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Characterization of Trichloroethylene Contamination in the Fractured Bedrock at the Smithville Site  
BY:  
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NWRI Contribution No. 97-140

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## MANAGEMENT PERSPECTIVE

- Title:** CHARACTERIZATION OF TRICHLOROETHYLENE CONTAMINATION IN THE FRACTURED BEDROCK AT THE SMITHVILLE SITE
- Author(s):** A. Brown, P. Lapcevic, K. Novakowski, S. Lesage, S. Brown, K. Millar, J. Voralek, and L. Zanini
- NWRI Publ. #:** 97-140
- Citation:** Required report to Smithville Phase IV management
- EC Priority/Issue:** The bedrock aquifer underlying the Smithville PCB transfer site was contaminated by PCB congeners, trichlorobenzenes and trichloroethylene (TCE) in the early 1980s. At a significant cost, an alternate water supply for the town of Smithville was provided by the Province of Ontario and preliminary site clean-up was undertaken. However, recent experience at Superfund sites in the US has shown that there are no adequate methods with which to remediate the contamination present at depth in the bedrock aquifer. This study is a preliminary effort to determine if there is sufficient natural degradation of the contaminants (particularly TCE) through aerobic and anaerobic processes such that present remediation through expensive pump-and-treat methods might be curtailed. This work supports COA Stream 1 activities. The EC Business Plan issue addressed by this study is Toxics in Groundwater.
- Current Status:** This report will act as a background document for a proposal to be submitted to the Smithville Phase IV management for further investigation of the degradation processes at the site.
- Next Steps:** To conduct a more detailed study of the degradation processes at the Smithville site. This will involve more detailed sampling for degradation products and several lab experiments conducted to simulate the anaerobic conditions in the subsurface.

## Executive Summary

This study has examined trichloroethylene (TCE) contamination and groundwater geochemistry of the bedrock units underlying the CWML site in Smithville. Two approaches were developed to measure the concentration of TCE in discrete fractures, and to examine the extent of contamination in the deeper rock units. The first approach used a small, 0.1 m sampling interval and a down-hole pneumatic pump to isolate and sample single discrete features, using existing transmissivity data to guide fracture location. The second approach focused on building a borehole concentration profile, using a larger submersible pump with a 1.5 m sampling interval. Geochemistry results, including anions, cations and dissolved oxygen, were obtained from most of the 0.1 m zones isolated. Trichloroethylene concentration, Eh, pH, TCE biodegradation products and trichlorobenzenes were all sampled for from the discrete features and larger zones.

Three boreholes were sampled over the course of this work. Borehole 54D, located to the north of the site was used to develop methods suitable for the location and sampling of discrete features using existing transmissivity data as a guide. The results from this site demonstrated a positive correlation between the volumes of water produced from a feature and the zone transmissivity. Background geochemical information was also collected from this site. Generally, results from this hole showed low redox potential, and evidence of sulfate reducing conditions in the deeper zones, including possible iron sulfate precipitate and hydrogen sulfide gas.

The principal borehole used in this study was borehole 56, which intersects the aqueous contaminant plume, down gradient from the source area. Twelve discrete features were successfully located in ten high transmissivity zones ( $T > 10^{-6}$  m<sup>2</sup>/s). Samples were obtained for the measurement of TCE, TCBs and PCBs, anions, cations, Eh, pH and dissolved oxygen.

Concentrations of TCE measured were between 0 and 18  $\mu\text{g/L}$ , which were consistently below measured openhole concentrations. The highest concentrations of TCE observed were in features of mid-depth, between 175 and 168 masl in the lower Eramosa and upper Vinemount units. Cis-dichloroethylene (c-DCE) was qualitatively observed in all but the uppermost features in the Eramosa unit, suggesting that biodegradation of TCE is occurring. The presence of TCBs in the uppermost zones, which have no detectable c-DCE nor TCE suggests that some other mechanism, possibly aerobic biodegradation, is removing TCE from these features.

Sampling of borehole 56 between occurred through the Eramosa, Vinemount, Goat Island and Gasport units of the Lockport formation (183 and 150 masl) using a 1.5 m sampling zone. Measured concentrations of TCE ranged from below detection limits to 11  $\mu\text{g/L}$  in these zones with c-DCE and 1,2,3 and 1,2,4 TCB qualitatively confirmed in some of the lower zones. The highest TCE concentration measured was 11  $\mu\text{g/L}$  at 180 masl in the upper Eramosa Unit, but consistently high concentrations between 5 and 10  $\mu\text{g/L}$  were observed through the mid-range of the borehole in the Eramosa and Vinemount units. Lower TCE concentrations measured in deeper zones with low redox potential ( $E_h < -50$  mV corrected) and c-DCE, suggests that anaerobic biodegradation of the TCE may be occurring at depth.

The final borehole investigated was borehole 34C, approximately 200m down gradient from the source area. This borehole was profiled continuously at 1.5 m intervals through all members of the Lockport formation (from 179 to 154 masl, except 177 to 171 masl). Concentrations of TCE observed ranged between 0 and 6  $\mu\text{g/L}$ , lower than concentrations observed at comparable depths at borehole 56. The highest concentrations of TCE measured (3 to 6  $\mu\text{g/L}$ ) were observed in the Vinemount unit (between 170 to 165 masl). Cis-dichloroethylene was also detected in all zones but those in the upper Eramosa unit.

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## Introduction

From the late 1970's through to the mid 1980's, Chemical Waste Management Limited (CWML), operating as a PCB storage and transfer facility in Smithville Ontario, received more than 400,000L of liquid waste, including PCBs and chlorinated organic solvents. In 1985, PCB contaminated oil was discovered in a shallow storm water lagoon onsite. Two years later, free and aqueous phase contamination was confirmed in the overburden and bedrock aquifer underlying the site. The Ontario Ministry of Environment and Energy initiated a four phase program to contain and remediate the CWML site. Phase I involved securing the site and the second phase found safe storage and transfer of the site contents. Destruction of the PCB contaminated overburden and the installment of a pump and treat system occurred in Phase III. Phase IV, currently underway, is conducted to investigate the remediation of the contaminants in the bedrock and groundwater beneath and adjacent to the site.

Site characterization has begun with the goal of developing a detailed conceptual model for groundwater flow and contaminant transport in the fractured rock at the Smithville site. Necessary to such a model is a full understanding of the properties of the fracture framework and the unfractured rock matrix, as well as the chemical properties of the groundwater system. Ongoing field work includes hydraulic testing, measurement of hydraulic heads, downhole camera work, point dilution experiments and groundwater sampling for inorganic geochemistry. The results of these studies will be used to build a conceptual model of the groundwater system, focusing on contaminant transport and the role of fractures in this system. This conceptual model is essential for the effective design and implementation of containment or remediation solutions at the Smithville site.



The chlorinated solvent trichloroethylene (TCE) was the focus of this study since it is one of the most toxic and mobile components of the CWML site. The site also contained PCBs, TCBS, and other solvents such as toluene and xylene (Golder Associates Ltd., 1995). Trichloroethylene is a toxic and possibly carcinogenic organic solvent that due to widespread industrial use, is currently a common groundwater contaminant and priority pollutant (CEPA, 1993). Chlorinated organic compounds are highly pervasive and persistent environmental contaminants. Conventional remediation of chlorinated solvents has usually relied on physical treatment approaches which transfer the contaminant to another media for ultimate treatment. Bioremediation is an alternative treatment approach that has the potential to completely reduce the TCE present in the groundwater to environmentally benign end-products. Anaerobic biodegradation sequentially dechlorinates TCE to dichloroethylene (DCE), vinyl chloride and finally ethene and even ethane (deBruin et al., 1992). Anaerobic biodegradation of TCE has been observed in the fractured dolomite at an American site, where degradation products such as DCE, vinyl chloride and ethene have been measured in the contaminant plume area. (Yager et al., 1997). In this study, it was found that the microorganisms present in the plume area had adapted to utilize and biodegrade the TCE at the site and contribute significantly to the decontamination of this site. Biodegradation of TCE can also take place in aerobic environments. TCE can be aerobically biodegraded to TCE epoxide and finally to organic acids and carbon dioxide. Enhanced aerobic biodegradation has been observed in environments with natural gas present (Little et al., 1988).

The goal of this project was to characterize trichloroethylene(TCE) contamination in the fractured bedrock underlying the aqueous plume area. The presence of organic solvents in discrete fractures was investigated, as well as the occurrence of contaminants in the deeper rock units at the site. Using this information, it may prove possible to identify major transport pathways or sources of contamination within these zones with an ultimate goal of proposing further steps for study and

remediation. This project will contribute the larger effort to characterize the bedrock units at the Smithville site as well as describe the physical and chemical hydrogeology of the area. To carry out this study, three boreholes were sampled in detail. Borehole 54D was selected to develop sampling methods and measure background geochemistry. Borehole 56 was investigated since it intersects the aqueous contaminant plume. Finally, borehole 34C down gradient of borehole 56 was chosen for comparison with borehole 56 results.

## Methods

### Field Methods

Three boreholes were used for sampling and field work for this project. The choice of boreholes was made using the following criteria; 1) borehole location, 2) open borehole (do not contain packers or Westbay equipment) 3) availability of complete vertical transmissivity profiles at 0.5 m test intervals. Considering these criteria, borehole 54D in the north cluster, borehole 56, the northernmost hole in the south cluster, and borehole 34C, down gradient from the plume, were chosen for this study (Figure 1). Borehole 54D was selected since it is situated north of the site away from the contaminant plume. Since regional groundwater flow is approximately north to south, borehole 54D provided background geochemical information and an opportunity to develop field methods in an uncontaminated area. Borehole 56 is in the southern cluster of holes, intersecting the aqueous contaminant plume. Also, borehole 56 has distinctive, high transmissivity features separated by low permeability zones, which was useful for discrete fracture location. Finally, borehole 34C, south-west from borehole 56 was chosen. This borehole was used to investigate TCE contaminant levels further down gradient and to compare these results with those from borehole 56.

Two approaches were employed to sample groundwater from the three selected boreholes. The first sampling approach focused on the location of discrete features in the borehole, and involved sampling from these zones. The second approach focused on building a complete profile of TCE concentrations throughout the borehole. Discrete fracture sampling used either a stainless steel plate mounted on a packer (Figure 2a), or a sampling interval between two smaller packers (Figure 2b) to isolate a length of borehole for sampling. A full borehole profile was developed using a much larger sampling interval and using a higher capacity submersible pump (Figure 2c).

