GREAT LAKES INSTITUTE REPORT
ON
AN ASSESSMENT OF SEEPAGE OF GROUNDWATER
INTO THE ST. CLAIR RIVER
NEAR SARNIA, ONTARIO, CANADA

FINAL REPORT
FOR
ENVIRONMENT CANADA
OTTAWA, ONTARIO

BY
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SUMMARY

The main objective of this research program has been to determine the quantity, quality and source(s) of groundwater seepage from the streambed into the St. Clair River in the vicinity of Sarnia, Ontario, Canada.

We installed 17 survey lines on the bed of the St. Clair River in a 100 m by 7 km band between Sarnia Bay and the Sarnia Indian Reserve. The survey lines extended 100 m from shore at an angle of approximately 90° to the shore. We collected soil cores along the survey lines in conjunction with river bottom descriptions to characterize the river bed. On the survey lines which had at least 100's of mm of granular material, we installed seepage meters to measure seepage rates. Significant seepage was noted on two of the seven survey lines that contained the granular bottom sediments. We used minipiezometers on these two survey lines to collect streambed groundwater from depths of 1.0 and/or 1.5 m below the river bed. We determined the electrical conductivity, pH and temperature of the streambed groundwater and river water samples in the field. Selected river water and streambed groundwater samples were also analyzed for: chlorinated hydrocarbons, polychlorinated biphenyls, trihalomethanes, EPA Priority Pollutants (extractables), total organic halides (TOX), chloride, and natural isotopes (oxygen-18, deuterium, and tritium).

Some of our most important observations are that:

1. the average observed seepage rate of 1.4×10^{-8} $m^3/s/m^2$ suggests higher than expected hydraulic conductivity or hydraulic gradients in

the streambed, 2 to 4 orders of magnitude greater than determined in other studies,

2. detectable but not excessive levels of some organic contaminants were found in the streambed groundwater samples, ie., <0.0067 ug/L total chlorinated hydrocarbons, <0.026 ug/L PCB, <2.77 ug/L trihalomethanes, and <2.4 ug/L base neutral extractables,

3. isotopic and electrical conductivity data indicate that:
   - the streambed groundwater is not just river water
   - 'virgin' groundwater from the freshwater aquifer does not apear to be a significant component of the streambed groundwater
   - some of the streambed groundwater may be partially derived from shallow groundwater
   - an unidentified source of water contributes to the streambed groundwater,

4. from isotopic data there are indications that previously undocumented parts of the freshwater aquifer in Lambton County have been affected by waste injection.

ACKNOWLEDGEMENTS

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AN ASSESSMENT OF SEEPAGE OF GROUNDWATER
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1.0 INTRODUCTION

Between 1958 and 1975, several industries in Lambton County, Ontario, Canada, used on site "deep well" disposal systems for their liquid waste disposal. They injected over 8 x 10^6 m^3 of liquid industrial waste into 16 wells completed to the Detroit River Group limestone formation, approximately 205 m below the ground surface. The injected wastes included a wide range of both organic and inorganic substances produced as by-products of the petrochemical industry, however, the exact nature of these wastes is not well-documented (Rathbone, 1983). In addition to the waste compounds injected into the wells, the products of downhole chemical reactions amongst the various injected wastes and between the wastes and the disposal unit rocks are another potential source of contaminants in the disposal unit. There have been several indications that the waste has migrated at least 1 or 2 km from the injection wells and that above-ground head conditions have developed over a considerable area (Rathbone, 1983).

The main water supply aquifer in Lambton County, the "freshwater aquifer", consists of a relatively thin deposit of granular overburden overlying the bedrock surface. Above the aquifer most of the overburden is low permeability silty clay till (Quigley and Ogunbedjo, 1976; Desaulniers et al., 1981) which varies in thickness from about 15 m in the eastern part of Lambton County to about 45 m near the St. Clair River in the west. Under natural flow conditions, the hydraulic head in the Detroit River Formation was reported to be some 60 m below the base of the freshwater aquifer (Rathbone, 1983). However, even though the disposal unit is overlain by about 150 m of shale and dense carbonate rock and 45 m of overburden, it is believed this formation is too shallow to ensure the safe disposal of liquid waste (Simpson, 1978).

The occurrence of contaminated, shallow, flowing water wells in the Sarnia area of Lambton County in the early 1970's, coincident with the greatest subsurface waste injection activities, strongly indicates that the deep well disposal of wastes pressurized the Detroit River Formation to such an extent that at least localized contamination occurred in the freshwater aquifer. Piezometric data from the Canadian side of the St. Clair River (Vandenberg et al., 1977) suggest that flow in the freshwater aquifer is toward the St. Clair River. Although there is a considerable thickness of low permeability clayey till between the streambed and the freshwater aquifer, it is conceivable that there are fractures in the till and that there is a sufficient upward hydraulic gradient to move contaminated water from the freshwater aquifer into the river.

2.0 OBJECTIVES AND SCOPE OF STUDY

The main objective of this research program has been to determine if there is any discharge of the freshwater aquifer into the St. Clair River, and if there is, to determine the quantity, quality and source(s) of the seepage. The problem was approached and studied in several ways:

1. streambed sediment sampling, seepage meters, and minipiezometers were

used to map the distribution of groundwater seepage from the St. Clair River streambed and to obtain samples for organic contaminant analyses, and

2. in order to determine the source(s) of the water in the streambed sediments, field measurements of pH, electrical conductivity (EC), and laboratory analyses of environmental isotopes (oxygen-18, deuterium, and tritium) were used to compare the streambed water to the river water, shallow groundwater from fractured clayey deposits near ground surface, and groundwater from the freshwater aquifer.

3.0 DISCUSSION OF TECHNIQUES

The field studies involved river bottom characterizations, core sampling, and the use of seepage meters and minipiezometers to determine the nature of the river bottom and distribution of groundwater seepage. Seepage flux rates were determined through the use of the seepage meters, and chemical analyses were performed on water samples collected from the minipiezometers.

3.1 RIVER BOTTOM CHARACTERIZATION/CORE SAMPLING

We installed 17 survey lines on the bed of the St. Clair River in a 100 m by 7 km band between Sarnia Bay and the Sarnia Indian Reserve (Figure 1, map of survey lines and study area) (Appendix 1, survey line locations). During the survey line installation, our divers collected stream bed core samples to aid us in the selection of appropriate sites for later seepage meter and minipiezometer installation. The divers used modified Oakfield Model C Soil Samplers which they tapped into the river bottom to a depth of 46 cm. They

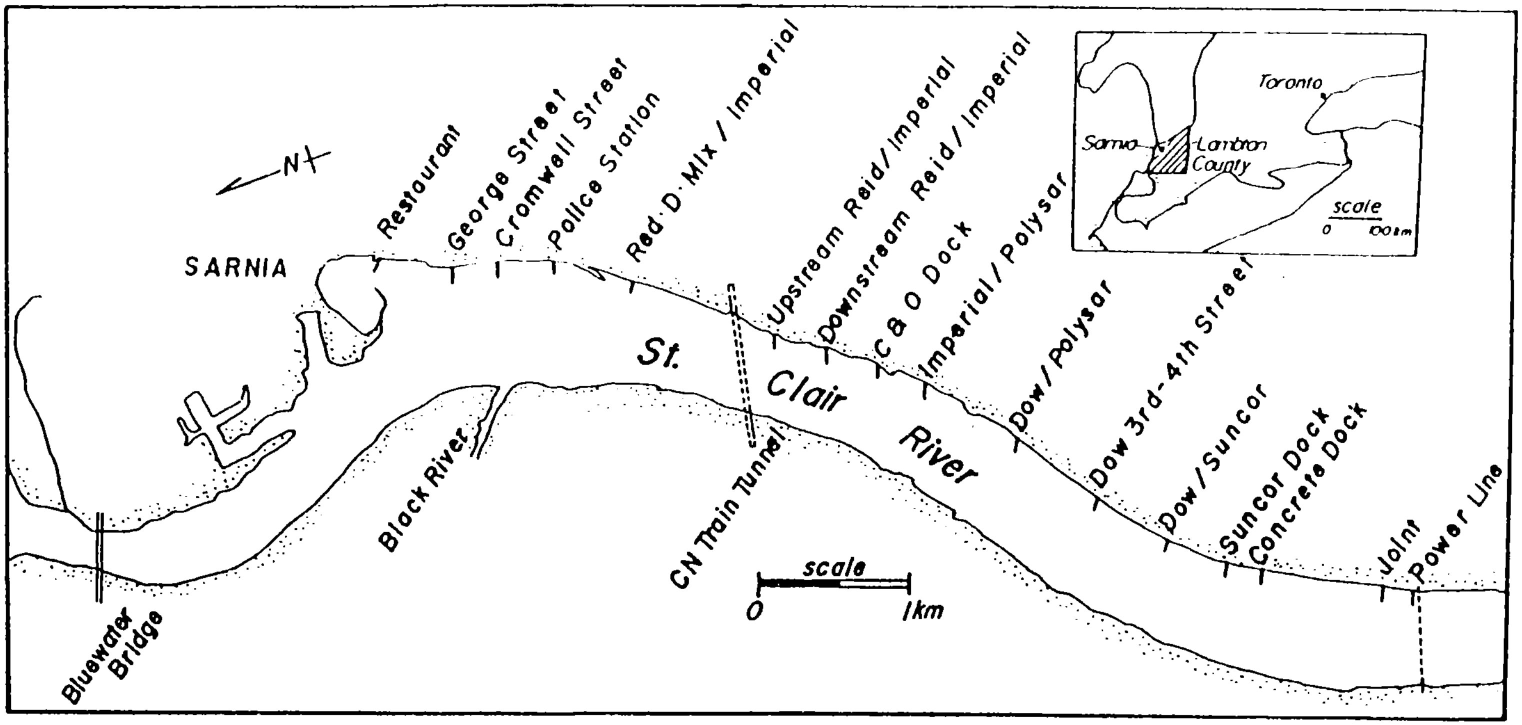


Figure 1. Map of streambed survey lines and study area.

collected bottom cores at the midway points between adjacent stations (between 5 m and 85 m from shore). After pulling the sampler from the stream bed, the divers slipped the core tube into a PVC plastic tube to bring it to the surface.

Once the divers returned to the boat with the samples, the core tubes were examined for core recovery and core description. We assumed that zero recovery or missing core sections represented either a plugged corer, or granular material which had been blown of the core tube by the river current during delivery to the boat.

3.2 SEEPAGE METERS

The surface water-groundwater interaction in lake bottoms and stream beds is often controlled at or near the sediment-water interface (Lee, 1977). Depending upon the interaction, groundwater flow in lake bottoms and stream beds can be upward, downward or horizontal. The direction and rate of flow is dependent upon the texture, statigraphy and physiography of the subsurface materials (Lee and Cherry, 1978). Local flow can vary considerably from one location to another providing a variety of observational conditions within a single study area.

We studied the nature of the hydrologic interactions between the groundwater and the river water in the St. Clair River primarily by using two devices: seepage meters and minipiezometers.

The seepage meters, installed in the sediment on the river bed, were used to identify groundwater inflow into the river and to determine the spatial and temporal variations in seepage flux through the river bottom sediments. The principle of the seepage meter is that the seepage flux between the groundwater and the overlying surface water can be measured directly by covering a known area of river bottom sediment (by an open-bottomed seepage meter) and measuring the collection time and water volume change in a sample bag attached to the seepage meter.

The seepage meters were installed on 8 survey lines where bottom cores indicated the existence of considerable granular material. During installation, the seepage meters were twisted into the bottom sediments in such a manner to insure that the vent hole was elevated slightly allowing any gas from the sediment to freely escape (Figure 2).

Seepage meters used in this study were a modified version of Lee's (1977) seepage meter design. Modifications were necessary to adapt these seepage meters for use in the fast flowing and deep water in the St. Clair River, groundwater of unknown quality, and a need to reuse the meters several times.

The seepage meters were fabricated from 1.6 mm thick, #304 stainless steel, rolled and welded into 50 cm diameter cylinders, 15 cm high. A top was constructed of the same material and welded to each cylinder. A single 10 mm O.D., 0.035 " wall #304 stainless steel tube, located 5 cm from the edge of the top, allowed seepage to escape. A brass quick connect/disconnect mechanism at the end of this tube was attached to our collection bag appartus. The quick connect/disconnect mechanism prevented any loss or

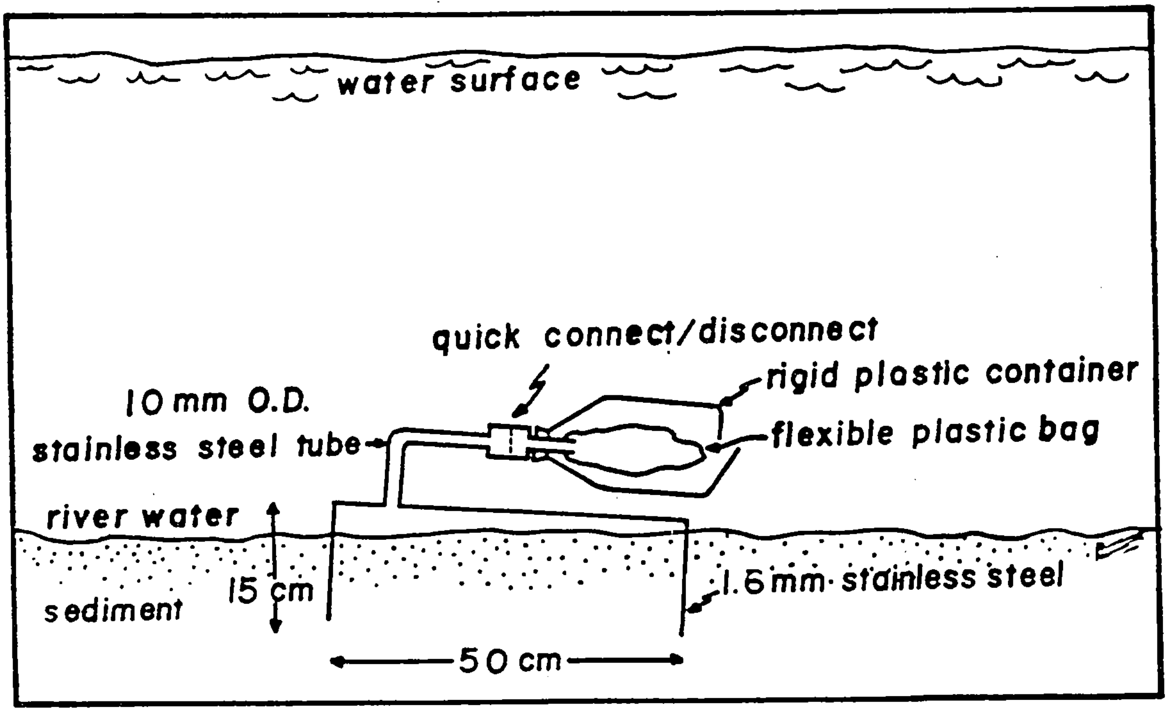


Figure 2. Schematic diagram of modified seepage meter.

addition of water during collection and transport of the collection bag.

The collection bag apparatus contained a flexible plastic bag placed inside a rigid plastic container which was used for protection from the river current. The brass connect/disconnect was attached to a stainless steel tube that extended through a hole in the plastic bottle cap into a rubber stopper fit into the neck of the bottle. An opening was cut into the bottom of the rigid plastic bottle which allowed examination of the collection bag and aided in keeping the bag at an ambient river bottom hydraulic head.

The collection assemblies were replaced every one to three days with several assemblies being left on the seepage meters for up to nine days in order to determine any temporal variations in seepage rates. The accumulated seepage in the collection bags was measured in a plastic graduated cylinder after every recovery. Samples of seepage water were retained for field measurements of pH, electrical conductivity (EC) and temperature. No further chemical parameter testing was done on any of these samples due to the generally low seepage rates (and the resultant incomplete displacement of river water by seepage water in the meter) and because of the possible contamination from surface sediments.

3.3 MINIPIEZOMETERS

The second device used to determine the quality and source(s) of seepage water from the bed of the St. Clair River was the minipiezometer. We installed minipiezometers at sites where significant seepage was measured. The minipiezometers designed for this study had to address several potential problems including: the difficulty in installing any tall or wide instruments in the strong river current, unknown streambed material below a depth of about 50 cm, ease of installation by the divers, ease of attachment to the pumping equipment, and potentially contaminated surface sediments.

The minipiezometers were constructed of 10 mm O.D., 0.89 mm wall thickness #304 stainless steel tubing, 1.0 and 1.5 m in length (Figure 3). The bottom of each piezometer contained a #304 stainless steel screen (0.15 mm diameter holes, 0.64 mm spacing between hole centres) which permitted the entry of pore water from the river bed sediments. This screen was kept in place by a stainless steel spring which allowed removal for cleaning.

Prior to installation of the minipiezometers, a 50 cm stainless steel casing, with a cap on the bottom, was driven through the upper sediment to ensure that the minipiezometer tip did not come into contact with the upper sediments (especially those which may have been contaminated). This cap was released as the minipiezometer was pulled back about 2 cm. Drive heads were welded to the minipiezometer and the casing to aid in installation. Figure 3 shows the small diameter outlet end which accepted the small diameter teflon tube that was used during sampling.

The minipiezomters provided a means of sampling the water at and beneath the river bed to depths ranging from 1.0 m to 1.5 m below the river bottom. Prior to and during installation, the minipiezometers were pre-washed by pumping distilled water through the teflon tube. This pre-pumping also aided in keeping the screen clean during installation. Upon installation and prior to sample collection, water was drawn through the teflon tube from the minipiezometer by a Masterflex Model 7570 peristaltic pump. Water was drawn

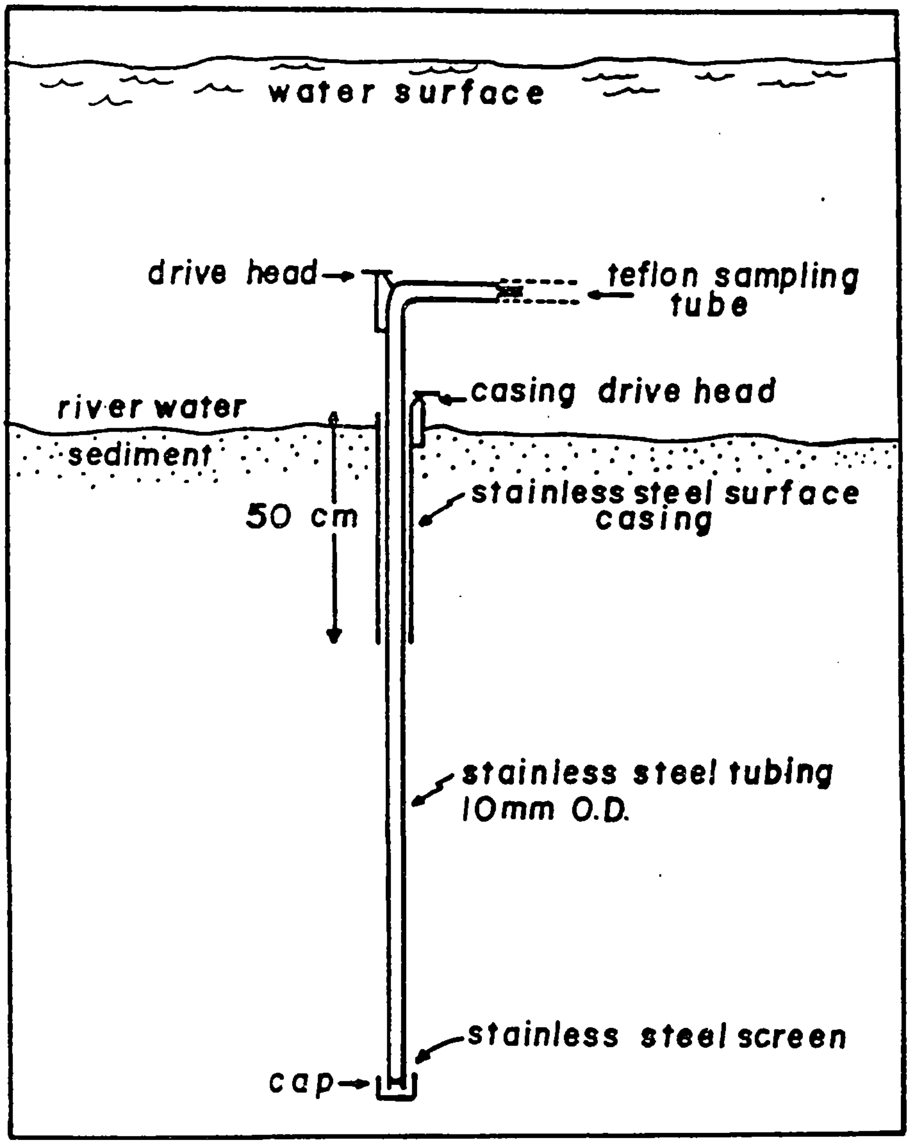


Figure 3. Schematic diagram of a minipiezometer.

for a minimum of 10 minutes and until the electrical conductivity stabilized, before samples were collected and the pH, EC and temperature were recorded. Waiting for the stabilization of the EC was necessary to ensure that adequate purging of the pre-pumped distilled water had taken place before sample collection. The temperature measurements were not considered representative of the bottom sediment environment since the extracted water had to pass through at least 10 m of teflon tubing before reaching the surface for collection. The pH was measured in a closed flow cell to prevent exposure of the water to the air.

During sample collection three samples of water were collected at each location: a 1L amber bottle (no head space) with metal lined cap was collected for TOX and GC/MS analysis, a 40 mL amber glass vial (no head space) with a teflon coated septum lined cap was collected for chlorinated hydrocarbons and volatiles, and a 250 mL nalgene plastic bottle (no head space) was collected for isotopic analysis. For the volatile samples, the pump was stopped prior to sampling and the minipiezometer was allowed to recover in order to reduce the formation of gas bubbles in the teflon tubing and to minimize the potential for loss of volatiles.

Once the streambed groundwater samples at depths of 1.5 m and 1.0 m were collected, the teflon tube was disconnected from the minipiezometer and river water was pumped until a constant electrical conductivity was attained, at which time samples of river water were collected. Temperature, pH and electrical conductivity were measured on river water and streambed groundwater samples at the time of collection. Selected samples of river water and streambed groundwater were analyzed for; chlorinated hydrocarbons, polychlorinated bihpenyls, trihalomethanes, EPA Priority Pollutants (extractables), total organic halides, chloride, and nautral isotopes (oxygen-18, tritium and deuterium).

After collection, the samples were stored on the boat in a cooler with cold packs until they could be refrigerated on shore. They were sent by courier as soon as possible to Zenon Environmental Inc., of Burlington, Ontario for organic analysis. Samples for isotopic analysis were sent to the Isotope Laboratory, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario.

We had intended to use the minipiezometers to determine the hydraulic gradient in the streambed sediments. Due to excessive gas bubble formation in the teflon tubing, accurate measurements of hydraulic heads in these piezometers were prohibited.

3.4 ENVIRONMENTAL ISOTOPES

Environmental isotopes are naturally occurring isotopes which can be used in investigations of groundwater and surface water systems. Oxygen-18 (^{18}O), tritium (^{3}H or T) and deuterium (^{2}H or D), are the three most commonly used environmental isotopes in hydrogeological studies and were the isotopes used in this study. These isotopes are commonly used largely because they are constituent parts of water molecules. Tritium is normally used as a guide to the age of groundwater while ^{18}O and D are used mainly to provide information on the type, origin and movement (transit time) of groundwater and surface water. Generallly, if the isotopic content does not change within the aquifer, this lack of change will reflect the origin of the water. If the isotopic content does change, this change will reflect the history of the water. The orgin deals with the location, period and process of recharge, while the history encompasses the mixing, movement and discharge processes (Fritz and Fontes, 1980). The natural isotopes were very important in this study, for their concentrations and distributions provided information on the age and origin of the waters collected in the minipiezometers.

The stable isotopic compositions such as ^{18}O and D are normally measured with reference to a standard. The commonly accepted international standard is Standard Mean Ocean Water (SMOW). The isotope ratios (ratios of heavy to light isotopes) are expressed in delta units ($\underline{\delta}$) as per mil differences (parts per thousand or ‰), relative to this standard (Craig, 1961a):

$$\delta^{18}O \text{ or } \delta D = [(R_x - R_{standard}) / R_{standard}] \quad X \quad 1000 \ (‰)$$

where: R_x and $R_{standard}$ are isotope ratios of $^2H/^1H$ or $^{18}O/^{16}O$, of the sample and the standard respectively. Analytical precisions for oxygen-18 and deuterium analyses by mass spectrometry are better than 0.2 ‰ and 2.0 ‰ , respectively.

The various isotopic forms of water have slightly different vapour pressures and freezing points. These two properties give rise to differences in ^{18}O and D concentrations in the water in the various parts of the hydrologic cycle. These variations are primarily the result of fractionations caused by phase transitons, chemical or biological reactions and transport processes.

In shallow groundwater flow regimes with normal temperatures, ^{18}O and D are non-reactive, naturally occurring tracers. Their concentrations, under these conditions, are altered only by physical processes such as: mixing, diffusion, dispersion, and radioactive decay. These concentrations are determined by the isotopic composition of the precipitation that falls on the ground surface and by the amount of evaporation that occurrs before the water penetrates below the upper part of the soil zone. Once this water moves below the upper part of the soil zone, the ^{18}O and D concentrations become a characteristic property of the subsurface water mass. These characteristics enable the source areas and mixing patterns to be determined by sampling and analysis for these isotopes (Freeze and Cherry, 1979).

Craig (1961b) found that the concentrations of ^{18}O and D in unevaporated meteoric waters are linearly related through the well known meteoric water line:

$$\delta D = 8\delta^{18}O + 10$$

Waters which have been evaporated plot below the meteoric water line on straight lines with slopes of between 2 and 5 (Fontes, 1980).

The number of condensation stages resulting in precipitation and ambient conditions of subsequent evaporation basically control the stable isotope concentrations or enrichment in waters. The degrees of enrichment of these stable isotopes are different during evaporation and condensation. It is this variation that causes a departure of ^{18}O and ^{2}H concentrations from the meteoric water line. The condensation process, referred to as "isotopic fractionation" (the partioning of isotopes between two substances with two different isotopic ratios), is mainly temperature dependent and to a lesser degree affected by pressure change. The causes of the temperature variaton can be translated in terms of altitude, amount, distance to source of vapor, paleoclimate and seasonal and/or short term variations (Fritz and Fontes, 1980).

Dansgaard (1964) and others have demonstrated that isotopic variations in precipitaion around the globe are linearly related to mean annual temperature (Figure 4). This relationship has been used by Fritz et al. (1974), Desaulniers et al. (1981) and others to estimate the age of groundwater. Fritz et al. (1974) used the oxygen-18 content of fossil shells to demonstrate that the climatic conditions in southern Canada have remained much the same for about the last 10,000 years and that much colder temperatures prevailed prior to that time (Figure 5). Based on this argument, Desaulniers et al. (1981) have suggested that: (1) the $\delta^{18}O$ values of shallow groundwater in southwestern Ontario which are similar to the current rain $\delta^{18}O$ values (approximately -10 ‰), represent recent recharge (<10,000 years) compared to (2) the $\delta^{18}O$ values of deep groundwater in southwestern Ontario which are very depleted in oxygen-18 relative to current precipitation (approximately -17 ‰) which represent recharge which occurred more than about 10,000 years ago, and (3) intermediate $\delta^{18}O$ values which represent mixtures of older and younger waters.

For a given atmoshperic vapor, the more pronounced the cooling process, the more depleted in ^{18}O and ^{2}H is the vapor phase. Multi-stage cooling gives a condensed phase (liquid or solid) progressively depleted in heavy

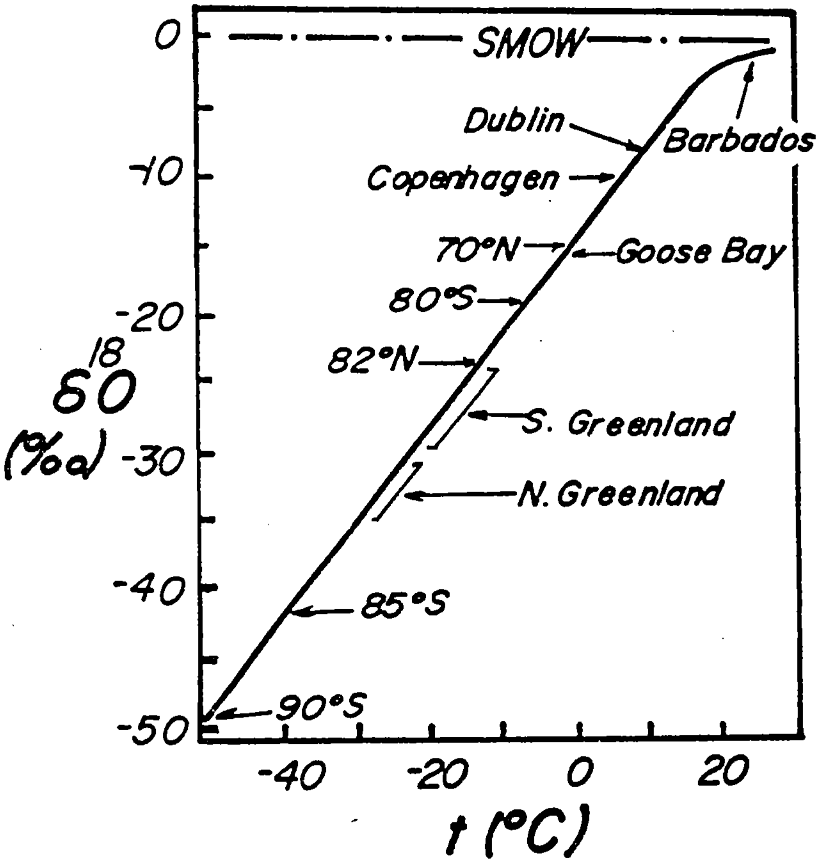


Figure 4. Oxygen-18 in precipitation versus temperature (after Fontes, 1980).

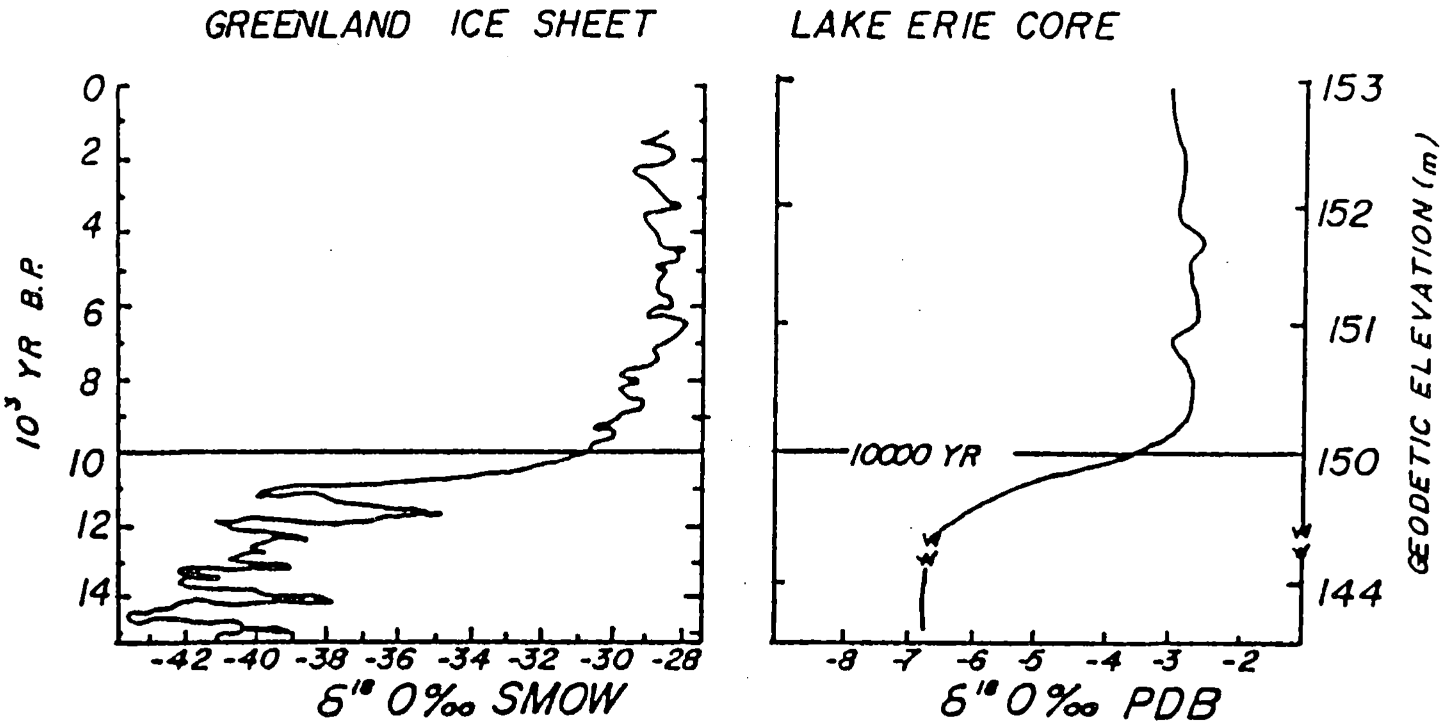


Figure 5. $\delta^{18}O$‰ in meteoric water over the past several thousand years (after Fritz et al., 1974).

isotopes. The evaporation process tends to increase the isotope content of the remaining liquid phase. This enrichment is inversely correlated with relative humidity, i.e. with the density of water vapor molecules depleted in heavy isotopes whose condensation at the liquid surface counteracts the enrichment due to evaporation. Evaporated water can be distinguished by the fact that it contains relatively more ^{18}O than prescribed by the meteoric water line, plotting below this line. Unevaporated meteoric water is depleted in heavy isotopes relative to SMOW (δ values are negative) (Fritz and Fontes, 1980). Thus, it is possible to determine whether groundwater has undergone appreciable open surface evaporation prior to infiltration. Water falling close to the meteoric water line indicates that they are isotopically unaltered meteoric waters (Fritz and Fontes, 1980).

Tritium is a radiogenic isotope whose half-life is approximately 12.35 years. Natural tritium is produced in the upper atmosphere by cosmic neutron bombardment of nitrogen-14. Since 1952, the natural background has been loaded by enormous amounts of man-made tritium which were injected into the stratosphere during thermonuclear tests and have since been the dominate source of tritium in precipitation (Figure 6). A tritium unit (1 TU) corresponds to a concentration of one atom of T in 10^{18} atoms of ^{1}H. Tritium contents are determined as concentrations and not as per mil or percent variations from a standard.

Both natural and bomb produced tritium appear to a large extent, in the form of tritiated water and can be used to distinguish different age zones within the modern (post-1952) water part of the groundwater flow systems, or distinguish zones of mixing between two adjacent flow zones. Two

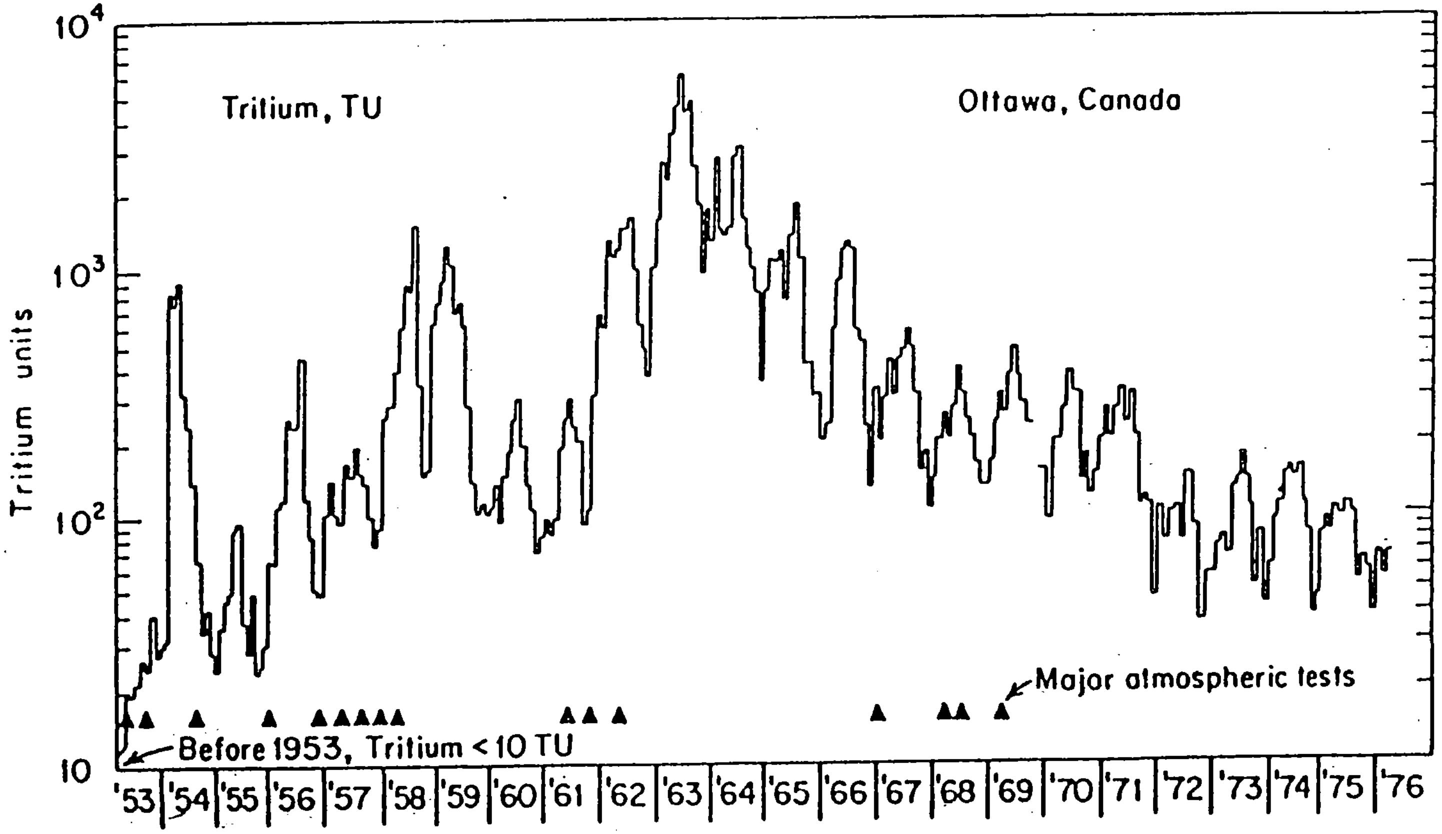


Figure 6. Tritium in precipitation versus time (after Freeze and Cherry, 1979).

attributes make tritium an excellent indicator of young groundwaters: the conservative nature of tritium and the temporal variations in the tritium concentrations in precipitation over the past 40 years. Tritium concentrations in precipitation before 1952 have been estimated to range from 4 to 25 TU however, thermonuclear tritium concentrations of up to three orders of magnitude greater than the natural levels have completely masked the natural levels (Gat, 1980). Since the half-life of tritium is 12.35 years, any water recharged before 1952 would have tritium concentrations less than about 5 TU, conversely, waters recharged after 1952 would have more than about 5 to 10 TU (Fontes, 1982).

3.5 CHEMICAL ANALYSIS

Selected river water and streambed groundwater samples collected during the minipiezometer survey were analyzed for the following parameters: chlorinated hydrocarbons, polychlorinated biphenyls, trihalomethanes, EPA Priority Pollutants (extractables), TOX, chloride and the natural environmental isotopes (oxygen-18, deuterium and tritium).

