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2018

Canada

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2018

Permanent link: https://doi.org/10.4095/311182

This publication is available for free download through GEOSCAN (http://geoscan.nrcan.gc.ca/).

Recommended citation
Stepner, D.A.J., Knight, R.D., Bajc, A.F., and Russell, H.A.J., 2018. Geochemistry of surficial sediment cores, Dundas buried bedrock valley area, southwestern Ontario; Geological Survey of Canada, Open File 8300, 1 .zip file. https://doi.org/10.4095/311182

Publications in this series have not been edited; they are released as submitted by the author.

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1.0 Introduction

Over the past 20 years, the Geological Survey of Canada (GSC) and the Ontario Geological Survey (OGS) have carried out numerous studies on the glacial sediments of southern Ontario (Fig. 1). Much of this work is summarized in the Canadian Journal of Earth Sciences, Special Issue: Quaternary geology of southern Ontario and applications to hydrogeology (e.g., Russell et al., 2018). These studies utilized basin analysis techniques to study sediments within this region, but there is a general lack of information on the regional geochemistry of sediments. Geochemical studies are crucial for defining chemical and mineralogical variations within sediments and supplement sediment description, grain size data, downhole geophysical and stratigraphic correlations (Crow et al., 2015a; 2015b) and provide a geochemical baseline for interpreting host sediment (rock) composition and ambient groundwater chemistry. Geochemical data collected from cores provide the opportunity to establish a chemo-stratigraphic framework that complements other stratigraphic correlation techniques, such as litho-stratigraphy, event stratigraphy, and biostratigraphy.

