AN INVESTIGATION OF THE GROUNDWATER ZONE IN FRACTURED SHALE AT A LANDFILL

by

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ABSTRACT

The results of a hydrogeologic investigation at an inactive landfill in Burlington, Ontario are presented in two parts. Part 1 describes water level measurements, rising-head response tests and the distribution of tritium used to characterize groundwater movement in the Queenston Formation, an extensively fractured shale bedrock. Fractures in a vertical rock core are spaced between 5 and 35 cm apart and appear to have developed along horizontal bedding planes. Subhorizontal, slickensided fracture surfaces, also observed in the rock core, suggest the occurrence of soft-sediment deformation shear fractures that pass through the horizontal fractures at many locations in the shale. In outcrop in a quarry adjacent to the landfill, the latter were observed to extend several meters in the horizontal direction.

Groundwater conditions were monitored to a depth of 36 m using 33 conventional piezometers installed in well nests and 5 multilevel devices, each containing at least 10 discrete piezometers connected to 1 m sample intervals in a single borehole. Vertical hydraulic head profiles in the shale are irregular and do not correlate well between monitoring locations. Extreme hydraulic head values occur over narrow zones and differ by as much as 20 m between vertically adjacent piezometers. Marked low values are believed to be caused by major zones of groundwater transmission related to the major subhorizontal fractures.

Bulk hydraulic conductivity values from rising-head response tests range from 2.3×10^{-12} m/s to 1.8×10^{-6} m/s. No trend with depth was apparent below the shallow, weathered bedrock surface which is a zone of high hydraulic conductivi-

ty. Estimates of fracture porosity, generated using hydraulic conductivity values and fracture spacing in core samples as required by the Snow Method, range from 0.0007% to 0.1%.

The distribution of tritium (3 - 51 TU) and tritium-free groundwater is erratic. Levels typical of modern precipitation that occur at the maximum monitoring depth suggest significant vertical hydraulic connection in the shale. However, the absence of tritium at shallower depths suggests that there are zones hydraulically isolated from active groundwater flow in other regions of the fracture network and/or the ground surface. The poor correlation between hydraulic-head profiles, and the erratic distribution of tritium may be related to the arcuate, soft-sediment deformation shear fractures characteristic of the Queenston Formation.

Part 2 describes the inorganic, bulk organic and trace organic constituents in groundwater used to delineate the extent of landfill-derived contamination and estimate contaminant transport. Major ion concentrations give no reliable indication of the zone of contamination and while organic nitrogen, DOC and phenol concentrations are above background levels at least 320 m downgradient of the landfill, they may be influenced by natural organic matter derived from the shale. Three synthetic organic compounds, 1,1,1-trichloroethane (TCA), chlorobenzene (CB) and paradichlorobenzene (PDCB) were found at trace levels in groundwater using down-hole sampling with adsorption/thermal desorption cartridges. Their distributions indicate more conclusively that contamination extends at least to a depth of 35 m and 825 m downgradient of the landfill, the vertical and lateral limits of the groundwater monitoring network. Sorption of TCA, CB and PDCB is expected to be minimal because the total organic carbon content of the shale is < 0.01%. The distance to which they have moved downgradient of the landfill is

consistent with observed biodegradation trends for TCA, CB and PDCB under moderately anaerobic conditions.

At 30 of 35 monitoring locations, groundwater was found to contain tritium and the three chlorinated compounds. Tritium was first input to the hydrogeologic system at high levels beginning in 1953, followed 8 years later by the chlorinated organics which began to be input when the landfill began operation in 1961. At the remaining 5 monitoring locations, the chlorinated organic compounds were found in non-tritiated groundwater which suggests a higher relative loss of tritium by diffusion to the rock matrix. Estimates of effective diffusion coefficients for the shale were used to show the effect of such a loss in a model which represents transport in a single fracture. Using De values of 2.4×10^{-9} cm^2/s and 8.9×10^{-10} cm^2/s for tritium and TCA, respectively, the maximum travel distance for these two parameters after 25 years is 200 m less for tritium than for the TCA.

A mass balance of water that has infiltrated the landfill since its completion and groundwater contained in the shale indicates that a zone of contamination should extend at least 0.8 km downgradient of the landfill. This is based on the assumption that the water emanating from the refuse and moving through the fractures is in equilibrium with that in the matrix and occupies the total rock porosity, essentially equal to a matrix porosity estimated to be about 5%. Using a fracture porosity of 0.1%, the zone of contamination should extend all the way to Lake Ontario. The distance to which TCA was found downgradient of the landfill produces a minimum transport velocity through the shale of about 35 m/yr. Values estimated using the Darcy equation and equivalent porous-medium concept are generally at least one order of magnitude less than this. Combined in this way, groundwater flow parameters therefore do not provide a reliable basis

for predicting the lateral migration rate of a zone of landfill-derived groundwater contamination in the fractured shale.

ACKNOWLEDGEMENTS

It is with sincere gratitude that I acknowledge the guidance and counsel of Dr. John A. Cherry throughout every aspect of this research. I would also like to acknowledge the contributions of Drs. R.W. Gillham, J.F. Barker and D.J. Russell through discussions and a review of the manuscript.

Funding for this research was provided by an NSERC Grant to J.A. Cherry in 1982 and 1983 and by the Province of Ontario Lottery Fund in 1984. The Regional Municipality of Halton and National Sewer Pipe Limited, owner of the land adjacent to the Bayview Park landfill, contributed directly to drilling costs for the installation of multilevel devices in 1982. Access for drilling and groundwater monitoring was also provided by National Sewer Pipe Limited. An elevation survey of the multilevel devices was conducted by the City of Burlington.

Dr. J.F. Pankow is responsible for the development of the down-hole ATD sampling device. Trace organic analyses were conducted in his laboratory as part of a co-operative research project between the Oregon Graduate Centre and the Universtiy of Waterloo. Dr. Pankow's contributions during field sampling and data interpretation in addition to his reviews of the manuscript were most helpful.

In 1982, enriched tritium analyses were provided by Dr. Robert Buddemeir of the Lawrence Livermore Laboratory at the University of California. Subsequent tritium analyses and all of the oxygen 18 analyses were provided by the Environmental Isotope Laboratory of the University of Waterloo.

I would like to thank several people for their invaluable expertise in the field. Paul Johnson co-ordinated the construction, installation and testing of multilevel devices placed in boreholes drilled by Mike Pollice of All-Terrain Drilling Limited. Robert Ingleton devised a system to seal these devices and participated in piezometer development, groundwater sampling and response testing. I am particularly indebted to Robert for his resourcefulness and amicable assistance under even the most inclement field conditions.

Of all the graduate students who have shared the progress of my research, I would especially like to thank Glenn Reynolds, Carol Ptacek and Ronald Wall for numerous consultations and impromptu discussions. They have become very special friends.

Finally, I would like to dedicate this thesis to my parents, whose love and trust have helped me reach this important goal.

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Part 1

GROUNDWATER FLOW AND TRITIUM OCCURRENCE

Chapter I

INTRODUCTION

As new landfills continue to be developed and as leachate continues to be produced from old landfills, the need to acquire a better understanding of the transport of landfill-derived contaminants in groundwater persists. Investigations of the influence of groundwater flow on contaminant migration, while extensive, have been mainly focused on sand and gravel aquifers. A limited knowledge of flow in fractures has hindered research in rock despite the great potential for rapid and extensive contaminant transport in this type of environment. Large groundwater velocities and small fracture surface areas can lead to relatively high contaminant mobility and reduced influences of chemical and physical attenuation processes.

In the Niagara Region of Southern Ontario, one of the major industrial regions in Canada, many active and inactive landfills and other waste disposal facilities are situated on fractured shale. The movement of contaminants introduced to groundwater by these sites has for some time, not been considered great. Detailed investigations of groundwater contamination trends are now necessary to evaluate this claim.

The Bayview Park landfill, reported on in this paper, has features typical of many waste disposal sites found in the Niagara Region. It is located in Burlington, about 3.5 kilometers north of Lake Ontario (Figure 1). Between 1961 and 1974, waste from the surrounding community was deposited in shale quarry excavations at this site. The waste was largely municipal in origin, but because the

landfill was one of only two major waste disposal sites in the region, it is reasonable to expect that it also received some industrial waste. When landfilling was completed, the refuse was covered, graded to be nearly flat, and then grassed.

The investigations at the Bayview Park site began in 1982 for the purpose of evaluating the use of conventional approaches for determining the potential for large-scale migration of landfill-derived contaminants in fractured shale. The results are presented in two parts. The objective of Part 1 was to conduct a hydrogeological characterization of groundwater flow through the shale, based primarily on equivalent porous medium methods and concepts. Hydraulic conditions and the distribution of tritium, derived from detailed vertical groundwater monitoring provided by conventional piezometers and multilevel devices, are described. Tritium, a radioisotope released to the atmosphere during thermonuclear testing beginning in 1953, served as a tracer of young groundwater. The objective of Part 2 was to establish the distributions of landfill-derived contaminants in groundwater in the shale and to use these distributions for comparison with estimates of potential contaminant transport based on the hydrogeological characterization of Part 1.

The Bayview Park landfill occupies approximately 18 ha and sits directly on the shale of the Queenston Formation. In terms of the regional geology of Southern Ontario, the Queenston Formation occupies the flank of the Niagara Escarpment that slopes downward to the shores of Lake Ontario (Figure 2). It is believed to be the distal fine-grained element of the Queenston Delta deposited during Late Ordovician time (Russell and Harman, 1985). In the vicinity of the study site it is continuous to a depth of 135 m and is underlain by dark grey shales of the Georgian Bay Formation.

The rock of the Queenston Formation is commonly referred to as a "shale", but is more accurately described as a red, silty mudstone (Russell and Harman, 1985). The characteristic red colour of the shale, imparted by a small percentage of hematite, is occasionally interrupted by grey-green bands. These bands contain relatively higher amounts of calcite and were found to be less than 0.2 m in thickness. The Queenston Formation is overlain by the Halton Till which has a thickness of only a few meters or less over most of the study site.

From an examination of rock core, horizontal fracturing in the top 47 m of the Queenston Formation is quite extensive. Fracture spacings range from 5 to 35 cm. The fractures appear to have developed along horizontal bedding planes but do not necessarily appear to be coincident with changes in colour. The permeability attributable to the fractures is orders of magnitude greater than that attributable to the matrix, so groundwater flow can be expected to occur largely through the fracture network between relatively impermeable blocks of rock matrix.

Chapter II

STUDY METHODS

The groundwater monitoring network at the Bayview Park site consists of 33 conventional piezometers installed during 1979 and 1980 by Morrison Beatty Limited and 5 multilevel devices installed in 1982 as part of this investigation. A schematic representation of these two types of devices is shown in Figure 3. In total, they provided 84 sampling points in the shale.

The conventional piezometers, denoted by the prefix "OW" (Figure 4), were constructed of 3.17 or 3.81 cm OD PVC pipe and were placed in individual 12.70 cm OD boreholes. Boreholes, commonly grouped in nests of 3 and 4, were drilled to a maximum depth of 28 m using either the hollow-stem auger or mud rotary methods. The bottom 1 - 3 m of the PVC pipe, slotted to serve as a screen, was surrounded by a sand and gravel filter and then sealed from the rest of the borehole using a bentonite plug.

Multilevel devices were recently developed for use in fractured rock and their design allows discrete fractures or sets of fractures to be isolated anywhere along a borehole (Cherry and Johnson, 1982). Sample intervals are separated from one another by chemical packers which expand to press against the borehole wall when the multilevel device is in place. The expansion is activated when the packer material reacts with water pumped into the centre stock for this purpose. A sample port accessing each interval is attached to a piezometer tube that leads to the surface to facilitate water level measurements and groundwater sample collection. A detailed discussion of the construction and installation of these multilevel devices is given by Cherry et al. (1985).

To maximize groundwater monitoring along boreholes to be drilled at this site, multilevel devices were assembled to isolate several vertical sampling intervals. These intervals were long enough to ensure intersection with several fractures based on the high frequency of horizontal fractures observed in a 47 m vertical cored hole drilled beneath the landfill. Boreholes for the multilevel devices were drilled using an air-tricone method which does not provide a log of precise fracture locations but proceeds twice as quickly as conventional coring methods and significantly reduces the amount of foreign water introduced to the formation.

Boreholes produced by the air-tricone method were 11.43 cm OD and ranged in depth from 37 to 46 m. The multilevel devices installed in these boreholes, denoted by the prefix "WAT" (Figure 4), were constructed of nominal 7.62 cm PVC casing which contained 1.27 or 1.59 cm OD piezometer tubes. Sampling intervals in these devices average 1.1 m in length. They were generally spaced 60 cm apart and isolated at the top and bottom with packers 46 cm in length. As most of these devices contain 12 sampling intervals, between 23 and 45% of the total borehole length was monitored.

Following installation, several standing volumes of water were pumped from all monitoring devices. Single standing volumes range from less than 50 mls to almost 6 L for piezometer tubes in multilevel devices and from about 1 to 20 L for conventional piezometers. The annulus between the PVC casing and the borehole wall corresponding to each multilevel sample interval contains about 4 L of water.

During the period of piezometer development and initial hydraulic testing, the water levels in many of the piezometers in each multilevel device repeatedly equilibrated to the same position. This suggested hydraulic connection between

the inside of the PVC casing and the individual sample intervals. The casing of each multilevel device was then filled with a thick bentonite slurry to seal leaks and prevent the influence of hydraulic "short-circuiting".

The differences in equilibrium water levels between most sampling intervals became distinct following bentonite installation. At major leakage points however, bentonite that moved into sample sections caused clogging of the sample port. As a result, 7 piezometers, of a total of 58 contained in all multilevel devices, were no longer useful for hydraulic testing.

Sixteen conventional rising-head response tests were performed to determine bulk hydraulic conductivity values for the shale. Tests were conducted in multilevel piezometer tubes at depths between 2 and 32 m below the bedrock surface. For each response test a triple tube pump, of the type described by Robin et al. (1982), was used to lower the water level between 10 and 15 m below equilibrium position. This is equivalent to a maximum volume of 1.1 litres in a 0.95 cm ID piezometer tube and 1.9 litres in a 1.27 cm ID piezometer tube.

Following groundwater evacuation, the triple tube pump was immediately withdrawn from the piezometer tube. The recovery of the water level toward its equilibrium position was monitored with time, in general until it had returned to within at least 50% of the initial level. As part of the rising-head response test procedure, water levels in sampling intervals above and below the test interval were recorded both before and after the evacuation of groundwater.

To determine the distribution of tritium in groundwater, between ten and twenty groundwater samples were collected annually between 1982 and 1984 from a total of seventeen conventional piezometers and nine multilevel piezometer tubes. Each year at least six monitoring locations were repeat-sampled to observe trends with time. Tritium data obtained by Morrison Beatty Limited (1980, 1981) was also used for this purpose.

In 1982, samples for enriched tritium analysis were collected from conventional piezometers while in subsequent years, samples were collected from both conventional piezometer nests and multilevel devices. In 1983, six of the samples were also analyzed for oxygen 18.

Water levels in all of the monitoring devices were recorded several times a year through all phases of the research. Measurements were made using a water level tape consisting of an electric water-sensitive probe attached to the end of a very narrow, calibrated coaxial cable (Roctest Model). This water level tape allows easy access to piezometer tubes as small as 0.95 cm ID, and provides water level measurements accurate to within 1 cm.

Chapter III

RESULTS AND DISCUSSION

3.1 Hydraulic Head

Equilibrium water levels for all piezometers, except those clogged with bentonite, were used to produce vertical profiles of hydraulic head in the shale (Figure 5). Equilibrium levels were established during 3 months of detailed monitoring and confirmed by the recovery of water levels to these positions following repeated hydraulic testing and groundwater sampling. They are plotted at the midpoint elevation of each sample interval.

