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TRITIUM TRANSPORT THROUGH A FRACTURED TILL IN MICHIGAN

By

John Maris Gobins

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

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ABSTRACT

TRITIUM TRANSPORT THROUGH A FRACTURED TILL IN MICHIGAN

By

John Maris Gobins

The concentration of tritium in 40 ground-water samples collected from a fractured clay-rich till in southeastern Michigan was found to range from 0 to 44 TU. Bomb tritium was identified in samples at depths of 1.5 to 42 m below the water table while pre-bomb tritium was identified in samples from depths of 5.0 to 54 m. The distribution of tritium in the ground-water reservoir was simulated using a one-dimensional solute transport model. Based on the shallowest occurrence of non-tritiated water, the dispersivity value of the matrix flow system in the upper till unit was found to be less than 0.025 m. Bomb tritium penetration to depths beyond those predicted by the model can be explained by the presence of a fracture flow system.

ACKNOWLEDGEMENTS

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Mitchell Adelman collected and delivered the water samples.

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University are thanked for permission to use the liquid scintillation counters.

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Mīļš paldies maniem vecākiem!

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INTRODUCTION

The clay-rich tills which characterize much of the Great Lakes basin have traditionally been viewed as low permeability deposits that have limited potential for water supply (Norris, 1963). For this reason, they have been commonly used for containment of waste material and it has even been proposed that, in places, the tills may provide a suitable media for the disposal of hazardous waste (Desaulniers et al., 1981).

Within the last several decades, however, researchers have increasingly noted the occurrence of fractures within till deposits of the British Isles and Great Plains region of North America (Horberg, 1952; Fookes, 1965; Kazi and Knill, 1973; Grisak et al., 1976; Eyles and Sladen, 1981; Hendry, 1982; Keller et al., 1986; Cravens and Ruedisili, 1987). These fractures may have openings as large as several centimeters and have been observed to depths of over 10 meters (Eyles and Sladen, 1981; Keller et al., 1986). The presence of such fractures in tills of the Great Lakes basin would be of considerable interest since a regional low-level radioactive waste disposal facility could be associated with till deposits within Michigan (MILLRWC, 1987).

The purpose of this study is to examine the ground-water flow system in a fractured clay-rich till in southeastern Michigan and to determine the effect of the fractures on the movement of "bomb" tritium through the till. After a ground-water flow model is developed for the till, a one-dimensional solute transport model is employed to simulate the distribution of bomb tritium with depth.

STUDY AREA

The study area for this investigation is the Berlin and Farro Liquid Incineration Facility (BFLIF) which is located approximately five and one-half kilometers south of the town of Swartz Creek, Gaines Township, Genesee County, Michigan (T. 6 N., R. 5 E., Sec. 23). The 0.14 km^2 facility lies exclusively on till plain (Figure 1) and at one time included an incinerator, a sludge lagoon, and a landfill. As a result of repeated improper handling of toxic and hazardous wastes by the facility operators during the 1970's, the facility is currently included in the CERCLA (Superfund) National Priority List for remedial action and is presently under the control of the Michigan Department of Natural Resources (D' Appolonia, 1983).

Since 1982, several hydrogeologic studies have been initiated at the BFLIF, mainly at the request of the Michigan Department of Natural Resources, to provide the state with information necessary to meet Environmental Protection Agency requirements for federal funding of cleanup operations. These studies include magnetometer, resistivity, and seismic surveys, fracture trace analysis, test drilling, and ground-water and soil sampling (Woodward and Clyde, 1989). To date, 56 observation wells and more than 100 test borings have been drilled on or near the facility. The majority of observation wells are screened in glacial drift, but some are completed in bedrock. Remedial action has included removal of landfill and lagoonal contents and excavation of buried drums.

GEOLOGY

The BFLIF is located on a gently rolling till plain, deposited by the Saginaw glacial lobe, which is bordered on the north by the Flint moraine and on the south by the

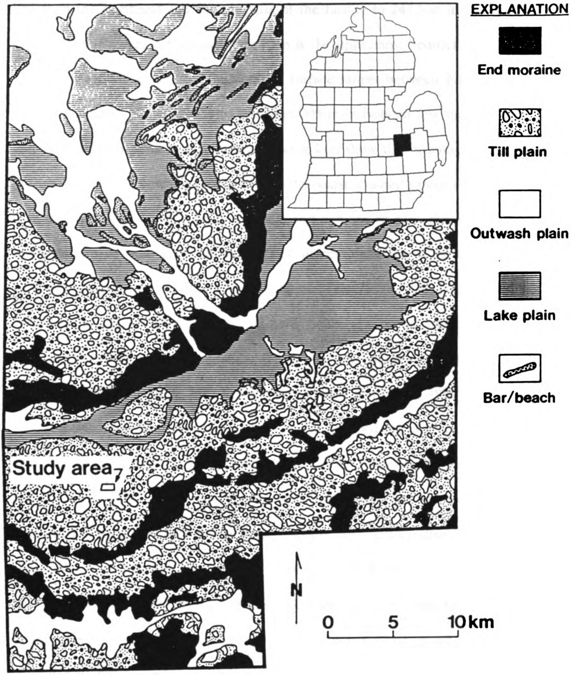

Figure 1. Geologic map showing location of study area and surficial deposits of Genesee County (after Wiitala et al., 1963).

Gaines moraine (Levrett and Taylor, 1915; Figure 1). Surface elevation ranges between 250 m in the northeast and central parts of the facility to 247.5 m in the western part.

The Pennsylvanian Saginaw Formation is the uppermost bedrock formation beneath the facility. The elevation of the bedrock surface ranges between 220 m along the eastern boundary of the facility to less than 205 m in isolated low spots in the central and southwestern parts of the facility. Boring logs show that it consists of light gray to grayish-brown and brownish-gray very fine- to coarse-grained sandstone. Interbedded with the sandstone are thin layers of shale and laminae of dark gray clays. Crossbedding in the sandstone is common and consists of alternating bands of dark and light, fine- and coarse-grained quartz. Cements are usually non-calcareous. The interbedded shale is typically gray to dark gray, firm to very hard, fissile, micaceous, and thinly bedded. Although the rock quality designation (RQD) for the Saginaw ranges from 0% to 98%, the average RQD value is 75% to 90% (Woodward and Clyde, 1989).

The unconsolidated sediments which overlie the bedrock are glacial in origin and were deposited during the Woodfordian stage of the Wisconsinan glaciation (Farrand and Eschman, 1974). Based on monitor well and boring logs, two relatively distinct layers of till, separated by a 0-5 m thick, discontinuous and variable, water-bearing sand and gravel layer, underlie the facility (Figures 2, 14, and 15).

The lower till is an 18 to 27 m thick, very stiff to hard, moist to dry, gray clayey silt to silty clay with occasional sand lenses and trace amounts of gravel. Characteristic of this till is its resistance to penetration with blows per foot typically exceeding 50. The sand and gravel lenses within this till vary in composition from silty sand to fine-grained sand to coarse-grained sand and gravel and are typically dense and wet. In areas

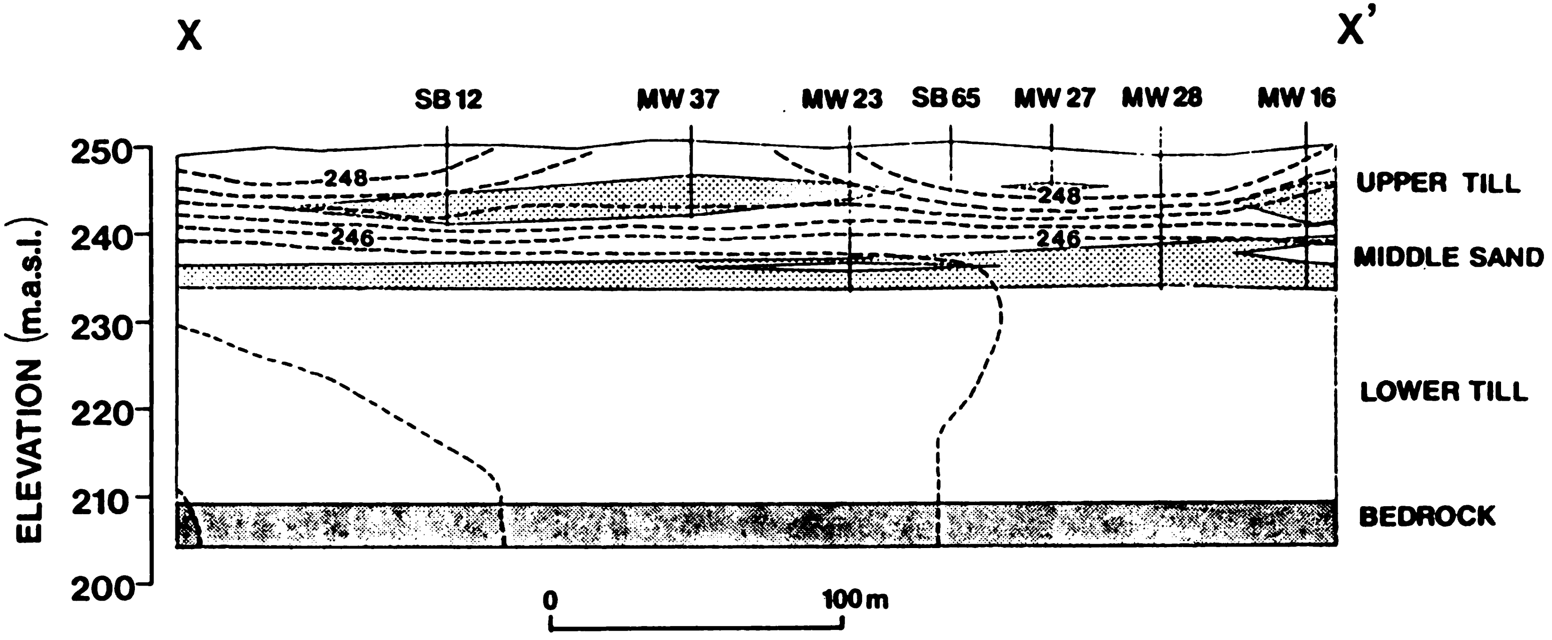

Figure 2. Geologic cross section showing simulated head distribution along line X-X' of Figure 4 (contour interval = 0.5 m). All elevations in m.a.s.l.

where the bedrock surface consists of shale, shale fragments have been incorporated into the base of the lower till, and in areas where the bedrock surface consists of sandstone, the lower till is sandier at its base.

The upper till is a 12 to 18 m thick, soft to stiff, moist to dry, brown to gray, silty to sandy to gravelly clay with occasional sand and gravel lenses and stringers. The penetration resistance of this till varies between 10 and 40 blows per foot but may be less in some of the sand lenses. The sand and gravel lenses vary in composition from silty sand and clayey gravel to fine-grained sand to coarse-grained sand and gravel and are typically loose and wet.

The large number of soil borings makes it possible to analyze in some detail the distribution of sand lenses within the upper till unit. Equal elevation sections of soil texture were generated at 0.3 m vertical intervals, starting at the surface and continuing to a depth of 12 m. These were subdivided into two textural classes. The coarse textural class includes gravel and sand and is described in the Unified Soil Classification System by the symbols GW, GP, GM, GC, SW, SP, SM, and SC. The fine textural class includes silt, clay, and organic deposits and is described in the same system by the symbols ML, CL, OL, MH, CH, and OH. Intervals not recovered were recorded as part of the coarse textural class. The percent of wells and borings indicating coarse material at each vertical interval was calculated and plotted as a function of depth (Figure 3). One curve was generated based on all of the study area logs and another was based on logs from the western half of the site where sand lenses appeared to be more common.

The findings indicate the presence of a 5 m thick zone in the upper till unit, characterized by intervals of coarse sediment, approximately 4 to 5 m below the surface

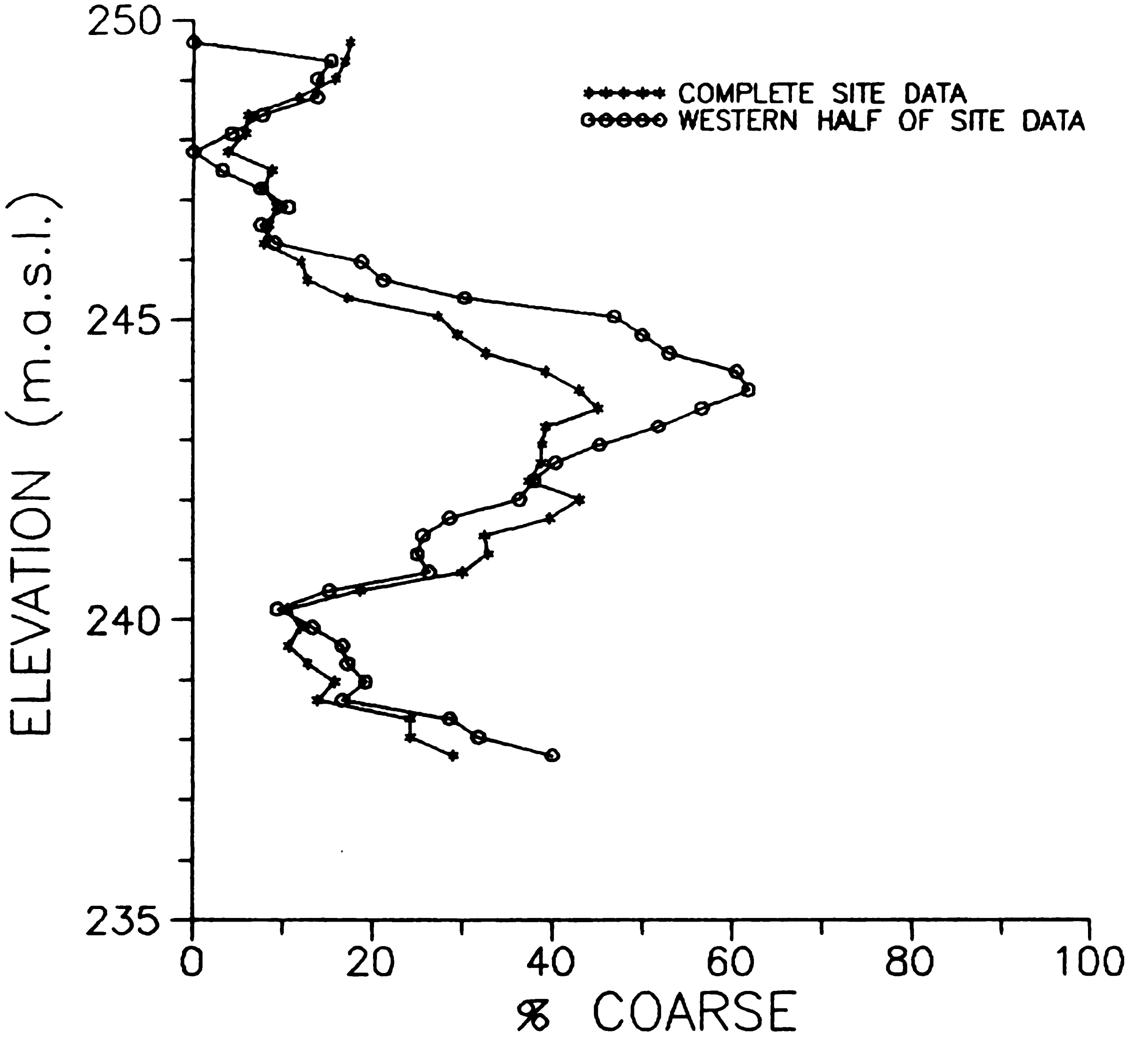

Figure 3. Elevation versus percentage of soil borings indicating coarse material (asterisks- all borings, circles- western half of site data).