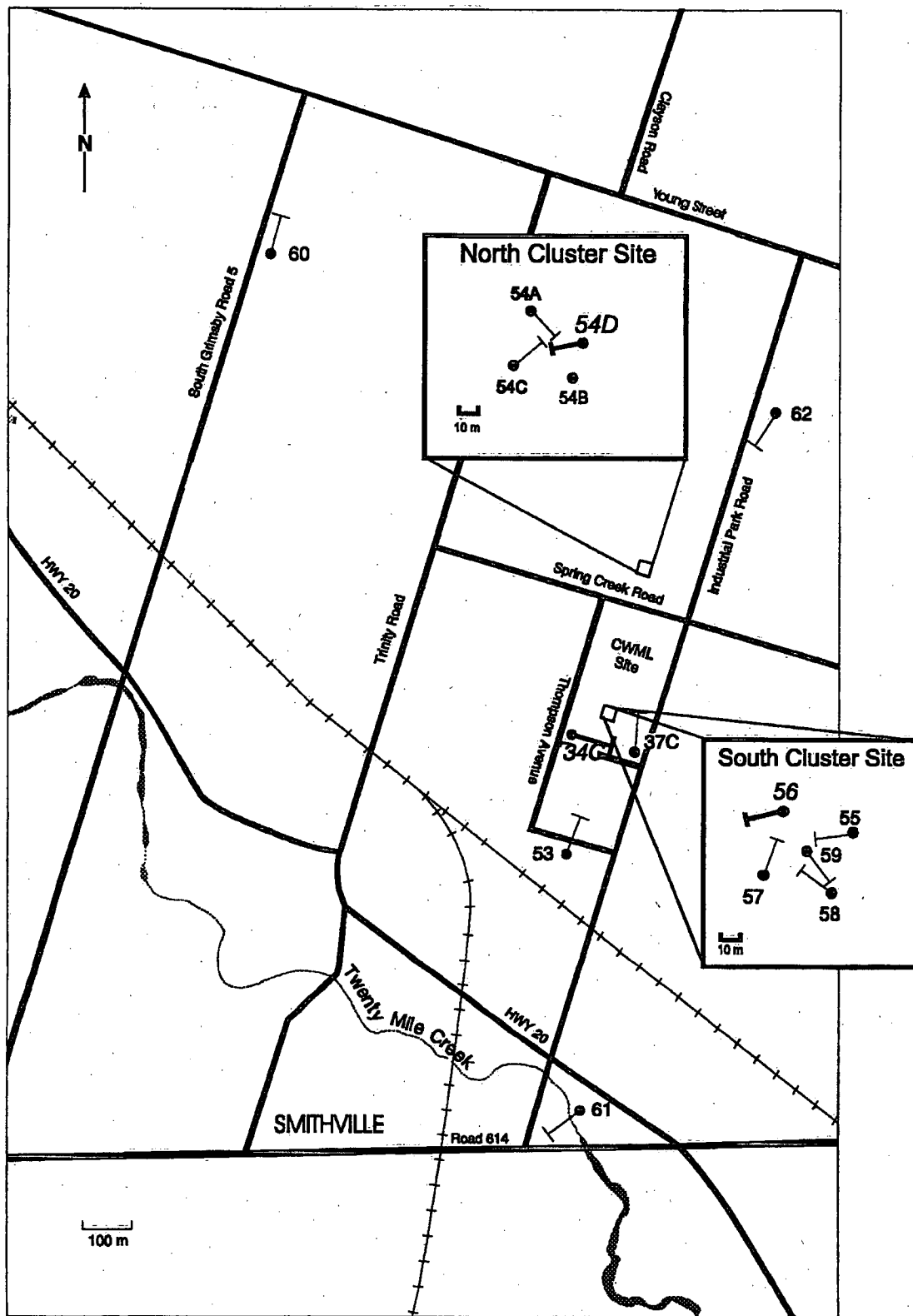
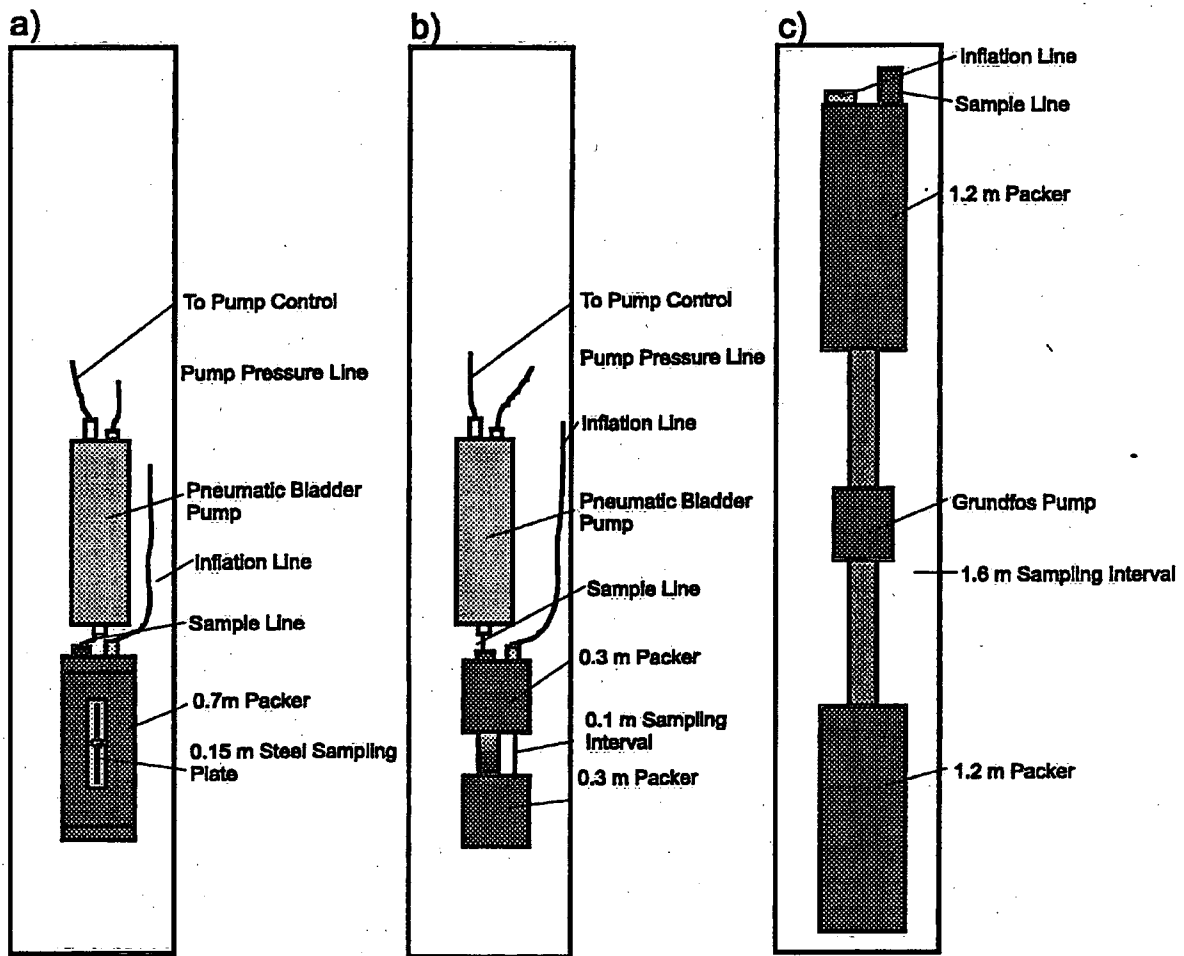


Figure 1: Site Map



**Figure 2. Sampling Equipment: a) Plate and Packer Sampler b) Double Packer Sampler c) Submersible Pump System**

Specific feature sampling required that small zones be reliably isolated and sampled. The 2 m and 0.5 m interval transmissivity profiles were used to establish zones that might contain fractures and could consequently be sampled (BH54D and BH34C transmissivity data from Groundwater Remediation Project Report, NWRI, 1997, and BH56 transmissivity data from unpublished NWRI data). Areas of high transmissivity ( $T > 10^{-6} \text{ m}^2/\text{s}$ ) were used to guide the fracture location process.

The first sampling system employed a single packer fitted with a stainless steel plate (Figure 2a). When the packer was inflated, the plate lay sealed against the borehole wall for sampling. A hole at the center of plate connected to a sample line that ran to the surface. Along a 0.15 m length of the plate was a 1 mm deep groove to channel water from across the plate's length. The principal advantage of this system was to minimize the zone volume and allow direct sampling of specific features.

The second system used a double packer arrangement. Two packers were separated by a 0.1 m slotted stainless steel sampling tube (Figure 2b). When both packers were inflated, a 0.1 m zone of less than 1 L volume was isolated and water could be pumped from fractures, independent of the packer orientation, rather than within the narrow width of the steel plate. This system was used for most intervals in borehole 54D and for all intervals in borehole 56.

Both packer-sampler systems were used in combination with a down-hole pneumatic pump. The pump was made from a narrow plastic cylinder with an inner Teflon bladder. An inflation line was connected, via a solenoid valve, to a nitrogen tank. When the solenoid valve was off, for the exhaust cycle, water filled the pump casing around the bladder due to the hydrostatic pressure down-hole. During the charge cycle, when the solenoid valve was on, nitrogen gas filled the bladder inside the pump, forcing the water between the bladder and casing through the sample lines to surface. The rate of pumping was controlled by varying the length of the exhaust and charge cycles. The charge and exhaust cycles were initially set to 5 and 8 seconds respectively to quickly pump small volumes to surface and fill the sample line with water. After water had been brought to surface, both cycles were increased. The charge cycle was set to coincide with the length of time required to completely discharge the volume of water sitting in the pump. The exhaust cycle was reduced while maintaining the current flowrate. The pump nitrogen pressure

was set to 30 psi initially, and increased approximately 10 psi for every 10 m additional depth below the water table. Withdrawal flowrates varied from 0.1 to 0.4 L/min depending on the transmissivity and depth of the sampled zone.

Once a fracture yielding consistent and abundant flow had been found, withdrawal rate was measured. Due to the pulsing action of the pneumatic pump, this was taken as the total volume collected over several minutes and averaged. Water from pumping was then directed through a flow through cell that contained either an Eh or pH probe. Both probes were left to stabilize for at least 15 minutes prior to taking a measurement. Dissolved oxygen (DO) was also measured from the flow-through-cell using colorimetric methods. When a stable Eh value was recorded, samples were assumed to then be reasonably representative of the feature water and samples for TCE, anions, trace metals, sulfide, PCBs and trichlorobenzenes (TCBs) analysis were collected. It is important, when examining TCE contamination and possible biodegradation activity, to also characterize other water quality parameters. The chemical characteristics of the water, such as concentrations of major cations and anions, Eh, pH and dissolved oxygen may be used to describe the type of environment in which activity is occurring and also, to understand the mechanism of possible biodegradation activity (Roberts et al., 1990).

The second sampling approach focused on sequential sampling at 1.5 m intervals. This method used a submersible Grundfos® pump supported by a stainless steel pipe between two 1.2 m packers (Figure 2c). This system had a 1.6 m sampling zone and approximately a 10 L volume was isolated between the packers. At each sampling depth, prior to packer inflation, water from the open hole was pumped for several minutes to clear any old water from the lines. Pump speed was set by varying the frequency of pump operation, usually within the range of 150 to 300Hz which produced flow rates between 2 and 6 L/minute. Samples for TCE analysis and for Eh and pH

measurement, were then collected from the open hole. Once the packers were completely inflated to isolate the zone, pumping was resumed. The pump frequency was increased until water was pumped to surface. If no water could be brought to surface, the zone was abandoned and the packers deflated and moved to the next 1.5 m zone. If water did reach the surface, the pump was set to withdraw water at approximately 3 L/min. This rate was sufficient to keep the sample lines completely filled with sample water, minimizing volatilization losses and drawdown. Deeper, low transmissivity zones were pumped at rates of less than 1 L/min. At regular intervals, samples were collected for later TCE analysis. After 50-70 L had been purged, additional samples were collected for Eh and pH measurement. Both sampling approaches are summarized in Table 1.

**Table 1. Summary of Sampling Approaches**

	<i>Submersible Pump and Packers</i>	<i>Discrete Fracture Sampler - Plate and Packer</i>	<i>Discrete Fracture Sampler - Straddle Packer</i>
<b>Zone Width</b>	1.6 m	0.15 m	0.1 m
<b>Purge Volume</b>	10 L	0.2 L	1 L
<b>Eh and pH Measurement</b>	-obtained after 50-70L purged	-monitored continuously using the flow-cell	-monitored continuously using the flow-cell
<b>Sampling Regime</b>	TCE, Eh, pH	Eh, pH, TCE, trace metals, anions, sulfide, PCBs, TCBs, DO	Eh, pH, TCE, trace metals, anions, sulfide, PCBs, TCBs, DO
<b>Locations Sampled</b>	34C, 56	54D	54D, 56
<b>Volumes Purged</b>	80-100L	20-60L	20-60L

Redox potential (Eh) and pH were measured using an Orion® 96-78-00 platinum electrode and a Corning® 3-in-1 combination electrode. The Eh probe was calibrated each sampling day using Zobel's solution while the pH probe was calibrated using a set of buffer solutions with pH's of 4, 7 and 10. Calibration solutions were kept as near to 10 °C (the temperature of the groundwater) as possible. Calibrations were repeated during the course of the day's sampling if erratic readings were observed. Measurements were made from a flow-through-cell during discrete fracture



sampling. The flow-cell was a 0.15 L glass jar, sealed with a rubber stopper that also held the probe and sample lines in and out of the cell. Because of the higher flow rates and resulting pressures, the flow-cell could not be used with the submersible pump. Eh and pH were measured from 0.04 L samples obtained after at least 50 L had been purged from the system. Both approaches usually required approximately 10-20 minutes for Eh measurements to stabilize. All Eh values reported in this study have been corrected (+200 mV as per electrode solution used given groundwater temperature).

