



122
918
THS

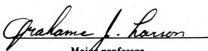


L

This is to certify that the
thesis entitled
AN ISOTOPIC INVESTIGATION OF GROUNDWATER
IN LEELANAU COUNTY, MICHIGAN
presented by
DAVID PHILIP REGALBUTO

has been accepted towards fulfillment
of the requirements for

MS degree in Geology


Major professor

Date May 22, 1982



RETURNING MATERIALS:
Place in book drop to
remove this checkout from
your record. FINES will
be charged if book is
returned after the date
stamped below.

JUL 1 1994 094 242 JUL 16 1994 200 Aug 15 Jan 5	MAR 21 2005 092304 SEP 19 2005	
---	---	--

AN ISOTOPIC INVESTIGATION OF GROUNDWATER
IN LEELANAU COUNTY, MICHIGAN

By

David Philip Regalbuto

A THESIS

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

MASTER OF SCIENCE

Department of Geological Sciences

1987

©1988

DAVID PHILIP REGALBUTO

All Rights Reserved

ABSTRACT

AN ISOTOPIC INVESTIGATION OF GROUNDWATER IN LEELANAU COUNTY, MICHIGAN

By

David Philip Regalbuto

Tritium and the stable isotope ratios of hydrogen and oxygen are used to study the timing, components and rates of recharge to a glacial drift aquifer system.

Bomb-tritiated waters are found from 0 to 25.0 meters below the water table. Dead waters are found below 19.2 meters. The bomb-tritium interface is placed from a minimum of 20.6 to a maximum of 25.2 meters below the water table. These depths are used to calculate an average recharge rate of 17 cm/year.

δD values ranged from -92.2 (0/00) to -82.4 (0/00). $\delta^{18}O$ ranged from -13.03 (0/00) to -11.81 (0/00). These ratios indicate of recharge during the cool months of the year.

A one-dimensional transport code is used to model the influence of lake-effect snowfall on tritium concentrations in groundwaters. The model shows that this input is responsible for low observed tritium concentrations relative to those predicted by the tritium input function.

ACKNOWLEDGEMENTS

The author wishes to extend his gratitude to those who have made this study both possible and rewarding. First of all is my appreciation of the advice and friendship extened to me freely by the thesis advisor, Grahame J. Larson, who on many occasions has gone the extra mile in supporting me. I wish to thank the other guidances commitee members, Duncan F. Sibley and Roger B. Wallace, for their insights and suggestions. A special word of thanks also to Duncan Sibley, for being there when the one who was down under could not.

I am indebted to the Sentiniel, G.W. Monoghan, who created the amazing code which saved me hundreds of hours in doing science, and to Manrico Delcore, whose guidance on the fine art of liquid scintillation counting was irreplacable.

Most of all I thank Caroline Olmsted and my parents for their endless encouragement and support.

The Michigan State University Foundation provided funds for stable isotope ratio analyses.

TABLE OF CONTENTS

LIST OF TABLES.....	vi
LIST OF FIGURES.....	vii
INTRODUCTION.....	1
Tritium.....	1
Stable Isotopes.....	2
SCOPE OF RESEARCH.....	4
Tritium.....	6
Stable Isotopes.....	9
STUDY AREA.....	12
Geology.....	13
Hydrology.....	18
METHODS.....	22
Sampling.....	22
Tritiated Sample Preparation.....	23
Analysis.....	25
RESULTS.....	26
Tritium.....	26
Stable Isotopes.....	28
DISCUSSION.....	28
Recharge Rates.....	28
Stable Isotope Ratios.....	33
The Possible Effect of Lake Michigan Water on Tritium Activities in Groundwaters.....	34
CONCLUSIONS.....	39

RECOMMENDATIONS FOR ADDITIONAL RESEARCH.....	42
APPENDICES.....	44
APPENDIX A - QUENCH MONITORING AND COUNTING EFFICIENCY.....	44
APPENDIX B - TRITIUM COUNTING DATA.....	46
APPENDIX C - TRITIUM ACTIVITY CALCULATIONS.....	47
BIBLIOGRAPHY.....	50

LIST OF TABLES

Table 1. Discharge characteristics of the Boardman River drainage basin.....	20
Table 2. Comparison of average observed tritium concentration with average simulated values, at varying solute exchange fractions.....	40

LIST OF FIGURES

Figure 1. Location of study area in Leelanau County.....	5
Figure 2. Tritium input function for the study area.....	7
Figure 3. Mean annual (Lamb, 1961) and growing season (Bernabo, 1981) temperature curves for the past 1100 years in the northern hemisphere.....	10
Figure 4. Stable isotope input function.....	11
Figure 5. Quaternary deposits of the study area (After Martin, 1957).....	14
Figure 6a. Cross section A-A'	15
Figure 6b. Cross section B-B'	16
Figure 6c. Cross section C-C'	16
Figure 7. Till thickness in the study area.....	17
Figure 8. Piezometric surface of the study area.....	21
Figure 9. Theoretic flow, in two dimensions, at a groundwater divide, in an unconfined aquifer (after Toth, 1962).....	22
Figure 10. Sampling locations.....	24
Figure 11. Plot of tritium concentration vs. depth.....	27
Figure 12. Plot of δD and $\delta^{18}O$ vs. depth.....	29
Figure 13. Plot of δD vs. $\delta^{18}O$	30
Figure 14. Comparison of simulated tritium concentrations when $D=0$ and $D=10E-4$ m /day.....	36
Figure 15. Comparison of maximum observed tritium concentration with simulated values, at varying solute exchange fractions.....	38
Figure 16. Quench curve for tritium counting window 170-225.....	44