(Figure 3). Individual borings typically encounter 1 to 3 m of coarse sediment in the upper 12 m of the drift. The cumulative thickness of the coarse sediment in each boring may be represented by a single sand layer or by several layers separated by clay stringers. Since the thickness of the coarse zone and the thickness of the lenses is different, it can be inferred that some vertical offset exists between the lenses. Laterally, almost 50% of all wells and borings indicate coarse material at an elevation of 244 m and, when logs from only the western half of the site are used, this value increases to nearly 65%. This indicates that, at this elevation, the majority of coarse-grained lenses occur in the western half of the study area. Lateral extent of individual lenses is more difficult to determine but in some instances, a lens encountered in one boring has not been encountered in another boring as little as 5 m away.

Fractures within the upper till unit have been intersected by approximately one-third of the soil borings at depths of 1 to 5 m. These fractures are typically vertical to sub-vertical and discontinuous and may be empty or filled with trace amounts of sand and/or root material. The fracture aperture is generally less than several millimeters and fracture spacing near the surface is approximately 5-10 cm based on observations at a excavation 1 km north of the facility. Walls of the fractures are typically smooth and contain a thin brown oxidation rind developed on the gray matrix material. Fractures with this type of appearance in tills have also been described by other workers in North America (Williams and Farvolden, 1969; Grisak et al., 1976; Hendry, 1983a). Brown and gray mottles are often associated with the fractures within and just beneath the soil zone.

AGE AND ORIGIN OF THE DRIFT

While an exact age has not been assigned to the drift beneath the facility, it is believed to be Late Wisconsinan. A similar drift stratigraphy has been described for Saginaw Lobe drift approximately 100 to 150 km southwest of the study area by Monaghan and Larson (1986) and has been correlated with drift sequences of the Lake Michigan Lobe in southwestern Michigan and the Huron-Erie Lobe in central Ohio. They describe two tills separated by an intervening variable sand and gravel unit. The lower and upper tills have been assigned ages of approximately 16,500 yr B.P. and 14,780 yr B.P., respectively. They associated the sand and gravel unit which separates the two tills with the Erie Interstade (15,500 to 15,000 yr B.P.) which represents a major retreat of the ice from the region (Dreimanis and Goldthwait, 1973).

As a result of its hardness and scarcity of sand and gravel lenses, the lower till at the facility is believed to represent lodgement till. The propensity of sand lenses in the upper till and its lesser consolidation, on the other hand, would suggest that it formed as ablation till.

HYDROLOGY

The ground surface at the facility generally slopes westward and, accordingly, surface water is removed in that direction. Approximately 150 m west of the facility, Slocum Drain collects the runoff.

Three "water-bearing" zones have been identified at the facility (Figure 4). The uppermost zone includes the sand lenses in the upper till unit between an elevation of approximately 240 m to 245 m. The middle zone includes the sand layer which

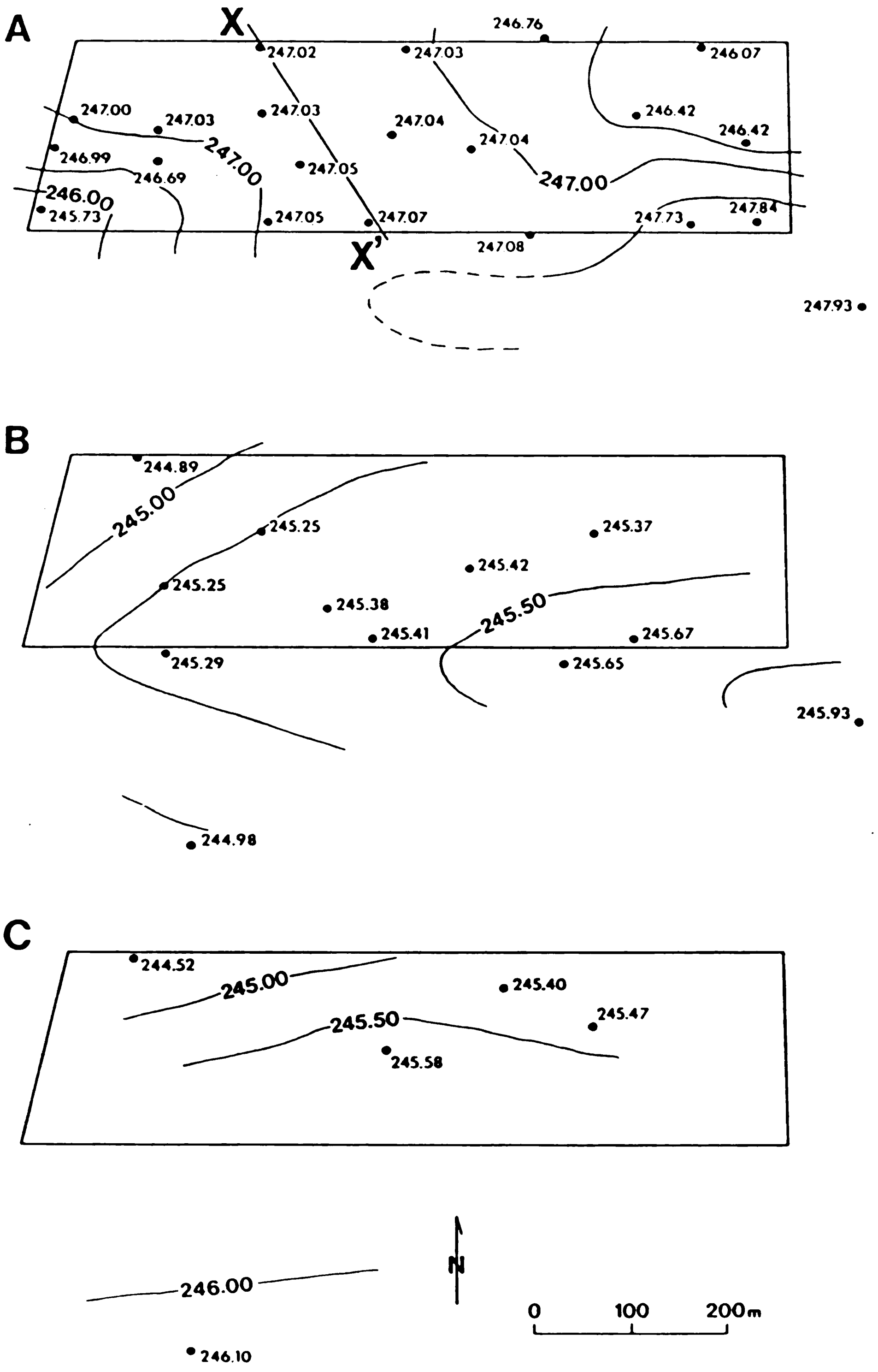

Figure 4. Observed potentiometric surface contour maps and location of cross section X-X' (all elevations in m.a.s.l.).
A Upper Till (contour interval = 0.5 m)
B Middle Sand (contour interval = 0.25 m)
C Bedrock (contour interval = 0.5 m)

separates the upper and lower tills and whose elevation ranges from 230 m to 240 m. The lowermost water-bearing zone is represented by the bedrock. The potentiometric surfaces of all three water-bearing zones are shown in Figure 4.

The potentiometric surface of the upper water-bearing zone slopes southwestward and northeastward from a northwest-southeast-oriented divide and has a horizontal hydraulic gradient of essentially zero in the central part of the facility to 0.01 in the southwestern and southeastern parts. The potentiometric surface of the middle water-bearing zone, on the other hand, slopes toward the northwest and has a horizontal hydraulic gradient of approximately 0.00125. The potentiometric surface of the lower water-bearing zone slopes to the north and has a horizontal hydraulic gradient of approximately 0.005.

Vertical hydraulic gradients between the various water-bearing zones were calculated using water levels recorded in nested wells two weeks before sampling. The average vertical hydraulic gradient between the upper till unit and the middle sand unit is 0.22 and downward. Between the middle sand unit and the bedrock, the vertical hydraulic gradient in the northwest part of the facility is 0.013 and downward. However, in the eastern part and south of the facility, the average vertical hydraulic gradient between the bedrock and middle sand unit is 0.01 and upward. Also, the similarity of water levels recorded in the upper till unit near the center of the facility suggests that some of the sand lenses may be hydraulically interconnected. Although some shallow wells did show annual water level fluctuations as great as 2 m, annual water level fluctuations for most of the monitor wells were generally less than 1 m.

Slug and bail tests were performed in the bedrock and drift to obtain hydraulic conductivity values. In the bedrock wells, inflatable packers were used to isolate several zones for testing. In the drift wells, however, the interval tested was represented by the length of the screened interval. The Hvorslev (1951) method was used to calculate hydraulic conductivity. The average for 20 bedrock hydraulic conductivity measurements was found to be 9.9 x 10^{-7} m/s and to range from 4.6 x 10^{-8} to 1.0 x 10^{-5} m/s. The average hydraulic conductivity of the lower till unit, based on one measurement, was found to be 6.7 x 10^{-8} m/s. The average hydraulic conductivity for the middle sand unit, based on 11 measurements, was found to be 4.4 x 10^{-5} m/s and to range from 1.9 x 10^{-6} to 2.0 x 10^{-4} m/s. The average hydraulic conductivity of the sand lenses in the upper till unit, based on nineteen measurements, was found to be 5.1 x 10^{-5} m/s and to range from 7.1 x 10^{-7} to 2.1 x 10^{-4} m/s.

NUMERICAL SIMUALTION OF GROUND-WATER FLOW

A three-dimensional finite-difference flow model (McDonald and Harbaugh, 1988) was applied in two dimensions along a northwest-southeast-oriented cross-section X-X' through the central part of the facility area (Figures 2 and 4). The modeled section was divided into 336 rectilinear nodes, 21 in the horizontal direction (X) and 16 in the vertical direction (Z). The upper till unit was divided into eight layers, the middle sand unit into two layers, the lower till unit into five layers, and the bedrock into one layer. The top layer was modeled as unconfined while the remaining layers were modeled as confined. A recharge well was used for the bedrock layer along the southeastern boundary of the cross section to account for flow across that boundary. No recharge wells, however, were used for the drift along the southeastern boundary of the cross section because flow across that boundary was assumed to be negligible. Discharge wells were used for the bedrock and the drift along the northwestern boundary of the cross section to account for flow across that boundary. Recharge was applied evenly across the entire cross section at a rate of 0.10 m/yr. To obtain this value, peak discharge rates for Swartz Creek, which drains the till plain containing the facility and has a gaging station approximately 12 km northeast of the facility, were subjected to baseflow separation (U.S.G.S, 1980).

The horizontal hydraulic conductivity (K_h) values used in the simulation were those obtained from the slug and bail tests. For the bedrock and middle sand units, the highest field-measured K_h values were applied because most of the water in these areally relatively extensive geologic units would move through the zones of highest permeability. For the lower till unit, the K_h value obtained from the one field measurement was applied. For the clay-rich zones of the upper till unit, the K_h value applied was ten times greater than the value used for the lower till to account for the effects of weathering (Keller et al., 1986; Cravens and Ruedisili, 1987). For the sand lenses in the upper till unit, the average of their field-measured K_h values was applied. Vertical hydraulic conductivity (K_v) values were estimated by assuming certain anisotropies: 1:1 for sand and gravel and 1:10 for clay, silt, and bedrock.

The simulated head distribution beneath the study area is shown in Figure 2 and is in general agreement with observed heads. Slight adjustments were made to the recharge rate but the hydraulic conductivities, anisotropies, and recharge/discharge well flow rates were not adjusted.

Equipotential data generated from the model indicate that between the land surface and the middle sand unit, ground-water flow direction is predominantly near-vertical and downward. Along the modeled cross section, the sand lenses in the upper till unit have little effect on the ground-water flow direction. The simulated horizontal gradient in the middle sand unit is very small and is in agreement with gradients obtained from measured water levels in the same unit.

The use of a recharge well in the bedrock along the southeastern boundary of the model simulates the observed upward hydraulic gradients between the bedrock and middle sand unit along the southern part of the facility. However, further to the north, equipotential lines indicate mainly downward hydraulic gradients between the middle sand unit and the bedrock and are in agreement with observed heads. The northward decreasing head values simulated by the model are consistent with measured head values.

Since there was some uncertainty as to the composition of the upper till unit in the northern third of the simulated cross section, a sensitivity analysis was performed by treating the composition of that part of the cross section as either all clay, all sand, or a clay/sand mixture with a distribution similar to that beneath the facility. The results indicate that the composition of the upper till unit in the northern part of the cross section has little influence on the hydraulic head distribution beneath the facility (Figure 16).

Ground-water velocity (V) can be calculated from the flow model using

$$V = \frac{K_v i}{n}$$

where **i** is the simulated hydraulic gradient, **K** is the hydraulic conductivity, and **n** is the porosity. The vertical ground-water velocity for the upper till unit is 4.8 x 10^{-9} m/s when applying a K_v of 6.7 x 10^{-9} m/s, an effective porosity of 0.35 (Hendry, 1988), and an average vertical hydraulic gradient of 0.25 which was derived from the flow model.

SAMPLING METHODS

Ground-water samples from 40 monitoring wells were collected by the Michigan Department of Natural Resources field personnel during the second week of October, 1987. These wells, terminating in glacial deposits and bedrock, have, at their bases, screened intervals of 1.5 and 3 m, respectively, and are completely cased down to the tops of these intervals. The elevations and lengths of screened intervals, as well as the geologic units that they draw from, are shown in Figure 5.

Before collecting water samples, each well was purged to insure that the sample obtained is representative of water from the screened interval. Samples for tritium analysis were delivered to 1 liter Nalgene plastic bottles, tightly capped, and labeled. In addition, 125 ml plastic bottles were filled with water from six selected wells and shipped to the University of Waterloo Environmental Isotope Laboratory (UWEIL) for ^{18}O and ^{2}H analysis by mass-spectrometry. The accuracy of the analyses is +/- 0.2 o/oo for ^{18}O and +/- 2 o/oo for ^{2}H.