After Eh and pH were determined, samples for further laboratory analysis were collected. Samples were obtained for later analysis for volatile organic compounds, principally TCE and possible biodegradation products such as cis-dichloroethylene (c-DCE). These were taken in 40 mL glass vials with Teflon<sup>®</sup>-silicon septa with no headspace or bubbles. Two to three samples were collected for analysis by gas chromatograph and mass spectrometer and at least one additional sample was obtained for headspace analysis. A 1 L sample was collected in an amber glass bottle for measurement of trichlorobenzenes (TCBs) and total PCB concentrations. Triplicates of these samples were collected from two of the fractures for quality control purposes. Two samples were obtained for analysis for trace metals. These were collected in 125 mL Nalgene bottles and preserved with the addition of concentrated hydrochloric acid, to prevent the later precipitation of the metals. Similarly two samples were taken, again in 125 mL Nalgene bottles for sulfide analysis. These were collected with no headspace and treated with zinc acetate and sodium hydroxide. Samples for anion analysis were collected in 60 mL Nalgene bottles. The samples collected in the field were stored in either a cooler or an air conditioned field trailer, and returned to Burlington to be refrigerated as soon as possible. All samples, except those collected for volatiles and PCBs and TCBs, were filtered using 0.45 µm Gelman<sup>®</sup> in-line filters. The complete sampling protocol is summarized in Table 2.

**Table 2. Sampling Methods Summary**

	<i># Samples Collected</i>	<i>Sample Volume</i>	<i>Sample Treatment</i>	<i>Quality Control</i>
TCE and VOCs	2-3 for GC-MS analysis and 1-2 for headspace analysis taken at regular intervals per feature	40 mL collected in glass vials	unfiltered samples, collected with no headspace	triplicates obtained for GC-MS and some duplicates for headspace analysis
TCBs and PCBs	1 per feature	1 L collected in an amber glass bottle	unfiltered	2 sets of triplicate samples were submitted for analysis
Trace Metals	2 per feature	125 mL collected in a HDPE Nalgene bottle	filtered and treated with concentrated acid	duplicates of each sample taken
Sulfide	2 per feature	125 mL collected in a HDPE Nalgene bottle	filtered and treated with a strong base and Zinc Acetate	duplicates of each sample taken
Anions	2 per feature	60 mL collected in a HDPE Nalgene bottle	filtered	duplicates of each sample taken

Laboratory Methods

Samples for TCE analysis were kept inverted and refrigerated to minimize losses from possible volatilization and escape through the bottle cap. All samples were taken in triplicate and two or three of each set were analyzed within one to four days of their collection. Due to the trace levels of contaminants being measured, samples had to be quickly analyzed as even minute losses could influence results. Appreciable losses of greater than 30% were noted in TCE standards that had been kept for more than two weeks.

Samples were analyzed using a Hewlett Packard® 5890A gas chromatograph and mass spectrometric detector. A 10 mL volume was removed from each sample by the Dynatech® Precision Sampling PTA-30 Autosampler and purged with helium gas in the Envirochem Unacon®

Series 810 purge and trap concentrator. The resulting gas stream was passed through the gas chromatograph where it underwent a specific temperature program expressly designed to detect chlorinated organic compounds that were identified by a Hewlett Packard 5770 series mass selective detector. This program began at -15°C and increased at 10°/minute to a temperature of 35°C. From this point, the temperature is increased more slowly by 4°/minute to 150°C. The program then held the temperature at 150°C for one minute until the run finished. The injector and detector were held at 175°C for the duration. Between sample runs, the purge and trap equipment and connecting lines were flushed five times with a dilute solution of sodium hydroxide to prevent cross contamination and remove traces of hydrogen sulfide.

Quality control measures taken included the analysis of triplicate samples from each fracture. Also, each set of analyses began with a deionized water blank and another blank was run again after every 8-10 samples to ensure that there was no carry-over of compounds between samples. Trichloroethylene standards were also analyzed with runs to insure that the calibration remained valid. Using a range of standards between 0 and 25 µg/L, a consistent calibration with an  $r^2$  of greater than 0.95 was maintained over the course of the analysis period. A known quantity of another standard was also analyzed with each sample. The volatile organic compounds (VOCs) internal standard contains bromochloromethane, chlorobenzene-D5 and 1,4-difluorobenzene. Since the same amount of standard was automatically added to each sample, the calculation of concentration used a ratio of the analyte peak to the standard peak to minimize errors from variations in run conditions. The gas chromatograph and mass spectrometer analysis method has a detection limit of approximately 1 to 2 µg/L.

A specific ion measurement (SIM) method was developed for better detection of low level chlorinated organics. This method was developed to detect cis-dichloroethylene, (c-DCE),

trichloroethylene (TCE) and 1,2,3 and 1,2,4-trichlorobenzene (TCBs) as well as 1,4-difluorobenzene from the internal standard. The internal standard was diluted thirty to forty times to increase the overall sensitivity to better detect TCE, c-DCE and TCBs at levels of less than 0.1 µg/L. The SIM method was used to qualitatively confirm the presence of trace levels of biodegradation products such as c-DCE since they were below the quantitation limit.

Headspace analysis, with a Photovac® 10S Plus gas chromatograph was also used to measure the TCE concentrations in duplicates of the samples obtained. Once the samples were returned to the laboratory for analysis, an artificial headspace was created by removing 5 mL of the sample with an air-tight syringe and allowing an equivalent volume of air into the sample through a second needle. The samples were then inverted to prevent losses, and left for a minimum of one hour to allow the gas and liquid phase concentrations of the volatiles to equilibrate and for the samples to come to room temperature. A minimum of three additional standards were prepared in a similar manner for analysis with the sample series. Each sample or standard was analyzed by injecting 0.05 mL of the headspace into the gas chromatograph. Blanks of ambient laboratory air were analyzed after every 5 samples to insure that there was no carryover between runs. This analysis method has an approximate detection limit of 1 µg/L.

Samples and duplicates to be analyzed for trace metals were sent to National Laboratory for Environmental Testing at the National Water Research Institute. Similarly, samples and duplicates were sent to the Water Technology Institute for analysis for sulfide, TCB and total PCBs. Anion samples were analyzed at NWRI using ion chromatography.

## Results & Discussion

### Borehole 54D

Transmissivity data from borehole 54D, from 2 m and 0.5 m intervals (Figure 3 a and b) was taken as the basis for discrete feature location. Eight 0.5 m zones of high transmissivity ( $T > 10^{-7}$  m<sup>2</sup>/s) were located for sampling in borehole 54D at through the Eramosa, Vinemount and Goat Island members of the Lockport formation from 183.5 to 168.3 masl (Figure 3 b). The work done at this borehole provided an opportunity to develop and refine field methods. Initially, zones were sampled with the plate-packer sampler. Due to the variability of plate orientation, this approach provided inconsistent fracture locating, and variable withdrawal rates. All eight zones (Figure 3c) were re-examined with the double packer-sampler and samples for TCE, Eh (Figure 4) analysis were collected from each feature, with additional samples for measurement of metals, anions, pH and DO collected from the lowest three zones (Figure 5). Results from groundwater sampling at borehole 54D are summarized in Table 3. No TCE was found in any feature, as would be expected from a borehole up-gradient from the contaminant plume. Redox potential was high in the upper zone and sharply dropped in the lower zone, at approximately 175 masl. This depth corresponds to the contact between the Eramosa and Vinemount bedrock units (Figure 4). From the additional geochemistry results that include metals and anions, conditions in borehole 54D appear anoxic and sulfate-reducing, in the lower features (Figure 5). Evidence of a sulfate-reducing system includes observed hydrogen sulfide gas from the sample water, and abundant black precipitate, likely iron sulfide. Although no TCE or biodegradation products were detected with GC-MS analysis, large hydrocarbon peaks from propane and butane among others, were observed.