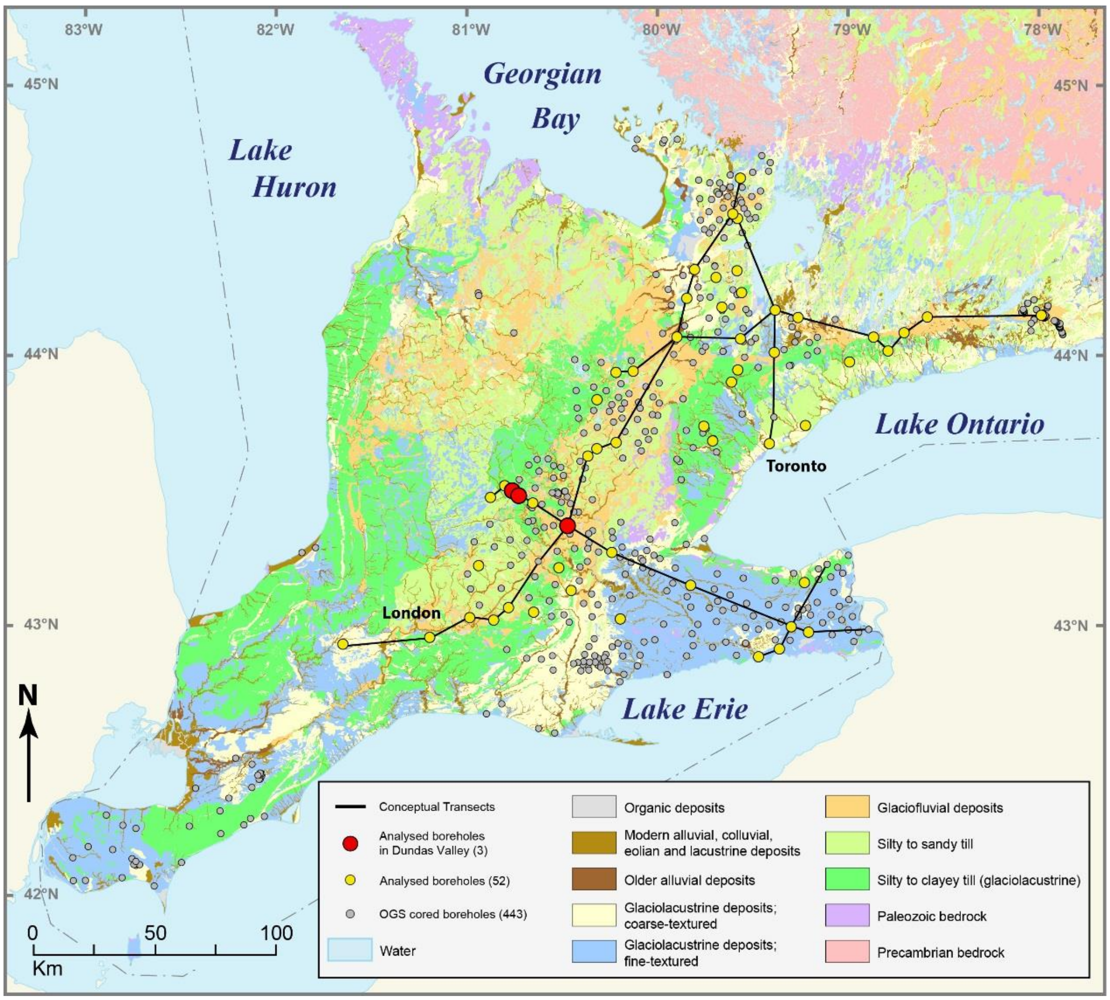

Figure 1: Map with the locations of Dundas Valley boreholes, in relation to other OGS and GSC cored borehole sites. Conceptual transects for this study shown as solid lines. Surficial geology of southern Ontario modified from OGS MRD128-Rev, (2010).

For groundwater studies, the collection of sediment geochemistry data is often beyond the scope (and budget) of many programs, and is generally not included as part of routine data collection. Portable X-ray fluorescent (pXRF) spectrometry has proven to be a successful tool for characterizing the chemostratigraphy of glacially derived sediments (e.g. Crow et al., 2012; Knight et al., 2015a, 2015b) as well as improving the interpretation of downhole geophysics, micropaleontology results, and pore water geochemistry (Medioli et al., 2012). Data collected using this method is now a routine part of borehole studies within the Groundwater Geoscience Program at the GSC (Knight et al., 2015a, 2015b, 2012).

The objective of this Open File is to release geochemical data and associated QA-QC for 235 sediment samples retrieved from three boreholes drilled during July 2011 in the Dundas Valley (Marich et al., 2011), located west and south of Waterloo, Ontario (Fig. 2). The report documents the contribution of these data to an emerging subsurface chemostratigraphic database for Southern Ontario.