A total of 29 samples of river water, streambed groundwater, blanks, spikes and duplicates analyzed for TOX by Zenon Environmental Inc. of Burlington, Ontario. Due to time restraints and budget, selection of additional samples for analysis was limited to samples showing elevated TOX levels. Eleven samples showing the elevated TOX levels were also analyzed for chlorinated hydrocarbons including polychlorinated biphenyls, and trihalomethanes. Five of these eleven samples were then analyzed for the EPA Priority Pollutant Extractables. All samples were analyzed in the field for pH and electrical conductivity.

Natural isotope analyses were performed on all 29 of the river water and streambed groundwater samples in addition to samples collected from wells on Suncor's property (Sarnia) and river water samples taken from the Chenal Ecarte in the St. Clair River Delta. Figure 7 shows the Chenal Ecarte sample locations.

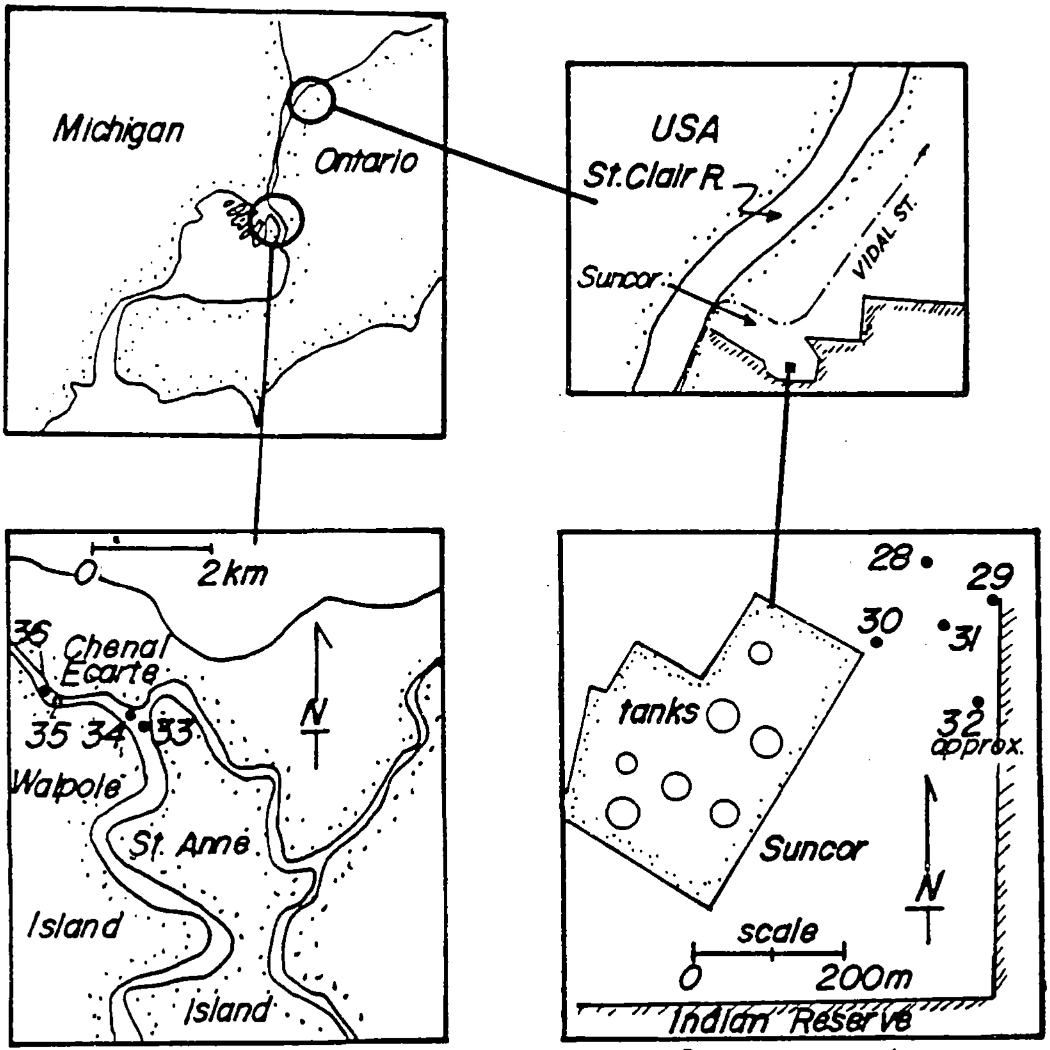
Table 1 contains a summary of the parameters, number of samples for each parameter, and the analytical method used during analysis of the samples. A brief summary of the methods follow (refer to Appendix 2 for the complete Work/QA Project Plan and detailed sampling procedures).

The overlap in test methods used during the water analysis, i.e., PCB analysis being done by two methods, were done for qualitative and quantitative confirmation of results from the other tests as well as to improve upon parameter detection limits from parts per million (ppm) to parts per trillion (ppt).

3.5.1. ISOTOPIC ANALYSIS

The isotopic analyses were performed under contract by the University of Waterloo. They used normal isotopic analysis procedures and standards recommended by the IAEA (International Atomic Energy Agency).

Oxygen-18, deuterium, and tritium were analyzed by standard methods used in isotopic analyses of water. A Micromass Model 903 mass spectrometer was



Chenal Ecarte samples

Suncor samples

Figure 7. Chenal Ecarte and Suncor sample locations.

TABLE 1. Parameter Table

Sample Matrix = all Streambed groundwater and river water

Parameter	Number of Samples	Analytical Method	Detection Limit	Precision Protocol
Total Organic Halides (TOX)	29	EPA Standard Method 9020	1-5 ug/L depending on compound	1 Blank 1 Duplicate and 1 spike /20 samples
Volatile Halogenated Organics (Trihalomethanes)	11	Modified ASTM Method D3973 (GC/ECD Pentane extraction Method)		1 Blank 1 Duplicate and 1 Standard /20 samples
Organo Chlorines Chlorinated Hydrocarbons/PCB	11	EPA Federal Register Method 608 (Dichloromethane extraction, silica cleanup, GC/EC)		1 Blank 1 Duplicate 1 Standard 20 samples
Semivolatile Organics (Base/Neutral and Acid Extractables)	5	EPA Federal Register Method 625 (with capillary column)		
Isotopic Analyses Oxygen, Deuterium and Tritium	29 oxygen 29 tritium 29 deuterium	Mass Spectrometry		1 Duplicate /15 samples
pH	22	Corning Combination Electrode and Model 103 Digital pH Meter		measurements on duplicate samples
electrical conductivity	22	YSI Conductivity Probe and Model 32 meter		measurements on duplicate samples
Phenols	5	Method 510, Standard Methods (4AAP and solvent extraction)		
Chloride	25	Specific Ion electrode		

used for oxygen-18 analysis, a modified Micromass 602 mass spectrometer was used for deuterium analysis, and Intertechnique or Beckman Model 7500 scintillation counters were used for tritium analysis. Analytical precisions for ^{18}O and D analyses by mass spectrometry are better than ±0.2 and ±2.0 ‰, respectively.

One in every 15 samples sent for analysis were split in order to evaluate the isotopic results. Internally, the University of Waterloo has a quality assurance program which includes a lab standard SWAT (Standard Waterloo Tap Water). This lab standard is run for each 5 oxygen-18 samples, each 6 deuterium samples, and each 10 tritium samples. SWAT has been related to three international standards: SMOW (Standard Mean Ocean Water), SLAP (Standard Light Artic Precipitation), and GISP (Greenland Ice Sheet Precipitaion). For each sample analysis, the results are an average of at least 5 sample-standard comparisons for oxygen-18 and deuterium and 500 to 660 minutes of tritium counting. Since there are no international standards for tritium, sample analyses are periodically compared with results from the Alberta Research Council and the Weizmann Institute in Israel.

3.5.2 TOTAL ORGANIC HALIDES

EPA Standard Method 9020 determines Total Organic Halides (TOX) as Cl^- in drinking and ground waters. This method uses carbon adsorption with a microcoulometric-titration dector. It requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 ug/L (SW-846, 2nd edition, 1982).

As described in SW-846 (1982), Method 9020 detects all organic halides containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine-containing species are not determined by this method. This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times. Method 9020 is provided as a recommended procedure that may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of TOX.

A method summary from SW-846 (1982) is as follows: a sample of water that has been protected against the loss of volatiles (by elimination of head space in the sample container), and that is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides, and is then analyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric dector.

3.5.3. BASE/NEUTRAL AND ACID EXTRACTABLES

EPA Federal Register Method 625 covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. Parameters may be quantitatively determined using this method. This method is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of a number of organic compounds found in municipal and industrial discharges (Federal Register, October 26,1984).

The following is a method summary from the Federal Register (1984): a measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses. Quantitative analysis is performed by using a single characteristic external or internal standard technique.

3.5.4. PHENOLS

Phenols are the hydroxy derivatives of benzene and its condensed nuclei, and may occur in industrial waste waters (Standard Methods, 1975). Of the several analytical procedures available to determine phenols under Method 510, the 4-aminoantipyrine colorimetric method (4AAP) was used by Zenon. This method determines phenol, ortho- and meta-substituted phenols, and under proper pH conditions, those para-substituted phenols in which the substitition is a carboxyl, halogen, methoxyl, or sulfonic acid group (Standard Methods, 1975).

The 4-aminoantipyrine method is given in two forms: Method B (which was used in this study) is normally used for extreme sensitivity, and is adaptable for use in water samples containing less than 1 mg/L phenol. This method concentrates the color in a nonaqueous solution. A universal standard containing a mixture of phenols is not available because the relative amounts of various phenolic compounds in a given sample are unpredictable (Standard Methods, 1975). For this reason, phenol itself has been selected as a standard for colorimetric procedures and any color produced by the reaction of other phenolic compounds is reported as phenol (Standard Methods, 1975). Because substitution generally reduces response, this value represents the minimum concentration of phenolic compounds.

Phenols are distilled from nonvolatile impurities. Standard Methods (1975), describes the method as follows: the steam-distillable phenols react with 4-aminoantipyrine at pH 7.9 + 0.1 in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is then extracted from the aqueous solution with $CHCl_3$, and the absorbance is measured at 460 nm. This method covers the phenol concentration >1.0 ug/L with a sensitivity of 1 ug/L. This method yields only an approximation and represents the minimum amount of phenols present. This occurs because the phenolic reactivity to 4-aminoantipyrine varies with the types of phenols.

3.5.5. CHLORINATED HYDROCARBONS AND PCB

The method used for the analysis of chlorinated hydrocarbons and PCB's in the water samples was an IWD (Inland Waters Directorate) method based on EPA Standard Test Method 608, Organochlorine Pesticides and PCBs. The IWD method contained several modifications to Method 608.

EPA Federal Register Method 608 is a gas chromatographic (GC) method applicable to the determination of a number of pesticides and PCB's that may be found in municipal and industrial discharges (Federal Register, July, 1982). When this method is used to analyze unfamiliar samples for any or all of the appropriate compounds, compound identifications should be supported by at least one additional qualitative techinque. Therefore, this method describes analytical conditions for a second GC column that can be used to confirm measurements made with the primary column. Method 625, discussed in a previous section, provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the appropriate parameters, using the extract produced by this method (Federal Register, July, 1982). Method 625 was used for this purpose.

A summary of the EPA test method is as follows: a measured volume of sample, approximately 1 L, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane, during concentration to a final volume of 10 mL or less. Gas chromatographic conditions are described which permit the separation and measurement of the parameters in the extract by electron capture GC (Federal Register, July, 1982). Method modifications by Zenon included: the measurement of parameters by electron capture GC, substitution of silica gel during the clean-up procedure, and use of capillary columns instead of packed columns (Foster, personal communication).

3.5.6. TRIHALOMETHANES

Trihalomethane analysis was performed by using a modified ASTM Method D3973, "Low-Molecular Weight Halogenated Hydrocarbons in Water". This method normally covers the analysis of drinking water but is also applicable to environmental and waste waters. ASTM Method D3973 covers the determination of halomethanes, haloethanes, and some related extractable organohalides amenable to GC measurement. The applicable concentration range for trihalomethanes is 1 to 200 ug/L. Detection limits depend on the compound and on the characteristics of the GC system (ASTM, 1982).

This method employs liquid/liquid extraction to isolate compounds of interest and provides a five-fold concentration enhancement prior to measurement. A 5 mL aqueous sample is extracted once with 1 mL of solvent. A 3 uL aliquot of the extract is analyzed in a GC equipped with an electron capture detector (ASTM, 1982). Modifications to this test procedure were the use of a larger quantity of sample and solvent (160 mL of sample and 2 mL of solvent) and the substitution of isopentane for isooctane as the solvent (Foster, personal communication).

3.5.7. CHLORIDES

A specific ion electrode was used to determine the chloride levels in the water samples. A specific method was not referenced by Zenon.

4.0 RESULTS AND INTERPRETATION

4.1 GROUNDWATER FLOW PATHS/HYDRAULIC GRADIENTS

To better understand the groundwater flow and its possible correlations to seepage into the St. Clair River, we conducted a literature review of the geology, hydraulic head distribution and groundwater flow in the freshwater aquifer and deep well disposal unit (Detroit River Group) for the Sarnia area.

Figure 8 is a schematic cross-section of Lambton County showing the relationship between the upper clay tills (which generally acts as an aquitard) and the thin sandy basal unit directly overlying the bedrock which is considered to be the freshwater aquifer in the Sarnia area.

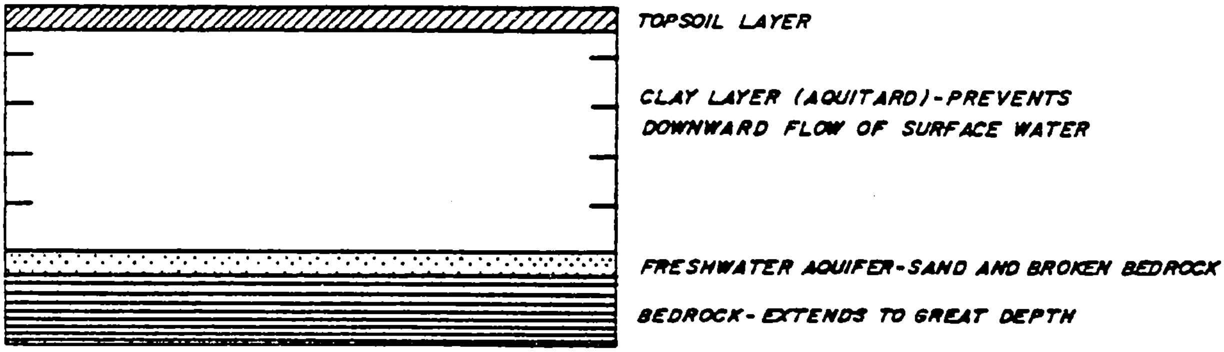


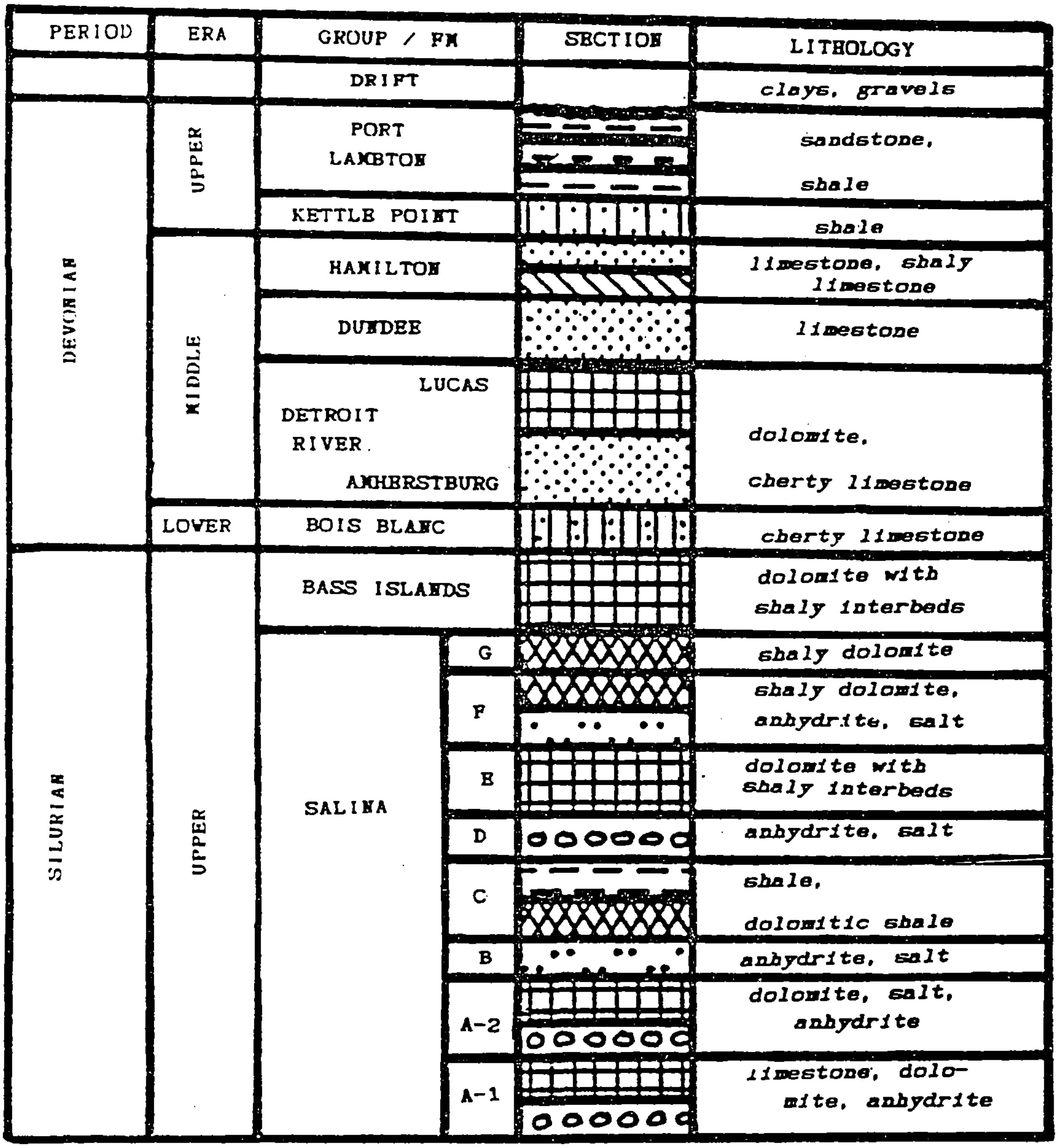
Figure 8. Schematic cross-section of Lambton County.

There are approximately 41 m (135 ft) of silty clay deposits which overlie the Devonian shales and limestones of the Lambton, Hamilton and Detroit River Groups (Figure 9). These silty clays vary in thickness from about 15 m in the eastern part of Lambton County to about 45 m near the St. Clair River in the west (Figure 10). On the basis of texture, homogeneity and slight over-consolidation, these deposits are considered to be water-laid, glacial tills (Quigley and Ogunbadejo, 1976). The intergranular hydraulic conductivity of these silty clays ranges from 8×10^{-10} to 9×10^{-10} m/s (Desaulniers et al., 1981).

Quigley and Ogunbadejo (1976) studied the tills near Sarnia within the boundaries of the city landfill site, located on the flat grasslands 7 km southeast of Sarnia. This study indicated that at least two tills could be distinguished within the upper 27 m (90 ft) of deposits. These till deposits contain 40-50% clay size material and were only slightly over-consolidated except for the desiccated crust above 7 m. A change in the moisture content profile occurs at 14 m, at which point the moisture content increases with depth. Pockets of silty sand, approximately 4 m thick ,were observed within the clayey soil sequence at a depth of about 18 m. Goodall and Quigley (1977), and Desaulniers et al. (1981), determined the vertical hydraulic gradient in the clayey deposits is downward with values between 0.01 to 0.18.

Weathering of this upper till has caused close-spaced fissuring apparently brought about by leaching and desiccation. The intensity of the fissuring decreases with depth with reported fissure spacings of about 1 m at a depth of 5 m (Quigley and Ogunbadejo, 1976). Desaulniers et al. (1981),

Figure 9. Partial stratigraphic column for southwestern Ontario (after Vandenberg et al., 1977).



PERIOD	ERA	GROUP / FM		SECTION	LITHOLOGY
		DRIFT			clays, gravels
DEVONIAN	UPPER	PORT LAMBTON			sandstone, shale
		KETTLE POINT			shale
	MIDDLE	HAMILTON			limestone, shaly limestone
		DUNDEE			limestone
		DETROIT RIVER	LUCAS AMHERSTBURG		dolomite, cherty limestone
	LOWER	BOIS BLANC			cherty limestone
SILURIAN	UPPER	BASS ISLANDS			dolomite with shaly interbeds
		SALINA	G		shaly dolomite
			F		shaly dolomite, anhydrite, salt
			E		dolomite with shaly interbeds
			D		anhydrite, salt
			C		shale, dolomitic shale
			B		anhydrite, salt
			A-2		dolomite, salt, anhydrite
			A-1		limestone, dolomite, anhydrite

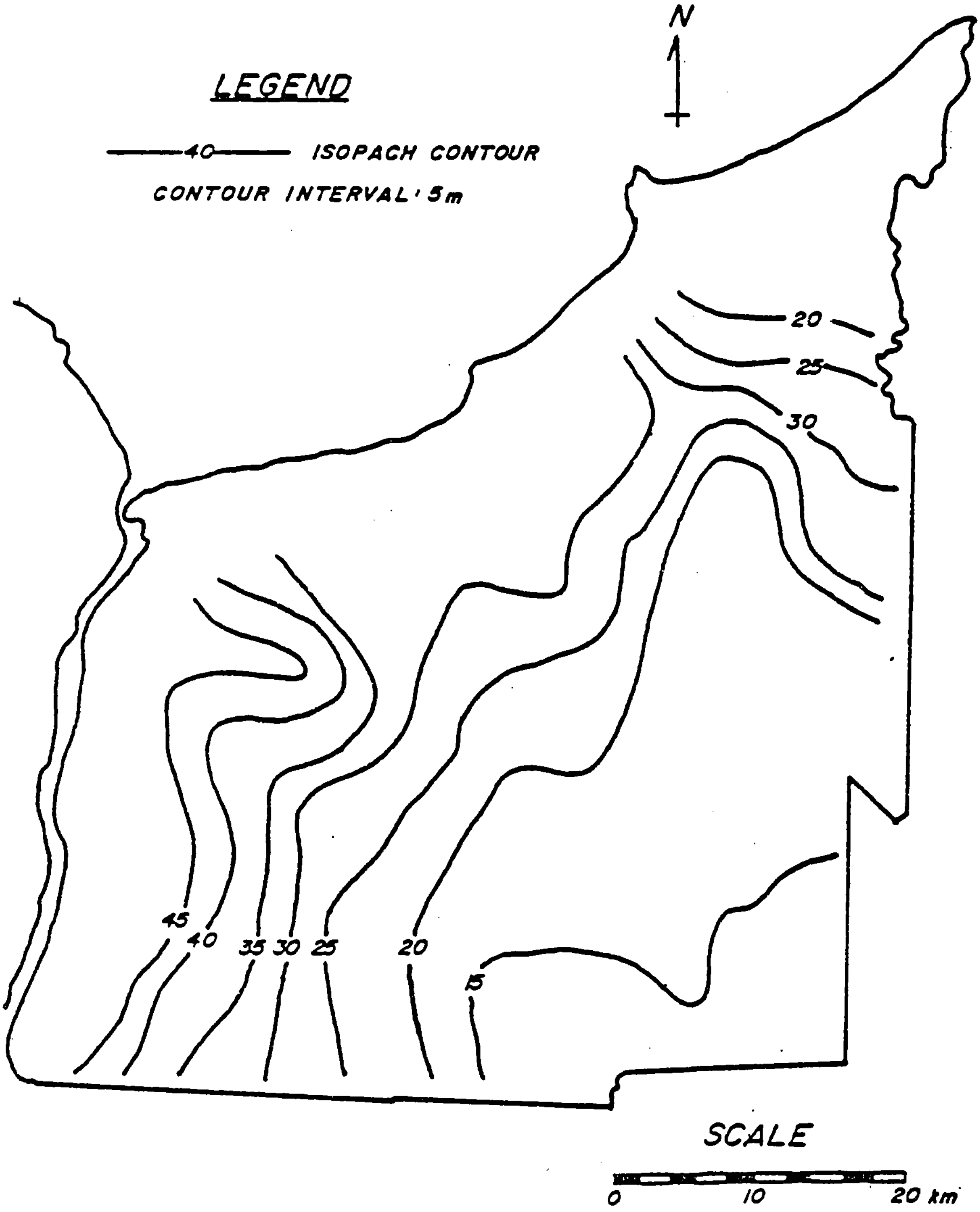


Figure 10. Isopach map of overburden in Lambton County.

concluded that the hydraulic conductivity of the clay and till was not greatly affected by the fractures.

The freshwater aquifer, the main source of potable groundwater in rural areas of Lambton County, has been identified as a thin layer of granular overburden directly overlying the bedrock. The aquifer appears as a thin layer of sand and gravel spread out unevenly over the bedrock surface, confined beneath by the shaley bedrock and above by the clay and till which forms the bulk of the overburden (Underground Resources Management, 1984).

The topography and piezometric head of the freshwater aquifer apparently follow the westerly trend of the bedrock surface. Figure 11 shows the elevation of the bedrock surface and thus the elevation of the sand and gravel aquifer. Figure 12 shows the piezometric head of the fresh water aquifer and the westerly direction of groundwater movement. Vandenberg et al. (1977) have identified regions of similar groundwater chemistry in the freshwater aquifer. The directon of groundwater movement, as inferred from these water chemistry types, correlates with the flow system revealed by the piezometric-head map (Figure 13, groundwater chemistry of Lambton County).

Regional recharge to the freshwater aquifer occurs in the high areas on the eastern border of the county where elevations range from 242 masl to 212 masl. The aquifer is believed to discharge into the St. Clair River and Lake Huron (Vandenberg et al, 1977), where the elevation along the river is 182 masl, and the elevation of the St. Clair River is 176 masl (NOAA, 1985).

The main disposal zone in Lambton County was the Lucas Formation of the

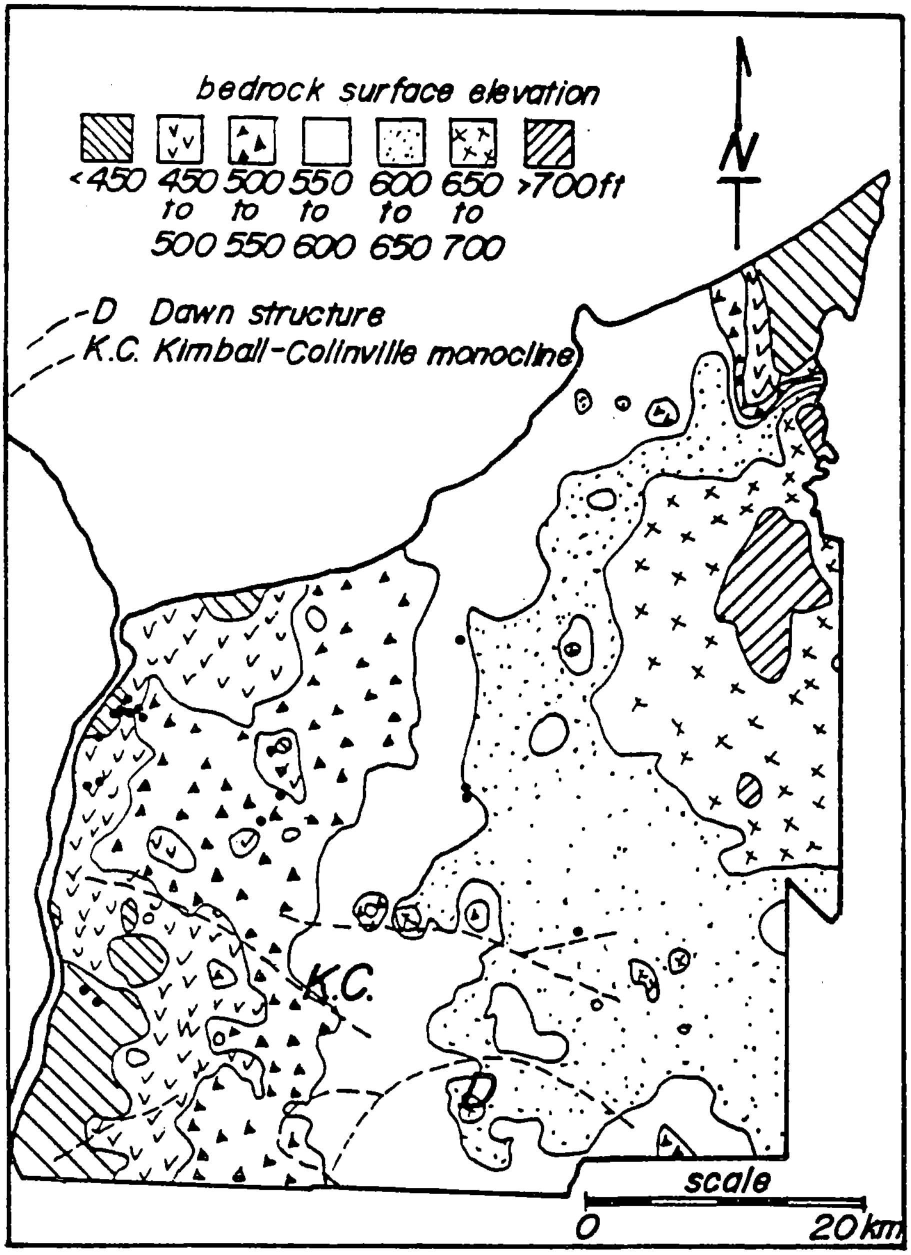


Figure 11. Elevation of the top of the bedrock (after Vandenberg et al., 1977).

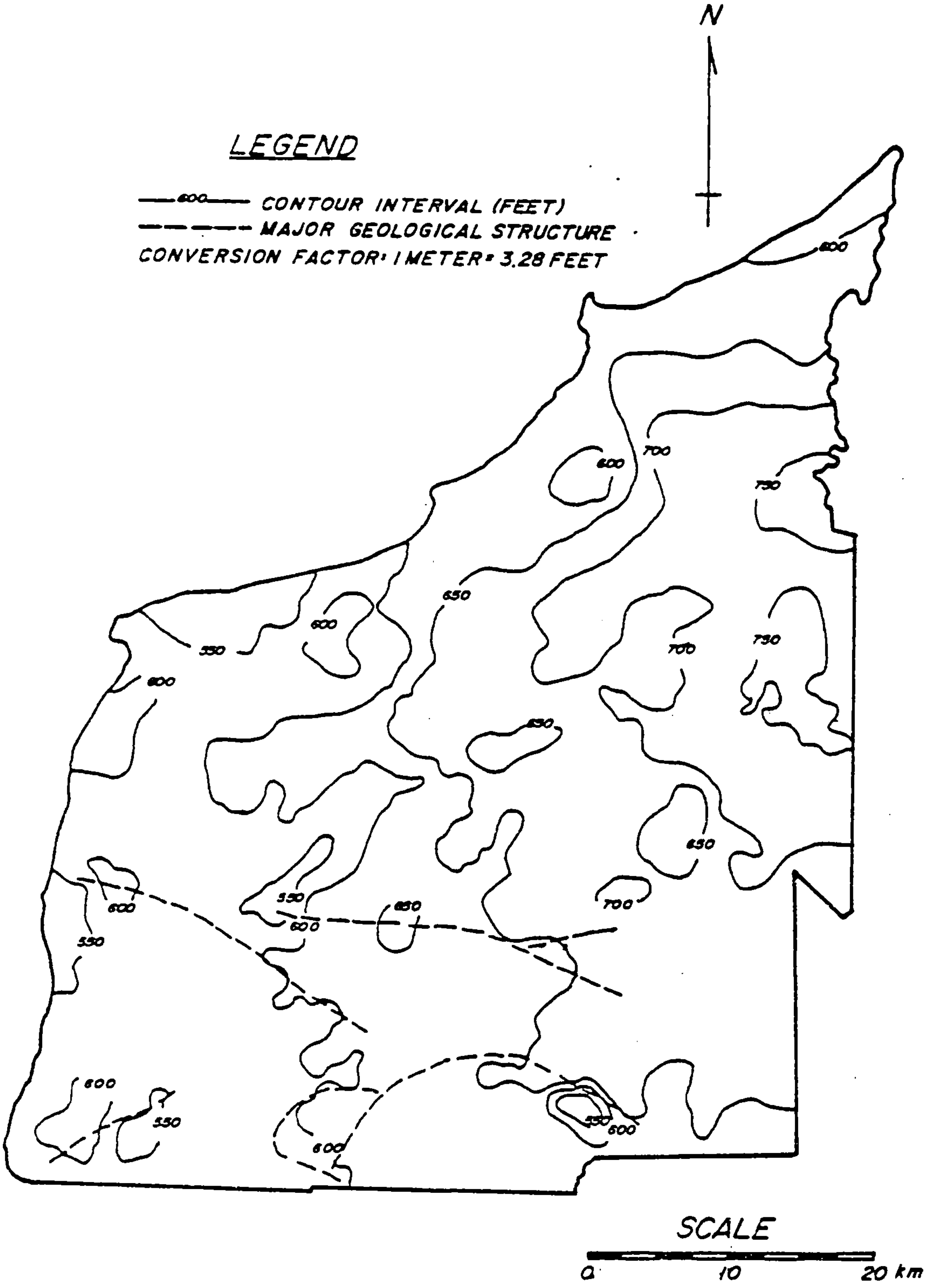


Figure 12. Piezometric head of the freshwater aquifer (after Vandenberg et al., 1977).

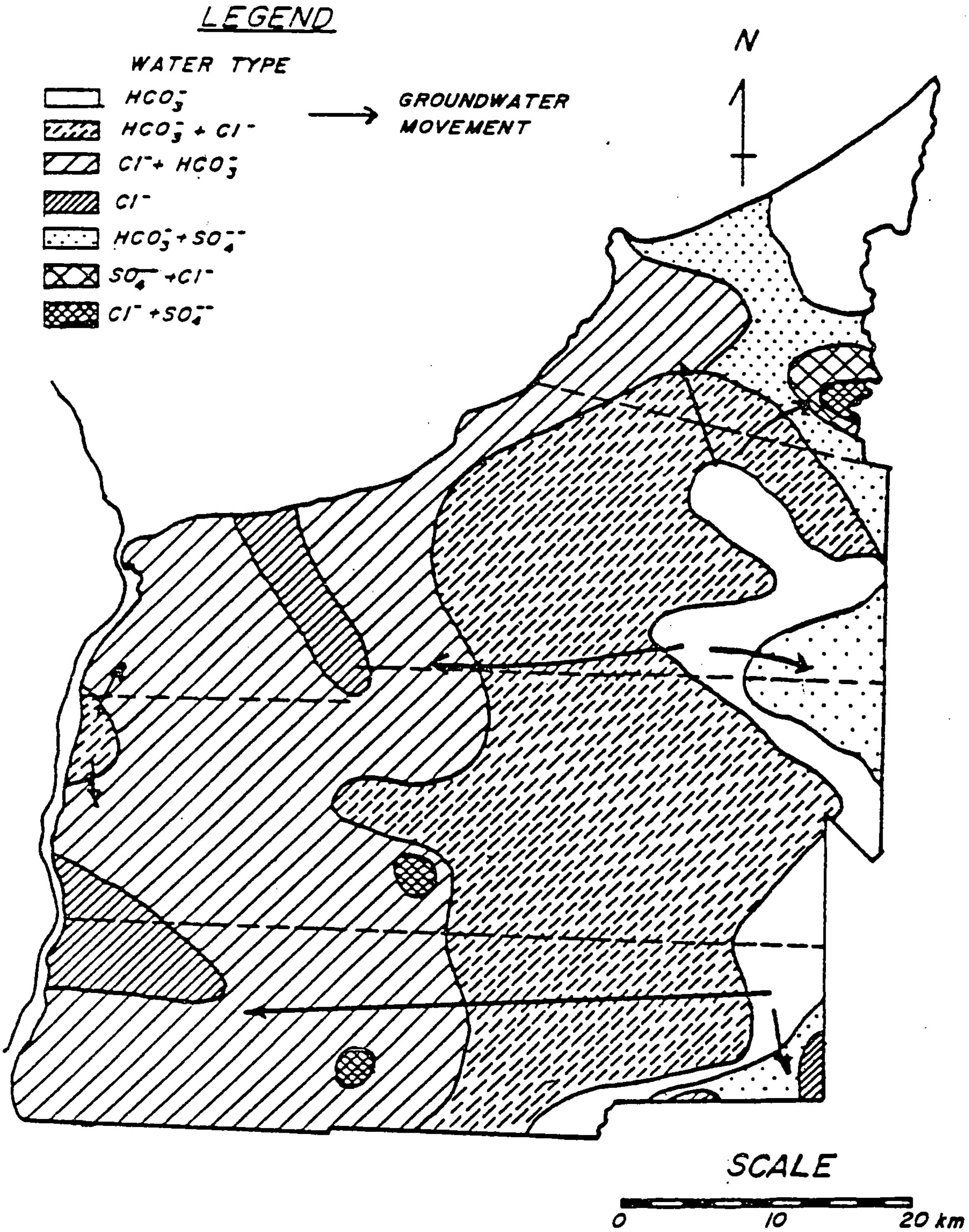


Figure 13. Groundwater chemistry of Lambton County (after Vandenberg et al., 1977).

Detroit River Group which consists of dolomite, limestone, and minor anhydrite beds in the lower part of the formation (Figure 14, location map of disposal wells in Lambton County). In Lambton County, the disposal formation thickness ranges from 91 m in the north to 61 m in the south with an apparent increase in thickness toward the northwest or centre of the Michigan Basin. The top of the formation dips westward from an elevation of 91 masl on the eastern boundary of the county to 30 mbsl (metres below sea level) on its western boundary (Vanderberg et al., 1977). The Detroit River Group, which underlies the tills, is found at depths ranging from 167 to 288 m below ground surface (Rathbone, 1983). There is also a reported localized thinning of the Dundee Formation (which directly overlies the Detroit River Group) (Figure 15, bedrock geology of Lambton County), and the Detroit River Group along the Dawn Structure in Lambton County. This localized thinning has been associated with leaching of salt from the underlying Salina Formation. The same process may have caused similar features along the Kimball-Colinville monocline and the unnamed trend east of this monocline. The collapse associated with such leaching may have produced an increase in vertical, as opposed to horizontal permeability, within the Detroit River Group and overlying formations in this particular area (Vanderberg et al., 1977).