Most of the vertical profiles are very irregular, exhibiting some large differences in hydraulic head over very small changes in depth. Vertical gradients range from 0.09 to 8.45 in the upward direction, while downward gradients are commonly over 1.0, but may reach as high as 8.70. At WAT 2, the gradual decrease in hydraulic head found in the upper portion of the rock is interrupted at the 140 masl elevation by a drop of over 12 m. Similar extreme changes in hydraulic head can be seen in profiles at WAT 4 and WAT 7. At WAT 4, the water level centred on the 100 masl elevation is 20 m below water levels for adjacent sampling intervals. At WAT 7, there are two vertical zones with water levels that deviate almost 3 meters from the general downward trend indicated by other water levels in the multilevel device. Absolute shifts in hydraulic head are smaller for the remaining multilevel devices and conventional well nests, but still produce variable profiles.

In most cases, extreme high and low hydraulic-head values occur over only 1 - 2 m vertical zones and do not correlate well between monitoring devices. The major changes in hydraulic head at WAT 4 and WAT 7 are not identifiable in vertical profiles for nearby monitoring devices. Distinct differences exist between profiles at WAT 3, WAT 4 and WAT 5, each separated by a distance of about 50 m. Hydraulic-head values at WAT 3 occur consistently between 120 - 130 masl, while a significant number of those found at WAT 4 are less than 120 masl. At WAT 5, values show the least amount of variability, and occur between 123 and 127 masl. As a result of these variations, hydraulic-head values are sometimes highest at WAT 5, suggesting local groundwater flow opposite to the regional topogaphic slope.

On a regional scale, using a broad contour interval, the hydraulic-head distribution in the shale shows a general trend (Figure 5). The study site appears to be on the edge of a recharge zone dominated by the highly permeable caprock of the Niagara Escarpment (Figure 2). Downward gradients predominate in the shale to some depth at which flowlines are believed to turn upward to discharge to the bottom of Lake Ontario.

Hydraulic-head values are greater than 130 masl immediately beneath the landfill and show a maximum decline of 27 m toward the south. The average horizontal hydraulic gradient between OW 15 and OW 13 is 0.054. The water table across the study site is situated in the till, generally within 1.5 m of ground surface. There are insufficient piezometers in the landfill to define a water table mound throughout the landfill.

The zones of extremely low hydraulic head in vertical profiles at WAT 2, 4 and 7 are believed to be major zones of groundwater transmission in the shale. These zones may be related to fractures that have developed in the Queenston

Formation along large, soft-sediment deformation shears due to stress release. Russell and Harman (1985) have described these fractures as curved partings that change dip with depth and range in orientation from horizontal to vertical. A vertical core through the Queenston Formation intersected several subhorizontal, slickensided surfaces with which Russell and Harman (1985) have associated these soft-sediment deformation shear fractures.

Evidence of the occurrence of these fractures in the Queenston Formation was much more obvious along quarry faces and outcrop surfaces immediately east of the landfill (Figure 4). Here they were traced over several meters in the horizontal direction. In another quarry about 50 km north of the Bayview Park site, groundwater movement has been observed along their length (D.J. Russell, personal communication). The limited extent and changing orientation of these soft-sediment deformation shear fractures appear consistent with the restricted lateral extent of zones of marked low hydraulic head in the shale.

3.2 Hydraulic Conductivity

Values of bulk hydraulic conductivity for the shale were determined using the standard Basic Time Lag Method described by Hvorslev (1951). The basic time lag, T_0, for each rising-head response test was taken from a semilog plot of water-level recovery versus time (Figure 6). Values of T_0 correspond to a head-equalization ratio of 0.37 or 63% water level recovery. If a response test was terminated before this point, T_0 was determined from an equation of the recovery line drawn through early time data.

The basic time lag values ranged from less than an hour to almost 200 days, although most were between 100 and 600 hours. Despite this range, most of the recovery plots were linear as predicted by Hvorslev in his original development of

the method for unconsolidated porous media. Six did show some instantaneous recovery at the beginning of the response test as residual water in the triple tube pump escaped into the piezometer as the pump was withdrawn. This small influence on water level recovery was removed during data analysis by using the first-recorded water level following evacuation as the maximum drawdown reference point.

The bulk hydraulic conductivity values range over six orders of magnitude with a maximum of 1.8×10^{-6} m/s and a minimum of 2.7×10^{-12} m/s (Table 1). The faster response times may represent a sample interval which intersects several fractures or a few large fractures while the slower response times may represent intervals intersecting very few or small fractures.

No trend is evident between values of bulk hydraulic conductivity and depth (Figure 7). The maximum value of hydraulic conductivity was measured at about 4 m below ground, coincident with a zone of weathered shale observed at the overburden/bedock contact. A value of 1.4×10^{-8} m/s, found at a depth of approximately 21 m, indicates that relatively high values are not restricted to shallow depth, however.

Although the sample intervals registering extremely low water levels are thought to represent zones of relatively high permeability, this was not confirmed by response test results. Bulk hydraulic conductivity values for these particular piezometers were on the order of 10^{-10} m/s or less. Local zones of high permeability positioned near a sample interval, rather than directly intersecting it, may influence hydraulic head. However, hydraulic conductivity values may not represent this permeability because rising-head response test results reflect conditions only in the immediate vicinity of the borehole.

Bulk hydraulic conductivity values generated during this investigation are, in general, three orders of magnitude lower than those reported elsewhere for the Queenston Formation. Most values cited by Morrison Beatty Limited (1980) from response tests in conventional piezometers at the Bayview Park site are on the order of 10^{-8} to 10^{-7} m/s. Gartner Lee Associates generated similar values during an investigation of groundwater movement in the Queenston Formation, 2 km east of the Bayview Park site. In both of these studies, decreasing bulk hydraulic conductivity was observed with depth.

The smearing of borehole walls during drilling is a possible explanation for the apparent low hydraulic conductivity values calculated for the Bayview Park site. However, the boreholes for the multilevel devices were drilled using an air-tricone drilling method, which uses only minor amounts of water. This drilling method appears to have less potential for borehole smearing than the augering method used to install most of the conventional piezometers.

Fracture porosity for the shale was estimated using the method developed by Snow (1968) for a parallel set of planar joints. This method is particularly amenable for use in the present study due to the extensive and often regular horizontal fracturing observed in the rock core. The Snow equation was rearranged to solve for insitu fracture aperture and then fracture porosity per unit volume of rock using fracture frequency and incorporating the fundamental relationship between intrinsic permeability and hydraulic conductivity. For each value of bulk hydraulic conductivity, estimates of fracture frequency were taken over vertical intervals in the rock core corresponding to the depths of sample intervals used in rising-head response tests.

Estimates of fracture aperture range from 1 to 50 μm and correspond to fracture porosities ranging from 0.0007% to 0.1% (Table 1). The maximum frac-

ture porosity was calculated for the zone of weathered shale that exists at the bedrock surface. Because hydraulic conductivity values are generally much lower than those in this shallow zone, fracture porosities at the lower end of the range are probably more representative of the shale. Fracture porosity values will be used in Part 2 to estimate groundwater velocities from the Darcy relation.

3.3 Tritium Distribution

Tritium was used to identify zones of greatest groundwater movement in the shale. Tritium is a non-chemically reactive radioisotope of hydrogen with a halflife of 12.3 years. It is incorporated into the water molecule in the atmosphere and introduced to the terrestrial water cycle by precipitation.

Prior to 1952, naturally-produced tritium levels in precipitation were between 5 and 20 TU so that groundwater of this age would currently contain less than 3 TU (Payne, 1972). Between 1952 and 1963, large-scale testing of thermonuclear bombs caused average monthly tritium levels in precipitation to rise to several hundred TU, so that even accounting for radioactive decay groundwater recharged since this time contains tritium at levels significantly greater than 3 TU. The occurrence of tritium can therefore be used to trace this younger groundwater in the shale.

Tritium values in groundwater are reported in tritium units (TU), where a tritium unit is defined as 1 tritium atom in 10^{18} atoms of hydrogen (Table 2). The analytical precision associated with each value represents a counting error equivalent to ±8 TU for samples analyzed during 1980 and 1981 and ±2 TU for the enriched tritium analysis done during subsequent years.

The most recent tritium values do not show any distinct depth in the shale below which groundwater can be considered "prebomb" due to the absence of tri-

tium (Figure 8). Low and high tritium values are found throughout the shale at varying depths. At WAT 3 and WAT 7, tritiated water is found at depths greater than 35 m, while at the same depth at WAT 4 virtually no tritium is found. Tritium values increase with depth at some locations, a trend opposite to expectations. Low values at shallow depth indicate zones that are hydraulically isolated from infiltrating rainwater as well as groundwater in other parts of the rock. Beneath these zones higher values can occur if there is connection to the ground surface or to another zone transmitting modern groundwater.

The oxygen 18 content in groundwater at six monitoring locations was also used to investigate groundwater movement through the shale. All values are approximately -10%, equivalent to the annual mean concentration found in precipitation currently falling in Southern Ontario. Occurring consistently at this level throughout the shale, the oxygen 18 results indicate no evidence of very old groundwater originating under climatic conditions different than those of the present.

The occurrence of tritium at depths as great as 35 m in the shale indicates that vertical movement of groundwater is not inhibited by the primarily horizontal orientation of fractures found in the rock core. Evidence of vertical fracture connection was not apparent during the rising-head response tests however, as groundwater evacuation from test intervals did not cause water level changes in sample intervals above and below.

The soft-sediment deformation shear fractures in the Queenston Formation, observed in outcrop and tentatively identified in rock core from beneath the study site, may facilitate the vertical movement of groundwater. From the description of these features given above, it is unlikely that they would be oriented to hydraulically connect two sample intervals. However, evidence suggests

that they may occur throughout the shale, changing in orientation from horizontal to vertical and extending over several meters.

Chapter IV

SUMMARY AND CONCLUSIONS

The hydraulic head distribution in the shale is very irregular. Equilibrium water levels can change by as much as several meters over a 2 m change in depth. Marked low values of hydraulic head may indicate the presence of major zones of groundwater transmission in the shale. These zones do not correlate between monitoring locations and therefore appear to have a restricted lateral extent. Bulk hydraulic conductivity values for the shale range from 2.3×10^{-12} to 1.8×10^{-6} m/s, reflecting the variability in the fracture network over sample intervals of regular length. Hydraulic conductivity values do not show any distinct trend with depth, except for particularly high values that are believed to be related to a weathered zone in the top few meters of the bedrock. Estimates of fracture porosity range from 0.0007% to 0.1%.

The distribution of tritium in groundwater did not exhibit any consistent spatial trends. Levels greater than 3 TU, representing groundwater input to the system since 1953, were found at various depths in the shale as great as 35 m. Oxygen 18 values typical of modern precipitation were also found throughout the shale. Tritium levels of less than 3 TU, representing pre-1953 groundwater, were found at shallower depths, however. This erratic distribution of values indicates some degree of vertical fracture connection in the shale between which certain zones can still remain hydraulically isolated.

The irregular and often large changes in hydraulic head in conjunction with the wide range of bulk hydraulic conductivity values and erratic tritium distribu-

tion indicate a very complex flow system in the shale. A distinct horizontal fracture network exists for groundwater movement with fractures spaced between 5 and 35 cm apart. Vertical fracture connection, suggested by the distribution of environmental isotopes, was not in evidence during hydraulic testing. However, downward movement of groundwater may be partly facilitated by soft-sediment deformation shear fractures. These features were observed on quarry faces near the study site and have been associated with subhorizontal, slickensided surfaces which were identified in the rock core from beneath the study site.

Chapter V

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Chapter VI

FIGURES

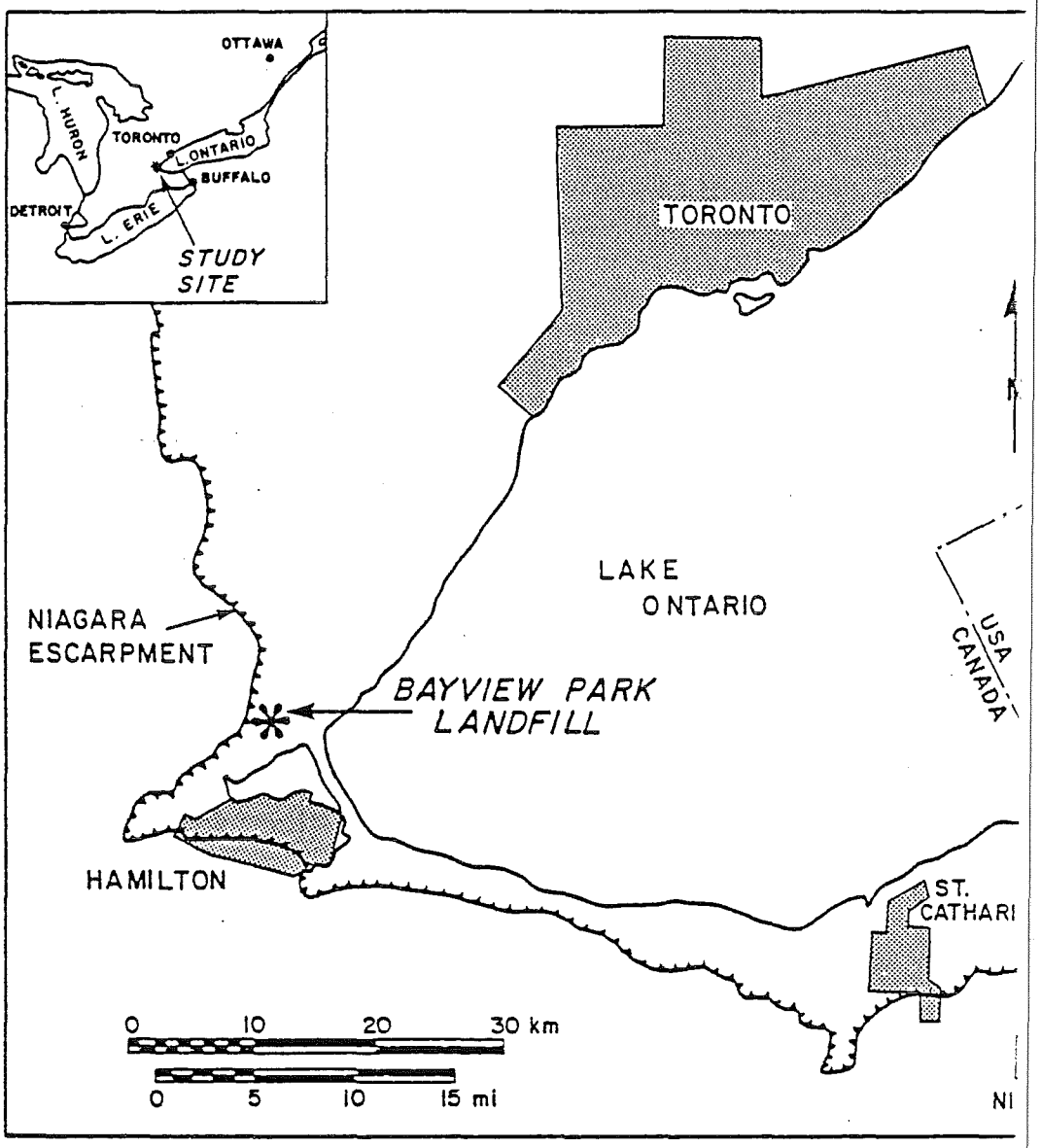


Figure 1: Study site location.