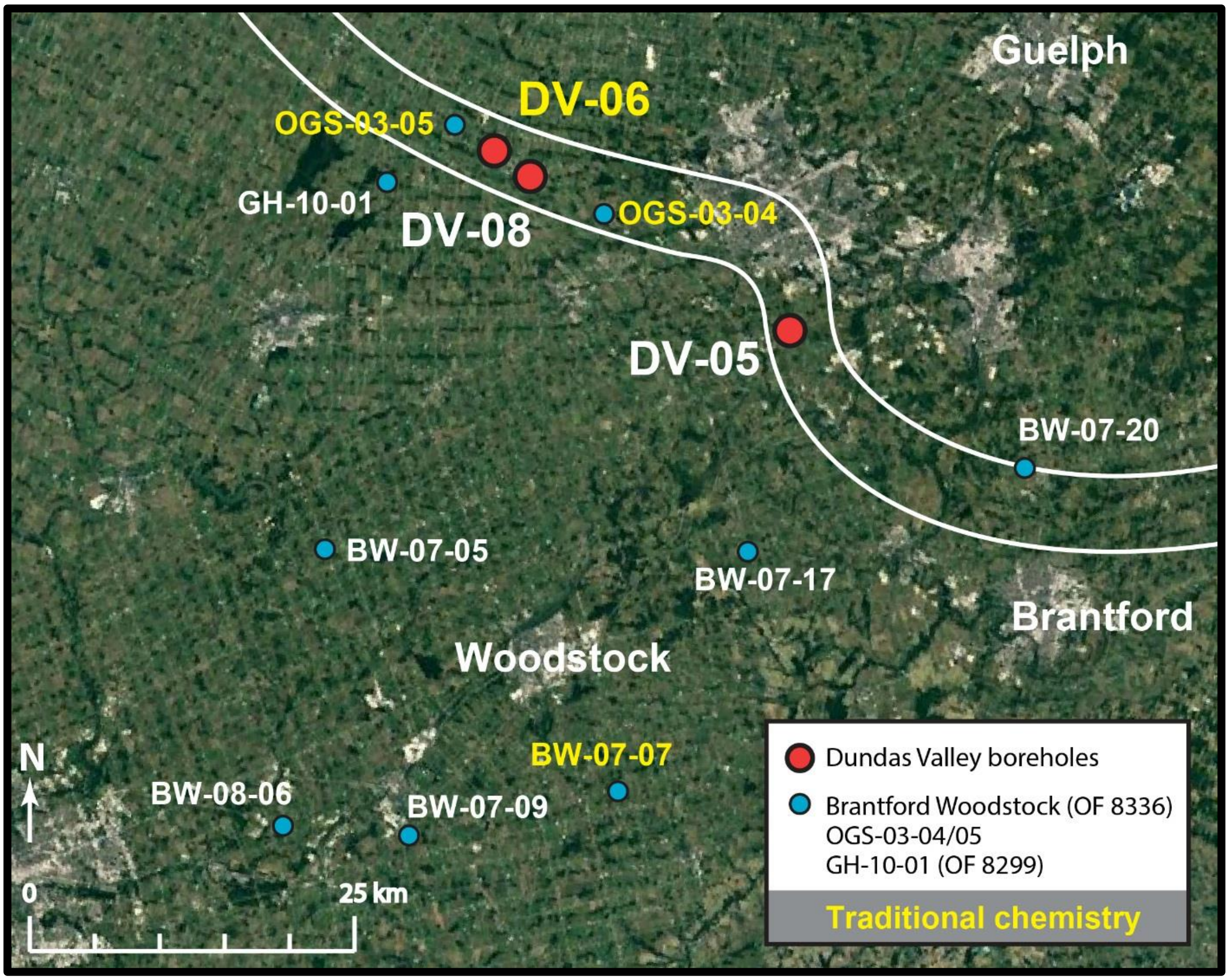

Figure 2: Location of chemostratigraphic boreholes within the Dundas Valley area drilled by the OGS and analyzed by the GSC. White text represents boreholes analysed by pXRF, yellow text represents boreholes analyzed by both pXRF and traditional geochemical methods (not reported here). Blue dots represent previously published borehole chemostratigraphic data. Image from Google Earth, 2017.

2.0 Study Area Geological Setting

Dundas valley is filled by 30 to > 200 metres of glacial sediment derived from the Huron-Georgian Bay and Erie-Ontario lobes. The 3 boreholes in this study intersected a series of till sequences separated by glaciolacustine sediments. The till units include; the Canning Till, the Catfish Creek Till, the Mayhill Till and equivalent Waterloo Moraine Deposits, the Tavistock Till, and the Mornington Till. Full descriptions are given in Marich et al., (2011) Karrow, (1993) and Bajc et al. 2018.

Older deposits

Overlying bedrock and underlying the Catfish Creek Till, in all three of the boreholes, are older till sequences, glaciolacustrine silt and sand and lacustrine sedimentary sequences. These sequences include diamicton and fine- to coarse-glaciolacustrine sediments which have been correlated, by Marich et al., (2011), to the Canning sediments in holes DV-06 and DV-08. Other till sequences, silts, sands and gravels record Late Quaternary geologic history for this region.

Catfish Creek Till

The Catfish Creek Till overlies the basal sedimentary sequence. The till is generally overconsolidated and is commonly referred to by water well drillers as hardpan. Pebble fabrics from subglacial facies generally indicate a southwesterly ice flow; however, early and late lobate facies of the till have been recognized regionally across southwestern Ontario. Pebble counts indicate a predominance of dolostones consistent with a northeastern source area as well as a number of easily recognized lithologies (Gowganda tillite, jasper conglomerate) derived from the Proterozoic terrane north of Lake Huron (Karrow 1993).

Maryhill Till

Maryhill Till overlies the Catfish Creek Till and is composed of a brown matrix of clayey silt to silty clay with few pebbles and is interbedded with glaciolacustrine silt and clay (Farvolden et al., 1987). These localized till sequences were most likely deposited by small-scale re-advances and retreats of the Huron-Georgian Bay and Erie-Ontario lobes. The upper sections of all 3 Dundas Valley boreholes are predominantly Waterloo moraine sediments (Marich et al., 2011).

Tavistock Till

The Tavistock Till overlies the Catfish Creek Till and N near Gads Hill, surface exposures of the till have a fine gritty, silty clayey texture with < 20% sand and ~30% clay. The till coarsens to the southeast. The pebble fraction is dominated by dolostones (53%), limestones (32%) and Precambrian lithologies (10%) with minor cherts and clastics (Karrow 1993). The upper portions of the till commonly contains clasts of red shale and erratics of jasper conglomerate in line with a Georgian Bay lobe source area (Karrow 1977). It is attributed by Dreimanis and Karrow (1972) to the Early Port Bruce Phase and deposition by the Huron-Georgian Bay ice lobe advance.