The tritium concentration of each sample was first analyzed by direct liquid scintillation counting in the tritium laboratory at Michigan State University (detection limit of approximately 12 TU and counting error of +/-10 TU). Samples which contained more than 12 TU were also analyzed by direct liquid scintillation counting at UWEIL (detection limit of 6 TU and counting error of +/- 8 TU). Samples which

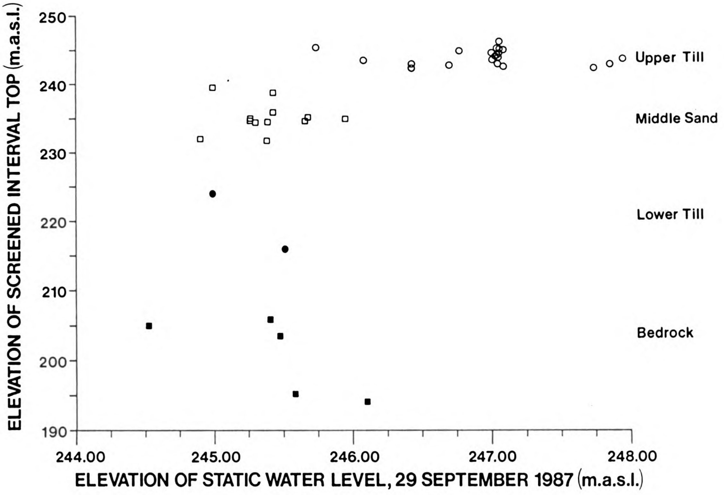

Figure 5. Elevation of screened interval top versus elevation of static water level and geologic units sampled. Open circles- upper till, open squares- middle sand, filled circles- lower till, filled squares- bedrock.

contained less than 12 TU were electrolytically enriched in the tritium laboratory at Michigan State University and counted at UWEIL (average detection limit of 1.5 TU and counting error of +/- 1.4 TU).

STABLE ISOTOPE RESULTS

The stable isotopes ^{18}O and ^{2}H (deuterium) are part of the water molecule and can therefore be used to trace the origin and history of a water mass. The mass differences of the various isotopic forms of water lead to slight differences in their vapor pressures, which in turn are responsible for the isotopic fractionation of water during evaporation and condensation stages of precipitation formation. The degree of fractionation depends on the rate of the reaction and the temperature, and increases with increasing rate of reaction and with decreasing temperature (Dansgaard, 1964). Unless high temperatures are encountered in the subsurface, exchange of ^{18}O with oxygen-bearing minerals can be considered negligible. The isotopic content of precipitation is also influenced by geographic factors in that it becomes increasingly lighter as its parent air mass moves over continental areas and preferentially releases the heavier isotopes.

It has been demonstrated by Craig (1961) that most precipitation, excluding that in tropical areas, falls on a meteoric water line which on a global basis is described by

$$\text{del } ^{2}H = 8 \text{ del } ^{18}O + 10.$$

Thus, a ground-water sample whose isotopic composition falls on the meteoric line can be used as an indicator of the average isotopic content of precipitation in its respective recharge area. Water samples whose isotopic composition falls off of the meteoric line can be said to have undergone evaporation, reaction with minerals, or mixing with water of non-meteoric origin.

Del values, in parts per thousand or mil (o/oo), are used to report the deviation of the isotopic ratios of the sample from those in an international standard. The deviations are calculated using the equation

$$\text{del sample} = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \text{X } 1000$$

where R is the abundance ratio ($^{18}O/^{16}O$ and $^{2}H/^{1}H$). The standard for reporting del ^{18}O and del ^{2}H is standard mean ocean water (SMOW). The results of the stable isotope analyses from the facility are shown in Table 1.

Table 1. Stable isotope data.

Sample #	Sampled Interval Elevation (masl)	del ^{18}O	del ^{2}H	Geologic Unit Sampled
BF-14	244.48 - 242.96	-9.01	-67.2	Upper Till
BF-15	238.81 - 237.29	-8.82	-67.0	Middle Sand
BF-5	223.94 - 222.41	-8.73	-66.5	Lower Till
BF-2	215.95 - 214.43	-8.90	-67.3	Lower Till
BF-11	205.86 - 202.81	-9.14	-67.2	Bedrock
BF-10	195.19 - 192.15	-9.25	-67.8	Bedrock

The isotopic composition of the four samples taken from drift wells is plotted in Figure 6 and is consistent with a trend observed in other samples taken from drift wells in Michigan (Regalbuto, 1987; Long et al., 1988; Long and Larson, 1988). These samples have been plotted against a meteoric line (del $^{2}H = 7.5$ del $^{18}O + 12.6$) for the Lake Simcoe, Ontario area which lies approximately 300 km east of the study area

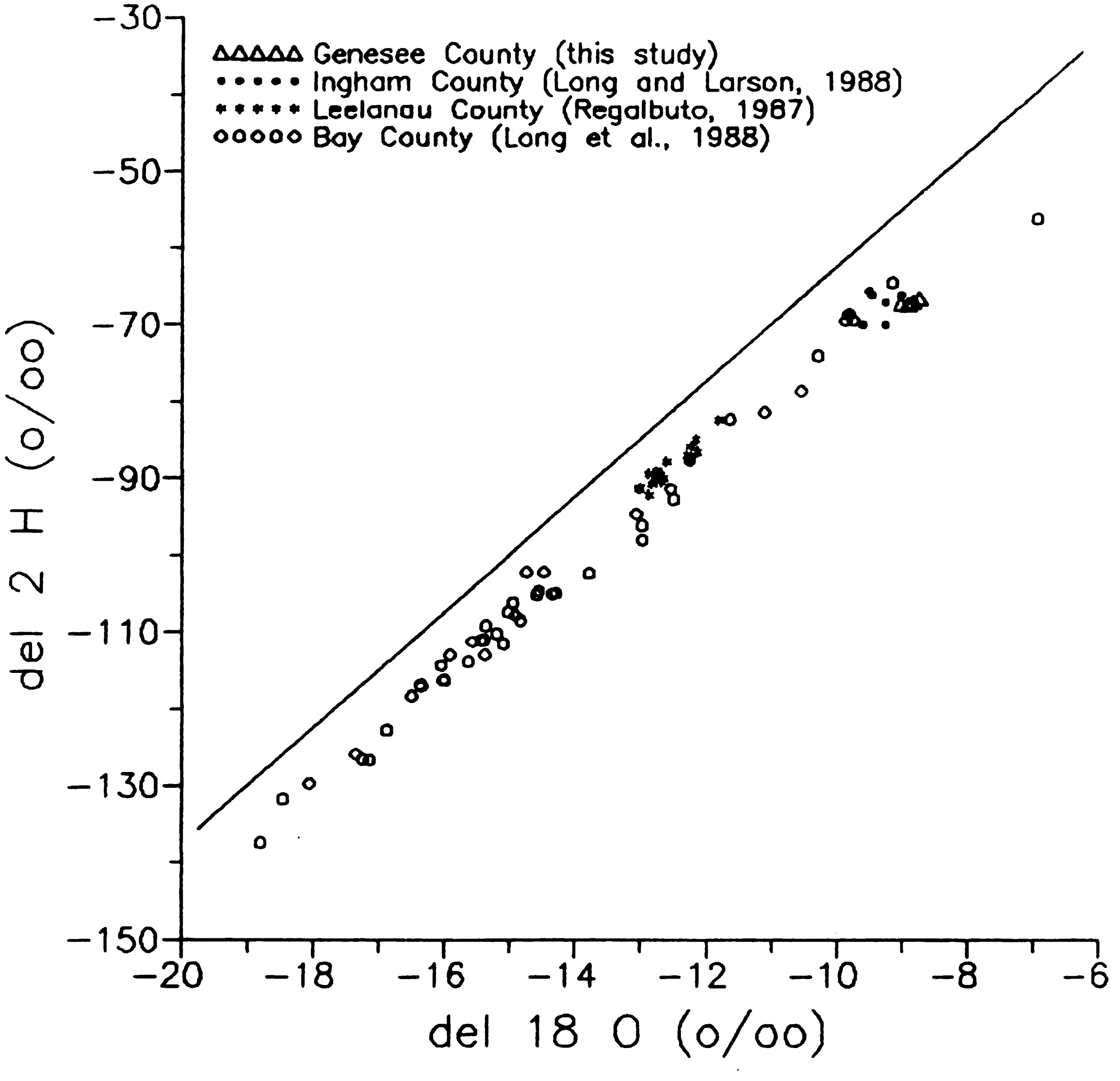

Figure 6. Stable isotope composition of water sampled from drift wells in Michigan. Solid line- Lake Simcoe meteoric line (Desaulniers et al., 1981).

(Desaulniers et al., 1981).

The results indicate no significant isotopic trends with depth. Unlike 60 km to the north in Bay County (Long et al., 1988) and 150 km to the east in southwestern Ontario (Desaulniers et al., 1981) where very negative values in thick clay sequences have been used to suggest the presence of water recharged when the climate was cooler during the late Pleistocene and early Holocene, no such extremely negative values have been measured in ground-water samples from the facility. Therefore, the stable isotopic contents of the samples suggest that the ground water beneath the facility was recharged during a climate similar to that of present and during the relatively recent geologic past.

TRITIUM RESULTS

Large amounts of tritium (^3H), a radionuclide of hydrogen with a half-life of 12.43 years (Mann et al., 1982), were introduced into the hydrologic cycle from 1953 to 1962 as a result of atmospheric nuclear weapons testing. Prior to 1953, the natural tritium concentration of precipitation was 3 TU, where 1 TU is equal to 1 tritium atom per 10^{18} hydrogen atoms (Robertson and Cherry, in press). Post-1953 precipitation is characterized by tritium concentrations which are several orders of magnitude higher than in pre-1953 precipitation. Therefore, any water which entered the ground prior to 1953 cannot have tritium contents in excess of 0.45 TU. For a review of tritium systematics, refer to Appendix F.

The results of the tritium analyses from the facility are shown in Table 2. Any sample whose tritium concentration is 0.45 TU above its counting error, expressed in TU, contains "bomb" tritium and can be considered to have recharged after 1953.

DIRECT COUNTING RESULTS

SAMPLE #	TU	+/- TU
STD		
BF-12	6.96	8.00
BF-13	16.41	8.00
BF-15	<6	8.00
BF-22	8.95	8.00
BF-25	<6	8.00
BF-27	16.90	8.00
BF-28	<6	8.00
BF-34	14.91	8.00
BF-35	44.74	8.00
BF-36	22.37	8.00
BF-37	21.87	8.00
BF-39	11.93	8.00

ENRICHED COUNTING RESULTS

SAMPLE #	GROSS CPM	NET CPM	Un	Ug	Ms (g)	EEs	DPMs	TU	+/- TU
ST-T1	118.21	114.58	1.22	1.22	13.15	.84	3.96	557.35	5.95
BF-9	3.70	.07	.26	.22	13.48	.84	.00	.35	1.28
BF-14	3.65	.02	.26	.21	13.52	.84	.00	.10	1.28
BF-16	3.76	.13	.26	.22	12.83	.84	.00	.62	1.22
BF-20	4.27	.64	.27	.23	13.16	.84	.02	3.12	1.32
BF-21	3.74	.11	.26	.22	13.82	.84	.00	.56	1.32
BF-29	3.69	.06	.26	.21	13.85	.84	.00	.31	1.31
BF-31	4.63	1.00	.28	.24	12.42	.84	.03	4.59	1.28
BF-33	3.90	.27	.26	.22	13.29	.84	.01	1.33	1.29
BF-40	4.27	.64	.27	.23	13.54	.84	.02	3.21	1.35
ST-T2	94.61	91.11	1.10	1.09	16.52	.84	4.00	562.92	6.70
BF-3	3.65	.15	.26	.21	12.85	.82	.01	.74	1.24
BF-4	3.80	.30	.26	.22	14.04	.83	.01	1.59	1.36
BF-6	3.71	.21	.26	.22	13.80	.83	.01	1.10	1.33
BF-17	3.58	.08	.25	.21	13.05	.83	.00	.40	1.24
BF-19	4.51	1.01	.28	.24	15.19	.83	.04	5.81	1.57
BF-23	3.70	.20	.26	.22	15.92	.84	.01	1.19	1.51
BF-26	3.77	.27	.26	.22	14.35	.83	.01	1.47	1.39
BF-32	3.77	.27	.26	.22	15.20	.84	.01	1.53	1.45
BF-38	3.71	.21	.26	.22	14.29	.83	.01	1.14	1.37
BF-41	4.71	1.21	.28	.24	15.30	.84	.05	6.92	1.59
ST-T3	98.73	95.23	1.12	1.11	15.30	.82	3.96	558.22	6.49
BF-1	3.77	.27	.26	.22	15.82	.82	.01	1.64	1.55
BF-2	3.77	.27	.26	.22	14.58	.82	.01	1.51	1.43
BF-5	4.65	1.15	.28	.24	15.78	.82	.05	6.95	1.67
BF-7	3.70	.20	.26	.22	13.76	.82	.01	1.05	1.34
BF-10	3.71	.21	.26	.22	15.11	.82	.01	1.22	1.47
BF-11	3.72	.22	.26	.22	13.34	.81	.01	1.14	1.32
BF-24	3.63	.13	.25	.21	16.41	.83	.01	.81	1.57
BF-30	4.27	.77	.27	.23	13.45	.81	.03	4.02	1.39
BF-42	4.38	.88	.27	.23	12.77	.81	.03	4.36	1.34

Table 2. Tritium data.

A plot of tritium concentration versus depth indicates that, with the exception of three samples from depths of 15, 26, and 45 m, bomb tritium has not penetrated deeper than 4 to 8 m below the ground surface and is therefore confined to the upper till unit (Figure 7). However, within the upper till unit, the concentration of tritium at any particular depth is not the same and indicates that tritium is not moving downward along a front. For example, a plot of the lateral distribution of tritium within the sand lenses of the upper till unit shows that in the central part of the study area, where water level readings suggest that the sand lenses may be interconnected, tritium is not evenly distributed (Figure 17). Pre-bomb or bomb tritium is also probably present in the middle sand unit at a depth of 17.5 m, in the lower till unit at a depth of 33 m, and in the bedrock at a depth of 55 m. These seemingly anomalous values could be attributed to fracture flow, leakage down the annular space of the casing, or analytical error.

DISCUSSION

In order to evaluate the effect of hydrodynamic dispersion (D) on the movement of bomb tritium through the upper till unit at the BFLIF, mathematical simulations were generated which take into account advection, dispersion, and diffusion. Implicit in these simulations is the assumption that ground-water flow through the upper till unit is vertical and downward. This is supported by the flow model already discussed. The middle sand, lower till, and bedrock were not included in the simulations because flow velocities and directions in those units are different from those in the upper till. The simulations are based on a computer code (Javandel et al., 1984) that generates analytical solutions to the following one-dimensional solute transport equation:

$$D \frac{d^2C}{dx^2} - \frac{vdC}{dx} - LC = \frac{dC}{dt}$$

$$D = av + D^*$$

where x is the vertical and downward distance of travel over time t, v is the average linear ground-water velocity in the x direction, C is the concentration of tritium (solute), L is the radioactive decay constant for tritium, and a and D^* are the coefficients of dispersivity of the aquifer material and effective molecular diffusion for tritium in the saturated porous medium, respectively. The method of superposition (Egboka et al., 1983) was applied to the simulations to account for the temporal variability of bomb tritium entering the till over a period of 34 years. The tritium input function used was generated from the tritium concentration in recharging precipitation for Chicago, Illinois (IAEA, 1969, 1970, 1971, 1973, 1975, 1979, 1983, 1986).