The regional groundwater flow in the bedrock disposal unit is shown to be similar to the regional shallow (freshwater aquifer) groundwater movement, which is generally to the west-northwest and also appears to be influenced by topography (Vandenberg et al., 1977). Locally, the potentiometric surface is irregular. These irregularities have been attributed to deep-seated geologic structures representing zones of variable permeability or irregular area-wide recharge of the groundwater from the glacial overburden (Underground Resource

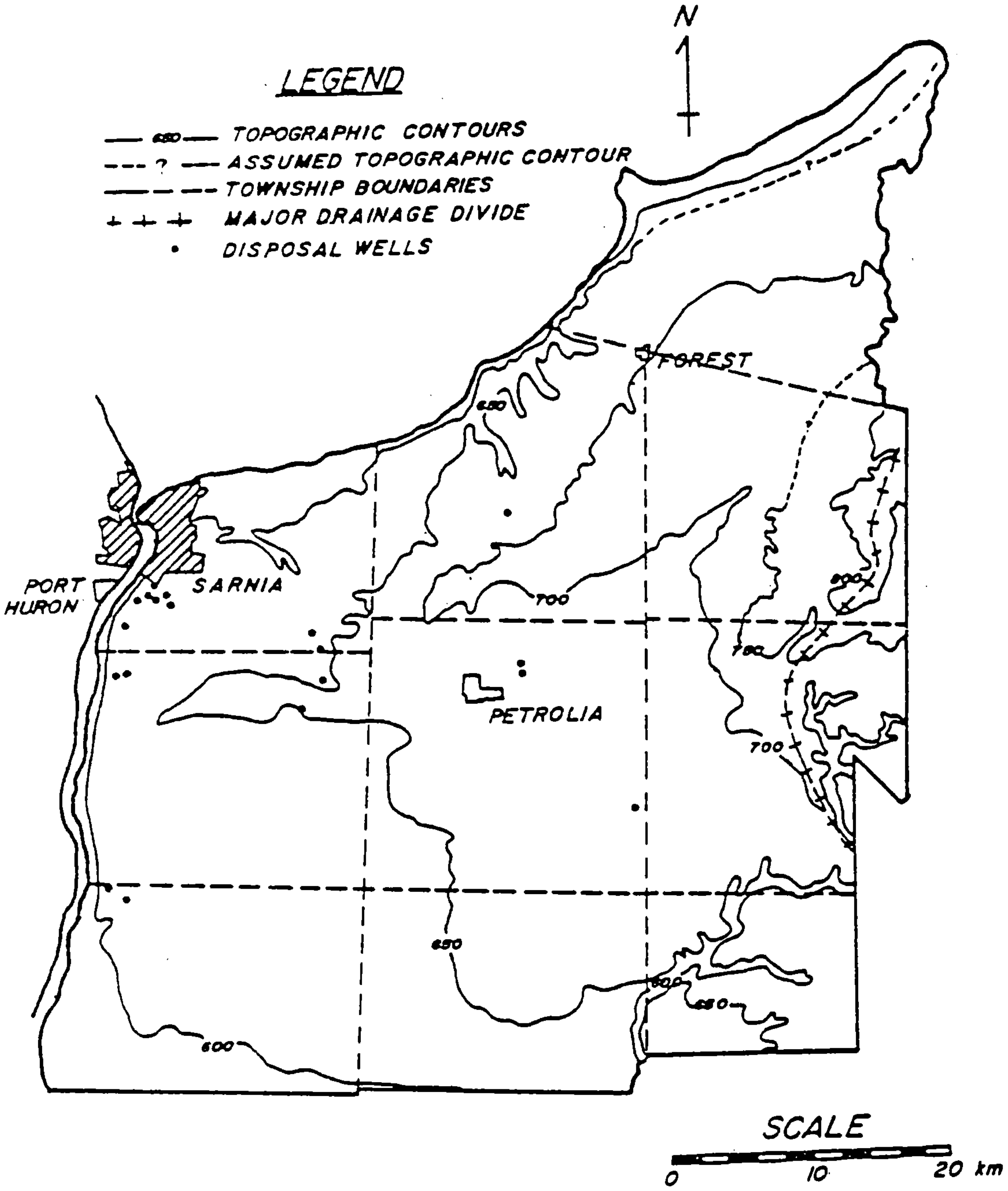


Figure 14. Location map of disposal wells (after Vandenberg et al., 1977).

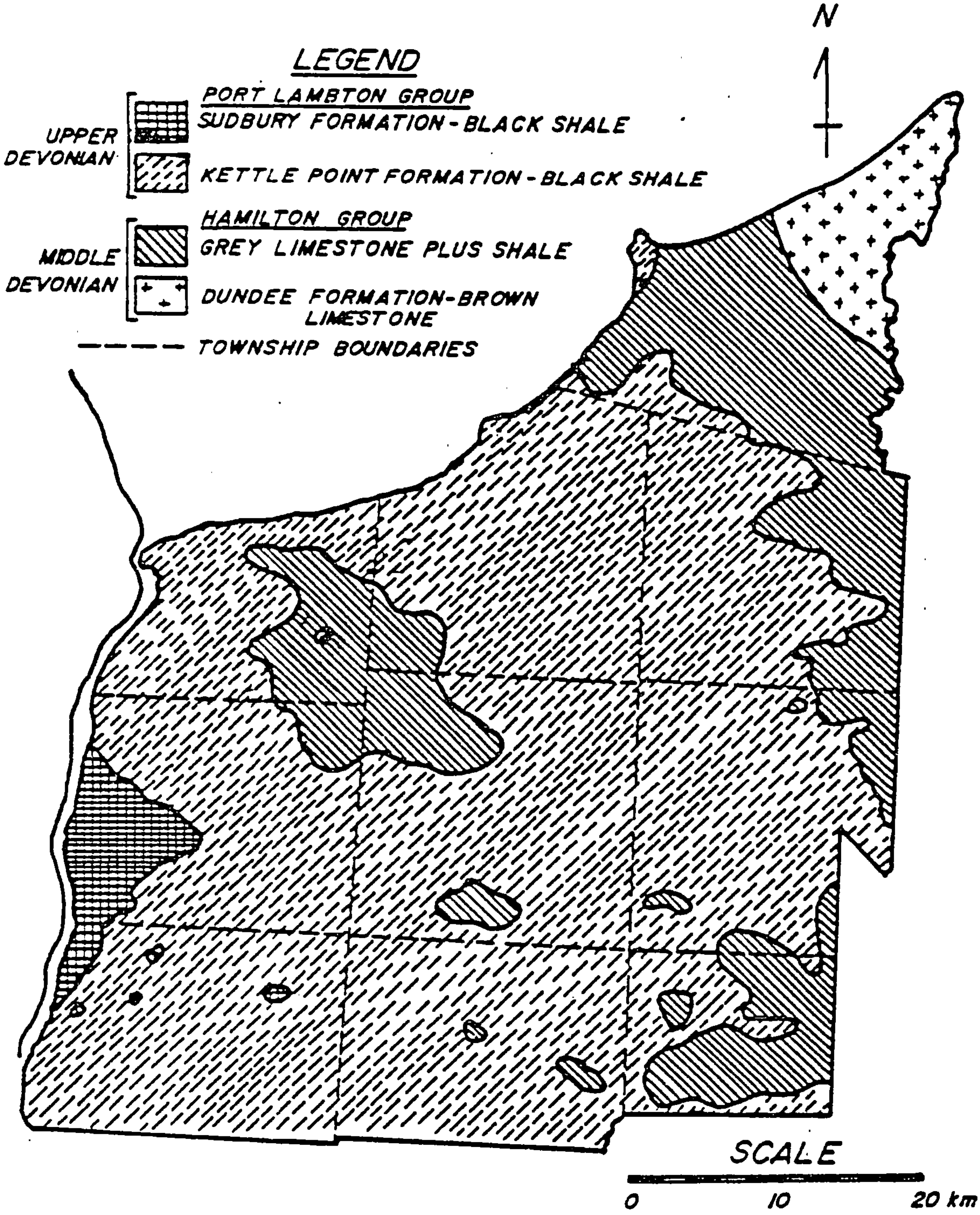


Figure 15. Bedrock geology of Lambton County (after Vandenberg et al., 1977).

Management, Inc., 1984). Figure 16 shows a piezometric map of the disposal zone from Vandenberg et al. (1977) which suggests a hydraulic gradient to the west.

The piezometric head in the disposal zone (the Detroit River Group in Lambton County), under natural conditions, has been reported to range from 60-90 m (Vandenberg et al., 1977) to 0-60 m (Rathbone, 1983) below the piezometric head in the shallow aquifer.

During the height of the deep well disposal practices in Lambton County (1967-1971), surface flows were reported at abandoned water wells, indicating static water levels well above the lower boundary of the upper aquifer (Rathbone, 1983). These outbreaks were thought to be the result of over-pressurization of the disposal formation during waste injection. Any modifications such as these to normal subsurface pressures can alter water levels from above normal to above surface. As the number of operating wells declined and injection pressures were reduced, static water levels in the Detroit River Group reportedly declined. Information on the rate of decline of pressures or current water levels in the deep disposal unit is not readily available.

A study conducted by GTC Geologic Testing Company Ltd. (1985) reported that only a few wells have had detailed pressure monitoring since the closure of the well. Pressure recovery information for a few of the disposal wells is given in Figure 17. Recovery information for the ESSO wells are complicated by the fact that the wells were filled with fuel oil. An equivalent water filled gauge pressure for ESSO NO. 5 was determined. The shape of the curve

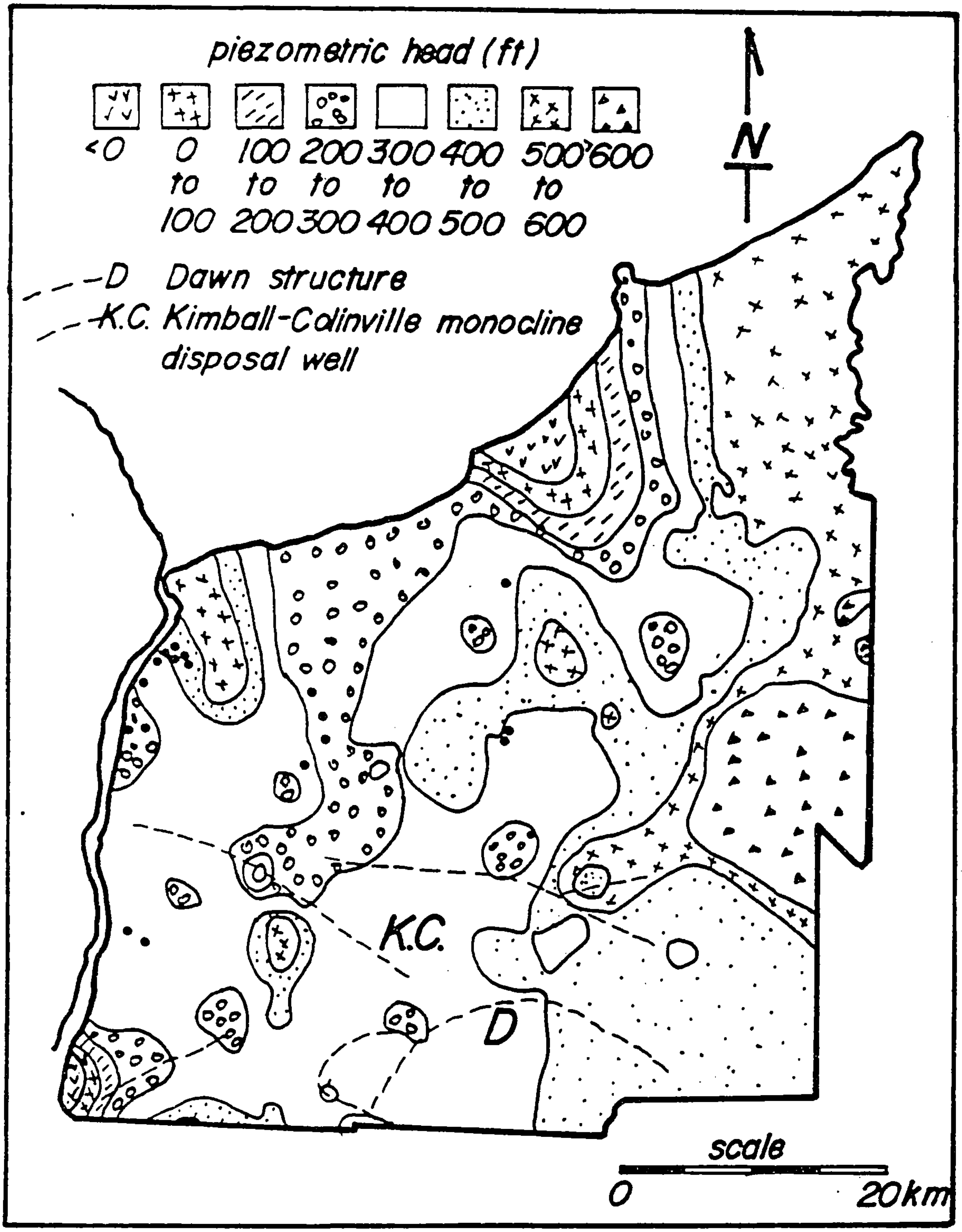


Figure 16. Piezometric map of the disposal zone (after Vandenberg et al., 1977).

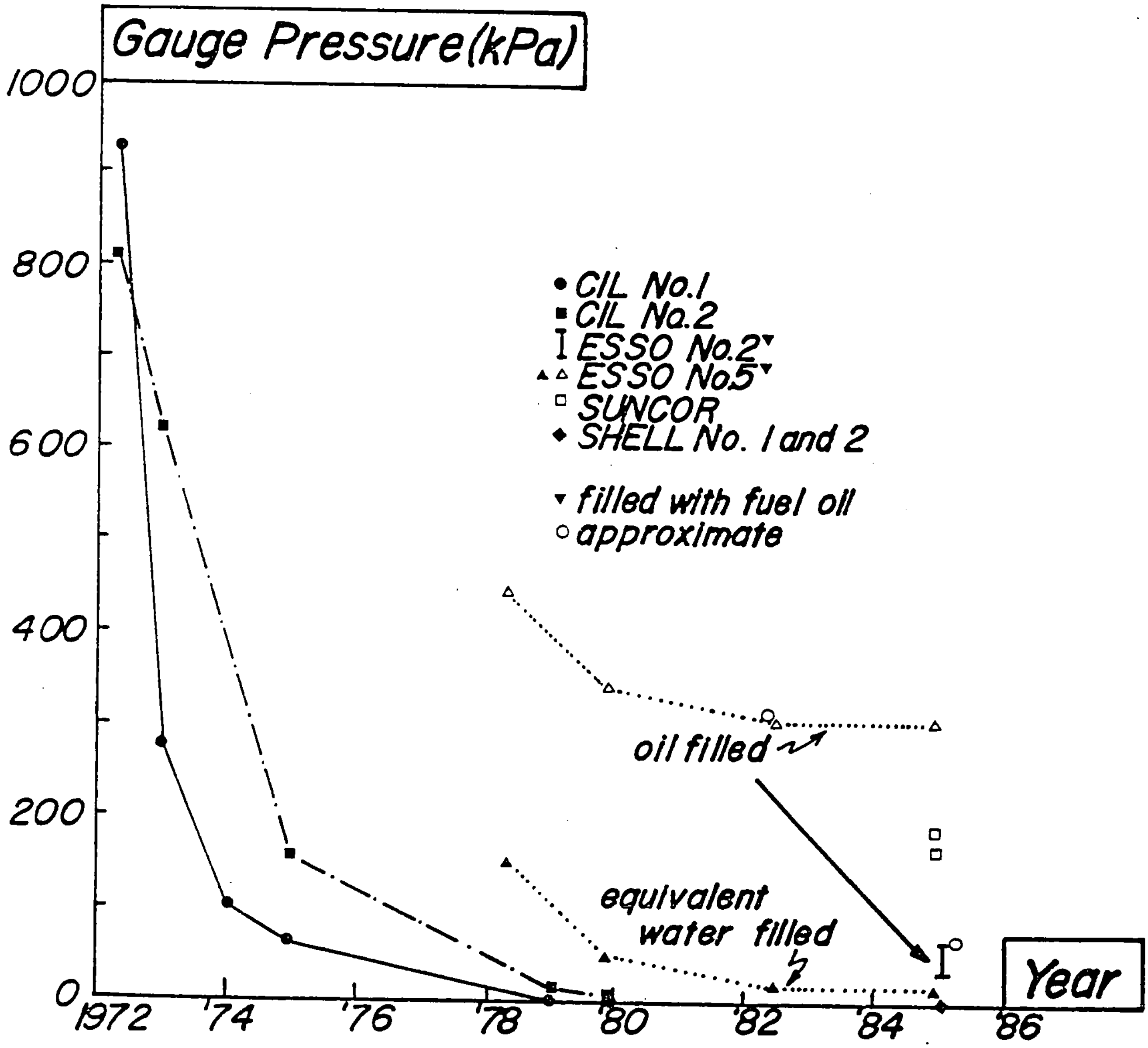


Figure 17. Pressure recovery data for several disposal wells (after GTC Geologic Testing Consultants Ltd., 1985).

indicates that the well is still recovering (GTC Geologic Testing Company Ltd., 1985). For the CIL wells, the formation pressure had recovered to below ground surface by about 1982, or after about 10 years of inactivity (GTC Geologic Testing Company Ltd., 1985). The Suncor well was at about 172 kPa gauge in December, 1984, but no information is available for the recovery prior to this date.

Despite the vast amount of data available on oil and gas wells drilled in Lambton County, the information is not appropriate for the evaluation of the hydrogeology of the disposal zone. Some of the problems in the interpretation of the data are related to the reliability of the data: the data may not reflect conditions throughout the system, considerable time delay may elapse between a change of area-wide head levels and subsequent responses of other strata, and the scarcity or unreliability of head measurements. These problems, coupled with the lack of sufficient information on current pressure gradients and water levels in the deep disposal zone, render any interpretation highly speculative.

Due to time limitations and problems with gas bubbles in the tubing (from the minipiezometers to the boat), hydraulic gradients were not determined for the streambed groundwater during the minipiezometer survey. However, a minipiezometer on the Cromwell Street survey line (station # 11, 100 m from shore) flowed, with a hydraulic head of approximately 70 cm above the river level. Additional work is necessary to better determine the groundwater flow paths and hydraulic gradients.

4.2 RIVER BOTTOM CHARACTERIZATION/SEDIMENT THICKNESS

We examined the type sand distribution of sediments on the bed of the river using both divers descriptions and sediment samples. We collected 71 core samples from various locations along 17 of the 18 survey lines installed for use during this study (Appendix 3 and 4 gives the results of these surveys). The Restaurant survey line was not used due to excessively silty conditions and strong currents.

Interpretation of the character of the river bottom was aided by a study recently conducted by Environment Canada and the Ontario Ministry of the Environment in the St. Clair River (Environment Canada and Ontario Ministry of the Environment, 1986) which has described the bottom profile of several distinct reaches of the river in the area of several of our survey lines. Their first area is the steep upper reach between Lake Huron and the mouth of the Black River, where the channel is approximately 450 m wide and 9 m deep, with a mean surface current of 1.5 m/s. The second has been identified as the middle reach which extends downstream to the river delta, having a variable width and depth of 600-900 m and 8-15 m respectively, and a mean surface current of 1 m/s. The reach of the St. Clair River along Sarnia's industrial shoreline is described as a stable channel which is 500-800 m wide and 9-15 m deep (Environment Canada and Ontario Ministry of the Environment, 1986). The adjacent, excessively altered, shoreline is low-lying with a height of less than 10 m. Considerable artificial smoothing of the industrial shoreline by landfilling occurred between 1955 and 1973 (Environment Canada and Ontario Ministry of the Environment, 1986).

The depth and shape of the channel is reported to vary with distance downriver. North of the CN railway tunnel the channel has steep, smooth sides and a central ridge separating Canadian and American sub-channels 2-4 m deep (Figure 18, cross-section A). The shape of the cross section gradually changes further south as the slope of the American shore decreases and the sub-channels become less prominent (Figure 18, cross-section B). These two profiles fall within close proximity to several of the survey lines we installed, cross-section A is close to the Red-D-Mix /Imperial line, and cross-section B is adjacent to the Dow-3rd-4th Street line (Figure 18, cross-section locations).

In addition, Environment Canada and the Ontario Ministry of the Environment, conducted a detailed morphology of the Canadian slope in the vicinity of a recent spill at Dow's property. The inshore slope is shown to be smooth and very steep with grades as high as 1 in 3 (18°). The bottom contours are generally parallel to the shore. The slope gradually decreases offshore for approximately 5 m then a pronounced break in the slope occurs. There is also an increase in bottom roughness between 50 and 100 m off shore at a depth of between 7 and 9 m. The local relief on the lower slope and in the adjacent channel floor ranges from 0.1 to 0.5 m.

From examination of our core samples and the river bottom descriptions noted by our divers, the bed of the St. Clair River in the study area can be broadly described as a clayey till overlain in areas by sand and gravel.

The river bed within 30 m of the shore is covered by sand size sediments and gravel varying in thickness and vegetative cover. Further from shore the vegetation is less dense with coarser sands and gravels overlying the clayey

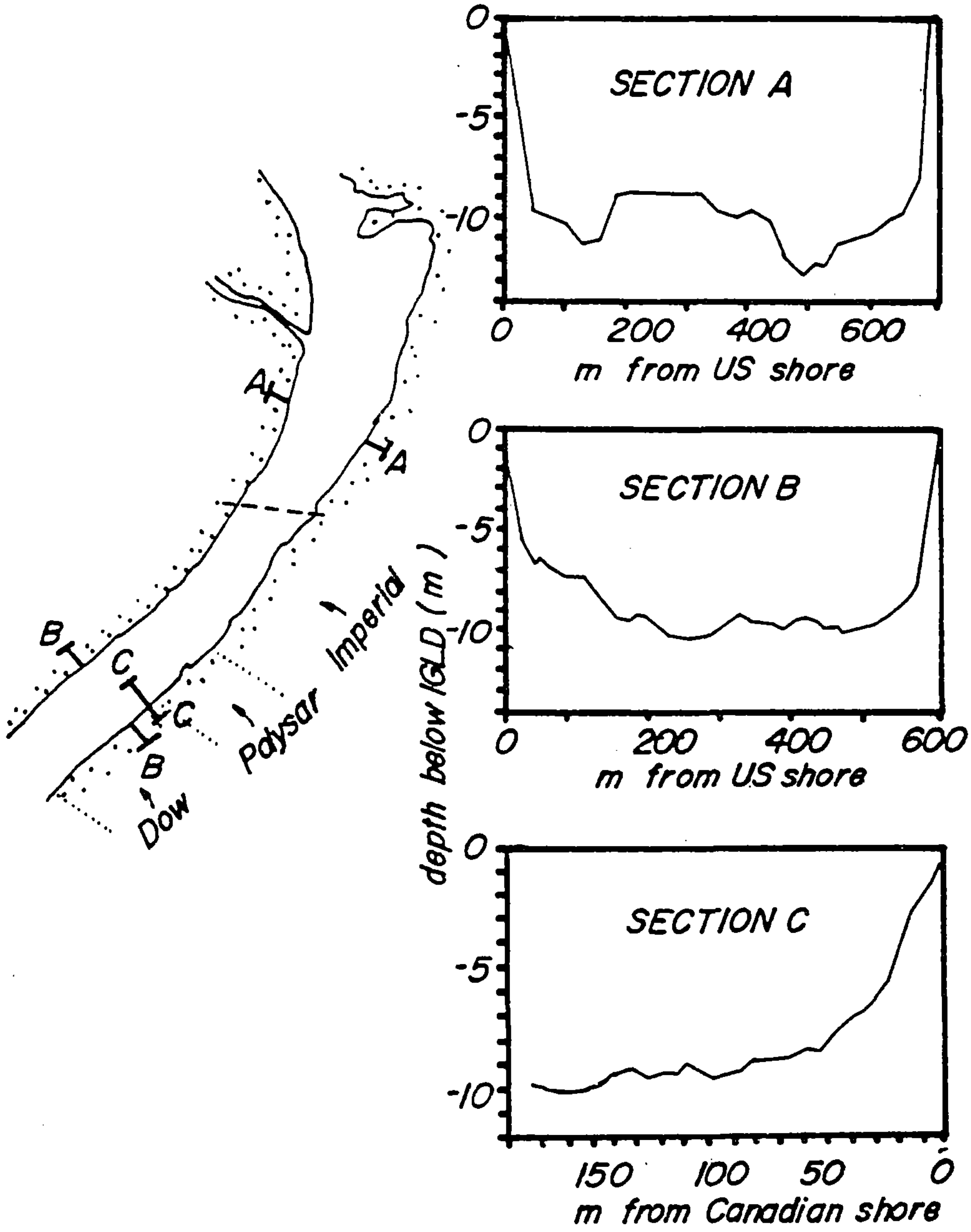


Figure 18. Profiles of the St. Clair River bottom and cross-section locations (after Environment Canada and Ontario Ministry of the Environment, 1986).

till. Clay is exposed or lightly covered by gravel in several areas along the survey lines. The divers reported seeing distinct benches up to 10's of cm in height, cut into the clayey till of the river bottom in numerous locations.

Some of our survey lines were completely mantled by fine-grained sand which ranged in thickness from 1-46 cm (total length of core sampler). The Restaurant survey line contained so much silt that core samples could not be taken. Various amounts of debris (rubble, piles, logs, boats, etc.) were noted by the divers over the entire length and width of the survey area.

Black oily sand and sediments were observed at several stations along 5 survey lines: C & O Dock (20-30 m from shore), Imperial-Polysar (20-30 m from shore), Cromwell Street (20-30 m from shore), Dow-Polysar (50 m from shore), and Dow 3rd-4th Street (30-50 m from shore). These were described either in the sample cores or bottom descriptions as black, oily sand, varying in thickness from 5-46 cm thick (as determined from core samples). Data on the observed sand and clay thicknesses from cores taken along the 17 survey lines are presented in Figure 19.

There does not appear to be any correlation between distance from shore and lithology. A zero recovery was reported at numerous locations throughout the survey, this could have been due to conditions such as: an all rock and/or coarse gravel core area, or fine sand being blown out of the corer by the river current during transport to the boat.

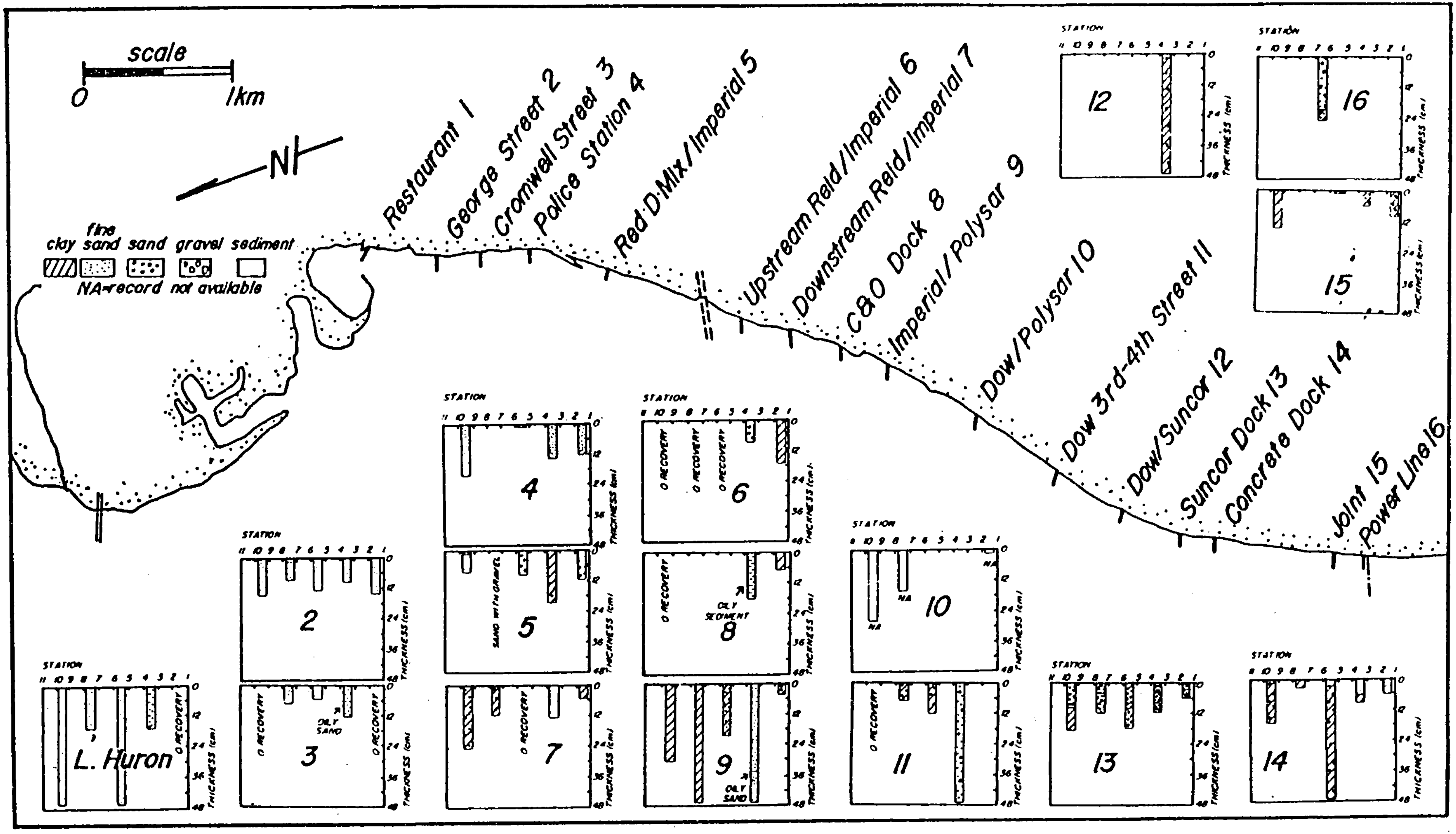


Figure 19. Distribution of sediment thickness along the survey lines.

4.3 SEEPAGE DISTRIBUTION

As previously discussed, we installed seepage meters along eight survey lines which contained enough granular material to adequately seat the seepage meters. Once installed, the water collection assemblies on the seepage meters were repalced every one to three days, with several assemblies left on longer to determine any temporal variation.

From our seepage meter survey, we determined field values of pH, electrical conductivity and temperature of water collected from the seepage meters. We also measured volumes of seepage, and from determining the time elapsed between measurements, the seepage rates for a number of stations along the survey lines were calculated.

The seepage rates varied both temporally and areally. Table 2 shows the average seepage rates for the seven survey lines where seepage meters could be installed (Appendix 5 contains the field data on the seepage study). The data in Table 2 represent the re-calculated means of the seepage values at each station after seepage rates differing from the mean by more than two standard deviations were removed.

There appears to be no simple relationship between the observed thickness of the granular sediment and the seepage rates (Figure 20), nor is there an obvious relationship between seepage rate and distance from shore (Figure 21). River stage fluctuations were also examined to determine if any correlation existed between average seepage rates and change in river elevations. Again, an obvious relationship was not evident.

TABLE 2. Groundwater seepage into the St. Clair River

SEEPAGE RATE (mL/h/m^2)
STATION NUMBER

LINE	1	2	3	4	5	6	7	9	11	$\overline{x}$	s
L. Huron	59	134	136	-	9	-	3	30	5	58	56
George	1	-	5	-	9	-	10	13	23	10	8
Cromwell	29	-	6	-	32	-	20	132	46	44	45
Police	7	-	21	-	61	-	34	14	49	31	21
Red-D-Mix	2	-	39	-	4	-	135	67	112	60	55
Suncor	-	-	19	-	19	-	61	-	176	69	74
Concrete	-	8	8	25	99	131	161	-	-	72	67

* distance from shore = (Station No. - 1) x 10 m
1 mL/h/m^2 = 2.8 x 10x-10 m^3/s/m^2

$\overline{X}$=mean S=standard deviation

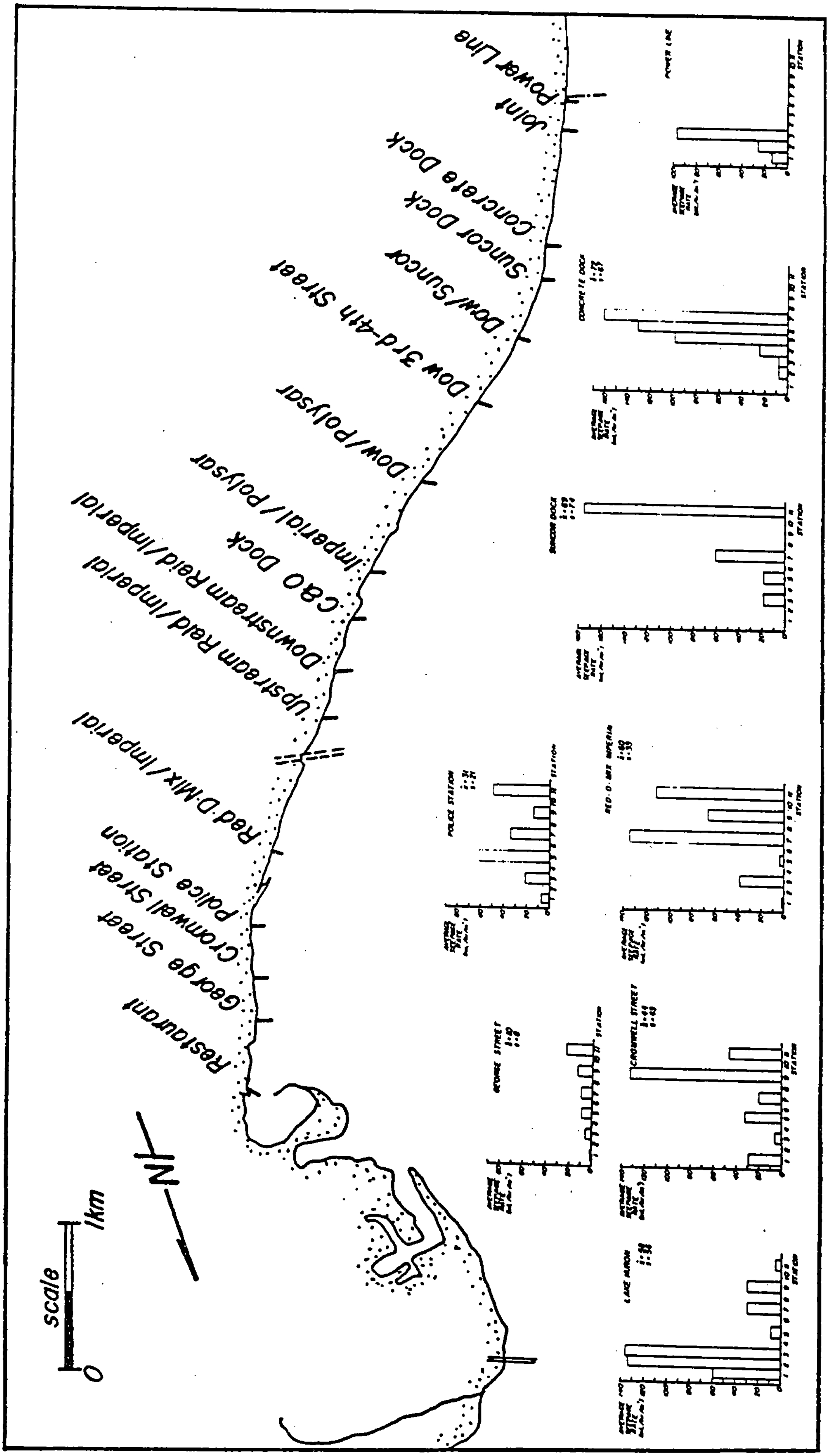


Figure 20. Seepage distribution along survey lines.

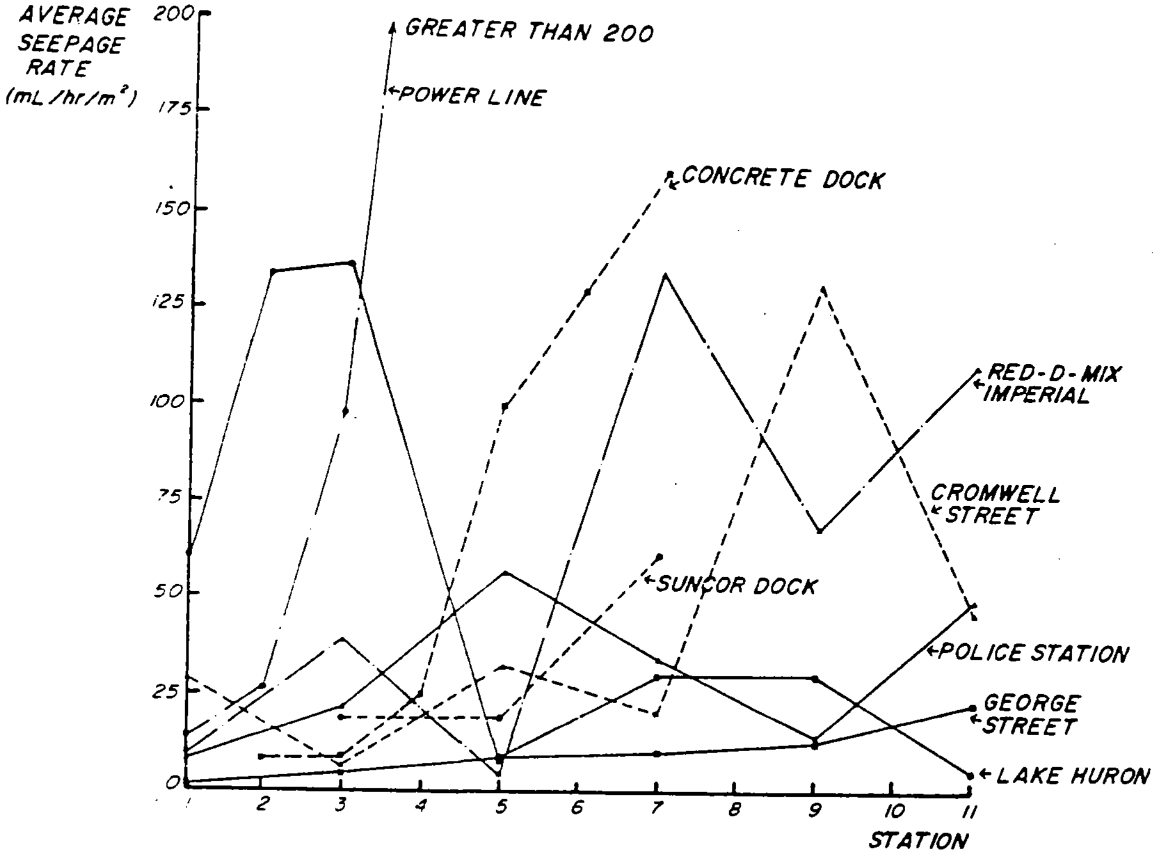


Figure 21. Relationship between distance from shore and seepage rate.

The electrical conductivity (EC) and pH values of the water collected from the seepage meters are similar to those of the river water. The mean and standard deviation of the river water EC and pH (n=7) were 204 and 50 uS/cm and 7.47 and 0.34, respectively. The seepage meter waters had EC values between 104 and 495 uS/cm and pH values between 5.9 to 8.7. Due to a malfunction of the temperature probe on the conductivity meter during field work, none of the EC values are temperature corrected to 25 C. However, since all of the samples collected were about the same temperature throughout the study, relative errors in the EC values should be small.

The similarity in EC and pH of the streambed groundwater and the river water can be explained in three ways: (1) river water leaked into the seepage meters, (2) the seepage was so slow that little displacement of the river water trapped during installation of the seepage meter, had occurred, or (3) the streambed groundwater had the same EC and pH as the river water. In situations where the granular deposits are thin and poor seals between the seepage meter and the clay could be expected, the leaking hypotheses is likely to be correct. The hypothesis that the EC and pH values of the streambed groundwater and the river water are the same is disproved by the minipiezometer data which will be discussed in the next session. The low seepage rate hypothesis seems to be the most likely.

Assuming the optimum seepage conditions (8 cm of the seepage meter buried and the maximum recorded seepage rate of 565 mL/h/m^2), the minimum time required to displace the river water would be over 5 days. Taking into consideration that the average seepage rate was an order of magnitude lower, complete displacement would require more than 50 days. Since we sampled our seepage meters every few days, and since no seepage meters were left in place for more than a few weeks, most of the water collected in the collection assemblies was displaced river water with some streambed groundwater.

Darcy's Law can be used to estimate complementary sets of hydraulic conductivity and hydraulic gradient values necessary to satisfy the observed seepage rates. Table 3 lists the calculated hydraulic gradients for given hydraulic conductivities, assuming that the average of the survey line average seepage rates (approximately 1.4×10^{-8} $m^3/s/m^2$ or 49 $mL/h/m^2$) represents the seepage rate from the streambed into the river.