Mornington Till

The Mornington Till is generally silty to clayey and is relatively stone-poor, with noticeably fewer pebbles than the underlying Tavistock Till. Karrow (1993) attributes the clayey texture is to an undiscovered, overridden lake source. Pebble fraction comprises 41% limestone, 40% dolostone, 4% chert, 5% clastics, and 10% Precambrian crystalline clasts (Karrow, 1993). Karrow, (1993) assigns the Mornington Till to a brief southeast re-advance of the Huron-Georgian bay lobe.

3.0 Sample Collection, Processing and Analytical Methods

The Dundas Valley boreholes are located south and west of Waterloo, ON (Fig. 2). Elevation (m.asl), easting and northing coordinates (UTM NAD 83 - Zone 17) are provided for each borehole in Table 1. Core from the three boreholes was logged, sampled and photographed by the OGS at the time of drilling during the 2010 field season (Marich et al., 2011). The OGS collected 235 samples for processing and analysis (Table 1). Samples of dried and sieved sediment where received for pXRF analysis during October and November 2016. The OGS processed sediment samples to <0.074 mm, which resulted in inclusion of a very fine sand component with the silt and clay size fraction (<0.063 mm) normally examined by the GSC. A comparative study between the <0.074 and <0.063 mm size fraction concluded that the difference in size fractions did not produce results greater than the margin of error for elements (Landon-Browne et al., 2017a).

Table 1 – Dundas Valley borehole location and elevation.

Borehole ID	Depth (m)	Number of Samples	Easting	Northing	Elevation (m.asl)
DV-05	109.7	60	541104	4800483	~352
DV-06	82.75	94	518276	4814982	~372
DV-08	79.85	81	520975	4812880	~352

The sieved samples were placed in 23 mm diameter plastic vials to an approximate thickness of 30 mm. This thickness has been found to meet the requirement of the pXRF manufacture for an infinitely thick sample (Knight et al., 2015c). The vials are sealed with 4 µm thick Chemplex Prolene Thin-Film. On occasion, sample volume was limited and an infinite thickness was not attainable. Sample thickness was recorded for ~23 samples when samples contained ≤ 5 mm in thickness of sediment (Appendix A). A table with a correction factor for data obtained from each borehole is included in Appendix A. Adjusted data using a correction factor are highlighted for the numerical data in Appendix A in light purple.

Elemental concentration data was collected using a handheld Thermo Scientific Niton XL3t GOLDD spectrometer equipped with Cygnet 50 kV 2-watt Ag anode X-ray tube and a XL3 silicon drift detector (SDD) with 180,000 counts per second (cps) throughput, mounted to a test stand (Fig. 3). In soil mode a 60 second dwell time per filter (Main, Low, High) was used for a total of 180 seconds, following the protocols developed in previous borehole studies (Knight et al., 2012, Knight et al., 2015a, Plourde et al., 2012). In mining mode, a 45 second dwell time was used per filter also for a total of 180 seconds of analysis. Soil Mode uses Compton normalization that is recommended by NITON for elements expected to occur with < 1% concentration (trace elements). Mining Mode uses Fundamental Parameters which is recommended for elements expected to exceed 1% concentration (major elements). Table 2 presents a summary list of elements detected and their X-ray intensities.

Table 2: Elements and corresponding X-ray energy intensities used to determine concentrations in Mining Mode and Soil Mode.

Element	Line	Energy (keV)	Window Low (keV)	Window High (keV)	Filter
As	$K\alpha_1$	10.54	10.33	10.73	Main
Ba	$K\alpha_1$	32.19	31.70	32.70	High
Ca	$K\alpha_1$	3.69	3.50	3.89	Low
Cr	$K\alpha_1$	5.41	5.24	5.59	Low
Cu	$K\alpha_1$	8.05	7.84	8.24	Main
Fe	$K\alpha_1$	6.40	6.20	6.60	Main
K	$K\alpha_1$	3.31	3.10	3.49	Low
Mn	$K\alpha_1$	5.90	5.70	6.10	Main
Ni	$K\alpha_1$	7.48	7.35	7.67	Main
Pb	$L\beta_1$	12.61	12.40	12.80	Main
Rb	$K\alpha_1$	13.39	13.18	13.60	Main
S	$K\alpha_1$	2.31	2.20	2.45	Low
Sr	$K\alpha_1$	14.16	13.95	14.38	Main
Th	$L\alpha_1$	12.97	12.80	13.15	Main
Ti	$K\alpha_1$	4.51	4.21	4.70	Low
V	$K\alpha_1$	4.95	4.80	5.10	Low
Zn	$K\alpha_1$	8.64	8.49	8.83	Main
Zr	$K\alpha_1$	15.77	15.53	15.98	Main

