

Inorganic Geochemistry of the Groundwater at the CWML site, Smithville, Ontario - Phase II and III Investigation, 1997

by:

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During the late 1970's and early 1980's a PCB waste management site was operating on the outskirts of the town of Smithville, located approximately 15 km south of Lake Ontario, on the Niagara escarpment. In 1985, it was discovered that PCB oils and associated solvents had penetrated the into the ground and pervaded the upper horizons of the bedrock underlying the site. This resulted in the closure of a local water supply which utilized groundwater from this aquifer. An ongoing investigation into the extent of groundwater contamination is currently underway.

A fraction of the PCBs and associated contaminants can migrate with the groundwater along the groundwater flow path. Thus, a conceptual model of the groundwater flow system is needed before any interpretation of contaminant migration with the groundwater is attempted. This study involves detailed analyses of the physical and inorganic chemical properties of both the fractured bedrock and groundwater at the site. By combining these data, a conceptual model of the groundwater flow system can be delineated. Such a model can be used in future numerical simulations that will provide valuable insight into the fate and transport of groundwater contaminants at the site.

This works supports EC priorities on Ecosystem Health and Ecosystem Initiatives under COA Stream 1.4 (contaminated sites) and Stream 1.6 (groundwater).

Current Status:

The report is intended to be released as a NWRI contribution and a less detailed version was submitted to a journal for publication.

Next Steps:

This study is currently completed and the objectives fulfilled. However, the results presented in the report will be used to aid future studies and develop a numerical model.

EXECUTIVE SUMMARY

During the year of 1997, a study was undertaken to chemically characterize the inorganic constituents in the fractured carbonate aquifer underlying the CWML site in Smithville, Ontario. At the onset of the study, samples were collected from seven boreholes drilled at the site (boreholes 11, 12, 21, 53, 60, 61 and 62). In May 1997, two new boreholes were drilled (boreholes 63 and 65) and also sampled in phase III of the investigation. The objective of this investigation is to combine previously accumulated hydraulic data (Lapcevic et al., 1996) and detailed rock geochemistry (Bickerton, 1997) with the measured inorganic groundwater chemistry to provide a conceptual model for groundwater flow in the fractured dolomitic aquifer underlying Smithville, Ontario.

Groundwater samples for inorganic geochemistry analyses were collected in February, July and November of 1997. Alkalinity, pH, Eh and electrical conductance were measured in the field. Collected samples were analyzed for trace metals by inductively coupled plasma spectrometry, anions by photometry and nutrients were analyzed using colourimetric techniques. Samples were also obtained to determine the stable isotopic composition (δ^{18} O and δ^{2} H) of the groundwater and to determine tritium (3 H) concentrations of the groundwater.

Both physical and chemical hydrogeological observations obtained from field investigations are used to interpret the groundwater flow system in the fracture network. Geochemical measurements indicate that the fractured dolomite is divided into two groundwater flow systems separated by an extensive unit of low transmissivity throughout the region. The upper flow system is characterized by water enriched in Mg and SO₄. Below the low transmissivity zone, groundwater increases in salinity, and is enriched in Ca and SO₄. Based on the geochemistry, the rate of groundwater migration in the lower flow system is surmised to be less than that in the upper

system. Measurements of hydraulic head in conjunction with the results of the analyses of the environmental isotopes (δ^{18} O and δ^{2} H) suggest that groundwater flow is mainly horizontal and likely governed by enlarged bedding plane fractures. The isotope geochemistry and topographical features further suggests that groundwater recharge is occurring just north of the site in a topographical low of minimal overburden thickness.

Sampling throughout the different seasons (winter, summer and fall), indicated that very little change was observed in the overall trends of the inorganic constituents with depth in each borehole. However, for individual zones sampled, dissolved ion concentrations may vary considerably. This may have resulted from changes in sampling methods and analyses.

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INTRODUCTION

The Niagara Escarpment is an extensive geological structure that extends along the western shoreline of Lake Ontario (Figure 1). This feature is comprised of a stratigraphic sequence of dolostone and shale units that includes the Lockport Formation as the cap rock (Tesmer, 1981). The Lockport Formation is an important source of water for many of the farming communities in the Niagara region. It also underlies numerous industrialized cities and towns. As a result, chlorinated solvents have contaminated the groundwater at several locations (Masalia and Johnson, 1984, Yager et al., 1997).

During the late 1970's and early 1980's a PCB management site was operating on the outskirts of the town of Smithville, located approximately 15 km south of Lake Ontario, on the Niagara escarpment (Figure 1). In 1985, it was discovered that PCB oils and associated solvents had penetrated the overburden and pervaded the upper horizons of the Lockport Formation. This resulted in the closure of a local water supply which utilized groundwater from this aquifer.

In order to develop a remedial strategy for the site, a conceptual model for regional groundwater flow and contaminant transport in the bedrock is required. The primary purpose of this study is to use both physical and geochemical hydrogeological observations in the construction of such a conceptual model. Physical hydrogeological observations include measurement of the distribution of transmissivity and measurement of hydraulic head at selected depth intervals in the Lockport Formation. Geochemical observations include measurements of the inorganic ionic content, stable isotopic (δ^{18} O, δ D) and tritium (3 H) composition of the groundwater, as well as determination of the chemical composition of the rock units. Inorganic ion concentration of the groundwater is used in conjunction with hydraulic measurements to determine preferential flow

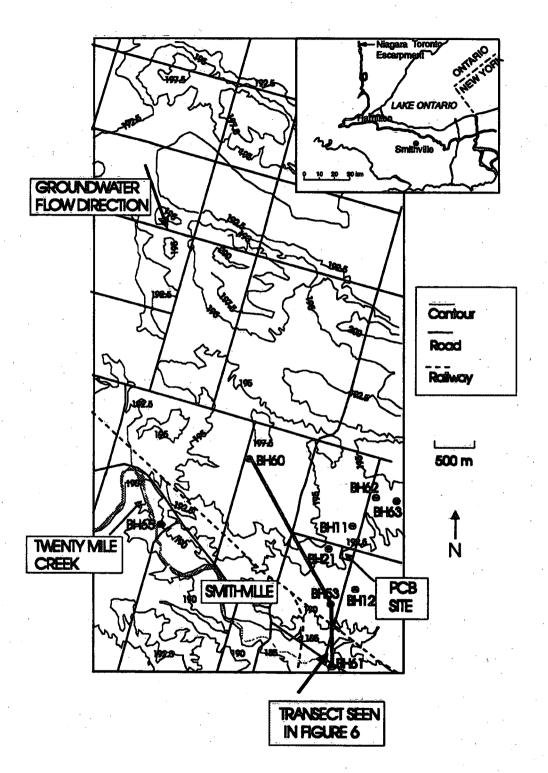


Figure 1: Topographical map of the Smithville field site and borehole locations

paths in the fracture network. Trends in the concentrations of dissolved inorganic ions are used to define differing groundwater flow regimes and isotopic composition is used as an indicator of groundwater recharge. Thus, the geochemical data provides information on the groundwater flow system that can not be deduced using hydraulic information alone. Recent application of this approach was used to develop a conceptual groundwater flow model for fractured granitic rock in Aspo, Sweden (Smellie et al., 1995) and for the fractured Chalk aquifer in the United Kingdom (Hisock et al., 1996).

SITE GEOLOGY AND HYDROGEOLOGY

The PCB contaminated site is located just north of the town of Smithville, Ontario (Figure 1). The surface topography (Figure 1) indicates the presence of a swale oriented in the east-west direction, located approximately 1.5 km to the north of the site and a river (20 mile creek) flowing from the north-west to the south-east, located approximately 1 km to the south of the site. The topographical gradient in the vicinity of the site, is relatively flat with a slight inclination of roughly 10 m/km south. Approximately 5 to 10 m of clay till overburden underlies the site (Figure 2). The clay till is of minimal permeability (K ~ 10⁻⁹ to 10⁻¹¹ m/s) although pervaded by sparse vertical fractures some of which may be fully penetrating (Golders Associates, 1995). The Lockport Formation underlying the clay till is comprised of four geological members consisting of fine to medium grained dolostone that dip in a southeasterly direction at an angle of 0.5° (Golders Associates, 1995). The upper member (Eramosa) of the Lockport Formation is 10 to 20 m in thickness and is fractured in a relatively uniform manner. Transmissivity of the fractures can be as high as 10⁻² m²/s (Golders Associates, 1995). The Vinemount member, which underlies the Eramosa, is characterized by a weathered vuggy zone (1 to 4 m thick) and a zone of unfractured

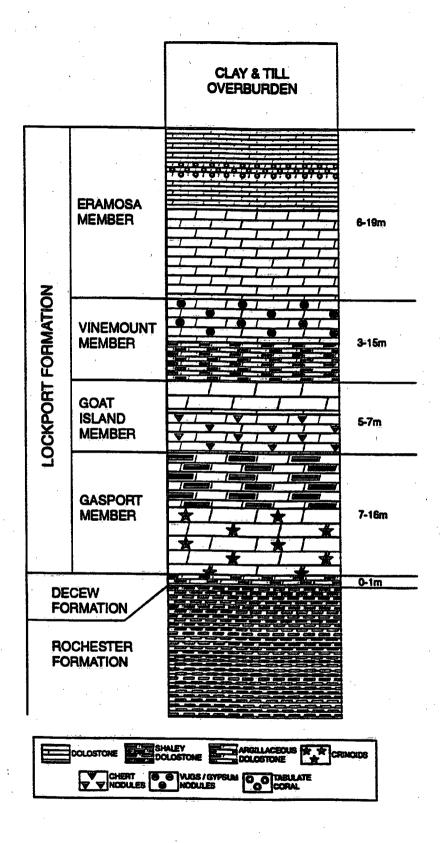


Figure 2: General stratigraphy of the Lockport Formation

rock of relatively low transmissivity (3 to 4 m in thickness). The lower members (Goat Island and Gasport) are 6 to 7 m and 8 to 10 m in thickness respectively. Fracture frequency in these units is more sparse, although transmissivity is no less than that observed in the Eramosa member. The Lockport Formation is underlain by an impermeable shale of up to 17 m in thickness and is considered a regional aquitard (Golders Associates, 1995).