Figure 7 shows the simulated and actual tritium concentrations for the upper till unit at the facility. The simulations were obtained by applying dispersivity values of 0.025, 0.25, and 2.5 m while maintaining a constant value of 2.1×10^{-9} m/s for velocity as calculated from laboratory permeability values for the till and vertical hydraulic gradients from the flow model. The radioactive decay constant value is 0.000153. A value of 5×10^{-11} m^2/s was used for the diffusion coefficient and is based on reported values for diffusion of conservative solutes in clayey materials (Freeze and Cherry, 1979; Grisak et al., 1980; Gillham et al., 1984).

The results of the simulations indicate that no single dispersivity value for the upper

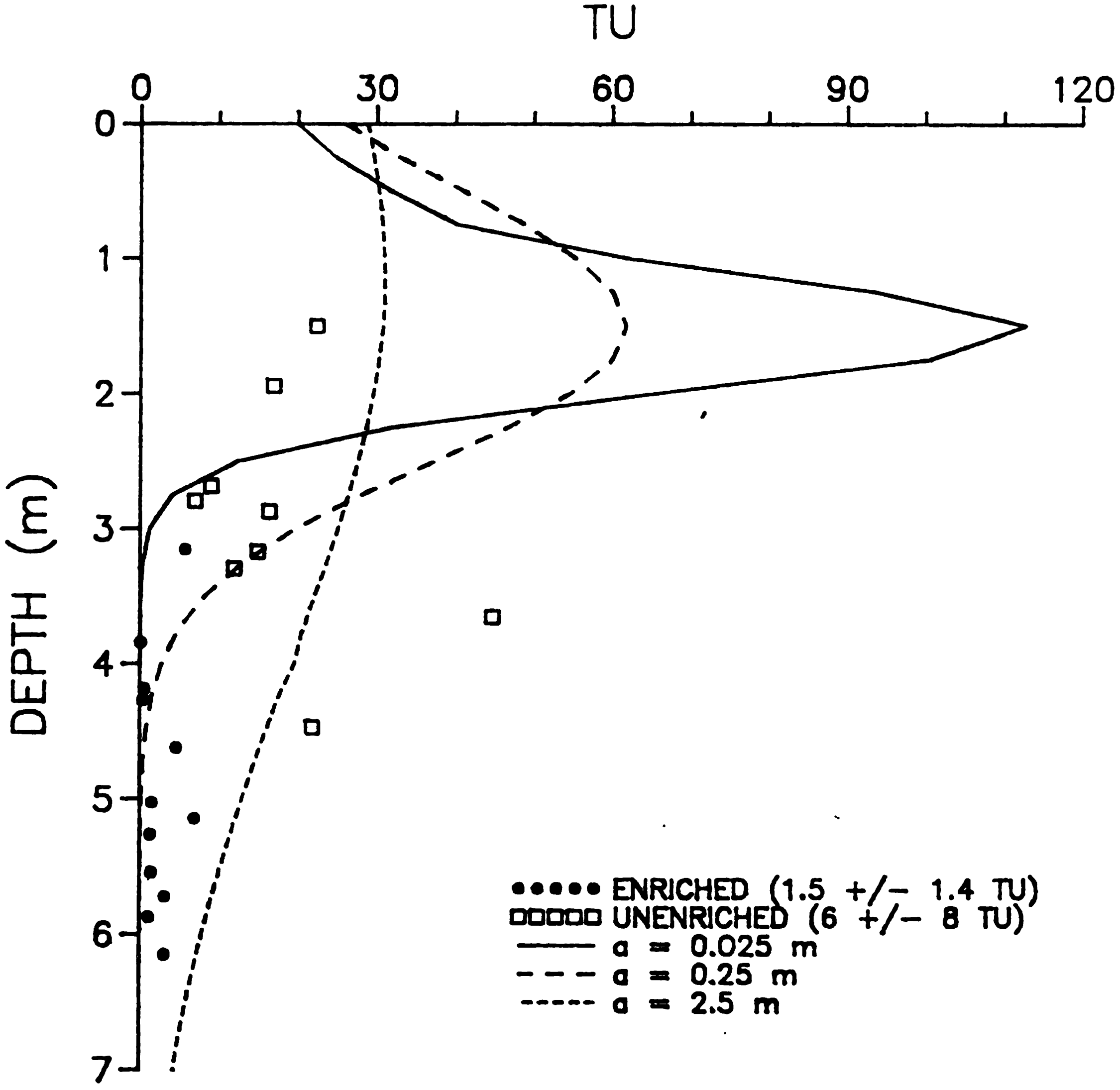

Figure 7. Simulated and observed tritium values in the upper till unit at the facility.

till unit can adequately account for the distribution of tritium. For example, when applying a dispersivity of 2.5 m, few measured concentrations correspond to predicted concentrations and most are significantly greater or less than predicted. Likewise, when a dispersivity of 0.25 m is applied, most measured concentrations are significantly greater or less than predicted.

The simulation generated using a dispersivity value of 0.025 m also does not explain all the tritium data in Figure 7, but it does explain the presence of non-tritiated water at a depth of 3.8 m, especially since the solute transport model assumes matrix flow. The presence of tritiated water below depths predicted can likewise be explained by fracture flow. Such a system has been presented by Williams and Farvolden (1969), Grisak and Cherry (1975) and Hendry (1983a). Also, Grisak and Pickens (1980) have mathematically simulated solute transport in such a system and have demonstrated that diffusive transport is usually dominant in the unfractured matrix of till and advective-dispersive transport is dominant in the fractures.

Although a one-dimensional solute transport model like the one applied in this study does not directly account for fracture flow, its application is justified by its usefulness as a preliminary indicator of the presence of a non-matrix flow system and by the minimum amount of data required. However, to accurately simulate the movement of solutes through deposits such as fractured tills, especially if tills are to be considered for containment of hazardous or low-level radioactive waste, solute transport models like the one developed by Grisak and Pickens (1980) should be applied. Such models normally require information about fracture aperture, spacing, and flow velocity, as well as diffusion and distribution coefficients, and porosity for the matrix material. It is probable, however, that the acquisition of such information would be considerably less difficult than the calibration of such models against field data.

CONCLUSION

The concentration of tritium in 40 ground-water samples collected from two till units and underlying bedrock in southeastern Michigan was found to range from 0 to 44 TU. Bomb tritium was identified in samples at depths of 1.5 to 42 m below the water table while pre-bomb tritium was identified in samples from depths of 5.0 to 54 m. The distribution of tritium in the ground-water reservoir of the upper till unit was simulated using a one-dimensional solute transport model which assumes matrix flow. Based on the shallowest occurrence of non-tritiated water, the dispersivity value of the matrix flow system in the upper till unit was found be less than 0.025 m. Bomb tritium penetration to depths beyond those predicted by the model is explained by the presence of a fracture flow system in the tills.

The results of this study demonstrate that the tritium distribution observed in Michigan tills is similar to that observed in tills in the Great Plains region and that further study of these deposits is required if they are to be used for containment of low-level radioactive or hazardous waste.

APPENDICES

APPENDIX A

REGIONAL GEOLOGIC ANALYSIS

More than 70 bedrock water well records within a 3.5 km radius of the study area were examined to define regional trends in the bedrock surface, bedrock potentiometric surface, drift thickness, bedrock surface composition, and height of potentiometric surface above bedrock surface.

Local bedrock was found to lie between 200 and 220 m in elevation and contain slopes of 12 to 20 m per km. However, no regional trends in bedrock surface are observed (Figure 8).

Approximately 60% of the wells indicate shale as the uppermost bedrock unit while the remaining 40% of the wells encountered sandstone as the uppermost bedrock formation (Figure 9). Although sandstone is encountered more toward the eastern and southeastern parts of the study area, it would be speculative to draw a contact based on this data because the Paleozoic formations are rather variable in their composition and irregular bedrock topography could explain some of the apparent lateral variability. The possibility of a contact in this area, however, should not be ruled out completely because regional maps indicate that a Saginaw-Marshall contact runs beneath southeastern Gaines Township. Apparently, the Michigan Formation is not represented in this area.

Local drift thickness ranges from more than 50 m in the southwest to less than 30 m in the northeast (Figure 10). Although drift thickness is largely a function of bedrock topography when dealing with a planar ground surface, a gradual increase in ground surface elevation to the south appears to account for the increasing drift thickness in that direction.

The local drift consists predominantly of clay with subequal amounts of silt, sand, and gravel. Most well records indicate the presence of 3 to 5 m of brown clay at the surface underlain by thick gray clay with occasional sand and gravel lenses. The brown and gray clay probably represent zones of oxidized and unoxidized material, repsectively (Williams and Farvolden, 1969; Grisak et al., 1976; Desaulniers et al., 1981; Hendry, 1982; Keller et al., 1986; Cravens and Ruedisili, 1987).

A north-south oriented surface water divide, located approximately 2 km southwest of the study area, separates the Flint River drainage basin to the east from the Shiawassee River drainage basin to the west. Locally, Kimball Drain removes any water east of the divide and Cargill Creek drains areas west of the divide. Drainage in the area is improved through extensive use of tile fields and drains.

Local ground water supplies include thin, shallow (10-20 m deep) sand and gravel layers within the thick clay sequences. These sand and gravel bodies may be related to the middle sand unit in the study area. These aquifers are typically confined and produce less than 10^{-3} m^3/s. The Saginaw Formation is the principal aquifer in the bedrock, producing water from fractured interbedded shale-sandstone sequences at the bedrock surface. The confined conditions of the Saginaw are attested to by the level of the water above bedrock surface which ranges from 50 m in the south to less than 30 m in the north (Figure 11). The bedrock potentiometric surface slopes to the north with a horizontal hydraulic gradient of 0.005 (Figure 12).

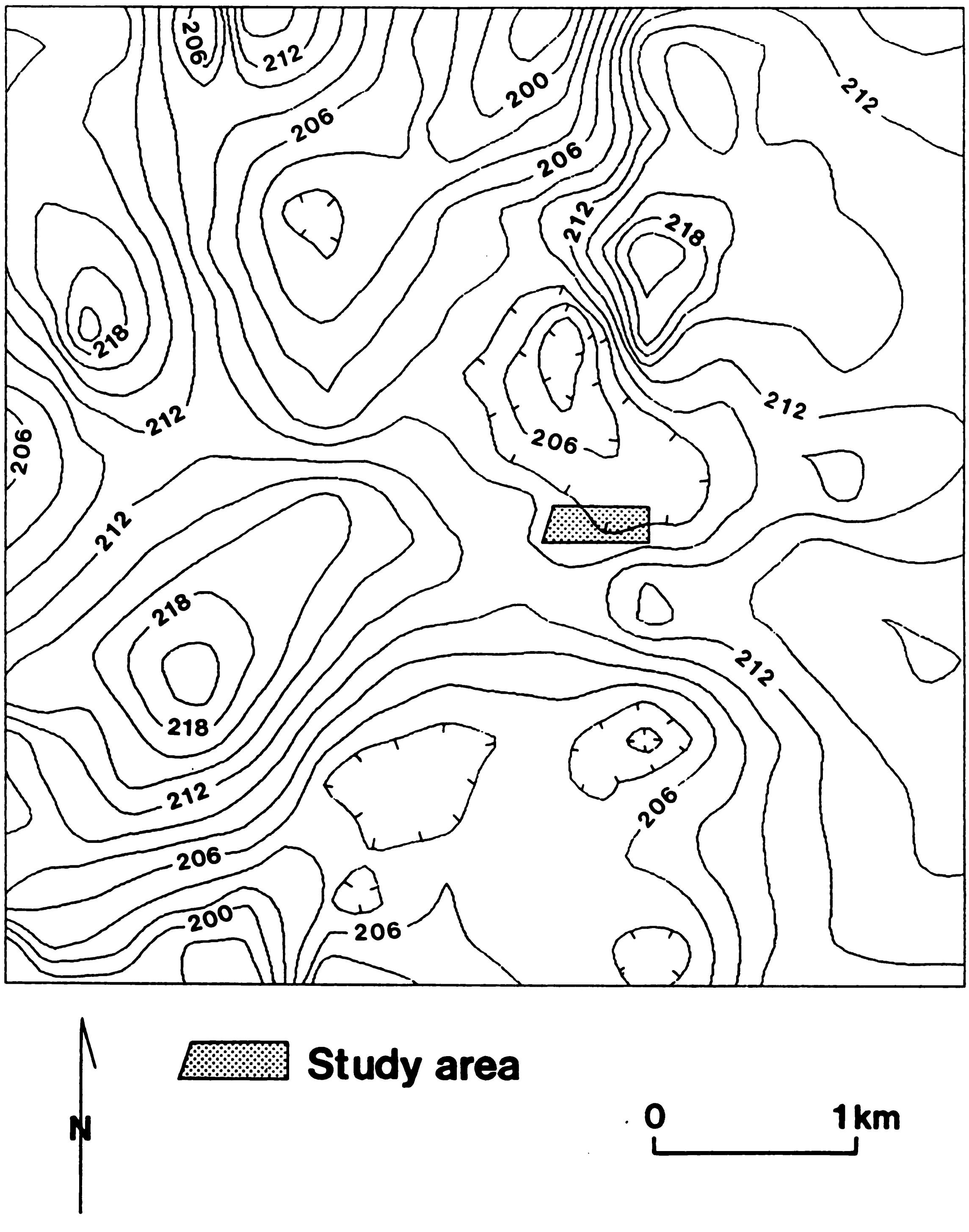

Figure 8. Regional bedrock surface contour map (contour interval = 2 m).