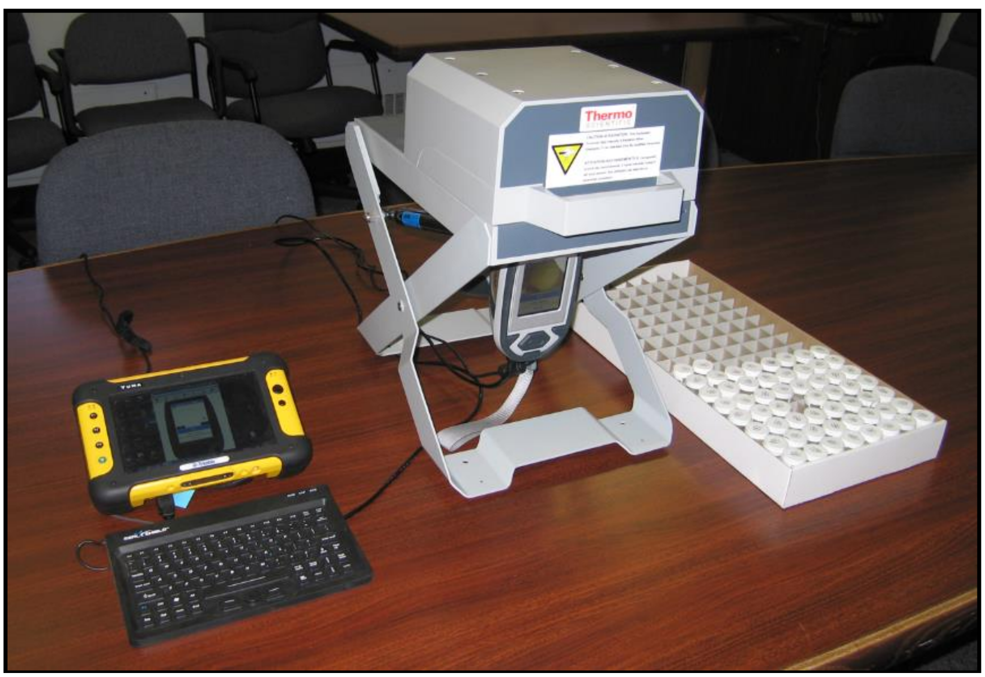

Figure 3: Example of pXRF spectrometer mounted in a test stand with micro-computer for analysis of processed sediment samples.

3.1 Reproducibility and Precision of Standards

Three standards (Till-1, Till-4, and TCA 8010) and 2 blanks (SiO_2 and Teflon) were analyzed at the beginning and at the end of each analytical session and after every 10 analyses of the borehole samples. The SiO_2 blank and Teflon blank were analysed to determine the cleanliness of the pXRF window and sample-stand environment.   After approximately 10 analyses the operating environment (test stand) was cleaned with compressed air and Kimwipes. The Teflon blank commonly returns values in the 10's of ppm Ti and may return trace amounts of Mo. The Chemplex® Prolene®thin-film that separates all samples except the Teflon blank from the spectrometer may contain trace amounts of Ca, P, Fe, Zn, Cu, Zr, Ti and Al. The SiO_2 blank in soil mode, Cd, Hg, K, Pd, Sr, and V returned values near or below the recommended limits of detection (<LOD, see pXRF Data in Appendix A). When analyzed in mining mode the SiO_2 blank also resulted in Al values below LOD. These elements are not listed as known impurities on the Chemplex® Prolene®thin-film and thus most likely represent internal detector noise. Calcium and Fe returned values above the limits of detection and may be associated with the impurities in Chemplex® Prolene®thin-film or represent contamination of the thin film. We replaced the Chemplex® Prolene®thin-film on a regular basis to avoid potential contamination. Information regarding quality control including precision, accuracy, instrument drift, dwell time optimization and calibration of pXRF spectrometry for reference materials including Till-1, Till-4, and TCA 8010 is available from Knight et al. (2013).

For each element detected in a given standard, the count, minimum value, maximum value, mean, standard deviation, relative standard deviation (% RSD), error and recommended values as determined by traditional wet chemistry methods are listed for both soil and mining mode for Till-1, Till-4 and TCA 8010 below each dataset collected from Dundas Valley boreholes in Appendix A. The percent error row contains the difference between the mean and recommended value. Low absolute values in this column indicate that the element is measured accurately; high absolute values indicate that a calibration curve is required to correct the data or that the data are not reliable. It is important to note that precision and accuracy are affected by concentration. Lower concentrations, especially those near the limit of detection (LOD) tend to result in lower precision and thus higher %RSD.