Groundwater flow in the fracture system is generally to the southeast, following stratigraphic dip of the geological units (Golders Associates, 1995). Based on the previous studies of the Lockport Formation conducted at this site and elsewhere in the region, it is inferred that groundwater flow is primarily governed by bedding plane fractures that are laterally extensive and have limited vertical interconnection (Novakowski and Lapcevic, 1988; Riechart, 1990; Golders Associates, 1995). Thus, it is assumed that groundwater flow in the Lockport Formation underlying the contaminated site is primarily in the horizontal direction, carried along bedding plane fractures of unknown lateral extent and unknown vertical interconnectivity. Previous site investigations (Golders Associates, 1995) indicate that some fractures, at least in the upper Lockport members, are observed to be laterally connected over a distance of 1 km as evidenced by the downgradient transport of aqueous-phase contamination emanating from the PCB source. Hydraulic gradients in this zone have been estimated to be 0.02 with initial estimates of groundwater velocity ranging 20 - 6000 m/a whereas hydraulic gradients in some of the lower dolostone members are estimated at values ranging from 0.001 to 0.007 (Golders Associates, 1995). Groundwater flow in localized areas may vary depending on the nature of the fracture system. The resulting variations in hydraulic gradient are subtle and therefore may be inadequate to identify fracture interconnectivity.

FIELD INVESTIGATION

To conduct the field study, six new 76 mm (N-sized) diameter boreholes (53, 60, 61, 62, 63 and 65) were drilled in 1996 and 1997 within the vicinity of the site (Figure 1) using a diamond core and triple-tube wireline techniques. The boreholes were drilled to penetrate the entire thickness of the Lockport; a depth of approximately 55 m below ground surface. Five of the boreholes are inclined at angles ranging from 55° to 57° with respect to the ground surface, and one borehole (borehole 65) is vertical. Boreholes 11, 12 and 21 (Figure 1) were completed in 1988 with 1.25 inch diameter PVC multilevel peizometers having varying screen lengths (Golders Associates, 1989).

Once drilling was completed, hydraulic tests using the constant-head injection method (Novakowski, 1988) were performed on boreholes 53, 60, 61, 62, 63 and 65 to obtain measurements of transmissivity over continuous 2 m depth intervals in each borehole. Minimum and maximum values of transmissivity ranging between 10⁻¹⁰ m²/s and 10⁻² m²/s were determined using this procedure (Lapcevic et al., 1996). Transmissivity tests were previously conducted by Golders Associates in 1988 at 3 m intervals in boreholes 11, 12 and 21 using a similar constant head packer testing method. This method has a lower minimum testing value (10^{-7.5} m²/s) than that used in the other boreholes (Golders Associates, 1989). After completion of the hydraulic testing, the new boreholes were instrumented with a series of permanently-emplaced packer systems (Black et al., 1987). There are 5 - 9 isolated depth intervals in each borehole. Hydraulic head measurements in each isolated interval were obtained using a pressure transducer. In the case of the multilevel piezometers, measurements were obtained with a water level meter. Measurements of hydraulic head were performed on a weekly basis over a two year period.

A total of 32 rock samples, collected from each of the geological units of the Lockport Formation, were submitted for chemical and mineralogical analyses (Bickerton, 1997). Samples were prepared by crushing the sample using a ceramic ball mill to a powder (<100 μm size fraction). Samples were analyzed for mineral content using X-Ray Diffraction (XRD) techniques. Concentrations of the major elements (SiO₂, TiO₂, Al₂O₃, Cr₂O₃, MnO, Fe₂O_{3 total}, MgO, CaO, Na₂O, K₂O and P₂O₅) and trace elements (Ba, Nb, Rb, Sr and Zr) were determined using wavelength dispersive x-ray fluorescence (XRF). Total concentrations of H₂O, CO₂ and S were determined using combustion followed by infra-red spectrometry (Bickerton, 1997).

Groundwater samples were collected in February, July and November of 1997, from the permanently-emplaced packer systems and the multilevel wells. Only data obtained in November is incorporated in the main text as this data was most complete and up to date. Data from the other sampling dates are provided in Appendix A, along with a brief description of seasonal variations in the measured parameters. The samples from boreholes 53, 60, 61, 62, 63 and 65 were collected using a stainless steel sampling chamber (volume of 500 mL) connected to an electronic actuating device that draws in groundwater from the isolated zone outside the packer system. As the volume of water external to the packer system is relatively small, mixing and diffusional processes equilibrate the geochemical parameters in each isolated groundwater zone relatively quickly. Thus, the need to purge the borehole of standing water is eliminated (Black et al., 1987). Samples from boreholes 11, 12 and 21 were obtained after purging the volume in each piezometer three times using a Waterra hand pump.

After drawing the sample to ground surface, electrical conductivity, Eh, and pH were measured in the field on unfiltered samples in enclosed containers. For boreholes 11, 12 and 21, these measurements were obtained using a flow through cell. A combination electrode with an

Ag/AgCl internal reference, calibrated against the buffers 4 and 7 were used to determine pH. Eh was measured using a combination platinum redox and Ag/AgCl reference electrode. Alkalinity was measured shortly after sample collection by titrating a known volume of filtered sample with 0.16N sulfuric acid using a HACH digital titrator. Groundwater samples collected for inorganic ions and dissolved organic carbon (DOC) analyses were filtered in the field using a 0.45 μm nylon filter. Samples submitted for cation analyses were preserved at the time of collection with ultrapure HCl.

Analyses for metals were performed in the laboratory using inductively coupled plasma spectroscopy (ICP-MS). Anions (Cl, SO₄ and SiO₂) were determined using ultraviolet photometry (COBAS). Concentrations of ammonia (NH₃-N) and nitrate (NO₃-N) were analyzed using a Bran+Luebbe TRAACS-800 continuous flow analyzer. Analyses for DOC were performed using ultraviolet digestion. Charge imbalances for the inorganic ions are less than 10% with the exception of 2 samples.

Samples were also collected for stable isotopes analyses (¹⁸O and ²H) in July and November of 1997. Analyses were performed using standard CO₂/water and H₂/water equilibration techniques. δ¹⁸O and δ²H data were normalized to VSMOW/SLAP and are reported relative to VSMOW with reproducibility of +/- 0.1 and +/- 2.0 respectively. Samples were analyzed for ³H by using direct scintillation methods obtaining a detection limit of 6TU, with a reproducibility of +/-8TU. Nineteen selected samples were re-analyzed for enriched ³H analyses in order to refine the estimate of concentration of ³H in the groundwater at a few locations. The enriched ³H analyses has a reproducibility ranging between +/-0.6 to +/- 1.3 TU.

Saturation indices of various mineral phases were calculated using groundwater chemistry and the geochemical speciation program PHREEQC (Parkhurst, 1995). Thermodynamic data used

Table 1: XRF and XRD analyses of rock samples collected from various geological units at the Smithville site.

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Calche (36)	8	,		
Gypeum (%)		3.4 7.7 3.6 7.4	6 4. 6 6.	ug.
Owarts (%)	2.5 2.9 2.0 2.4	0 1. 10		22.4 2.3 2.3 7.9 7.0 6.2 6.2 6.2
Dolomite (%)	97.3 93.7 97.1 87.0	989 9 1:1 989 8 1:1 989 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	983.7 96.4 96.4 96.6 96.6 96.6 96.6	94.5 97.6 96.3 92.1 91.2 92.0 93.0 73.3
e (journal)	1 1 2 2 3 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	162 13.4 9.98 13.7 7.17 2.12 9.05	2.5.8 2.1.5 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1 3.6.1	8-67 4-37 1-50 1-50 7-80 20.80 21.52
P (mmof)	0.14 0.28 0.70 0.14	28 24 24 25 25 25 25 25 25 25 25 25 25 25 25 25	0.28 0.28 0.28 0.14 0.14	2
(mmod)	1059 1059 1079 1079	961 973 973 973 996 996	976 1038 1068 1068 1045 1011	1008 1008 1008 1018 1018 1018 1083 1083
H,O (mmol)	33.3 27.8 33.3 11.1	666 666 666 666 666 666 666 666 666 66	25.2.2.2.3.8.2.2.3.8.2.2.3.8.2.2.3.8.2.2.3.8.2.2.3.8.2.3.3.2.3.3.2.3.3.3.2.3.3.3.3	88 20 2 4 20 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
(mmol)	0.64 0.21 0.00 0.00	13.4 8.07 8.07 8.08 9.382 4.25	6.37 0.21 0.21 1.06 0.42	7.43 2.65 10.6 8.49 0.85 2.87 2.87 30.4
Ce (mmoj)	638 546 539	481 504 504 614 614	2	447 621 637 637 648 698 697 698
Mg (mmol)	612 615 611 622 522	86 4 4 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8 8	50 473 516 518 508 68 68 68 68 68 68 68 68 68 68 68 68 68	422 498 498 498 498 398 398
litin (mmol)	0.42 0.70 0.85 1.41	0.86 0.85 1.13 1.27 1.97 1.13	0.88 0.88 1.13 1.13 0.85 1.27 1.27	1.55 0.58 0.09 0.09 1.41 1.27 0.06 0.06
Fo(total)	1.25 0.00 2.50 3.78	12.5 10.0 10.0 10.0 11.3 11.3	2. 7.51 2.78 3.78 3.78 5.01 5.01	10.0 6.28 6.28 6.01 10.0 17.5 17.5
A (mmol)	86.2 86.2 86.2 86.2 86.2 86.2 86.2 86.2	49.0 39.2 13.7 11.8 17.7 17.7	25.5 11.8 13.82 1.96 7.85 8.88	28.4 17.7 43.2 31.4 7.86 16.7 16.7 16.7 16.7
tr (mmot)	20.0 81.0 81.0 81.0 81.0 80.0	2.1.13 0.00 0.00 0.00 0.00 0.00 0.00 0.00	8 8 2 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	0.88 0.28 0.26 0.50 0.50 0.50 0.50
SE (mmod)	16.6 6.0 18.3 3.3 3.3	110 86.5 61.8 102 35.0 138 74.9	25.0 107 113.3 113.3 113.3 113.3 113.3 113.3 113.3	245 43.3 117 116 116 251 253
Elevation (mast)	183.3 179.9 176.1 171.6 168.5		168.7 167.6 167.6 160.8 160.8 160.8 160.8 160.8	160.3 153.8 161.5 164.6 153.1 147.1
Formetion Member	Eramosa Eramosa Eramosa Eramosa	Vinemount 2 Vinemount 2 Vinemount 1 Vinemount 1 Vinemount 1 Vinemount 1	Goet Island Goet Island Goet Island Goet Island Goet Island Gesport Gasport	Gasport Gasport Gasport Gasport Gasport Rochester Rochester
			, ·	- - - -

for these calculations were provided in the PHREEQC database. The PHREEQC model calculations are considered reliable in sodium chloride dominated waters with higher ionic strength (Parkhurst, 1995).