INTRODUCTION

Environmental isotopes, such as deuterium, tritium and oxygen-18 are attractive as either point or non-point tracers because they possess all the traits of the "ideal tracer", at least in shallow groundwater environments. They are essentially conservative in their reactions with the host porous medium; they experience no retardation with respect to groundwater flow; they are a part of the water itself and they are continuously added to the groundwater system in time and space. There does exist exchange of oxygen isotopes, and to a lesser degree hydrogen isotopes, between the liquid and solid phases in an aquifer, above all where carbonates and shales are the dominant lithology. This has been shown, however, not to be significant below formation temperatures of about 50° (C) (Clayton, 1961).

Tritium

Tritium became a useful tool in the field of subsurface hydrology beginning in the late 1950's. By this time atmospheric nuclear testing had resulted in elevated tritium levels (termed "bomb" tritium) in the atmosphere and precipitation, much higher than existed prior to late 1952, when such testing began.

The utility of bomb tritium as an age indicator lies

in its global distribution in meteoric waters and the ease of distinguishing between pre- and post-1953 groundwaters. For example, post-1953 tritium concentrations in recharged waters were found to be as much as four orders of magnitude higher than ambient conditions which existed prior to 1953 (Thatcher and Payne, 1965). Pre-1953 ambient background tritium concentrations have been estimated as being from 10 to 20 tritium units (TU) (Brown, 1961), with a TU being equivalent to one tritium atom per 10^{18} hydrogen atoms. As the half-life of tritium is 12.3 years, background concentrations in meteoric waters older than 1953 should not exceed 5 TU. Water of this age is commonly termed "dead".

Most tritium research applied to the subsurface utilizes the isotope to either delineate regional flow patterns (Rabinowitz, 1977; Wurzel, 1983; Kondoh, 1986), or to measure recharge rates (Andres, 1985; Offer, 1982; Sukhija and Shaw, 1976; Brendenkamp et al., 1974). Most recently, tritium has been used as an indicator of dispersion in unconfined aquifers (Egboka et al., 1983).

Stable Isotopes

By the late 1940's, research into the variability of stable hydrogen and oxygen isotopic ratios was well under way. Major advances were possible due to refined methods in mass spectrometry. The works of Craig (1961a), Dansgaard (1964) and Friedman et al. (1964) are recommended as early summaries of stable isotopic behavior, and the mechanisms

which account for their fractionation. The reader is referred to Ferronsky and Polyakov (1982) for a more recent comprehensive reviews of stable isotopes and their applications in hydrogeology.

Isotopic fractionation of deuterium and oxygen-18 occurs primarily as water is evaporated and precipitated. Since oxygen-18 (^{18}O) and deuterium (D) are heavier than oxygen-16 (^{16}O) and protium (H), respectively, their vapor pressures are lower than their lighter isotope counterparts at any temperature. For a pair of isotopes, however, the ratio of their vapor pressures, termed the fractionation factor, is not constant with respect to temperature. The fractionation factor of any isotopic pair increases as the temperature of evaporation decreases, such that at cooler temperature newly formed water vapor is preferentially enriched with respect to H and ^{16}O .

Stable hydrogen and oxygen isotopic ratios are normally given with respect to Standard Mean Ocean Water (SMOW), where:

$$\delta\text{D}(\text{O/00}) = \left[\left(\frac{\text{D}}{\text{H}} \right)_{\text{sample}} - \left(\frac{\text{D}}{\text{H}} \right)_{\text{SMOW}} \right] / \left(\frac{\text{D}}{\text{H}} \right)_{\text{SMOW}} \times 1000$$

and

$$\delta^{18}\text{O}(\text{O/00}) = \left[\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{sample}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{SMOW}} \right] / \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{SMOW}} \times 1000.$$

(Craig, 1961b).

Negative values would indicate "light" water, or preferentially enriched with ^{16}O or H. The opposite would be true

for positive values.

Thus, the utility of the stable isotopes D and ^{18}O in groundwater research is that their ratios, in meteoric waters, to H and ^{16}O are largely a function of the temperature of their evaporation and precipitation. As a result, the isotopic signature of a groundwater body can be tied to the climatic conditions of its formation and recharge.

Stable isotopic ratios have been used to differentiate between connate and meteoric waters of recent age (Clayton et al., 1966; Hitchon and Friedman, 1969; Graf et al., 1965). Since they are sensitive to temperature, stable isotopes can be used to identify climatic events in groundwaters whose flow patterns are understood. Of particular interest in temperate regions is the study of residence times of groundwaters since the end of the Pleistocene Epoch. At several locations in the Great Lakes region, groundwaters with very negative isotopic ratios have been interpreted as being of Pleistocene age (Clayton et al., 1966; Desaulniers et al., 1981; Long et al., 1986; Sklash et al., 1986).

SCOPE OF RESEARCH

The research presented in this paper uses tritium and stable isotopic ratios largely to understand the nature of recharge and the age of groundwaters in a heterogeneous drift aquifer system underlying part of Leelanau County, which is located in northwestern lower Michigan (Figure 1).