3.2 Limit of Detection

Thermo Scientific provides a list of the sensitivity or limits of detection for the pXRF (Themo Scientific, personal communication). The pXRF provides an error as 2 standard deviations for each element analysed. Some elements return results that are lower than the LOD. When this occurred, the point was plotted on the chemostratigraphy graph using the returned number however an arrow and title (LOD) was placed on the X-axis depicting the recommended LOD value.

3.3 Data Delivery

Results for each of the three boreholes are provided in Appendix A and subfolders. A Microsoft Excel® file contains two worksheets with data for each analyzed borehole and for data quality control standard reference materials. The first worksheet is for data collected in mining mode, the second worksheet is for data collected in soil mode. There are also individual files for mining and soil mode as .csv files of the same data. A single PDF file in Appendix B contains all three borehole stratigraphic logs, chemo-stratigraphic profiles and corresponding sand, silt and clay contents. The chemostratgraphic profiles display single element trends from the base to the top of the borehole. On these graphs, dashed horizontal lines correspond to the lithological breaks as defined by the OGS (Marich et al., 2011). The Dundas Valley – Chemostratigraphy .pdf file displays all three boreholes in a single file. OGS graphic logs presented in GSR-12 (Marich et al., 2011) display grain size, total carbonate, calcite/dolomite ratio, percent recovery, and stratigraphy.

4.0 Results and Surficial chemostratigraphy

Sediments in the Dundas Valley borehole DV-05 and DH-06 are generally silty to sandy with limited clay and gravel. For DV-08 the lower stratigraphy is sand rich with overlying sediments containing more silt and clay. Overall the stratigraphy and associated sedimentology is complex with a high degree of variability in sediment facies with horizons often being <10 meters in thickness. Differences in source material and depositional environments are reflected in particle size distribution geochemistry.

The following borehole discussion relates to analyses carried out in Mining mode. Figure 4 presents a legend for borehole sedimentology as assigned by the OGS.

Figure 4: Sedimentology of the boreholes as assigned by the OGS.

4.1 DV-05

The ~110 m deep borehole (Fig. 5) is located on a remnant upland of the Waterloo moraine and intersects limestone bedrock at its base (Marich et al., 2011). Geochemical analyses were carried out on 60 samples. Diamicton (Canning Till), gravel, sand, silt and minor clay horizons overlie bedrock to a depth of 78 m. Elemental concentrations vary throughout these sediments correlating roughly with changes in silt content. As noted by Marich et al. (2011) the upper contact of the diamicton at 95 m constitutes a weathering horizon suggesting a break in depositional history prior to further sediment deposition. This however is not reflected in any systematic variation in elemental concentrations suggesting no change in provenance between the underlying and overlying sediments. Sediments from a depth of 78-32 m also consist of diamicton (Catfish Creek Till), sand, silt and clay (Tavistock and Lower Maryhill Drift) and minor gravel. These sediments have a marked increase (e.g. Al, Ba, K, Rb) and decrease (Ca) in elemental concentrations from both the underlying and overlying sediments. The upper 32 m of the borehole consists of interbedded very fine- to coarse- sand with minor silt and clay. From a depth of 32-5 m sediments have consistent and lower concentrations for Al, K, Rb, and S than both the underlying and overlying horizons. The uppermost three samples for Ba, Sr, Th, Ti, Zr and the uppermost 2 samples for Al, K, and Rb all have an increasing trend in concentration towards the top of the borehole.

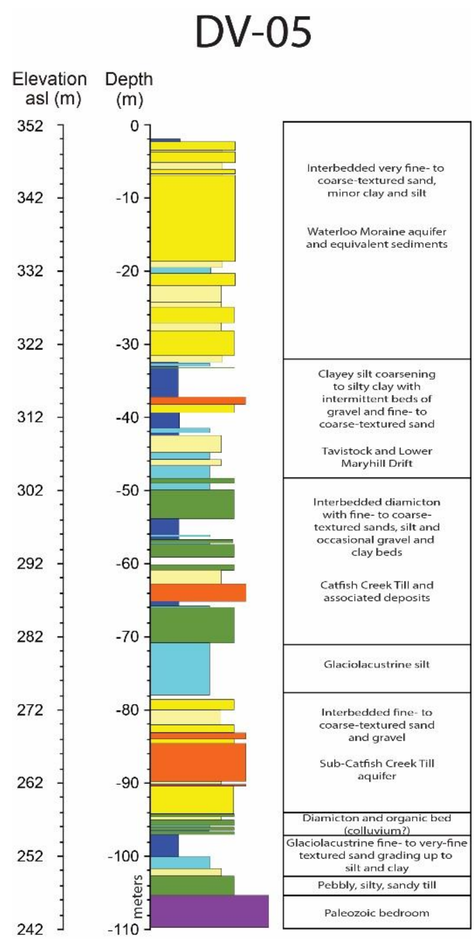

Figure 5. Sedimentology and stratigraphy for borehole DV-05.