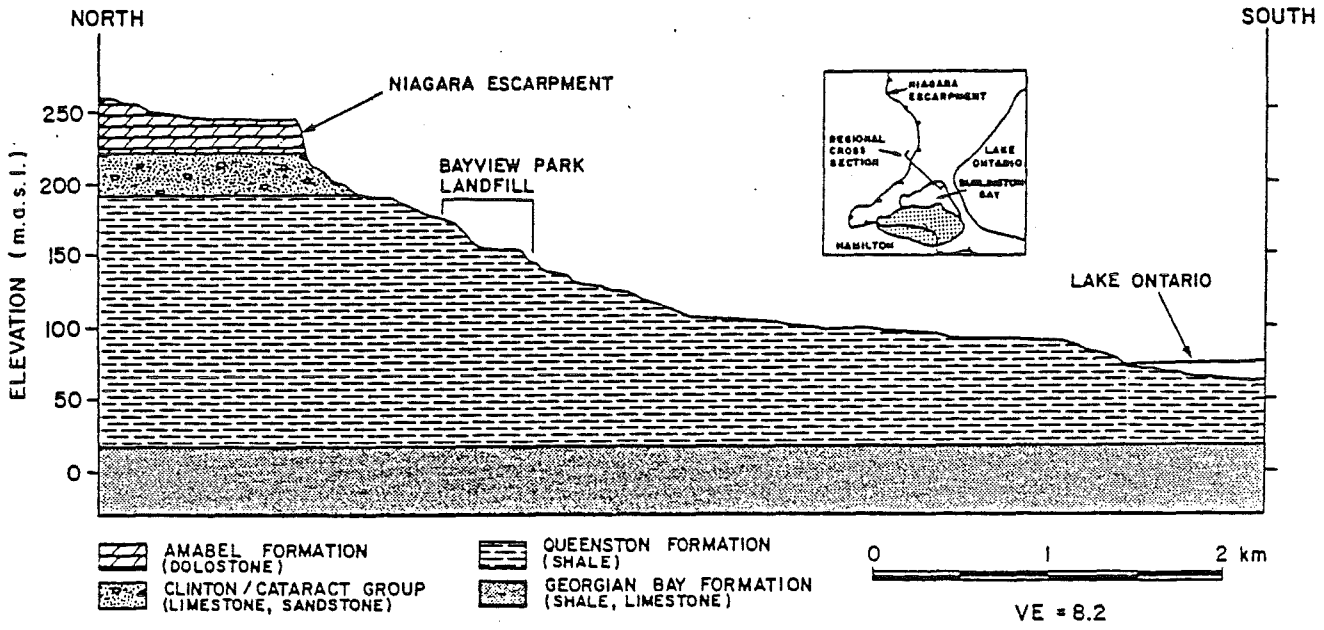


Figure 2: Longitudinal geological cross-section along the main direction of groundwater flow between the Niagara Escarpment and Lake Ontario.

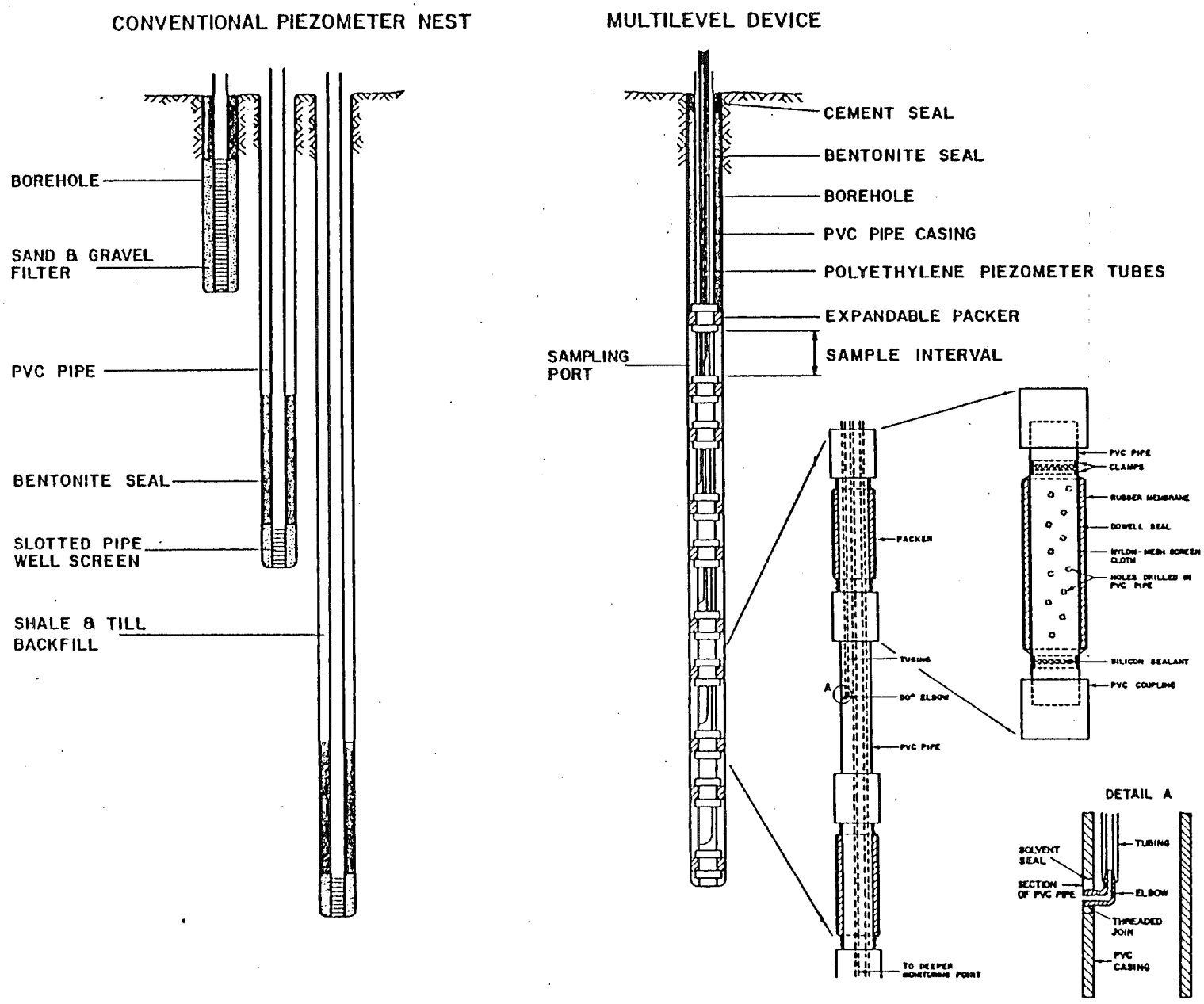


Figure 3: Conventional piezometer nests and multilevel devices used

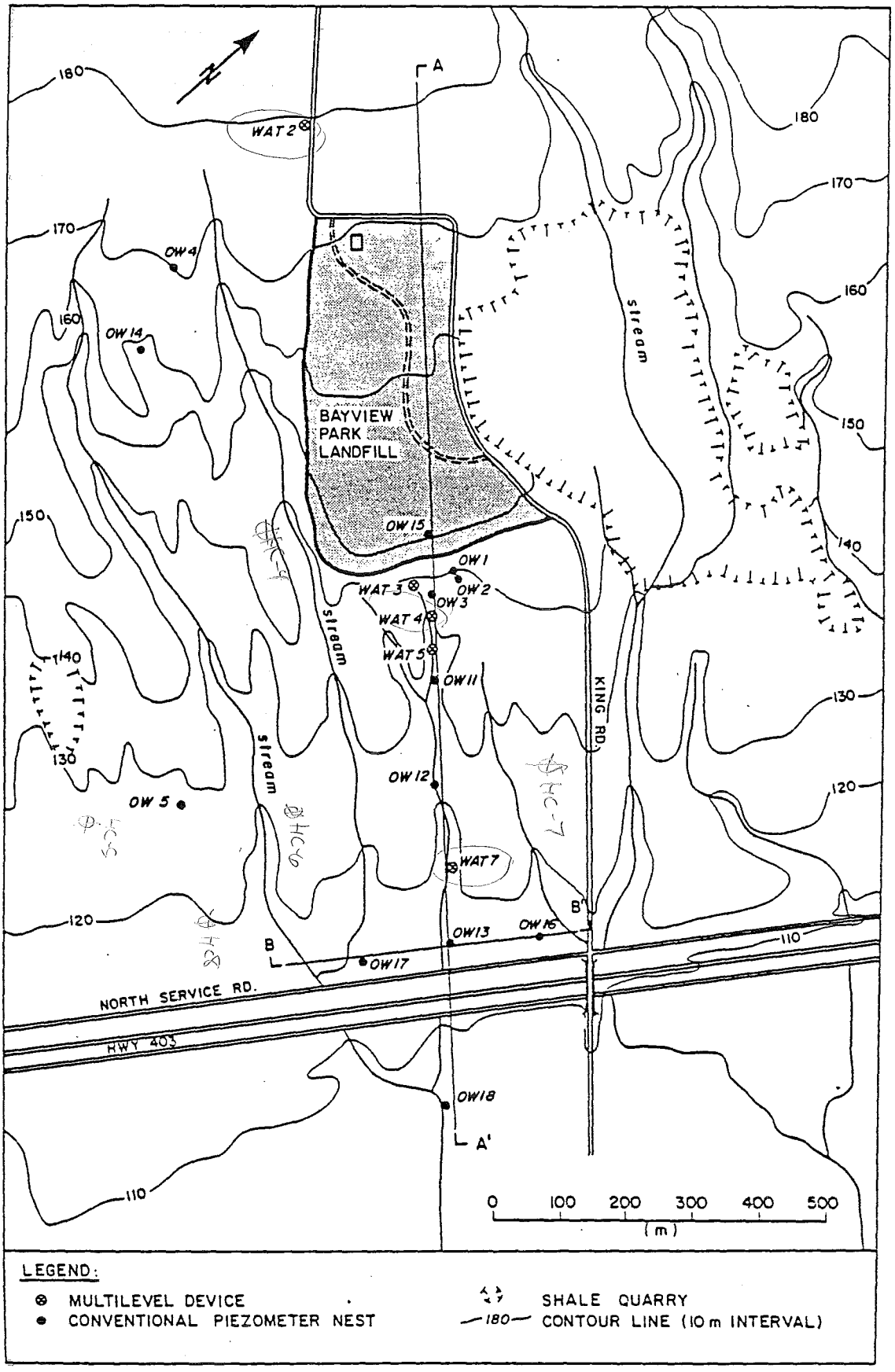


Figure 4: Study site topography and location of the groundwater

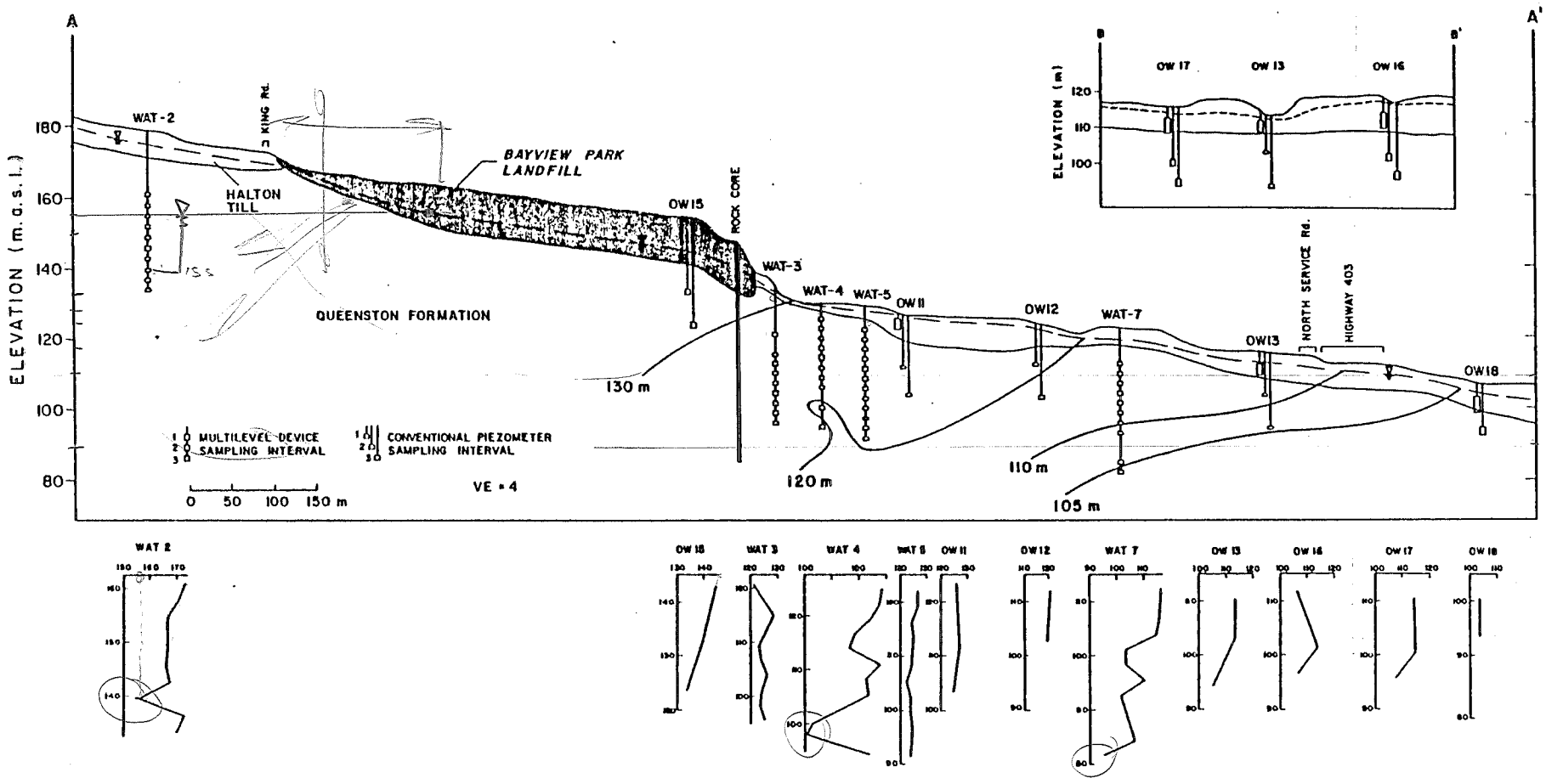
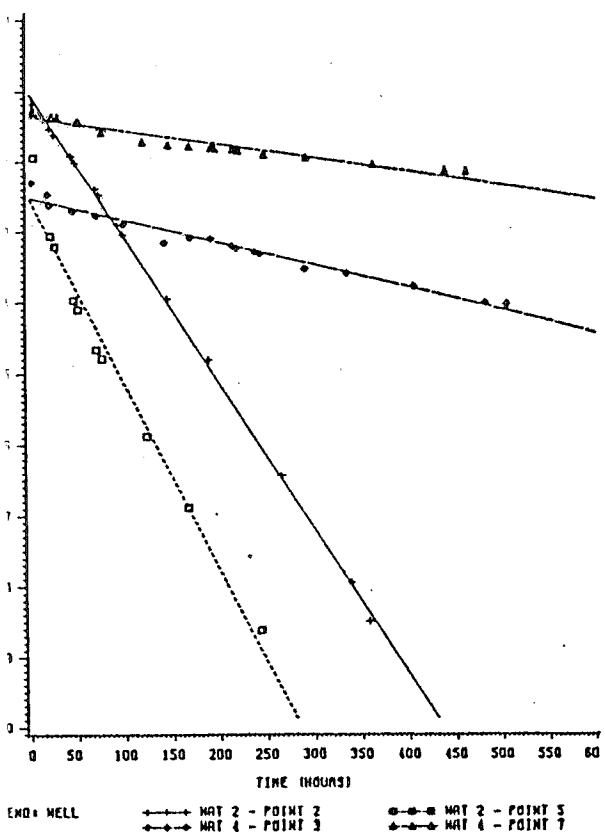
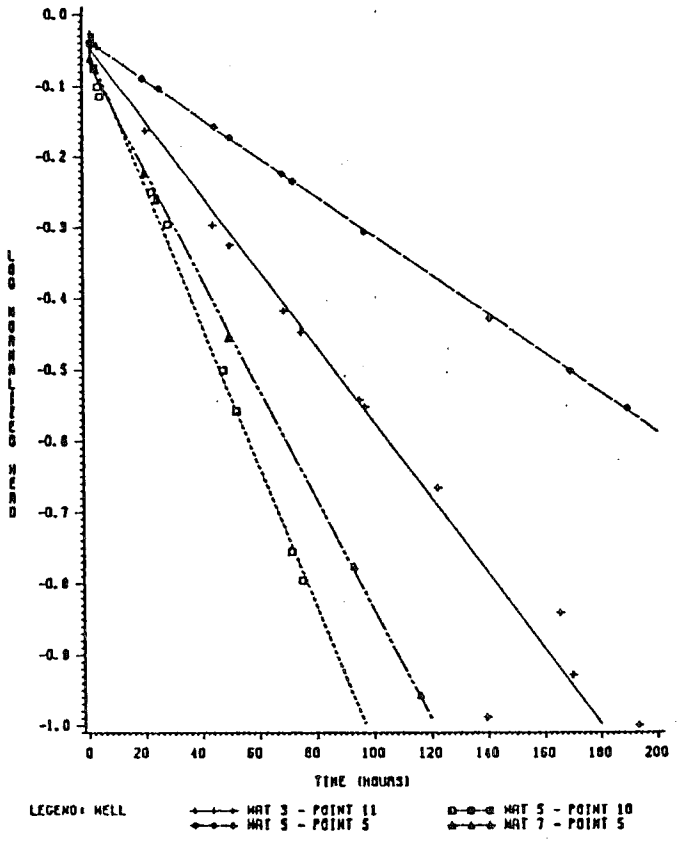


Figure 5: Hydraulic head distribution in the shale.