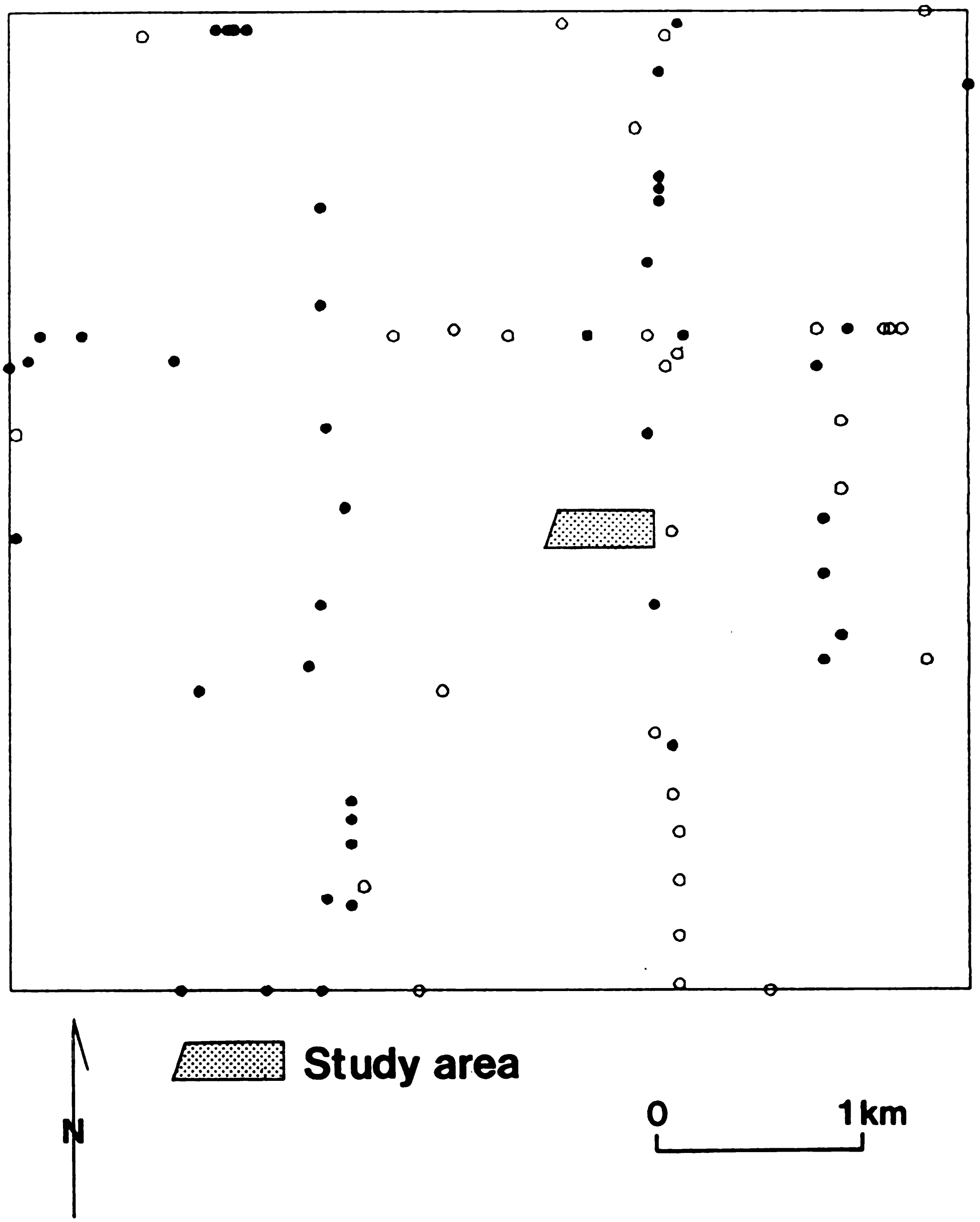

Figure 9. Regional bedrock surface lithology map (filled circles- shale, open circles- sandstone).

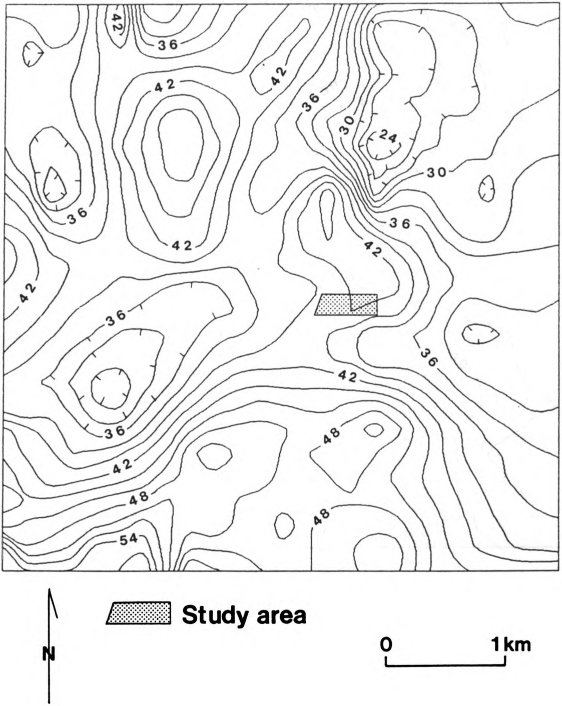

Figure 10. Regional drift isopach map (contour interval = 2 m).

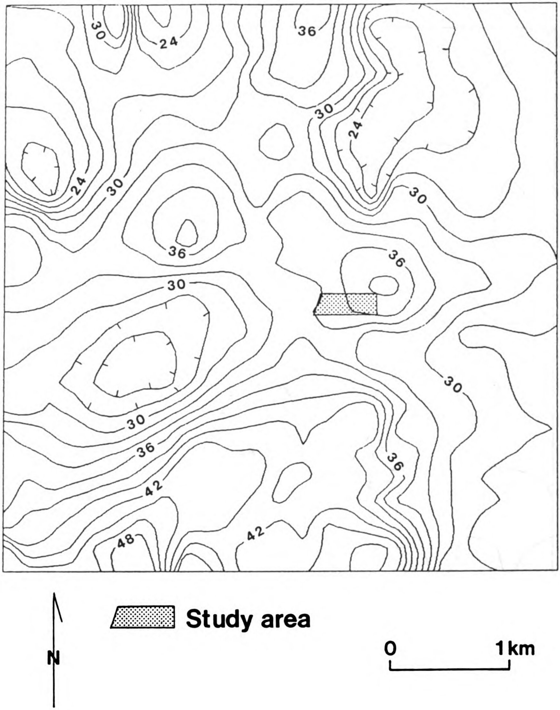

Figure 11. Regional map showing height of bedrock potentiometric surface above bedrock surface (contour interval = 2 m).

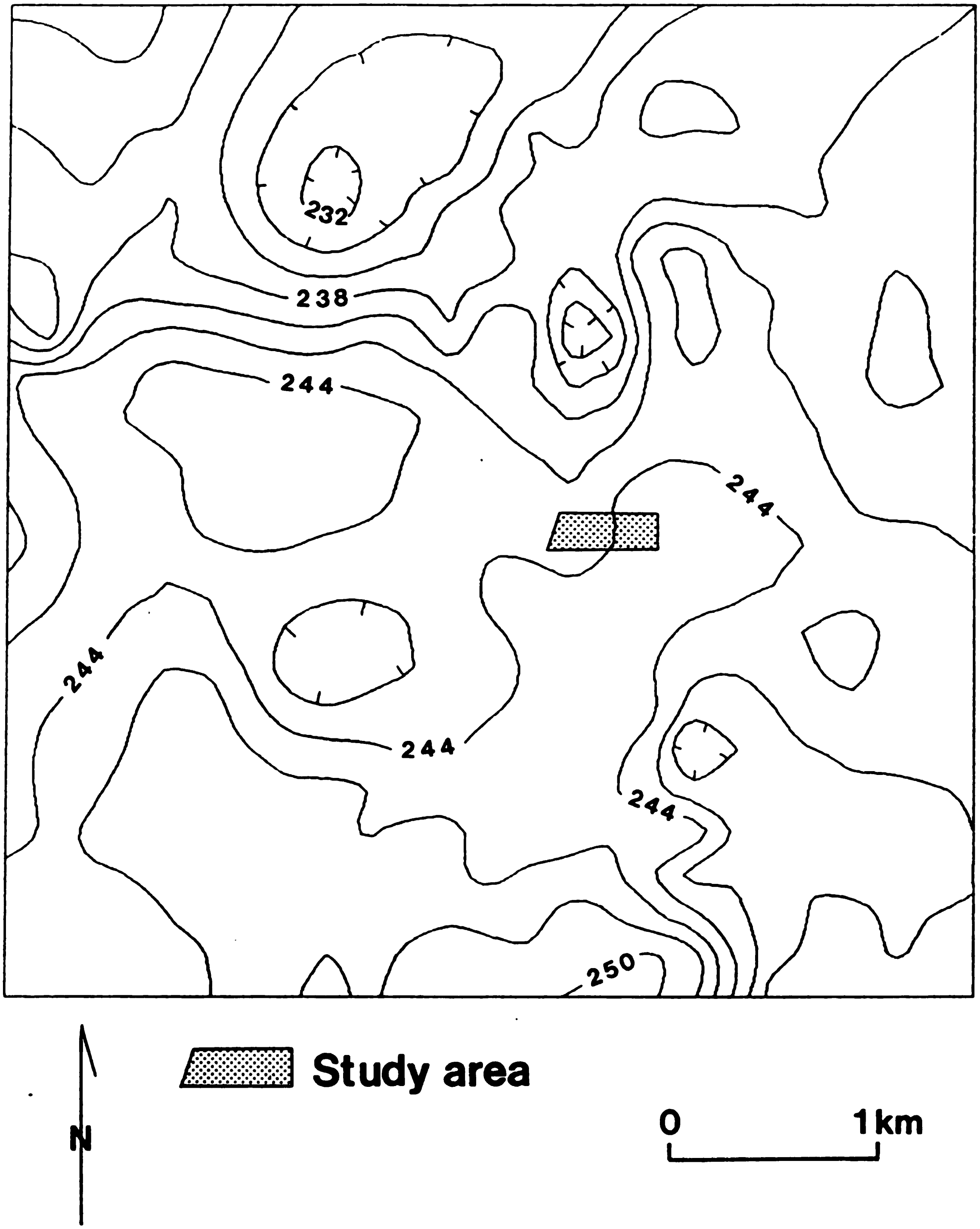

Figure 12. Regional bedrock potentiometric surface map (contour interval = 2 m).

APPENDIX B

CROSS SECTIONS THROUGH THE STUDY AREA

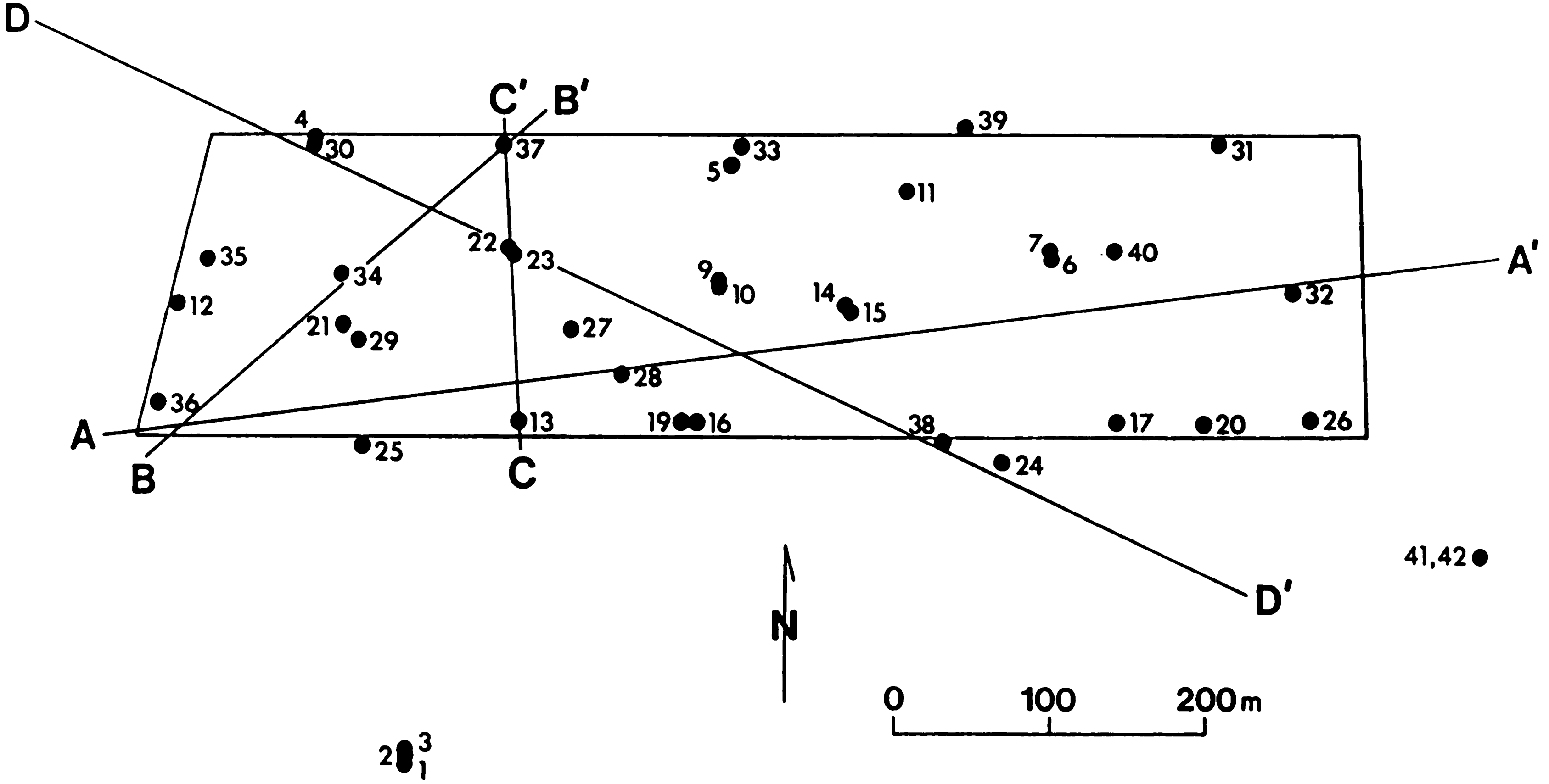

Figure 13. Map showing location of wells sampled and location of cross sections in relation to the Berlin & Farro site boundary.