4.1 DV-06

The ~83 m deep borehole (Fig. 6) is situated on Mornington Till plain and intersects limestone bedrock at its base (Marich et al., 2011). Geochemical analyses were carried out on 94 samples. Eight units can be identified using variations in elemental concentrations; however, no single element cannot be used to differentiate all units. Spikes in silt and clay content are often reflected in spikes in elemental concentrations. Contacts for the lowermost 3 units do not coincided with stratigraphic contacts as identified during OGS core logging. From the base of the borehole to a depth of ~76 m, approximately 4 m, Sr and Ti have an upward increase with K and S having a significant decrease in concentration. The upper contact is represented with a significant increase in silt content and a corresponding decrease in sand however the stratigraphic contact is in the middle of a sand horizon. A decrease in S concentration is noted from a depth of 76-71 m which corresponds to the upper contact of a diamicton assigned to Canning Till (Marich et al. 2011). Elevated concentrations of S occur from a depth of 71-53 m with upper contact being in a diamicton unit. Other elements do not change over this interval. This interval also has a high degree in variability in sand and silt content compared to the overlying sediments. Sediments from a depth of 53-35 m include diamicton of the Catfish Creek Till, a gravel horizon and a few meters of upper Canning Till. These sediments are distinguished by their consistent sand and silt content compared to both under and overlying sediments. A decrease in Al, Ba, and Sr with an increase in Ca is noted for this sequence. The upper contact is defined by a marked change in elemental concentration for Ba, Ca, Sr, Zn, and Zr whereas Al, K, and Rb has no change across this interval. Sediments from a depth of 35-29 m consist of interbedded very-fine to coarse sand, gravel, and silt that show a consistent upwards decrease in Ba and Zr with an increase in Rb and Sr. Sediments from a depth of 29-19m consist of silt, sand and clay of the Waterloo moraine. The significant increase and variability in clay content is reflected in the increase and variability in Al, Fe, K, Sr, Zn and a corresponding decrease in Zr. The upper contact, at 19m represents a transition from silt and clay to sand and is characterized by a marked decrease in Al, Fe, K, Sr, Zn and an increase in a concentration of Zr. At a depth of 7m to the top of the borehole sediments consist of a silt and clay diamicton of the Mornington Drift. The basal contact is reflected in a marked increase in Al, Fe, K, Rb, Ti and Zn concentration and a corresponding decrease in Ba.

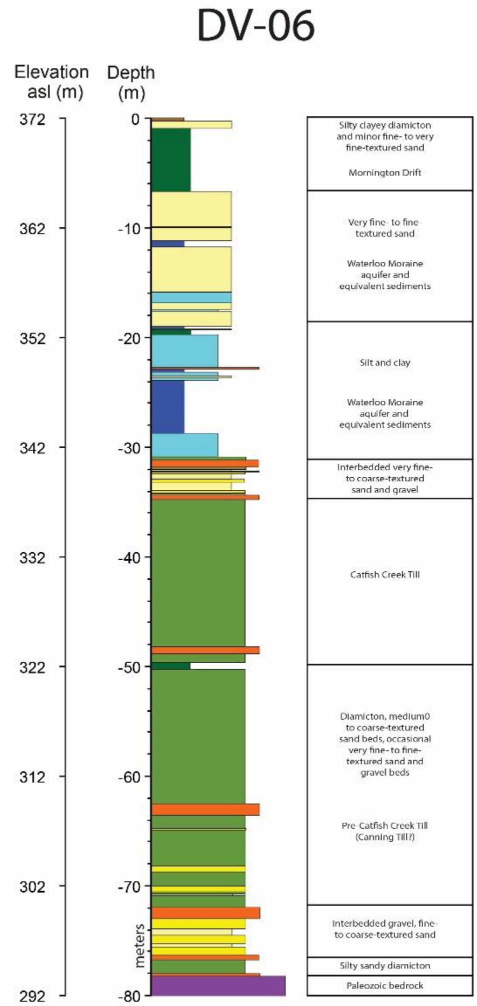

Figure 6. Sedimentology and stratigraphy for borehole DV-06.