Desaulniers et al. (1981) report that the hydraulic conductivities of the upper 20 m of till are in the order of 10^{-10} m/s. From Table 3, this magnitude of hydraulic conductivity suggests that either there is an extremely high hydraulic gradient in the streambed or that the hydraulic conductivities in the streambed are 2 to 4 orders of magnitude greater than the 10^{-10} m/s estimate. Isotopic and EC data for some streambed groundwater are consistent with water moving through the near-surface fractured clay which could have hydraulic conductivities of from 2 to 4 orders of magnitude greater than 10^{-10} m/s.

Assuming that the values of hydraulic conductivity determined by Desaulniers et al. (1981) do apply to the streambed and that hydraulic gradients are between 0.01 and 1, then it would take between 162 days and 44 years to completely displace the river water from the seepage meter. Since several of the seepage meters collected water with noticeably higher EC values than the river (perhaps a mixture of river water and groundwater) after only a

TABLE 3. Calculated hydraulic gradients in the streambed

HYDRAULIC CONDUCTIVITY (-log K in m/s)	HYDRAULIC GRADIENT
10	140
9	14
8	1.4
7	0.14
6	0.014
5	0.0014

few days, it is unlikely that the low hydraulic conductivities suggested by Desaulniers et al. (1981) can apply to the streambed.

4.4 MINIPIEZOMETER DATA

Due to time limitations on the field study, minipiezometers were installed on only 2 of the 17 survey lines, George Street and Cromwell Street. The minipiezometers were installed to depths of 1.0 and 1.5 m below the streambed, at 4 stations on the George Street line and 2 stations on the Cromwell Street line. Hydraulic heads were not measured because of generally slow response times, time constraints on the field work, and gas bubbles in the line. At Cromwell Street Station #11 (100 m from shore, 1.5 m depth), water flowed from the teflon tube to a height of approximately 70 cm above river level after the sampling tube was removed from the pump.

There is an apparently significant difference in the EC values of the streambed groundwater and the river water: the mean and standard deviation of 19 streambed groundwater samples are 996 and 328 uS/cm while the mean and standard deviation of 7 river water samples are 204 and 50 uS/cm (Appendix 6, complete field data). The EC values of the streambed groundwater are greater than the EC values in the freshwater aquifer near Sarnia (Scott and Sklash, 1986) (Figure 22). Due to the lack of domestic wells in and around Sarnia, the freshwater aquifer survey did not include samples adjacent to the St. Clair River near Sarnia, the 36 residental wells that were sampled were spread out throughout Lambton County (Scott and Sklash, 1986) (Figure 23, locations of wells sampled in the freshwater aquifer).

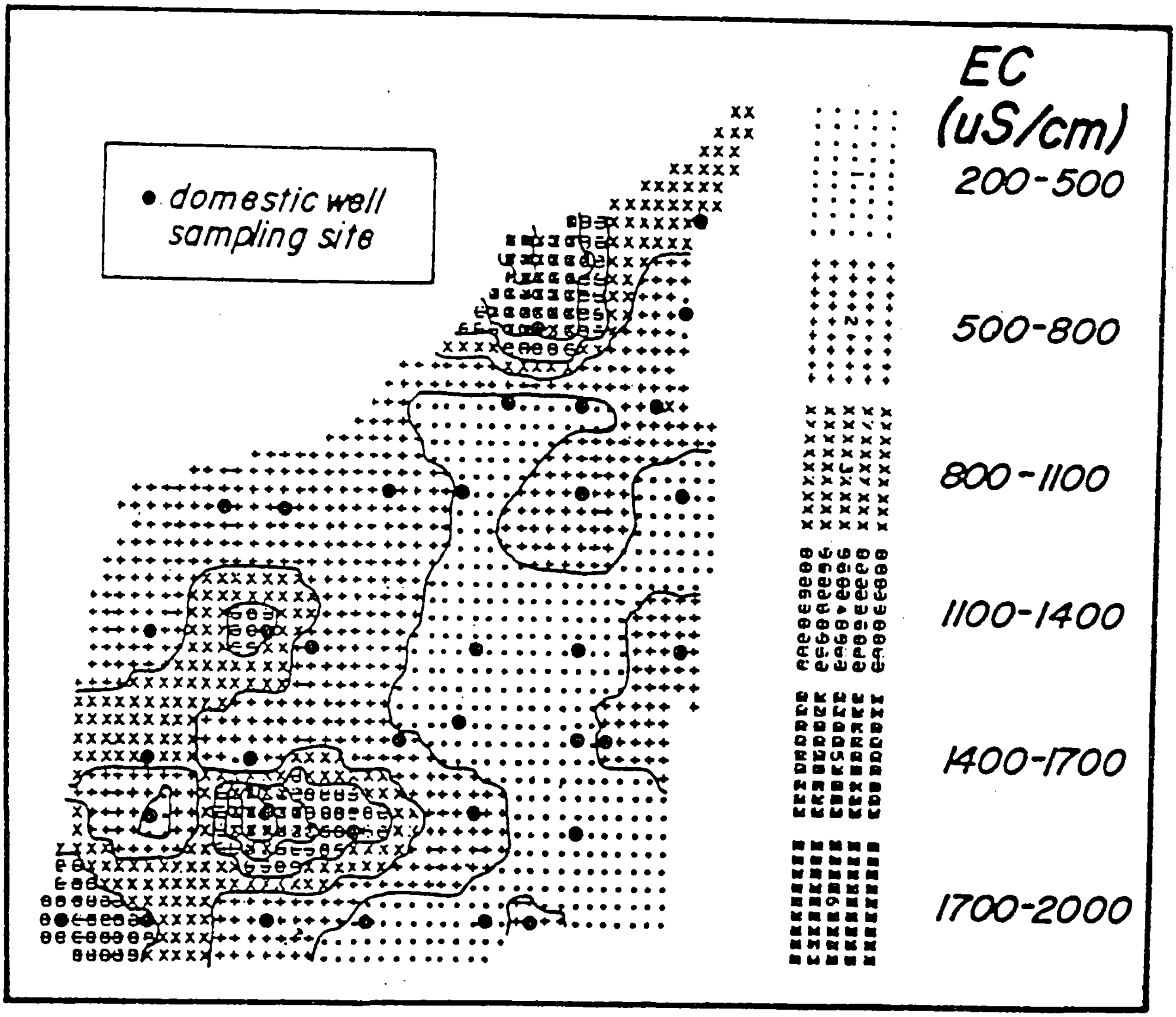


Figure 22. Contour map of electrical conductivity of the freshwater aquifer in Lambton County (after Scott and Sklash, 1986).

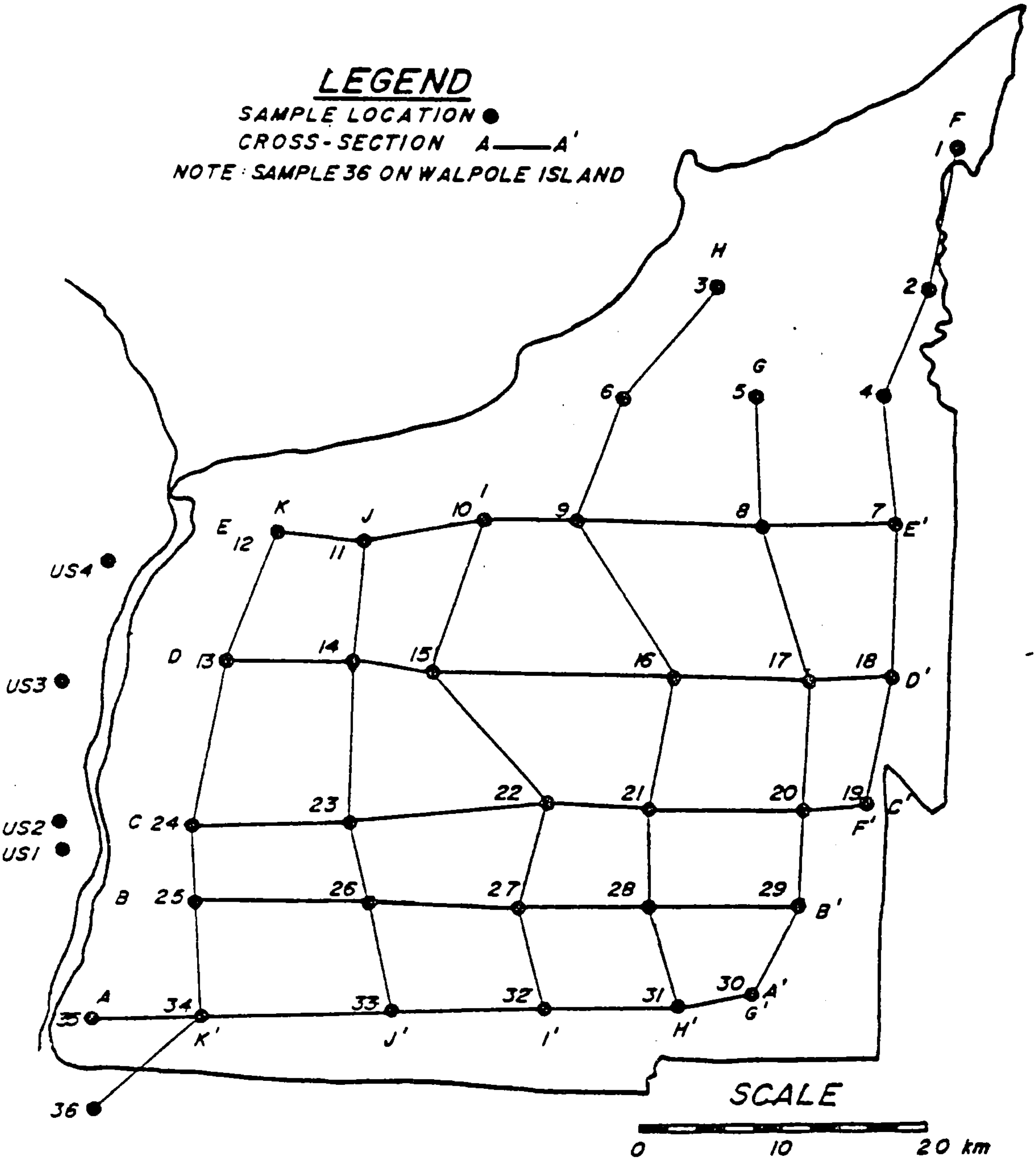


Figure 23. Locations of wells sampled in the freshwater aquifer (after Scott and Sklash, 1986).

The ranges of pH for the streambed groundwater and river water were not as noticeably different. For 19 streambed groundwater samples the pH ranged form 6.7 to 7.8, with a mean of 6.99 and a standard deviation of 0.32. The pH values of the river water were 7.0 to 7.8, with a mean of 7.47 and a standard deviation of 0.34 (n=7). The pH values of the freshwater aquifer near Sarnia are generally between 7.0 and 8.0 (Figure 24) (Scott and Sklash, 1986). Since the pH values of water from the river, streambed, and freshwater aquifer are all similar, pH is not a good tracer for determining the source(s) of water in the streambed.

4.5 CHEMICAL ANALYSES

4.5.1 CHLORIDE

Twenty-three river water and streambed groundwater samples were analyzed for chloride (Cl^-) (Appendix 7, analytical results). A statistical difference exists between the mean chloride concentrations of the river water and the streambed groundwater. The Cl^- levels in the river water ranged from 5.2 to 5.5 mg/L, with a mean of 5.34 mg/L and a standard deviation of 0.13 mg/L. In contrast, the Cl^- levels in the streambed groundwater ranged from 7.8 to 111 mg/L, with a mean of 33.9 mg/L and standard deviation of 37.9 mg/L. Of the 18 streambed groundwater and river water samples analyzed, 5 contained Cl^- levels in excess of 80 mg/L. These 5 samples were obtained from the George Street line (Station # 5), with 4 of the 5 samples being from the 1.0 m depth.

These Cl^- levels do not appear excessively high when compared to the Cl^- levels of the shallow groundwater reported by Vanderberg et al. (1977) of 332 to 2180 ppm (mg/L), or Desaulniers et al. (1981) of 0 to 10 mol/m^3 (0 to 350 mg/L), however, when the Cl^- values are plotted against tritium (Figure 25)

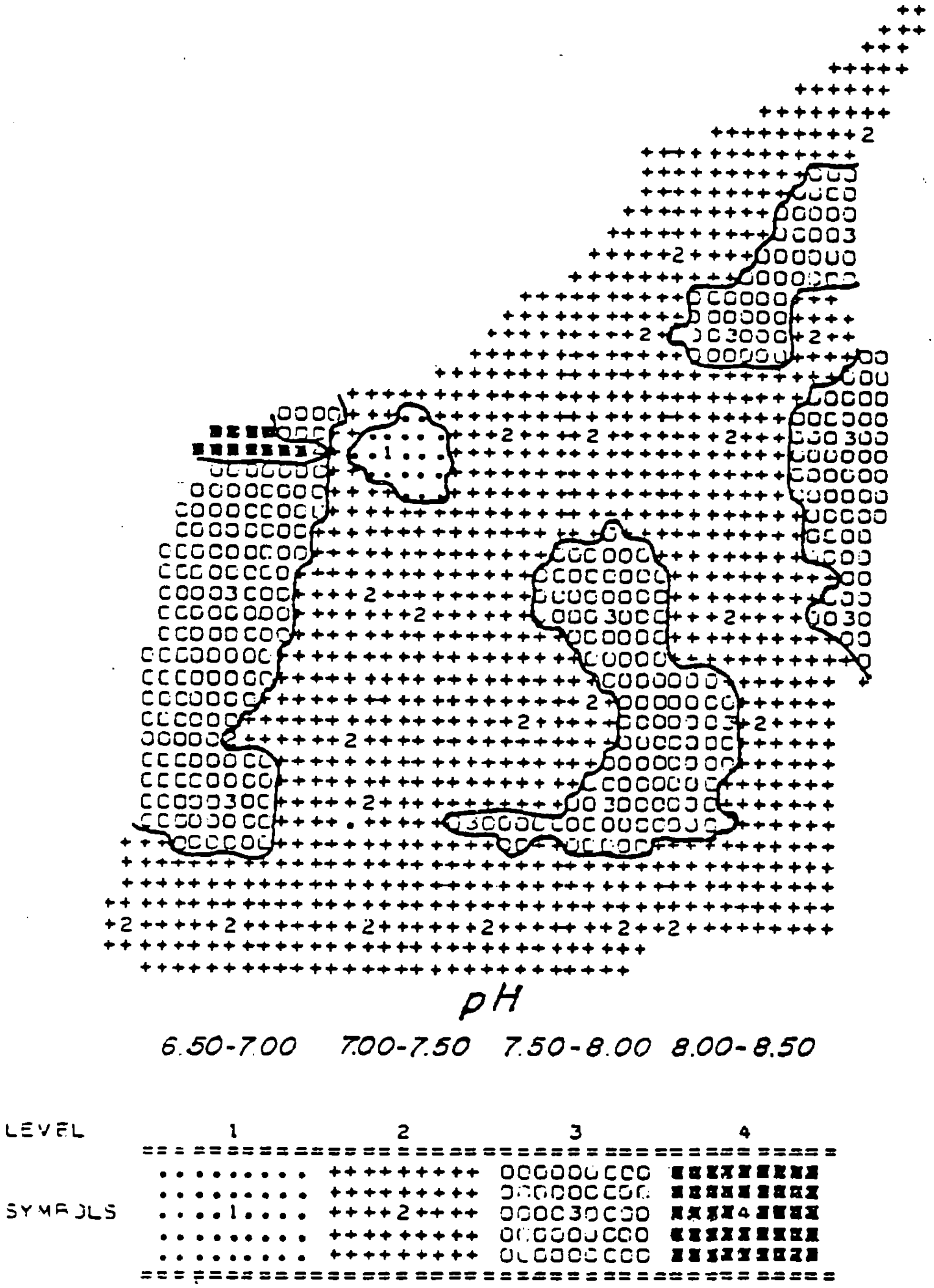


Figure 24. Contour map of pH values in the freshwater aquifer (after Scott and Sklash, 1986).

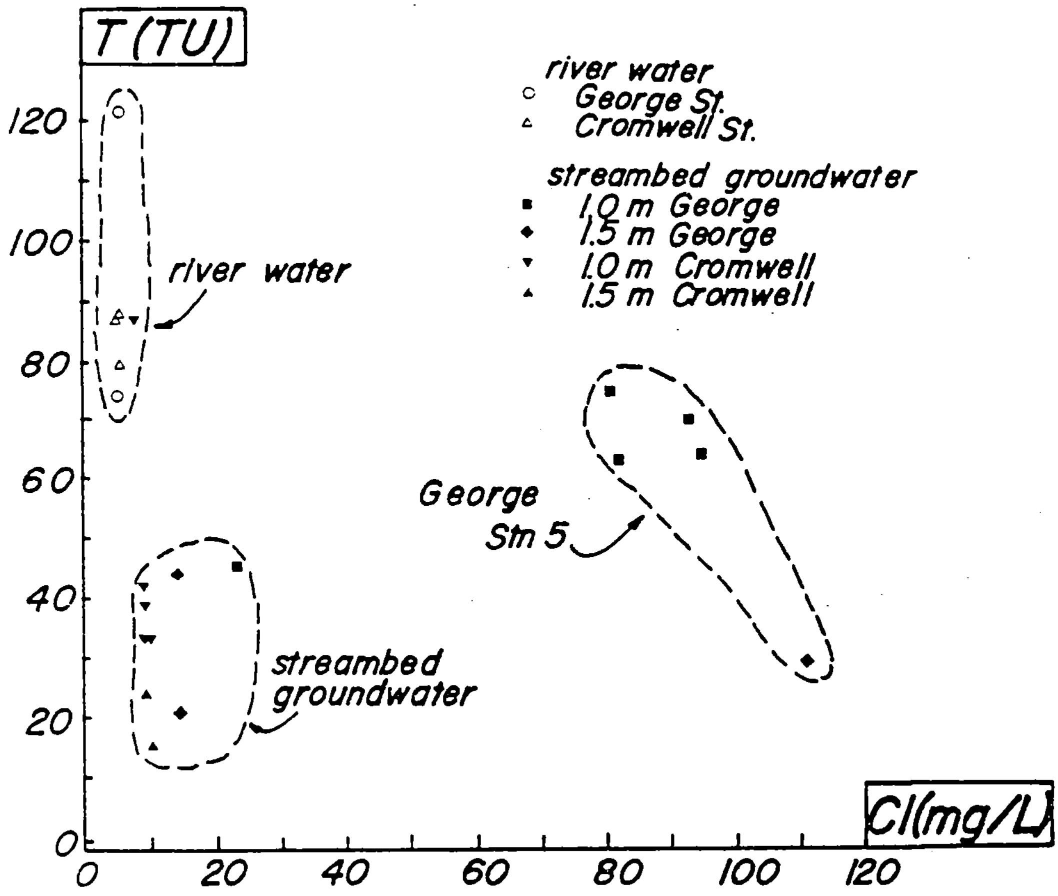


Figure 25. Plot of tritium versus chloride.

and ^{18}O (Figure 26), these 5 samples appear on each graph as an anomalous area. The TOX results for George Street Station # 5 also contained some of the highest levels reported in this study (discussed in the following section).

Another indication that the George Street Station 5 samples, especially from the 1 m level, are anomalous is the relationship between chloride and electrical conductivity (Figure 27). The obviously higher chloride and relatively low EC compared to the other streambed groundwater samples, suggest that the 1 m samples from George Street Station 5 are derived from a different source or sources than the other streambed groundwater samples.

Again, although the Cl^- values are not excessively high, they still may be indicative of contaminants entering the river at this location and warrant further investigation.

4.5.2 TOTAL ORGANIC HALIDES

There were a total of 29 samples of river water, streambed groundwater, blanks, spikes and duplicates analyzed for TOX by Zenon. Samples showing elevated TOX levels were selected for additional analyses, which included: 11 samples with the highest uncorrected TOX values analyzed for chlorinated hydrocarbons including polychlorinated biphenyls, and trihalomethanes, and 5 samples analyzed for the EPA Priority Pollutant Extractables. It should be noted that one of the two lab blanks supplied by Zenon, for use during water sampling, showed noticeable TOX values of 3.0 ug/L and 9.95 ug/L (9.95 ug/L is

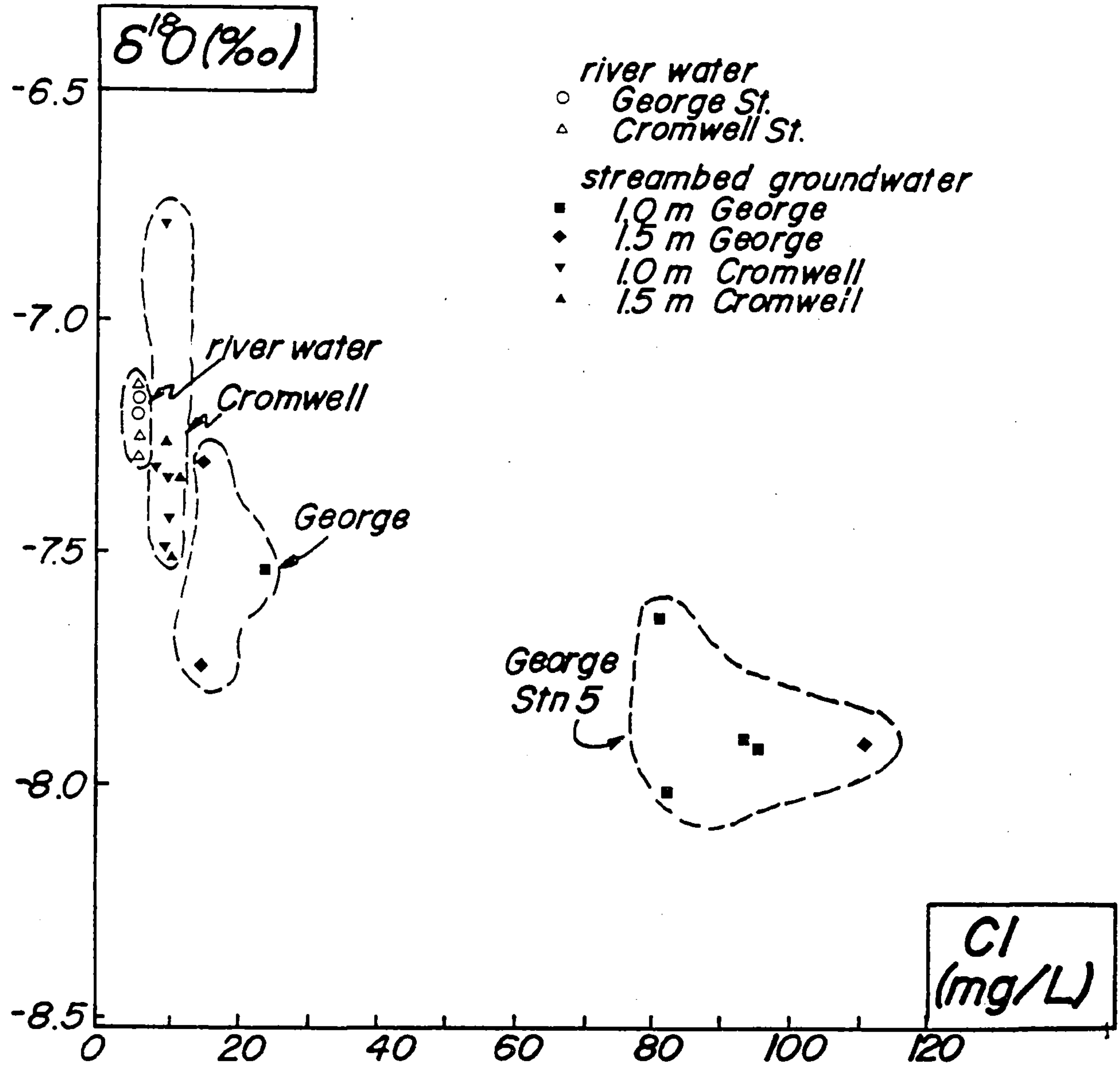


Figure 26. Plot of oxygen-18 versus chloride.

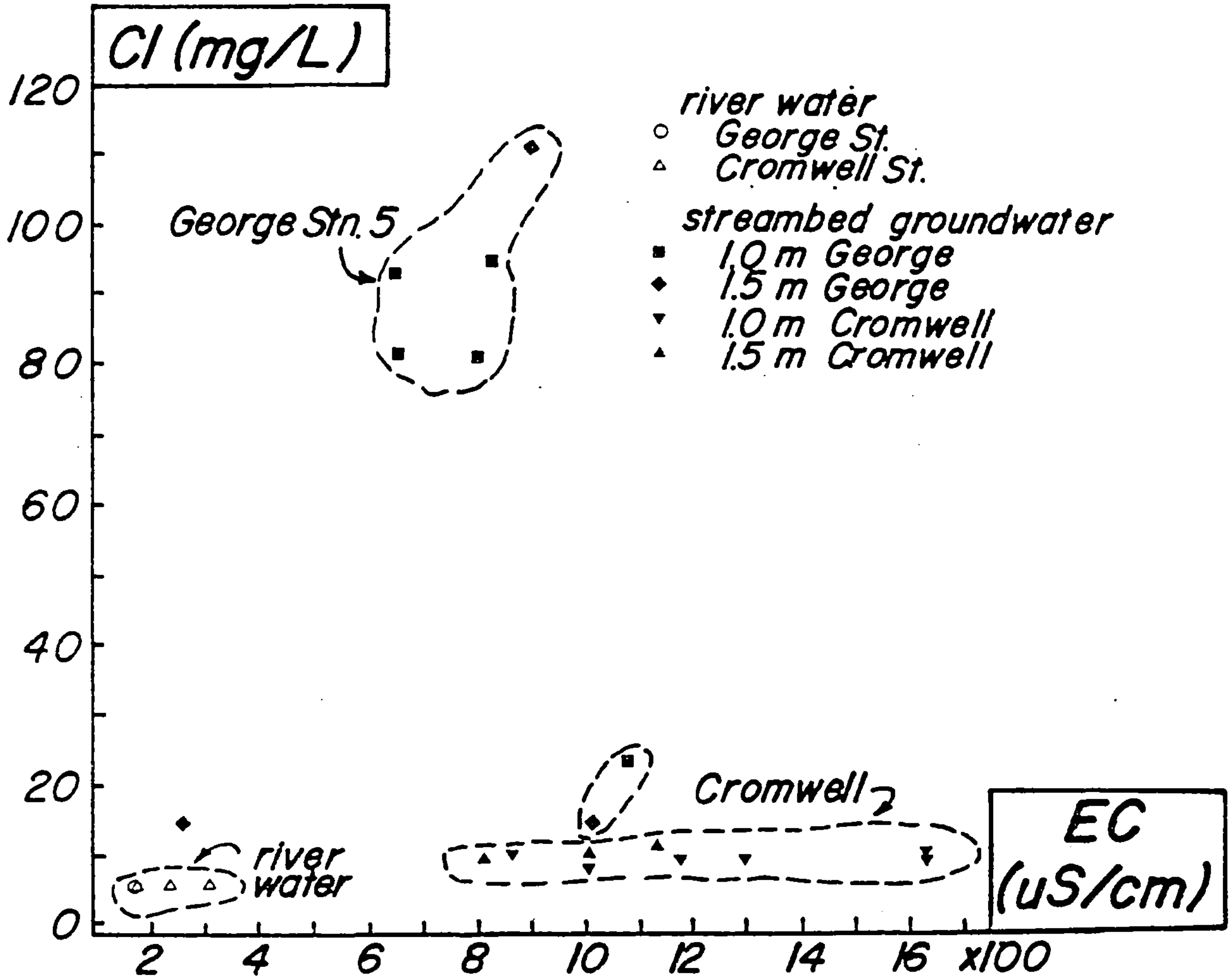


Figure 27. Plot of chloride versus EC. aquifer (after Vanderberg et al., 1977).

an average of a duplicate run on one of the blanks with reported values of 11.5 ug/L and 8.4ug/L) (Appendix 8, TOX results). These elevated values indicate possible lab interference introduced through sample bottles, blank water, or analytical procedures. These blank values were taken into consideration during the interpretation of the analytical results, however, the values reported do not reflect corrected values. Due to time limitations additional sampling and/or additional analyses were not performed to confirm or refute these results.

The uncorrected TOX values for the 29 samples ranged from <1 to 18.3 ug/L, with a detection limit of between 1 and 5 ug/L depending upon the compound (Foster, personal communication). When considering the blank values, elevated but not excessive TOX levels were detected. The highest TOX values were reported at George Street Station #11 (river water), and Station #5 (streambed groundwater), with values of 18.3 and 16.0 ug/L respectively. As previously discussed, George Street Station #5, showed anomalous results for EC, T, ^{18}O and Cl^-, and also contains a number of the highest TOX values reported. This water appears to be different from the water of other stations along the George Street line and from the water encountered on the Cromwell Street line at the same depth.

4.5.3 CHLORINATED HYDROCARBONS AND PCB

The 11 samples analyzed for chlorinated hydrocarbons and polychlorinated biphenyls (PCB) showed detectable levels of chlorinated hydrocarbons (<0.0027 ug/L) in particular: hexachlorobenzene (HCB) (<0.0027 ug/L), a-benzenehexachloride (<.00022 ug/L), g-benzenehexachloride (<0.0019 ug/L), and p,p'-DDE (<0.0014 ug/L). The total chlorinated hydrocarbons were <0.0067 ug/L, with the value of the lab blank reported at <0.0009 ug/L (Appendix 9). The St. Clair River Pollution Investigation (Environment Canada and Ontario Ministry of the Environment, 1986) reported appreciable concentrations of HCB in river water downstream of our survey lines, in the vicintiy of Dow's property, with elevated levels persisting for at least 25 km downstream. HCB concentrations ranged from 1.0 ng/L (ppt) at the mouth of the St. Clair River, to 15 ng/L just below Sun Oil Company Ltd. (Environment Canada and Ministry of the Environment, 1986). A reported value of 1.0 ng/L HCB was detected at a sample location in the area of our George Street and Cromwell Street lines (Figure 28). The highest concentrations of HCB were detected at sampling locations located from downstream of Dow Chemical to Sun Oil Company Ltd. (Figure 29) (Environment Canada and Ministry of the Environment, 1986).

Some interference was encountered during the analysis for PCB's thus reducing the number of PCB results to 8. Of these 8 samples, PCB was detected at several stations on both the George Street and Cromwell Street survey line. Values ranged up to 0.0026 ug/L.

4.5.4 TRIHALOMETHANES

Various trihalomethanes were evident in all the samples with values ranging from 0.04 to 2.77 ug/L (Appendix 10). A field blank, also analyzed for trihalomethanes, showed levels from 0.04 to 1.18 ug/L for various parameters. Carbon tetrachloride (CTC) (<0.29 to 1.76 ug/L), tetrachloroethylene (<0.08 to 1.18 ug/L) and chloroform (<0.47 to 2.77 ug/L) were detected in all the samples. The Environment Canada and Ministry of the Environment Study reported CTC levels in the range of 1 to 10 ng/L, these levels were detected in the river water at most stations along the western

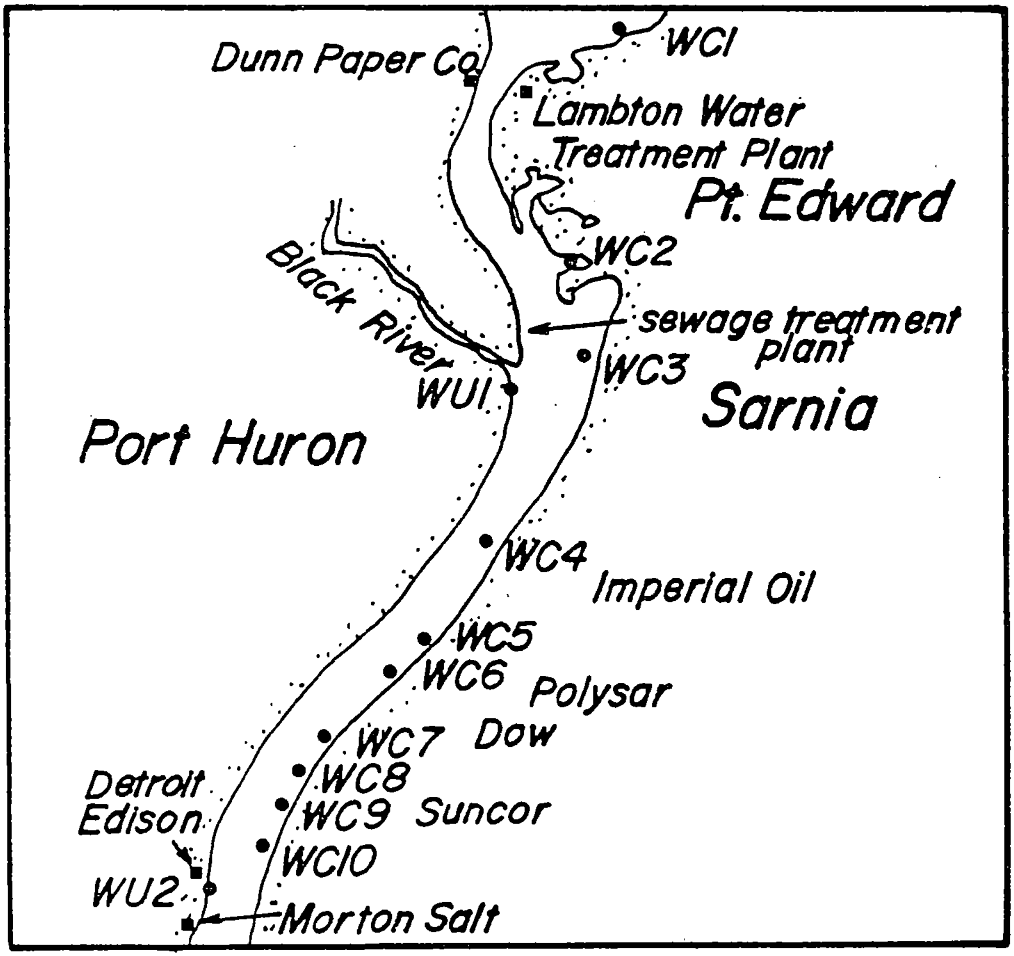


Figure 28. Water sample locations, St. Clair River Pollution Investigation (after Environment Canada and Ministry of the Environment, 1986).

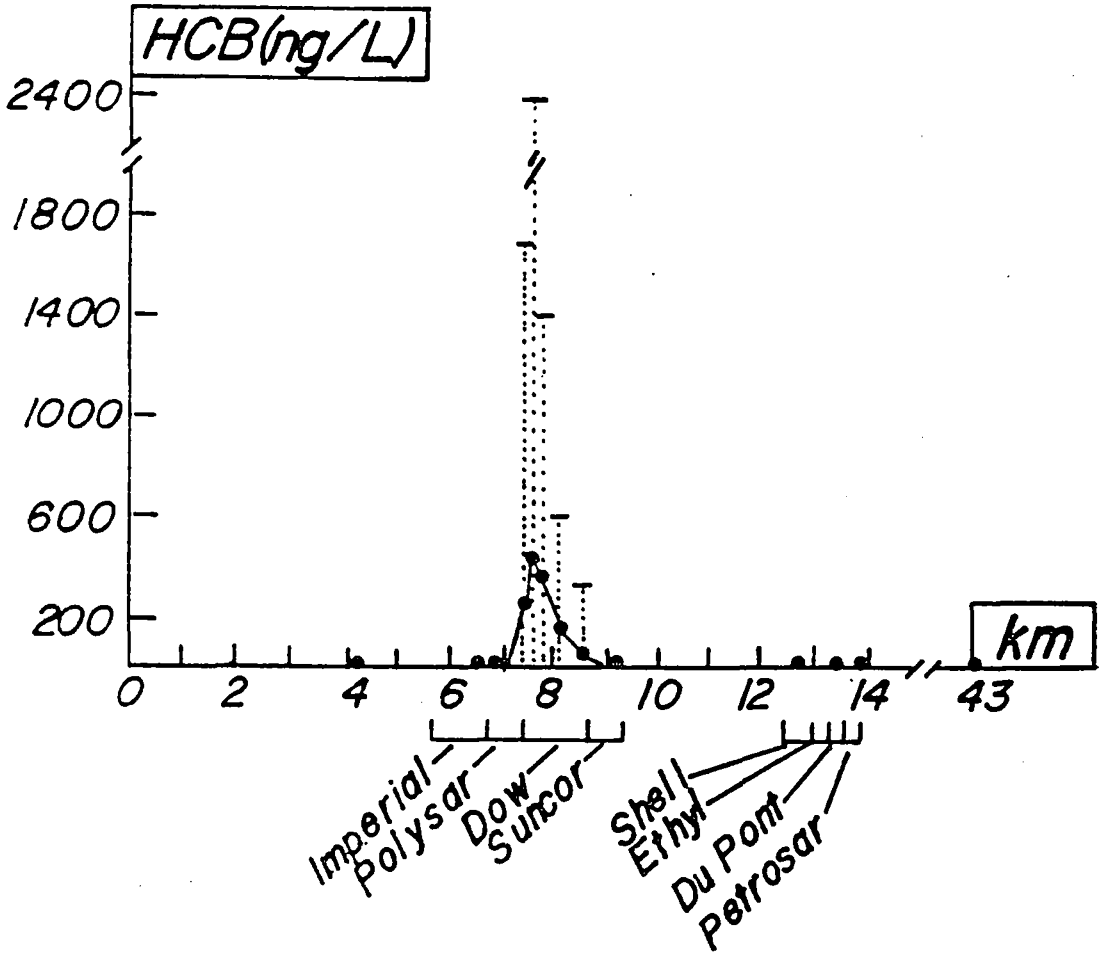


Figure 29. Hexachlorobenzene in river water, St. Clair River Pollution Investigation (after Environment Canada and Ontario Ministry of the Environment, 1986).

shore of the river, and upstream stations on the eastern shore. A CTC concentration of over 2000 ng/L was found at a station just upstream from the CN railway tunnel (downstream of our George Street and Cromwell Street lines). Elevated levels were also observed at downstream locations, with the CTC appearing primarily in the near shore zone (Environment Canada and Ministry of the Environment, 1986). Another parameter included in this study was chloroform, with levels of between 10 to 20 ng/L observed in the river water on both sides of the river. As noted in the report, chloroform is primarily a by-product of raw and waste water chlorination and the observed concentrations are expected from the large volume of cooling water discharged along the St. Clair River.

4.5.5 BASE/NEUTRAL AND ACID EXTRACTABLES

An EPA Priority Pollutant (base/neutral and acid extractable) analysis was performed on 5 samples. No acid extractables, including phenols, were detected in any samples (detection limits between 1 and 5 ug/L) (Appendix 11). Base/neutral extractables were detected at stations along both survey lines, George Street and Cromwell Street (Appendix 12). Of the base/neutral extractables detected, benzo(ghi)prylene (<2.4 ug/L), dibenzo(a,h,)anthracene (<0.4 ug/L), and indeo(1,2,3,-cd)pyrene (<2.4 ug/L) were the most prevalent, at detection limits of 0.05 to 1.0 ug/L. PCB's were not detected on this scan because of the higher detection limit of 2 ug/L.

As evidenced from our chemical analysis of the streambed groundwater and river water samples taken along the George Street and Cromwell Street survey lines, low to moderate concentrations of contaminants appeared in these water samples. This may be indicative of contaminants entering the river via streambed seepage, further investigation is warranted.

4.5.6 ISOTOPE DATA

As part of this study, we used natural tritium, oxygen-18 and deuterium concentrations in the river water and streambed groundwater to aid in determining the age, origin and movement of the groundwater in the study area. This data was also applied in the determination of potential impacts to the groundwater of the area caused by past deep well disposal practices.

Data compiled from several isotopic studies conducted in southwestern Ontario, particularly in the Sarnia area, (Brown, 1970; Desaulniers et al., 1981; Scott and Sklash, 1986), have supplied us with isotopic data for the, freshwater aquifer, shallow groundwater and river water in the study area. From this data and data collected during our investigation, we have attempted to determine the interrelationships between the groundwater in the shallow, fractured clay, the deep overburden aquifer (freshwater aquifer), the St. Clair river water, and the streambed groundwater.