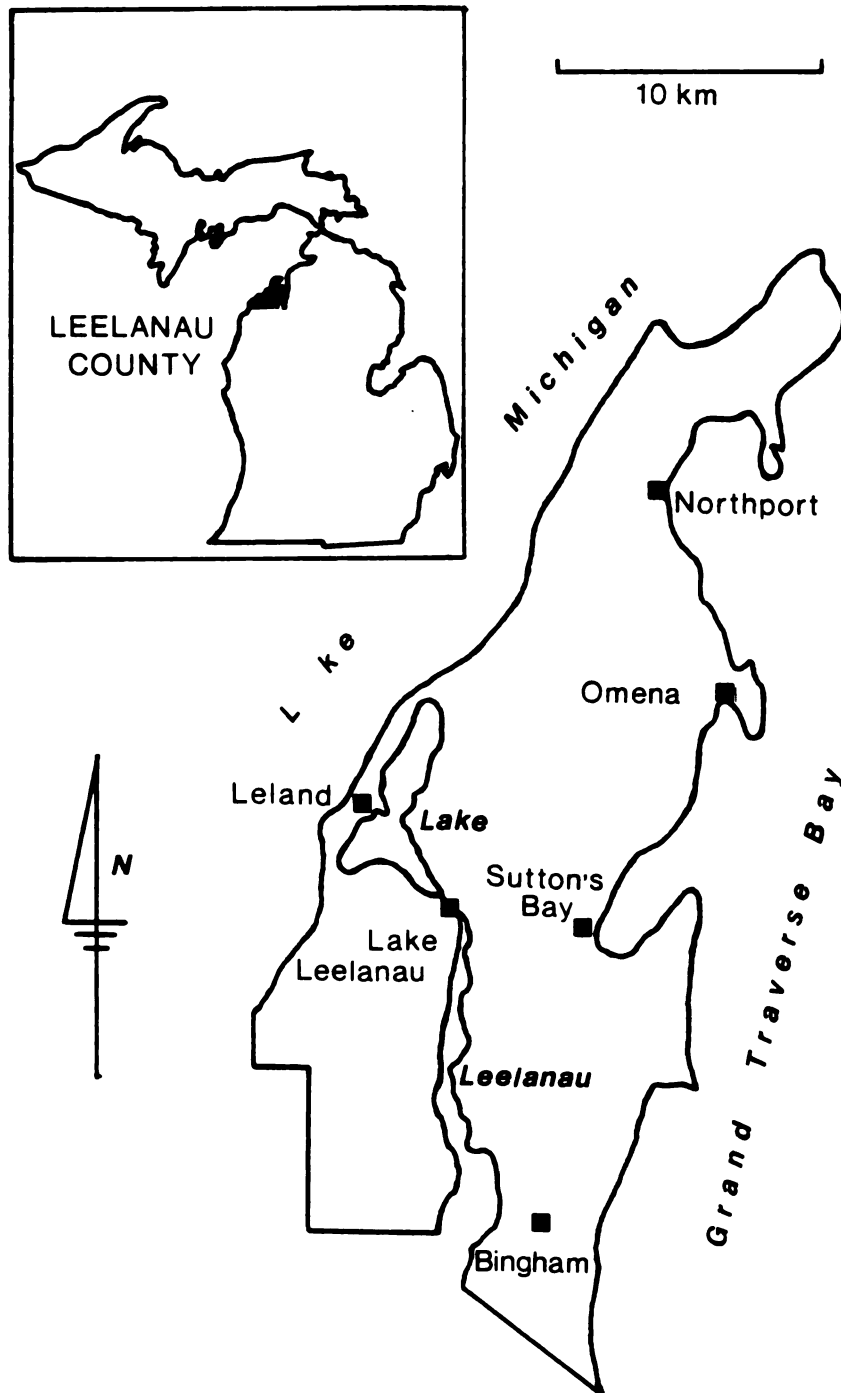


Figure 1. Location of study area in Leelanau County.

Tritium

The use of tritium to determine recharge rates involves sampling at different depths in a groundwater column in order to "sandwich" the depth of the interface between bomb-tritiated water and the dead water beneath it. The bomb-tritium interface method was first applied to studies of the unsaturated zone (Smith et al., 1970; Dincer et al., 1974; Zimmerman et al., 1967) and has been used within the 1980's to study recharge rates in the saturated zone (Andres, 1985; Maloszewski, 1980). The first studies of recharge in the saturated zone using tritium were performed on simple, relatively homogeneous, highly permeable aquifers (Offer, 1982; Larson et al., 1987). More recently, this method has been applied to more complex aquifer systems (Delcore, 1985; Delcore and Larson, 1987; Kondoh, 1986). One of the goals of this research is to attempt to extend the tritium interface method to a complex and heterogeneous drift aquifer system.