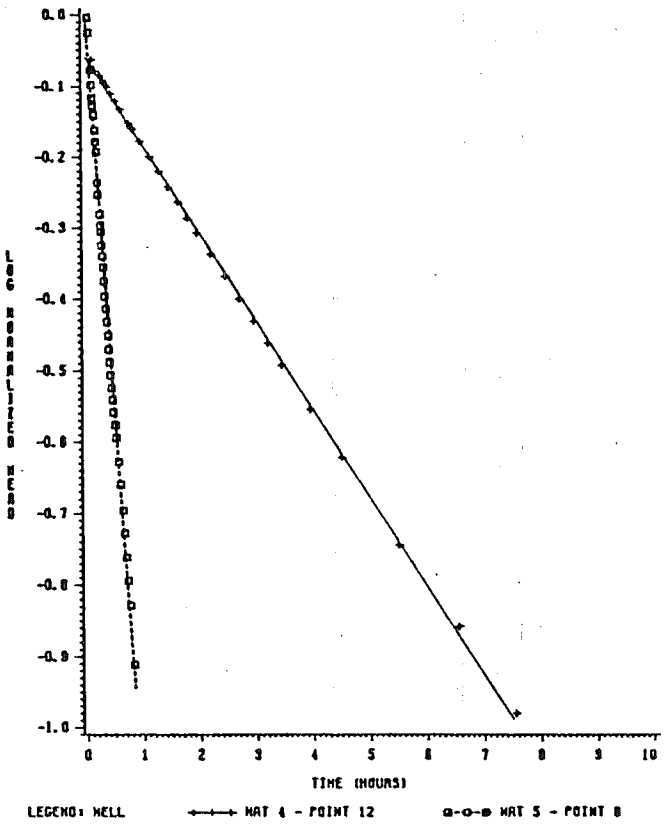


Figure 6: Response test recovery curves for graphical determination of basic time lag, T_0 .

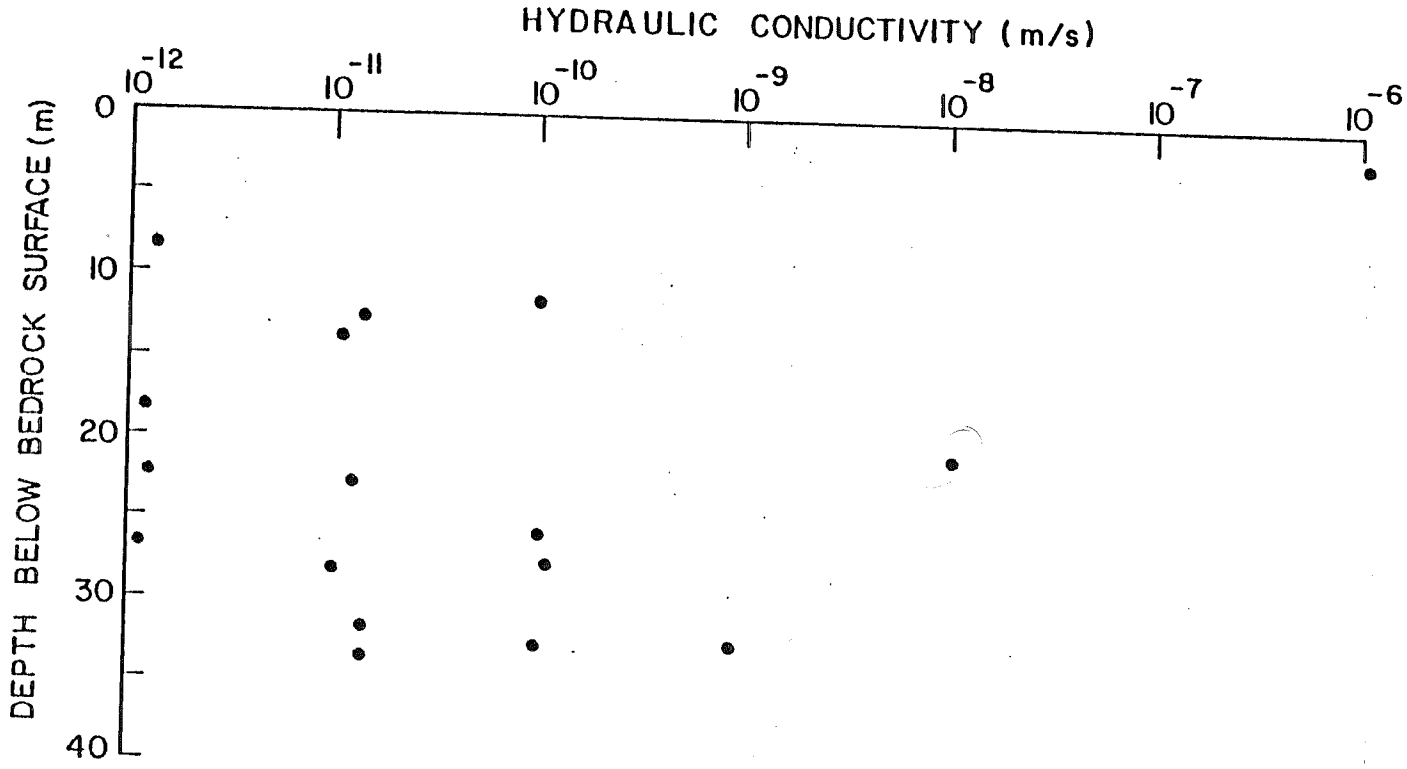


Figure 7: Bulk hydraulic conductivity values versus depth.

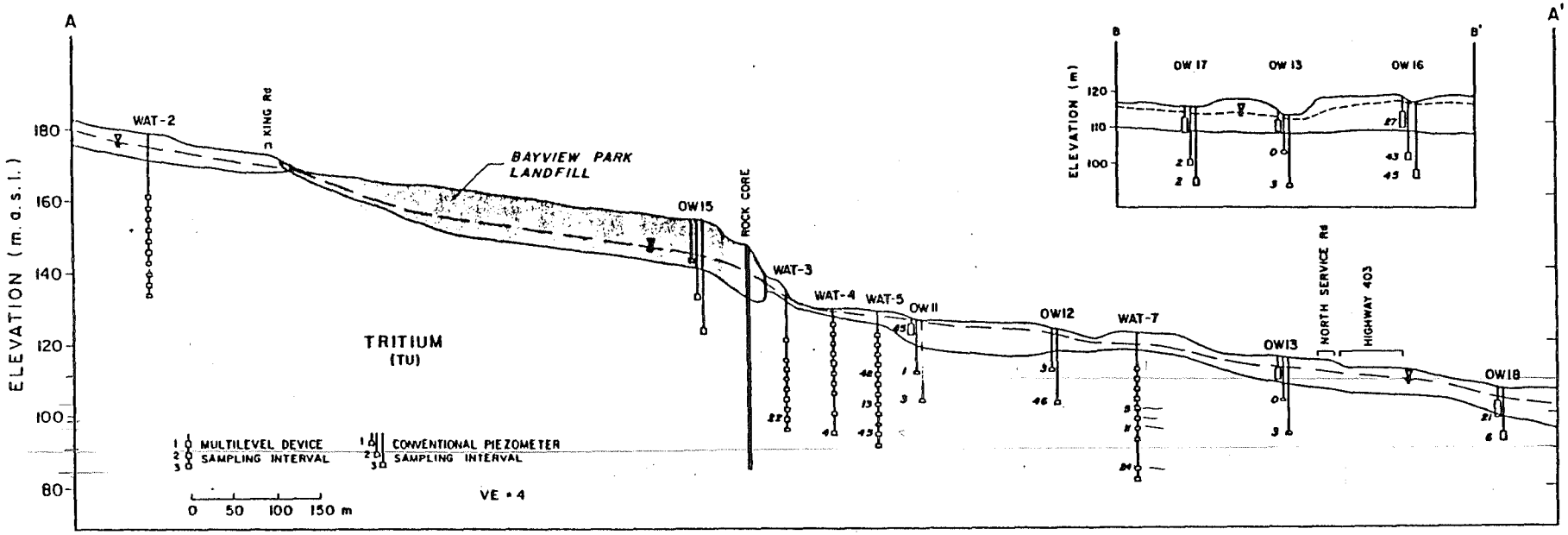


Figure 8: Distribution of tritium in groundwater, 1983,1984.

Chapter VII

TABLES

Monitoring Location	Bulk Hydraulic Conductivity (m/s)	Depth Below Bedrock Surface (m)	Fracture Porosity (%)
		E60	
WAT 2 - 2	2.0×10^{-11}	13.8	0.002
WAT 2 - 5	3.0×10^{-11}	22.7	0.001
WAT 2 - 8	4.0×10^{-11}	31.5	0.0009
135 WAT 3 - 9	1.3×10^{-11}	28.0 107	0.001
WAT 3 - 11	4.0×10^{-11}	33.3 102	0.001
129 WAT 4 - 3	3.5×10^{-12}	8.3 121	0.0007
WAT 4 - 7	2.7×10^{-12}	18.2 111	0.0009
WAT 4 - 10	2.3×10^{-12}	26.9 102	0.0009
WAT 4 - 12	9.8×10^{-10}	32.2 97	0.003
125 WAT 5 - 1	1.8×10^{-6} 10^{-4}	2.1 123	0.1
WAT 5 - 5	3.7×10^{-11}	12.6 112	0.003
WAT 5 - 8	1.4×10^{-8}	20.6 105	0.02
WAT 5 - 10	1.4×10^{-10}	25.8 99	0.001
118 WAT 7 - 5	1.1×10^{-10}	11.4 107	0.004
WAT 7 - 9	3.1×10^{-12}	22.1 96	0.001
WAT 7 - 11	2.1×10^{-10}	27.4 91	0.003

Table 1: Values of bulk hydraulic conductivity and fracture porosity for the Queenston Formation.

MONITORING LOCATION	TRITIUM (TU) Jan,1980	Jul,1981	Jul,1982	Nov,1983	May,1984
OW 1 - 2	44±8	54±8	41.5±6.1		51±2
OW 1 - 4	18±8		10.4±1.9		1±2
OW 11 - 1	85±8		74.7±3.7	45±2	
OW 11 - 2			4.9±2.2	1±2	
OW 11 - 3	20±8	9±8	6.5±2.1	3±2	
OW 12 - 2			3.3±4.9	3±2	
OW 12 - 3		15±8	39.1±2.5	46±2	
OW 13 - 1	40±8				
OW 13 - 2				0±2	
OW 13 - 3	12±8	-2±8		3±2	
OW 16 - 1				ND	27±2
OW 16 - 2				50±2	43±2
OW 16 - 3				42±2	45±2
OW 17 - 2				2±2	
OW 17 - 3				2±2	
OW 18 - 1				21±2	
OW 18 - 2				6±2	
WAT 3 - 11				20±2	22±2
WAT 4 - 12				4±2	
WAT 5 - 3				4±2	
WAT 5 - 5					48±2
WAT 5 - 8				23±2	13±2
WAT 5 - 10				20±2	45±2
WAT 7 - 5				17±2	5±2
WAT 7 - 7					11±2
WAT 7 - 11					24±2

Table 2: Tritium levels in groundwater, 1980-1984.

Part 2

CONTAMINANT DISTRIBUTION AND MIGRATION

Chapter VIII
INTRODUCTION

In Part 1 of this study, hydraulic head measurements, rising-head response tests, the distribution of tritium and fracture trends were used to describe hydrogeologic conditions in shale of the Queenston Formation. Based on irregular vertical profiles of hydraulic head, on hydraulic conductivity values that range from 2.3×10^{-12} to 1.8×10^{-6} m/s and on the erratic distribution of tritium, it was concluded that the groundwater flow system is very complex. There appears to be potential for contaminant migration downward through major fractures and laterally through smaller but more numerous horizontal fractures.

In this second part of the study, the chemistry of groundwater in the shale was investigated to determine the extent of landfill-derived contaminant migration. The objective was to evaluate the consistency between the observed trends in groundwater contamination and the physical hydrogeologic conditions described in Part 1. Groundwater contamination was mapped using conventional inorganic and bulk organic parameters as well as three synthetic organic compounds. Contaminant transport rates based on the travel distances of these groundwater constituents were compared to estimates of contaminant movement generated by the Darcy relation.

Chapter IX

STUDY METHODS

The groundwater monitoring network at the Bayview Park landfill consists of conventional piezometers, installed in individual boreholes grouped in nests, and multilevel devices designed to isolate several discrete vertical intervals in a single borehole. Although most of these monitoring devices are located within 600 m downgradient of the landfill a few are situated at a maximum distance of 825 m. Some are also located away from main groundwater pathways originating near the landfill (Figure 9).

Groundwater samples for analyses of inorganic constituents and bulk organic constituents such as dissolved organic carbon (DOC), organic nitrogen and phenol were collected from 25 conventional piezometers during January, 1980 and from 30 conventional piezometers during August, 1981. Several days prior to sampling, a stainless steel bailer was used to evacuate at least one standing volume of groundwater from each piezometer. Over half were actually bailed dry by this procedure. Samples, also collected using the bailer, were filtered through a USGS backflush filter (Kennedy et al., 1976) containing 0.45 µm filter paper at the end of each sampling day.

During March, 1983 samples for trace organic analysis were collected from 14 conventional piezometers using the syringe and cartridge sampling apparatus described by Pankow et al. (1984). This apparatus consists of a glass adsorption/thermal desorption (ATD) cartridge attached to the inflow end of a small diameter (3.3 cm OD) glass syringe. The ATD cartridge contains a sorbent which pref-

erentially retains dissolved organic compounds present in groundwater. The syringe contains a moveable Teflon plunger to draw a groundwater sample, generally 40 to 50 mls, through the cartridge under vacuum. The plunger is mobilized by a vacuum/pressure pump at the surface, connected to the syringe via 0.6 cm O.D. diameter polyethylene tubing.