Figure 30 is a plot of the oxygen-18 and tritium data for the streambed groundwater samples, the river water at the George and Cromwell Street lines, river water from the Chenal Ecarte (in the delta of the St. Clair River), and the shallow groundwater from the upper 10 m of clayey till at the Suncor landfarming site near the southern boundary of the study area. The oxygen-18 and tritium data for these water sources are summarized in Table 4 (Appendix 13 contains the complete isotope results).

There are several obvious groupings of the oxygen-18 versus tritium data

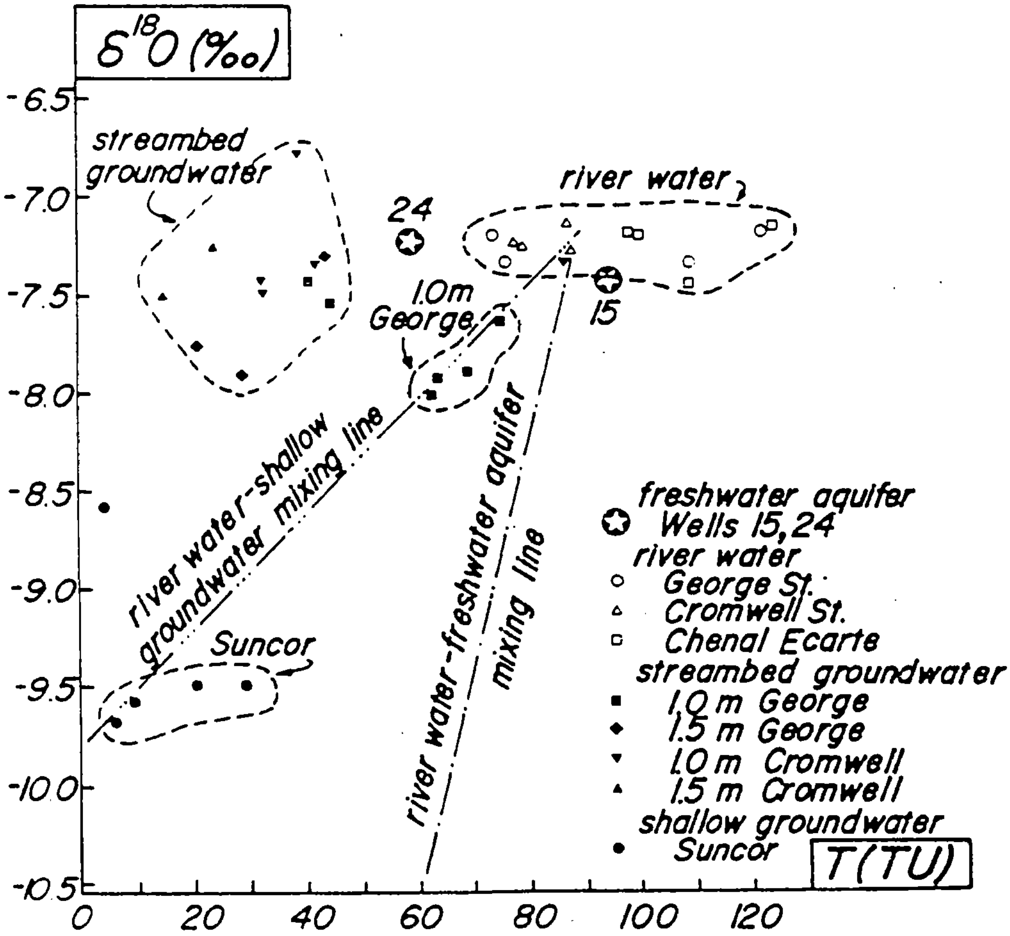


Figure 30. Plot of oxygen-18 versus tritium.

TABLE 4. Summary of oxygen-18 and tritium data

SOURCE	Oxygen-18 (‰)			Tritium (TU)		
	n	$\bar{x}$	s	n	$\bar{x}$	s
minipiezometer 1.0 m	11	-7.53	0.34	11	53.4	18.6
minipiezometer 1.5 m	6	-7.51	0.26	6	23.2	12.9
Suncor wells 10 m	5	-9.37	0.43	5	14.0	10.2
St. Clair River	8	-7.25	0.08	8	89.1	17.4
Chenal Ecarte	4	-7.25	0.13	4	108	11.8

n = number of samples, $\bar{x}$ = mean, s = standard deviation in Figure 30. The shallow groundwater samples from the Suncor wells are more depleted in oxygen-18 and much lower in tritium than the river samples which plot in the opposite corner of the figure. The oxygen-18 values of the Suncor samples are typical of the current mean annual rainfall oxygen-18 values for southwestern Ontario (Desaulniers et al., 1981). The low tritium values in the shallow groundwater can be expected when considering the the low matrix permeability of the clayey till, with higher values suggesting the influence of fractures. Both the oxygen-18 and tritium concentrations from the Suncor site are consistent with the values for shallow groundwater in the Sarnia area reported by Desaulniers et al. (1981).

The relatively enriched oxygen-18 values (due to evaporation in the lakes) and the characteristic tritium values (ranging from about 80 to 130 TU) for the river water, are consistent with the isotopic values of the water at the outlet of Lake Huron reported by Brown (1970). Brown noted tritium concentrations of 179 and 200 TU in 1966 and 1969, respectively. Considering the half-life of tritium and the effects of long residence times in the upper Great Lakes, the tritium values which we obtained for the river are reasonable.

The samples from the minipiezometers fall into two distinct groups in Figure 30. The 1.0 m samples from the George Street line fall on a mixing line between the shallow groundwater from the Suncor wells and the river water. The other streambed groundwater samples fall into a group which is slightly more depleted in oxygen-18 than the river water and which has less than one-half of the tritium of the river water samples. These samples do not fall along the river water-shallow groundwater mixing line and the source(s) of this water are currently unknown.

Cluster analyses were performed on the streambed groundwater and the river water samples. The cluster analysis for tritium (Figure 31) shows two distinct groups: one group consists of samples taken from the minipiezometers at depths of 1.0 and 1.5 m, the second group consists of predominately river water samples. Four samples taken from the 1.0 m depth (at Station # 5) on the George Street line, are similar in tritium content to the river water. These samples belong to the same group of samples that appeared as one of the distinct groups on the ^{18}O versus tritium plot, and they also form an anomalous group on the Cl^- versus EC plots and other plots. The ^{18}O cluster analysis indicates two main groupings: streambed groundwater, and a river water/streambed groundwater mixture (Figure 32). The cluster analyses confirms the presence of several distinct groups of water present in the study area.

Figures 33 and 34 are computer derived (SYMAP) contour plots of the oxygen-18 and tritium concentrations in the freshwater aquifer in Lambton County (Scott and Sklash, 1986). Scott and Sklash found that the oxygen-18 concentrations in the freshwater aquifer follow a trend from recent precipitation values ($\delta^{18}O$ of approximately -8 to -10 ‰) in the recharge area in the eastern part of Lambton County to very depleted values (about -17 ‰) near the St. Clair River in the west. These depleted values, according to the findings of Desaulniers et al. (1981), represent water which is in the order of 10,000 years old. The east to west gradation noted by Scott and Sklash can be considered as the horizontal equivalent of the vertical profiles in the aquitard noted by Desaulniers et al. (1981) except that more advective

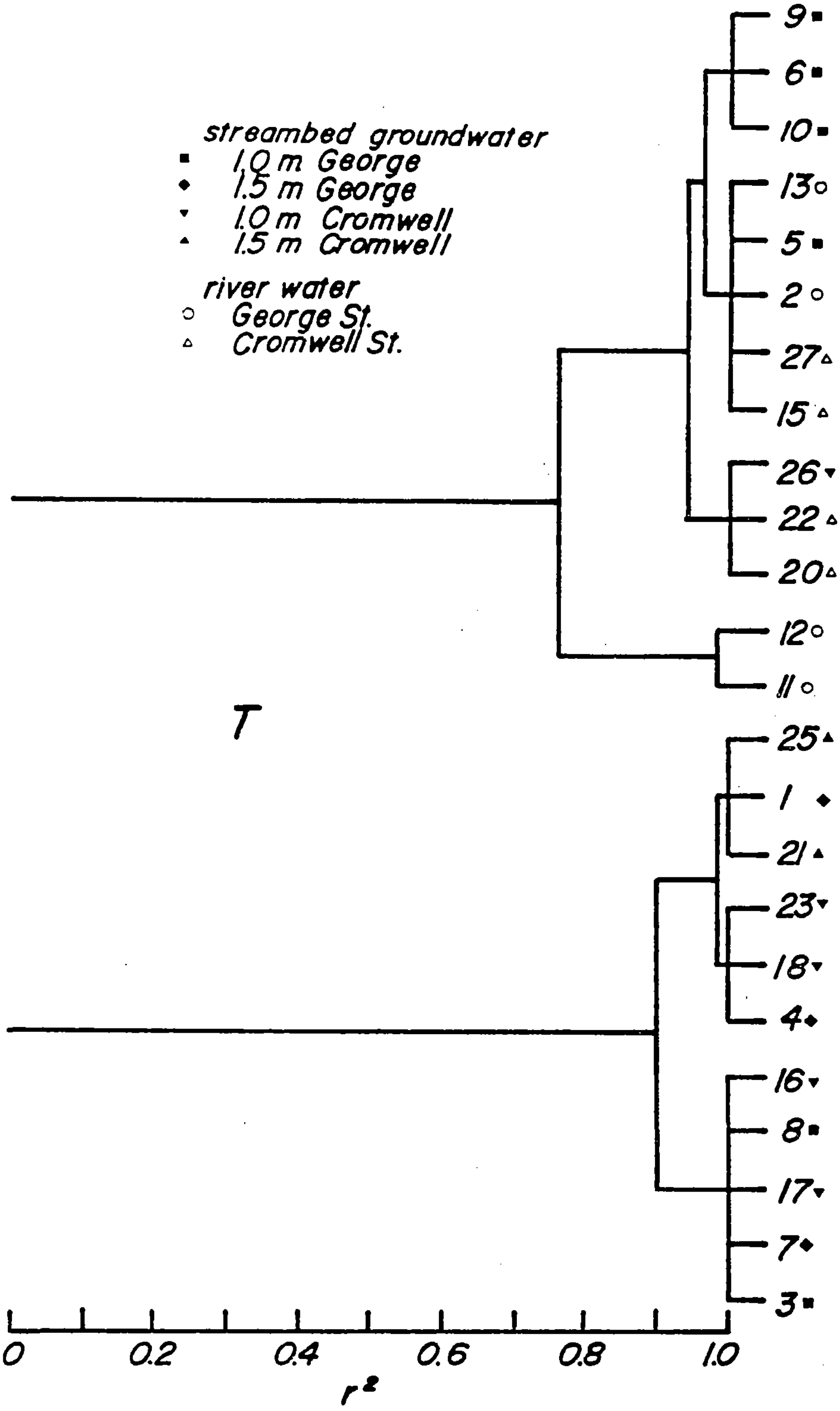


Figure 31. Cluster analysis for tritium data.

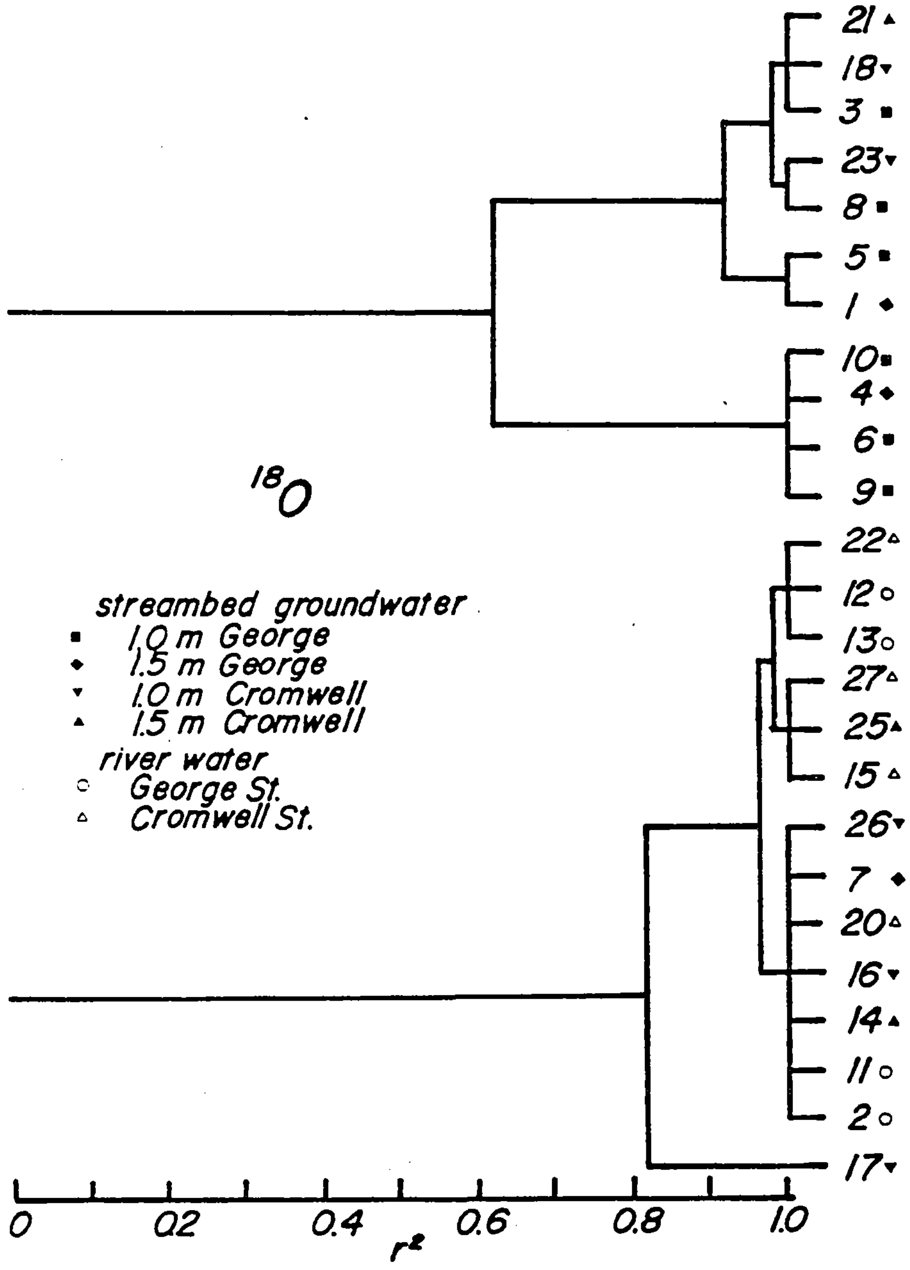


Figure 32. Cluster analysis for oxygen-18 data.

flux would be expected in the aquifer.

Scott and Sklash concluded on the basis of their tritium data from the freshwater aquifer, that in general, very young waters (<35 years old) occur in part of the recharge area in the eastern portion of the county and that most of the rest of the freshwater aquifer contains non-tritiated water.

Scott and Sklash also found strong evidence which suggests that the freshwater aquifer near Petrolia (near the Thompson Company injection wells) and south of Courtright (near the C.I.L. Injection Well #2), indicated by 15 and 24 on Figures 33 and 34, has been affected by deep well injection practices. GTC Geologic Testing Company Ltd. (1985) reported that both of these sites were suspected of causing problems: flowing wells near Courtright and oilfield problems near the Thompson wells. The anomalous domestic well near Courtright is close to a major bedrock structural feature. At both of these sites, anomalous ^{18}O and tritium values exist (Figures 33 and 34): -7.45 ‰ and 95 TU, and -7.24 ‰ and 58 TU, for the Petrolia and Courtright sites, respectively. These isotopic values are similar to the average river water values (-7.25 ‰ $\delta^{18}O$ and 89 TU) observed in this study.

Figure 35 is a plot of oxygen-18 versus deuterium for the various water samples. The meteoric water line based on a cross-section of freshwater aquifer samples and the shallow groundwater samples from Suncor is:

$$\delta D = 7.6 \delta^{18}O + 7.35$$

Since this line is parallel to the meteoric water line for southwestern Ontario (Desaulniers et al., 1981), it can be assumed that this line represents unevaporated meteoric water.

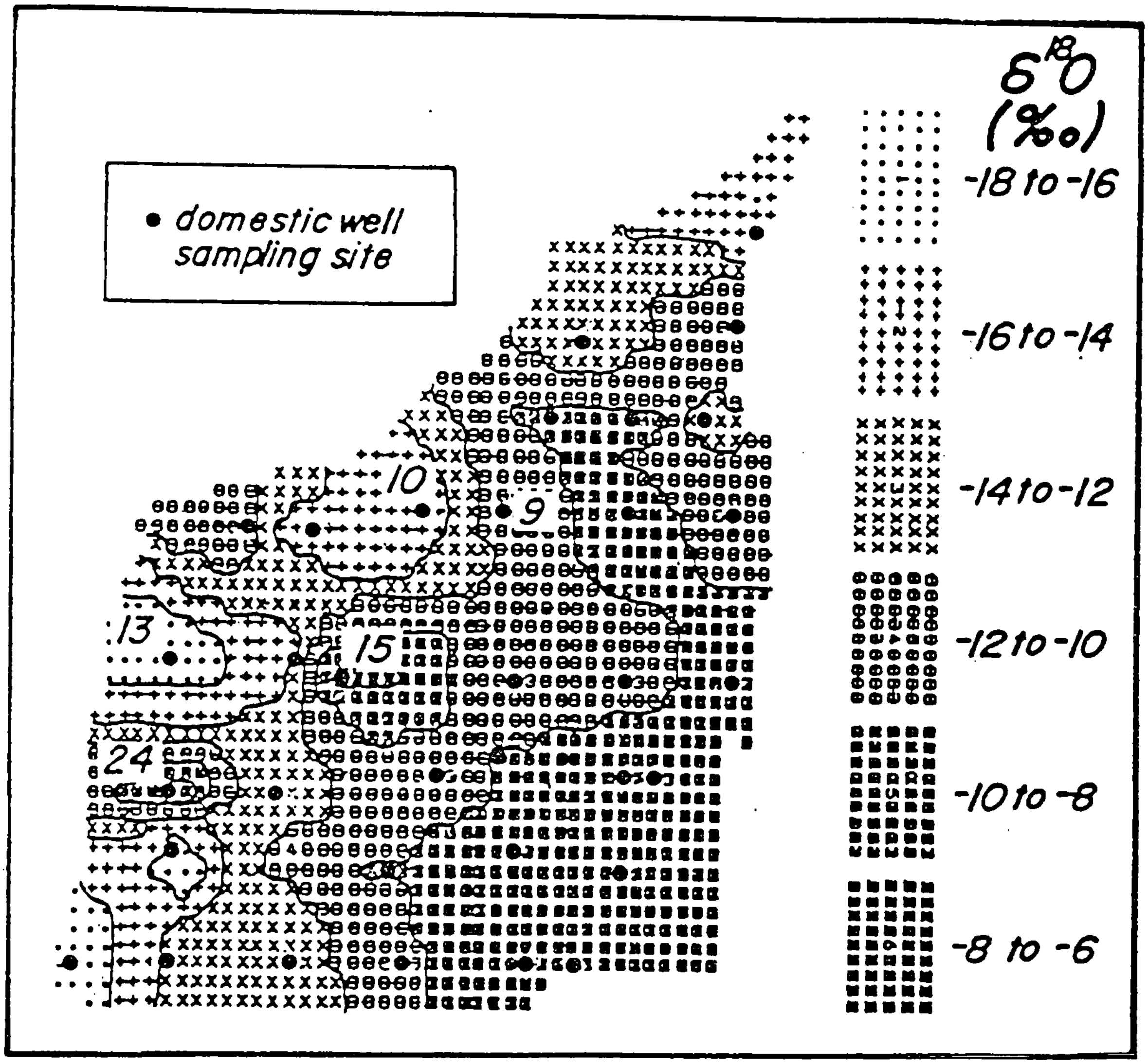


Figure 33. Contour map of oxygen-18 in the freshwater aquifer in Lambton County (after Scott and Sklash, 1986).

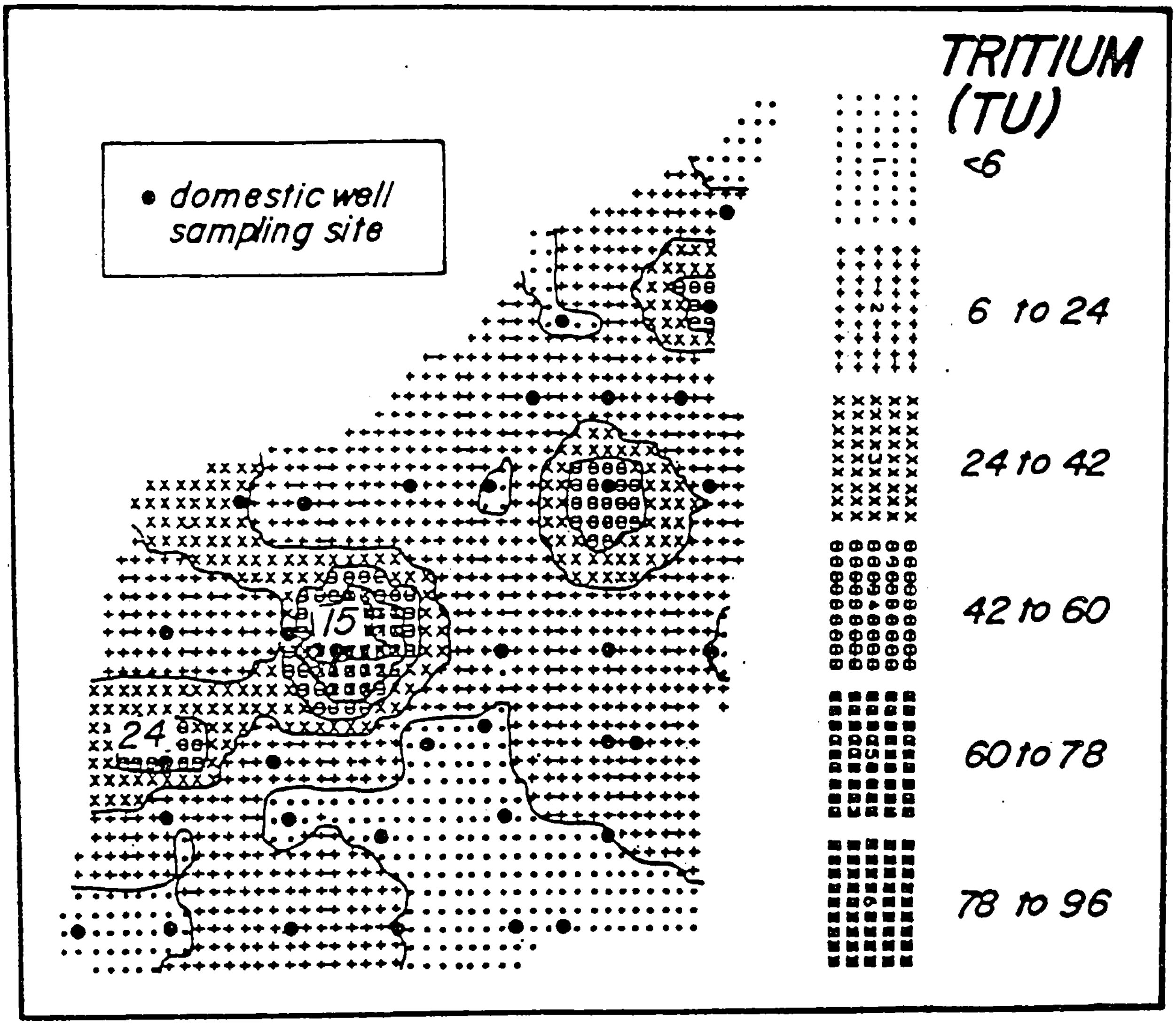


Figure 34. Contour map of tritium in the freshwater aquifer in Lambton County (after Scott and Sklash, 1986).

Also plotted on Figure 35 are some of the streambed groundwater samples and two river water samples. Since the river water samples fall below the meteoric water line, they represent evaporated water. These data are consistent with the findings of Brown (1970) who reported δD values of about -67 ‰ for the outlet of Lake Huron. The streambed groundwater samples also fall below the meteoric water line (between the river samples and the line) indicating either some evaporation of the streambed groundwater prior to recharge or that the streambed groundwater is mixed with evaporated water. Since the isotopic data for both the shallow groundwater at Suncor (except for one sample) and the freshwater aquifer near the St. Clair River (excluding the affected groundwater near Courtright) indicate that the groundwater is not evaporated, the mixture hypothesis is most likely to be true.

Table 5 summarizes the isotopic and EC information we have found for the various sources of water which may contribute to the streambed groundwater. One of the remaining unknowns is the isotopic character of the freshwater aquifer below the St. Clair River. Isotopic data is not yet available on the freshwater aquifer below the industrial complex in Sarnia.

Figures 36 and 37 are plots of oxygen-18 and tritium versus EC for the various types of water examined in this study. We have included estimated mixing lines between the river water and the shallow (Suncor) and deep (freshwater aquifer) groundwater. River water is considered to be one of the major influences on the streambed groundwater because the isotopic, EC and pH values of the streambed groundwater tend to move toward the river water values with decreasing depth in the streambed. Figures 36 and 37 indicate that

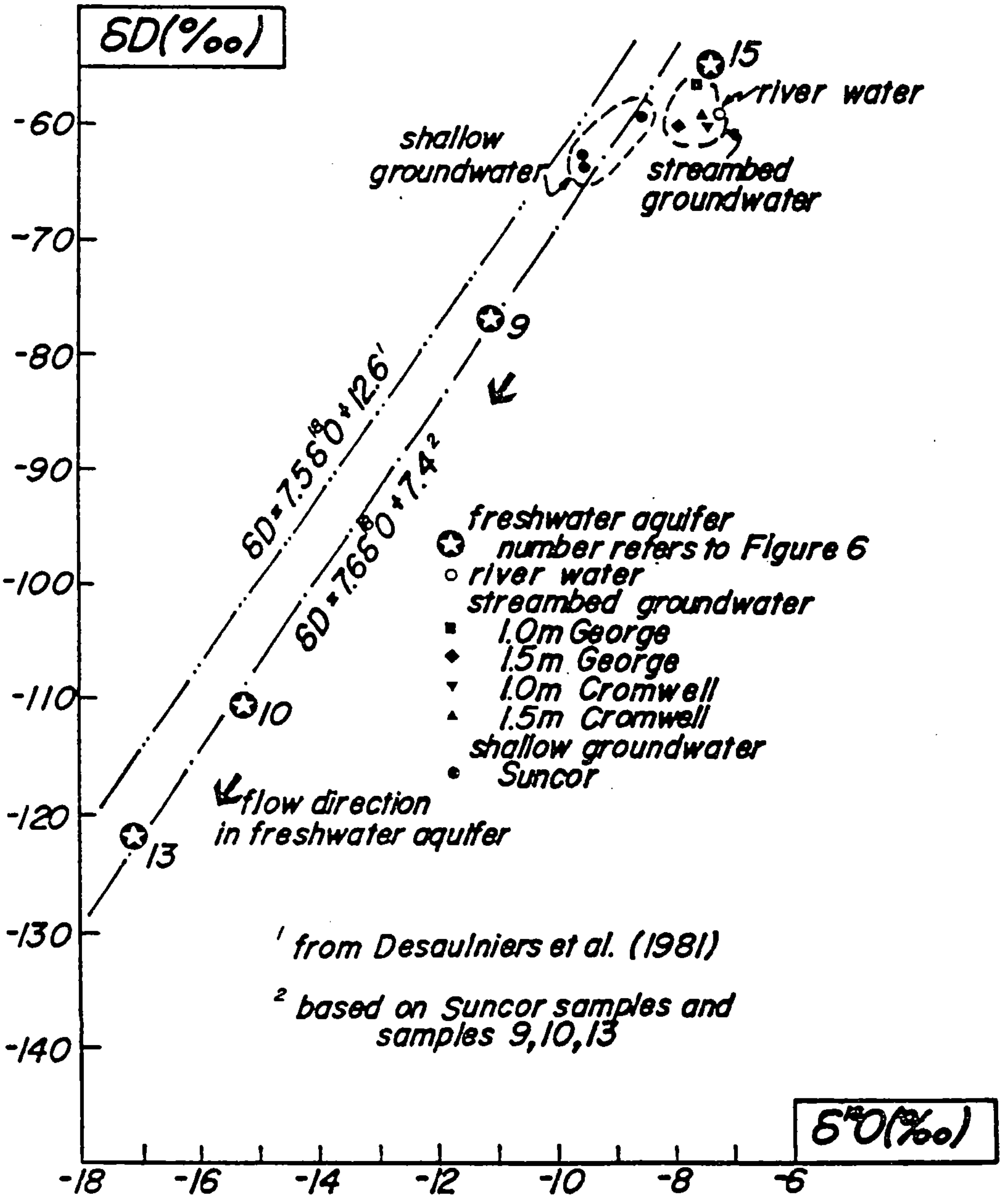


Figure 35. Plot of $\delta^{18}O$ versus δD for river water and groundwater.

TABLE 5. Summary of isotopic and EC data

SOURCE	EC (uS/cm)	OXYGEN-18 (‰)	TRITIUM (TU)	DEUTERIUM (‰)
river water	204	-7.25	89	evaporated
shallow groundwater	580-1350*	-9.37	14	unevaporated
freshwater aquifer** (virgin)	500-800	-17.5	0	unevaporated
freshwater aquifer** (Samples 15 & 24)	400	-7.5	58-95	evaporated
streambed groundwater	996	-7.5	38	evaporated?

* from Desaulniers et al. (1981)

** from Scott and Sklash (in preparation)

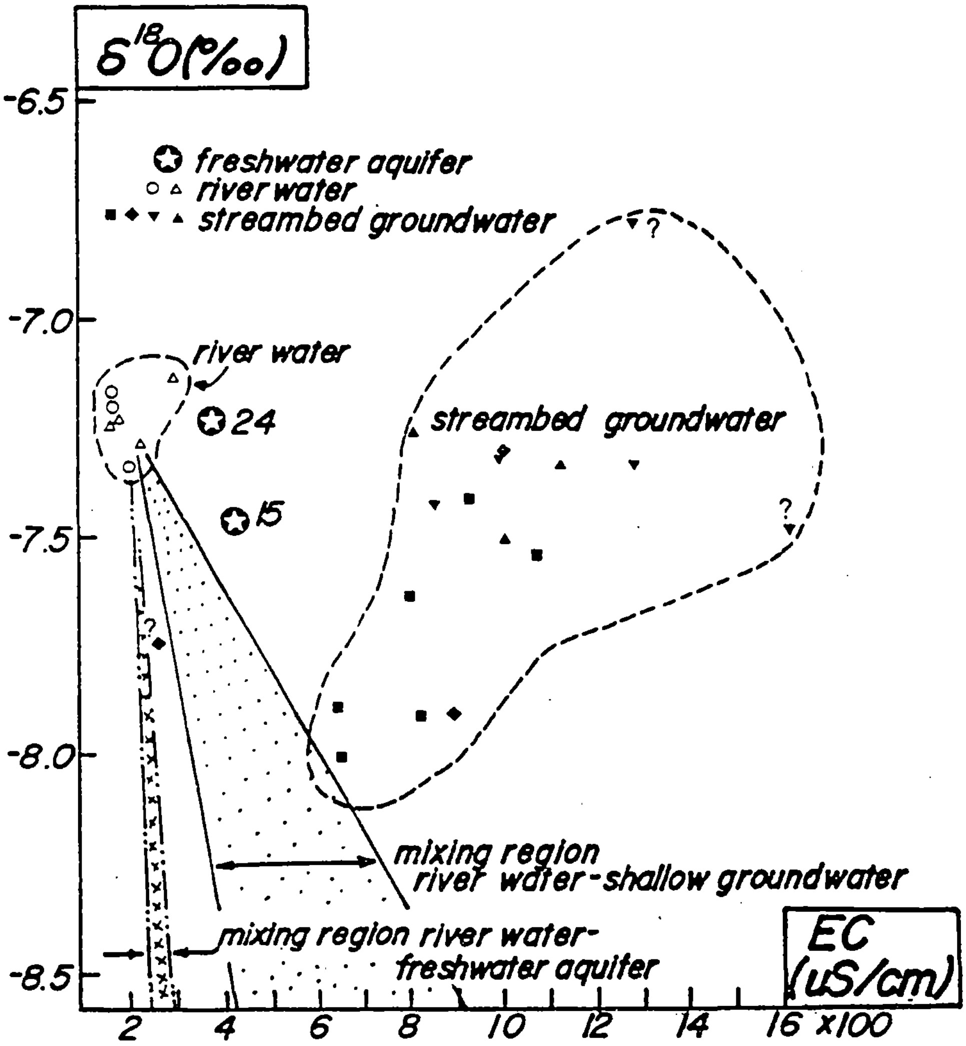


Figure 36. Plot of $\delta^{18}O$ versus EC.

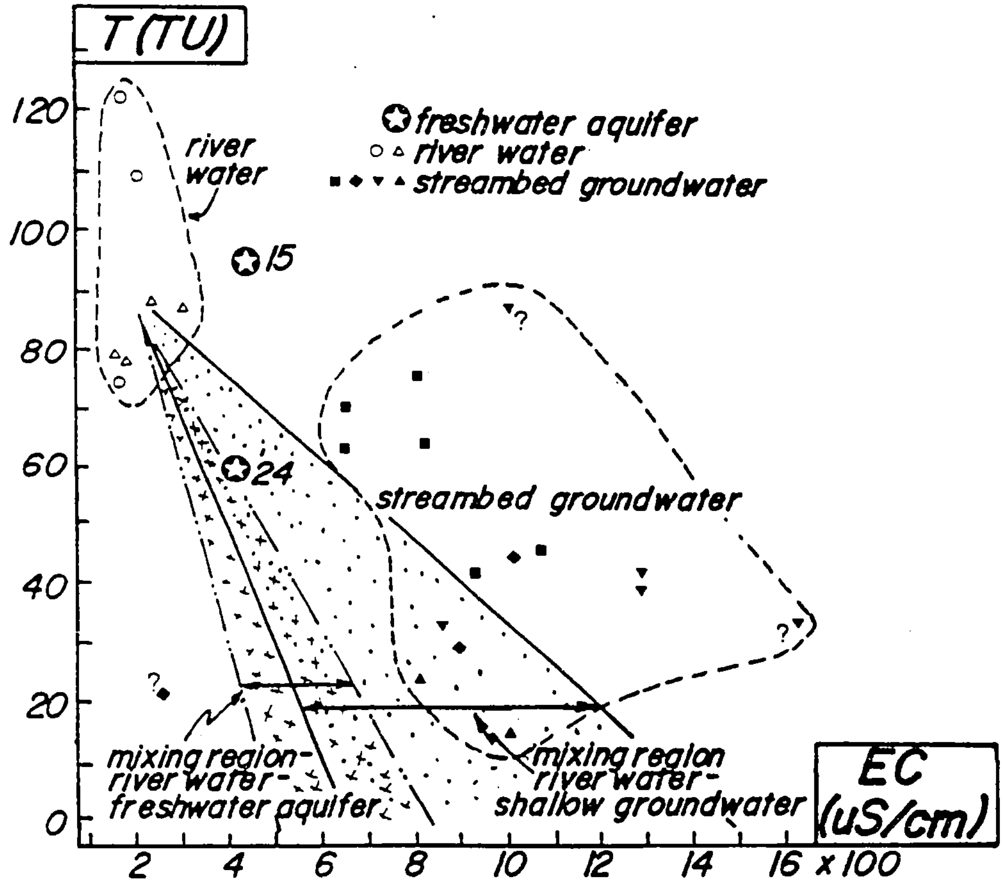


Figure 37. Plot of tritium versus EC.

there is a high EC source of water contributing to the streambed groundwater which we have not yet accounted for. One possibility is that the freshwater aquifer below Sarnia cannot be characterized in terms of EC of either the virgin groundwater or the affected groundwater near Petrolia and Courtright. The contaminated groundwater which rose to the surface around Sarnia in the 1960's and 1970's may be the unknown factor, for that water has been described as being high in chloride (GTC Geologic Testing Company, Ltd., 1985). Road salt and deep formation waters are other possible sources of high EC water.

The chloride values were plotted against tritium and oxygen-18 (Figures 25 and 26). Low chloride levels are evident on both plots for the river water and the majority of streambed groundwater samples, however, the George Street Station # 5, (1.0 and 1.5 m depth samples) show elevated chloride levels when compared with the other samples. From the chloride versus tritium plot (Figure 25) three groups are evident: river water with high tritium and low chloride, streambed groundwater with low tritium and low chloride, and the George Street Station # 5 group with tritium levels between river water and streambed groundwater, and high chloride levels. Figure 26 also indicates that there is a source of high chloride water contributing to the streambed groundwater at the George Street station, the oxygen-18 values for this group also appear to be more depleted than the other streambed groundwater. There is the possibility that seepage of contaminants near George Street Station # 5 could be affected by fractures in the till of the river bed.

Another unknown is the low tritium source of water which causes the streambed groundwater from the Cromwell Street and George Street 1.5 m samples to plot with a similar $\delta^{18}O$ value but much smaller tritium concentration than the river water in Figure 30. It is conceivable that this unknown source or the high chloride source at George Street Station # 5 could also be related to the contaminated waters which came to the surface in and around Sarnia. If these waters were injected early in the history of deep well disposal in the area and considering the residence time of the water in the upper Great Lakes, these waters could have little or no tritium.

5.0 CONCLUSIONS

The average observed seepage rate of groundwater into the St. Clair River near Sarnia was approximately 1.4×10^{-8} $m^3/s/m^2$, however, seepage varied both temporally and areally. This rate of seepage suggests that either the till in the bottom of the St. Clair River has a hydraulic conductivity which is 2 to 4 orders of magnitude greater than the values determined by Desaulniers et al. (1981) for the till in Sarnia or that the hydraulic gradient in the streambed is very large (>1.4). The isotopic content of some of the streambed groundwater samples (especially the George Street 1.0 m samples) is consistent with shallow groundwater moving laterally through the fractured till into the streambed and then into the river.

Detectable but not excessive levels of organic contaminants were found in the streambed groundwater and the river water: <0.0067 ug/L total chlorinated hydrocarbons, <0.026 ug/L PCB, <2.77 ug/L trihalomethanes, and <2.4 ug/L base neutral extractables.

The isotopic and EC data indicate that: (1) the streambed groundwater is lower in tritium content than the river water but higher than the shallow groundwater and virgin groundwater from the freshwater aquifer near the river, (2) some of the streambed groundwater appears to be mixed with shallow groundwater from the upper part of the till, (3) the streambed groundwater is either mixed with evaporated water which comes from the river (or perhaps the shallow groundwater from the fractured till) or it comes from another source of evaporated water which we have not yet identified, (4) the streambed groundwater is influenced by water which has a high EC value.

Even though EC, oxygen-18, deuterium, and tritium have been useful in distinguishing between the various possible sources of the streambed groundwater, the exact source(s) of the streambed groundwater are still unknown. The major remaining problem is a lack of information on the freshwater aquifer below the St. Clair River. It is conceivable that the unknown water mentioned above could be contaminated groundwater in the freshwater aquifer below the river.

6.0 RECOMMENDATIONS

Based on our observations and interpretations, the following studies should be undertaken:

(1) Determine the isotopic character of the freshwater aquifer adjacent to the St. Clair River, in order to use isotopic data to identify the source of seepage into the streambed of the St. Clair River.

(2) Delineate the extent of anomalous isotopic values in the freshwater aquifer in the vicinity of injection wells.

(3) Extend the domestic well isotopic survey to the American side of the river. Trans-boundary migration of injected fluids may be identified by isotopic studies.