4.1 DV-08

The ~80 m deep borehole (Fig. 7) is situated on Mornington Till plain and intersects limestone bedrock at its base (Marich et al., 2011). Geochemical analyses were carried out on 81 samples. Five units can be identified using variations in elemental concentrations. These units correlate closely with the borehole stratigraphy. From the base of the borehole to a depth of 66 m sediments consist of a cobble diamicton with a gravel bed at a depth of 74 m. The unit has consistent sand and silt content and for most elements (e.g. Al, Ca, Fe) consistent concentrations. From depth of 74-29 m a basal sequence (10 m) of gravel, with poor recovery, with few samples is overlain by 11 m of sand and minor gravel toped by ~14 m of diamicton assigned to the Catfish Creek Till. Although the sedimentology of theses horizons is different the elemental concentrations for Al, Ca, Fe, K, Mn, Rb, S, Sr, Th, Ti and Zn has little variation. Data spikes in this interval are often associated with spikes in silt content. From a depth of 29 m to the top of the borehole sediments consist of a ~21 m diamicton with fine to very-fine sand matrix overlain by 5 m of silt and 3 m of diamicton. These sediments are assigned to the Mornington Drift. Grain size data indicate an increase in clay content to the top of the borehole. For this sedimentary package elements such as Al, Ba, Fe, K, Rb, and Zr have variations in concentration most likely related to changes in silt content. Other than these variations concentrations are consistent throughout the sequence. At a depth of 8 m a 5 m thick silt horizon is differentiated from the underlying and overlying sediments by changes of Ca, Mn, Pb, Sr, Th, and Zn concertation.

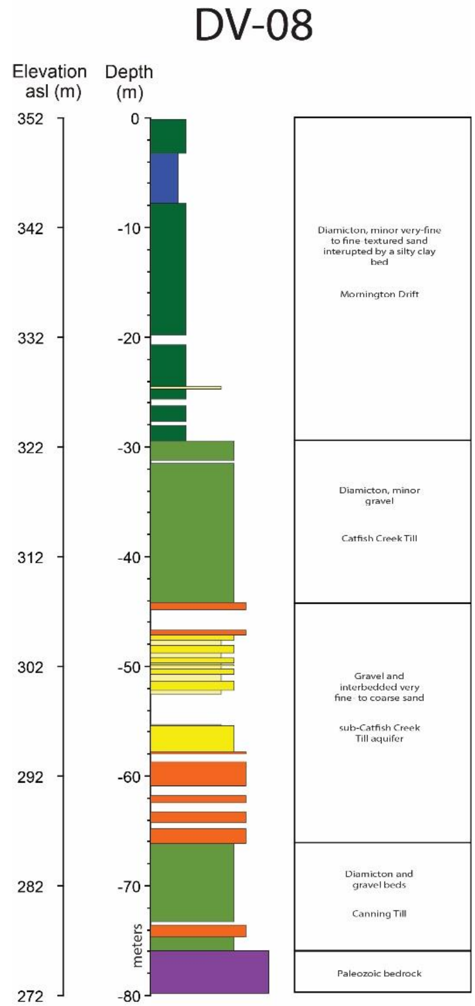

Figure 7. Sedimentology and stratigraphy for borehole DV-08.

5.0 Summary

This geochemical study expands the range of sediments that has been analyzed as part of an effort to characterize surficial sediment aquifers and aquitards across Canada and more specifically in southern Ontario. The boreholes contain sediments assigned to the Canning and Catfish Creek tills, Mornington and Port Stanley Drift and associated interbedded gravel, sand, silt and clays. For many elements (see Al, Ca, Si), variations in concentrations often reflect subtle changes in provenance as reflected in changes in sand, silt and clay contents. The descriptions presented in this open file are brief, and are provided as general contextual information to support the data release. Greater detail on shifts in elemental concentrations and geochemical relationships can be deciphered from a detailed examination of the numerical data present in Appendix A.

6.0 Acknowledgements

Samples from the Dundas Valley boreholes were collected by the Ontario Geological Survey. The analytical work was carried out at GSC-Ottawa under the Aquifer Assessments and Support to Mapping, Groundwater Inventory Project of the Groundwater Geoscience Programme. This work is a contribution of the GSC-OGS Southern Ontario project on groundwater 2014-2019.

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