In order to properly interpret tritium activities in groundwater profiles it is necessary to have a history of tritium levels in the meteoric waters available for recharge. The tritium input function for the Leelanau County area is shown in Figure 2. The years indicated on the input function are rearranged as water years, with a water year beginning in October. The input function gives mean tritium concentrations in precipitation occurring during the recharge season within a water year, and the depth of recharge season precipitation. Examples of tritium input

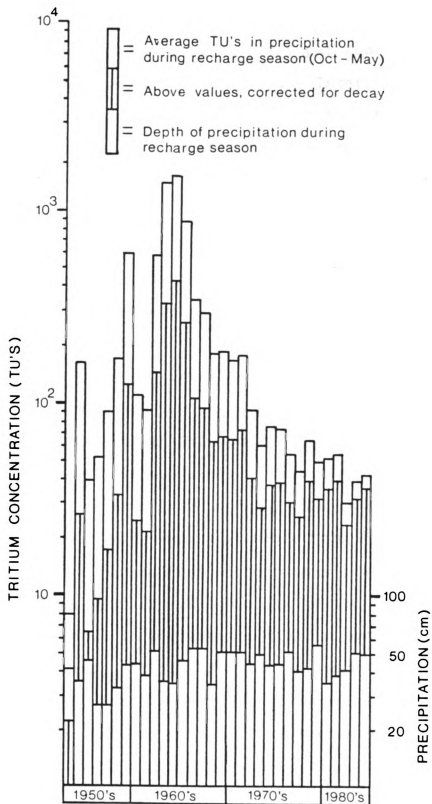


Figure 2. Tritium input function for the study area.

functions are found in Rabinowitz et al. (1977), Delcore (1985) and Offer (1982).

Tritium activities used in the input function are those reported for precipitation by the International Atomic Energy Agency (1969 through 1986) at its Ottawa, Canada, station. Data is also available from the Chicago, U.S. station, but the record isn't continuous from 1953 to the present.

One problem which has perplexed isotope hydrologists working with tritium is that tritium activities measured in groundwaters are commonly less than those measured in precipitation (Egboka et al., 1983; Delcore, 1985). The possibility of analytical error is an unacceptable explanation for this observation, for it is possible to accurately and precisely measure the activities of tritium standards in the laboratory. One explanation is that dispersion is responsible (Egboka et al., 1983). While this is certainly plausible, the input of nearly dead water from Lake Michigan in this study area is believed to be partly responsible for the observed low tritium values. One of the goals of this research, then, is to take the tritium activities from the input function, account for decay and dispersion, and attempt to match the observed tritium concentrations with a simulation by varying the amount of the suggested mixing in of the relatively dead water derived from Lake Michigan.

Stable Isotopes

D and ^{18}O in this study serve three purposes. First, the D/H and $^{18}\text{O}/^{16}\text{O}$ ratios of groundwater samples will be compared to those of present day snowmelt and rainfall, in order to get an idea of whether rainfall or snowmelt dominates the recharge.

The second usage is to test for the recharge of pre-Holocene ($>10,000$ yrs.) waters. The existence of pre-Holocene water in a shallow drift aquifer system would indicate very long residence times within the regional flow system and the existence of nearly impervious atrata overlying the aquifer. At a few sites within Michigan and Ontario, particularly beneath thick clay sequences, both deep and shallow groundwaters have shown extremely light (or negative) values for hydrogen and oxygen ratios (Clayton et al., 1966; Desaulniers et al., 1981; Long et al., 1986; Sklash et al., 1986). It is believed that these waters represent recharge during Pleistocene times, as the extremely cool climates during glacial events would have a profound fractionation effect.

Stable isotopes will be used thirdly to test whether the effect of a less severe but more recent climatic episode can be identified. A host of studies dealing with climatic changes over the past few thousand years are in close enough agreement to suggest that a significant cool period, termed the "Little Ice Age", persisted from about the 16th through 19th centuries (Williams and Wigley, 1983). Of particular interest is a growing season temperature curve

(Figure 3) established by Bernabo (1981) using ^{14}C -dated

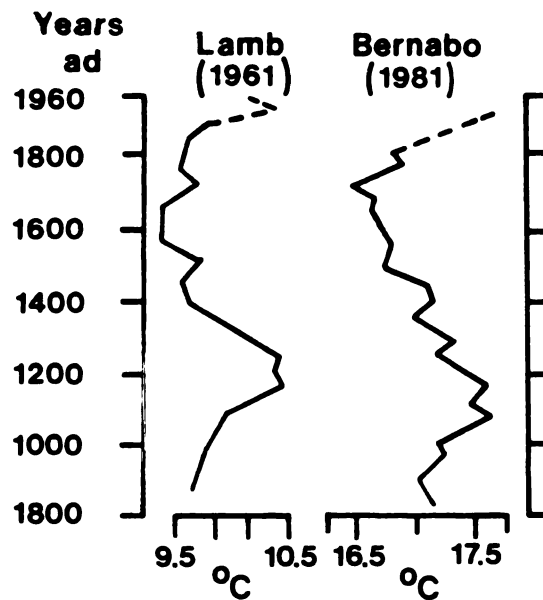


Figure 3. Mean annual (Lamb, 1961) and growing season temperature (Bernabo, 1981) curves for the past 1100 years, for two locations in the northern hemisphere, including the study area in Leelanau County.

palynomorphs from a lake some 15 miles east of the study area in Leelanau County. Based on Webb and Clark's (1977) transfer function, which relates pollen deposition to summer temperatures, Bernabo has calculated that temperatures during the late 17th to early 18th centuries were about 1°C cooler than the 30-year interval of 1931-1960 in northern Michigan. Bernabo's curve agrees qualitatively with

that proposed by Lamb (1961) for central England.