(4) Examine the isotopic content of groundwater from formations below the freshwater aquifer and from injection wells.

(5) Samples of the clayey till from the bottom of the St. Clair River should be squeezed and the water analyzed for environmental isotopes.

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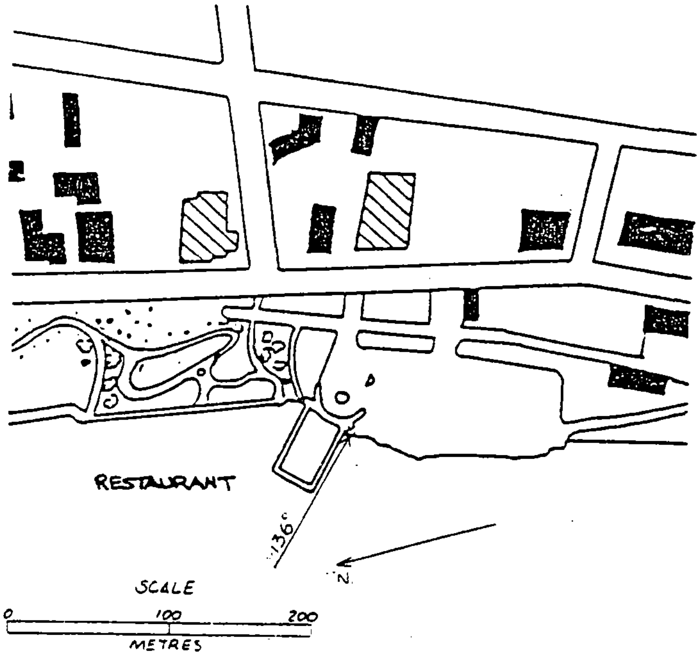
APPENDIX 1. Survey line locations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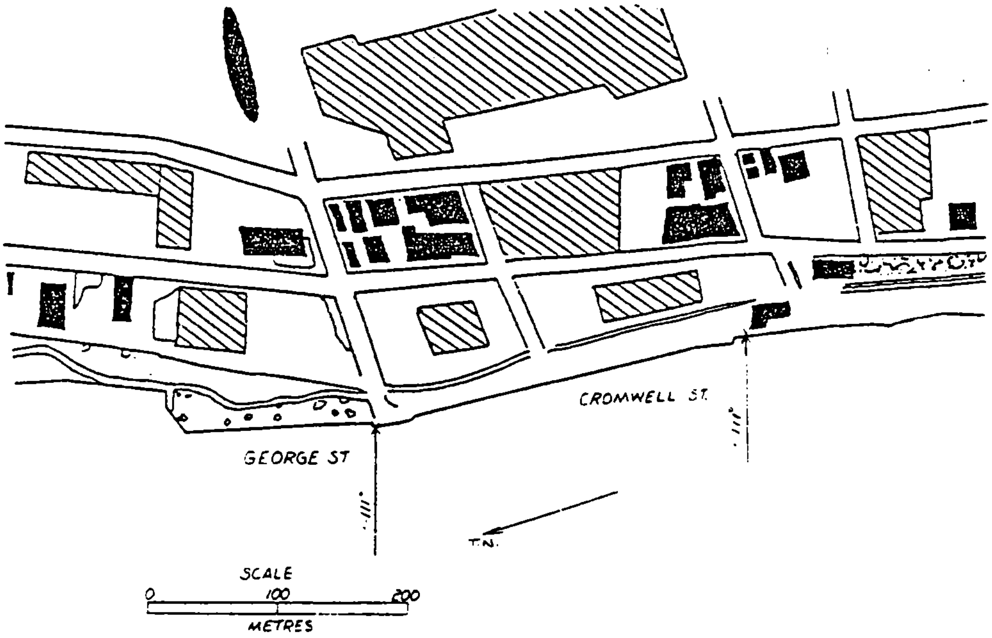
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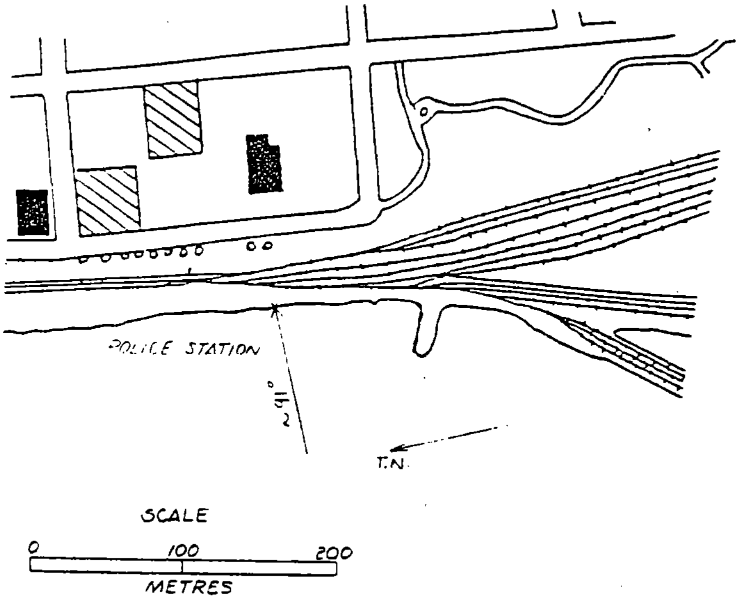
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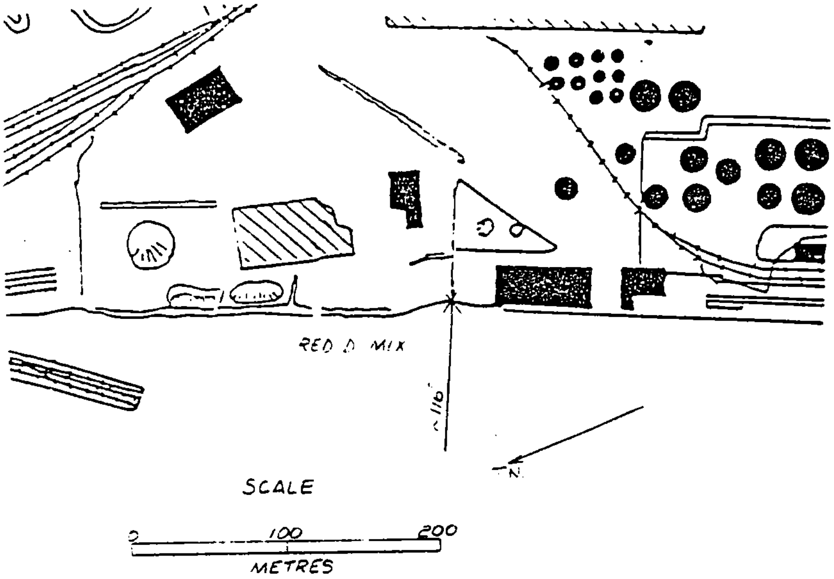
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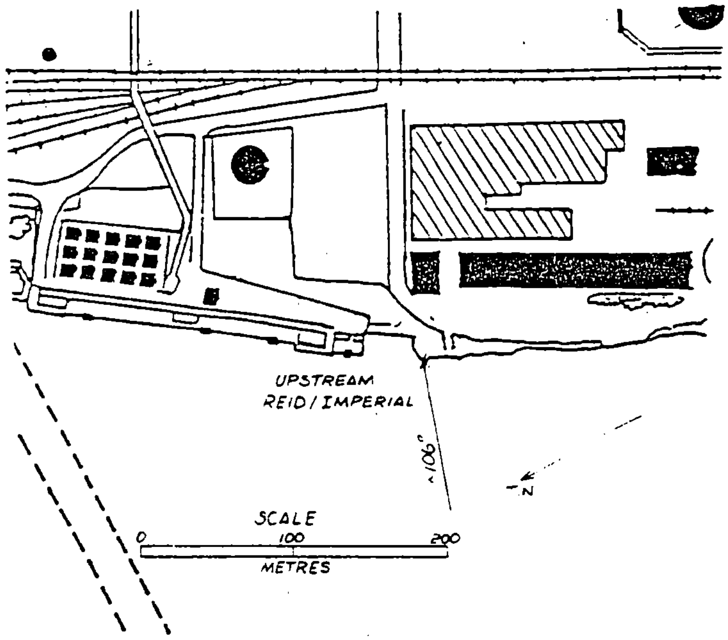
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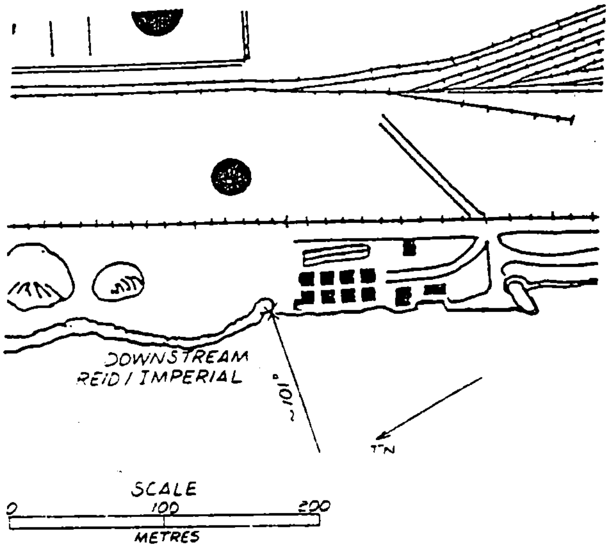
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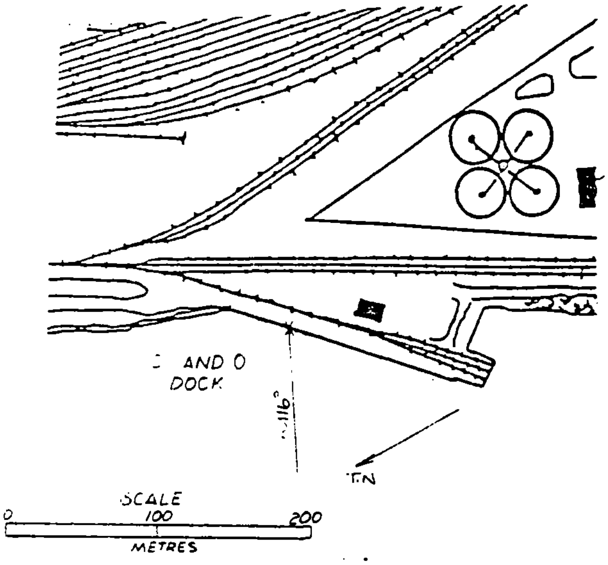

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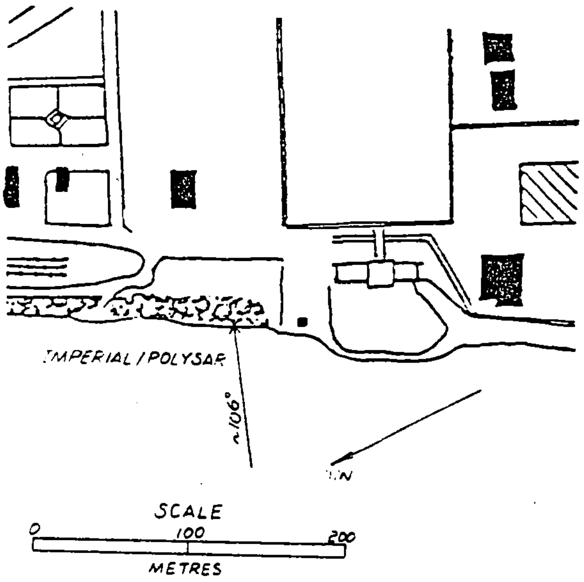

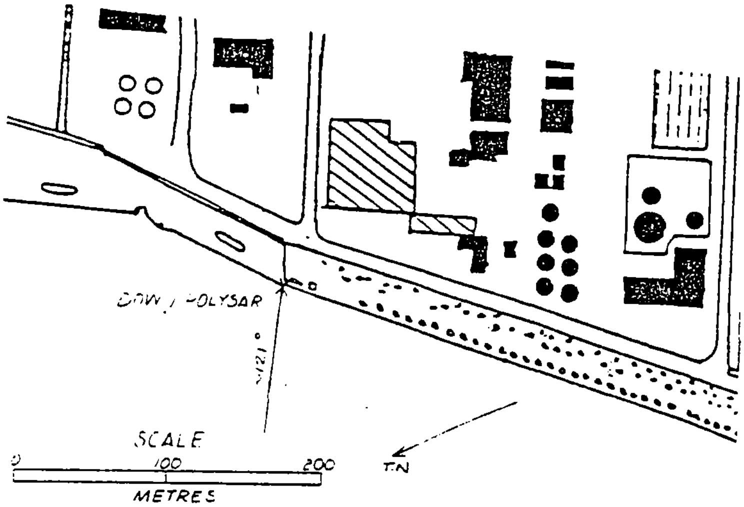
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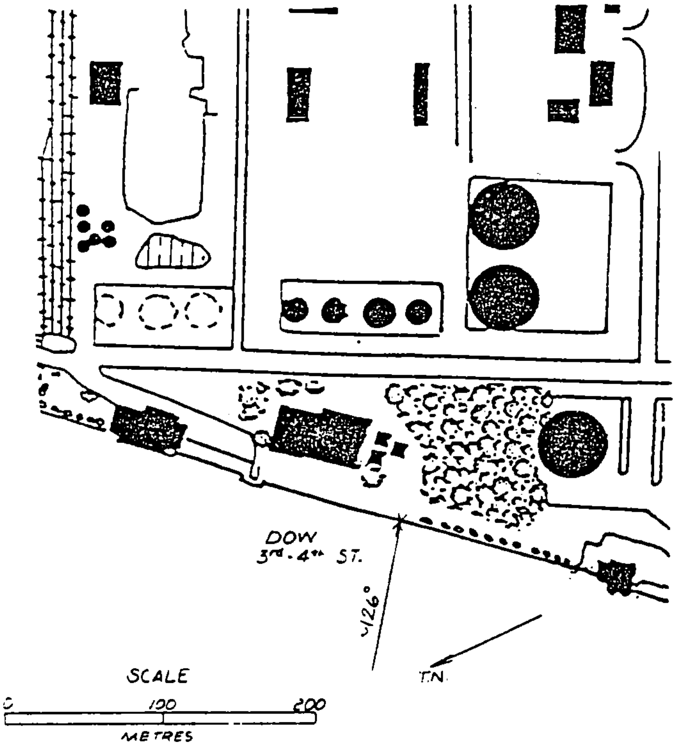
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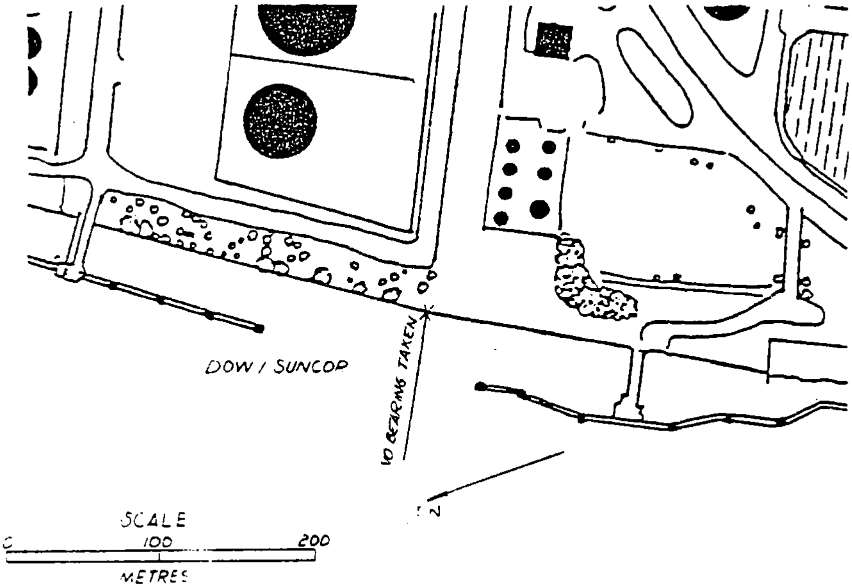
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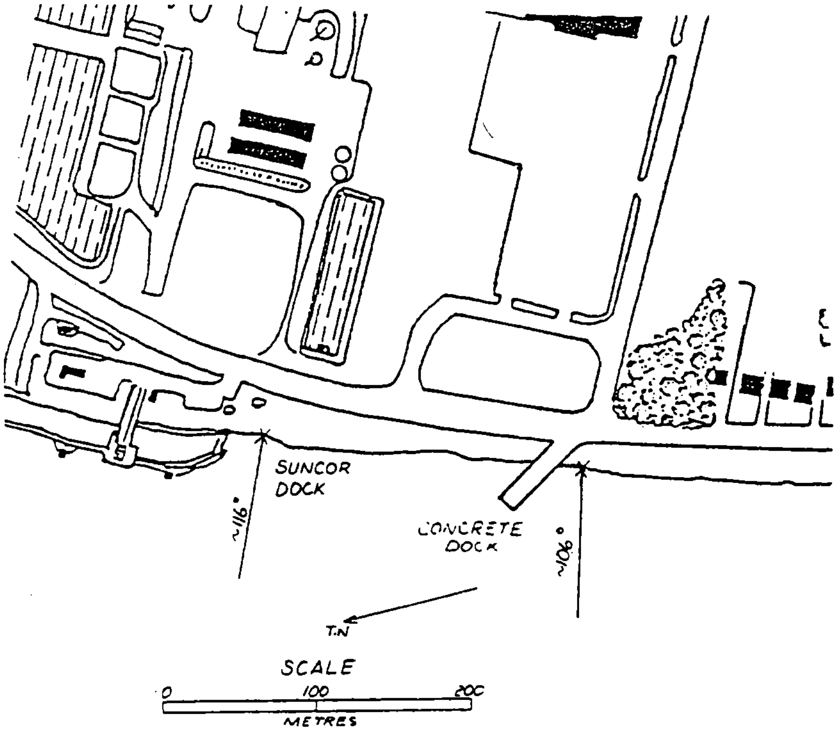
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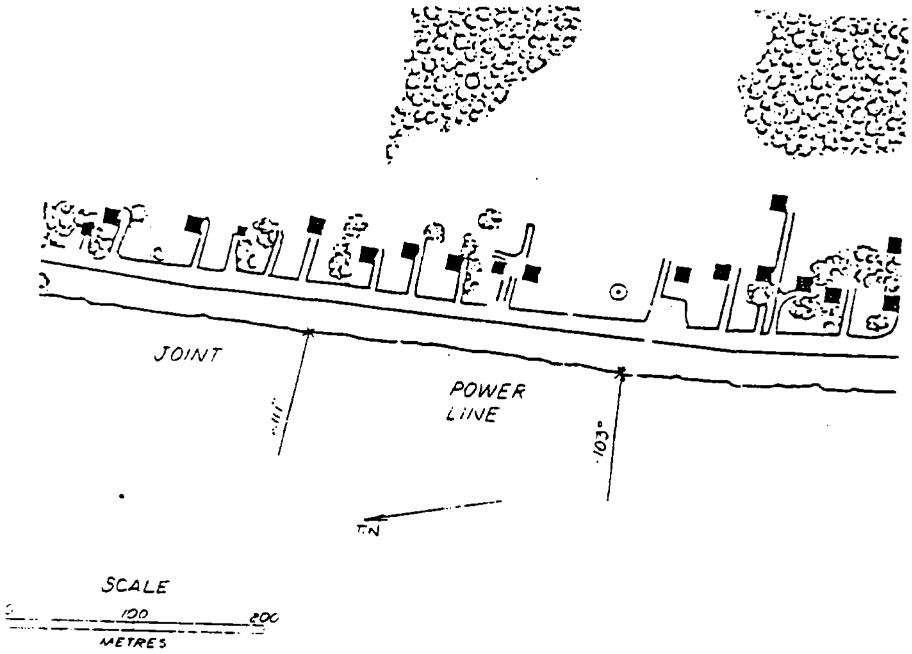
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APPENDIX 2. Work/QA plan

Zenon Environmental Inc.
845 Harrington Court, Burlington, Ontario L7N 3P3 Canada Telephone: (416) 639-6320 Telex: 061-8734

ST. CLAIR RIVER STUDY

PROTOCOLS & QA/QC

TOX
- carbon adsorption of aqueoul sample
- desorption of inorganic halide with aqueous KNO_3
- combustion of carbon in furnace tube
- titration of HX by microcoulometry
- blanks and duplicates performed once for every fifteen samples

VOLATILE ORGANICS
- EPA Method 624
- purge and trap of aqueoul sample followed by GC/MS analysis with capillary columns
- includes CH_2cl_2, $CHcl_3$, CCl_4, perchloroethylene, chlorobenzene, dichlorabenzene
- purge and trap system blank performed with each batch of samples, d_6-benzene added as internal standard to assess and analyte recoverablility in each sample

PESTICIDE/FULL SCAN CHARACTERIZATION
- EPA Method 625
- extraction of aqueous samples at basic and acidic pH, concentration
- analysis by full scan GC/MS with capillary columns
- method blank performed plus d_{10}-anthracene and d_3-2,4-dichlorophenol added as surrogate spikes prior to extraction d_{10}-phenanthrene added as an internal standard just prior to analysis

WORK/QA PROJECT PLAN

ACTIVITY E.6

AN ASSESSMENT OF SEEPAGE OF GROUNDWATER INTO THE ST. CLAIR RIVER

NHRI / UNIVERSITY OF WINDSOR GREAT LAKES INSTITUTE

(Project Officer's Signature) ____________________

(Project Officer's Name) Dr. Michael Sklash

(Project Quality Assurance Officer's Signature) ____________________

(Project Quality Assurance Officer's Name) Dr. Ronald J. Patterson

1. Project Name: AN ASSESSMENT OF SEEPAGE OF GROUND WATER INTO THE ST.CLAIR RIVER

2. Date of Project Initiation: July 1, 1985

3. Project Officer: Dr. Michael Sklash, Univ. of Windsor

4. Quality Assurance Officer: Dr. R.J. Patterson, NHRI

5. Project Description:

A. **Objective and Scope Statement** - The main objective is to assess the quantity and quality of ground-water seepage from the bed of the St. Clair River in the vicinity of Sarnia. Ground-water flow patterns will be interpreted from the literature and the distribution of seepage will be mapped using seepage meters, mini-piezometers and stream bed sampling.

B. **Data Usage** - Data will be used for identifying areas where contaminants are entering the river via seepage and for calculating loadings of contaminants.

C. **Monitoring Network Design and Rationale** -

1.0 Background

In an ideal situation, deep well disposal is a controlled injection of waste water into the subsurface in such a manner that all hazards to drinking water sources are minimized. In a well-designed system, the "disposal unit" is a porous, permeable, geological stratum which is vertically confined by low permeability rocks. The disposal unit should be deep enough and the ground-water velocities slow enough to isolate the wastes from the biosphere for a long period of time. The disposal unit should also be structurally simple with no natural or man-made conduits through the confining units.

Between 1958 and 1975, several Sarnia area industries used deep well disposal systems for their liquid waste, most of them using on-site wells. They injected over 8 x 10^6 m^3 of liquid industrial waste into 16 "deep wells" (Rathbone, 1983). The wastes included a wide range (several hundreds) of both organic and inorganic substances produced as by-products of the petrochemical industry, however, the exact nature of the injected wastes is not well-documented (Rathbone, 1983). In addition to the waste compounds injected into the wells, the products of downhole chemical reactions amongst the various injected wastes and between the wastes and the disposal unit rocks are another potential source of contaminants in the disposal unit.

The recognition of failures of the Sarnia area deep well disposal practices are well-documented in the literature. These failures have become extremely sensitive public issues because:

1. the area is along an international boundary,
2. the area is highly industrialized and heavily populated, and
3. much of the waste is toxic.

Three case histories serve to illustrate that the wastes have apparently migrated at least one or two kilometres and that above-ground head conditions developed over a considerable area. In 1967, several abandoned wells began to flow in Port Huron, Michigan, eventually yielding water which contained phenols, high hydrogen sulphide levels and unusually high pH. In 1972, an abandoned, 44 m deep water well began to flow behind the Capital Theatre in downtown Sarnia. The greenish discharge contained 2000 ppb phenol, 3960 ppm chloride and significant hydrogen sulphide and total organic carbon. In the same year, two water wells on the Imperial Oil Limited property began to discharge water with 500,000 ppb phenol, 6450 ppm chloride, and considerable hydrogen sulphide.

The disposal unit in the Sarnia area was the Detroit River Formation which consists of carbonate strata extending from about 154 to 244 m below ground. The disposal unit is overlain by approximately 150 m of shale and dense carbonate rock and about 45 m of overburden.

The main water supply aquifer in the Sarnia area consists of a relatively thin deposit of granular overburden which overlies the permeable bedrock surface. We call this the "fresh water aquifer". Above the aquifer, most of the approximately 45 m of overburden is low permeability silty clay till. Under natural flow conditions, the hydraulic head in the Detroit River Formation is some 60 m below the base of the fresh water aquifer. The occurrence of contaminated, shallow, flowing water wells in the Sarnia area in the early 1970's, coincident with the greatest subsurface disposal activity, strongly indicates that the deep well disposal of wastes pressurized the Detroit River Group to such an extent that some upward flow took place and at least localized contamination occurred in the fresh water aquifer.

The exact flow paths of the contaminants from the Detroit River Formation disposal unit to the fresh water aquifer are not known, however, several possibilities exist:

1. migration along natural or man-made fractures,
2. migration along abandoned well casings and exploratory holes, and
3. migration along poorly constructed wells currently in use.

The fresh water aquifer likely discharges on a regional scale into the St. Clair River and Lake Huron. The fate of contaminants from the deep well disposal activities once in the fresh water aquifer vis-a-vis the St. Clair River is the subject of this research.

2.0 Study Location and Sampling Strategy

The location of the study site is shown in Figure 1. Originally it was anticipated that seepage meters would be installed on a grid pattern comprising 40 lines oriented at right angles to the shoreline and spaced at 0.25 km intervals. Along each line, the seepage meters would be placed at 10 m intervals. Initial reconnaissance of the area indicated that much of the river bed is hard clay till which is unsuitable for installation of seepage meters. As a result, a bottom sediment survey was conducted to identify areas where sand or silt was present above the clay. Within these areas, seepage meters and associated minipiezometers have been emplaced at 10 or 20 m intervals along lines perpendicular to the shore. A 20 m spacing was generally selected because it will not be possible for the total number of sample locations to exceed about 50. The number of sample sites was reduced significantly from the original proposal because of unusually high river water conditions and because much of the river bottom was not suitable for seepage meter installation. The divers have to work at greater than anticipated depths and under high flow velocity conditions which greatly increase the time required for installation and sampling. These conditions also necessitated major modifications in sampling procedures.

3.0 Sampling and Monitoring Equipment and Methods

Sampling of river bottom sediments during the initial reconnaissance survey was conducted using an OAKFIELD Model C Soil Sampler. The sampler was driven to a depth of 50 cm into the river bed and recovered by hand. Often, sandy or silty sediments were not recovered due to washing by the strong current, however if clay was encountered it was retained in the sample tube. With this method, the minimum thickness of sand or silt above clay was determined.

Seepage meters (Fig. 2) were pressed and driven as far as possible into sandy or silty parts of the river bed to ensure an effective seal in the sediment. The plastic bag assembly was modified by the addition of a protective plastic bottle which prevented the strong current in the river from tearing the bag. A quick connect/disconnect valve was installed in the tube to facilitate removal and attachment of the bag. This valve also closed when disconnected preventing entry or loss of water from the bag during transport to and from the surface.

At most locations, the meters were installed and left in place for only two or three days. During this period three measurements of the amount of accumulated water in the bag and calculations of seepage rates were made. The seepage meters in one of the lines will remain in place for several weeks to permit monitoring of temporal changes in seepage rate.

When relatively significant seepage was measured, minipiezometers (Fig. 2) were installed. Small diameter, relatively short piezometers were necessary because installation was difficult due to high water velocities.

Prior to installation of a minipiezometer, a 50 cm stainless steel casing with a cap on the bottom was driven into the river bed. This casing prevented contact between the minipiezometer and surficial river bed sediments that might be contaminated. A minipiezometer of either 1 m or 1.5 m length was then inserted into the casing and driven, along with the bottom cap, to the desired depth. A screened section permitted the entry of pore water from the river bed sediments into the bottom of the piezometer.

3.0 Sampling procedures

To obtain samples from the minipiezometer, a prewashed (5 minutes of rinsing with distilled water) teflon tube (0.476 cm I.D., 0.051 cm wall thickness) secured to a nylon rope was attached to the top of the minipiezometer. Water was then drawn through the teflon tube from the piezometer by a Masterflex Model 7570 peristaltic pump for a minimum of 10 minutes and until the conductivity stabilized before samples were collected and pH, electrical conductivity and temperature recorded. Temperature measurements are not considered representative of the bottom sediment environment because the extracted water had to pass through at least 10 m of teflon tubing before reaching the surface. pH was measured in a closed flow cell to prevent exposure of the water to the air. At each location, three samples of water were collected; a one litre (no head space) amber glass bottle with a metal lined cap for TOX and GC/MS; a 40 ml amber glass vial (no head space) with teflon coated septum liner in the cap for chlorinated hydrocarbons and volatiles and a 250 ml nalgene plastic bottle (no head space) for isotopic analyses. Prior to collecting the sample for volatiles, the pump was stopped for a short period to allow the piezometer to recover. After recovery, the formation of bubbles in the teflon line was reduced and the bottle could be filled quickly with minimum potential for losses of volatiles. Following collection of these samples, the teflon tube was disconnected from the minipiezometer and river water was pumped until a stable conductivity reading was achieved. A fourth sample (250 ml nalgene plastic bottle) of river water was then collected for isotopic analysis. The conductivity and pH of the river water was also measured.

D. **Monitoring Parameters and their Frequency Collection** - Samples of pore waters from river bed sediments and river waters will be analyzed for some or all of: total organic halides (TOX) volatile and semi-volatile chlorinated hydrocarbons, phenols isotopes, pH, chloride and conductivity. Due to limitations of diving time, only about 3 locations where relatively high conductivities occur will be resampled. At at least one of these locations, a second sample will be collected after 1 day and a third after about 1 week.

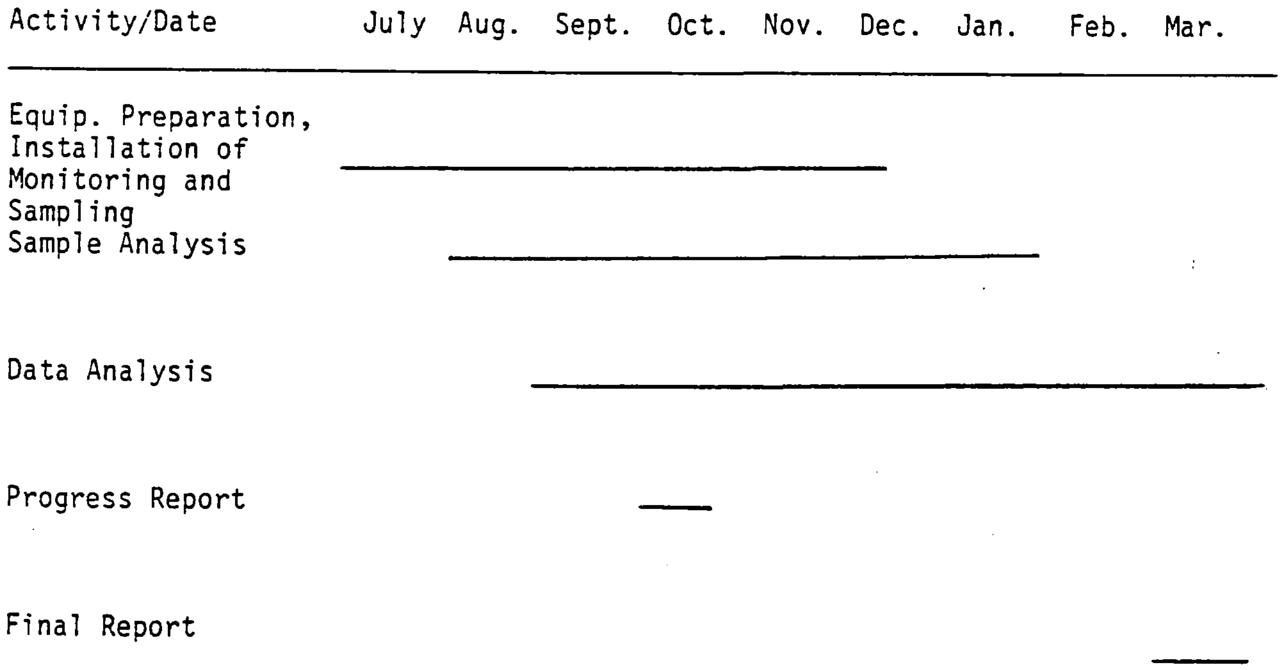
Parameter	Number of Samples	Sample Matrix	Analytical Method Reference	Sample Preservation	Holding Time
Total Organic Halides (TOX)	approx. 35	-Pore water from -river bed sediments -River Water	Method 9020.* Zenon Environmental Inc.	-	1 month
Volatile Halogenated Organics	approx. 20	"	GC/ECD Pentane extraction Method. Zenon Environmental Inc.	-	2 weeks
Organo Chlorines	approx. 20	"	Dichloromethane extraction, silica cleanup, GC/EC. Zenon Environmental Inc.	-	2 weeks
Semivolatile Organics	2	"	EPA 625 with capillary column Zenon Environmental Inc.	-	2 weeks
Isotopic Analyses Oxygen, Deuterium and Tritium	35 oxygen 30 tritium 15 deuterium	"	Mass Spectrometry*	-	3 months
pH	approx. 35	"	Corning Combination Electrode and Model 103 Digital pH Meter	-	None
Conductivity	approx. 35	"	YSI Conductivity Probe and Model 32 meter	-	None
Phenols	approx. 10	"	4AAP and solvent extraction*	C_uSO_4 and H_3PO_4	2 weeks
Chloride	approx. 10	"	Specific Ion electrode Zenon Environmental Inc.	-	2 months

* See Attachment 1

F. Analytical Method Documentation

- See Attachment 1

6. Schedule of Tasks and Products



7. Project Organization and Responsibility

Contractor:

Great Lakes Institute
University of Windsor
Windsor, Ont. N9B 3P4

Principal Investigator:
Dr. M. Sklash
519-253-4232 Ext. 2496

Contract and Project Q/A Officer:
Dr. R.J. Patterson
Contaminant Hydrogeology Section
National Hydrology Research Institute
Environment Canada
River Road Labs
Ottawa, Ontario K1A 0E7 Canada
613-998-8854

Responsibilities:

Dr. M. Sklash
- sampling operations
- sampling QC
- laboratory analyses
- laboratory QC
- data processing activities
- data quality review
- performance auditing
- systems auditing (on-site evaluations)
- overall project coordination
- data interpretation and reporting

Dr. R.J. Patterson
- overall QA

8. Data Quality Requirements and Assessments

Parameter	Sample Matrix	Detection Limit	Quantification Limit	Estimated Accuracy	Accuracy Protocol	Estimated Precision	Precision Protocol
Total Organic Halogens (TOX)	Pore waters from river bed sediments and river waters	1-5 µg/L depending on compound	SEE METHOD 9020 in **ATTACHMENT 1**		------------------------>		1 Blank 1 Duplicate and 1 Spike /20 Samples
Volatile Halogenated Organics	"	0.5 µg/L	EPA METHOD 5010		------------------------>		1 Blank 1 Duplicate and 1 Standard Addition /20 Samples
Organo Chlorines	"	0.001 µg/L	ENVIRONMENT CANADA WATER QUALITY BRANCH (IWD) METHOD		------------------------>		1 Blank 1 Duplicate and 1 Standard Addition /20 Samples
Semivolatile Organics	"	1.0 µg/L	EPA METHOD 625 WITH CAPILLARY COLUMN				-
Isotope Analysis	"	<----- SEE METHODS in **ATTACHMENT 1**			---------------------------------->		1 Duplicate /15 Samples
pH	"	-	-	±0.02 pH units	Standardization against buffers	± 0.1pH Units	Measurements on Duplicate Samples
Conductivity	"	-	-	±0.5%	Comparison with KCl solution	±5%	"
Phenols	"	<----- SEE METHOD (4AAP) in **ATTACHMENT 1**			------------------------>		
Chloride	"	SPECIFIC ION ELECTRODE - ZENON ENVIR. INC.			------------------------>		

Data Representativeness - Sampling could not be carried out on the basis of a regular grid but was restricted to certain areas where granular bottom sediments occur. The distribution of sampling points was further limited by water depth and current velocity, shipping traffic and debris on the river bed. The number of samples that could be collected was severely constrained by the high water level and current velocity in the river. Under these conditions, the time required by the divers to install and operate equipment was greatly increased. As a result of these limitations on sample distribution and density, a fully representative data set will not be obtained and extrapolation will be necessary. Nevertheless, the results should indicate whether significant quantities of contaminants are entering the river via seepage in the Sarnia area under current conditions. Fluxes may not represent long term averages, however, because present seepage rates are probably reduced by the prevailing high river levels.

Data Comparability - Laboratory analytical protocols will be identical to those in Activity E:5 - both studies are using Zenon Environmental Inc. for water analyses. No other similar seepage studies are being conducted in the UGLCCS.

Data Completeness - Data concerning the quantity and quality of seepage will be obtained in the study. However, anticipated "short falls" relate to the distribution and density of sampling.

9. **Sampling Procedures - See 5C.**

10. **Sample Tracking Procedures** - Samples are retained in locked storage and packed by University of Windsor staff prior to shipping by courier to Zenon Environmental Inc. laboratories in Burlington, Ontario.

11. **Calibration Procedures and Preventive Maintenance -**

Field equipment checklist:

Peristaltic pump	- battery charged and operation checked each morning
pH electrode and meter	- calibrated against two buffers at the beginning and end of each day and against a single buffer between readings
Conductivity electrode and meter	- calibrated against KCl standard daily.

12. Documentation, Data Reduction, and Reporting

A. **Documentation** - Data obtained in the field is recorded and transcribed nightly. A separate activity log (plus two carbon copies) is maintained by Dr. Chris Pugley on a daily basis. The location of samples lines are documented with Polaroid photographs. All lines will be located on high resolution air photos. Analytical results are stored in triplicate by Dr. Sklash.

B. **Data Reduction and Reporting** - Data will be cross-checked for accuracy prior to reporting by Drs. Sklash and Pugsley and Ms. Sharon Mason.

13. **Data Validation** - The validity of analytical results will be assessed on the basis of results for duplicate samples , repeat samples, blanks and spiked samples. In addition, anticipated correlations between parameters will be evaluated. Any unusual or anomalous values will be recalculated or if possible confirmed by reanalysis.

14. **Performance and Systems Audits** - Zenon Environmental Inc. is one of the laboratories participating in the UGLCCS and will be assessed by the Quality Management Work Group.

15. **Corrective Action** - Samples are being submitted for analysis as soon as collected so that data will be received before the field program is completed. Early data will be assessed to indicate whether problems are present and changes in procedure need to be implemented.

16. **Reports** - A progress report summarizing activities completed and presenting initial results will be submitted by October 31, 1985. A final report will be submitted by March 31, 1986.