RESULTS

Mineralogy

X-Ray Diffraction analyses (Table 1) indicate that the three principal minerals present in all members are dolomite (86-98 wt%), quartz (2-15 wt%) and gypsum (3-8 wt%). However, none of the samples from the Eramosa member are observed to contain any measurable gypsum. X-Ray Fluorescence analyses indicate that all samples have a Ca:Mg ratio between 1.03-1.09:1 (Table 1; Bickerton, 1996). Thus, most of the Ca in the samples is likely contained within the dolomite mineral structure. Any excess Ca concentrations will presumably exist as either calcite and/or gypsum. X-Ray Fluorescence analyses also indicates that both a small percentage of Fe and Al are present in the rock samples. Based on normative analyses of the rock chemistry and visual identification in the rock core, much of the Fe is likely incorporated in sulfide minerals (pyrite) whereas Al is likely to occur in clays (Bickerton, 1997).

Water Chemistry

Groundwater underlying the Smithville site (Table 2) is mainly reducing (Eh <0) at depths greater than 20 to 30 m below ground surface (bgs). At shallow depths, conditions are more aerobic (Eh>0 mV). Increased concentrations of HS in solution and subsequent decrease in Fe concentrations, suggest that redox conditions change from iron reducing to sulfate reducing with increasing depth. An exception is observed in borehole 63, were redox conditions remain aerobic

Table 2: Summary of inorganic groundwater chemistry

Festbey boreholos		Brifforn Pone	Top zone	_ T	Œ	Alleghthy	,8	2	2	¥	2	os.	5	2	os o
Annehoto Z	•	fmeel)	(mass)		SE		(mg/L)	(MOM)	(mg/L)	(mgg/)	(mg/L)	Tage (Z Z	Z	T day
anna la		478.A	401.9	â	8		588	477	127	7.00	1.67	2810	2	900	6.3
2	- c	130	1 X X	7.5	2		214	72	32.2	2.40	0.35	828	8,3	0.02	12.7
	·	10.0	6 6 6		Ę		182	6	41.0	2.60	0.46	618	16.2	000	13.8
		97.0	1.0.E	, c	§ 8		5	125	2	4.20	0.16	8	24.7	0.79	12.9
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and Fe concentrations in solution actually increase with depth. The pH of the groundwater is near neutral (6.8) to slightly alkaline (7.7). Temperature of the groundwater ranges from approximately 10 to 11 °C. In general, ion concentrations that increase with depth in solution are: Ca, Na, K, HS, Cl and SO₄ and those that decrease are: Mg and Fe. Alkalinity also decreases slightly with depth.

Hydraulic Properties

Constant head injection tests performed at continuous two meter depth intervals on the Westbay installed boreholes (53, 60, 61, 62, 63 and 65) indicate that transmissivity ranges between the testing limits of 10⁻¹⁰ m²/s and 10⁻² m²/s. Highest transmissivities measured at the maximum level (10⁻² m²/s) of the transmissivity test (3% of the total number of tests) are observed in boreholes 61, 63 and 65 at ~165, 155 and 170 meters above sea level (masl) respectively. Approximately 9% of the testing zones in these boreholes measured below the minimum testing limit (10⁻¹⁰ m²/s). In boreholes 11, 12 and 21 transmissivity ranges from the minimum testing limit of 10^{-7.5} m²/s to 10⁻² m²/s. In these holes, approximately 22 % of the testing zones measure below the minimum testing limit. Most of these low transmissivity zones are concentrated in the lower Vinemount and upper Rochester units. However, a few low transmissivity measurements are also observed at the top of the Goat Island (boreholes 11, 12, 60 and 62) adjacent to the Vinemount/Goat Island bedrock contact. The Eramosa, upper Vinemount and Gasport units are characterized by high transmissivities ranging from 10⁻⁵ to 10⁻² m²/s.

Hydraulic head measurements range from 181 masl to 192 masl. Highest head measurements are observed in the Eramosa member of boreholes 60, 62 and 63. In these boreholes, hydraulic head decreases sharply below the Eramosa member. Hydraulic head is

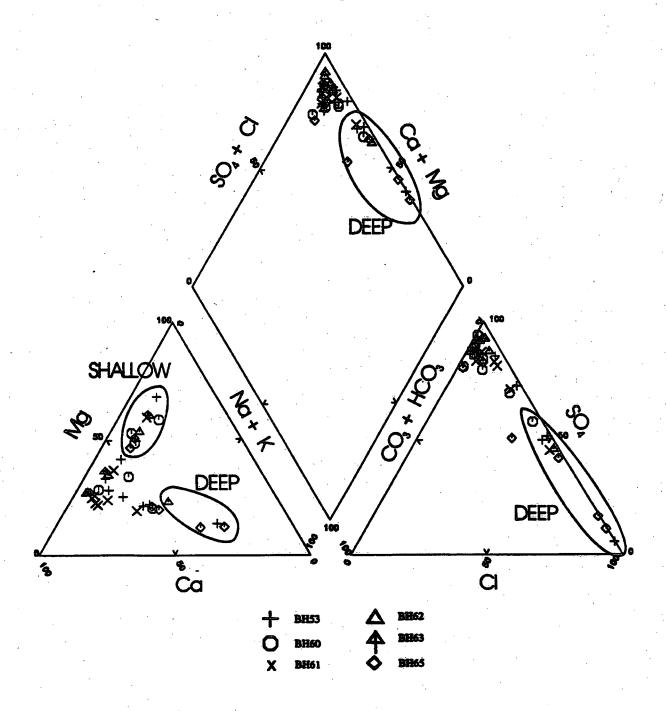


Figure 3a: Piper diagram for groundwater chemistry of samples collected from Westbay packer installed boreholes

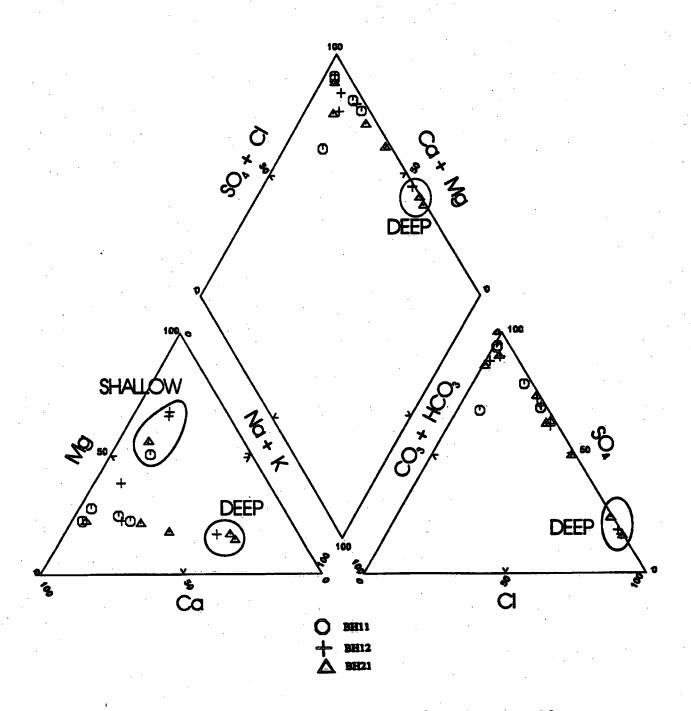


Figure 3b: Piper diagram for groundwater chemistry of samples collected from multilevel piezometers

observed to be almost uniform with depth in boreholes 11, 12, 21, 53 and 65 with values ranging between 184 and 185 masl. In borehole 61 head is observed to be highest at an intermediate depth (at an elevation of 160 masl), resulting in an artesian condition.

Environmental Isotopes

In general, stable isotopic composition of the groundwater ranges widely from -9 to -14 % and -50 to -110 % for δ^{18} O and δ^{2} H respectively. The isotopic composition of the groundwater is relatively enriched (-9 to -11 % and -50 to -80 % for δ^{18} O and δ^{2} H respectively) and changes little with depth in boreholes 11, 60, 61, 62 and 63 whereas values become significantly depleted at ~155 to 165 masl and below in boreholes 12, 21, 53 and 65. Tritium values vary from below detection to values greater than 25TU.

DISCUSSION

Major ion analyses of the groundwater samples indicate that three chemically distinct zones are present in the flow system (Figure 3 a, b). At shallow depths (elevations > 170 masl) Mg and SO₄ are observed to be the highest concentration of ions in solution. At elevations between approximately 150 to 170 masl, Ca and SO₄ enriched waters dominate. At greatest depth (elevations <150 masl) in boreholes 12, 21, 53, 61, 63 and 65, the groundwater chemistry approaches brine conditions, characterized by high concentrations of Na and Cl.

The location of these chemical zones can be readily explained as a consequence of mineral dissolution and precipitation reactions. For instance, calculated saturation indices (Figure 4 a, b) indicate that groundwater in most boreholes is undersaturated (SI ~-0.5 to -1.0) with respect to gypsum at shallow depths (~ 20 to 30 m bgs or >165 masl). Below this, groundwater is observed

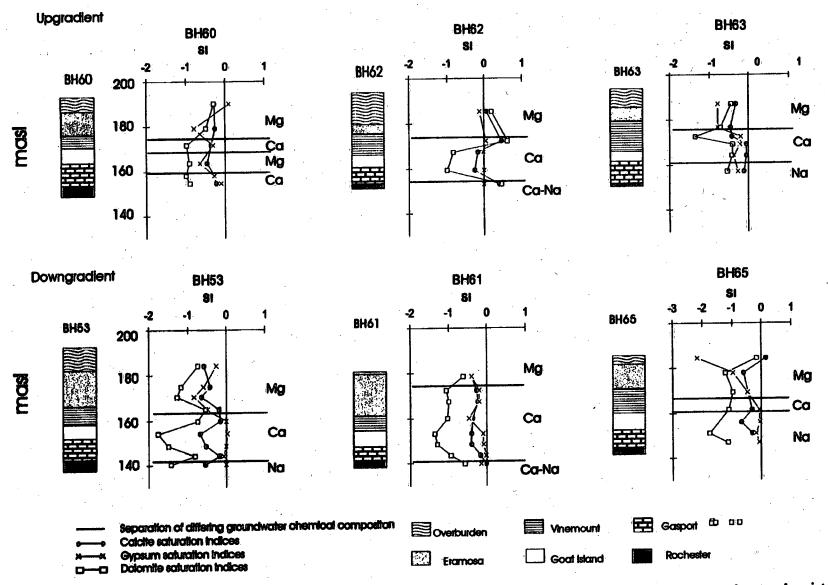


Figure 4a: Calculated saturation indices using PHREEQC for dolomite, gypsum and calcite calculated with groundwater chemistry from Westbay packer installed "upgradient" boreholes 60, 62 and 63 and "downgradient" boreholes 53, 61 and 65