If real recharge rates are small enough in the study area, that is, on the order of a few centimeters per year, it should be possible to sample water two to three hundred years old, for the at this rate the isotopically light water recharged during this cool period would not have exceeded the depths of the existing well coverage in the study area, from about 10 to 30 meters below the water table. In this case, a curve relating isotopic ratios to depth will mimic Bernabo's temperature curve, as ratios should become increasingly negative with depth to the point in time when the Little Ice Age reached its zenith. This relationship is demonstrated in a stable isotope input function (Figure 4).

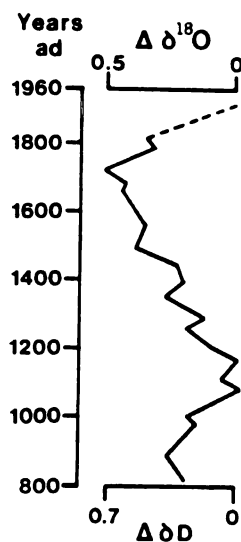


Figure 4. Stable isotope input function.

The stable isotope input function integrates Bernabo's temperature curve and Dansgaard's theoretical calculation (1964) of a 0.5 ‰ and 0.70 ‰ shift per 1° (C) in temperature. By knowing the depth at which the groundwater is lightest, it might be possible to calculate a recharge rate for the past two to three centuries.

It is expected that actual recharge rates to the drift aquifer system in the Leelanau area are much too high for Little Ice Age water to be sampled. The drift in this area, however, is known to contain clay-rich strata. It may be possible that, given a till with a high enough clay fraction, hydraulic conductivities are low enough to limit recharge rates to fractions of an inch per year.

STUDY AREA

The study area (Figure 1) is the peninsula of Leelanau County, located in the northwest part of Michigan's lower peninsula. The study area on the Leelanau Peninsula covers approximately 500 square kilometers. The peninsula is bounded on the west by Lake Michigan and on the east by the west arm of Grand Traverse Bay.

The Leelanau Peninsula was selected as a study area because while it offers a relatively complex glacial geological environment in which to test the bomb tritium interface method, local flow patterns are simplified by the presence of major discharge boundaries (Lakes Leelanau, Michigan and Grand Traverse Bay) close to one another. By

knowing precisely where the piezometric surface is lowest, the groundwater divides between Grand Traverse Bay and Lake Leelanau, and between Lakes Leelanau and Michigan can be accurately defined.

Geology

The surficial Quaternary deposits of the Leelanau Peninsula, shown in Figure 5, are of Woodfordian age, being formed most likely during the Great Lakean readvance (Even-son et al., 1976). The southern end of the peninsula east of Lake Leelanau is underlain by a segment of the Manistee Moraine. The till associated with the moraine consists chiefly of a poorly sorted mixture of coarse-grained sand and stones, most of which are carbonates. In most areas the till is poorly sorted, although well-sorted sands were observed during field reconnaissance. Some clay-rich areas are present in the region between the town of Bingham and the southern boundary of the study area. Ice-contact structures, chiefly slumped and convoluted beds of till and outwash, are exposed in a few roadcuts and gravel pits along the eastern flank of the moraine.

Highly drumlinized till plains are developed west and north of the Manistee moraine. Between Lakes Leelanau and Michigan some very localized outwash deposits cover the till plain along its western and eastern flanks. The texture of the till is fairly consistent from north to south. It is predominantly stony and sandy but with a much higher clay content than the till observed on the Manistee moraine.

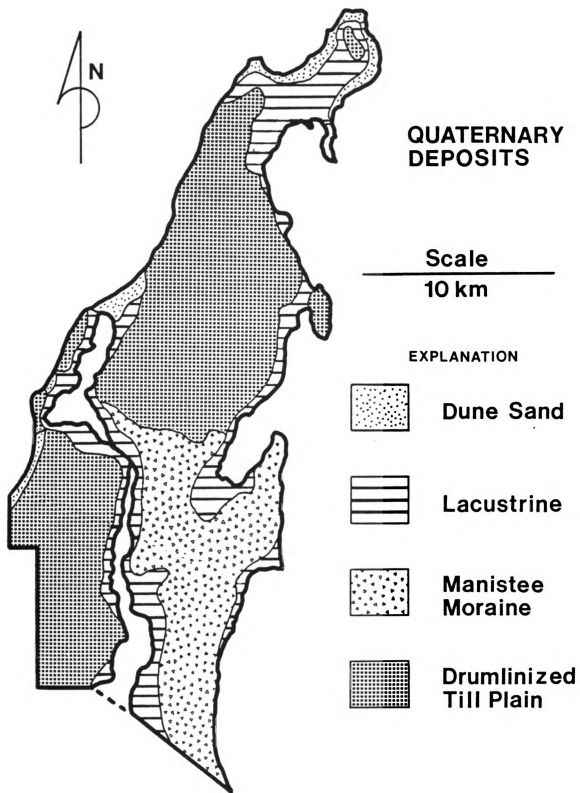


Figure 5. Quaternary deposits of the study area (after Martin, 1957).

Geologic cross sections of both till plains and the Manistee Moraine are shown in Figure 6. Correlations based on drillers logs are tenuous at best, given the variable nature of the drift, the distances between control wells and the interpretive nature of formation logging during drilling.