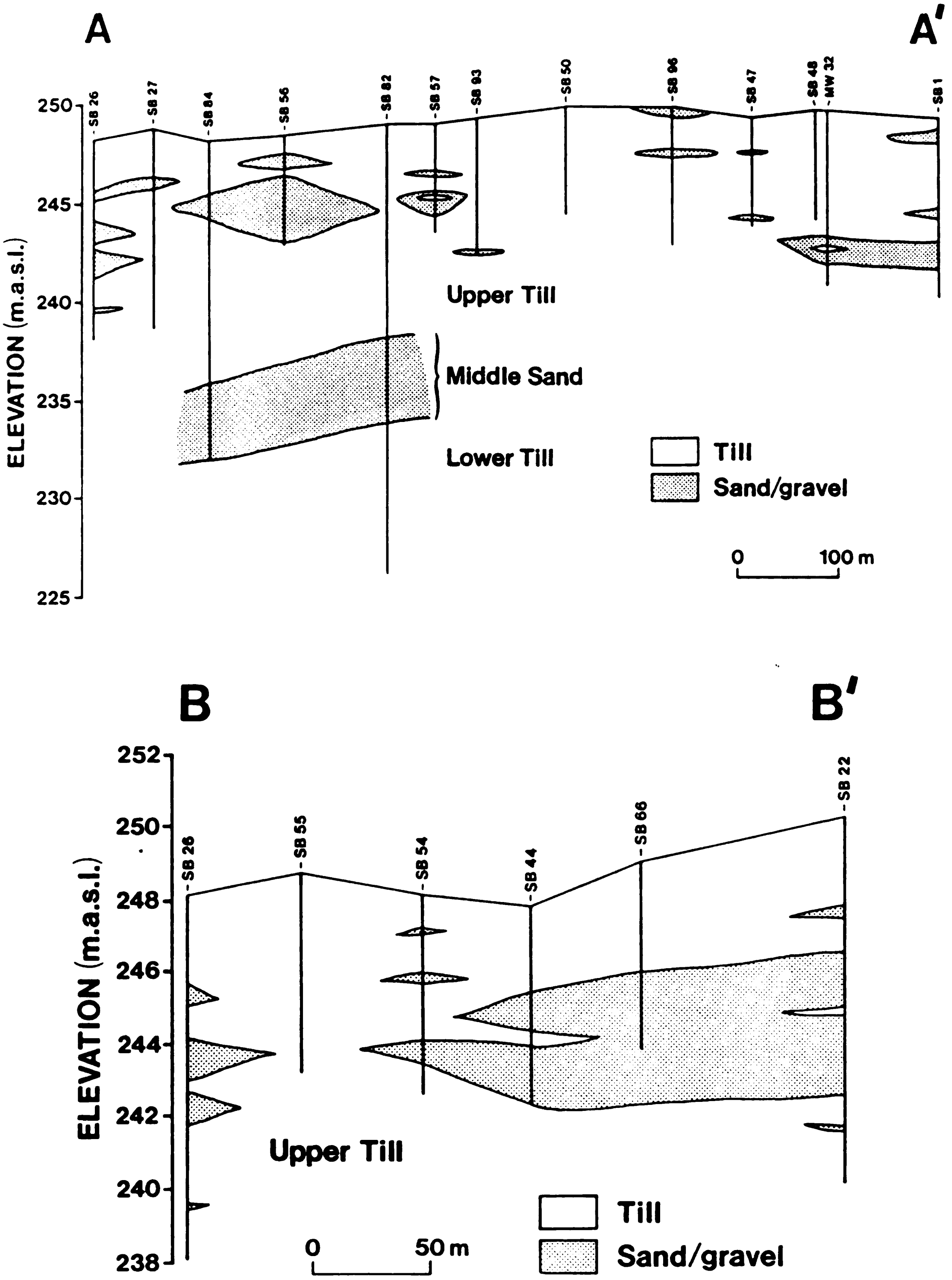

Figure 14. Cross sections A-A' and B-B'.

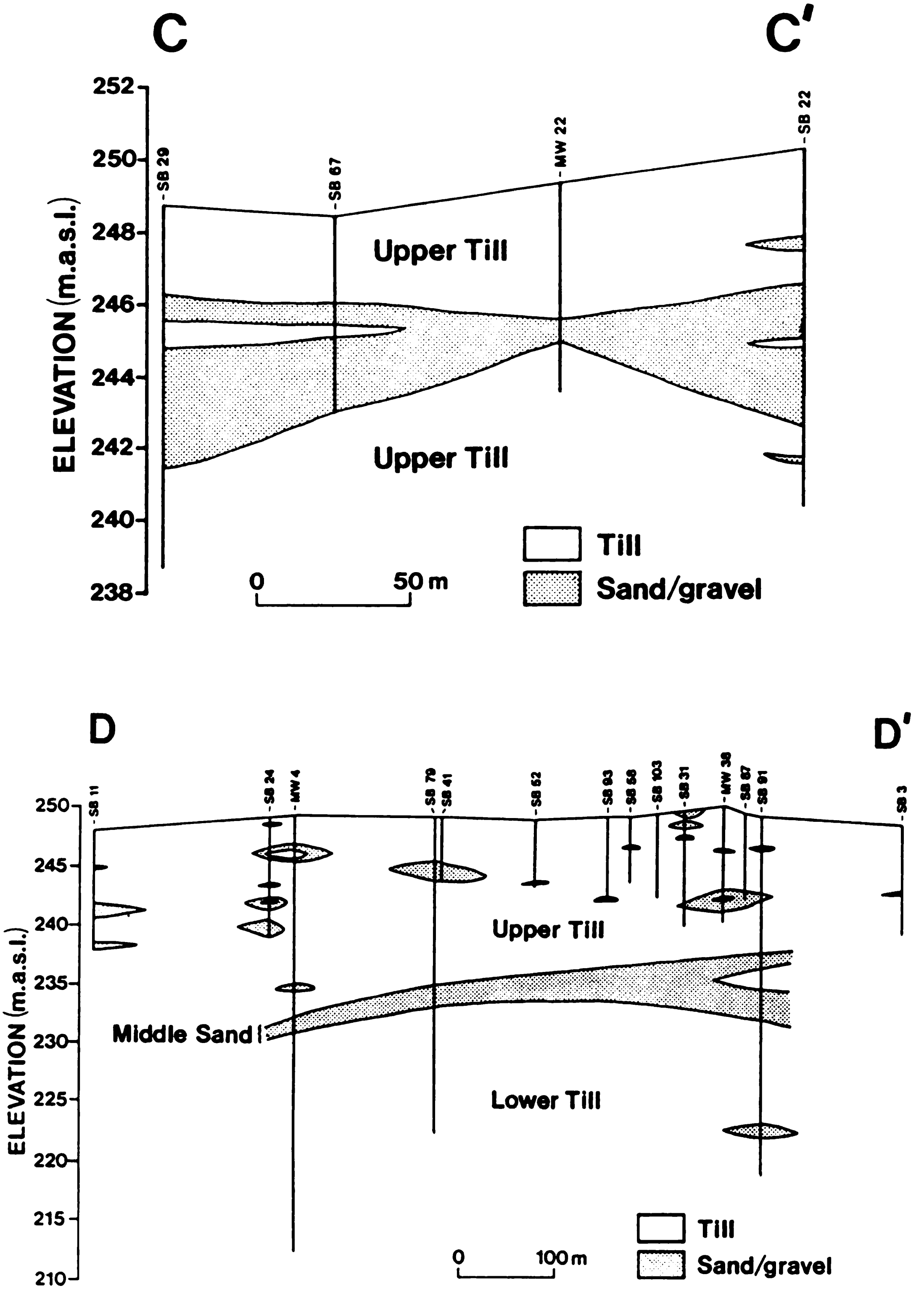

Figure 15. Cross sections C-C' and D-D'.

APPENDIX C

SIMULATED HYDRAULIC HEAD DISTRIBUTIONS

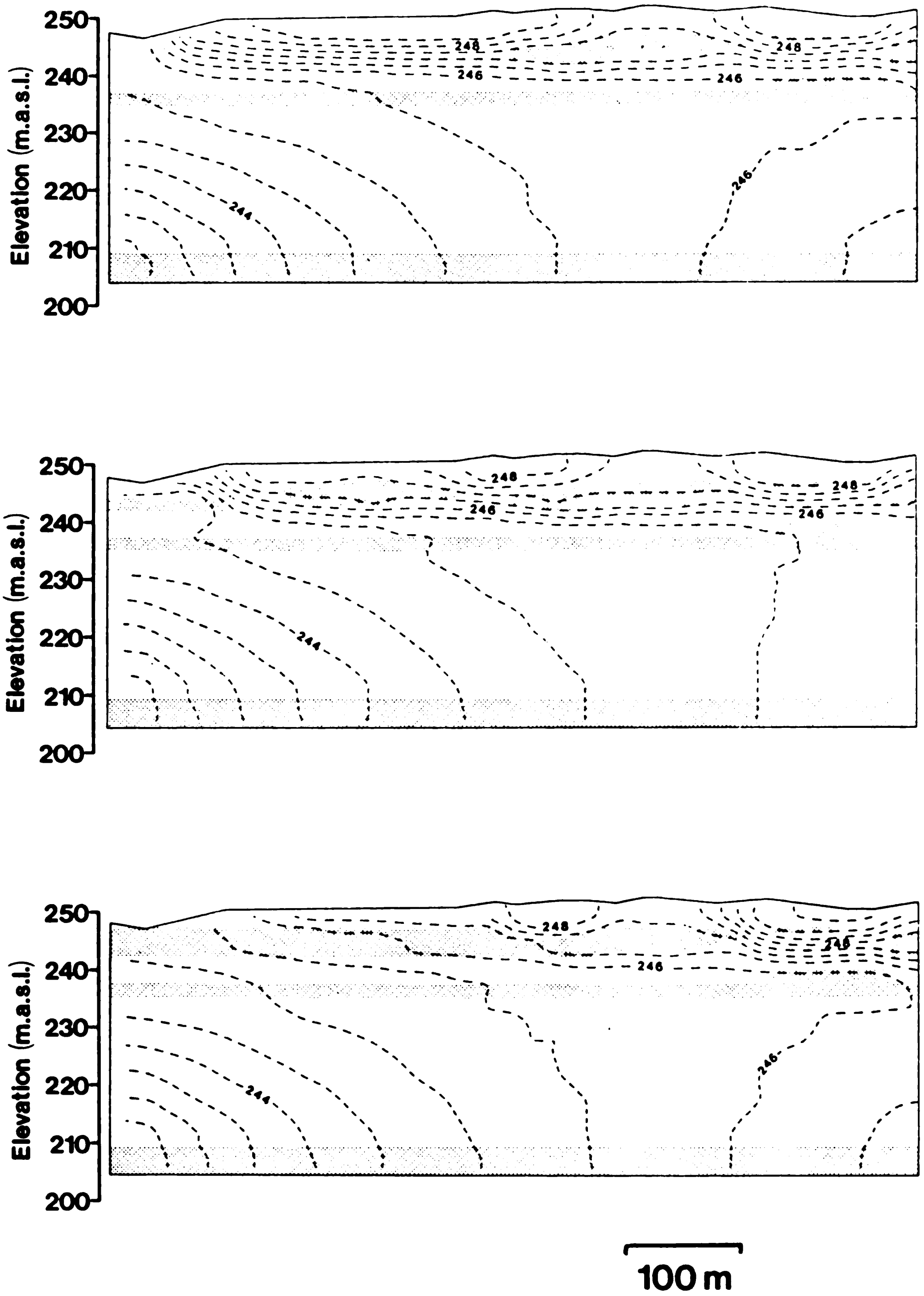

Figure 16. Figure showing the effect of varying lithologies on simulated head distribution along cross section X-X' in Figure 4 (contour interval = 0.5 m).

APPENDIX D

LATERAL TRITIUM DISTRIBUTION

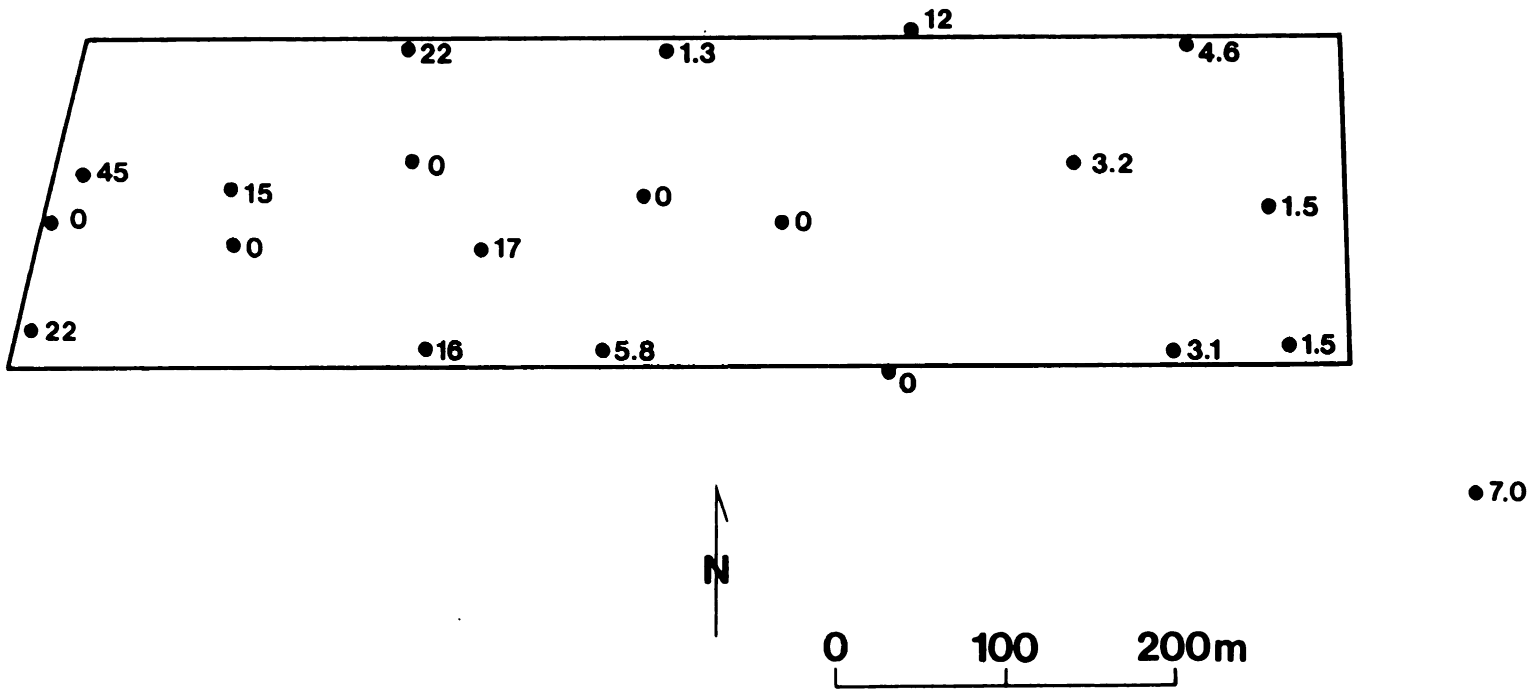

Figure 17. Lateral distribution of tritium within the upper till unit (all values in TU).

APPENDIX E

SITE SOIL TYPES

The soils at the BFLIF are representative of the Del Rey-Lenawee association and are level to gently sloping, somewhat poorly drained and poorly drained silt loams and silty clay loams having a silty clay loam substrate (Holcomb, 1972). Soils of the Metamora series and the Selfridge series are also represented at the site. The Metamora series consists of nearly level to gently sloping soils formed in sandy and loamy deposits underlain by light sandy clay loam. The Selfridge series consists of somewhat poorly drained, nearly level to gently sloping loamy sands having a silty clay loam substrate. The characteristics of each soil type, as described in the Genesee County soil survey of 1972, are summarized below (Holcomb, 1972).

The Del Rey silt loam is the dominant soil in the undulating areas of the heavier textured till plains and borders of lake plains. Typical areas have short, complex slopes, wet depressions, and random drainage ways that empty into well-defined drainage channels. These soils have a moderate shrink-swell potential, and grain size analysis indicates that 55-90 percent pass sieve No. 200. As these soils are nearly level to gently sloping, runoff is slow or very slow and some depressions are ponded. Permeability is moderately slow to slow. Del Rey soils are found in the eastern half of and along the southern border of the site, as well as in the extreme northwest corner of the site.

Lenawee silty clay loam is extensive on lake plains but may be found on till plains. It is developed in drainage channels within areas of undulating soils and is generally associated with the higher, somewhat better drained Del Rey soils. The Lenawee soils have moderate shrink-swell potential, and 85-90 percent pass sieve No. 200. As these soils are level or nearly level, runoff is very slow or ponded, and the high content of fine silt and clay results in moderately slow or slow permeability rates. These soils occur in isolated bands in the western, northern, and southeastern parts of the site.