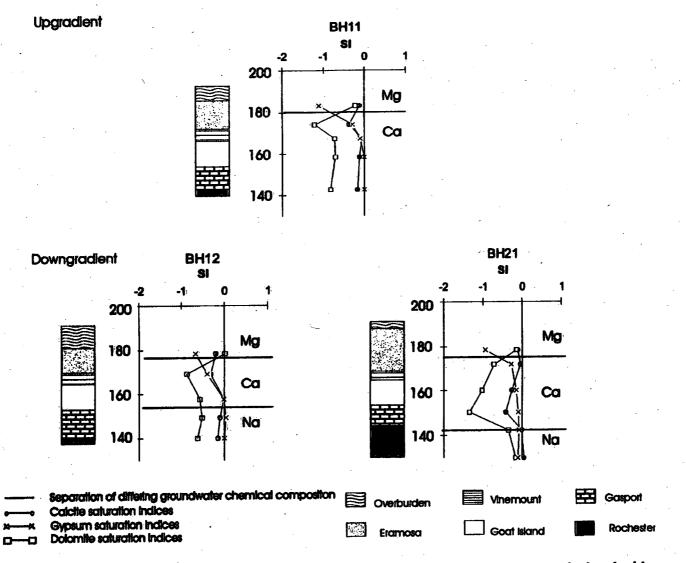


Figure 4b: Calculated saturation indices using PHREEQC for dolomite, gypsum and calcite calculated with groundwater chemistry from multilevel piczometer installed "upgradient" boreholes 11 and "downgradient" boreholes 12 and 21

to be close to equilibrium with gypsum (SI ~ 0) suggesting that the amount of Ca in the groundwater is controlled by chemical equilibration reactions with gypsum. At all depths groundwater tends to be undersaturated or near saturation with respect to both dolomite and calcite (Figure 4 a, b).

Mineralogical studies indicate that the geological members in the lower units contain a small percentage of gypsum whereas no gypsum was observed in the upper Eramosa member. Thus, the dissolution of dolomite and calcite alone may control the amount of Ca concentrations in the groundwater located in this upper unit. The presence of gypsum in the lower formation members indicates that undersaturated water (i.e. recharge water) has not extensively reached this horizon. The high Na concentrations and overall salinity observed in groundwater at greater depth (elevations of approximately 150 masl or less; Figure 3, Table 2) indicates high residence time and therefore sluggish groundwater velocity.

The measured hydraulic parameters (transmissivity and hydraulic head) in each borehole are compared to measured geochemical parameters (Figure 5). The boreholes are arranged based on location upgradient (boreholes 60, 62, 63 and 11; Figure 5a, b) of the PCB contaminated site, in an area of possible groundwater recharge versus those located either immediately adjacent to the site (boreholes 12, 21 and 53, Figure 5b, c) or in possible areas of discharge along the river (boreholes 61 and 65; Figure 5c). Superimposed on these Figures are the distribution of the three chemically distinct groundwater zones discussed above.

Upgradient boreholes

Although the overburden is relatively thick in the vicinity of boreholes 11, 60, 62 and 63, it was initially surmized that these boreholes are situated immediately downgradient from a potential

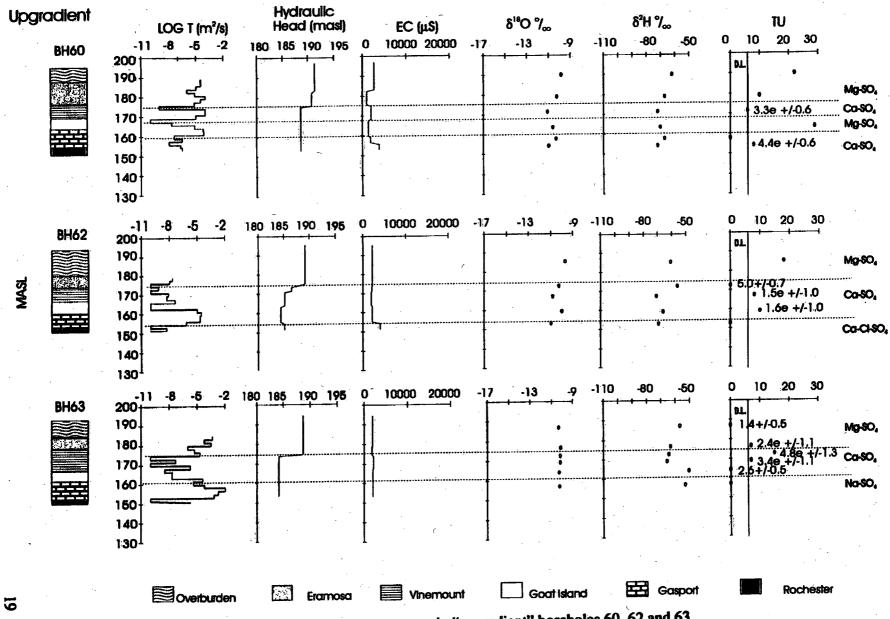


Figure 5a: Composite diagram of measured parameters in "upgradient" boreholes 60, 62 and 63

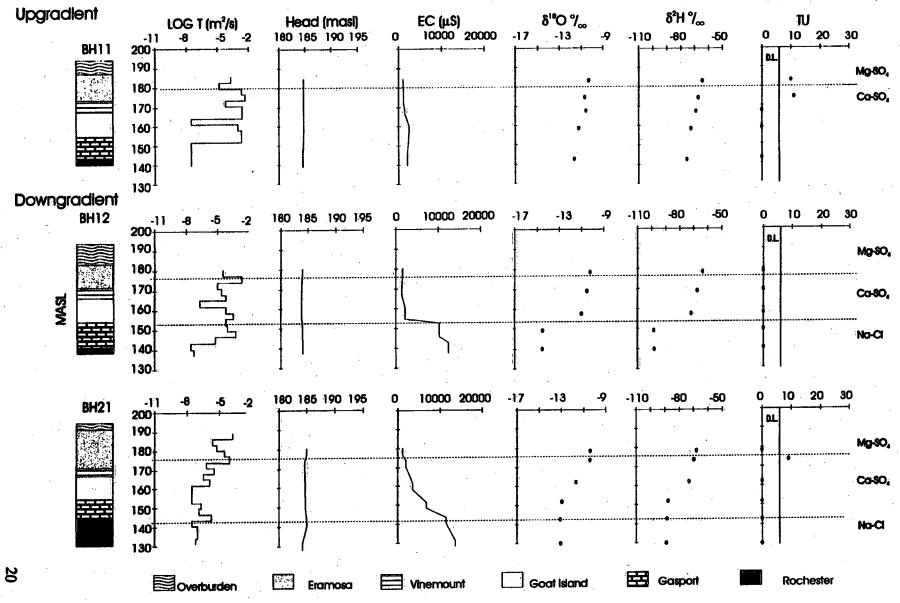


Figure 5b: Composite diagram of measured parameters in "upgradient" borehole 11 and "downgradient" boreholes 12 and 21

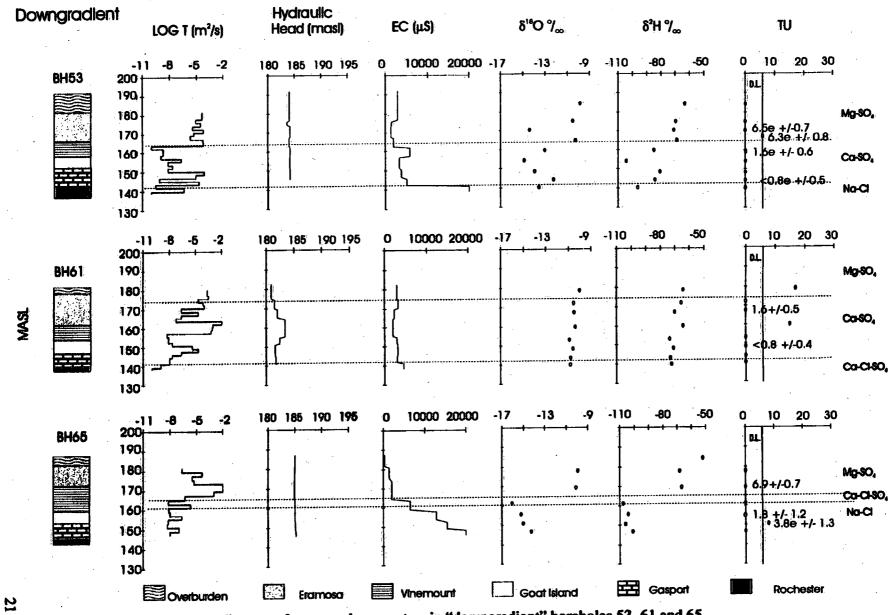


Figure 5c: Composite diagram of measured parameters in "downgradient" boreholes 53, 61 and 65

zone of recharge. These boreholes are located approximately 2 km south of a swale which trends east-west. Due to a slight southward dip in the bedding planes, the thickness of the Eramosa member in these boreholes is less than that observed in the downgradient wells (Figures 5 a, b). The distribution of transmissivity follows the general observations (i.e. high transmissivity in the Eramosa, Goat Island and Gasport members). Lower transmissivities are observed in the middle to lower Vinemount member. An exception to this is borehole 62 which exhibits lower transmissivity throughout the base of the Eramosa, Vinemount and Goat Island members, with higher transmissivity evident only in the Gasport member. Lowest transmissivity in borehole 11 is observed mainly in the Goat Island, Gasport and Rochester units.

The distribution of hydraulic head indicates a persistently downward gradient with increasing depth in boreholes 60, 62 and 63. In each case, the transition between higher and lower hydraulic head occurs at the base of the Eramosa member or top of the Vinemount member, across a discrete zone of low transmissivity. In the case of borehole 60 and 63, the hydraulic head below the low transmissivity zone is uniform. The steady decrease in hydraulic head with depth observed in borehole 62 may indicate vertical fracture connection through these units within the immediate vicinity of this borehole. The hydraulic gradient in borehole 11 is observed to be uniform with depth, indicating predominantly horizontal groundwater flow in this vicinity.

Electrical conductivity is relatively uniform with depth in all these boreholes, ranging from ~2000 μ s to 4000 μ s. Similarly, stable isotopic composition of the groundwater sampled is also uniform with depth, ranging from -9% to -12% and -60% and -80% for δ^{18} O and δ^{2} H respectively. Average δ^{18} O and δ^{2} H values in precipitation collected in Simco, Ontario, (located approximately 100 km to the east) during the period from 1975 to 1982, are approximately -10% and -70%, respectively (IAEA/WMO). Thus, the groundwater is of recent origin. In addition,

many of the sampled zones contain measurable concentrations of ³H indicating that groundwater in these zones is of post WWII age. In boreholes 60 and 62, ³H concentrations are highest in the shallow depths (elevations >165 masl). However, high transmissivity zones in the lower Vinemount and Goat Island to upper Gasport also exhibit moderate to very high ³H concentrations.

