Whiteside, Canada, 803 p.

Singer, S.N., Cheng, C.K., and Scafe, M.G., 2003. The hydrogeology of southern Ontario; Ontario Ministry of Environment, Environmental Monitoring and Reporting Branch, 395 p.

Skuce, M., 2014. Isotopic fingerprinting of shallow and deep groundwaters in southwestern Ontario and its applications to abandoned well remediation. University of Western Ontario, MSc thesis, Electronic thesis and dissertation repository, Paper 1926, 267 pp., http://ir.lib.uwo.ca/do/search/?q=skuce&start=0&context=686929

Skuce, M., Longstaffe, F.J., and Potter, J., 2015. The isotopic characterization of water in Paleozoic bedrock formations of southwestern Ontario; Oil, Gas and Salt Resources Library, Open File Data Release 2015-3.

Skuce, M., Longstaffe, F.J., Carter, T.R., and Potter, J., 2015. Isotopic fingerprinting of groundwaters in southwestern Ontario: application to abandoned well remediation; Applied Geochemistry 58, p.1-13.

Somers, M., and Fortner, L. Paleozoic bedrock geology of southern Ontario; Oil, Gas and Salt Resources Library, Open File Data Release 2017-2.

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