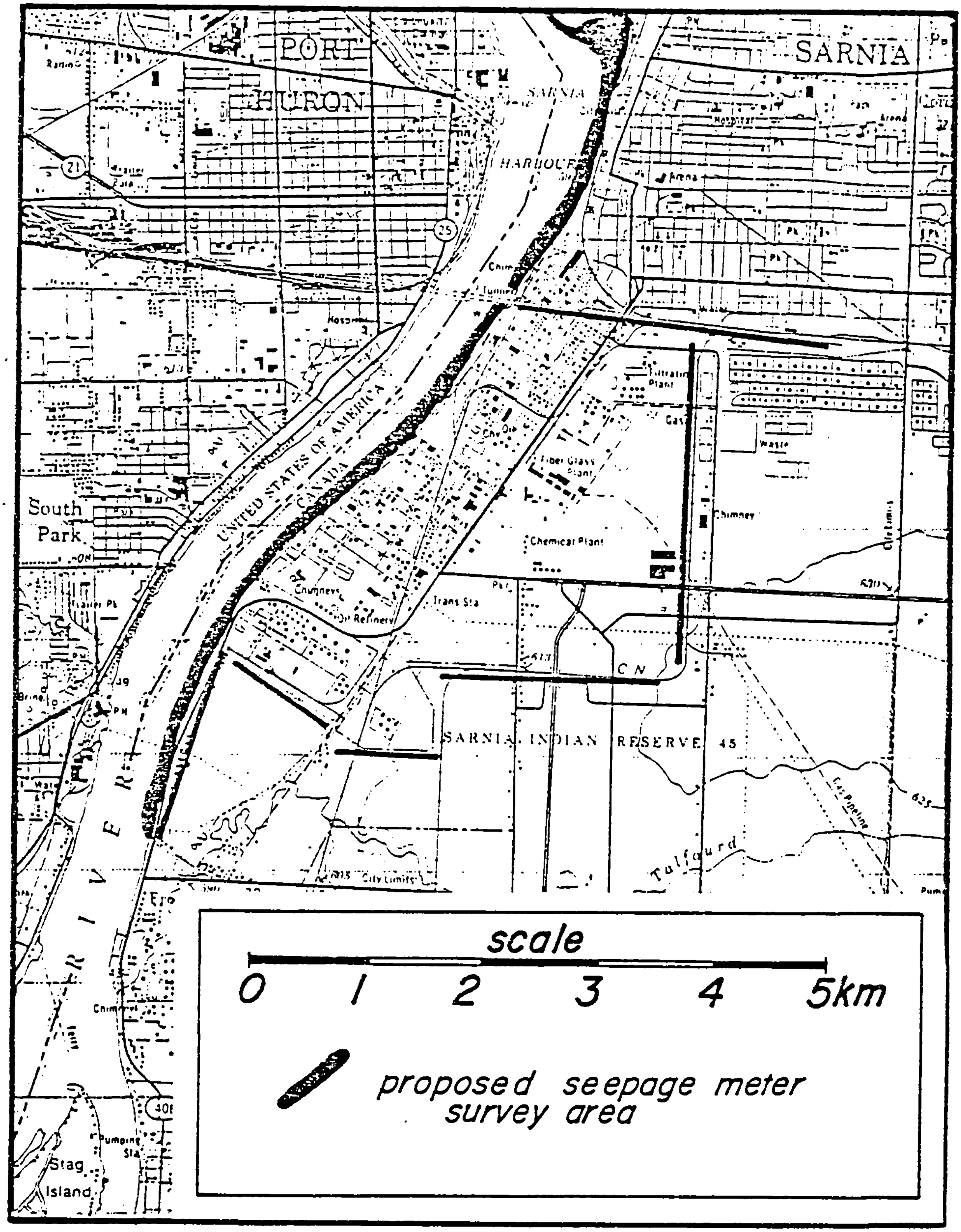
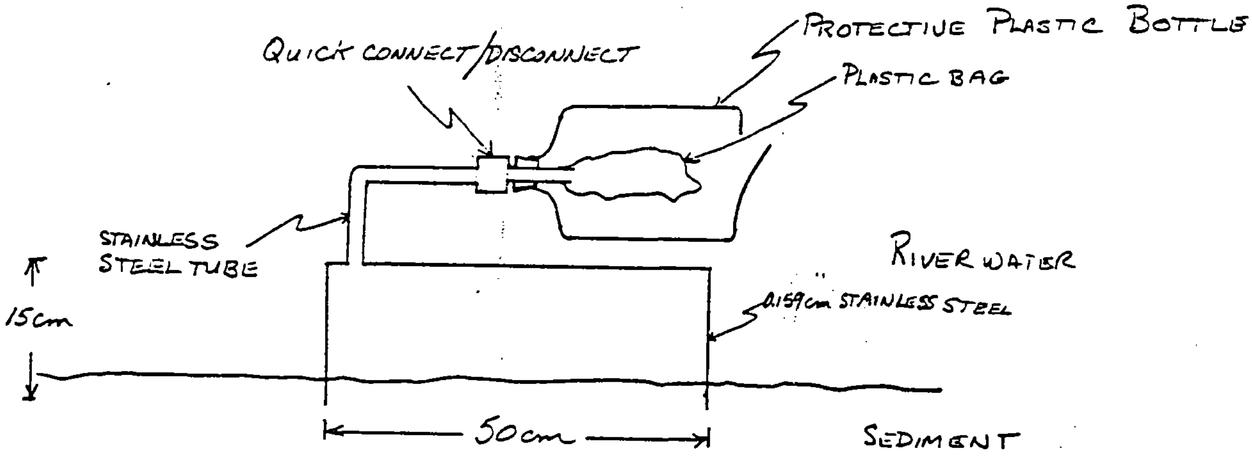


Figure 1. Study Site.

SEEPAGE METER



MINI PIEZOMETER

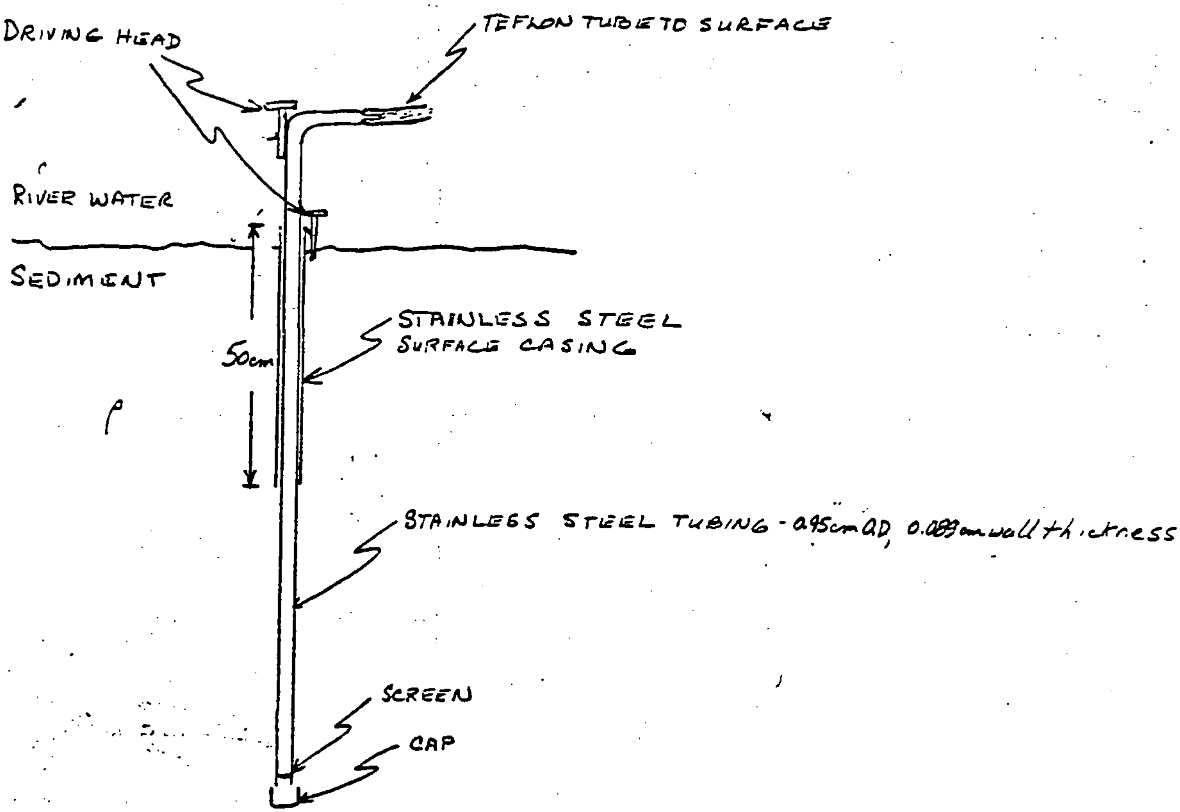


FIGURE 2. SEEPAGE METER AND MINIPIEZOMETER

ATTACHMENT 1

Isotopic Methods

Methods, Test Procedures, Sample Analysis

The isotopic analyses will be performed under contract by the University of Waterloo. They use the normal isotopic analysis procedures and standards recommended by the IAEA (International Atomic Energy Agency).

Oxygen-18, deuterium, and tritium will be analyzed by standard methods used in isotopic analyses of water. A Micromass Model 903 mass spectrometer is used for oxygen-18 analysis, a modified Micromass 602 mass spectrometer is used for deutrium work, and Intertechnique or Beckman Model 7500 scintillation counters are used for tritium analysis.

One in every 15 samples sent for analysis will be split for evaluating the isotopic results. Internally, the University of Waterloo has an elaborate quality assurance program. Waterloo's lab standard SWAT (standard Waterloo tap water) is run for each 5 oxygen-18 samples, each 6 deuterium samples, and each 10 tritium samples. SWAT has been related to the three international standards: SMOW (standard mean ocean water), SLAP (standard light Arctic precipitation), and GISP (Greenland Ice Sheet Precipitation). For each sample analysis, the results are an average of at least 5 sample-standard comparisons for oxygen-18 and deuterium and 500 to 660 minutes of tritium counting. As there are no international standards for tritium, sample analyses are periodically compared with results from the Alberta Research Council and the Weizmann Institute in Israel.

METHOD 9020

TOTAL ORGANIC HALIDES (TOX)

1.0 Scope and Application

1.1 Method 9020 determines Total Organic Halides (TOX) as Cl^- in drinking and ground waters. The method uses carbon adsorption with a microcoulometric-titration detector. It requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/l.

1.2 Method 9020 detects all organic halides containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine-containing species are not determined by this method.

1.3 Method 9020 is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

1.4 Method 9020 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

1.5 This method is provided as a recommended procedure. It may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of TOX (i.e., by comparison of sensitivity, accuracy, and precision data).

2.0 Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides, and is then analyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3.0 Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400° C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

4.0 Apparatus and Materials

4.1 Adsorption system

4.1.1 Dohrmann adsorption module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.2.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000 mg Cl^- equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville), or equivalent: Form this material into plugs using a 2-mm-I.D. stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

4.1.5 Column holders (available from Dohrmann).

4.1.6 Volumetric flasks: 100-ml, 50-ml. A general schematic of the adsorption system is shown in Figure 1.

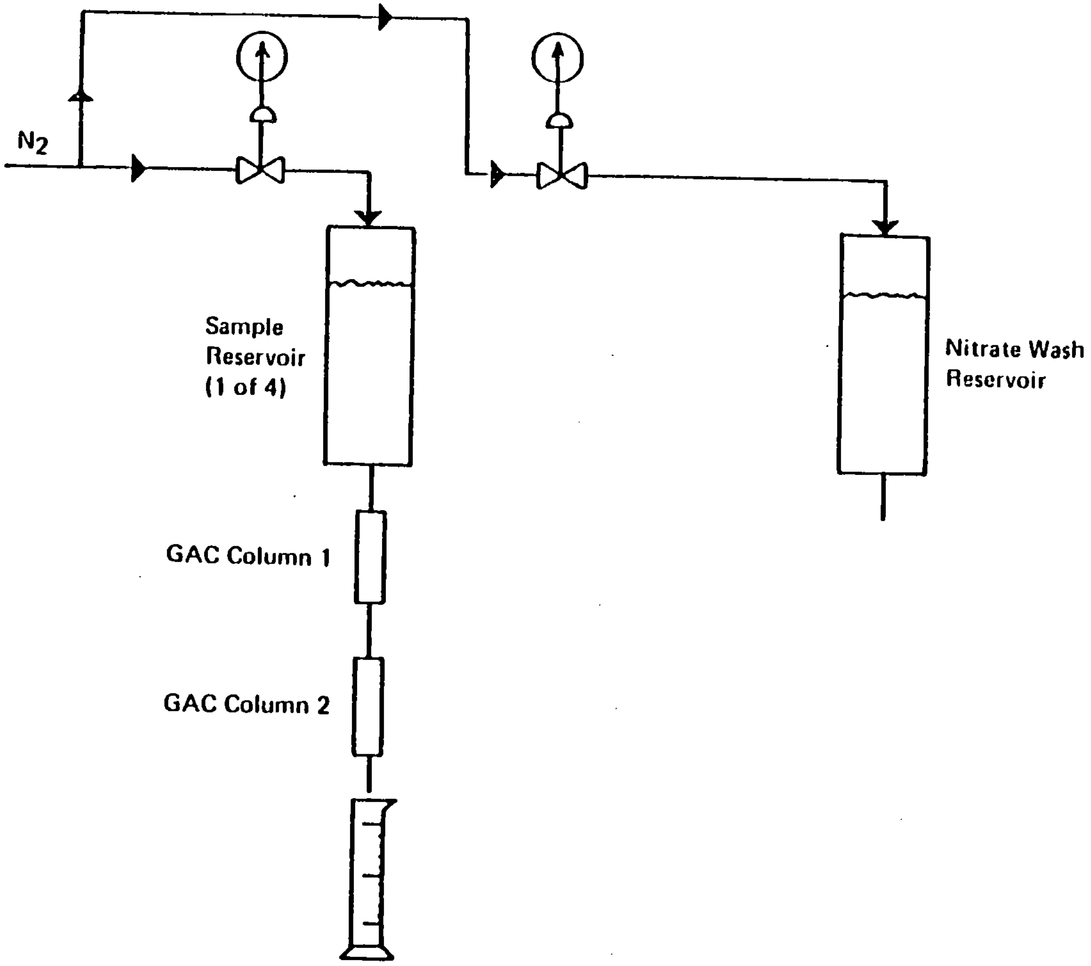


Figure 1. Schematic of Adsorption System.

4.2 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

4.2.1 Boat sampler.

4.2.2 Pyrolysis furnace.

4.2.3 Microcoulometer with integrator.

4.2.4 Titration cell: A general description of the analytical system is shown in Figure 2.

4.3 Strip chart recorder.

5.0 Reagents

5.1 Sodium sulfite: 0.1 M, ACS reagent grade (12.6 g/liter).

5.2 Nitric acid: Concentrated.

5.3 Nitrate-wash solution (5000 mg NO_3^-/l): Prepare a nitrate-wash solution by transferring approximately 8.2 g of potassium nitrate into a 1-liter volumetric flask and diluting to volume with reagent water.

5.4 Carbon dioxide: Gas, 99.9% purity.

5.5 Oxygen: 99.9% purity.

5.6 Nitrogen: Prepurified.

5.7 70% acetic acid in water: Dilute 7 volumes of acetic acid with 3 volumes of water.

5.8 Trichlorophenol solution, stock (1 µl = 10 µg Cl^-): Prepare a stock solution by weighing accurately 1.856 g of trichlorophenol into a 100-ml volumetric flask. Dilute to volume with methanol.

5.9 Trichlorophenol solution, calibration (1 µl = 500 ng Cl^-): Dilute 5 ml of the trichlorophenol stock solution to 100 ml with methanol.

5.10 Trichlorophenol standard, instrument-calibration: First, nitrate-wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µl of the calibration solution.

5.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/liter): Prepare an adsorption-efficiency standard by injecting 10 µl of stock solution into 1 liter of reagent water.

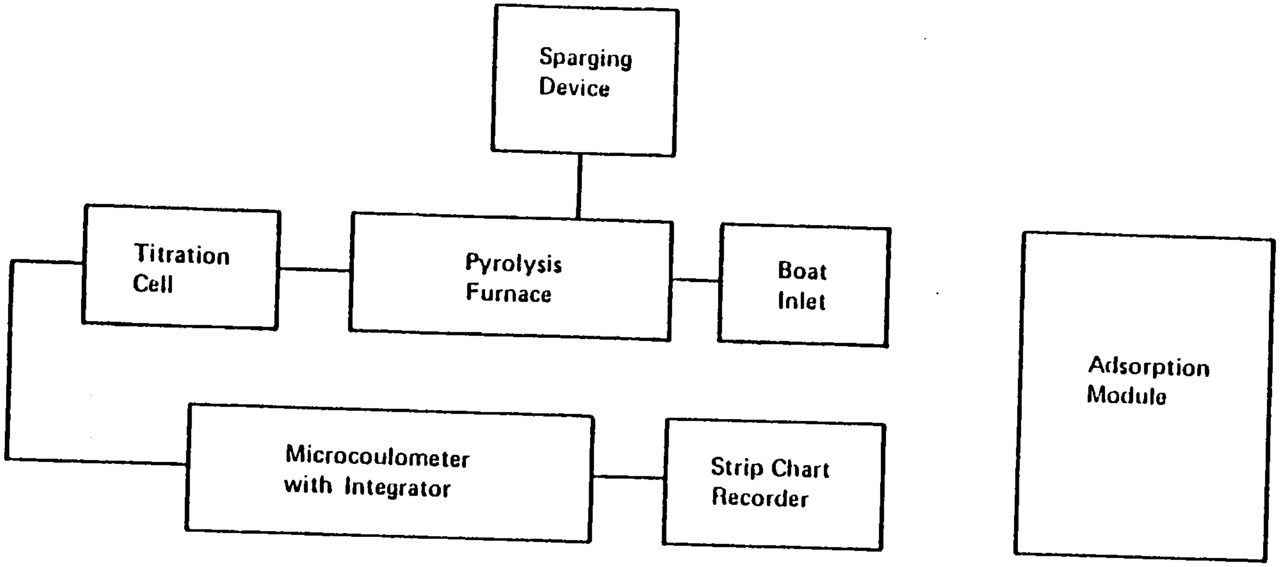


Figure 2. Schematic diagram of CAOX analysis system.

5.12 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.13 Blank standard: The reagent water used to prepare the calibration standard should be used as the blank standard.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples should be collected in bottles with teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass, 250-ml, fitted with teflon-lined caps. Foil may be substituted for teflon if the sample is not corrosive. Samples must be protected against loss of volatiles by eliminating headspace in the container. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400° C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in 3.1.1.

7.0 Procedure

7.1 Sample preparation

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

7.1.2 Reduce residual chlorine by adding sulfite (1 ml of 0.1 M per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4° C without headspace.

7.1.3 Adjust the pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

7.2 Calibration

7.2.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 ml of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.2.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

7.3 Adsorption procedure

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 ml/min. NOTE: 100 ml of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/l; 50 ml for 501 to 1000 µg/l, and 25 ml for 1001 to 2000 µg/l.

7.3.3 Wash the columns-in-series with 2 ml of the 5000-mg/l nitrate solution at a rate of approximately 2 ml/min to displace inorganic chloride ions.

7.4 Pyrolysis procedure

7.4.1 The contents of each column are pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

7.4.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to ensure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere. NOTE: The quartz sampling boat should have been previously muffled at 800° C for at least 2 to 4 min as in a previous analysis, and should be cleaned of any residue by vacuuming.

7.4.3 Transfer the contents of each column to the quartz boat for individual analysis.

7.4.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCTS-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

7.4.5 Position the sample for 2 min in the 200° C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

7.4.6 After 2 min, advance the boat into the 800° C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 min to complete.

7.5 Detection: The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

7.6 Breakthrough. The unpredictable nature of the background bias makes it especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10% of the two-column total measurement. If the 10% figure is exceeded, one of three events can be happening. Either (1) the first column was overloaded and a legitimate measure of breakthrough was obtained, in which case taking a smaller sample may be necessary; or (2) channeling or some other failure occurred, in which case the sample may need to be rerun; or (3) a high random bias occurred and the result should be rejected and the sample rerun. Because it may not be possible to determine which event occurred, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analysis that is rejected should be repeated whenever sample is available. If the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

7.7 Calculations: TOX as Cl^- is calculated using the following formula:

$$\frac{(C_1-C_3) + (C_2-C_3)}{V} = \mu g/l \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in liters.

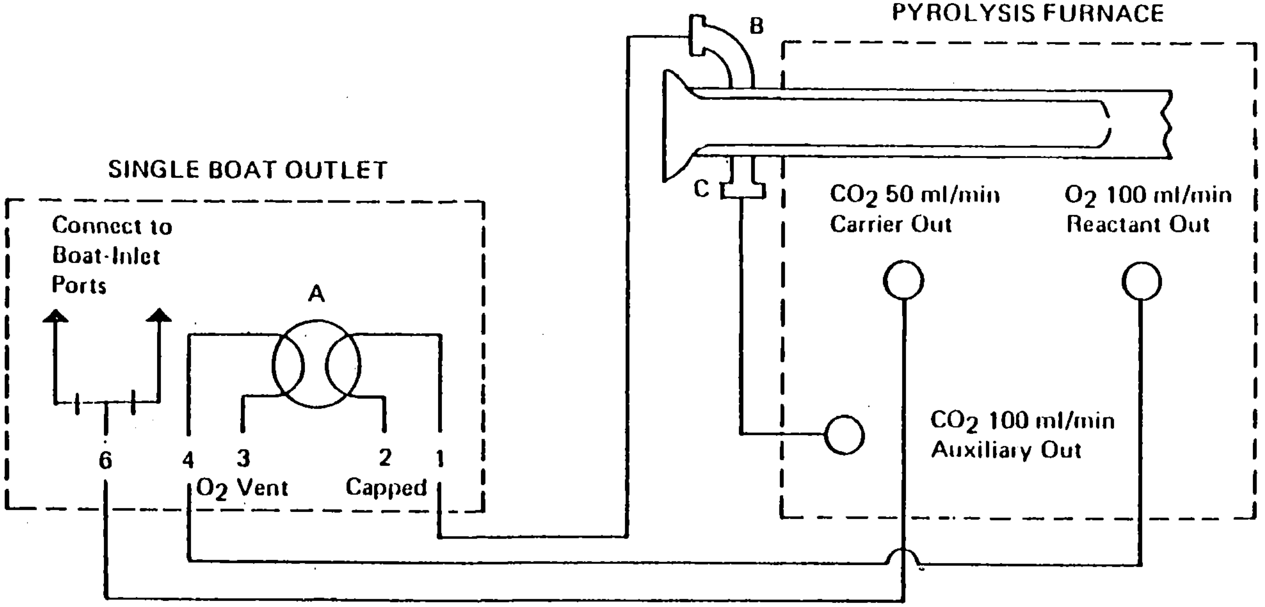


Figure 3. Rear-view plumbing schematic for MCTS–20 System. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by analyzing appropriate quality-control check samples.

8.3 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Run check standard after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparations process.

8.7 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

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STEERE, N.V., ed. 1971. Handbook of Laboratory Safety. Chemical Rubber Company, Cleveland, Ohio.

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U.S. ENVIRONMENTAL PROTECTION AGENCY. 1976. Analysis of Pesticide Residues in Human and Environmental Samples. Environmental Toxicology Div., Health Effects Laboratory, Research Triangle Park, N.C.

Chlorinated Phenoxy Acid Herbicides

METCALFE, L.D. & A.A. SCHMITZ. 1961. The rapid preparation of fatty acid esters for gas chromatographic analysis. *Anal. Chem.* 33:363.

GOERLITZ, D.F. & W.L. LAMAR. 1967. Determination of phenoxy acid herbicides in water by electron-capture and microcoulometric gas chromatography. U.S. Geol. Surv. Water-Supply Paper 1817-C.

510 PHENOLS

Phenols, defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewaters, natural waters, and potable water supplies. Chlorination of such waters may produce odorous and objectionable-tasting chlorophenols. Phenol removal processes in water treatment include superchlorination, chlorine dioxide or chloramine treatment, ozonation, and activated carbon adsorption.

Of the three analytical procedures offered here, two use the 4-aminoantipyrine colorimetric method that determines phenol, ortho- and meta-substituted phenols, and, under proper pH conditions, those para-substituted phenols in which the substitution is a carboxyl, halogen, methoxyl, or sulfonic acid group. The 4-aminoantipyrine method does not determine those para-substituted phenols where the substitution is an alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde group. A typical example of these latter groups is paracresol, which may be present in certain industrial wastewaters and in polluted surface waters. The third procedure is a direct aqueous gas-liquid chromatographic technic.

1. Selection of Method

The 4-aminoantipyrine method is given in two forms: Method B, for extreme sensitivity, is adaptable for use in water samples containing less than 1 mg phenol/L. It concentrates the color in a nonaqueous solution. Method C retains the color in the aqueous solution. Because the relative amounts of various phenolic compounds in a given sample are unpredictable, it is not possible to provide a universal standard containing a mixture of phenols. For this reason, phenol (C_6H_5OH) itself has been selected as a standard for colorimetric procedures and any color produced by the reaction of other phenolic compounds is reported as phenol. Because substitution generally reduces response, this value represents the minimum concentration of phenolic compounds. Method D, a gas-liquid chromatographic procedure, may be applied to samples or concentrates that contain more than 1 mg phenolic compounds/L.

2. Interferences

a. Interferences such as phenol-decomposing bacteria, oxidizing and reducing substances, and alkaline pH values are dealt with by acidification with phosphoric acid (H_3PO_4). Some highly contaminated wastewaters may require specialized technics for eliminating interferences and for quantitative recovery of phenolic compounds.

b. Eliminate major interferences as follows (see Section 510A for reagents):

1) Oxidizing agents, such as chlorine and those detected by the liberation of iodine on acidification in the presence of potassium iodide (KI)—Remove immediately after sampling by adding excess ferrous sulfate ($FeSO_4$). If oxidizing agents are not removed, the phenolic compounds will be oxidized partially.

2) Sulfur compounds—Remove by acidifying to pH 4.0 with H_3PO_4 and aerating briefly by stirring. This eliminates the interference of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2).

3) Oils and tars—Make an alkaline extraction by adjusting to pH 12 to 12.5 with NaOH pellets. Extract oil and tar from aqueous solution with 50 mL chloroform ($CHCl_3$). Discard oil- or tar-containing layer. Remove excess $CHCl_3$ in aqueous layer by warming on a water bath before proceeding with the distillation step.

3. Sampling

Sample in accordance with the instructions of Section 105.

4. Preservation and Storage of Samples

a. Phenols in concentrations usually encountered in wastewaters are subject to biological and chemical oxidation. Preserve and store samples at 4 C or lower unless analyzed within 4 hr after collection.

b. Acidify to pH 4.0, or slightly below, with H_3PO_4. If H_2S or SO_2 is known to be present, briefly aerate or stir sample with caution. Store at 4 C or lower.

c. Analyze preserved and stored samples within 24 hr after collection.

510 A. Cleanup Procedure

1. Principle

Phenols are distilled from nonvolatile impurities. Because the volatilization of phenols is gradual, the distillate volume must ultimately equal that of the original sample.

2. Apparatus

a. Distillation apparatus, all-glass, consisting of a 1-L borosilicate glass distilling apparatus with Graham condenser* (see Figure 323:1.)

b. pH meter.

3. Reagents

Prepare all reagents with distilled water free of phenols and chlorine.

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*Corning No. 3360 or equivalent.

a. Phosphoric acid solution, H_3PO_4, 1 + 9: Dilute 10 mL 85% H_3PO_4 to 100 mL with water.

b. Methyl orange indicator solution.

c. Special reagents for turbid distillates:

1) *Sulfuric acid,* H_2SO_4, 1*N*.

2) *Sodium chloride,* NaCl.

3) *Chloroform,* $CHCl_3$, *or methylene chloride,* CH_2Cl_2.

4) *Sodium hydroxide,* NaOH, 2.5*N*: Dilute 41.7 mL 6*N* NaOH to 100 mL or dissolve 10 g NaOH pellets in 100 mL water.

4. Procedure

a. Measure 500 mL sample into a beaker, adjust pH to approximately 4.0 with H_3PO_4 solution using methyl orange indicator or a pH meter, and transfer to distillation apparatus. Use a 500-mL graduated cylinder as a receiver. Omit adding H_3PO_4 if sample was preserved as described in 510.4*b*.

b. Distill 450 mL, stop distillation and, when boiling ceases, add 50 mL warm water to distilling flask. Continue distillation until a total of 500 mL has been collected.

c. One distillation should purify the sample adequately. Occasionally, however, the distillate is turbid. If so, acidify with H_3PO_4 solution and distill as described in ¶ 4*b*. If second distillate is still turbid, use extraction process described in ¶ 4*d* before distilling sample.

d. Treatment when second distillate is turbid: Extract a 500-mL portion of original sample as follows: Add 4 drops methyl orange indicator and make acidic to methyl orange with 1*N* H_2SO_4. Transfer to a separatory funnel and add 150 g NaCl. Shake with five successive portions of $CHCl_3$, using 40 mL in the first portion and 25 mL in each successive portion. Transfer $CHCl_3$ layer to a second separatory funnel and shake with three successive portions of 2.5*N* NaOH solution, using 4.0 mL in the first portion and 3.0 mL in each of the next two portions. Combine alkaline extracts, heat on a water bath until $CHCl_3$ has been removed, cool, and dilute to 500 mL with distilled water. Proceed with distillation as described in ¶s 4*a* and *b*.

NOTE: CH_2Cl_2 may be used instead of $CHCl_3$, especially if an emulsion forms when the $CHCl_3$ solution is extracted with NaOH.

10% REPLICATES

510 B. Chloroform Extraction Method

1. General Discussion

a. Principle: Steam-distillable phenols react with 4-aminoantipyrine at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a colored antipyrine dye. This dye is extracted from aqueous solution with $CHCl_3$ and the absorbance is measured at 460 nm. This method covers the phenol concentration range from 1.0 µg/L with a sensitivity of 1 µg/L.

b. Interference: All interferences are eliminated or reduced to a minimum if the sample is preserved, stored, and distilled in accordance with the foregoing instructions.

c. Minimum detectable concentration: The minimum detectable quantity is 0.5 µg phenol when a 25-mL $CHCl_3$ extraction with a 5-cm cell or a 50-mL $CHCl_3$ extraction with a 10-cm cell is used in the photometric measurement. The minimum detectable quantity is 1 µg phenol/L in 500 mL distillate.

2. Apparatus

a. Photometric equipment: A spectrophotometer for use at 460 nm equipped with absorption cells providing light paths of 1 to 10 cm depending on the absorbances of the colored solutions and the individual characteristics of the photometer.

b. Filter funnels: Buchner type with fritted disk.[*]

c. Filter paper: Alternatively use an appropriate 11-cm filter paper for filtration of $CHCl_3$ extracts instead of the Buchner-type funnels and anhydrous Na_2SO_4.

d. pH meter.

e. Separatory funnels, 1,000-mL, Squibb form, with ground-glass stoppers and TFE stopcocks. At least eight are required.

3. Reagents

Prepare all reagents with distilled water free of phenols and chlorine.

a. Stock phenol solution: Dissolve 1.00 g phenol in freshly boiled and cooled distilled water and dilute to 1,000 mL. Ordinarily this direct weighing yields a standard solution; if extreme accuracy is required, standardize as follows:

1) To 100 mL water in a 500-mL glass-stoppered conical flask, add 50.0 mL stock phenol solution and 10.0 mL 0.1*N* bromate-bromide solution. Immediately add 5 mL conc HCl and swirl gently. If brown color of free bromine does not persist, add 10.0-mL portions of bromate-bromide solution until it does. Keep flask stoppered and let stand for 10 min; then add approximately 1 g KI. Usually four 10-mL portions of bromate-bromide solution are required if the stock phenol solution contains 1,000 mg phenol/L.

2) Prepare a blank in exactly the same manner, using distilled water and 10.0 mL 0.1*N* bromate-bromide solution. Titrate blank and sample with 0.025*N* sodium thiosulfate, using starch solution indicator.

3) Calculate the concentration of phenol solution as follows:

$$\text{mg phenol/L} = 7.842\,[(A \times B) - C]$$

where:

A = mL thiosulfate for blank,
B = mL bromate-bromide solution used for sample divided by 10, and
C = mL thiosulfate used for sample.

b. Intermediate phenol solution: Dilute 10.0 mL stock phenol solution in freshly boiled and cooled distilled water to 1,000 mL; 1 mL = 10.0 μg phenol. Prepare daily.

c. Standard phenol solution: Dilute 50.0 mL intermediate phenol solution to 500 mL with freshly boiled and cooled distilled water; 1 mL = 1.0 μg phenol. Prepare within 2 hr of use.

d. Bromate-bromide solution, 0.10*N*: Dissolve 2.784 g anhydrous $KBrO_3$ in water, add 10 g KBr crystals, dissolve, and dilute to 1,000 mL.

e. Hydrochloric acid, HCl, conc.

f. Standard sodium thiosulfate titrant, 0.025*N*: See Section 421B.2*e*.

g. Starch solution: See Section 421B.2*d*.

h. Ammonium hydroxide, NH_4OH, 0.5 *N*: Dilute 35 mL fresh, conc NH_4OH to 1 L with water.

i. Phosphate buffer solution: Dissolve 104.5 g K_2HPO_4 and 72.3 g KH_2PO_4 in water and dilute to 1 L. The pH should be 6.8.

j. 4-Aminoantipyrine solution: Dissolve 2.0 g 4-aminoantipyrine in water and dilute to 100 mL. Prepare daily.

k. Potassium ferricyanide solution: Dissolve 8.0 g $K_3Fe(CN)_6$ in water and dilute to 100 mL. Filter if necessary. Store

[*] 15 mL Corning No. 36060 or equivalent.

in a brown glass bottle. Prepare fresh weekly.

l. Chloroform, $CHCl_3$.

m. Sodium sulfate, anhydrous Na_2SO_4, granular.

n. Potassium iodide, KI, crystals.

4. Procedure

Ordinarily, use Procedure *a*; however, Procedure *b* may be used for infrequent analyses.

a. Place 500 mL distillate, or a suitable portion containing not more than 50 μg phenol, diluted to 500 mL, in a 1-L beaker. Prepare a 500-mL distilled water blank and a series of 500-mL phenol standards containing 5, 10, 20, 30, 40, and 50 μg phenol.

Treat sample, blank, and standards as follows: Add 12.0 mL 0.5*N* NH_4OH and adjust pH to 7.9 ± 0.1 with phosphate buffer. About 10 mL phosphate buffer are required. Transfer to a 1-L separatory funnel, add 3.0 mL aminoantipyrine solution, mix well, add 3.0 mL $K_3Fe(CN)_6$ solution, mix well, and let color develop for 3 min. The solution should be clear and light yellow.

Extract immediately with $CHCl_3$ using 25 mL for 1- to 5-cm cells and 50 mL for a 10-cm cell. Shake separatory funnel at least 10 times, let $CHCl_3$ settle, shake again 10 times, and let $CHCl_3$ settle again. Filter each $CHCl_3$ extract through filter paper or fritted glass funnels containing a 5-g layer of anhydrous Na_2SO_4. Collect dried extracts in clean cells for absorbance measurements; do not add more $CHCl_3$.

Read absorbance of sample and standards against the blank at 460 nm. Plot absorbance against micrograms phenol concentration. Construct a separate calibration curve for each photometer and check each curve periodically to insure reproducibility.

b. For infrequent analyses prepare only one standard phenol solution. Prepare 500 mL standard phenol solution of a strength approximately equal to the phenolic content of that portion of original sample used for final analysis. Also prepare a 500-mL distilled water blank.

Continue as described in ¶ *a*, above, but measure absorbances of sample and standard phenol solution against the blank at 460 nm.

5. Calculation:

a. For Procedure a:

$$\mu\text{g phenol/L} = \frac{A}{B} \times 1{,}000$$

where:

A = μg phenol in sample, from calibration curve, and
B = mL original sample.

b. For Procedure b, calculate the phenol content of the original sample:

$$\mu\text{g phenol/L} = \frac{C \times D \times 1000}{E \times B}$$

where:

C = μg standard phenol solution,
D = absorbance reading of sample,
E = absorbance of standard phenol solution, and
B = mL original sample.

6. Precision and Accuracy

Because the "phenol" value is based on C_6H_5OH, this method yields only an approximation and represents the minimum amount of phenols present. This is true because the phenolic reactivity to 4-aminoantipyrine varies with the types of phenols. Using the extraction procedure for concentration of color, six laboratories analyzed samples at concentrations of 9.6, 48.3, and 93.5 μg C_6H_5OH/L with standard deviations of, respectively, ±0.99, ±3.1, and ±4.2 μg/L.