The fact that there is little change in electrical conductivity and in the stable isotopic signature with respect to depth suggests that in the upgradient boreholes, groundwater in both the upper Eramosa member and the in the lower members are of a common origin. The presence of ³H at various depths (i.e. shallow and deep) further indicates that younger water is infiltrating the flow system. As the clay till overburden is thick and relatively impermeable overlying these boreholes, this suggests that recharge is localized to the swale and a bedrock ridge which lies immediately to the north of the swale. Overburden thickness along this swale is minor and ranges from 1 to 2 m in thickness. The bedrock ridge immediately north of the swale has a topographic high of 10 - 15 m above the swale and consists of Eramosa member rocks. North of this ridge towards the escarpment, overburden thickness increases. Thus, recharge to the area is most likely located in the ridge and swale area where infiltration is facilitated.

Downgradient boreholes

In general, the lithology logs for boreholes 12, 21, 53, 61 and 65 show a diminished overburden thickness and an increase in the thickness of the Eramosa member in the downgradient direction (Figure 5b, c). The elevation of the top of the Rochester formation (the underlying aquitard) is ~8 m below that of the upgradient boreholes.

The distribution of transmissivity in these boreholes is similar to that for the upgradient boreholes. Low transmissivity zones in the middle to lower Vinemount and high transmissivity zones in the Eramosa/Upper Vinemount, Goat Island and Gasport members are observed. The exception, is boreholes 21 and 65, which has more sparsely distributed zones of limited transmissivity (10⁻⁷ to 10⁻⁸ m²/s) in the Goat Island and Gasport members.

Contrary to many of the boreholes located upgradient, boreholes 12, 21, 53 and 65 have a relatively uniform distribution of hydraulic head with depth. The hydraulic head distribution in borehole 61 is dissimilar to all other boreholes in that the highest hydraulic head is observed at 160 masl corresponding to the high transmissivity zone (10⁻² m²/s) that straddles the Eramosa-Vinemount member contact. This zone is artesian, resulting in vertically upward and downward gradients emanating from this horizon.

The electrical conductivity in boreholes located downgradient generally increases with depth (Figure 5b,c) with the exception of borehole 61. The most profound change in electrical conductivity is observed in boreholes 12, 21, 53 and 65 where measured values range from ~1500 µs in the shallow zones to values greater than 20,000 µs in the deepest zones. Electrical conductivity in boreholes 21 and 65 is observed to steadily increase with depth, whereas in boreholes 12 and 53 electrical conductivity mainly increases at the Goat Island/Gasport contact and below the Eramosa/Vinemount contact respectively. In borehole 61 electrical conductivity increases only slightly from ~2000 to 5000 µs.

In boreholes 12, 21, 53 and 65, δ^{18} O and δ^{2} H concentrations are relatively enriched in groundwater located in the Eramosa and Upper Vinemount members (>165 masl) with values ranging between -9 % and -11 % and -50 % to -80 % respectively. Below the Vinemount member, the isotopic signature becomes significantly more depleted with values ranging between

 $-13^{\circ}/_{\infty}$ to $-17^{\circ}/_{\infty}$ and $-80^{\circ}/_{\infty}$ to $-110^{\circ}/_{\infty}$ for $\delta^{18}O$ and $\delta^{2}H$, respectively. The change in isotopic signature occurs below the low transmissivity zone located in the Vinemount member. In boreholes 12, 53 and 65, ^{3}H (analyzed by direct methods) is not observed in any of the sampled groundwater. However, enriched ^{3}H values obtained from borehole 53, indicate that the presence of ^{3}H (6.3 enriched TU +/- 0.8) at 175 masl, close to the contact between the Eramosa and Vinemount units. A small amount of ^{3}H is observed at ~175 masl in borehole 21.

The isotopic composition of the groundwater in borehole 61 varies little with $\delta^{18}O$ and $\delta^{2}H$ ranging from $-9^{\circ}/_{\infty}$ to $-11^{\circ}/_{\infty}$ and $-55^{\circ}/_{\infty}$ to $-80^{\circ}/_{\infty}$ throughout the borehole depth. This signature is similar to that for the upgradient boreholes. As with the upgradient boreholes, substantial ^{3}H concentrations are also observed in borehole 61, particularly at the shallowest interval and the high transmissivity zone located in the middle of the Eramosa member. In borehole 65, a small amount of ^{3}H is observed at 150 masl. A second sample from this zone obtained 5 months later confirmed the presence of ^{3}H (3.8TU enriched +/- 1.3). However, this zone is of low transmissivity ($\sim 10^{-8}$ m²/s) and it is likely that drill water was entrapped during installation of the permanent packer system. Dissolved chloride concentrations are elevated (~ 8000 mg/L) in this zone but not as elevated as that observed at the deepest levels in borehole 53 ($\sim 19,000$ mg/L) which may suggest that drill water has not entirely equilibrated with groundwater.

The pronounced shift with depth in isotopic composition and electrical conductance observed in boreholes 12, 21, 53 and 65 suggests that two distinct flow systems are present. As with the upgradient boreholes, the low transmissivity zone in the Vinemount unit or upper Goat Island appears to be the dividing horizon between older water at depth and younger water present in the Eramosa unit. In boreholes 12 and 21, this area of low transmissivity zone is observed to be in the upper Goat Island. The absence of ³H concentrations observed in groundwater from the

upper Eramosa unit in boreholes 21 and 65 suggests that, although this water is young, recharge in the immediate vicinity is unlikely.

Tritium, δ^{18} O and δ^{2} H concentrations in borehole 53 show the presence of recent water in the high transmissivity zone at the base of the Eramosa and the upper Vinemount. A value of 6.3TU +/-0.8 TU for enriched 3 H was obtained for this interval. The source for this water is likely through connection with the upgradient recharge area. Considering that groundwater velocities in the fractures within the lower Eramosa range from 10 to 30 m/day (Radcliffe, 1997) and matrix porosities range from 5 to 15% (unpublished data), transport of the 3 H from the recharge area in a horizontal fracture can be simulated. Using the Tang et al (1981) solution, simulation of transport in a discrete fracture having an aperture of 500 μ m, a velocity of 30 m/day and adjacent matrix porosity of 5% shows that 3 H concentrations as high as 15 TU are possible at borehole 53 when input conditions at borehole 60 (i.e. 30 TU) are employed. The low concentrations of 3 H present in the low transmissivity zone in the upper Goat Island may be remnant drill water.

The results for borehole 61 are complicated by the presence of the artesian hydraulic head in the high transmissivity zone in the Lower Eramosa and Vinemount units. The water in this zone is observed to contain ³H (15TU +/- 8) and shows a similar isotopic signature to water from the recharge area. The source of this water is uncertain. Hydraulic connection from the recharge zone may be present. However, the upper Eramosa is exposed on the river bottom at several locations both upstream and downstream from borehole 61. Thus, it is also likely that the source of this water may be from a connection with river water in the stream direction of river flow.

Groundwater in the stratigraphic intervals above and below the artesian zone show stable isotopic signatures similar to that in the artesian zone. Although these waters contain low or

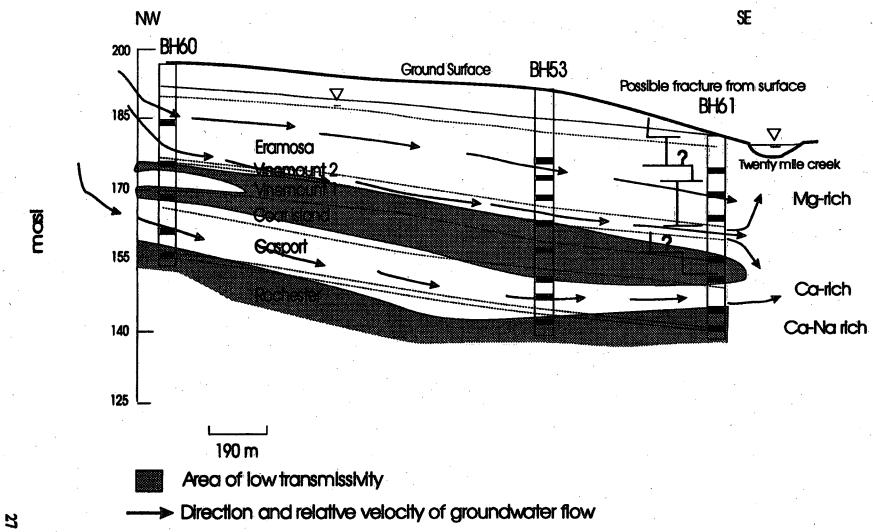


Figure 6: Conceptual model of two dimensional groundwater flow at the Smithville site

immeasurable concentrations of ³H, it is likely that they originate from the artesian zone, through vertical connections, or are recharged at locations further up the river valley.

CONCEPTUAL MODEL AND CONCLUSIONS

Since fracture networks are, in general, complex with the nature of fracture interconnection being uncertain, interpretation of groundwater flow from borehole to borehole using hydraulic parameters is also complex. The previous discussion supplements the hydrological data with geochemical data to provide evidence for hydraulic interconnection on a large scale. The conceptual model (Figure 6) represents a two dimensional cross-section, using three selected boreholes located in the direction of groundwater flow (northwest to southeast). For the conceptual model, only data from boreholes 53, 60, 61, 62, 63 and 65 are considered.

Transmissivity tests conducted on boreholes 11, 12 and 21 are less sensitive than those conducted on the other boreholes and sample intervals are coarser. Also, zones sampled are much smaller and more infrequent in these boreholes and thus provide less reliable information.

Hydraulic head and measurements of transmissivity can provide only a general idea of groundwater flow in the immediate vicinity of a particular borehole. For example, the uniform distribution of hydraulic head in boreholes 53 and 65 coupled with large variations observed in transmissivity measurements may indicate that groundwater flow is primarily horizontal in the vicinity of these boreholes, with little interaction between the individual fracture planes.

Alternatively, the uniformity of the hydraulic head distribution could imply that the horizontal fracture planes are extremely well connected such that no vertical gradient could exist. However, the chemistry and isotopic composition of the groundwater in these boreholes shows the water

above the Vinemount to be markedly different than that below, suggesting that little interaction between the water in these two horizons has occurred.