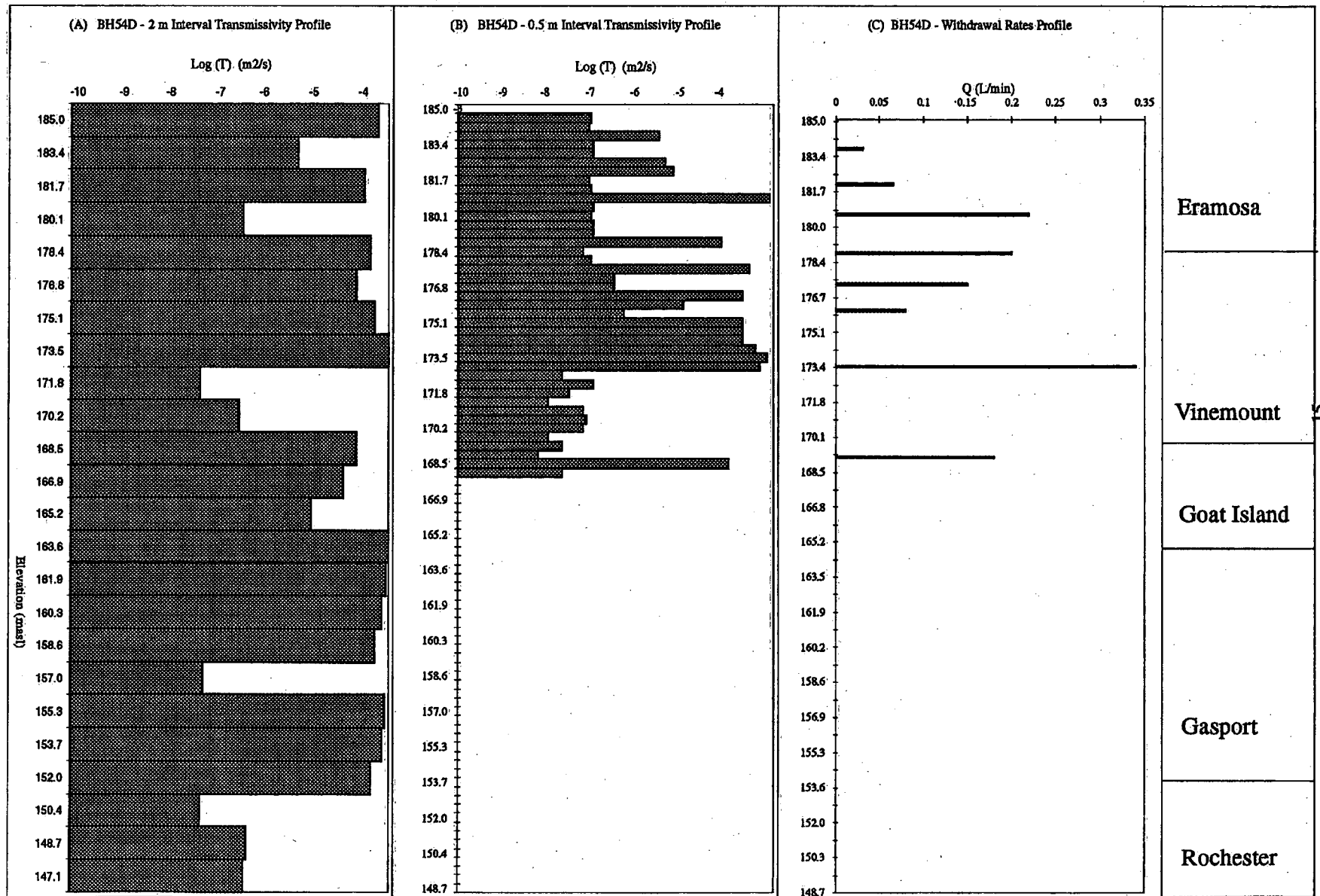


Figure3: BH54D results

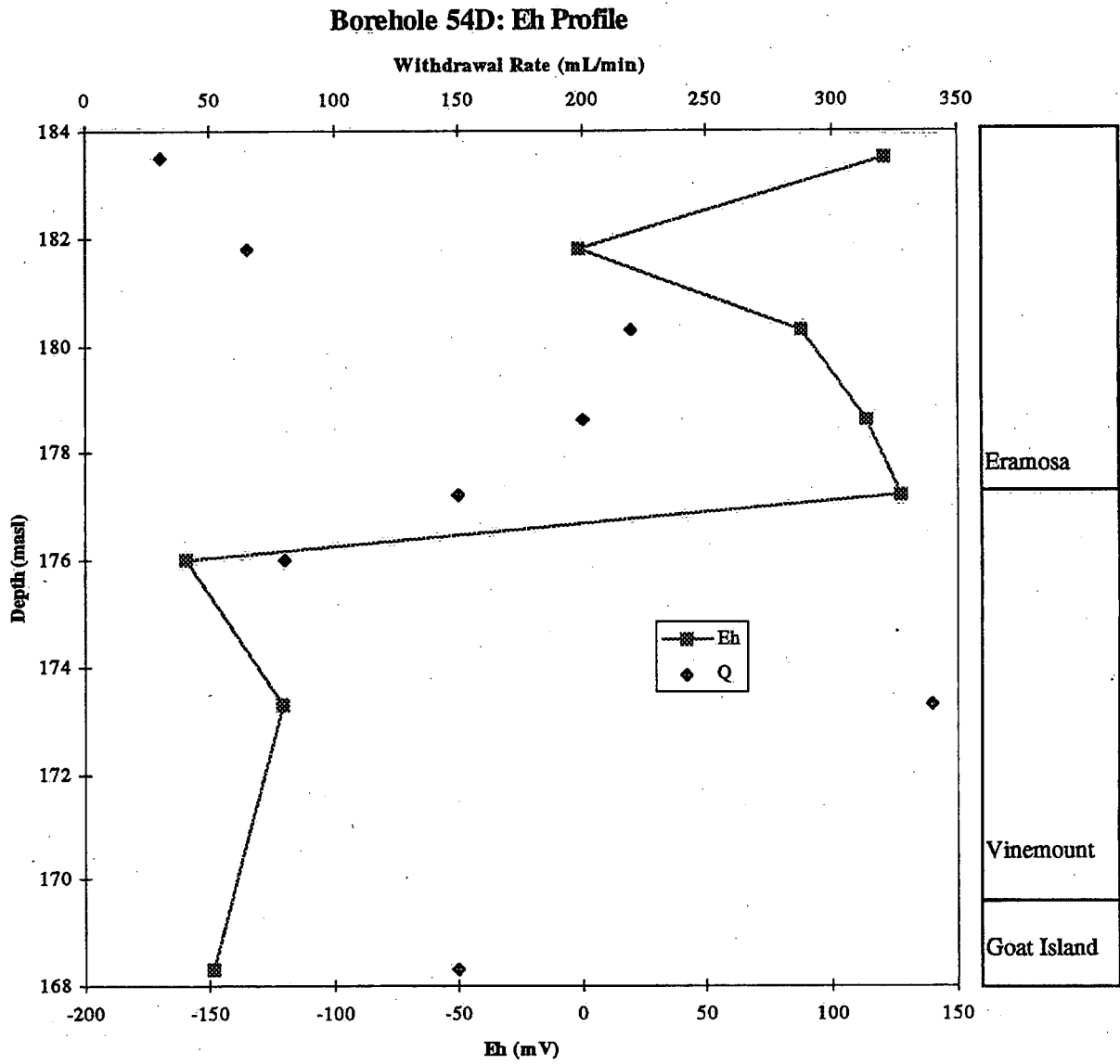


Figure 4: Borehole 54D redox potential profile

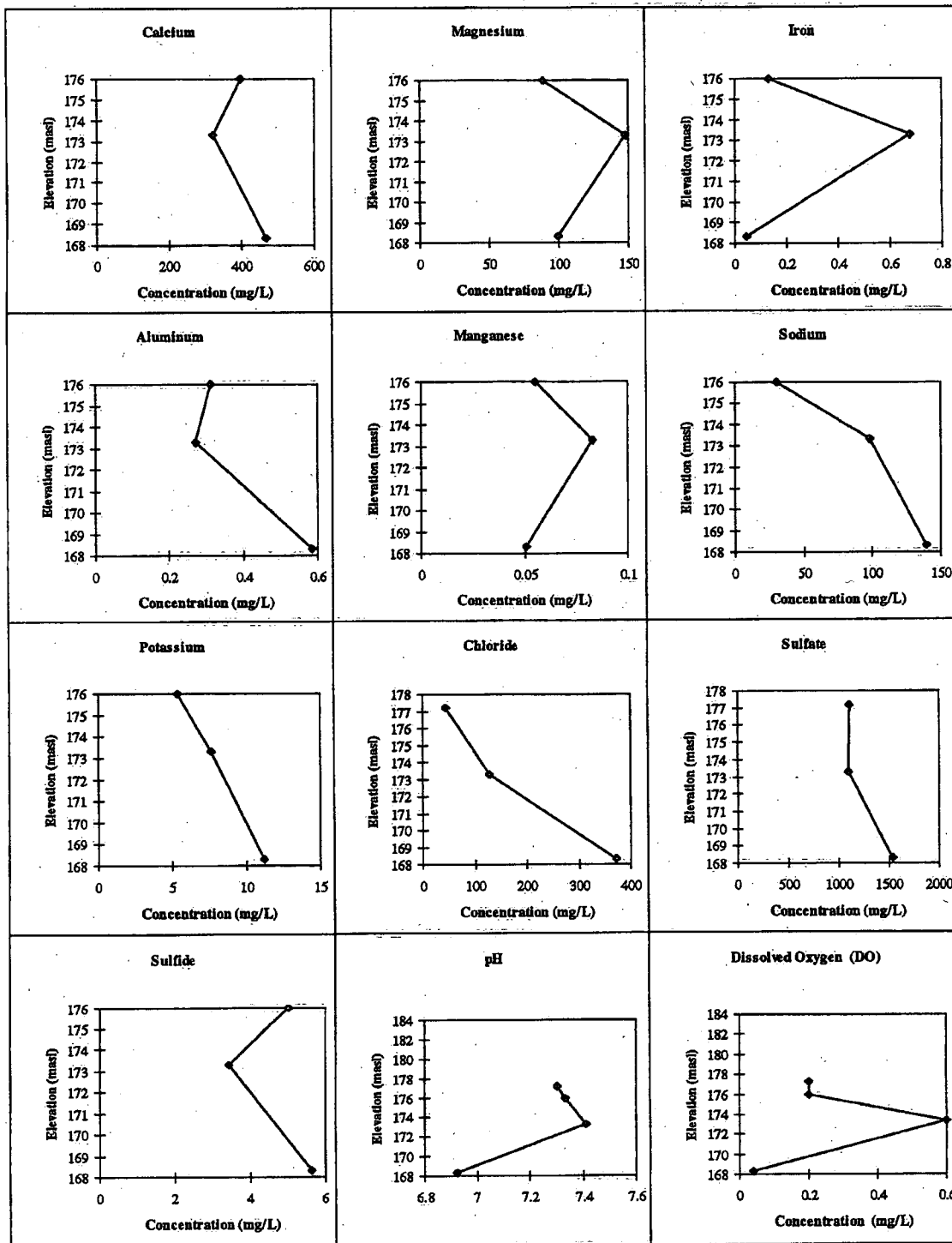


Figure 5: Geochemical results from discrete feature sampling at BH54D



**Table 3: BH54D Discrete Feature Results**

Zone Elevation		Total Volume Purged (L)	TCE (µg/L)	Eh (mV)	pH	Dissolved Oxygen (mg/L)	Iron (mg/L)	Sulfide (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Lockport Formation Member	T (m <sup>2</sup> /s)
Start (masl)	End (masl)											
183.5	183.4	10	0	121							Eramosa	3 E-07
181.8	181.7	15	0	-1							Eramosa	6 E-07
180.4	180.3	35	0	88							Eramosa	8 E-05
178.6	178.5	20	0	114							Eramosa	7 E-06
177.2	177.1	20	0	128	7.3	0.2			1113	43.8	Eramosa	3 E-05
176.0	175.9	20	0	-160	7.3	0.2	0.1295	5.03			Vinemount	2 E-05
173.4	173.3	40	0	-121	7.4	0.6	0.675	3.43	1099	127.1	Vinemount	6 E-05
168.3	168.2	30	0	-149	6.9	0.04	0.0455	5.62	1531	371	Goat Island	1 E-05

### Borehole 56

Transmissivity results from 2 m and 0.5m testing were used as the basis for discrete sampling and profiling work done at borehole 56 (Figure 6a and b). Borehole 56 was profiled at 1.5 m intervals down the hole using the larger submersible pump with 1.6 m packer spacing, which allowed a 0.1 m overlap between zones. Eleven zones from the Eramosa, Vinemount, Goat Island and Gasport units (between 184 to 151 masl), were developed using the submersible pump and TCE concentrations from these zones were measured (Figure 6c). Time series of samples were collected for TCE analysis to roughly establish the number of purge volumes necessary to obtain a representative sample (Figure 7). Based on these results, samples after 3 to 5 purge volumes can be reasonably considered representative since variation after 5 zone volume purges was usually less than 1 µg/L which is close to instrument accuracy. The stable TCE concentrations measured are plotted in Figure 6c and decrease with depth down the hole. Concentrations observed in the lower Eramosa and upper Vinemount units, between 170 and 166 masl, were consistently between 7 to 8 µg/L. Redox potential results are plotted in Figure 8 where it can be seen that deeper zone TCE concentrations generally occurred with low Eh zones. A summary of the complete borehole profile is included in Table 4.

**Table 4: 1.5 m Profiling Results from BH56**

Zone Elevation		Q	Total Volume Purged	TCE Concentration	Eh	pH	Lockport Formation Member	T	SIM Results		
Start (masl)	End (masl)	(L/min)	(L)	µg/L	(mV)			(m <sup>2</sup> /s)	c-DCE	1,2,4 TCB	1,2,3 TCB
182.7	181.4	3	90	1.8	165	7	Eramosa	3 E-05	no	yes	no
181.4	180.2	3	90	11	123	7	Eramosa	7 E-05	no	yes	no
180.2	178.9	3	105	0.9	-59	7.02	Eramosa	8 E-07	yes	yes	yes
177.7	176.4	3	90	0	80	7.1	Eramosa	1 E-04			
174	182	3.1	93	7.5	150	7.03	Eramosa	2 E-04			
170.2	169	2.8	84	5.9	145	6.99	Eramosa	2 E-05			
169	167.7	2.8	84	7.1	180	6.99	Vinemount	2 E-05			
167.7	166.5	3	90	7.1	143	6.99	Vinemount	1 E-04			
161.5	160.3	3	90	7.1	160	7	Vinemount	2 E-05	yes	yes	yes
156.5	155.3	0.7	42	4.2	-121	6.92	Goat Island	6 E-06	yes	yes	yes
153.2	152	0.6	30	3	-66	7.04	Gasport	3 E-08	yes	yes	yes