The Metamora sandy loam occurs on till plains and outwash plains and occupies low, smooth ridges and knolls and short slopes of drainageways. The shrink-swell potential of these soils is low to moderate, and, depending upon the horizon analyzed, 20-90 percent pass sieve No. 200. Permeability is moderately rapid in the upper layers but moderate to moderately slow in the deeper, finer textured material. Metamora soils occupy a small area in the northwest quarter of the site.

Selfridge sandy loam is developed in outwash and may be transitional between the till plains and lake plains. The soil occurs on hills, knolls, and short slopes bordering intermittent upland drainageways. The shrink-swell potential of these soils is low to moderate, and, depending upon the horizon analyzed, 15-90 percent pass sieve No. 200. These sandy, nearly level or gently sloping soils have slow or very slow runoff and readily absorb most of the rainfall. The upper sandy layers have moderately rapid permeability, but the finer textured underlying material has moderately slow permeability. The Selfridge soils are found in the northeast corner of the site.

A zone of brown and gray mottles at various depths in the soil profile records the fluctuation in water level. This mottled zone is typically underlain by a brown zone which marks the upper and lower limits of oxidizing conditions below the water table. Beneath the brown zone, reducing conditions below the water table are indicated by a gray zone. Although the mottled zone is usually within a meter or two of the ground surface, the contact between the base of the brown zone and the underlying gray zone has been recorded as deep as 5 m in some soil borings.

APPENDIX F

TRITIUM SYSTEMATICS

A variety of tracers can be used to determine rates of water movement in geologic systems. Traditionally, tracers have been categorized according to detection means. Dyes are detected by color, electrolytes are detected by conductivity, and radioisotopes are detected by nuclear radiations. Ideally, a tracer should accurately describe water flow for the system under study. To this end, the tracer should not appreciably change the hydraulic or chemical properties of the water, and it should not alter the transmission characteristics of the medium through which the water is flowing. Hydrogen isotopes meet these requirements because they are part of the water molecule, and therefore, do not appreciably change the properties of water or the porous medium. The additional advantage of tritium is its radioactivity which can, with proper instrumentation, be detected in minute quantities. Tritium occurs naturally in the water cycle and is continuously, in time and space, added to the ground-water system.

The natural production of tritium takes place primarily in the atmosphere, but small amounts are produced in the lithosphere and hydrosphere. Solar radiation or reaction of cosmic rays with other gasses in the upper atmosphere produces neutrons which cosmically radiate ^{14}N to produce ^{12}C and ^{3}H (tritium). The rate of production of tritium is greatest at a height of approximately 10 km and for neutrons of 15-20 MeV, and its mean lifetime in the stratosphere is about 2 years (Vinogradov et al., 1968). The tritium so formed combines readily with oxygen atoms in the stratosphere and mixes with molecular water in the atmosphere and on the surface of the earth. Analysis of natural water for tritium is based on detection of the beta radiation which accompanies the radioactive decay of ^3H (tritium) to ^3He (helium). The utilization of tritium as a tracer assumes that it is being produced at a constant rate in the upper atmosphere and that it has reached a state of equilibrium between production and decay.

Inception of atmospheric nuclear weapons testing in the early 1950's served to introduce large quantities of artifical tritium into the hydrologic cycle. It is estimated that prior to 1953, cosmic-ray produced tritium concentrations were in the 5-10 TU range (Payne, 1972), although more recent studies suggest that this value may have been as low as 3 TU (Robertson and Cherry, in press). A water of concentration 1 TU has 1 tritium atom for every 10^{18} hydrogen atoms. The tritium unit is useful because it represents the order of magnitude of tritium in natural waters prior to 1953, and it is the approximate limit of activity detectable using present day counting systems.

Artificial tritium input into the hydrologic cycle continued for about 10 years during which time tritium concentrations in precipitation increased to levels which were as much as four orders of magnitude greater than pre-1953 levels. It is estimated that during the 10-year period prior to the test ban treaty of 1962, approximately 200 kg of artificial tritium were added to the planet. Calculations based upon formation rates of natural tritium suggest that the planet contained less than 2 kg of tritium prior to 1953 (Vinogradov et al., 1968).

The use of tritium in hydrologic investigations was first proposed in 1953, and shortly thereafter came the realization that tritium could be used to determine the age of ground water relative to 1953 (Libby, 1953). Waters which enetered the ground after 1953 have tritium concentrations which may be several orders of magnitude higher than waters which entered the ground prior to 1953. Since the half-life of tritium is 12.43 years (Mann et al., 1982), and almost three half-lives have elapsed since 1953, the waters which entered the ground before 1953 should presently have tritium concentrations of less than 0.4 TU. This pre-1953 water is commonly referred to as "dead" or "pre-bomb" water whereas post-1953 water is referred to as "tritiated" or "bomb" water.

Tritium has been applied as a tracer for calculating circulation and residence times (Begemann and Libby, 1957; Brown, 1961; Dincer and Payne, 1971; Hendry et al., 1983b), ground-water age (von Buttlar and Wendt, 1958; von Buttlar, 1959; Nir, 1964), storage (Eriksson, 1958), recharge rates and flow velocities in coarse-grained materials (Allison and Hughes, 1972; Allison and Holmes, 1973; Atakan et al., 1974; Dincer et al., 1974; Vogel et al., 1974; Allison and Hughes, 1975; Rehm et al., 1982; Andres and Egger, 1985; Knott and Olimpio, 1986; Delcore and Larson, 1987), recharge rates and flow velocitites in fine-grained materials (Hendry, 1982; Hendry, 1983a; Bradbury, 1984; Keller et al., 1986; Cravens and Ruedisili, 1987; Hendry, 1988), diffusion rates in fractured materials (Foster, 1975), and dispersion in coarse-grained materials (Rabinowitz et al., 1977; Egboka, 1983; Larson et al., 1987; Robertson and Cherry, in press).

APPENDIX G

SAMPLE PREPARATION FOR TRITIUM ANALYSIS

PRE-DISTILLATION

The intial step in the analysis of ^{3}H consists of the complete distillation of the sample to remove all dissolved solids and suspended particles. The system used consists of a boiling flask, Kjeidahl bulb, Allihn condenser, and receiving flask (refer to Delcore, 1985 or Regalbuto, 1987 for an illustration of the apparatus). The system is first dried under vacuum, and once drying is complete, dry air is admitted to the system. Approximately 70 g of glass beads are placed in the boiling flask to insure more even boiling of the sample, and afterwards, 225 ml of undistilled sample are poured into the flask. Then, 0.25 g of copper powder are added to the sample to aid in retention of sulfur, the radioisotope of which is a beta-emitter and whose energy emission spectrum overlaps that of tritium. Vacuum is reapplied to the system and removed when bubbling of the sample, due to degassing, stops. Dry air is readmitted to the system, the line is connected to a pressure compensator, and heat is applied to begin distillation. If, during distillation, the pressure compensator indicates excess pressure, vacuum is applied momentarily. When the level of the sample in the flask reaches the top of the glass beads, the heat is removed to allow any water in the Kjeidahl bulb to drain. The receiving flask, with the distilled sample, is removed from the apparatus and sealed from the atmosphere. To prevent any possibility of sample cross-contamination, a heat source is lightly applied to the Kjeidahl bulb and connecting glass, and air is pumped through the condensing tube until the system is completely dry.

For direct counting, 10 ml of this pre-distilled sample are pipetted into a plastic liquid scintillation vial to which 13 ml of scintillation cocktail are added, and the vial is placed in the dark for one to two hours before counting. Direct counting is done in groups of twelve samples and consists of one standard (40 DPM/ml), two dead water samples to monitor background, and nine unknown samples.

ELECTROLYTIC ENRICHMENT

Enrichment of the samples is necessary because specific tritium activities in natural waters are very low. Electrolytic enrichment is used because it has been proven to yield reproducible results and is a simple process in which large numbers of samples can be enriched at the same time (Florkowski, 1981).

The electrolysis system consists of: gas exhaust lines, a low-temperature bath, Ostlund electrolysis cells, electrodes, and a power supply. Electrolysis is simultaneously performed on twelve samples of which ten are unknown samples, one is a standard (4 DPM/ml), and one is a sample of dead water. The dead water is obtained from a 600 m deep well at a fish hatchery in Thompson, Michigan, and a supply of the water is distilled in the tritium laboratory prior to use with electrolysis. A 160 ml quantity of distilled sample water is transferred to an Ostlund cell, and to this, a 5 ml aliquot of electrolyte is added. The electrolyte used is 4 molar NaOH solution with dead, distilled water as the solvent. The cells are set in the water and glycol bath, and the electrodes are put into the cells and connected to the electrical wires. The iron electrode is the cathode and the nickel electrode is the anode. The cells are capped, connected to the exhaust fan by way of gas exhaust lines, and allowed to equilibrate with the temperature of the bath for about 15 minutes. The electrolysis process is most efficient at low temperatures, and therefore, the water bath and cells are kept at 1 degree Centigrade (Hoffman and Stewart, 1966). To insure that an equal amount of current will pass through each cell, the electrodes are connected in series to the power supply unit.

The current used is calculated based on a total electrode area of 34 square centimeters and a maximum current density of 0.09 amps per square centimeter (Ostlund and Werner, 1962). Since electrolysis efficiency decreases as the electrolysis temperature increases, and since heat dissipation is a function of the water level inside the cell, it is necessary, as the volume of sample in the cell decreases, to limit the amount of heat produced by electrolysis. Therefore, the current supplied to the electrodes is decreased as the volume of sample in the cells decreases, and a circulation pump is used in the bath to provide circulation of the coolant. When the volume of the samples in the cells has been reduced to between 11 and 13 ml, the power unit is shut off, the electrical and exhaust connections are removed, and, to minimize atmospheric contamination, capped distillation heads are substituted for the electrolysis heads.

POST-DISTILLATION

Upon completion of electrolysis, 11 to 13 ml of enriched sample usually remain in the cell. This water must be quantitatively removed from the cell and separated from the NaOH. These two steps are accomplished by freeze-up distillation. The post-distillation line consists of Ostlund cells, modified distillation heads, weighing bulbs, liquid nitrogen, pressure compensator (balloon), vacuum, and dry air (Delcore,1985; Regalbuto, 1987). The weighing bottle, modified distillation head, and balloon are weighed before and after each post-distillation.

The Ostlund cells are removed from the cooling bath and connected to the weighing bulbs via the modified distillation heads. The balloon is mounted onto the stem of the distillation head and secured with a rubber band. Vacuum is then applied, and if the system appears vacuum-tight, the vacuum is shut off at the stopcock. The weighing bottle is submerged in the liquid nitrogen to a level approximately 2 cm below the point at which the bottle neck begins to widen. One flexible heating coil is wrapped around the lower part of the cell and heated to 60 degrees Centigrade while the other heating coil is wrapped around the upper part of the cell and the distillation head and heated to 100 degrees Centigrade. During heating, the point at which the bottle neck begins to widen should be the transition zone between the hot bottle neck above and the cold bulb below; some adjustment of the liquid nitrogen level will probably be necessary. Heating is continued for an additional 30 minutes beyond apparent dryness, during which period it will probably become necessary to submerge the weighing bottle another 1-2 cm into the liquid nitrogen.

When heating has been completed, the weighing bottle is weighed to determine the exact amount of sample in it. Lastly, 10 ml of the enriched, post-distilled sample are pipetted into a plastic liquid scintillation vial in preparation for liquid scintillation counting.

APPENDIX H

LIQUID SCINTILLATION ANALYSIS

INTRODUCTION

The concentration of natural tritium in ground water samples is difficult to determine because it is often low (less than 1 TU) and because the energy of the beta emission spectrum of tritium is low (less than 18.6 keV). Traditionally, internal gas or liquid scintillation counters have been used to measure the low concentrations. Although internal gas counting yields low background counting rates and is very sensitive while not requiring enrichment, conversion of the sample to hydrogen gas and destruction of the sample itself are just two of the disadvantages with this generally time consuming and complicated procedure. Liquid scintillation counting requires that the water sample be mixed with a liquid scintillation solution (cocktail), and, because this procedure is known to yield reproducible results while being far simpler, it was chosen as the counting technique for this study.

THEORY OF LIQUID SCINTILLATION COUNTING

Liquid scintillation counting is an analytical technique which is defined by the incorporation of a radionuclide into uniform distribution with a liquid chemical medium capable of converting the kinetic energy of nuclear emissions into emitted photons (Packard, 1987). The rate that these light scintillations are produced within a finite time period is proportional to the rate of radioactive decay, and the number of photons or intensity of the light scintillations is proportional to the energy of the decaying beta particle (Beckman, 1976).

Radioactive decay of an element is the initial step in the scintillation process and is the result of an imbalance between the nuclear components of the atom, the proton and neutron. This imbalance, which results in an unstable elemental condition, eventually yields to rearrangement and subsequent energy release in the form of radiation. For tritium, the radiation emitted consists of a beta particle, which is an electron originating in the nucleus, and a neutrino. The energy of the radiation is characteristic of the radionuclide and, in the case of tritium, it is 18.6 keV. This energy is shared between the beta particle and the neutrino and, in any particular radiation, the beta particle can contain all, some, or none of this energy (Packard, 1987).

The second step in the scintillation process entails efficient transfer of the beta particle energy to the cocktail. This requires a cocktail that consists of a solvent and solute and acts as a solvent for the sample material. While solvent molecules, in an excited state, are not readily recognizable, they are, nontheless, capable of transferring energy from one another and to the solute molecules. This transfer of kinetic energy to the solute results in flourescence of the solute and emission of light energy as photons (Packard, 1987).

The final step in liquid scintillation analysis involves the detection of the emitted photons and the conversion of light energy into an electrical signal. This conversion can be achieved with a device known as a photomultiplier tube (PMT), and a pair of these, one on either side of the sample, is usually employed in a scintillation counter. If both PMTs record an event over a very short time interval, the machine circuitry is instructed to record that event as a true count and to convert the energy of the event to a digital value. As a result of each PMT producing a signal from the same event, the geometrical location of the event within the vial becomes less significant (Packard, 1987).

FACTORS AFFECTING COUNTING EFFICIENCY

Liquid scintillation counting of tritium decay events is an inefficient process and the result of various inherent interferences. These interferences include other solutes within the sample or cocktail, photoluminescence, vial material, reaction of the cocktail with the vial material (wall effect), type and volume of cocktail, and background radiation.

The most important type of interference internal to the sample is quenching, and it can result in a loss of counting efficiency exceeding 50 percent and a shift of the energy spectrum toward lower energies. The three types of quenching, caused predominantly by the cocktail, include photon quenching, in which there is incomplete transfer of beta particle energy to solvent molecules, chemical quenching, in which energy is lost as it is transferred from solvent to solute, and color quenching, in which light photons are attenuated in the solution (Packard, 1987). The energy loss in chemical quenching takes place when impurities quench the sample by either competing with the solute for energy transfer or by chemically making the solute less reactive to energy transfer (Beckman, 1976). Most sample material causes little or no quenching as any quenching agents in the sample are removed by distillation prior to counting; however, in solute-rich samples (e.g. brines), some quenching agents may pass through the distillation process. These effects are generally insignificant when compared with quenching caused by the cocktail.