The syringe component of this sampling apparatus is reusable, but ATD cartridges and needle flow restrictors are dedicated to single samples. Four syringes were used during the sampling. Two were used exclusively for samples collected at the edge of the landfill and at the maximum sampling distance, respectively. The remaining two syringes were each used to collect several samples in order of decreasing distance from the landfill.

Duplicate and triplicate samples were collected from 10 and 4 piezometers, respectively. At regular intervals during the sampling program, blank cartridges were removed from their protective containers as if they were sample cartridges. Rather than actually being attached to a polyethylene sampling tube however, each blank cartridge was exposed to the atmosphere for several seconds and then resealed. A total of 5 blank cartridges were exposed in this way.

Based on the success of the down-hole technique, the sampling apparatus was modified to access multilevel device piezometer tubes as small as 0.95 cm ID by eliminating the glass syringe (Pankow et al., 1985). With the new assembly, consisting of only the ATD cartridge and a Teflon sampling tube, water pressure in the piezometer replaces suction created in the syringe as the driving force for groundwater movement through the sample cartridge (Figure 10).

The rate at which water passes through the cartridge depends on the depth below the water surface to which the cartridge is submerged. A needle flow restrictor set in the outflow end of each sample cartridge ensures a maximum

flowthrough that does not effect sorption efficiency, and prevents groundwater that has moved into the tubing during sampling from passing back through the cartridge as it is being brought to the surface.

Groundwater samples were collected using the tube and cartridge assembly during November, 1983. Duplicates were taken in 31 piezometers and triplicates in 4 piezometers, generating a total of 74 sample cartridges and 20 blank cartridges. During sampling, cartridges were placed between 1 and 8 meters below the water level in a piezometer. Duplicate and triplicate samples were collected at 1 and 2 m depths, respectively, below that of the original cartridge.

The down-hole exposure time required to pass approximately 50 mls of groundwater through a sample cartridge ranged from 15 minutes for a cartridge 8 m below water level, to 70 minutes for a cartridge 1 m below water level. The groundwater sample volume that passed through each cartridge remained in the Teflon tubing until it was measured at the surface.

During sampling, the exposed cartridges were sealed in Pyrex culture tubes with Swagelok endcaps, wrapped in aluminum foil and stored at 10° C. They were returned to the laboratory for analysis at the completion of field sampling. The ATD GC/MS analytical procedure used by the laboratory has been described by Pankow (1982).

Chapter X

RESULTS AND DISCUSSION

10.1 Inorganic Constituents

Groundwater analyses were carried out for all major ions. Background concentrations of these parameters in the shale were established using three piezometers, OW 4 and OW 14 located west of the landfill and OW 5 located directly south of the landfill. Although the latter is downgradient, it is shallow in depth and therefore unlikely to be influenced by landfill-derived groundwater which appears to flow southwestward to Lake Ontario.

Concentrations of most major ions at each of these background locations exhibit distinct differences which appear to be related to depth. At OW 14, the deepest background piezometer at a depth of 22 m, concentrations are considerably higher than those at OW 4 and OW 5 which extend to depths of 12 and 6 m, respectively (Table 3).

The range in concentration differences between the two shallower piezometers and the deep piezometer is defined by the magnesium and chloride ions. The magnesium concentration at OW 14, 190 mg/L, is at least double that at OW 5 and six times as great as that at OW 4. The chloride concentration at depth is 4690 mg/L, which is greater than a factor of 30 above levels in groundwater in the two shallower background piezometers.

Directly beneath and immediately downgradient of the landfill, concentrations of the major ions in groundwater do not exceed the maximum background level. At the two most shallow piezometers at OW 15 and the most shallow pie-

zometers at OW 1 and OW 2, concentrations are actually some of the lowest found in the shale for many of the major ions (Figure 11, 12 and 13). Chloride and sodium levels range from about 500 mg/L to 4300 mg/L and 450 to 900 mg/L, respectively. Maximum background concentrations for these two ions are 4690 mg/L and 2600 mg/L. Sulphate levels between 1 and 2000 mg/L are less than the maximum background concentrations of 2860 mg/L.

The trend of increasing concentrations with depth observed between the three background locations is even more consistent downgradient of the landfill. As a result, maximum concentrations of Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+} and K^+ are found at depth in the shale rather than directly beneath the landfill. In the deepest piezometer of each conventional well nest, some reach as high as tens of thousands of mg/L (Figures 11, 12).

For chloride and sodium in particular, concentrations at this depth do not show a gradual decrease with distance from the landfill. Because of this trend and because levels of these two constituents far exceed those found at other landfills in Ontario, they are probably not landfill-derived. At three sites situated on sand and gravel deposits investigated by Cherry (1983), contaminanted groundwater was characterized by chloride and sodium concentrations in the range of 100's to 1000's of mg/L.

The source of these two constitutents is more likely related to the high chloride and sodium content of water that exists in pores in the shale matrix derived from saline water of marine transgressions during Late Ordovician time. These salts are currently diffusing into meteoric groundwater flowing through the fractures. The range in hydraulic conditions found in the shale causes considerable spatial variability of chloride and sodium in groundwater moving through the shale.

On the basis of a comparison with background concentrations, chloride, sodium, sulphate, magnesium, calcium and potassium are not effective tracers of landfill contamination. An interpretation of their source in groundwater is also complicated by a trend of increasing concentration with depth which appears to occur naturally in the shale.

10.2 Bulk Organic Constituents

Organic nitrogen, dissolved organic carbon (DOC) and phenol were used as indicators of the bulk organic content of groundwater in the shale. Unlike the trends of most inorganic constituents described above, background concentrations of these parameters do not increase significantly with depth. Organic nitrogen, the difference between total kjeldahl nitrogen and free ammonia, has a maximum background level of 0.3 mg/L. DOC values range between 2.5 and 4.0 mg/L and phenol has a maximum level of 2 µg/L. Although low in absolute terms, phenol and organic nitrogen concentrations exceed the limits recommended for drinking water quality in Ontario (Ontario Ministry of the Environment, 1978). These are 0.001 µg/L for phenol and 0.15 mg/L for organic nitrogen.

Concentrations of phenol and DOC in groundwater immediately beneath and downgradient of the refuse establish the landfill as a major source of dissolved organic compounds (Figure 14, 15). They are significantly above background in the two most shallow piezometers at OW 15 and in the shallowest piezometers at OW 1 and OW 2. DOC also exceeds background levels in the deepest piezometer at each of these locations. Organic nitrogen concentrations exceed background concentrations at the more shallow depths at OW 1 and OW 2 and at all three levels of OW 3.

Above-background levels of phenol, DOC and organic nitrogen persist in groundwater downgradient to at least OW 13. Organic nitrogen shows the most gradual concentration reduction over this 600 m distance with concentrations generally less than 1 mg/L above background. Trends in phenol and DOC concentration are much more erratic, but appear quite consistent for these two parameters. At most well nests downgradient of OW 11, concentrations are often near background levels in one piezometer but closer to concentrations found near the landfill in the other piezometers.

The distributions of the three bulk organic parameters described above suggest that the zone of leachate-contaminated groundwater in the shale is much more extensive than indicated by the major ions. However, because there is a possibility that natural organic matter in the shale causes some of the higher phenol, dissolved organic carbon and organic nitrogen values, these parameters cannot be used to definitively delineate the full extent of the zone of contamination, particularly at considerable distance from the landfill. Thus, trace organic compounds in groundwater in the shale were determined as an additional, more diagnostic meaning of mapping landfill-derived groundwater contamination.

10.3 Trace Organic Constituents

An initial characterization of trace organic compounds was based on groundwater from 14 conventional piezometers, two at background locations and the rest at various distances downgradient of the landfill. The down-hole syringe and ATD cartridge method used to collect these samples allowed compound detection to concentrations as low as 0.001 µg/L.

Over 70 trace organic compounds were tentatively identified in groundwater, however a source for most of these may be the shale itself. The most abundant of

these compounds were alkylated or polynuclear aromatics and straight-chain hydrocarbons. Only about 10% of the organic compounds were classified as synthetic, chlorinated aliphatics or aromatics and of these, 1,1,1-trichloroethane (TCA), chlorobenzene (CB) and paradichlorobenzene (PDCB) were most prevalent. TCA in pure product form has a solubility in water of 4400 mg/L at 20°C. It is a constituent of many industrial and domestic solvents. CB is used in the manufacture of pesticides and industrial solvents and in pure product form has a solubility of 500 mg/L (20°C). PDCB has a solubility of 79 mg/L (20°C), and of the three compounds has the most diverse industrial, household and agricultural sources. It is a constituent of moth repellants, air deodorizers, dyes, soil fumigants and pesticides.

Because TCA, CB and PDCB have relatively high solubilities and occur in a variety of household and industrial products, they are becoming quite common in the groundwater environment. In the Netherlands, trace levels of TCA have been detected in groundwater pumped for drinking water supply and CB and PDCB occur in leach water from waste disposal sites (Zoeteman et al., 1980, 1981). The persistence and transportability of these compounds have also been observed by Reinhard et al. (1984) at two landfill sites on sand in Ontario. CB and PDCB persist in groundwater at least 800 m downgradient of one landfill and TCA occurs at a distance of 50 m beyond another landfill site.

To better define the distribution of TCA, CB and PDCB at the Bayview Park site groundwater was sampled more extensively, including piezometers as deep as 35 m and as far downgradient as OW 18 (Figure 17). Compound concentrations were determined from the mass found on each ATD sample cartridge and the groundwater sample volume. Duplicate and triplicate sample concentrations were averaged. Mean blank levels for each compound, determined on the basis of the

20 blank cartridges, represent contamination from sources other than groundwater and were subtracted from each average concentration.

These adjusted concentrations were compared to a sampling limit of detection (cl) established for each compound using a t-test criterion. It was assumed that blank level contamination was normally distributed and that the blank level standard deviation was the same as sample standard deviation for concentrations near the blank level (Pankow et al., 1985). Blank level standard deviations (sb) are 2.3×10^{-2}, 9.6×10^{-3} and 5.0×10^{-4} for TCA, CB and PDCB, respectively. Using the appropriate blank level standard deviation, the sampling limit of detection for each compound was determined at a 99% confidence level using the following equations: cl=2.60 sb for a single sample, cl=1.88 sb for duplicate samples and cl=1.56 sb for triplicate samples.

Concentrations were considered statistically significant if they were greater than the appropriate limit of detection for a particular compound. Concentrations below these limits were within the range of possible blank level contamination and were therefore considered to represent a non-detectable level of organic compound.

10.4 Distribution of Three Chlorinated Organic Compounds in Groundwater

The main source of the three chlorinated organic compounds in groundwater is the landfill, however small amounts may also be imparted by materials used to construct the multilevel devices. Background levels of TCA, CB and PDCB were therefore established using WAT 2, a multilevel device located about 200 m upgradient of the landfill, and OW 5, a conventional piezometer used previously for background levels of inorganic and bulk organic constitutents.

CB was not found at either of the above locations. TCA and PDCB were not found in groundwater at OW 5 but were present at significant levels in the piezometers at WAT 2 (Figure 17). Any influence on TCA levels by packers used to isolate sample intervals at this location and known to contain this compound, is not expected to be great and will be discussed later.

A more likely explanation for the anomalous results at WAT 2 involves hydraulic conditions within the rock. Hydraulic head profiles are typically very irregular with depth in the shale so a zone may exist beneath the refuse in which hydraulic head is higher than that at the two sample piezometers at WAT 2. If a fracture connection exists between the locations, it is conceivable that contaminants could move with groundwater to WAT 2 in response to the head differential.

Downgradient of the landfill, TCA and PDCB were identified throughout the monitoring network to the furthest monitoring site, OW 18, a distance of 825 m from the landfill (Figure 17). The distribution of chlorobenzene was more restricted, extending only 320 m to OW 12. In proximity to the landfill the three compounds are found at relatively high concentrations and their distribution indicates substantial downward movement of leachate-impacted, groundwater, consistent with the distribution of dissolved organic carbon and to a lesser extent, phenol in this area. Concentrations in the deepest sample piezometers at WAT 3, WAT 4 and WAT 5 are at least as high as those in the most shallow sample piezometers.

A wide range of concentrations was observed for each of the three chlorinated compounds but in general, concentrations decrease with distance downgradient of the landfill. TCA was present between 1 and 25 µg/L. Concentrations of CB are lower, between 0.6 and 15 µg/L, but have a much more restricted lateral distribution in the shale. The distribution of PDCB is very similar to TCA although at significantly lower concentrations, generally between 0.005 and 0.5 µg/L.

While the highest concentrations of the two aromatic compounds are found immediately downgradient of the landfill this is not the case for TCA. At OW 13 and WAT 7, concentrations are as high as those directly beneath the landfill. The maximum TCA value, 26 µg/L, actually occurs at WAT 7 at a depth of 32 m.

TCA is a component of the Dowell seal packer material, which is used in the construction of multilevel devices. Although these devices have rubber sheaths to isolate packers from groundwater, TCA may be diffusing through this membrane. In addition, some of these sheaths may have leaked because of faulty seals where they attach to the PVC casing or acquired holes due to irregularities on the borehole walls during installation. As a result, it is also conceivable that some TCA may be derived from direct groundwater contact with the packer material.

TCA concentrations in the monitoring network are consistent between multilevel devices and nearby conventional piezometers so it is concluded that the influence of the packer material on the observed distribution is negligible. The occurrence of PDCB, not a component of the packer material, at WAT 2 suggests that the TCA at this location is probably landfill-derived. In addition, groundwater collected from WAT devices does not contain fragments of packer material or have a characteristic green colour imparted by it as evidence of this type of contamination. The concentrations at WAT 7-11, WAT 2-3 and WAT 2-7 therefore, are believed to represent conditions in groundwater uninfluenced by the packer material.

The different concentration ranges observed for the three chlorinated compounds is probably due, in large part, to their variable input to the groundwater system. Unlike chloride salt for which the refuse acts more or less as a continuous source, these chlorinated compounds are not necessarily ubiquitous in a landfill. They probably occur as more local sources of contamination so that their

time, location and quantity of input can be a primary influence on the concentration distribution observed in groundwater.

The distribution of the three chlorinated compounds may also be influenced by sorption to particles within the shale and by biotransformation. As uncharged molecules, TCA, CB and PDCB are subject to hydrophobic sorption. On the basis of laboratory experiments, a strong correlation has been established between this sorption process and organic matter contained in natural sediments (Karickhoff, 1979, 1981). Solid material scraped from fracture surfaces and from deeper in the shale matrix was found to have a solid TOC content of less than 0.01%. This extremely low organic carbon content in the shale suggests that sorption may not be a major influence on the rate of migration of TCA, CB and PDCB in the groundwater zone.

The effect of biotransformation on the distribution of dissolved organic compounds in groundwater is a function of their structural susceptibility to microbial attack and the redox conditions favourable for this attack. Biotransformation of the aromatic compounds, observed under aerobic conditions (Tabak et al., 1981), involves cleavage of the benzene ring with compounds becoming much more resistent as the number of component halide atoms increases. It follows therefore, that the two chlorine atoms found in PDCB make it relatively more resistant than CB. The alkane structure of TCA is considered much less reactive than both aromatic structures but it has been observed to undergo microbial dehalogenation under extremely reducing conditions in the laboratory (Bouwer and McCarty, 1983).

There is no way to determine which combination of factors has produced the distributions of TCA, CB and PDCB in Figure 17, however if we assume conditions in the groundwater zone to be moderately anaerobic the distributions of the

three compounds are generally consistent with observed biodegradation trends. TCA, largely recalcitrant under these conditions, exists throughout the system with relatively high concentrations found 400 m downgradient of the landfill at WAT 7. The aromatic compounds may be susceptible to biotransformation however, PDCB, like TCA, is found as far as OW 18, but much less consistently. Beyond OW 12 it occurs only at extremely low levels, in some cases below the level of detection. CB, structurally the most susceptible to biotranformation, was not found downgradient of OW 12.