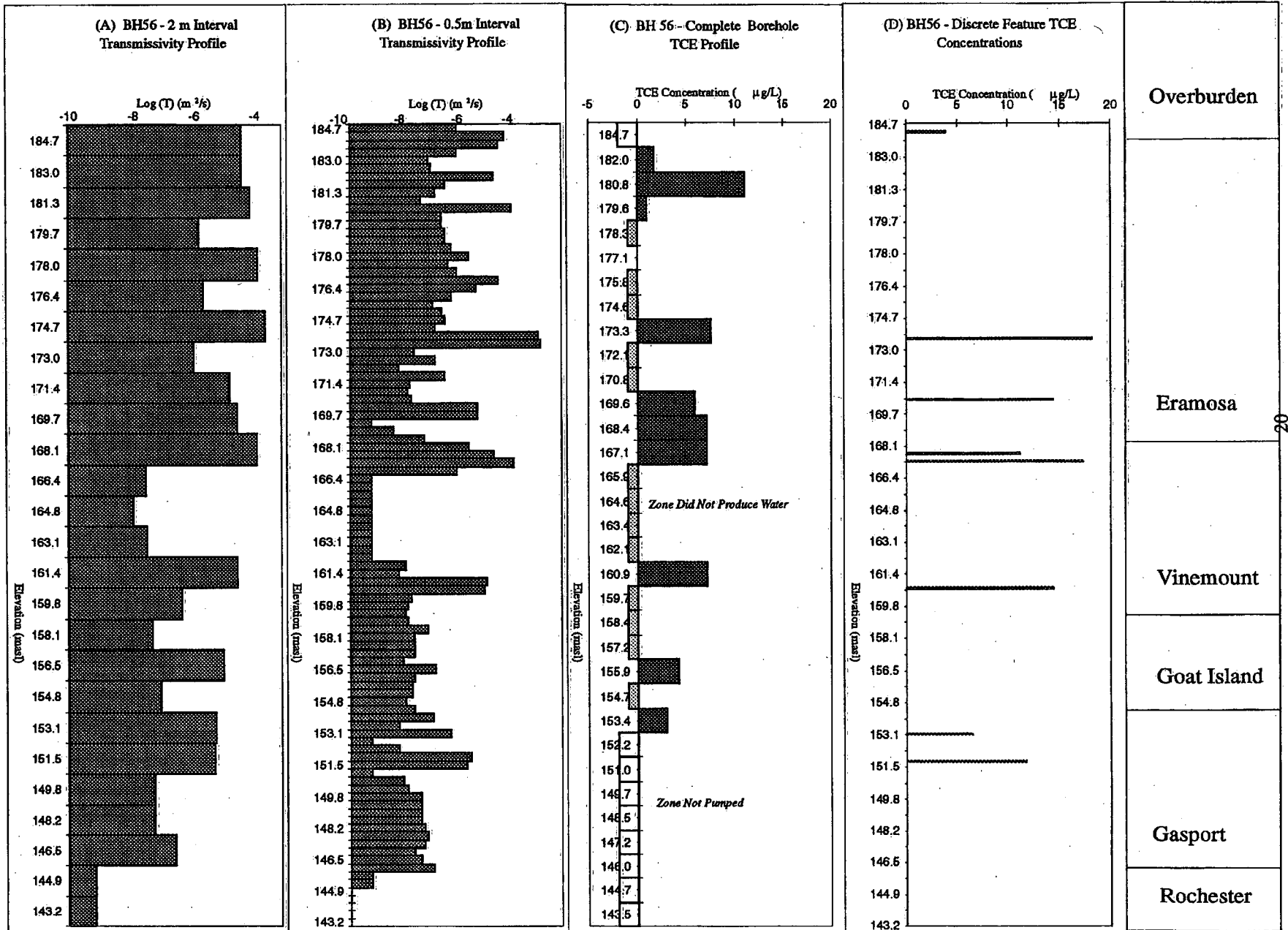


Figure 6: BH56 results

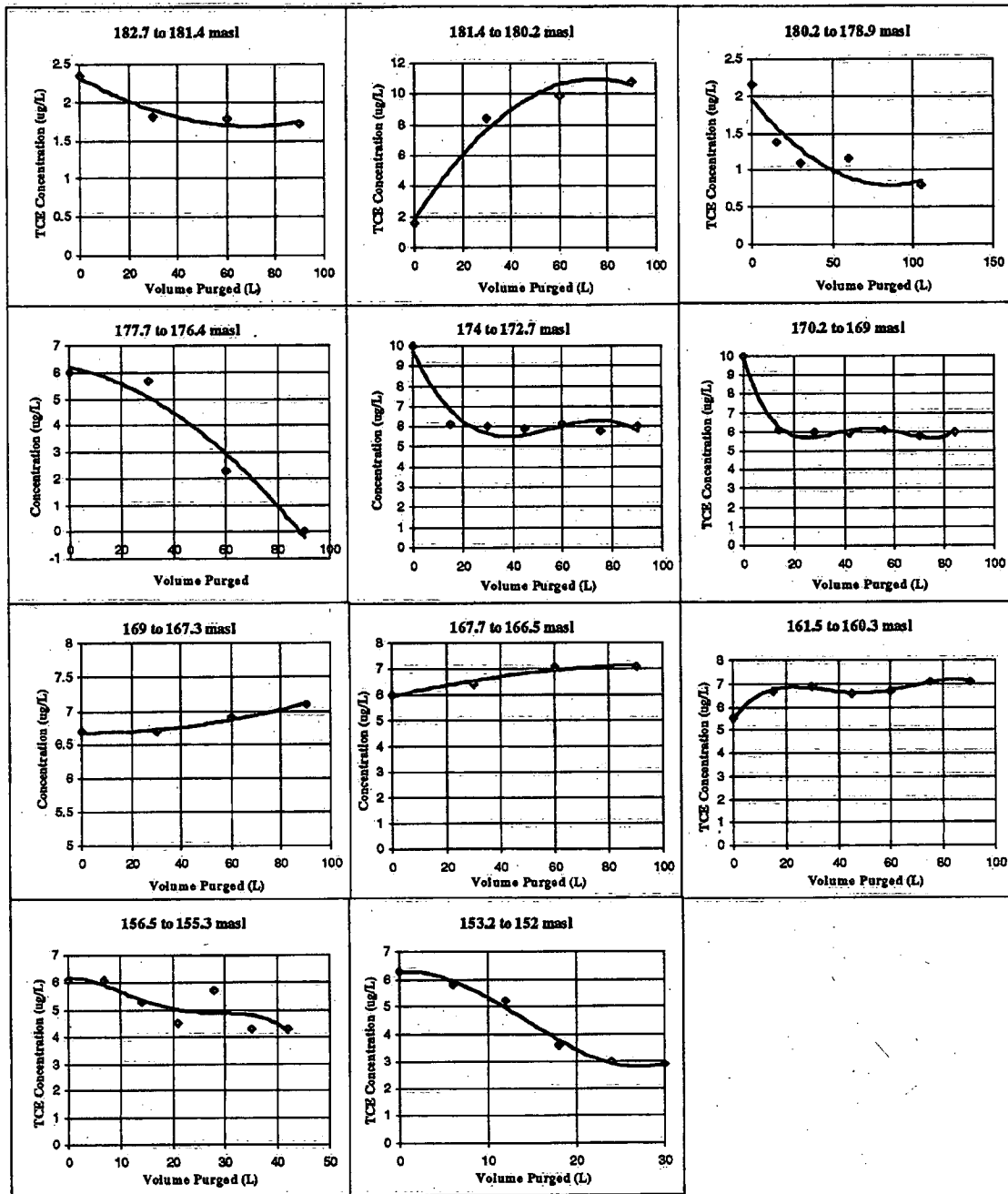


Figure 7: BH56 1.5 m profile time series results

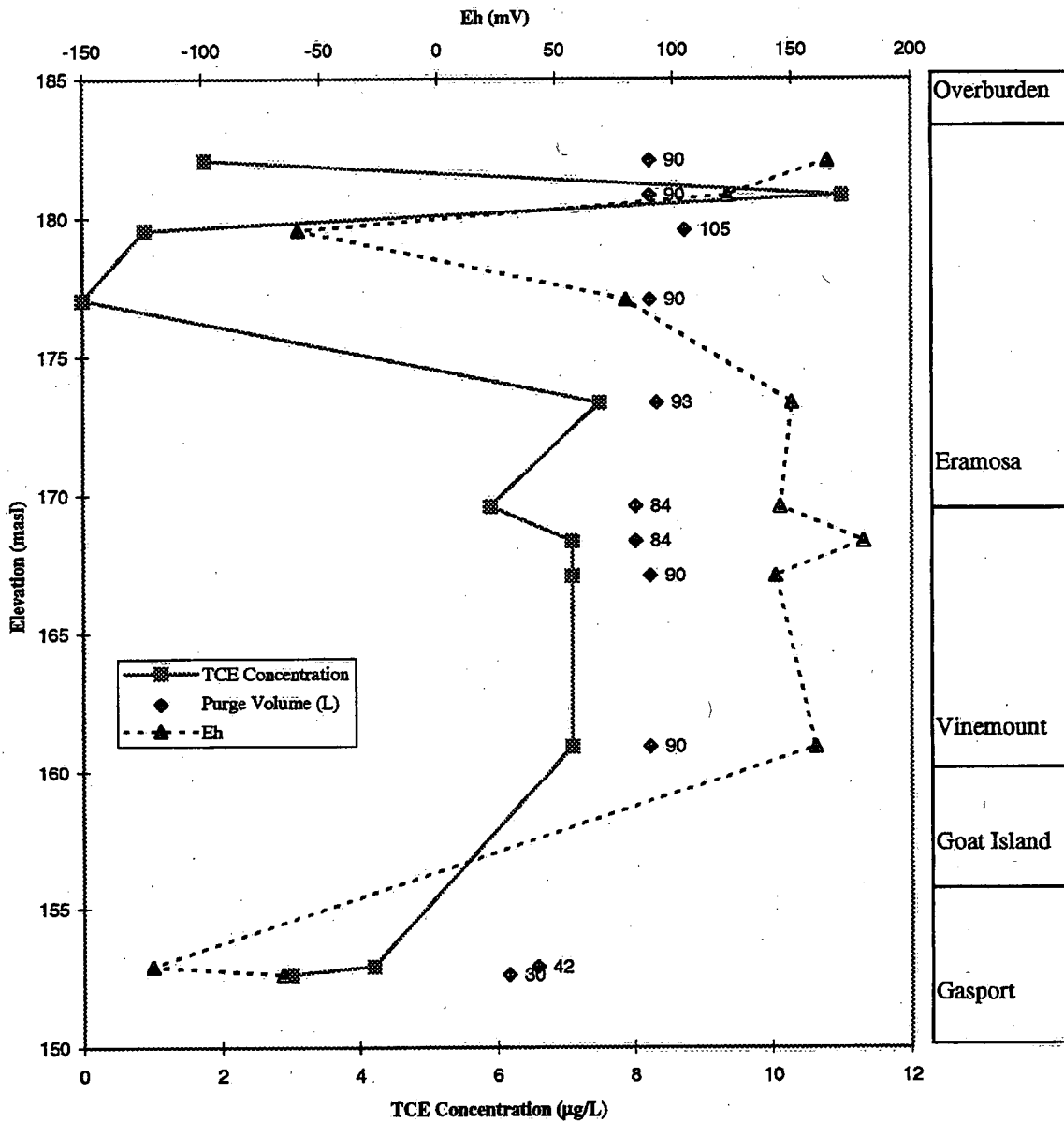


Figure 8: Borehole 56 - TCE concentration, Eh and purge volume comparison

\*The presence of C-DCE could not be confirmed in these samples because of problems with the quality control blanks

Borehole 56 had 10 targeted high transmissivity ( $T > 10^{-6} \text{ m}^2/\text{s}$ ) zones (Figure 6 a and b), in which 12 features were successfully isolated (Figure 6 d). The double packer-sampler was used exclusively for discrete feature location and sampling. TCE concentrations measured from discrete feature samples ranged between 0-17  $\mu\text{g/L}$  with little to no TCE observed in some features in the upper Eramosa (Figure 9). High TCE concentrations were generally associated with higher Eh (Figure 10), low dissolved oxygen (Figure 11) and high iron and sulfate concentrations (Table 5). Trichlorobenzenes were also detected throughout the fractures sampled, these concentrations generally followed the TCE profiles, but at levels of less than 1  $\mu\text{g/L}$  (Figure 12). Since TCE and TCB were both present in the original plume, a plot was prepared of the ratio of TCE concentration to TCB concentration (Figure 13). Where this ratio decreases, TCE is decreasing relative to TCB levels measured. All total PCB results were below the minimum detection limits. Results of discrete feature sampling are summarized below in Table 5.