APPENDIX 3. Bottom cores

Bottom Cores

Survey Line	Sample Location	Distance from shore (m)	Recovery[*] (cm)	Description
Power Line (07-18-85)	Between Stn. 6-7	55	20 50	Sand and gravel Clay with sand and gravel
Joint (07-30-85)	Between Stn.			
	1-2	5	10	Clay with gravel
	3-4	25	7	Clay with gravel
	5-6	45	1	Clay
	9-10	85	15	Clay
Police (S-3) (07-30-85)	Between Stn.			
	1-2	5	12	Sand (coarser sand at top of core)
	3-4	25	14	Sand, fine-grained
	5-6	45	1	Sand, fine-grained
	9-10	85	20	Sand, fine-grained
Suncor Dock (07-31-85)	Between Stn.			
	1-2	5	7	Sand with gravel
	3-4	25	12	Sand with gravel
	5-6	45	18	Gravel
	7-8	65	12	Sand with gravel
	9-10	85	19	10 cm gravel 9 cm clay (at bottom of core)
George Street (07-31-85)	Between Stn.			
	1-2	5	14	Sand, fine-grained
	3-4	25	8	Sand, fine-grained (with small chunks of wood)
	5-6	45	13	Sand, fine-grained
	7-8	65	8	Sand, fine-grained
	9-10	85	14	Sand, fine-grained
Downstream Reid Imperial (08-1-85)	Between Stn.			
	1-2	5	12	Sandy clay
	3-4	25	13	Sand, fine-grained
	5-6	45	0	-
	7-8	65	11	Clay with gravel
	9-10	85	25	Sandy clay

[*] Total length of core barrel - 46 cm

NA - not available

Survey Line	Sample Location	Distance from shore (m)	Recovery* (cm)	Description
Dow-Polysar (08-1-85)	Between Stn.			
	1-2	5	1	NA
	7-8	65	16	NA
	9-10	85	28	NA
	6	50	NA	NA
C and O Dock (S-4) (08-2-85)	Between Stn.			
	1-2	5	7	Clay
	3-4	25	17	Oily sediment
Dow 3-4th St. (S-10) (08-2-85)	Between Stn.			
	1-2	5		Sediment (with wood at top of corer)
	3-4	25	46	Sand with gravel
	5-6	45	12	Clay with gravel
	7-8	65	7	Clay with gravel
	9-10	85	0	-
Red-D-Mix Imperial (08-9-85)	Between Stn.			
	1-2	5	11	Sand with gravel (at bottom of corer)
	3-4	25	20	Clay with gravel (at bottom of corer)
	5-6	45	10	Gravel (at bottom of corer)
	7-8	65	NA	Sand with gravel
	9-10	85	8	1 cm clay (at top of corer) 7 cm sand (at bottom of corer)
Restaurant (08-14-85)				Very silty (line not used current too strong)
Upstream Reid-Imperial (08-14-85)	Between Stn.			
	1-2	5	17	Clay (at bottom of corer)
	3-4	25	8	Gravel (at bottom of corer)
	5-6	45	0	
	7-8	65	0	
	9-10	85	0	

Survey Line		Distance from shore (m)	Recovery* (cm)	Description
Concrete Dock (08-16-85)	Between Stn.			
	1-2	5	6	Sand, fine-grained (at top of corer)
	3-4	25	9	Sand, fine-grained (at top of corer) clay at bottom
	5-6	45	46	Clay with gravel
	7-8	65	3	Clay (at bottom of corer)
	9-10	85	17	Clay with gravel
Imperial-Polysar (08-19-85)	Between Stn.			
	1-2	5	4	Clay with gravel (at bottom of corer)
	3-4	25	46	Oily sand, fine-grained
	4	30	NA	Clay
	5-6	45	21	Sandy clay (at bottom of corer
	7-8	65	46	Clay
	9-10	85	31	Clay (at bottom of corer)
Cromwell Street (8-19-85)	Between Stn.			
	1-2	5	0	
	3-4	25	12	Oily sand, black (at bottom of corer)
	5-6	45	5	Sand, fine-grained (at bottom of corer)
	7-8	65	7	Sand, fine-grained (at bottom of corer)
	9-10	85	0	
Dow-Suncor (8-21-85)	Between Stn.			
	3-4	25	46	Clay with gravel

Survey Line	Sample Location	Distance from shore (m)	Recovery* (cm)	Description
Lake Huron (8-22-85)	Between Stn.			
	1-2	5	0	All rock
	3-4	25	16	Sand, medium-grained
	5-6	45	46	Sand, fine-grained
	7-8	65	17	Sand, fine-grained
	9-10	85	46	Sand, fine-grained
Lake Huron #1 (8-27-85)	2 cores from 1.5 m radius around site		17	Clay with sand
			19	Clay with sand

APPENDIX 4. River bottom descriptions

Description of River Bottom

Survey Line	Location on Line	Description
Joint (7-18-85)	Near shore	Sandy, much vegetation
	0-30 m (from shore)	Vegetation, coarse sand, gravel, debris
	30-60 m (from shore)	Less vegetation, coarse sand, debris, logs, boulders, steeper slope
	50-100 m (from shore)	Gravel bottom, boulders, debris
Power Line (7-19-85)	Station	
	1-5 (0-40 m from shore)	Sand over clay, vegetation Stn. 1: 17 cm coarse gravely sand Stn. 2: Clay with less than 2 cm sand Stn. 3: Clay with 5 cm sand Stn. 4: Coarse sand and gravel
	5-7 (40-60 m from shore)	Fine sand
	7-9 (60-80 m from shore)	Stn. 7: Sand bar, 10 cm sand over clay
	9-11 (80-100 m from shore)	Sand (less than 5 cm), clay, debris
Reid-Imperial (8-1-85)	Near shore	Sand, gravel underlain by clay, exposed clay in areas
Dow-Polysar (8-1-85)	Station	
	1-4 (0-30 m from shore)	Sand, vegetation
	4-5 (30-40 m from shore)	Sand (5 cm thick), clay
	6 (50 m from shore)	Oily sediments
Dow 3-4th St. (S-10) (8-2-85)	Station	
	1-4 (0-30 m from shore)	Sand, clay, vegetation
	4-6 (30-50 m from shore)	Black sediments
	7-10 (60-90 m from shore)	Clay, gravel
Red-D-Mix Imperial (8-9-85)	Station	
	1-2 (0-10 m from shore)	Fine to coarse sand, vegetation
	3-4 (20-30 m from shore)	Coarse sand
	5-6 (40-50 m from shore	Boulders, gravel, clay
Imperial-Reid (8-14-85)		Clay, rubble
Restaurant (8-14-85)		Very silty

APPENDIX 5. Seepage meter data

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Lake Huron	Position #1 1/km	08-26	7.40	177	19.6	1450	72.07	102.650
		08-27	7.70	185	19.9	55	19.5	14.390
		09-06	7.44	188	28.2	1745	NA	NA
	2/10	08-23	8.29	200	24.0	1205	23.57	260.838
		08-29	NA	NA	NA	95	66.67	7.270
	3/20	08-23	7.31	192	22.5	1240	23.57	268.415
		08-29	NA	NA	NA	110	66.67	8.418
	5/40	08-23	7.17	197	23.8	65	23.57	14.070
		08-29	NA	NA	NA	50	66.67	3.826
	7/60	08-23	7.65	188	21.9	260	23.57	56.281
		08-26	7.36	184	19.5	1190	72.55	83.686
		08-29	NA	NA	NA	45	66.67	3.444
	9/80	08-23	7.10	186	21.5	370	23.57	80.091
		08-26	-	-	-	NR	-	-
		08-29	NA	NA	NA	125	66.67	9.566
	11/100	08-23	7.01	133	21.3	25	23.57	5.412
		08-26	7.87	184	19.6	55	72.55	3.868
		08-29	NA	NA	NA	275	66.67	21.045

NR - no recovery (dry)
NA - not available
EC - Electrical conductivity

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates ($ml/hr/m^2$)
George Street	1/shore	08-08	-	-	-	NR	-	-
		08-09	-	-	-	NR	-	-
		08-12	6.87	135	22.8	20	69.4	1.469
		08-13	-	-	-	NR	-	-
		08-16	6.90	271	22.7	55	78.38	3.582
		08-20	7.00	241	19.3	40	92.12	2.214
		08-21	-	-	-	NR	-	-
		08-22	-	-	-	NR	-	-
		08-23	7.81	125	22.0	15	24.63	3.107
		09-14	7.35	268	20.7	105	222.07	2.412
	3/20	08-08	-	-	-	NR	-	-
		08-09	6.45	140	26.6	25	27.66	4.612
		08-12	7.40	245	22.0	90	69.4	6.617
		08-13	7.28	162	26.6	20	28.72	3.551
		08-16	7.12	262	21.9	70	78.38	4.556
		08-20	6.99	161	19.3	35	92.12	1.939
		08-21	-	-	-	NR	-	-
		08-22	7.78	285	22.4	95	19.7	24.602
		08-23	7.83	154	22.4	45	24.63	9.321
		08-30	7.28	125	22.0	180	146.25	6.281
		09-05	7.71	322	23.4	90	140.10	3.278
		09-14	7.51	235	19.3	625	222.07	14.360
	5/40	08-08	7.20	225	25.6	262.5	25.92	51.668
		08-09	6.92	210	26.0	55	27.66	10.143
		08-12	7.14	124	22.8	50	69.4	3.679
		08-13	7.04	268	26.4	60	28.72	10.658
		08-16	6.65	265	21.7	120	78.38	7.811
		08-20	7.18	257	19.3	230	92.12	12.740

EC - Electrical conductivity
NR - No recovery (dry)

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
George Street (cont'd)	5/40	08-21	-	-	-	-	-	-
		08-22	7.40	289	22.6	65	19.7	16.837
		08-23	7.48	202	22.6	170	24.63	35.214
		08-30	7.45	253	22.4	240	146.25	8.372
		09-05	8.05	328	23.5	205	140.10	7.466
		09-14	7.52	308	20.1	65	222.07	1.493
	7/60	08-08	6.85	206	25.8	315	25.92	62.005
		08-09	6.93	257	25.0	345	27.66	63.638
		08-12	7.12	272	22.2	195	69.4	14.337
		08-13	7.49	322	26.3	75	28.72	13.321
		08-16	7.04	172	21.9	45	78.38	2.929
		08-20	7.05	335	18.9	92.5	92.12	5.123
		08-21	7.60	353	20.1	125	29.13	21.893
		08-22	7.33	386	22.6	245	19.7	63.454
		08-23	7.64	405	23.4	70	24.63	14.500
		08-30	7.23	225	22.1	280	146.25	9.770
		09-05	7.54	449	23.1	1395	140.10	50.802
		09-14	7.70	204	21.3	40	222.07	0.919
	9/80	08-08	7.06	214	28.0	340	25.92	66.924
		08-09	6.94	244	26.5	50	27.66	9.225
		08-12	7.12	281	22.1	140	69.4	10.291
		08-13	7.32	340	26.0	82.5	28.72	14.658
		08-16	7.21	293	21.8	292.5	78.38	19.041
		08-20	7.09	359	19.1	290	92.12	16.061
		08-21	7.34	382	19.8	60	29.13	10.510
		08-22	7.58	432	22.8	80	19.7	20.719
		08-23	7.34	463	23.9	60	24.63	12.429
		08-30	7.23	279	22.3	180	146.25	6.281
		09-05	7.86	495	23.5	430	140.10	15.659
		09-14	7.73	438	20.6	110	222.07	2.527

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
George Street (cont'd)	11/100	08-08	6.97	199	25.7	1370	25.92	269.668
		08-09	7.05	212	24.1	295	27.66	54.413
		08-12	7.40	235	22.0	575	69.4	42.270
		08-13	7.10	289	25.4	425	28.72	75.500
		08-16	7.12	286	21.5	210	78.38	13.668
		08-20	6.91	298	19.2	290	92.12	16.061
		08-21	7.29	305	20.2	105	29.13	18.393
		08-22	7.30	176	22.8	40	19.7	10.357
		08-23	7.52	195	24.8	20	24.63	4.143
		08-30	7.49	172	22.4	80	146.25	2.791
		09-05	7.78	426	24.0	130	140.10	4.734
		09-14	8.04	402	19.8	210	222.07	4.825

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (μS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Cromwell Street	1/shore	08-21	7.95	191	19.6	935	30.63	155.743
		08-22	7.02	229	22.1	110	19.72	28.460
		08-23	7.36	273	26.1	220	24.30	46.191
		08-26	7.29	248	19.7	360	75.40	24.360
		08-28	7.15	325	24.5	160	45.17	18.072
	3/20	08-21	7.06	179	19.3	65	30.63	10.827
		08-22	1.17	203	22.6	75	19.72	19.404
		08-23	7.30	208	25.3	30	24.30	6.300
		08-26	7.15	114	19.4	50	75.40	3.383
		08-28	7.87	180	25.4	20	45.17	2.259
	5/40	08-21	7.00	180	19.5	1050	30.63	174.899
		08-22	7.12	235	22.8	170	19.72	43.983
		08-23	8.10	253	24.7	305	24.30	64.038
		08-26	7.23	227	19.5	140	75.40	9.473
		08-28	8.04	276	25.9	90	45.17	10.166
	7/60	08-21	6.88	186	19.7	275	30.63	45.807
		08-22	6.95	230	23.6	30	19.72	7.762
		08-23	8.01	331	25.5	495	24.30	103.930
		08-26	7.66	289	19.7	330	75.40	22.330
		08-28	8.63	242	27.2	25	45.17	2.824
	9.80	08-21	6.93	181	19.8	1955	30.63	325.645
		08-22	7.25	232	22.5	965	19.72	249.669
		08-23	8.22	252	24.3	1620	24.30	340.136
		08-26	7.98	245	19.7	1430	75.40	96.763
		08-28	7.48	323	25.2	430	45.17	48.569
	11/100	08-21	7.36	180	19.4	590	30.63	98.276
		08-22	7.15	211	22.7	730	19.72	188.869
		08-23	7.68	269	25.4	165	24.30	34.644
		08-26	7.82	241	19.6	475	75.40	32.142
		08-28	7.87	314	26.7	165	45.17	18.637

EC - Electrical Conductivity

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (μS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Police Station (S-3)	1/shore	08-13	6.67	130	26.7	42.5	22.75	9.531
		08-15	6.80	211	19.8	200	48.98	20.855
		08-19	6.95	223	19.1	77.5	97.23	4.067
	3/20	08-13	7.02	226	26.5	107.5	22.75	24.109
		08-15	6.81	209	20.3	525	48.93	54.743
		08-19	6.86	228	19.4	330	97.23	17.316
	5/40	08-13	6.51	217	26.3	1330	22.75	298.273
		08-15	6.74	211	20.3	885	48.93	92.281
		08-19	7.02	252	19.3	550	97.23	28.861
	7/60	08-13	7.20	217	25.1	797.5	22.75	178.854
		08-15	6.65	245	20.0	365	48.93	38.059
		08-19	6.98	273	19.1	560	97.23	29.385
	9/80	08-13	6.90	216	26.1	730	22.75	163.714
		08-15	6.91	206	19.4	155	48.93	16.162
		08-19	7.11	240	18.8	220	97.23	11.544
	11/100	08-13	6.87	220	26.0	1145	22.75	256.284
		08-15	6.76	211	19.5	355	48.93	37.017
		08-19	7.16	229	19.5	1150	97.23	60.345

EC - Electrical conductivity

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Red-D-Mix Imperial	1/shore	08-13	5.94	212	27.7	12.5	20.05	3.181
		08-15	6.81	183	19.2	215	51.93	21.123
		08-20	-	-	-	NR	-	-
		08-21	7.09	104	20.4	20	29.12	3.504
	3/20	08-13	7.36	130	29.0	40	20.05	10.179
		08-15	6.74	241	19.6	135	51.93	13.264
		08-20	6.97	192	19.0	2145	115.92	94.409
		08-21	7.06	182	19.6	1810	29.12	317.126
	5/40	08-13	-	-	-	NR	-	-
		08-15	6.81	203	19.2	120	51.93	11.790
		08-20	-	-	-	NR	-	-
		08-21	6.98	181	19.6	1155	29.12	202.365
	7/60	08-13	6.87	220	27.7	230	20.05	58.527
		08-15	6.70	187	19.5	2545	51.93	250.042
		08-20	6.60	187	19.0	2180	115.92	95.949
		08-21	6.90	179	19.6	2085	29.12	365.308
	9/80	08-13	6.72	222	26.6	260	20.05	66.161
		08-15	6.64	190	19.1	175	51.93	17.194
		08-20	6.65	205	19.1	2655	115.92	116.856
		08-21	7.07	179	19.6	2080	29.12	364.432
	11/100	08-13	6.47	13	28.2	30	20.05	7.634
		08-15	6.84	186	19.3	2220	51.93	218.112
		08-20	6.47	186	19.1	2475	115.92	108.933
		08-21	7.04	180	19.5	1620	29.12	283.836

NR - no recovery (dry)
EC - Electrical conductivity

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Suncor Dock	3/20	08-08	6.84	395	26.8	330	30.58	55.058
		08-09	6.80	383	26.8	75	27.70	13.814
		08-12	7.15	213	24.9	45	69.5	3.304
		08-13	-	-	-	NR	-	-
		08-14	7.08	343	24.0	135	30.05	22.921
		08-16	7.00	344	21.3	742.5	43.35	87.388
	5/40	08-08	7.02	193	31.0	25	30.58	4.171
		08-09	-	-	-	NR	-	-
		08-12	7.10	363	22.9	1190	69.5	87.359
		08-13	6.26	22	29.2	20	23.53	4.337
		08-14	-	-	-	NR	-	-
		08-16	6.82	322	21.9	1240	43.35	145.941
	7/60	08-08	6.70	311	31.2	57.5	30.58	9.593
		08-09	7.23	274	26.2	1055	27.70	194.320
		08-12	7.53	263	23.7	1235	69.5	90.662
		08-13	6.07	11	29.2	30	23.53	6.505
		08-14	6.88	270	23.9	2345	30.05	398.146
		08-16	6.70	146	22.8	42.5	43.35	5.002
	9/80	08-13	6.89	250	29.3	2522	23.53	546.849
		08-14	7.01	215	23.8	2312.5	30.05	392.628
	11/100	08-12	7.64	213	23.7	2400	69.5	176.186
		08-13	6.53	231	28.0	2605	23.53	564.846
		08-14	6.90	209	23.9	2375	30.05	403.240

EC - Electrical conductivity
NR - No recovery (dry)

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (μS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Concrete Dock	2/10	08-20	6.94	317	18.0	180	96.17	9.55
		08-21	7.37	335	20.8	50	20.42	2.65
		08-22	-	-	-	-	22.55	-
		08-23	7.59	427	21.4	70	24.85	14.37
		08-26	7.68	459	20.0	385	75.35	4.74
		08-28	8.01	580	25.9	250	45.12	28.27
	3/10	08-20	6.64	301	17.5	160	96.17	8.49
		08-21	7.02	191	21.5	20	20.42	1.06
		08-22	-	-	-	-	22.55	-
		08-23	7.20	193	21.8	20	24.85	20.95
		08-26	7.46	356	19.9	65	75.35	1.35
		08-28	8.20	440	27.1	315	45.12	35.62
	4/30	08-20	7.03	273	18.1	380	96.17	20.16
		08-21	6.85	145	22.8	30	20.42	1.59
		08-22	7.93	118	20.4	15	22.55	3.39
		08-23	7.27	325	22.3	365	24.85	74.94
		08-26	7.95	305	20.3	1595	75.35	24.69
		08-28	7.68	355	25.1	1300	45.12	147.01
	5/40	08-20	6.54	220	18.6	1915	96.17	101.597
		08-21	6.82	143	22.7	35	20.42	1.857
		08-22	7.17	221	20.3	1665	22.55	376.71
		08-23	7.39	228	21.8	1535	24.85	315.15
		08-26	7.40	218	20.4	1210	75.35	103.94
		08-28	8.40	245	24.2	1660	45.12	187.72

EC - Electrical conductivity
NR - No recovery (dry)

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (μS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Concrete Dock	6/50	08-20	6.28	128	18.5	2195	96.17	116.45
		08-21	6.88	241	21.8	1185	20.42	62.87
		08-22	7.18	227	20.9	2050	22.55	463.82
		08-23	8.14	217	22.3	2040	24.85	418.84
		08-26	7.54	210	20.0	385	75.35	138.13
		08-28	8.44	240	24.8	1830	45.12	206.95
	7/60	08-20	6.86	217	18.6	1850	96.17	98.15
		08-21	7.01	236	21.9	1535	20.42	81.43
		08-22	7.16	237	21.5	2050	22.55	463.82
		08-23	7.30	215	22.8	1480	24.85	303.86
		08-26	7.51	199	20.0	1215	75.35	100.21
		08-28	8.33	226	25.0	1945	45.12	219.95

Seepage Meter Data

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (μS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Power Line	1/shore	07-16	6.99	269	22.5	230	94.03	12.480
		07-17	8.04	304	23.0	75	27.45	13.939
		07-19	7.47	266	22.0	62.5	22.12	14.418
	RW	07-19	7.90	211	20.0	-	-	-
	2/10	07-16	7.65	334	21.0	1210	94.03	65.653
		07-17	7.89	399	21.5	65	27.45	12.082
		07-19	-	-	-	NR	-	-
	RW	07-19	8.33	200	20.5	-	-	-
	3/20	07-16	7.48	138	27.0	1012	94.03	54.913
		07-17	7.64	315	21.0	1075	27.12	202.240
		07-19	7.84	334	21.5	600	22.12	138.393
	RW	07-19	8.46	194	20.5	-	-	-
	4/30	07-16	7.79	240	21.0	1985	94.03	107.709
		07-17	7.75	258	22.0	2010	27.12	378.138
		07-19	8.02	254	21.0	1930	22.12	445.158
	RW	07-19	8.48	230	20.5	-	-	-
	5/40	07-16	7.66	209	20.5	2170	94.03	117.745
		07-17	7.82	230	21.0	1670	27.12	314.174
		07-19	7.92	199	21.0	1105	22.12	254.873
	RW	07-19	7.96	176	20.5	-	-	-
	6/50	07-19	8.16	198	21.0	1655	22.68	372.306
	7/60	07-19	8.02	143	21.0	1525	23.0	338.286

EC - Electrical conductivity
NR - No recovery (dry)
RW - River Water

Survey Line	Station # (m from shore)	Date (1985)	pH	EC (µS/cm)	Temp. (C°)	Vol. (ml)	Duration (hrs)	Seepage Rates (ml/hr/m^2)
Power Line (cont'd)	8/70	07-19	8.45	186	21.0	2270	23.0	503.551
	9/80	07-19	8.55	187	22.0	2340	23.0	519.077
	10/90	07-19	8.66	187	21.0	2380	23.0	527.949
	11/100	07-19	8.63	188	21.5	2195	23.0	486.912
	RW	07-19	8.35	188	21.5	-	-	-

APPENDIX 6. Minipiezometer data

Minipiezometer Data

Survey Line	Station # (m from shore)	Time of Sample	Depth of Piezometer (m)	pH	EC (µS/cm)	Temp. (C°)	Sample #	Remarks/ Appearance
George St.	11*/100	11:00 am	1.5	7.03	532	18.6		- Clear
08-30-85			1.0	6.80	585	19.9		- Silty
			1.0	7.61	508	18.0		- Slightly yellow
			0.5	7.00	367	19.6		- Silty
			RW	7.79	183	19.3		- Slightly silty
			RW	8.26	172	19.2		- Clear
			RW	8.33	172	19.3		- Clear
			RW	8.25	173	19.0		- Clear
	11/100	3:45 pm	1.5	7.85	259	18.9	(1345)	
			1.5	7.36	373	18.8	(1346)	
			1.5	6.96	449	18.9	(1347)	
		4:30 pm	RW	NA	NA	NA	(1348,1349, 1350)	
George St. 09-03-85	6/50	pm	1.0	7.20	1075	26.6	(1351,1352, 1353)	- Groundwater had strong odor
			RW	7.90	185	21.4	(1354)	
George St. 09-04-85	5/40	am	1.5	7.20	898	20.9	(1355,1356, 1357)	- Clear with slight odor
			RW	7.42	204	22.7	(1358)	- Many gas bubbles
			1.0	7.25	801	22.3	(1359, 1360, 1361)	- Cloudy
George St. 09-05-85	5/40	am	1.0	7.55	824	24.8	(1363,1364, 1365)	
			RW	7.72	182	20.9	(1373)	

*Preliminary samples taken to test equipment

RW - River water

NA - Data not available

EC - Electrical conductivity

Survey Line	Station # (m from shore)	Time of Sample	Depth of Piezometer (m)	pH	EC (µS/cm)	Temp. (C°)	Sample #	Remarks/ Appearance
George St. 09-05-85	7/60	am	1.5	7.11	1012	22.7	(1367,1368, 1369)	
			RW	7.61	181	21.6	(1366)	
		am	1.0	7.18	935	20.5	(1370,1371, 1372)	
George St. 09-14-85	5/40	am	1.0	6.99	650	19.8	(1394,1395, 1396,1397, 1398,1399)	
			RW	7.80	171	18.7	(1400,1401, 1402,1403, 1404,1405)	
Cromwell St. 09-05-85	6/50	pm	1.5	6.76	1130	26.0	(1374,1375, 1376)	- rusty oily and hydrogen-sulfide odor
			RW	7.13	179	18.8	(1377)	
			1.0	6.73	1290	23.5	(1379,1380, 1381,1382, 1383,1384)	
			RW	-	-	-	(1378)	- gas
Cromwell St. 09-06-85	6/50	pm	1.0	6.70	1627	31.4	(1385,1386, 1387,1388, 1388,1390)	
			RW	7.30	233	26.9	(1391,1392, 1393)	

Survey Line	Station # (m from shore)	Time of Sample	Depth of Piezometer (m)	pH	EC (µS/cm)	Temp. (C°)	Sample #	Remarks/ Appearance
<u>Cromwell St.</u> 09-15-85 Lab Samples	6/50	10:11 am	1.5	6.80	1005	18.9	(1406,1407, 1408)	- Scum floating on top of water
		10:50 am	RW	7.00	303	20.0	(1409,1410, 1411)	
		11:45 am	1.0	6,83	860	26.2	(1412,1413, 1414)	Strong odor
		1:45 pm	1.0	6.78	1173	19.9	(1415,1416, 1417)	Hydrogen sulfide
	11/100	3:15 pm	1.5*	6.80	814	18.8	(1424,1425, 1426)	
		3:00 pm	1.0	6.71	1002	19.1	(1427,1428, 1429)	
		3:15 pm	RW	7.81	165	18.8	(1430,1431, 1432)	

*Flowing

Note: Sample 1418-1423 - blanks - organic free water

APPENDIX 7 Chloride results

UNIVERSITY OF WINDSOR (mg/l)

	CHLORIDE
1345	14.5
1348	-
1351	23.4
1355	111
1359	81
1363	95
1367	14.6
1374	11.3
1379	9.4
1382	9.2
1385	9.2
1388	10.3
1392	5.4
1394	82
1397	93
1400	5.5
1403	5.2
1406	10.1
1409	5.2
1412	9.6/9.9
1415	9.0
1424	9.2
1427	7.8
1430	5.4
1619	7.0

- indicates broken sample

APPENDIX 8. TOX results

SAMPLE I.D.						TOX CONCENTRATION (ug/l)
83085		George St.	11	1.5 m	1345	10.0
83085	4115	George St.	11	RB	1348	18.3
9385		George St.	6		1351	7.1
9485	1124	George St.	5		1355	16.0, 11.5
9485		George St.	5	1 m	1359	<1, <1
9585	1000	George St.	5	1 m	1363	5.7
9585	1002	George St.	7	1.5 m	1367	6.4
9585	1254	George St.	7	1 m	1370	9.2
9685	1530	Cromell	6	1 m	1388	4.2
9685	1534	Cromell	6	1 m	1385	7.5
9685	1559	Cromell	6	RB	1392	3.4
95	1823	Cromell	6	1 m	1382	2.3
95	1809	Cromell	6	1 m	1379	5.7
95	1718	Cromell	6	1.5 m	1374	4.7
91585		Blank			1421	3.0
915	1515	Cromell	11	1 m	1424	5.7
915		Cromell	6	1.5 m	1406	<1
915	1225	George St.	5	RB	1403	<1
		Cromell	6	1 m	1412	7.3
91585		Blank ZENON			1418	11.5, 8.4
915	1700	Cromell	11	1 m	1427	<1
914	1219	George St.	5	RB	1400	10.4
914	1156	George St.	5	1 m	1397	<1
		RB			1430	<1
914	1135	George St.	5	1 m	1394	5.8
91585	1345	Cromell	6	1 m	1415	<1
915		Cromell	6	RB	1409	3.1
		River Water			1619	2.0
928		80' hole		20 m	1625	2.3

APPENDIX 9. Chlorinated hydrocarbon/PCB results

CHLORINATED HYDROCARBONS AND POLYCHLORINATED BIPHENYLS

UNIVERSITY OF WINDSOR (ug/l)

	1345	1348	1351	1355	1367	1370
HEXACHLOROBENZENE	0.0000	0.0012	0.0003	0.0003	0.0004	0.0011
a-BENZENEHEXACHLORIDE	0.0002	0.0022	0.0006	0.0000	0.0002	0.0005
g-BENZENEHEXACHLORIDE	0.0005	0.0007	0.0015	0.0000	0.0006	0.0017
HEPTACHLOR	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ALDRIN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
OXYCHLORDANE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
HEPTACHLOR EPOXIDE	0.0000	0.0000	0.0000	0.0009	0.0000	0.0000
a-CHLORDANE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
g-CHLORDANE	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
a-ENDOSULFAN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
p,p'-DDE	0.0004	0.0014	0.0000	0.0000	0.0000	0.0000
DIELDRIN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ENDRIN	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
p,p'-DDD	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
o,p'-DDT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
p,p'-DDT	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
PHOTOMIREX	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MIREX	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHOXYCHLOR	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL PCB	0.000	0.000	0.019	0.026	0.000	*int

*int indicates interference

CHLORINATED HYDROCARBONS AND POLYCHLORINATED BIPHENYLS

UNIVERSITY OF WINDSOR (ug/l)

	1385	1388	1412	1421	1424
HEXACHLOROBENZENE	0.0010	0.0012	0.0027	0.0003	0.0014
a-BENZENEHEXACHLORIDE	0.0000	0.0003	0.0013	0.0002	0.0006
g-BENZENEHEXACHLORIDE	0.0019	0.0012	0.0013	0.0004	0.0000
HEPTACHLOR	0.0000	0.0000	0.0000	0.0000	0.0000
ALDRIN	0.0000	0.0000	0.0000	0.0000	0.0000
OXYCHLORDANE	0.0000	0.0000	0.0000	0.0000	0.0000
HEPTACHLOR EPOXIDE	0.0000	0.0000	0.0006	0.0000	0.0000
a-CHLORDANE	0.0000	0.0003	0.0000	0.0000	0.0000
g-CHLORDANE	0.0000	0.0003	0.0000	0.0000	0.0000
a-ENDOSULFAN	0.0000	0.0000	0.0000	0.0000	0.0000
p,p'-DDE	0.0000	0.0003	0.0000	0.0000	0.0000
DIELDRIN	0.0000	0.0000	0.0000	0.0000	0.0000
ENDRIN	0.0000	0.0000	0.0017	0.0000	0.0000
p,p'-DDD	0.0000	0.0000	0.0000	0.0000	0.0000
o,p'-DDT	0.0000	0.0000	0.0000	0.0000	0.0000
p,p'-DDT	0.0000	0.0000	0.0000	0.0000	0.0000
PHOTOMIREX	0.0000	0.0000	0.0000	0.0000	0.0000
MIREX	0.0000	0.0000	0.0000	0.0000	0.0000
METHOXYCHLOR	0.0000	0.0000	0.0000	0.0000	0.0000
TOTAL PCB	0.015	0.000	*int	0.000	*int

*int indicates interference

APPENDIX 10. Trihalomethane results

TRIHALOMETHANES

UNIVERSITY OF WINDSOR (ug/l)

	1347	1352	1356	1368	1371
CHLOROFORM	1.89	2.77	1.09	0.62	0.56
CARBON TETRACHLORIDE	0.78	1.76	0.91	0.30	0.30
TRICHLOROETHYLENE + BROMODICHLOROMETHANE	1.57	ND@0.01	1.76	0.15	0.16
DIBROMOCHLOROMETHANE	0.15	0.23	0.62	ND@0.01	ND@0.01
TETRACHLOROETHYLENE	0.16	0.98	1.18	0.09	0.09
BROMOFORM	ND@0.01	ND@0.01	ND@0.01	ND@0.01	ND@0.01

	1386	1389	1413	1419	1425
CHLOROFORM	0.85	0.67	0.61	1.18	0.47
CARBON TETRACHLORIDE	0.40	0.34	0.39	0.40	0.29
TRICHLOROETHYLENE + BROMODICHLOROMETHANE	ND@0.01	0.43	0.14	0.41	0.15
DIBROMOCHLOROMETHANE	ND@0.01	ND@0.01	ND@0.01	0.04	ND@0.01
TETRACHLOROETHYLENE	0.16	0.13	0.24	0.17	0.08
BROMOFORM	ND@0.01	ND@0.01	ND@0.01	ND@0.01	ND@0.01

APPENDIX 11. Acid extractable results

UNIVERSITY OF WINDSOR EPA PRIORITY POLLUTANTS: EXTRACTABLES (ug/l)

ACID EXTRACTABLES	DETECTION LIMIT	1348	1355	1370	1412	1424
4-Chloro-3-methylphenol	1	ND	ND	ND	ND	ND
2-Chlorophenol	1	ND	ND	ND	ND	ND
2,4-Dichlorophenol	1	ND	ND	ND	ND	ND
2,4-Dimethylphenol	1	ND	ND	ND	ND	ND
2,4-Dinitrophenol	5	ND	ND	ND	ND	ND
2-Methyl-4,6-dinitrophenol	5	ND	ND	ND	ND	ND
2-Nitrophenol	1	ND	ND	ND	ND	ND
4-Nitrophenol	5	ND	ND	ND	ND	ND
Pentachlorophenol	1	ND	ND	ND	ND	ND
Phenol	1	ND	ND	ND	ND	ND
2,4,6-Trichlorophenol	1	ND	ND	ND	ND	ND

APPENDIX 12. Base/neutral results

BASE NEUTRALS	DETECTION LIMIT	1348	1355	1370	1412	1424
Acenaphthene	0.1	ND	ND	ND	ND	ND
Acenaphthylene	0.1	ND	ND	ND	ND	ND
Anthracene	0.1	ND	ND	ND	ND	ND
Aldrin	0.1	ND	ND	ND	ND	ND
Benzidine	0.1	ND	ND	ND	ND	ND
Benzo(a)anthracene	0.1	ND	ND	ND	0.4	0.2
Benzo(b)fluoranthene	0.1	ND	ND	ND	0.6	0.7
Benzo(k)fluoranthene	0.1	ND	ND	ND	ND	ND
Benzo(a)pyrene	0.1	ND	ND	ND	0.4	0.3
Benzo(ghi)perylene	0.1	0.8	0.8	ND	2.4	1.3
Benzylbutylphthalate	1	ND	ND	ND	ND	ND
a-BHC	0.1	ND	ND	ND	ND	ND
b-BHC	0.1	ND	ND	ND	ND	ND
c-BHC	0.1	ND	ND	ND	ND	ND
Bis(2-chloroethyl)ether	0.1	ND	ND	ND	ND	ND
Bis(2-chloroethyloxy)methane	0.1	ND	ND	ND	ND	ND
Bis(2-ethylhexyl)phthalate	1	ND	ND	ND	ND	ND
Bis(2-chloroisopropyl)ether	1	ND	ND	ND	ND	ND
4-Bromodiphenylether	0.1	ND	ND	ND	ND	ND
Chlordane	0.1	ND	ND	ND	ND	ND
2-Chloronaphthalene	0.1	ND	ND	ND	ND	ND
4-Chlorodiphenylether	0.1	ND	ND	ND	ND	ND
Chrysene	0.1	ND	ND	ND	ND	ND
4,4'-DDD	0.1	ND	ND	ND	ND	ND
4,4'-DDE	0.1	ND	ND	ND	ND	ND
4,4'-DDT	0.1	ND	ND	ND	ND	ND
Dibenzo(a,h)anthracene	0.1	0.1	ND	ND	0.4	0.2
Di-n-butylphthalate	1	ND	ND	ND	ND	ND
Di-n-octylphthalate	1	ND	ND	ND	ND	ND
1,2-Dichlorobenzene	1	ND	ND	ND	ND	ND
1,3-Dichlorobenzene	1	ND	ND	ND	ND	ND
1,4-Dichlorobenzene	1	ND	ND	ND	ND	ND
3,3'-Dichlorobenzidine	1	ND	ND	ND	ND	ND
Dieldrin	1	ND	ND	ND	ND	ND
Diethylphthalate	1	ND	ND	ND	ND	ND
Dimethylphthalate	1	ND	ND	ND	ND	ND
2,4-Dinitrotoluene	0.1	ND	ND	ND	ND	ND

UNIVERSITY OF WINDSOR EPA PRIORITY POLLUTANTS: EXTRACTABLES (ug/l)

BASE NEUTRALS (CONT.)	DETECTION LIMIT	1348	1355	1370	1412	1424
2,6-Dinitrotoluene	0.1	ND	ND	ND	ND	ND
Endosulfan I	0.1	ND	ND	ND	ND	ND
Endosulfan II	0.1	ND	ND	ND	ND	ND
Endosulfan Sulfate	1	ND	ND	ND	ND	ND
Endrin	0.1	ND	ND	ND	ND	ND
Endrin Aldehyde	0.1	ND	ND	ND	ND	ND
Fluoranthene	0.1	ND	ND	ND	ND	ND
Fluorene	0.1	ND	ND	ND	ND	ND
Heptachlor	0.1	ND	ND	ND	ND	ND
Heptachlorepoxide	0.1	ND	ND	ND	ND	ND
Hexachlorobenzene	0.1	ND	ND	ND	ND	ND
Hexachlorobutadiene	0.1	ND	ND	ND	ND	ND
Hexachlorocyclopentadiene	0.1	ND	ND	ND	ND	ND
Hexachloroethane	0.05	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	0.1	0.2	ND	0.1	2.4	1.3
Isophorone	0.1	ND	ND	ND	ND	ND
Naphthalene	0.1	ND	ND	ND	ND	ND
Nitrobenzene	0.1	ND	ND	ND	ND	ND
N-Nitrosodi-n-propylamine	0.1	ND	ND	ND	ND	ND
N-Nitrosodimethylamine	0.1	ND	ND	ND	ND	ND
N-Nitrosodiphenylamine	0.1	ND	ND	ND	ND	ND
PCB-1016	2	ND	ND	ND	ND	ND
PCB-1221	2	ND	ND	ND	ND	ND
PCB-1232	2	ND	ND	ND	ND	ND
PCB-1242	2	ND	ND	ND	ND	ND
PCB-1248	2	ND	ND	ND	ND	ND
PCB-1254	2	ND	ND	ND	ND	ND
PCB-1260	2	ND	ND	ND	ND	ND
Phenanthrene	0.1	ND	ND	ND	ND	ND
Pyrene	0.1	ND	ND	ND	ND	ND
Toxaphene	1	ND	ND	ND	ND	ND
2,3,7,8-TCDD	0.01	ND	ND	ND	ND	ND
1,2,4-Trichlorobenzene	0.1	ND	ND	ND	ND	ND
d-10 ANTHRACENE % REC.		39	10	70	44	37

APPENDIX 13 Oxygen-18/tritium/deuterium results

Sample Conversion Numbers

Field Sample Number for O-18 and T		Report Sample Number
1346	George Street	1
1353		3
1357		4
1361		5
1365		6
1369		7
1372		8
1396		9
1399		10
1408	Cromwell Street	21
1376		14
1381		16
1384		17
1387		18
1414		23
1426		25
1429		26
1349	George Street	2
1358		11
1402		12
1405		13
1377	Cromwell Street	15
1391		20
1411		22
1432		27
1A	Suncor Wells	28
2A		29
4A		30
5A		31
6A		32
NA	Chenal Ecarte	33
NA		34
NA		35
NA		36

ISOTOPE RESULTS

Sample No.	Location	Station	Depth	O-18 (‰)	T (TU)	D(‰)
1	George Street	11	1.5m	-7.75	21+7	
3		6	1.0	-7.54	45+8	
4		5	1.5	-7.91	29+7	-59.9
5		5	1.0	-7.64	75+8	-56.0
6		5	1.0	-7.92	64+8	
7		7	1.5	-7.31	44+8	
8		7	1.0	-7.42	41+8	
9		5	1.0	-8.01	63+8	
10		5	1.0	-7.90	70+8	
21	Cromwell Street	6	1.5	-7.51	15+7	-59.2
14		6	1.5	-7.34	6+7	
16		6	1.0	-7.34	42+8	
17		6	1.0	-6.79	39+8	
18		6	1.0	-7.49	33+8	-59.6
23		6	1.0	-7.43	33+8	
25		11	1.5	-7.26	24+8	
26		11	1.0	-7.32	87+8	
2	George Street	11	rw	-7.34	76+8	
11		5	rw	-7.34	109+8	-58.7
12		5	rw	-7.17	122+8	
13		5	rw	-7.20	74+8	
15	Cromwell Street	6	rw	-7.23	78+8	
20		6	rw	-7.29	88+8	-58.6
22		6	rw	-7.14	87+8	
27		11	rw	-7.25	79+8	
28	Suncor Well No.	1A	6.1m	-8.61	6+9	-59.1
29		2A	6.1	-9.50	29+6	-68.3
30		4A	6.1	-9.50	20+7	
31		5A	9.9	-9.58	9+6	-65.1
32		6A	NA	-9.68	6+6	
33	Chenal Ecarte (near Walpole Island)		rw	-7.4	109+9	
34			rw	-7.20	98+9	
35			rw	-7.19	100+9	
36			rw	-7.15	124+9	

* analyses in progress
rw river water
NA not available

O-18 and T values for the Lambton County Fresh Water Aquifer Samples

Sample No.	O-18 (‰)	T (TU) (+6-8)	D (‰
1B	-15.73	6	
2B	-10.18	51	
3B	-13.49	6	
4B	-13.15	6	
5B	-9.58	11	
6B	-9.88	17	
7B	-10.48	19	
8B	-9.14	55	
9B	-11.10	6	-77.0
10B	-15.26	8	-110.6
11B	-14.84	12	
12B	-10.47	33	
13B	-17.14	13	-121.7
14B	-15.22	22	-55.0
15B	-7.45	95	
16B	-10.74	6	
17B	-10.83	18	
18B	-9.12	6	
19B	-8.44	13	
20B	-8.65	8	
21B	-9.88	<6	
22B	-10.68	<6	
23B	-13.54	7	
24B	-7.24	58	
25B	-16.60	<6	
26B	-11.92	<6	
27B	-9.94	<6	
28B	-9.31	<6	
29B	-9.31	<6	
30B	-9.07	<6	
31B	-8.57	<6	
32B	-10.09	<6	
33B	-13.40	17	
34B	-13.37	<6	
35B	-17.42	<6	
36B	-15.16	8	
US1B	-14.78	<6	
US2B	-16.42	23	
US3B	-16.19	<6	
US4B	-12.78	<6	