Conversely, in the upgradient boreholes and borehole 61, transmissivity measurements are equally varied, yet distribution of hydraulic head with depth is not uniform. The change in hydraulic gradient with depth may suggest a large amount of vertical groundwater interaction or this could be just another manifestation of horizontal flow. Evidence for horizontal flow is provided by the geochemical results which show that the sharp change in hydraulic head distribution occurring at 175 masl in the upgradient boreholes (60, 62 and 63) divides two separate flow systems. The presence of ³H at depths below the low transmissive zone (e.g., borehole 60) suggests that even though there is limited vertical hydraulic connection, there is enough to allow for the penetration of some freshwater across the low transmissive barrier. Thus, in both the upgradient and downgradient vicinities groundwater flow is predominantly horizontal. Flow is likely controlled by large bedding plane fractures that have been observed in the Lockport formation (Tesmer, 1981, Novakowski and Lapcevic, 1988, Yager and Kappel, 1998). The presence of bedding-plane partings is common in sedimentary rock sequences and are usually caused by stress changes. Enlarged bedding plane partings have been found to control groundwater flow in the Lockport formation at Niagara Falls Ontario, and in the Newark Basin, New Jersey (Novakowski and Lapcevic, 1988, Michalski and Britton, 1997).

The uniformity of the stable isotope composition with depth in the upgradient holes (60, 62 and 63) and the overall similarity to that of recent precipitation values, suggests that groundwater recharge is occurring upgradient of these boreholes. Groundwater recharge for the area likely occurs through the Eramosa unit and is localized to the swale and ridge located immediately north of the upgradient boreholes, where overburden thickness is minimal.

In all boreholes, a zone of low transmissivity is located in the middle to lower Vinemount member. This zone of low transmissivity varies in thickness yet appears ubiquitously. It is this horizon of low transmissivity that separates groundwater flow into the upper and lower flow regimes in the region. The upper flow regime is present in the Eramosa member, the lower flow regime is present mainly in the Gasport and Goat Island members (Figure 6).

Inorganic ion concentrations of groundwater and subsequent geochemical speciation modeling suggests that these regimes are physically and chemically related to the geological bedrock. Shallow groundwater is found to be dominated by high Mg concentrations due to equilibrium reactions with dolomite which control the amount of Ca and Mg in solution. However, in the lower flow regime, groundwater is dominated by high Ca and SO₄ concentrations due to the higher amount of gypsum minerals present in the rocks.

Transmissivity measurements in the lower flow regime are observed to be just as high as that in the upper flow regime. Thus, calculations based on equivalent aperture width would suggest that groundwater velocity in both flow regimes should be similar. However, the high electrical conductivity observed in the downgradient boreholes 53 and 65 at depth indicates that groundwater residence time in this zone is much greater than in the upper zone. Also, the observed depletion in stable oxygen and hydrogen isotopes at depth in these boreholes suggest that there is relatively less dilution from younger recharge water. As recharge is observed to occur in both regimes in the upgradient boreholes, it is therefore implied, through geochemical observation, that groundwater velocity in the lower flow regime is considerably slower than that in the upper flow regime.

Groundwater discharge from the flow system is less well defined. In borehole 61, located downstream from the town center, groundwater appears to interact with the river water, at least

within the upper flow system. In this same borehole, a high transmissivity zone in the Goat
Island/Gasport exhibits the lowest hydraulic head at depth of any of the boreholes. This indicates
that the lower flow system appears to completely underflow the river.

ACKNOWLEDGEMENTS

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APPENDIX A

Inorganic Ion Concentrations in the Groundwater related to Seasonal Changes

Before speculating on the changes in ion concentration with each sampling session, there are several factors that must first be taken into consideration. Firstly, samples obtained in February of 1997 were sent to Water Technologies Institute (WTI) for analyses, whereas all other samples were analyzed at the National Laboratories for Environmental Testing (NLET). Both of these institutions are located in Burlington, Ontario. Subsequently, anions from the February sampling session were analyzed by ion chromatography and by ultraviolet photometry in the other sessions.

During the second round of sampling, NLET had determined that the high SO₄ concentrations in the groundwater were causing interference effects when trying to determine the concentrations of cations in the groundwater. As a result, spiked samples had a low percentage of recovery. It was then determined that for major cation analyses (Ca, Na, Mg, K), a 1 to 10 dilution with double distilled water provided the best recovery rate, and was optimum for analyses. Thus, during the third round of sampling, dilutions were performed for all cation samples submitted to the laboratory for analyses.

Finally, no comparison can be made using wells 63 and 65, as these wells were sampled only once, in November of 1997. As these wells were first drilled in May, 1997, some time was required before inorganic ion concentrations in the groundwater are considered representative.

Despite these few differences, some obvious observations can still be made. In each individual sampling zone, the concentrations of dissolved ions may vary considerably (Tables A1 a, b and c). However, sampling throughout the different seasons (winter, summer and autumn) indicated that very little change was observed in the overall trends of the inorganic constituents. For example, in all sampling sessions, cations that increase with depth are: Ca, Na, K, HS, Cl and SO₄. Those that decrease with depth are: Mg and Fe (Tables A1 a, b and c). The fact that there

is little or no change in trends throughout the seasons suggest that recharge rates may be too low to cause a significant change in groundwater chemistry or that chemical reaction rates between infiltrating groundwater and rock are very fast that slight changes in recharge throughout the seasons cannot be observed.

Table A1: Summary of inorganic groundwater chemistry from February, 1997 sampling

Westbey bo		Bottom zone	Top zone	pH	Eh	Alkalinity	Ca	Mg	Ma	K	Fe	8Q,	CI	HB	SIO
Boreholo	Zone	(maei)	(mael)	P -1,	(MV)	(mg/L CaCO ₂)	(mg/L)	(mg/L)	(mgA.)	(mg/L)	(mg/L)	(mg/L)	(mp/L)	(mg/L)	(mg/L
58	1	176.4	191.8	7.4	220	420	278	482	150	9,81	1.52	2240	122	0.00	•
	2	173.9	175.7	7.3	161	275	219	84	36	2.9	0.671	701	8.8	0.00	•
	8	167.6	179.2	7.4	163	173	159	87	42.9	3.28	0.788	520	23.5	0.00	-
	Ä	162.6	168.9	7.0	28	295	263	114	49.9	4.63	0.16	899	35.4	0.07	•
	5	157.6	161.9	7.2	-19	206	774	224	686	37.6	1.85	1830	1710	2.13	-
	6	151.9	158.8	7.0	-100	220	573	163	151	29.3	0.026	1850	281	2.31	•
	/· 7	146.8	150.5	7.3	-64	213	605	162	223	22	0.038	1840	475	2.20	-
	8	142.6	145.5	7.0	-104	205	676	174	449	31.9	0.014	1840	1050	2.55	• •
	9	139.0	141.7	6.8	-80	161	2890	1170	7630	155	<u> </u>	1900	19900	2.73	
60	1	183.1	197.0	7.0	157	405	316	511	143	8.21	12.4	2690	16.5	0.01	•
	2	175.7	182.4	7,3	139	262	-	-	•	•	•	•	.•	-:	-
	3	168.2	174.9	7.1	-21	250	282	148	108	7.09	0.17	979	229	1.73	•
	4	159.9	167.4	7.1	- 3 .	285	148	121	47.1	5.03	0.536	619	32.1	0.42	•
	5	156.6	159.2	7.3	25	310	448	128	46.9	3.43	2.84	1450	18.5	0.11	•
	6	153.0	155.8	7.3	:-44	310	508	137	187	17.7	0,244	1580	298	0.12	
61	1	175.0	182.2	6.9	233	348	228	270	93.7	5.53	1.03	1440	42.4	0.01	. •
	2	170.1	174.8	7.0	68	268	421	102	53.7	5.98	0.112	1280	50.3	1.05	•
	3	165.2	169.4	7.1	14	303	410	102	52.7	3.82	0.052	1220	52.4	1,17	-
	4 .	165.4	164.5	7.0	87	253	295	113	51.4	2.98	0.024	909	45.1	0.40	•
	5	161.7	154.6	7.0	-40	240	591	116	96.1	5.64	0.022	1660	127	0.57 0.31	-
	6	145.5	150.9	7.1	-53	218	511	116	110	7.85	0.019	1480	208		•
	7	141.9	144.8	7.1	18	226	592	112	119	9.4	1.84	1710 1710	198	0.40	•
	8	138.4	141.1	7.5	71	177	582	115	257	23.6 5.7	13.6 8.99	3050	440 39.8	40.99	
62	1	175.0	195.4	7.8	118	283	428	588	166	13.3	7.78	auau	38.6	40.00	•
	2	171.3	173.4	7.7	43	208	510	185	89.3 45.5	14.9	0.102	1690	28.9	29.77	_
	3	163.9	170.6	7.1	-00	221	573 554	138 123	37.4	11.9	0.098	1650	31.3	32.24	
	4	155.2	163.1	7.1	-96	212	224	120	37.4	11.0	0.000	1000	01.0		
		151.4	154.5	7.7	29	216		 -	 -	:=:			<u>-</u> -		
63	1	179.6	194.8	•	•	-				-	_	_	_	-	•
	5	174.7	178.6	•	•	• .			-	-	-				
	8	171.4	179.7	•	-	•					-			•.	
	4	167.7	170.4 166.7	•	•	-									
	5	161.6	160.7	•	•	-,				•		•			
~		1594	180.5				-					•	·		
65	8	176.2	174.0	.•	-	•	-							:•.	-
	8	164.7	163.5	-	-	-		•					• . •	•	
	4	150.2	158.0	•	-	-									
	•	153.7 149.2	152.5	•		-		•	•	•		•			
	2	145.6	148.0	-	-			_			-			.=:	