**Table 5: Discrete Feature Results from BH56**

Zone Elevation		Total Volume Purged	TCE Conc.	c-DCE	Eh	pH	Dissolved Oxygen	Iron	Sulfide	Sulfate	Chloride	Lockport Formation Member	T
Start (masl)	End (masl)	(L)	$\mu\text{g/L}$		mV		mg/L	mg/L	mg/L	mg/L	mg/L		( $\text{m}^2/\text{s}$ )
184.3	184.2	15	3.9	yes	195	6.81	0.05	0.701	0.007	1511	20.1	Eramosa	2 E-04
183.8	183.7	8	0	no	178	6.86	0.05	1.07	0.018	3614	56.6	Eramosa	1 E-04
182.1	182.0	20	0	no	174	7	0.1	0.841	0.01	1027	9.1	Eramosa	6 E-05
179.9	179.8	22	0	no	164	7.09	1.5	0.478	0	353	7.4	Eramosa	4 E-04
176.8	176.7	70	0	yes	-36	7.23	0.5	0.132	0.0925	248	1.45	Eramosa	1 E-04
173.6	173.5	50	17.4	no	184	6.91	0.3	1.515	0	1193	19.5	Eramosa	8 E-03
170.5	170.4	60	14.4	no	228	6.9	0.02	1.33	0.0355	1155	13.3	Eramosa	1 E-05
167.7	167.6	40	11.2	no	200	6.91	0.04	2.12	0	1155	13.25	Vinemount	6 E-05
167.3	167.2	50	17.3	no	169	6.97	0.04	1.525	0	1160	31.4	Vinemount	5 E-04
160.8	160.7	45	14.4	no	172	6.86	0.2	1.225	0			Goat Island	3 E-03
153.1	153.0	60	6.5	yes	-86	6.9	0.08	1.08	0.897	1568	79.1	Gasport	5 E-07
151.7	151.6	65	11.7	yes	-65	6.86	0.06	0.099	0.24	1758	50.6	Gasport	1 E-06