Lacustrine clays are confined to the areas immediately adjacent to the lakes, although much of the area from Cathead Bay to the end of the peninsula is underlain by sand, gravel and stones associated with the Algonquin and Nipissing strandlines (Martin, 1957).

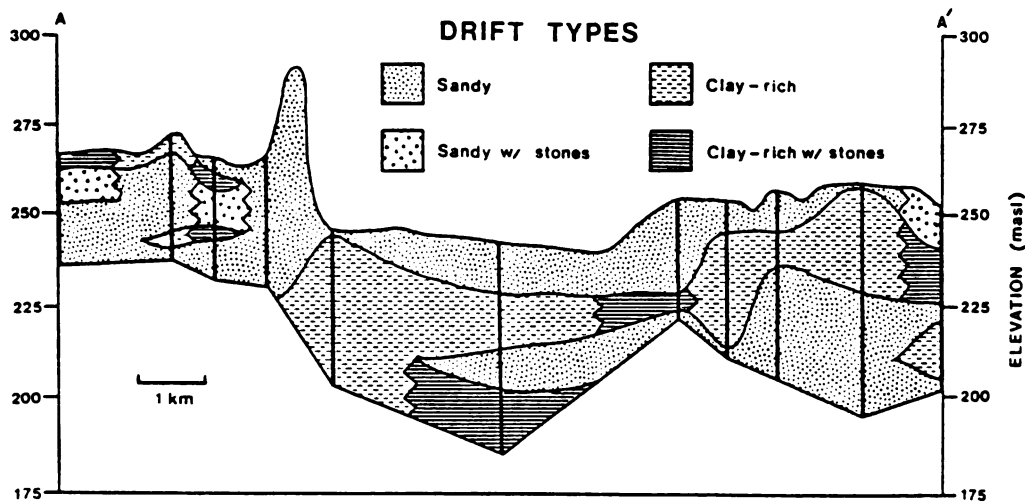


Figure 6a. Cross section A-A'.

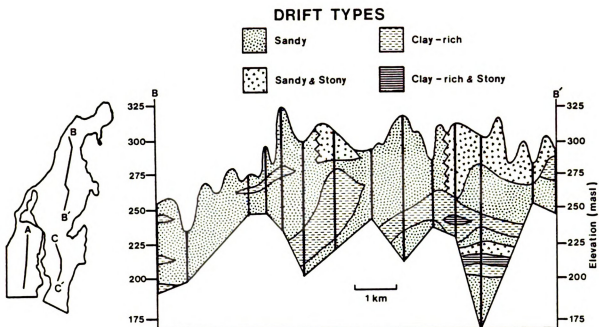


Figure 6b. Cross section B-B'.

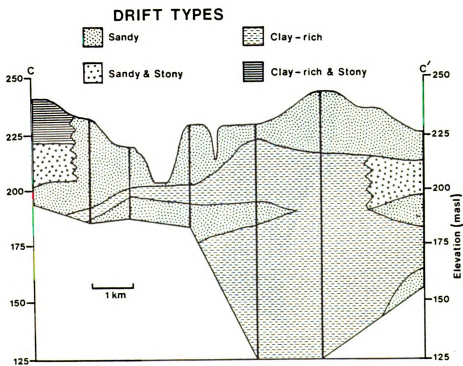


Figure 6c. Cross section C-C'.

Till thickness, shown in Figure 7, increases from north to south. North of Northport it is in the range of 50 to 75 meters, increasing to about 75 meters near Omena, then thickens to over 150 meters just two to three kilometers south of Omena. This marked increase lies at about the same

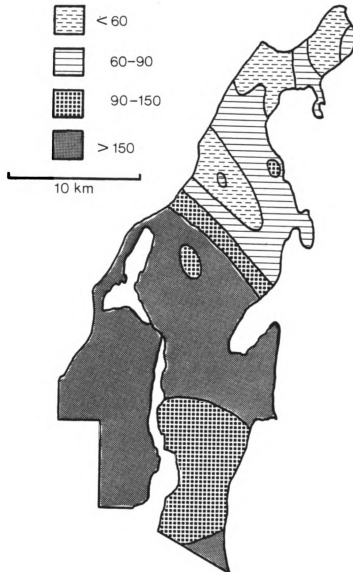


Figure 7. Till thickness in study area.

subcrop location of the contact between the Traverse Limestone and the Ellsworth Shale. It is thought that the increase in till thickness results from the relatively easier scouring of the Ellsworth by glacial ice.

Based on drillers logs isolated lenses of clay-rich drift are known to exist in the subsurface, to the base of the drift, throughout the peninsula.

Hydrology

Annual precipitation decreases from west to east across Leelanau County, from about 90 centimeters/year to 76 cm in the immediate Traverse City area. Precipitation on the peninsula, as recorded for the period of 1953 to 1985 (corresponding to the time covered by the tritium input function) is approximately 81 cm/year (Nurnberger, 1952-85). As seen by the tritium input function (Figure 2), the recharge season during these years experienced an average of 44 cm of precipitation per year.