The distributions of TCA, CB and PDCB downgradient of the landfill provide an indication that extensive groundwater pathways exist from the landfill through the shale. In addition, the maximum vertical and lateral occurrence of these compounds establishes minimum limits on a zone in which groundwater has probably been affected by the landfill operation that began 23 years ago. The distribution of the chlorinated organic compounds provides conclusive evidence that groundwater contamination related to the landfill exists as deep as 35 m and as far as 875 m downgradient. It is possible that groundwater monitoring at greater depth and at greater distance would show that the zone of contamination extends much deeper and much farther toward Lake Ontario than these minimum limits.

10.5 Comparison With Distribution of Tritium in Groundwater

As a geochemically-inert radioisotope, tritium was used in Part 1 to identify zones of greatest groundwater movement in the shale. These were indicated by measurable tritium, typical of water input since 1953 when thermonuclear testing in the atmosphere began. Where tritium occurs therefore, landfill-derived contaminants might also be expected to occur. The absence of tritium in groundwater does not imply a similar absence of contaminants, however. The distributions

of tritum and all other dissolved constituents in groundwater are influenced by relative losses to the matrix by diffusion.

The occurrence of detectable tritium in the shale is fairly consistent with the occurrences of CB and PDCB (Figures 17 and 18). At locations OW 1, OW 11, OW 12 and OW 13 and OW 17 tritium values between 0 and 3 TU coincide with non-detectable or extremely low concentrations of the organic compounds. These concentrations are generally much lower than others in this same region of the shale, suggesting that they are a function of distinct flow paths rather than dispersion with distance from the landfill.

Unlike the distributions of CB and PDCB, TCA is found at concentrations greater than 2.5 µg/L at the eight sampling locations where tritium values are between 0 and 3 TU. This difference may be attributable to a relatively higher diffusive loss of tritium to the shale matrix. The actual rate of diffusion for a particular dissolved compound is dependent on its effective coefficient of molecular diffusion in the shale matrix as well as the rate at which advection in each fracture causes concentration gradients to develop.

Tritium, which exists as part of the water molecule, would be more susceptible to diffusive loss than the larger halogenated TCA molecule because there is a 2.7 factor of difference between the free solution coefficient for tritium, 2.4×10^{-5} cm^2/s (Wang et al., 1953), and the free solution coefficient for n-butane, 8.9×10^{-6} cm^2/s (Bonoli and Witherspoon, 1969). Like TCA, n-butane is an aliphatic structure with a molecular weight slightly less than half that of TCA. To estimate the effects of different diffusion coefficients on the diffusive loss of dissolved groundwater constituents, a range of conditions were simulated using a model that represents transport through a single planar fracture with diffusive loss to a homogeneous porous matrix (Tang et al., 1981).

Values of effective diffusion coefficients in the Queenston shale required for this solution are currently being measured in the laboratory but results have not yet been obtained. No values for other shales have been reported in the literature, however effective diffusion coefficients for chloride, which as a non-reactive ion would behave similar to tritium in groundwater, were found by Feenstra et al., (1984) to range from 3.8×10^{-7} cm^2/s to 3.6×10^{-6} cm^2/s in a porous sandstone. The porosity of shale is generally at least a factor of two greater than that of shale so even the minimum estimates reported by Feenstra et al., may be considerably larger than actual effective diffusion coefficients of tritium in the Queenston Formation.

To illustrate the sensitivity of contaminant movement through a fracture to different values of effective diffusion coefficients, D_e values of 2.4×10^{-8}, 1.2×10^{-8} and 2.4×10^{-9} cm^2/s were selected for tritium. D_e values for the organic compounds were selected as 8.9×10^{-9}, 4.4×10^{-9} and 8.9×10^{-10} cm^2/s to maintain the relative difference between the reported free solution diffusion coefficients. Input to the analytical solution along with a groundwater velocity of 2 m/day and an aperture of 10 μm, these De values produce significant differences in the relative travel rates of tritium and organics with diffusion characteristics similar to n-butane in groundwater moving along a fracture. In all three cases the organic compound front, defined as $C/C_o = 0.01$, had advanced at least one hundred meters farther than a comparable front for tritium (Figure 19). If we assume that the input conditions are representative of those in the shale then, the smallest of the De values used for tritium and organics in the simulations are the most consistent with the distribution of TCA observed in the field.

If diffusion into the rock matrix can separate the advance of dissolved constituents as significantly as shown in Figure 19, it would be a viable explanation

for the inconsistency between the distributions of TCA and tritium in the shale. On the basis of a single fracture, idealized to be extensive in length, the groundwater found at distances equivalent to those between OW 13/OW 17 and the landfill would contain TCA but not contain tritium. Assuming both parameters were input to the system approximately 25 years ago, then relative diffusion loss to the rock matrix would result in detectable TCA to a distance of 660 m while tritium would be detected only at distances of less than 400 m. A contaminant moving through the fracture under the same flow conditions, but not exhibiting any diffusion to the matrix (De = 0), would have travelled a distance equivalent to that between the landfill and Lake Ontario in only 5 years.

Chapter XI

OBSERVED AND PREDICTED SIZE OF THE CONTAMINATED ZONE

Independent of measured groundwater flow parameters, an initial estimate of the extent of potential groundwater contamination in the shale can be made using estimates of the infiltration flux through the landfill. This involves calculating the volume of shale necessary to contain cumulative infiltration through 78% of the total landfill surface, the 14 ha portion that is flat, grassed and underlain by at least a few meters of refuse. The peripheral regions of the landfill, which constitute the remaining area, were excluded from the infiltration calculation because they do not overlie the area where waste was actually deposited.

From twenty years of climatological data collected at a weather station near the site, average annual precipitation falling on the Bayview Park landfill is approximately 80 cm/yr. Assuming a 50% loss due to evapotranspiration and minimal runoff, the annual infiltration flux for the landfill area is 5.60×10^4 m^3. If this annual flux is applied to the landfill since its completion in 1972, a total volume of approximately 6.72×10^5 m^3 has passed downward through the refuse. A worst case calculation assumes that this entire volume is input to the shale at the bottom of the refuse and that a negligible volume is lost to shallow local discharge from seeps near the edge of the landfill. Discharge may be as high as 1 L/min at these locations in the spring, however the total discharge flux is still less than 10% of the infiltration flux through the landfill.

The maximum depth to which infiltrating groundwater might move in the system was selected as 70 m, twice the maximum depth at which organic contaminants were found but above the depth at which flow lines are believed to turn upward toward Lake Ontario. The transverse extent of this infiltrated volume downgradient of the landfill would not be expected to be greater than about 230 m, the maximum width of the landfill. Given these dimensions, the distance downgradient to which the infiltrated water might exist in the shale depends on the storage volume provided by the rock porosity. This distance would be maximized if the rock matrix was non-porous and only the fracture porosity was available for storage. Even using a fracture porosity of 0.1% as suggested in Part 1, a volume of rock between the landfill and the shore of Lake Ontario, a distance of 3.5 km with the width and depth specified above, would contain groundwater which had infiltrated through the landfill in only 1 year.

If the contaminants diffuse fully into the matrix as the contaminant front advances toward Lake Ontario, this calculation must be based on the total porosity of the rock. In this case it is essentially equivalent to the matrix porosity. When a porosity of 5% is used and assuming concentrations in the matrix water have reached equilibrium with the water in the fractures, the volume of rock occupied by contaminants would extend 0.83 km downgradient. More accurate estimates of the extent of groundwater contamination could only be made in this way with effective diffusion coefficients for the shale and more detailed information on the dimension of the matrix blocks to determine the degree of equilibrium between groundwater contained in the matrix and in the fractures.

An estimate of the velocity of contaminant transport in the shale was determined using TCA. The widespread distribution of this compound and low relative diffusion losses suggested by the model simulations, indicate that it is the most

conservative of those identified in groundwater. The occurrence of TCA at OW 18 establishes the 825 m between this sampling point and the landfill as a minimum travel distance. Assuming that this compound was input early during landfill operation, this suggests a minimum transport velocity of 35 m/yr since landfilling began in 1961.

Estimates of average linear groundwater velocity for comparison purposes were determined from the modified Darcy equation based on the equivalent porous medium concept. Bulk hydraulic conductivities and hydraulic gradients required in the equation were determined from rising-head response tests and water level measurements in the field as described in Part 1. Fracture porosities were also calculated in Part 1 using the method develped by Snow (1968) for a parallel set of planar joints.

Bulk hydraulic conductivities and fracture porosities, in conjunction with a horizontal gradient measured between OW 15 and OW 13, produce a large range in average linear groundwater velocities. The majority are less than 10 m/yr, however in a few cases values are at least an order of magnitude above this (Table 4). The high permeability of the weathered bedrock surface produces a maximum velocity of 3000 m/yr.

The rate of contaminant transport based on the distribution of TCA therefore falls at the high end of this range of calculated groundwater velocities. Considering that it is a minimum velocity, it can be considered largely inconsistent with the high frequency of calculated velocities below 10 m/yr. At these rates, contaminant transport during the 25 year period since landfilling began would be just over one quarter of the 825 m minimum distance suggested by TCA.

Although some calculated velocities are greater than 35 m/yr, the distribution of TCA is not consistent with a contaminant migration concept involving

only a few high velocity zones within a rock mass primarily characterized by low velocities. If this were the case, isolated occurrences of organic compounds would be expected, especially near the landfill and perhaps becoming less erratic with distance due to dispersion in the fracture network. The distributions of all three chlorinated compounds do not support this type of contaminant advance and TCA in particular, occurs at all levels in the shale along the entire length of the cross section. Changes in concentration are somewhat irregular but not greatly different than those seen downgradient of landfills over similar distances in sand and gravel deposits (Reinhard et al., 1984).

The discrepancies between the observed and calculated transport velocities are probably due to uncertainties in the estimates of bulk hydraulic conductivity and fracture porosity. If the bulk hydraulic conductivities used to calculate average linear groundwater velocities are too low by a factor of three or four and estimates of fracture porosity are too high by a similar factor this would account for an order of magnitude, the margin which separates the majority of calculated transport velocities and the one derived from the distribution of TCA.

Vertical boreholes and short sample intervals introduce uncertainties into the small-scale measurement of bulk hydraulic conductivity which might cause these values to be lower than those determined on the basis of a pumping test. While the Snow Method provides an initial approximation of fracture porosity, it is based on a simplified and idealized fracture network which may overestimate the fracture porosity associated with the complex and extensive fracture network in the Queenston Formation. Without a fracture porosity determined from a tracer test, with which to compare these calculated estimates, this error cannot be quantified. These possible influences on bulk hydraulic conductivity and fracture porosity may contribute to the poor indication of the potential for large-scale contaminant migration through the shale given by the Darcy equation.

Chapter XII

SUMMARY AND CONCLUSIONS

Chloride and sodium, which can be effectively used to map landfill-related groundwater contamination at landfills on sand and gravel, as well as calcium, magnesium, potassium and sulphate, gave no reliable indication of the zone of contamination at the Bayview Park site. The distributions of phenol, DOC and organic nitrogen suggest that groundwater contamination might extend several hundred meters downgradient of the landfill. However, the potential influence of natural organic matter on the bulk organic concentration trends necessitated the use of more diagnostic tracers of groundwater contamination. Three chlorinated organic compounds, 1,1,1- trichloroethane, chlorobenzene and paradichlorobenzene, were identified in groundwater and used in this capacity. Their distribution confirmed the downward movement of landfill-derived contaminants to as great as 35 m.

Downgradient of the landfill, concentrations of these three compounds decrease gradually as far as OW 12, a distance of 320 m. At greater distances, CB is not detectable and PDCB concentrations approach non-detectable limits. TCA is found in groundwater as far downgradient as OW 18. Although the input of these compounds to the groundwater flow system is unknown, the distances downgradient to which each occur, appear consistent with what is known about their tendencies to biotransform under moderately anaerobic conditions.

The occurrence of CB and PDCB is largely coincident with tritiated groundwater, in zones of most active groundwater movement in the shale. The occur-

rence of TCA in non-tritiated groundwater suggests differential loss of these two parameters to the shale matrix by diffusion. A model that represents advective transport through a single, planar fracture and accounts for this diffusive loss based on different estimates of effective diffusion coefficients for the shale, produces maximum transport distances for an organic compound similar to n-butane and tritium that differ by at least 100 m after 25 years. The larger diffusive loss for tritium by this type of process may be responsible for detectable TCA and non-detectable tritium at distances as great as 600 m downgradient of the landfill.

As the most widespread of the three chlorinated compounds in groundwater, TCA was used to determine a transport velocity in the shale. Assuming it was introduced to groundwater early during landfill operation, its occurrence at OW 18 suggests a minimum transport rate of 35 m/yr. This is inconsistent with the average linear groundwater velocities determined using the Darcy equation based on the equivalent equivalent porous medium concept. Hydraulic conductivities from rising head tests, fracture porosities from the Snow Method and an average hydraulic gradient combined in this equation produce velocities that range from 0.1 to 3000 m/yr. Nearly all are less than 10 m/yr, however.

Compared to the rate of transport and distribution of TCA, these calculated velocities provide a poor indication of contaminant movement through the shale. Uncertainties associated with determining bulk hydraulic conductivity values in the field and estimating fracture porosity based on an idealized fracture network may account for this. These uncertainties underscore the importance of establishing diagnostic tracers whose distribution in groundwater can most accurately serve to indicate large-scale contaminant transport in this type of fractured media.

Chapter XIII

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Chapter XIV

FIGURES

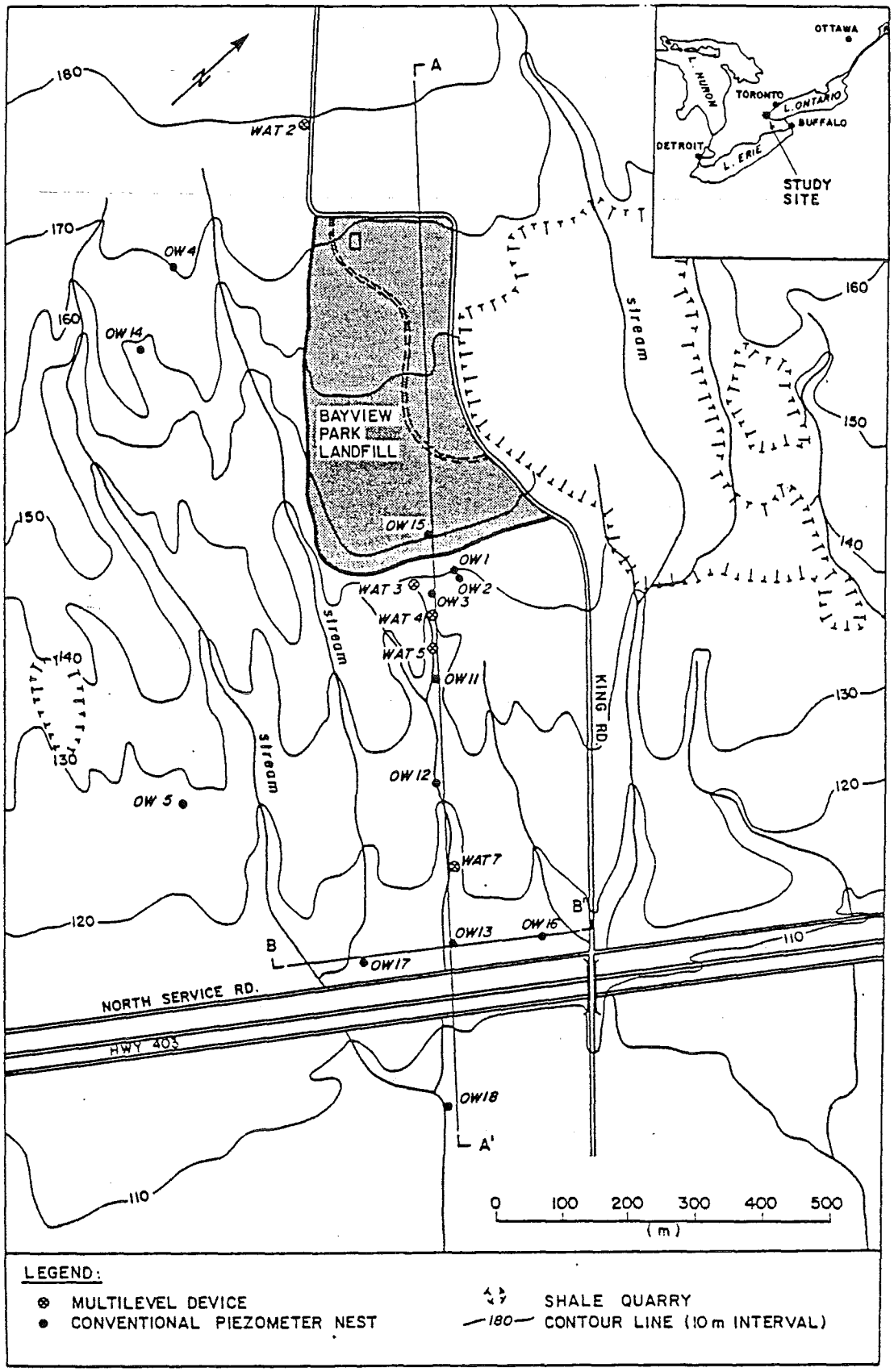

Figure 9: Physical setting of the Bayview Park landfill and the location of the groundwater monitoring network.