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Sample	Zone	B1. of Screen MASL	Top of Screen	pH	Eh (mV)	Alkelinity (mg/L CaCO ₂)	Ca (mg/L)	(mg/L)	No (mg/L)	K (mg/L)	Fe (mg/L)	80 ₄ (mg/L)	CI (mg/L)	H8 (mg/L)	810 ₁ (mg/L)
		181.6	184.7	7.81	-8	261	96.5	84.5	43.2	0	0.62	299	28.6	0.02	•
•••	ė	172	176.8	7.08	-112	227	354	85.4	20.8	4.4	0.02	883	15.6	5.67	•
	-	166.6	188.4	7.04	-98	250	449	88.5	29.5	5.8	0.07	1160	32.1	5.46	•
	.		180.1	7.05	-120	217	622	140	181	18	0.04	1630	156	2.19	•
	. •	157		7.08	-121	350	692	148	245	16.5	0.09	1610	565	2.51	•
	<u> </u>	139.6	145.6				97.5	125	52.8	2.2	0.96	478	19.7	0.00	
12	1	176.2	180.3	7.28	51	306						665	24.5	0.21	
	. 2	166.5	171 <i>.</i> 4	7.16	-57	800	180	126	52.9	2.9	0.78				•
	3	154.9	160.2	7.03	-71	25 9	651	· 118	103	8.9	0.11	1570	834	1.00	•
	. Ā	145.9	152.8	7.42	-115	283	741	171	528	28.5	0.04	1730	1190	7.70	•
		187.8	142.6	7.19	-89	220	1190	383	2370	65.9	0.03	1790	5110	7.10	
21		180.2	176.5	7.2	-29	291	123	116	43	2.3	8.51	470	9.53	0.08	•
		170.1	173.6	7.2	-133	246	463	88.9	93.2	3.5	0.06	1080	140	2.54	.=
•	ž				-143	250	528	108	196	18.5	0.08	1390	833	2.98	-
	3	158.3	161.8	7.8						38.2	0.09	1700	2350	6.17	_
	4	148.5	151.8	7.4	-132	198	863	231	1080						-
	5	140.4	143.5	7.1	-131	256	3910	474	2480	74.8	0.12	1820	6010	1:09	•
	Ā	128.2	131.2	7.11	-131	185	4700.	4160	2170	194	0.11	1650	28890	5.94	:-

Table A2: Summary of inorganic groundwater chemistry from July, 1997 sampling

Westbay bo		Bottom zone	Top zone	pH	Eh-	Alkelinity	Ca	Mg	Na	K	Fe	80,	CI	HS	810,
Bareholo	Zone	(mast)	(meel)		(mV)	(mg/L CaCO ₂)	(mg/L)	(mg/L)	(mgfL)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
3	1	176.4	191.8	6.91	126	. 391	233	432	128	7.20	1.30	2350	134	0.00	16.3
	2	173.9	175.7	7.18	399	185	215	70.4	31.2	2.10	0.38	786	5.7	0.03	13.3
	9	167.6	179.2	7.38	216	219	137	102	43.4	2.50	0.80	549	11.7	0.01	13.6
	4	162.6	166.9	7.18	10	260	. 250	125	51.6	4.00	0.12	869	28.9	0.83	13.4
	5	167.6	181.9	•	•	•	•:	•	:•		•	•	•	-	-
	6	151.3	156.8	7.12	-152	228	427	113	85.1	15.20	0.08	1740	183	5.92	6.B
	7	148.9	150.5	7.25	-95	212	430	108	147	13.30	0.06	1700	417	4.69	8.37
	8	142.5	145.5	7.08	-118	180	489	115	285	17.60	0.05	1520	889	15.04	8.53
	-9	189.0	141.7	6.65	-121	124	2560	1030	6180	117.00	0.06	1480	17700	1.98	11.3
0	1	183.1	197.0	7.1	172	400	289	497	131	5.90	8.08	2260	9.4	0.00	17
	2	175.7	182.4	7.21	303	243	129	99.9	31.4	2:10	1.88	430	7.8	0.03	13.2
	3	168.2	174.9	7.08	-91	248	300	132	108	7.20	0.10	958	242	4.68	10.5
	4	159.9	167.4	7.25	-10	294	154	116	47.3	4.40	0.11	1440	38.1	1.52	13.7
	5	156.6	159.2	7.04	114	281	417	112	45:1	4.90	1.64	796	94.3	0.26	9.59
	6	153.0	155.8	7,15	-69	276	501	124	247	15.60	0.20	2350	184	0.78	18.3
1	1	175.0	182.2	7.11	263	303	241	308	95	5.90	1.12	1690	29.1	0.00	14.7
*	2	170,1	174.8	7.16	-77	204	407	89.6	48.9	4.20	0.05	1170	48.8	2.26	12
	-3	165.2	169.4	7.15	-71	180	391	89.8	48.3	4:10	0.05	1060	51	0.00	12.5
	4	155.4	184.5	7.05	-61	243	253	91.9	43.5	3.70	0.03	987	34.9	2.11	18
	5	161.7	154.6	7.08	-114	195	440	99.7	131	7.60	0.18	1460	327	11.02	9.68
-	6	145.5	150.9	7.25	-91	232	•				•	-	•		
	7	141.0	144.8	6.88	-110	190	339	76.1	72.5	5.80	0.53	1440	193	6.47	9.95
		138.4	141.1	7.22	74	240	492	96.6	244	16.80	2.58	1720	937		7.1
2	1	175.0	195.4	7.92	68	256	348	418	134	4.50	10.30	2140	140	0.02	11.4
	2	171.3	178.4	7,61	46		404	142	63.6	9.90	4.40 0.10	1800 1390	87.4 32.6	5.98	6.96 7.71
	3	163.9	170.6	6.98	-150	226	417	94.2	25 37.6	9.10 7.60	0.09	1240	66.1	6.15	6.31
	4	155.2	163.1	7.14	-137	168	367 493	91.4 153		17.90	4.05	1750	523	0.10	9.31
		151.4	154.6	7.63	-11	-	490	100	340 ·	17.50	4.09.	1700	929		9.91
3	. 1	179.6 174.7	194.3 178.6	•	•	•	•	•		•		_	_		
	2	171.4	179.7	•	•		•	-		_		•:			
	3	167.7	170.4	•	•				_		_	_	· .	-	-
	4		168.7	-	•	•		_	-	_	-	-			
	9	161.6 153.4	160.6	•			<u>.</u>	-		-					
5	2	175.2	180.5		-					- :					-
7	2	164.7	174.0			-			-					:•	-:
	4	159.2	169.5	-	-	-	•		-						•
	7	159.7	158.0		-	-	-	-	•					٠.	•
	0	149.2	152.5	-	•										-
	9	145.6	148.0	-	-		•	-	-				•		

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Sample	Zone	St. of Screen MASL	Top of Screen	n pH	Eh (mV)	Alkelinity (mg/L CoCO ₂)	Ca (mg/L)	Mg (mg/L)	Ne (mg/L)	K (mg/L)	Fe (mg/L)	80 ₄	CI (mg/L)	H8 (mg/L)	SIO ₂ (mg/L)
11		181.6	184.7	7.16	22	229	90	78.3	41.8	2.30	0.55	303	20.7	0.04	14.70
•••		172	176.8	6.92	-79	172	305	72.6	18.8	4.40	0.04	875	9.8	5.65	13.40
	-	166.5	168.4	6.93	-90	217	339	61.9	17.3	4.30	0.08	1020	11.4	6.26	13.10
		157	160.1	7.98	-118	190	483	111	130	11.40	0.10	1320	335	4.61	9.85
	- 1	139.8	145.6	6.95	-98	185	403	89.4	147	11.20	0.11	1620	540	5.57	8.75
12		176.2	160.3	7.17	172	321	129	270	90.7	3.60	1:57	1480	10,1	0.02	12.80
		166.5	171.4	7.08	-82	217	340	74.5	36.3	4.10	0.13	1260	55	6.00	12.90
	3	154.9	160.2	6.98	-97	188 /	377	71.8	65.6	6.50	0.07	1390	174	5.62	10.80
		145.9	152.8	6.76	-146	168	1210	300	2860	58.60	0.05	1710	6900	5.94	7.69
		137.3	142.6	6.76	-112	205	1220	310	2700	57,40	0.05	1790	7150	1.86	7.63
21	-	180.2	176.5	7,14	-65	205	164	103	38.7	3.10	~ 0.30	656	6.9	0.78	13.70
		170.1	173.6	7.14	-29	270	122	107	39.9	2.80	0.33	417	8.6	0.41	13.50
		158.3	161.6	7.15	-155	202	613	116	298	13.40	0.04	1580	823	6.08	10.40
		148.5	151.6	7.07	-144	208	503	128	511	22.00	0.08	1350	1290	6.71	9.30
		140.4	143.5	7.06	-154	166	736	177	1210	31.60	0.10	1440	8000	3.87	9.05
		1989	131.2	7.18	-141	56	1140	359	2510	53.90	0.03	1770	6420	7.19	11.20

Table A3: Summary of inorganic groundwater chemistry from November, 1997 sampling