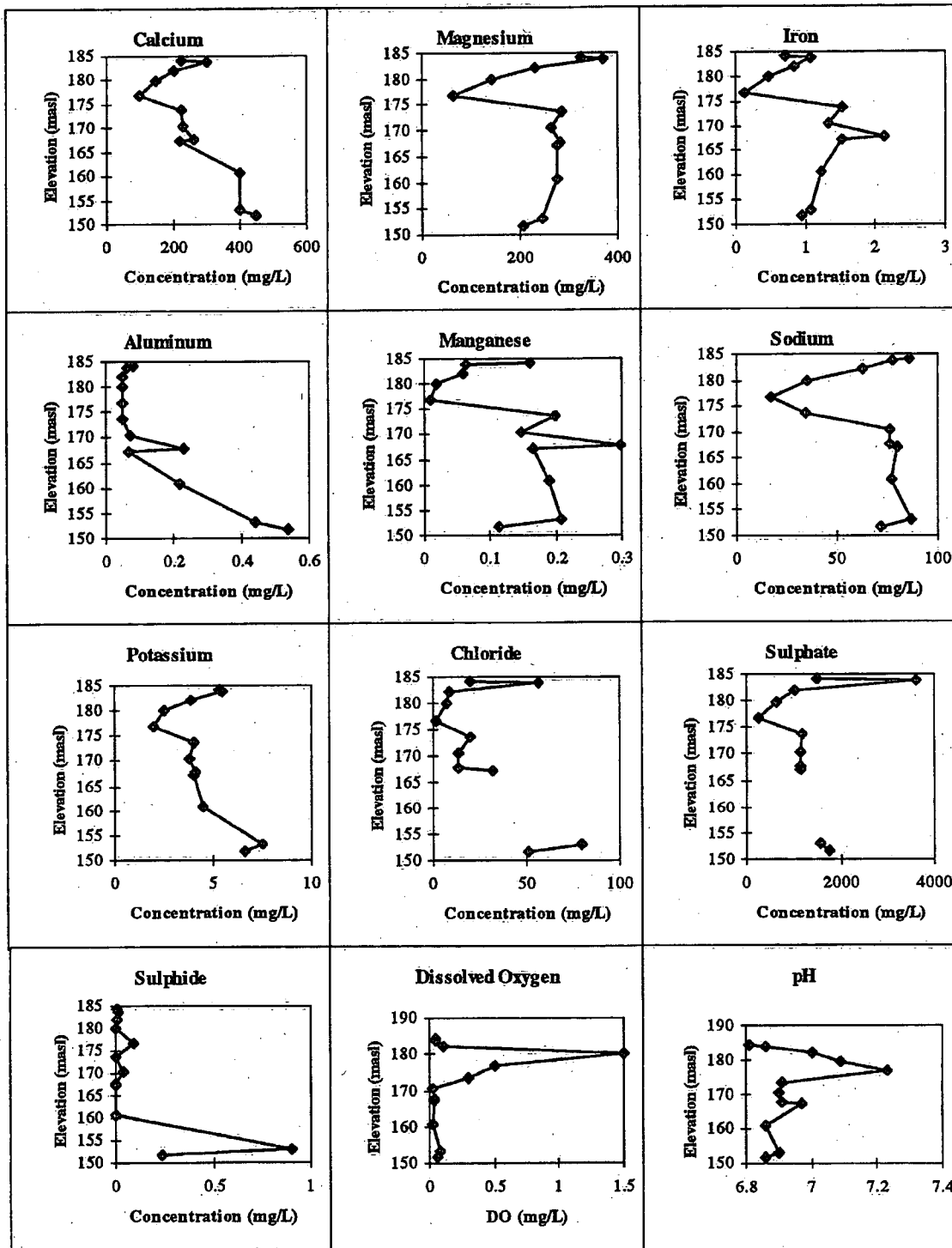


Figure 9: Geochemical results from discrete feature sampling at BH56

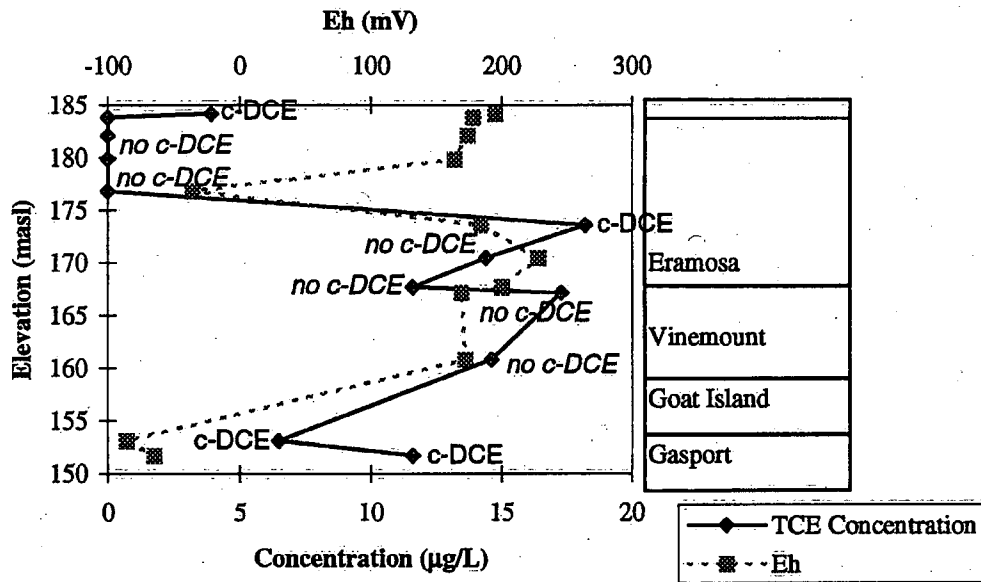


Figure 10: BH56 TCE and EH results

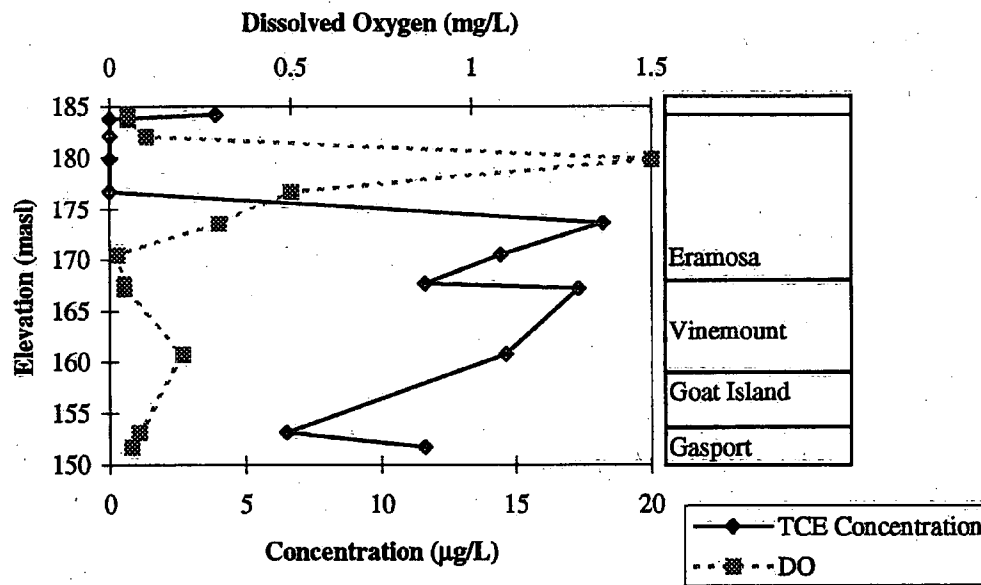


Figure 11: BH56 TCE and dissolved oxygen results



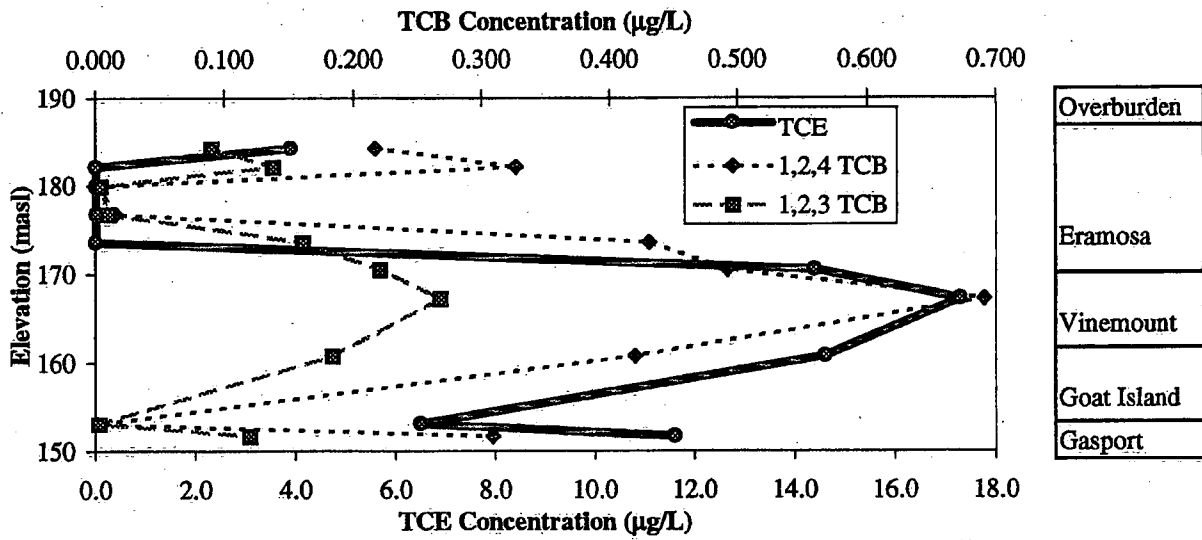


Figure 12: BH56 TCE and TCB concentration profiles

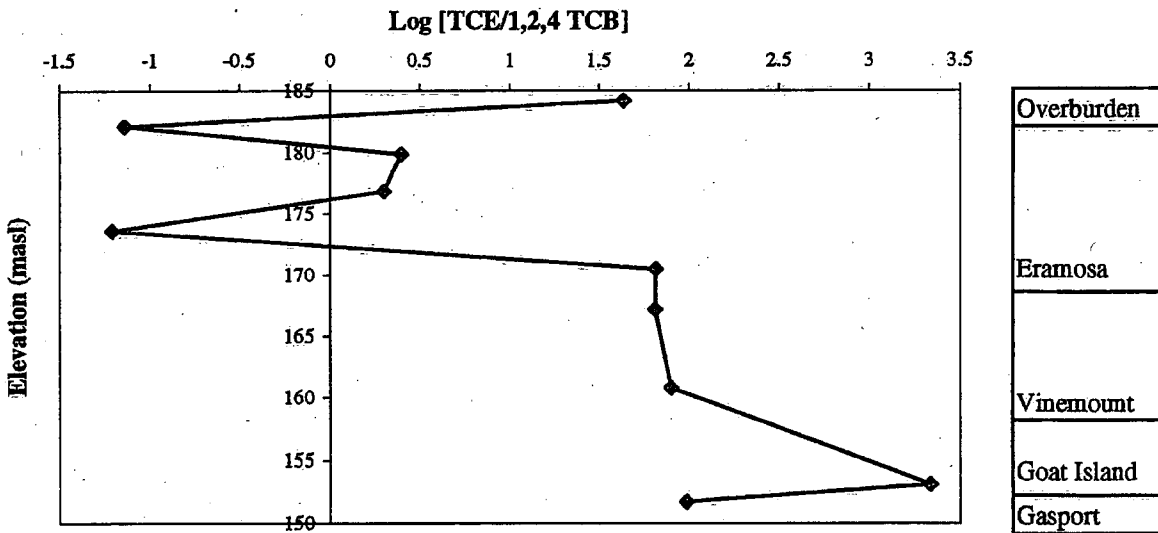


Figure 13: Ratio of TCE and 1,2,4 - TCB Concentrations at BH56

### Borehole 34C

A borehole profile including 15 sampled zones was developed at borehole 34C. Profiling occurred between 179 and 153 masl, through the Eramosa, Vinemount, Goat Island and Gasport units based on 2 m and 0.5 m hydraulic testing data (Figure 14 a and b), and excluded 171 to 177 masl due to cavities in this range. A complete summary of zone results is included in Table 6. TCE concentrations between 0 and 6 µg/L were observed in borehole 34C (Figure 14c). There were two distinct zones of relatively higher contamination in borehole 34C in the Vinemount and Goat Island units (175 to 160 masl and 165 to 159 masl), which also corresponded to higher redox potential zones (Figure 15). Contamination appeared to be vertically stratified, and separated by a zone of older, uncontaminated water in the lower Vinemount. Using SIM GC-MS analysis, c-DCE was also observed in all but the uppermost zones (Figure 15). TCE concentrations observed in borehole 34C were lower than those observed in borehole 56 (Figure 16), but zones of comparable concentration were observed between the holes, suggesting that attenuation is occurring and zones may be connected.

**Table 6: Borehole 34C Results**

Zone Elevation		Total Volume Purged	TCE Concentration	SIM Method Results			Eh	pH	Lockport Formation Member	T
Start (masl)	End (masl)	L	µg/L	c-DCE	1,2,4 TCB	1,2,3 TCB	(mV)			(m2/s)
178.8	177.52	80-100	0	no	yes	yes	133	7.06	Eramosa	1.E-04
171.2	169.97	80-101	0.7	no	yes	yes	-90	6.96	Eramosa	1.E-04
170.0	168.71	80-102	0	yes	yes	yes	-130	6.91	Eramosa	1.E-04
168.7	167.45	80-103	2.8	yes	yes	yes	150	7.02	Vinemount	1.E-04
167.5	166.20	80-104	4.5	yes	yes	yes	170	7.00	Vinemount	1.E-04
166.2	164.94	80-105	3.9	yes	yes	yes	170	7.00	Vinemount	1.E-04
164.9	163.68	80-106	2.1	yes	yes	yes	120	7.19	Vinemount	2.E-04
162.4	161.16	80-107	0.5	yes	yes	yes	-113	7.14	Vinemount	2.E-04
160.3	159.06	80-108	0.2				105	7.00	Goat Island	2.E-04
159.9	158.64	80-109	6.1	yes	yes	yes	190	7.10	Goat Island	2.E-04
158.4	157.09	80-110	1.2	yes	yes	yes	-109	7.00	Goat Island	2.E-04
157.8	156.55	80-111	3	yes	no	no	0	7.08	Gasport	2.E-04
156.3	155.00	80-112	4.1	yes	no	no	190	7.10	Gasport	2.E-04
156.1	154.87	80-113	5.62	yes	no	no	105	7.15	Gasport	2.E-04
154.9	153.61	80-114	6				150	7.16	Gasport	2.E-04