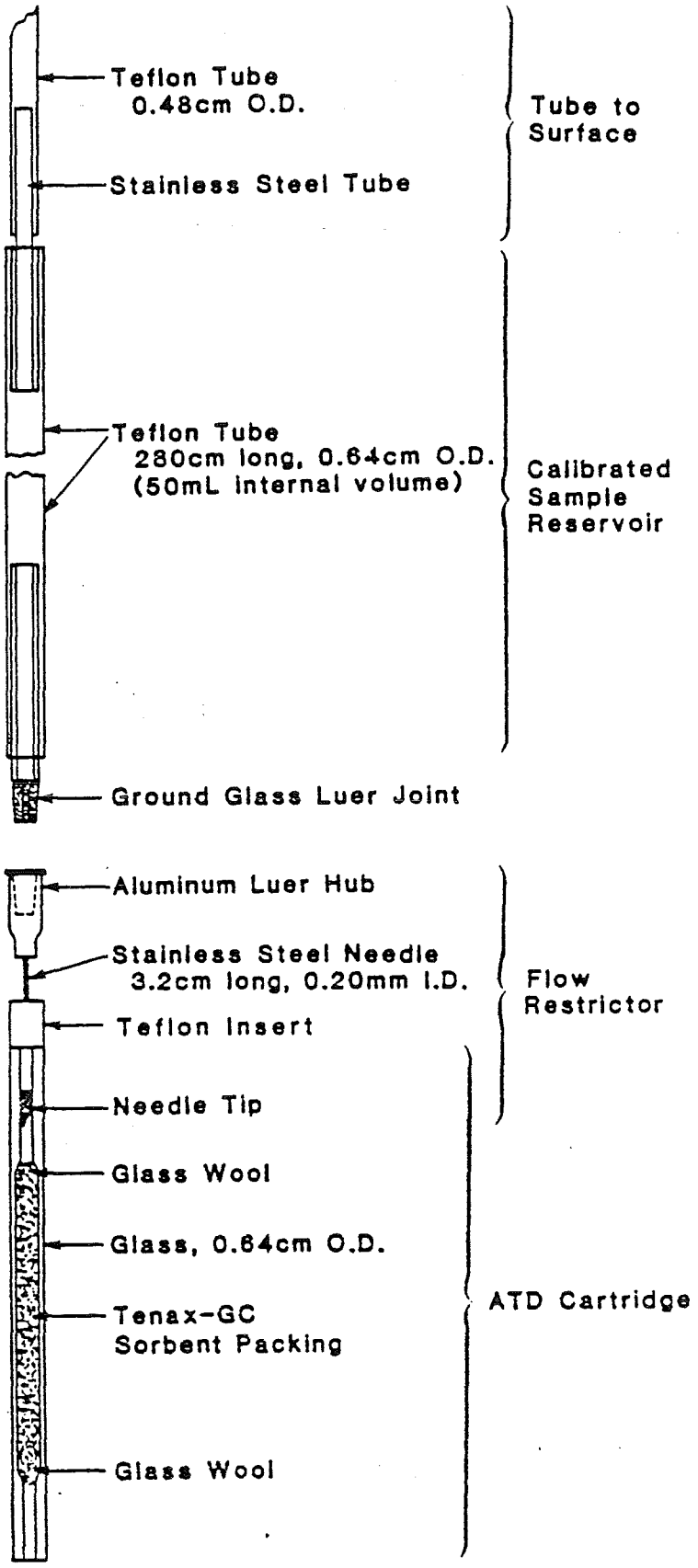

Figure 10: Schematic representation of the tube and ATD cartridge assembly for down-hole trace organic sampling.

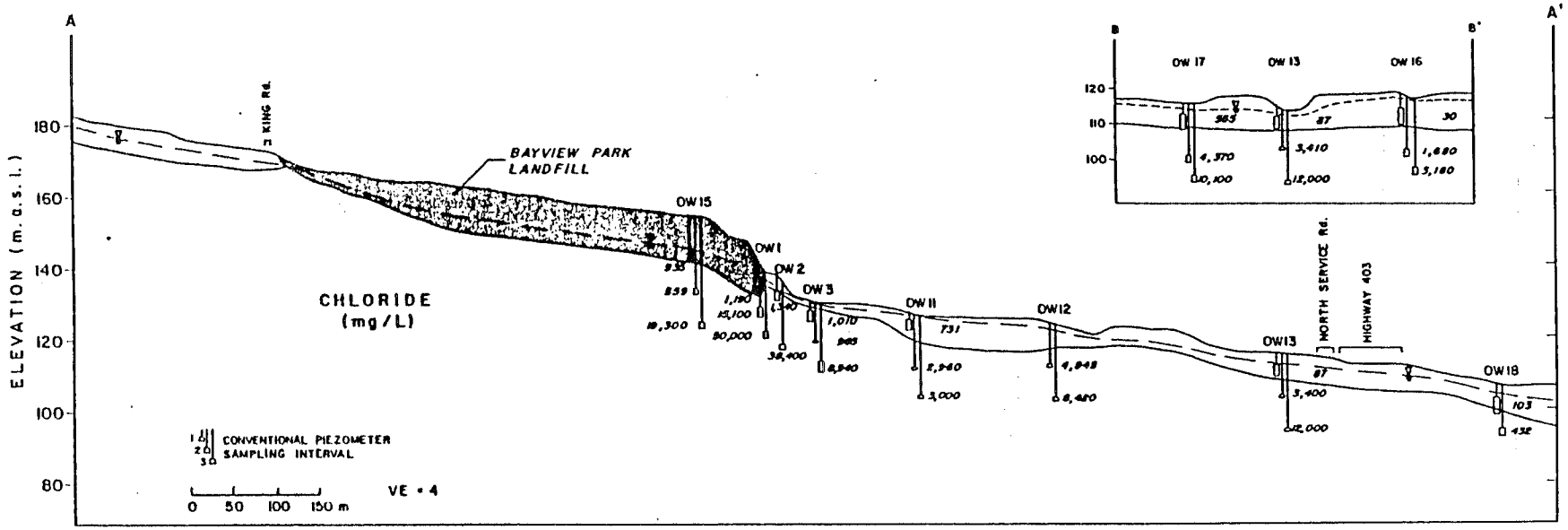

Figure 11: Distribution of chloride in groundwater downgradient of the landfill.

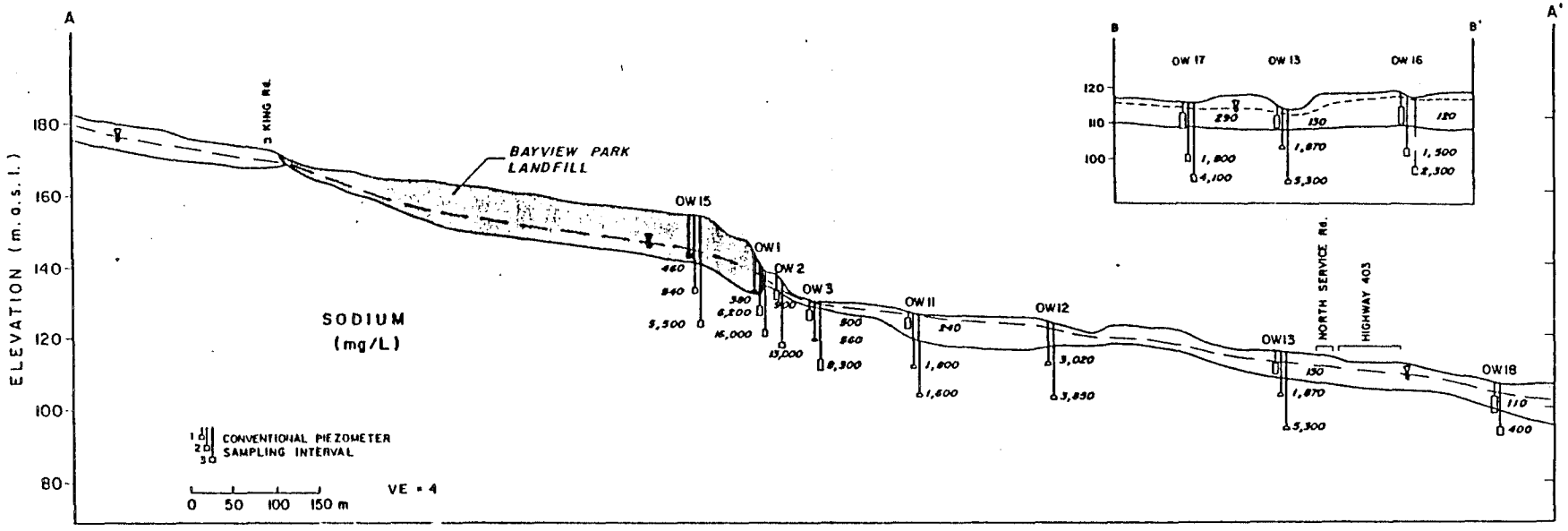

Figure 12: Distribution of sodium in groundwater downgradient of the landfill.

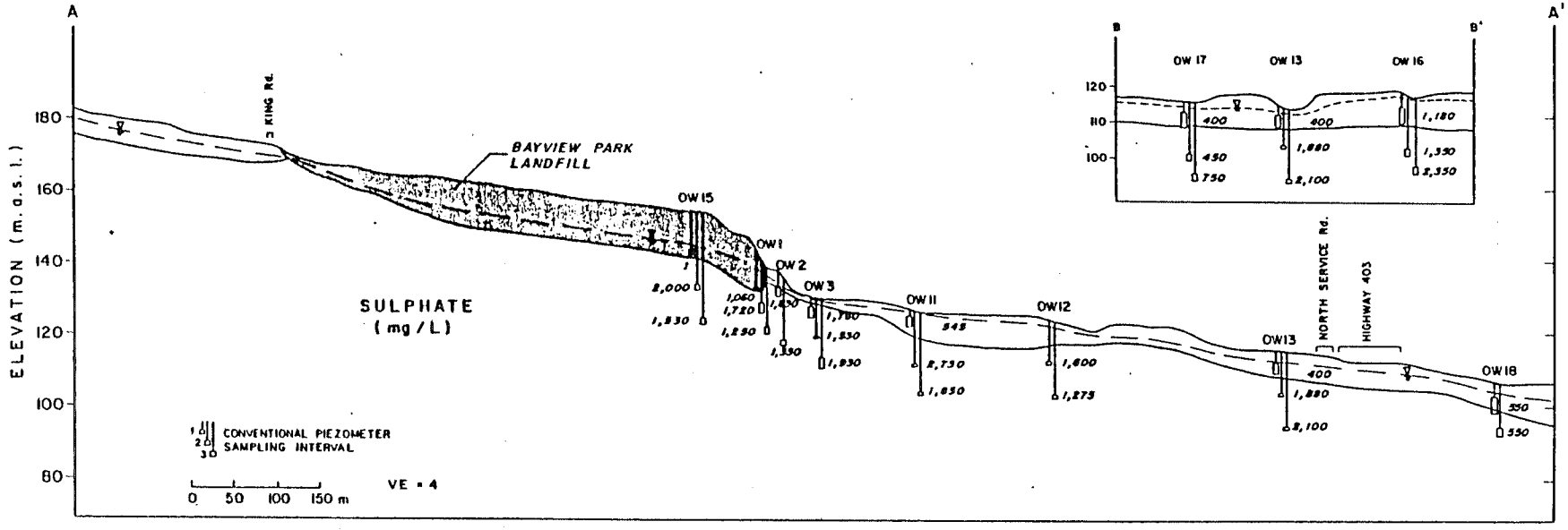

Figure 13: Distribution of sulphate in groundwater downgradient of the landfill.

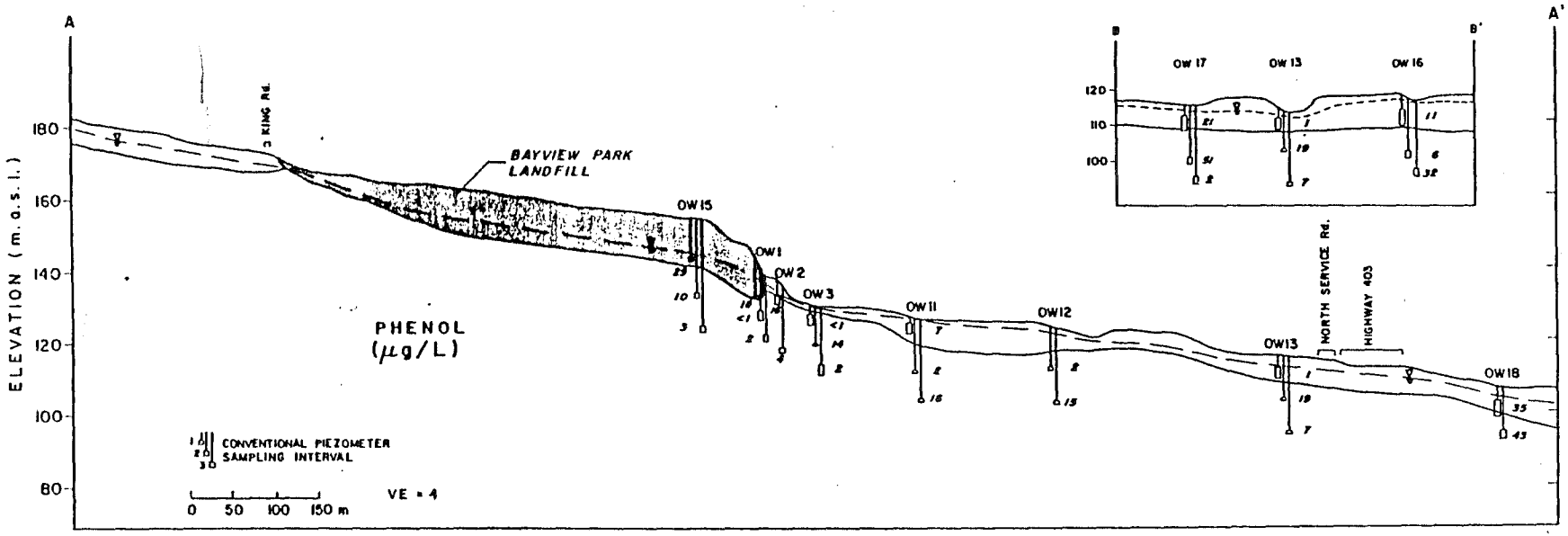

Figure 14: Distribution of phenol in groundwater downgradient of the landfill.