Westbay bo		Bottom zone	Top zone	pH*	2h	Alkelinity	Ca	Mg	No	K	Fo	80,	CI	HB	810,
Borehole	Zone	(mael)	(masi)	•	(mV)	(mg/L CeCO ₂)	(mgfL)	(Jam)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
3	1	176.4	191.8	6.9	320	300	268	477	127	7.00	1.67	2810	84.2	0.00	16.3
~	ž	178.9	175.7	7.2	259	160	214	72	32.2	2.40	0.35	628	6.70	0.02	12.7
	. 3	167.6	178.2	7.2	195	125	132	97	41.0	2.60	0.46	519	16.2	0.00	13.3
	Ā	162.6	166.9	7.2	29	257	250	126	59	4.20	0.16	847	84.7	0.79	12.9
	Ř	157.6	161.9	7.3	-30	138	662	178	451	25.3	0.13	1840	1290	8.42	7.48
	Ā	151.8	156.8	6.6	-100	209	558	154	116	12.5	0.09	2105	216	4.48	7.08
	7	146.3	150.5	7.0	-80	127	575	163	206	10.5	0.07	1920	514	5.88	8.32
	8	142.5	145.5	6.9	-94	292	663	184	407	5.91	0.05	1495	1061	5.58	8.50
	ě	139.0	141.7	6.3	-103	180	2900	847	7000	137	0.05	1457	18917	5.68	26.4
0		183.1	197.0	6.9	98	400	400	520	260	5.70	10.60	2943	19.4	0.09	15.0
•	ż	175.7	182.4	7.2	155	291	140	110	81.3	2.20	0.01	616	11.4	0.04	13.0
	ā	168.2	174.9	7.0	-78	234	338	136	119	8.10	0.05	1185	315	5.81	10.2
	Ă	159.9	167.4	7.1	-63	248	173	122	51.9 ·	5.20	0.09	794	72.5	2.31	12.7
	B	156.6	159.2	7.0	93	268	842	90	45.1	5.40	1.13	1172	80.6	0.27	13.7
	ě	153.0	155.8	7.0	-62	265	507	127	370	19.3	0.06	1679	:864	3.64	11.7
31	1	175.0	182.2	7.0	-9	800	248	285	92.9	6.20	1.00	1480	34.8	0.29	14.9
•	ż	170.1	174.8	6.9	-13	310	987	89	44.4	4.40	0.09	1265	58.0	3.35	12.5
	√8	165.2	169.4	7.0	-25	218	447	103	56	3.80	0.06	1120	58.5	3.07	12.3
	4	155.4	164.5	7.0	-22	237	278	112	51.7	4.00	0.03	763	38.7	1.77	12.8
	5	151.7	154.6	6.9	-65	204	465	91	70.8	6.50	0.08	1443	163	6.13	9.83
	6	145.6	150.9	6.8	-63	232	538	121	127	6.90	0.07	1450	373	5.81	9.38
*	7	141.9	144.8	7.0	-28	230	562	107	100	6.70	0.09	1678	224	2.13	11.0
	8	138.4	141.1	7.1	10	231	600	125	324	13.7	2.08	1198	1025	0.13	9.42
2	1	175.0	195.4	7.4	- 118	285	392	341	129	5.00	9.69	2270	164	0.00	12.7
	2	171.8	173.4	7.7	- 47	245	651	197	85.0	10.2	5.20	2350	75.2	0.00	7.48
	8	163.9	170.6	7.1	-82	208	537	127	36.0	10.2	0.05	1745	44.5	5.85	7.90
	4	155.2	163.1	7.1	-96	176	520	120	80.4	7.70	0.08	1933	67.5	5.11	7.41
		151.4	154.5	7.6	28	204	710	238	704	25.5	4.52	1903	1654 11.1	0.01	7.42 14.5
13	1	179.6	194.8	7.3	162	214	149	177	65	2.80	1.83	672 742	14.8	0.00	13.9
	2	174.7	178.6	7.3	153	204	139	167	53.9	2.60	1.7	/42 1310	17.4	0.00	13.0
	8 .	171.4	173.7	6.9	103	224	376	88.7	32.4	4.50	1.77 5.95	1834	31.1	0.12	11.8
	4	167.7	170.4	7.3	92	231	352	129	48.1	4.40	5.43	923	37.4	0.10	11.9
	5	161.6	166.7	7.3	101	216	823	117	39.1	4.50		1176	31.0	0.10	11.1
	6	158.4	160.6	7.3		193	<u> 859</u>	134	43.5	4.80	3.38		8.2	0.78	16.6
5	2	175.2	180.5	7.1	14	204	114	68	32.0	2.60	0.232	418 912	70.0	0.49	12.9
	8	184.7	174.0	7.0	179	229	268	170	72.0	5.40	2.98 0.053	1390	1410	4.83	6.84
	4	159.2	163.5	6.9	-115	177°	769	191	624	32.0 31.6	0.058	1440	1300	4.42	6.24
	5	153.7	158.0	6.9	-60	•: • • • •	1010	273	1500		0.049	1450	5480	3.58	6.27
	6	149.2	162.5	6.7	-105	145	798	225	2190	42.6		1280	7700	3.00	6.65
	7	145.6	148.Q	6.8	-105	144	1650	340	2900	57.1	0.051	1200	7 (04		0.00

Derrof		

Sample	Zone	Bt. of Screen MASL	Top of Screen	pH.	Eb (mV)	Alkalinity (mg/L CaCO ₂)	Ce (mg/L)	ûlg (mg/L)	Na (mg/L)	K (mg/L)	Fo (mg/L)	80, (mg/L)	CI (mg/L)	H8 (mg/L)	810; (mg/L)
11	1	181.6	184.7	7.52	130	256	94.9	77.1	40.5	2.40	0.46	328.0	29.2	0.02	13.6
••	ė	172	176.6	7.19	-55	146	821	77.3	20.6	4.60	0.03	1087	11.8	5.38	12.7
	i	166.5	168.4	7.24	-27	164	464	84.0	24.0	4.50	0.09	1380	15.0	5.11	12.3
	4	157	160.1	7.2	-69	197	651	188	154	10.1	0.07	1908	935	5.69	8.74
	ž	139.8	145.6	7.17	-86	172	593	138	235	18.4	0.09	1847	588	4.74	8.41
12		176.2	180.3	7.38	31	336	132	254	87.8	3.50	1.52	1256	18.80	0.02	18,9
12	,	166.5	171.4	7.28	-67	167	249	107	48.9	4.00	0.48	1077	39.80	3.49	13.9
			160.2	7.27	-70	191	590	130	165	48.9	0.08	1720	762	4.99	9.67
		154.9					1220	414	2540	43.6	0.04	1954	6518	3.69	7.58
	- 4	145.9	152.8	6.94	-107	221				49.2	0.08	1840	7077	5.25	7.51
	<u> </u>	137.3	142.6 ·	6.9	-62	207	1200	441	2680			493.0	3.60	0.04	12.7
21	1	160.2	176.5	7.69	60	167	109	104	38.0	2.90	0.36	;; -			
	2	170.1	173.6	7.43	-24	164	335	61.2	25.1	3.20	0.04	1040	33.80	4.75	19.0
	ā	158.3	161.6	7.05	-83	200	470	110	240	11.1	0.05	1880	571	6.09	10.2
	Ă	148.5	151.6	7.05	-92	140	541	124	480	19.4	0.08	1613	1228	4.73	8.51
	Ž	140.4	143.5	7.27	-125	189	743	266	2160	42.4	0.06	2039	5018	2.85	9.21
	2	190.7	191 2	7.98	-191	138	973	392	2620	50.8	0.14	1605	6453	0.03	18.3

APPENDIX B

Table B: List of isotopic analyses from groundwater samples collected in July and November ,1997

Sample	depth bot* (m)	Bottom zone MASL	Top zone MASL	Oxygen Standerdized Delta	Hydrogen Standerdized Delta	Tritlum TU	Enriched TU
BH60-15	15	183.11	197.04	-9.82	-61.92	22	
BH60-18	18	175.65	182.37	-10.26	-66.82	10	•
BH60-27	27	168.19	174.91	-11.08	-71.87	6	3.3 +/-0.6
BH60-36	36	159.90	167.44	-10.61	-69.98	29	
BH60-46	46	156.58	159.15	-10.33	-67.01	≪6	•
BH60-50	50	153.02	155.84	-10.98	-71.92	8	4.4 +/-0.6
BH62-23	23	175.01	195.45	-0.7	-60.8	18	•
BH62-26	26	171.30	173.44	-10.26	-56.12	<6	5.0 +/-0.7
BH62-30.5	30.5	163.88	170.56	-10.8	-70.75	8	1.5 +/-1.0
BH62-39.5	39.5	155.23	163.14	-9.99	-66.21	10	1.6 +/-1.0
BH62-50	.50	151.36	154.49	-10.96	-69.32	≪6	•
BH53-16.5	16.5	176.45	191.75	-9.83	-63.23	<6	
BH53-19.5	19.5	173.93	175.69	-10.51	-69.47	<6	•
BH53-22.5	22.5	167.64	173.18	-14.4	-70.97	<6	6.5 +/- 0.7
BH53-30	30	162.61	166.89	-10.25	-68.89	<6	6.3 +/-0.8
BH53-36	36	157.58	161.85	-13.03	-84.83		1.6 +/-0.6
BH59-42	42	151.29	156.82	-14.87	-104.29	≪6	
3H53-49.5	49.5	146.26	150.53	-13.94	-80.63	≪6	
BH53-55.5	55.5	142.48	145.50	-12.22	-84.22	<6	<0.8 +/-0.5
BH53-60	60	138.96	141.73	-13.54	-96.37	<6	
BH61-7	7	175.03	182.24	-10.01	-64.22	17	
BH61-10	10	170.12	174.29	-10.52	-65.63	-:- <6	
3H61-16	16	165.20	169.38	-10.5	-70.09	<6	1.6 +/-0.5
3H61-22	22	155.37	164.46	-10.38	-64.27	15	
BH61-34	34	151.68	154.63	-10.91	-73.53	.c <6	-
BH61-37.5	37.5	145.54	150.95	-10.59	-70.92	<6	<0.8 +/-0.4
BH61-46	46	141.85	144.80	-10.8	-72.88	<6	
BH61-51	51	138.41	141.12	-10.86	-72.21	<6 ⋅	
3H63-15	15	179.60	194.35	-10.32	-56.92	<6	1.4 +/-0.5
BH63-19.5	19.5	174. 69	178.62	-10.15	-63.44	7	2.4 +/-1.1
3H63-25.5	25.5	171.41	173.71	-10.18	-64.66	15	4.8 +/-1.3
3H63-29.5	29.5	167.73	170.43	-10.17	-65.94	7	3.4 +/-1.1
BH63-34	34	161.58	166.74	-10.3	-50.73	≪6	2.6 +/-0.5
3H63-41.5	41.5	153.39	160.60	-10.25	-53.43	<6	2.0 11-0.0
3H65-4	4	181.66	187.16	-6.9	-52.08	65	
3H65-7	7	175.16	180.46	-0.91	-68.27	≪6	_
3H65-13.5	13.5	164.66	173.96	-10.08	-66.91	46	6.9 +/-0.7
3H65-24	24	159.16	163.46	-16.07	-107.72	46	المحقد عند
3H65-29.5	29.5	153.66	157.96	-15.21	-104.15	~	1.8 +/-1.2
3H65-35	35	149.16	152.46	-15.01	-105.97	8	3.8 +/-1.3
BH65-39	39	145.59	147.96	-14.24	-101.05	3.0 11 -1.3
River Water	by 61			-12.39	-87.31	16	
River Water		•		-8.6	-62.78	10	-

		•					
Sample	depth bct* (m)	MASL	Top of Screen MASL	Oxygen Standerdized Delta	Hydrogen Standerdized Delta	Tritium	Enriched TU
BH11a	53.8	139.8	145.6	-11.63	-75.69	<6	•
BH11c	36 .6	157	160.1	-11.21	-72.43	<6	•
BH11d	27.1	166.5	168.4	-10.55	-68.94	<6	•
BH11e	21.6	172	176.8	-10.68	-67.56	11	•
BH11f	12	181.6	184.7	-10.33	-64.5	10	•
BH21a	66	128.2	131.2	-13.08	-89.19	≪6	-
BH21b	54.1	140.4	143.5	-13.11	-88.47	≪6	•
BH21c	46	148.5	151.6	-12.96	-87.77	≪6	•
BH21d	36.2	158.3	161.6	-11.69	-73.23	⊲ 6	•
BH21e	24.4	170.1	173.6	-10.43	-69 .74	9	. •
BH21f	18	180.2	176.5	-10.39	-67.95	≪6	3
BH12a	54	137.3	142.6	-14.54	-0 8.19	<6	•
BH12b	45.4	145.9	152.8	-14.49	-98.44	<6	
BH12c	36.4	154.9	160.2	-10.97	-71.63	≪6	. •
BH12d	24.8	166.5	171.4	-10.5	-67.43	≪6	
BH12e	15.1	176.2	180.3	-10.23	-63.69	€6	•





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