The nearest drainage basin whose discharge is gaged is that of the Boardman River, which drains some 530 square kilometers of mostly outwash, developed between the Manistee and Port Huron moraines, to the southeast of the study area. For the 33-year interval from 1953 to 1985, the mean annual discharge of the Boardman was equivalent to 36.6 cm of total runoff from the basin (USGS, 1953-1986). Hydrograph separations, using three different techniques, were performed on flow data from the water years of 1957, 1964, 1971, 1973 and 1985. These techniques - the sliding interval, the fixed

interval and the local minimum are described in detail by Petrie (1985). Annual mean discharges of the Boardman river and the percentages of the baseflow components are summarized in Table 1 for the years of records mentioned above. It was found that that average base flow, based on the five sets of hydrograph separations, is about 82 percent of the total runoff, or about 30.0 cm per year for the drainage basin.

Aquifer conditions on the Leelanau Peninsula are mostly unconfined although semiconfining conditions do exist locally where lenses of clay-rich till occur in the saturated zone. The many flowing wells located close to the shores of Lake Leelanau and Sutton's Bay are strong evidence that confined conditions exist in areas underlain by lake clays.

A water table elevation map of the peninsula is shown in Figure 8. It is based on a total of 414 well logs whose locations could be verified with confidence. As might be expected, the two major groundwater divides follow closely the traces of topographic divides.

The major uses of groundwater in the study area, besides domestic consumption, are for irrigation and cherry cooling. These large capacity wells, which account for only a small percentage of the wells on record in the area, produce up to 500 gallons a minute. Cherry cooling is limited chiefly to the month of July.

Table 1. Discharge characteristics of the Boardman River drainage basin.

Water Year	Total Runoff (in.)	Percent of Total Runoff as Baseflow					
		Local		Sliding		Fixed	
		7-day	15-day	7-day	15-day	7-day	15-day
1953	37.8						
1954	37.8						
1955	37.9						
1956	34.9						
1957	35.1	84.4	79.3	84.6	80.6	84.2	81.0
1958	30.4						
1959	32.0						
1960	15.2						
1961	34.1						
1962	38.3						
1963	32.7						
1964	30.4	79.0	71.0	80.1	73.2	80.2	72.3
1965	32.3						
1966	36.8						
1967	42.6						
1968	36.5						
1969	39.8						
1970	38.7						
1971	40.7	82.2	73.3	84.3	77.6	85.3	77.3
1972	34.9						
1973	33.0						
1974	34.9						
1975	36.8						
1976	43.7						
1977	33.6						
1978	35.5	87.5	84.8	91.7	86.9	91.5	86.1
1979	37.0						
1980	35.6						
1981	27.8						
1982	30.1						
1983	37.4						
1984	36.6						
1985	43.6	84.3	80.4	85.7	80.2	85.1	80.4
Means:	36.6	83.5	77.8	85.4	79.7	85.3	79.4

Mean of three methods = 81.9%

Baseflow of total runoff = recharge = (36.6 cm/yr)(0.82)

= 30.0 cm/yr.

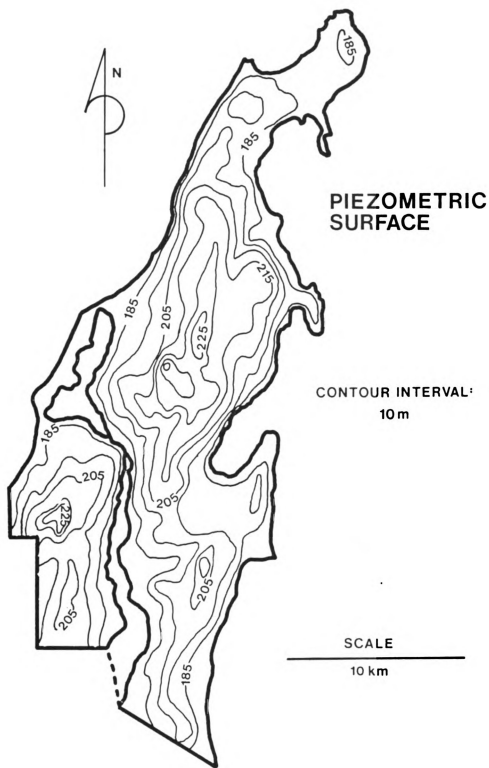


Figure 8. Piezometric surface of study area.

METHODS

Sampling

Sampling locations for all isotopic analyses were limited to the wells which fall on or immediately adjacent to the two major groundwater divides discussed above. Where an environmental tracer is being used to determine recharge rates, it is essential that sampling be done on a divide for it is here that movement in an aquifer is essentially vertically downward, as suggested by Toth (1962) (Figure 9). Sampling off a groundwater divide results in values which are less than actual since a component of flow is horizontal.

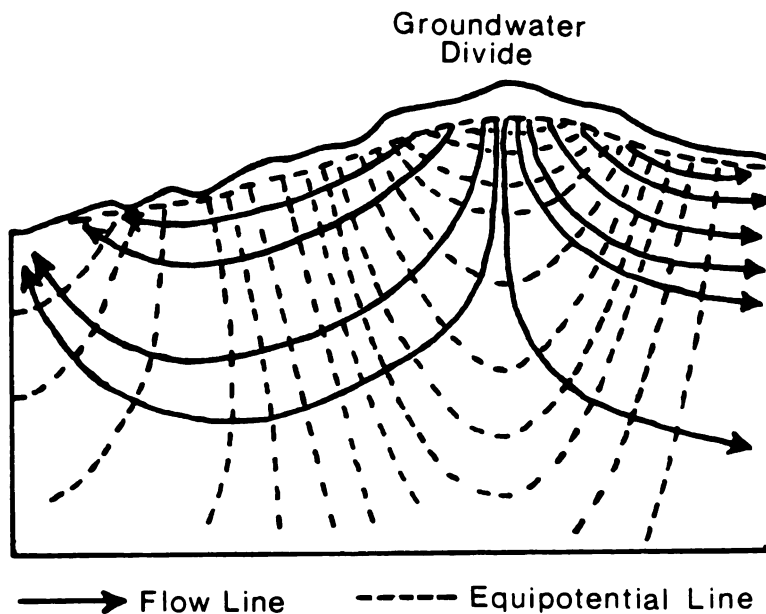


Figure 9. Theoretical flow, in two dimensions, at a groundwater divide in an unconfined aquifer (after Toth, 1962).