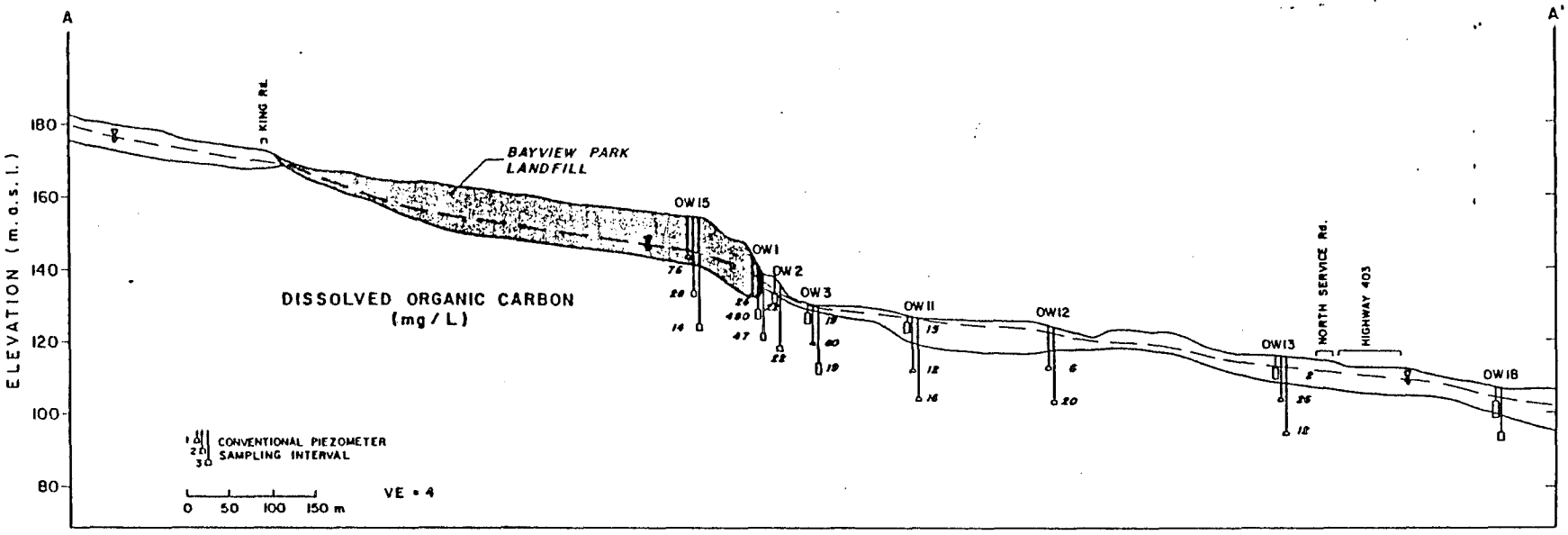

Figure 15: Distribution of dissolved organic carbon in groundwater downgradient of the landfill.

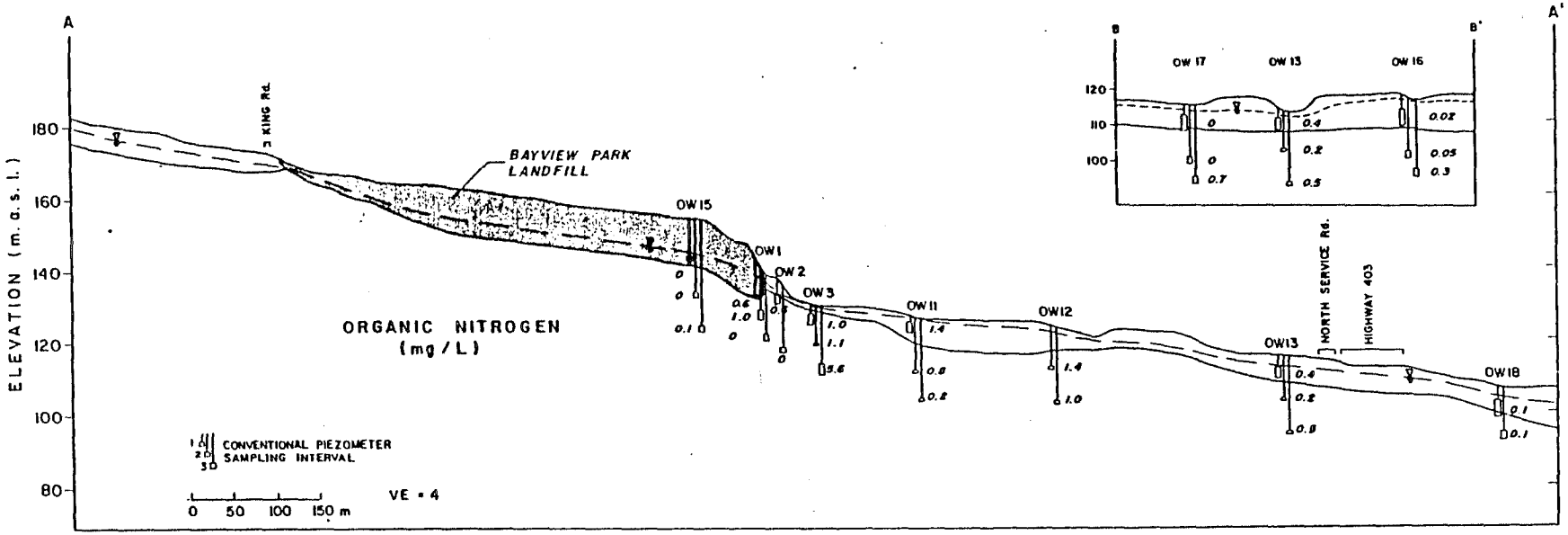

Figure 16: Distribution of organic nitrogen in groundwater downgradient of the landfill.

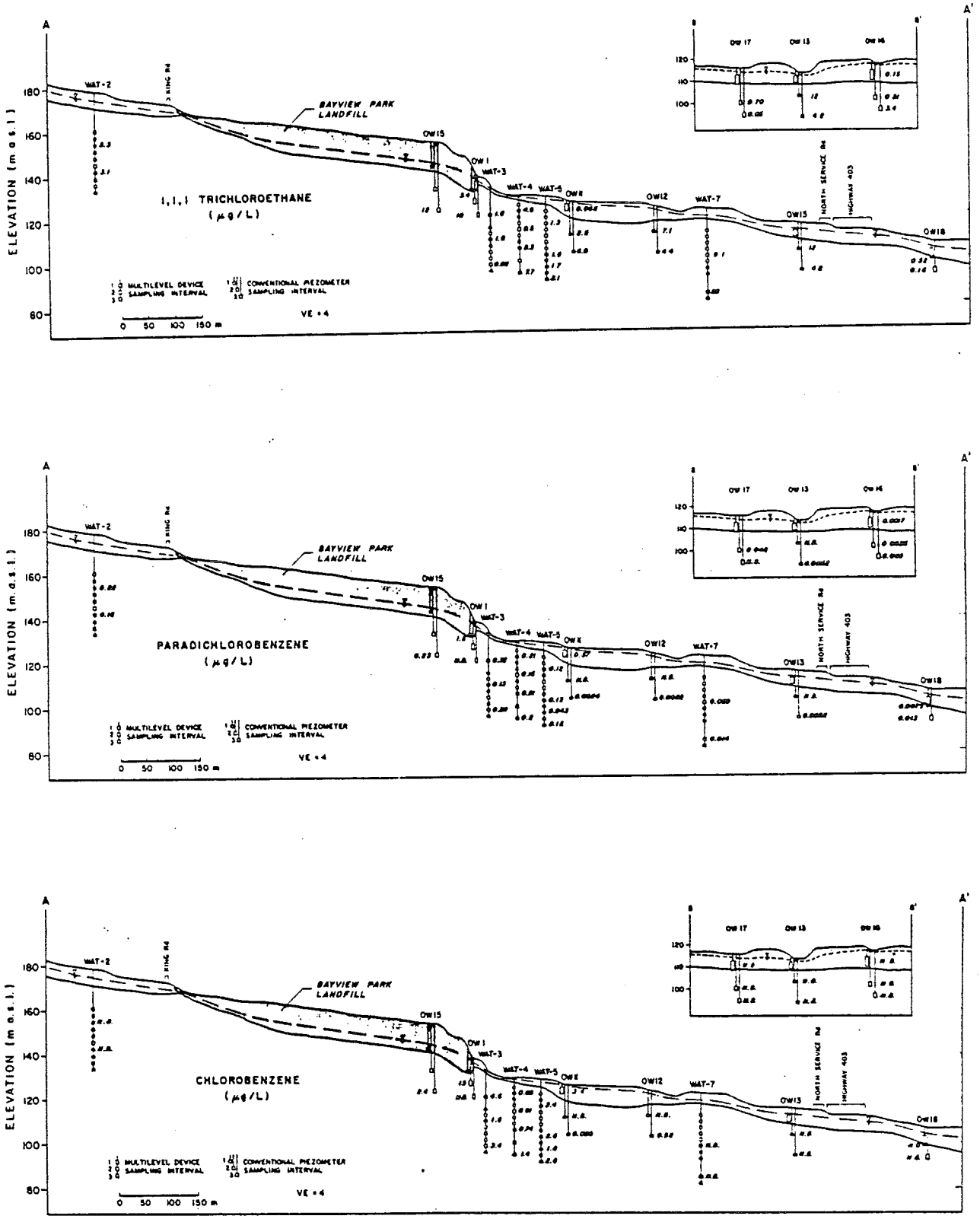

Figure 17: Distributions of 1,1,1-trichloroethane, chlorobenzene and paradichlorobenzene in groundwater downgradient of the

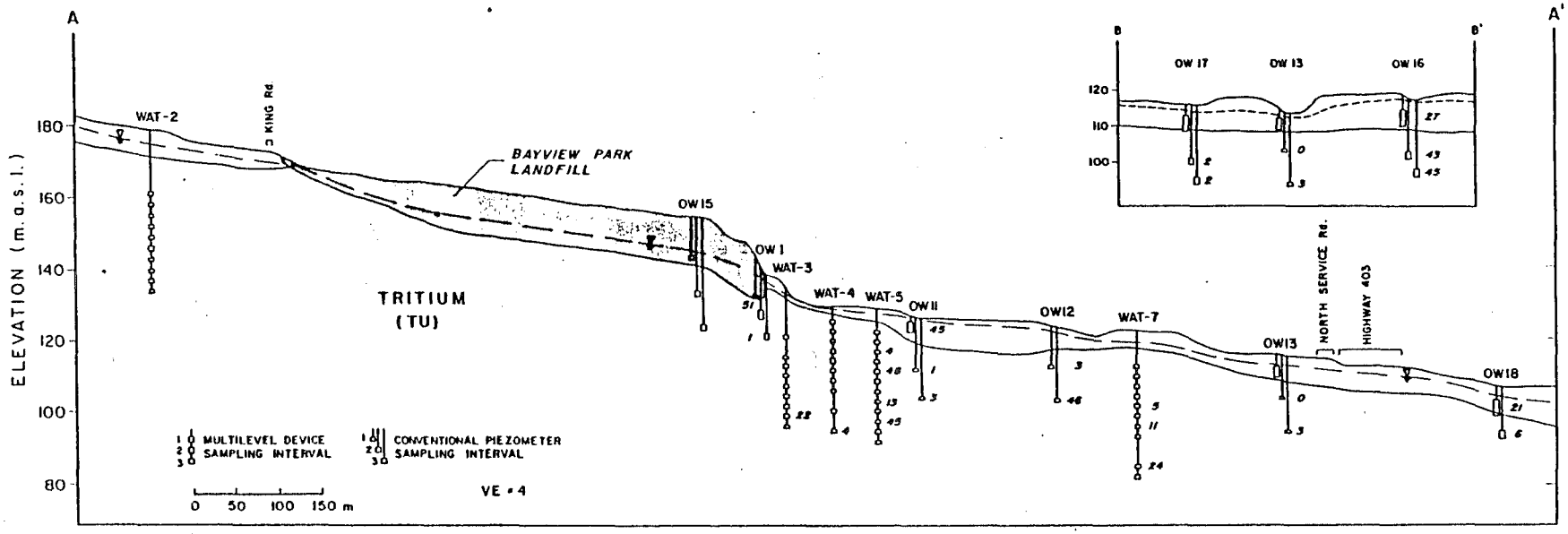

Figure 18: Distribution of tritium in groundwater, 1983, 1984.

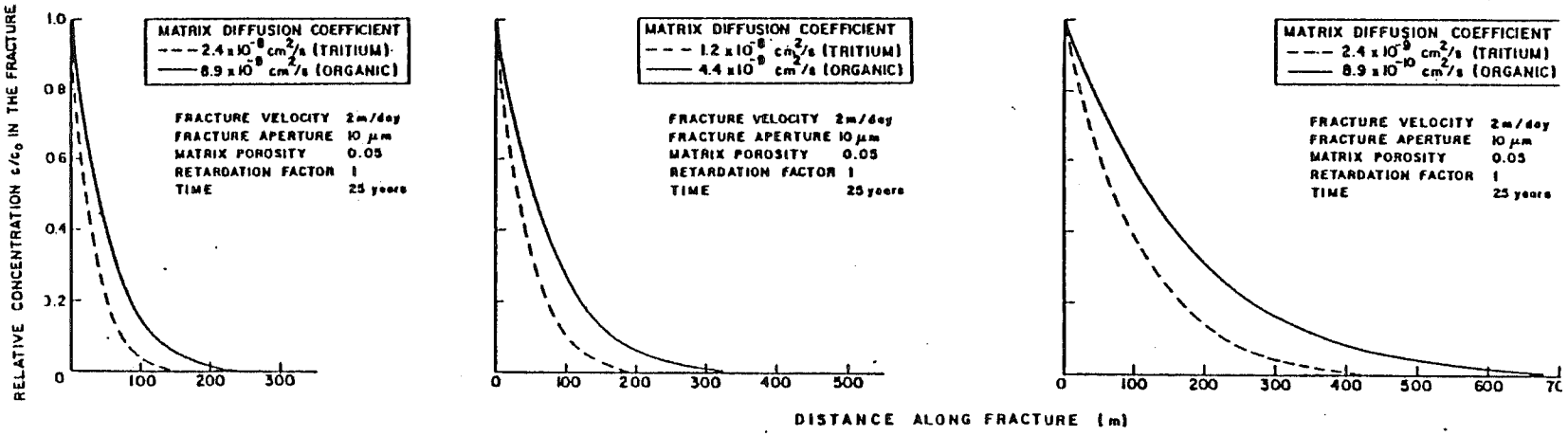

Figure 19: The effect of matrix diffusion on the migration of tritium and an organic compound in a fracture.

Chapter XV

TABLES

Parameter	Concentrations (mg/L) Background			Maximum in Shale
	OW 5	OW 4	OW 14	
Calcium	144	83	700	12,000
Magnesium	79	33	190	2,300
Sodium	165	49	2,600	16,000
Potassium	13	24	780	320
Chloride	160	14	4,690	50,000
Sulphate	410	50	2,860	2,350
Field pH	7.2	7.2	7.1	5.7
Phenol	<1 ug/L	<1 ug/L	64 ug/L	29 ug/L
DOC	4.0	3.8	2.7	76
Organic N	0.3	0.3	0.0	5.6

Table 3: Concentrations of inorganic constituents in groundwater at background locations and downgradient of the landfill.