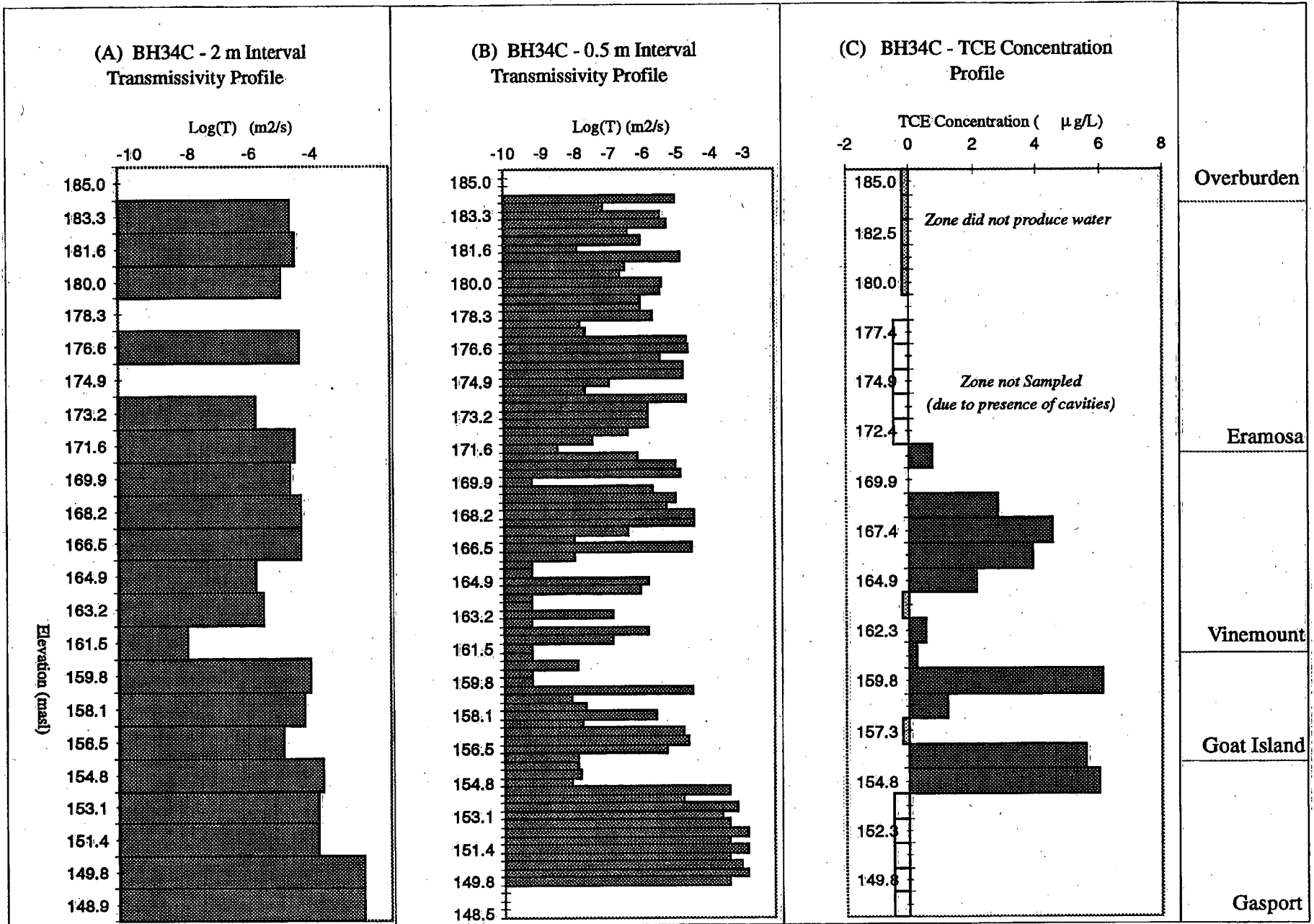


Figure 14: BH34C Results

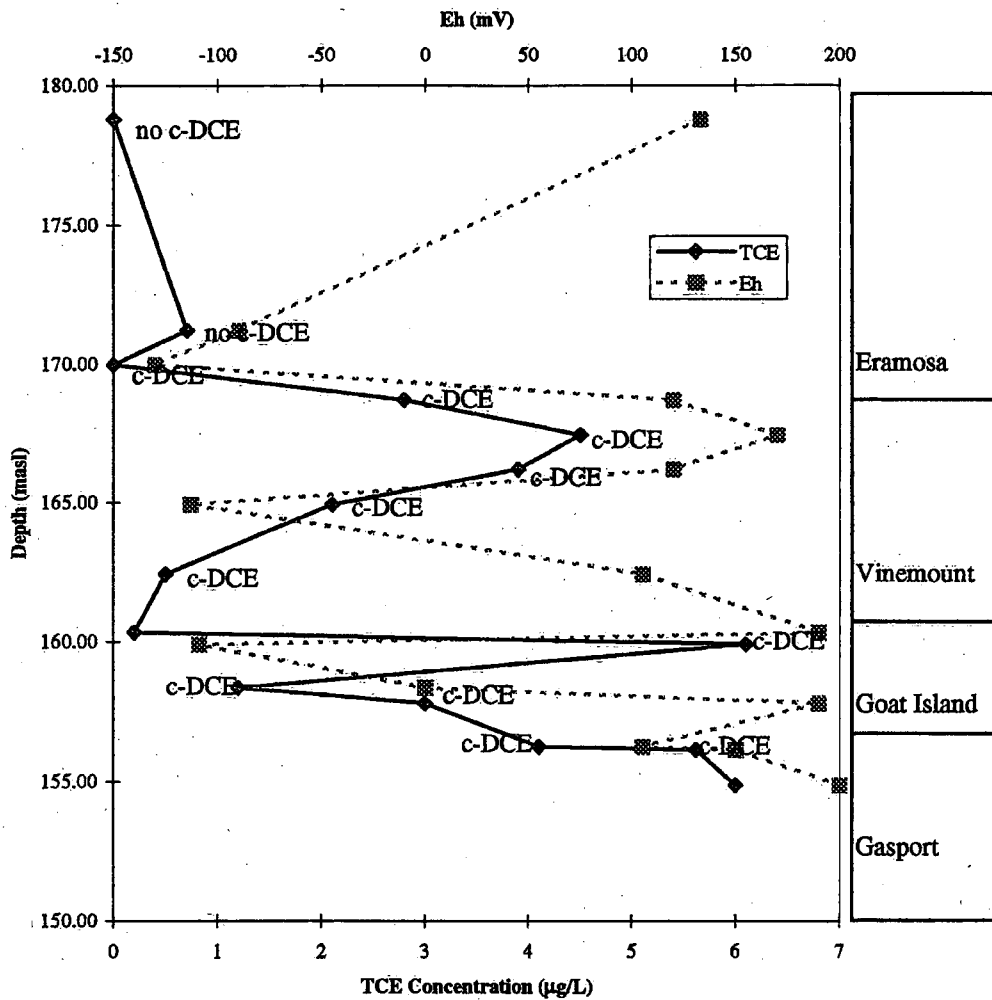


Figure 15: BH34C TCE and Eh results

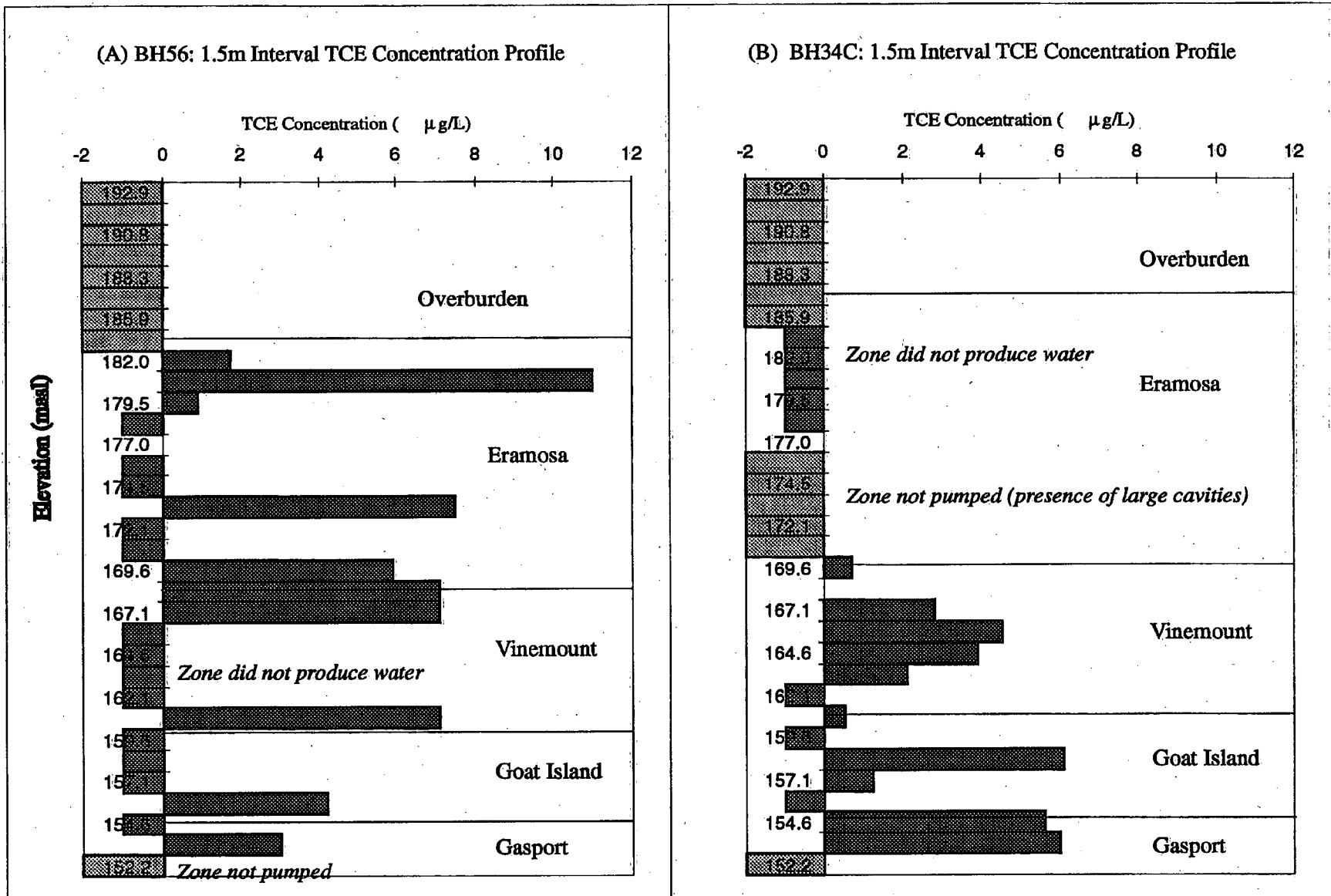


Figure 16: Comparison of BH56 and BH34C 1.5 m profile results

The principal objective of this study was to examine TCE contamination in the bedrock beneath the CWML site, specifically, the contamination of discrete rock features. TCE results from this work confirm contamination in large 1.5m zones throughout boreholes 56 and 34C (Figure 16) as well as in features in borehole 56 (Figure 6d). The highest concentrations observed were in discrete features, where TCE levels ranged from below detection limits to 18  $\mu\text{g/L}$ . This discrete feature concentration corresponds to a 1.5m zone with an observed concentration of 7.5  $\mu\text{g/L}$ . Concentrations were generally lower in the larger zones, likely due to dilution effects, since it is probable that multiple features of varying concentrations were contributing to the sample. Also, the larger pump, lines and higher flowrates ( $Q > 2 \text{ L/min.}$ ) may have also contributed to greater volatilization losses. Some of the larger zones sampled were in medium transmissivity areas. This might guide future fracture location work since fracture location focused on zones with transmissivities greater than  $10^{-6} \text{ m}^2/\text{s}$  which consequently overlooked medium transmissivity zones ( $10^{-7} < T < 10^{-6}$ ).

Since this study was conducted to investigate the presence of extremely volatile organic compounds at levels near instrument detection limits, it was important to ensure that results were representative of phenomena occurring in the groundwater in the study boreholes. Volatile organic compounds such as TCE and associated biodegradation products can volatilize, partition and further degrade which can alter measured concentrations. These factors were minimized by consistent sample preparation and storage and through other quality control measures. Another important consideration was whether a sample was representative of a larger zone possibly containing multiple features or a single feature. The presence of the borehole means that borehole water has mixed with water from different features. Sampling zones are generally purged to ensure that standing waters do not contribute to the sample. Traditionally zones are purged by flushing an arbitrary number of zone volumes, usually a minimum of three, or flushing until some field water

quality characteristics; such as Eh, pH, temperature or dissolved oxygen, stabilize (Gibbs and Imbriogiotta, 1990). Time series samples obtained from 1.5 m zones at borehole 56 demonstrated that a minimum of 3-5 purge volumes were required before TCE concentrations reached stable values (Figure 7). Even then, some samples responded differently to purging, with concentrations in certain zones decreasing to a stable value while other zones showed an increase in concentration. Representative samples appear, from this work to depend entirely on specific zone properties, including the number and transmissivity of features being sampled, as well the nature and extent of contamination. Time series results demonstrate that each zone behaves uniquely, depending on whether or not pre-existing contamination was or was not being diluted from openhole mixing. Redox potential is another possible indicator since Eh generally required at least 5 purge volumes to stabilize. However, since Eh is chemically unrelated to TCE concentration, it is not an absolute guideline (Gibbs and Imbriogiotta, 1990). Future work should continue to use time series data to ensure that samples are reproducible and representative.

The inorganic geochemistry results from this study were compared to recent results from site boreholes (Zanini et al., 1997). Similarities were noted between BH54D and geochemistry results from BH60, which is located approximately 1 km north-west of 54D. Borehole 60 has two zones located at elevations of 183 and 168 masl in the Eramosa and Vinemount units, which coincided with discrete features located in borehole 54D. The redox potential profiles in both holes were similar, positive in the shallow zones, and dropping sharply at approximately 175 masl, near the contact between the Eramosa and Vinemount units. A comparison of redox species profiles was difficult since only three features were analyzed at borehole 54D. However, metals and anion concentrations were comparable, though iron concentrations were more than 10 mg/L higher in the uppermost zone at BH60. When borehole geochemistry results from 54D were compared with similar results from BH62, which is approximately 700 m north east from 54D and has possibly



two overlapping zones in the Vinemount and Goat Island units (175 and 164 masl), no similar trends were observed.

Geochemistry results from BH56 in the aqueous contaminant plume were found to share some characteristics with borehole 53, a borehole located approximately 500 m directly south-west from borehole 56. Specific features located in borehole 56 are observed at similar depths in 5 zones in borehole 53 in the Eramosa, Vinemount, Goat Island and Gasport units (174, 168, 163, 151 and 146 masl). Both boreholes had maximum iron concentrations near the contact between the Vinemount and Goat Island units at approximately 160 masl which also coincided with low sulfate concentrations. Anion and cation profiles from the two boreholes had most maximum and minimum metals and anion concentrations occurring at comparable depths. Redox potentials between the two holes were generally quite different since Eh in borehole 53 decreased with depth and Eh in borehole 56 varied with specific features.

It is difficult to determine, how significant a comparison between a single feature and a larger zone of several metres can be, since a larger zone likely contains multiple features and it is not known if these are extensive or even interconnected. Also, samples obtained through Westbay instrumentation may be slightly different from those obtained via pumping. A qualitative comparison however does demonstrate that discrete feature sampling results resemble results from elsewhere on site. This similarity suggests that samples obtained from discrete features are comparable to, and consistent with site geochemistry, and likely representative of specific borehole geochemistry.

The findings of this study indicate that anaerobic biodegradation of TCE in the bedrock may be occurring in some zones and features. The presence of c-DCE supports this conclusion since no c-

DCE was in the original contaminant spill (Golder Associates Ltd., 1995). The anaerobic biodegradation pathway of TCE is first to cis or trans and then to vinyl chloride and to ethene (deBruin et al., 1990). These results are only qualitative since all c-DCE measurements had low signal to noise ratios of less than 5, preventing quantitative detection.

Evidence of TCE removal from some upper features was provided by the presence of trichlorobenzenes in discrete features. TCBs are more resistant than TCE to biodegradation, and may be used as tracers, marking the movement of the contaminant plume. The presence of TCB and a lack of c-DCE in the uppermost features suggests that TCE is being removed by a mechanism other than the typical anaerobic pathway. For example, aerobic biodegradation of TCE can cometabolize both TCE and natural gas to reduce TCE to TCE epoxide and finally to organic acids and carbon dioxide (Wilson and Wilson, 1985). Since TCBs are present in several of the uppermost features, the plume may be assumed to have spread through these fractures. The decline of the ratio of TCE to TCB concentrations in these upper features (Figure 13) indicates that TCB from the plume is moving through these features, and TCE has been removed. Since no c-DCE was detected, and the uppermost zones have high Eh and dissolved oxygen (Figures 10 and 11), biodegradation activities would likely be aerobic. While present evidence supports the possibility aerobic biodegradation, since no effort was made to determine if aerobic biodegradation products were present, this possibility can not be verified as yet.

Results from this work confirm that contamination extends into the deeper units of the Lockport formation, however, the presence of anaerobic biodegradation products suggests that bioremediation is also occurring in all but the most oxic features and zones. The lower TCE concentrations measured in the uppermost features may also be a function of continuing pump and treat operations around the perimeter of the contaminant source area. The treatment wells extend

to the upper bedrock and may be reducing contamination in some of the highest features. The presence of TCBs in these same zones however indicates that the contaminant is migrating through these features, if at reduced levels. As previously mentioned, the low ratio of TCE to 1,2,4-TCB concentrations (figure 13) also indicates that there is a decline in TCE relative to TCB levels in these upper features of the Eramosa from 173 to 183 masl. Since trichlorobenzenes were a component of the original contaminant spill, they indicate the presence of the plume.

## Conclusions

The findings of this study confirm TCE contamination in larger 1.5 m zones and in discrete features throughout the Lockport formation underlying the CWML Smithville site. Results from larger zones, discrete features, time series and geochemical data demonstrate that the field methods developed specifically for this work yield reproducible and representative results. No single source of TCE contamination was isolated, but rather, zones and features with a range of concentrations of TCE from 0 to 17  $\mu\text{g/L}$  were located in borehole 56, approximately 100m from the source area. Concentrations observed in discrete features were higher than those observed in the larger, corresponding zones. This suggests that fractures are the principal transport pathways for TCE and it is likely that less contaminated features in the larger zones contribute to the dilution and averaging of concentrations across the 1.5m sampling interval. TCE contamination has also been observed in both boreholes 56 and 34C in the Gasport unit (150 masl), confirming that TCE has been carried to depth, in both boreholes down gradient from the source of contamination. Biodegradation of TCE is observed to occur, since c-DCE, an anaerobic biodegradation product has been confirmed in most lower zones and features. The lowest contaminant concentrations coincide with low redox potential zones, suggesting enhanced biodegradation in more anoxic environments. Trichlorobenzenes have also been measured in these features, and since these resist degradation, higher TCB concentrations at depth act as tracers which suggest natural biodegradation of TCE. Low TCE and high TCB concentrations in the uppermost zones which have higher dissolved oxygen and high Eh suggest that aerobic biodegradation may be occurring. Future work may be focused on the development of techniques for the measurement of aerobic biodegradation products, including carbon dioxide, and organic acids.

Biodegradation offers a potential solution for the contamination problem in the CWML site bedrock. However, more knowledge about the mechanism of this process is required in order to determine if the process can be artificially enhanced and accelerated. Information about the substrate type and availability for both aerobic and anaerobic biodegradation should be determined since substrate addition may enhance natural biological activity leading to the complete removal of TCE from the groundwater system. If possible, current methods should be modified to measure the trace levels of biodegradation products present and assess the rate of biodegradation. Field work might also be conducted to measure methane levels, since aerobic biodegradation may occur through cometabolism of methane and TCE. In situ bioremediation including the possible aerobic and anaerobic biodegradation of the TCE in the groundwater at the CWML should be further investigated to evaluate its remediation potential.

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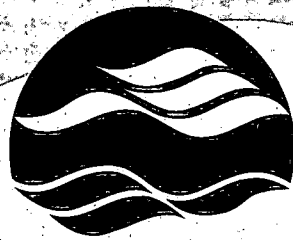


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