Photoluminescence occurs when the cocktail is activated by sunlight or flourescent lights in the laboratory. The decay of photoluminescence appears to be a function of the severity of exposure but is usually quite rapid (less than 0.1 hr) (Packard, 1987). This type of interference can best be avoided by storing the samples in dark areas, loading them into the machine while the room is dark, and keeping the smoked glass cover on the machine closed at all times. This phenomennon was recorded on several occasions with blank samples which, having been exposed to sunlight during transport, yielded abnormally high initial readings followed by gradually decreasing readings to a stable level.

The influence of the vial composition on the overall background counting rate was determined by measuring background with polyethylene and borosilicate vials that contained dead water. The findings indicated that background readings were higher with the borosilicate vials, and therefore, polyethylene vials were chosen for this study.

When polyethylene scintillation vials are used, the counting accuracy of the sample is affected by the reaction of the cocktail with the vial material. Long-term background measurements using blank water tend to increase with time as the cocktail reacts with the vial material, but the same trend is not observed with borosilicate vials. The smell of cocktail emmanating from the plastic vials after one or two days suggests that the vial walls are not impermeable to fluid and/or vapor movement. Corroborating these findings is the observation that sample vials, which have been sitting on the shelf for several months, have lost about one-half of their contents, which, incidently, is approximately equal to the amount of cocktail added to each vial. Borosilicate vials which, in some cases, were more than one year old, did not show any appreciable loss of contents. The counting efficiency of a sample is also a function of the cocktail type because all cocktails do not use the same solvent and/or solute. Currently, Insta-Gel and Pico-Flour LLT are the two most commonly used cocktails for counting water of low tritium content. Experimentation with the two cocktails indicated that Pico-Flour LLT yields higher efficiencies and lower background values and was, therefore, chosen for this study.

Significant quenching of the sample can also be brought about by varying the sample-to-cocktail ratio in the vial. Excess cocktail serves to reduce efficiency by providing excess solvent molecules which may absorb beta energy but fail to transfer it to the solute molecules. Insufficient volumes of cocktail do not provide enough solvent molecules to transfer the beta energy to the solute molecules. There should exist, therefore, an optimum sample-to-cocktail ratio that maximizes counting efficiency and minimizes lower limit of detection. Experimentation with sample-to-cocktail ratios ranging from 0.3 to 3.0 indicated that a ratio of 0.75 yields excellent efficiency while preserving a low limit of detection. Since the scintillation vials used for this study had a capacity of 23 ml, addition of 10 ml sample and 13 ml cocktail would result in a ratio of 0.77; therefore, this ratio was selected.

External to the sample, fluctuating background radiation is the most important interference because measurement of environmental samples for tritium typically yields values which are slightly above background radiation levels. In this study, background radiation generally comprised more than 75 percent of the total sample counts amassed. For this reason, it is very important to minimize all of the possible interferences internal to the sample.

In order to gain a better understanding of background radiation fluctuations, several long-term measurements of background radiation were made. These indicate that background may vary by as much as 25 percent. Daily cyclical patterns were observed in background levels, but, contrary to conventional thinking, the highest background levels were not always recorded during the day. These variations could also be a function of the daytime activity in the laboratory where the scintillation counter is located. It has been reported that longer term fluctuations in background are indeed real and related to seasonal variation and sunspot activity (Hut, 1986). The intercomparison study also indicates that at most of the laboratories, scintillation counters are placed in the basement so as to minimize background radiation even more.

QUENCH MONITORING AND CURVE GENERATION

Although all samples were distilled prior to counting, quench was initially monitored so as to confirm the efficiency of the distillation process. The Packard Tri-Carb 1500 liquid scintillation analyzer used for this study monitors quench using the transformed spectral index of the external standard (tSIE). After the sample vial has been lowered into the counting chamber, an external gamma source (Barium-133) is momentarily positioned next to the vial and an artificial excitation of the solvent molecules takes place. The resultant Compton spectrum shows a shift toward lower energies when compared with the spectrum of the unquenched standard, and the tSIE value is calculated from this difference. Quench monitoring in this study indicated that the distillation process is indeed effective for reducing the amount of quenching in all samples to a similar level.

A quench curve shows the relationship between counting efficiency and the quench indicating parameter (tSIE) and provides information necessary to calculate the true sample activity of the particular radionuclide. To generate a quench curve, a series of hot standards of various quench are counted and quench is monitored. These standards may be purchased, made in the laboratory, or quench curves may already be stored in the memory of the counter. For this study, a set of quenched standards was made in the laboratory because greater curve resolution was desired in the region encompassing the quench values of the unknown samples. These quenched standards were generated by mixing 4 drops of carbon tetrachloride from a Pasteur pipette and 52 ml of cocktail in a beaker. After stirring, 13 ml of this quenched cocktail were pipetted into a scintillation vial which contained 10 ml of 40 dpm/ml standard. The second standard was made by using 11 ml of quenched cocktail and 2 ml of unquenched cocktail. The third, fourth, fifth, and sixth standards were mixed with 9, 7, 5, and 3 ml of quenched cocktail, respectively and 4, 6, 8, and 10 ml of unquenched cocktail, respectively. These six standards, a standard containing no carbon tetrachloride, and one blank sample were then counted and provide the data for the quench curve. The data was plotted and the equation for the quench curve was defined as the line of best fit.

The study indicated that the pre-distillation process was effective in reducing quench in all samples to a similar level. Therefore, the counting efficiency for a known standard was used to calculate the tritium activity of its respective batch of unknown samples.

COUNTING WINDOW GENERATION

Although the energy distribution of tritium ranges from 0-18.6 keV, the distribution of decay events across this range is not even. Therefore, a series of experiments was conducted to determine the optimum channel setting that would best reproduce standards of known concentration. A 56.6 dpm/ml standard and a blank were counted in 0.5 keV increments, beginning at 0 keV and ending at 9.0 keV. The efficiency of each 0.5 keV increment was calculated and the efficiency of a sum of increments could be obtained by summing the efficiencies for those increments.

The data indicate that, although background intensity is fairly even from 0-9.0 keV, tritium energy distribution is actually centered in the 0-6 keV range. The incremental counts per minute (cpm) of the standard and background across this range were summed and then each of the incremental values was normalized. The 0-0.5 keV part of the spectrum was not used because the amount of efficiency gained by including it would be minimal and because that part of the spectrum could be susceptible to distortion caused by wall effect (Packard, 1987). Three channel settings were tested: 0.6-5.4 keV, 0.8-3.2 keV, and 0.7-4.3 keV. The first window was selected simply because it represents most of the usable part of the spectrum. However, the second and narrowest window was obtained by plotting the normalized cpm for the standard and the blank on a graph of normalized cpm versus keV. Since distribution of the background intensity is fairly even across the 0-6 keV range, a line of best fit was calculated to define the background distribution. The intersection of this line and the normalized cpm curve of the standard define the upper and lower limits of the window. The third window is simply an arithmetic intermediate between the first and second windows.

To test the performance of the various windows, the 100 T.U. standard from the 1986 International Atomic Energy Agency intercomparison study was counted. In addition, several dilutions of the standard were made to determine the performance of the windows at lower tritium concentrations. The results indicate that the best approximation of the true tritium content could be obtained by averaging the values obtained by the three windows. Rarely did all three windows yield the same results; more typically, one window indicated a value 5-10 % too high, another indicated a value 5-10 % too low, and the remaining window indicated the true value. It is anticipated that background fluctuations which occur in the higher energy regions of some windows and not others, result in the inconsistency of window performance.

APPENDIX I

TRITIUM ACTIVITY CALCULATIONS

The formulae used to calculate tritium activities from counting data are described by Wyerman (1978). Counting parameters which are required for calculation of electrolytically enriched tritium standard activities include:

Initial standard volume (ml)	V_o
Final standard volume (ml)	V_f
Initial standard activity (DPM/ml)	DPM_o
Gross standard counting rate (cpm)	CPM_{sg}
Background counting rate (cpm)	CPM_b
Standard counting efficiency (%)	EFF_s

The enrichment factor obtained for the standard is used to calculate the activities of the unknown samples in the particular electrolysis batch.

The background counting rate was determined by counting the sample of blank water which had been electrolyzed with each particular batch. The net standard counting rate (CPM_{sn}) is obtained by subtracting the background counting rate (CPM_b) from the gross standard counting rate (CPM_{sg}),

$$CPM_{sn} = CPM_{sg} - CPM_b.$$

The electrolytic efficiency of the standard (EE_{es}) is determined by multiplying the ratio of the final to the initial volumes of the standard (V_f/V_o) and the ratio of the final to the initial activities of the standard (DPM_f/DPM_o),

$$EE_{es} = (V_f/V_o) * (DPM_f/DPM_o).$$

During electrolysis, gases, which bubble through the liquid and eventually escape from the system, may carry away both water vapor and spray. Variable vapor loss may be the result of uneven cooling of cells in the water bath, electron density differences due to unequal electrode areas, and electrode spacing variations (Hufen et al., 1969). The variable vapor loss is compensated for by the electrolysis fractionation factor (B),

$$B = \ln (V_o/V_f)_{es} / -\ln EE_{es}.$$

The electrolysis fractionation factor of the standard is then used to calculate the electrolysis efficiency of the unknown samples (EE_{us}),

$$EE_{us} = (V_o/V_f)_s^{-(1/B)}.$$

At this point, the gross counting rate of the unknown sample (CPM_{usg}) can be used to calculate its tritium content (TU_{us}),

$$TU_{us} = (CPM_{usg} - CPM_b) / (EE_{us}) * (V_o/V_f)_s * V * EFF_s * K,$$

where $K = 0.0071$ DPM/ml, a TU conversion factor.

Direct count sample tritium contents are calculated with the following equation:

$$TU_{us} = (CPM_{usg} - CPM_b) / V * EFF_s * K.$$

APPENDIX J

TWO SIGMA ERROR DETERMINATION

All samples, enriched and unenriched, were counted to a two-sigma error (confidence level of 95.5 %). Since the gross count rate (CPM_g) is a combination of the net sample count rate (CPM_n) and the background count rate (CPM_b), the uncertainty in the net sample count rate (U_n) can be determined from the uncertainty in the gross count rate (U_g) and the uncertainty in the background count rate (U_b). The following equations are adapted from Packard (1987), and uncertainties are indicated as counts per minute.

The uncertainty in the background count rate (U_b) is defined by:

$$U_b = 2\sqrt{(CPM_b * t_b) / t_b^2},$$

where 2 = sigma error desired and t_b = total counting time of background, in minutes.

The uncertainty in the gross counting rate (U_g) is defined by:

$$U_g = 2\sqrt{(CPM_g * t_g) / t_g^2},$$

where 2 = sigma error desired and t_g = total counting time of sample, in minutes.

Therefore, the uncertainty in the net count rate (U_n) is defined by:

$$U_n = \sqrt{(U_b)^2 + (U_g)^2}.$$

Since the uncertainty in background count rate is an important component of the net count rate uncertainty when dealing with low tritium concentrations, it is necessary to count samples for longer periods of time to insure that background fluctuations are smoothed. Therefore, samples were counted until the returns in certainty from additional counting became minimal. This usually corresponded to a counting time of 480 minutes for the standard and unknown samples and 960 minutes for the blank samples. The twelve-position sample chamber allowed one standard, two blanks, and nine unknown samples to be counted over a four-day period. The lowest limit of detection (LLD) was defined as the minimum tritium concentration at which the net sample count rate (CPM_n) exceeded the uncertainty in the net count rate (U_n).

APPENDIX K

TRITIUM INPUT FUNCTION

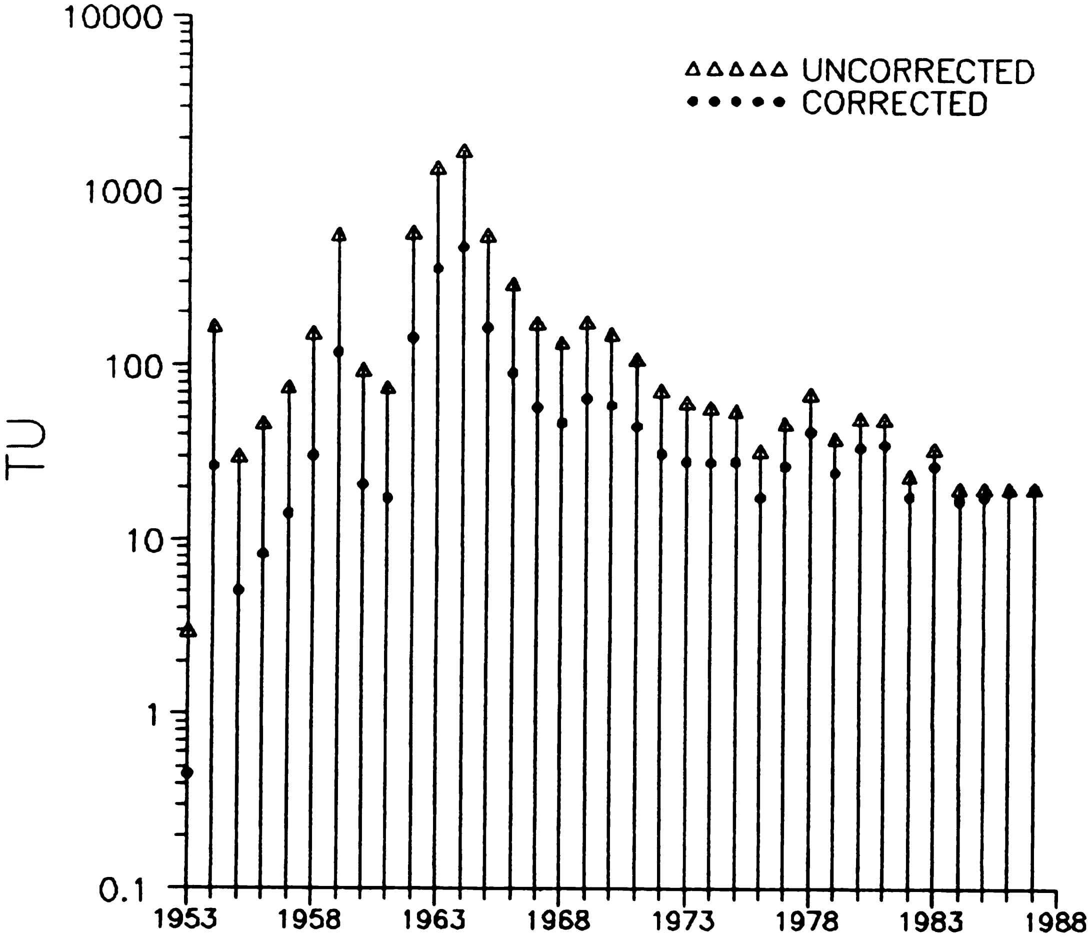

Figure 18. Tritium input function.

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