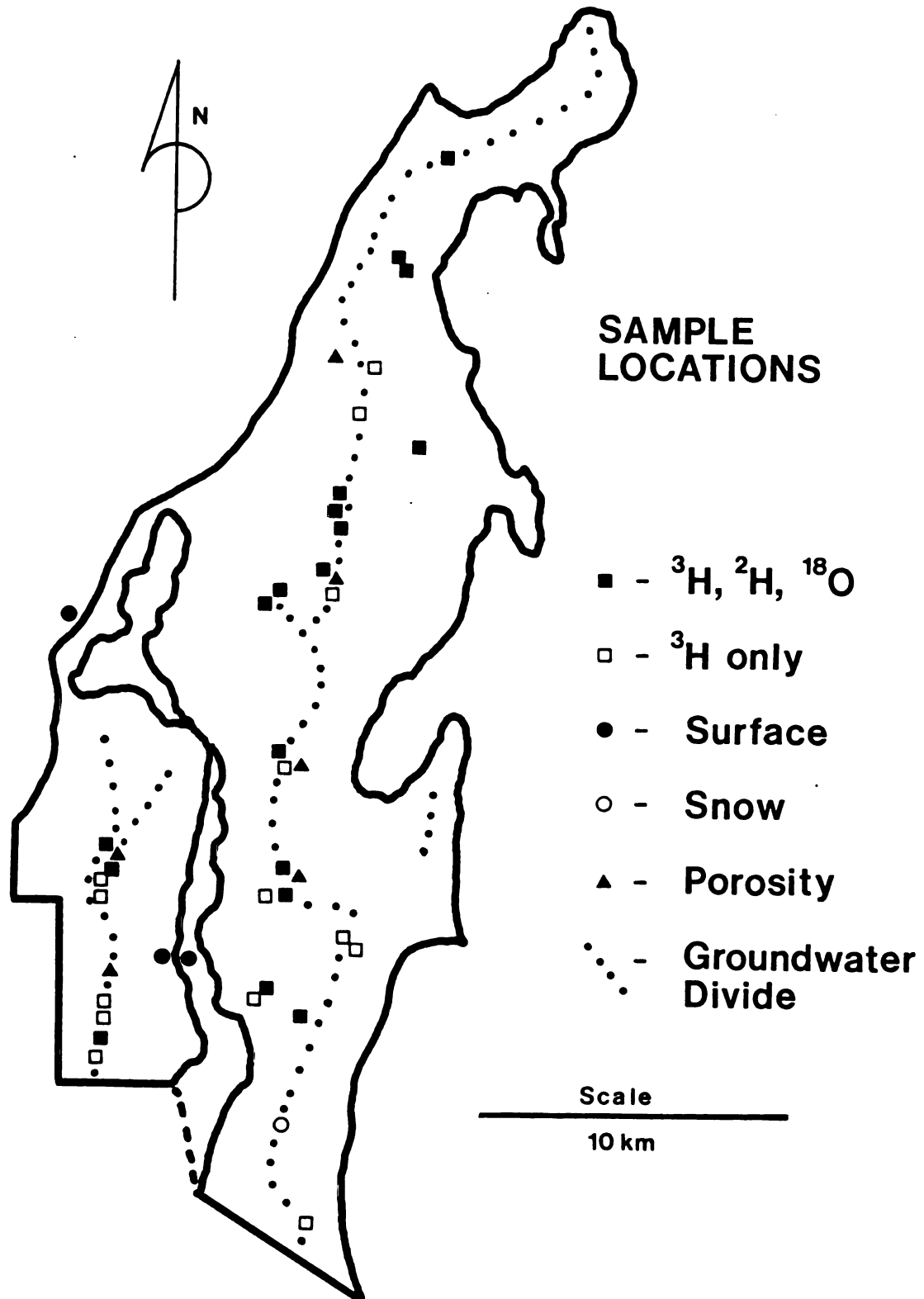


Figure 10. Sampling locations.

Twenty nine domestic wells were sampled for tritium. Depths of domestic wells ranged from 7 to 28 meters below the water table. Well screens are normally 1.2 to 1.6 meters (4 to 5 ft) long.

Eighteen wells, including one high production well, were sampled for stable isotopes. Their depths ranged from 8 to 91 m feet below the water table. Five of these are deeper than 27 m.

Samples were taken by simply turning on a tap or spigot served by the domestic well, and letting it run for about two minutes. This serves to stabilize the well system temperature and ensure that the sample hasn't undergone exchange with any of the well components. Samples were delivered to 500 ml Nalgene plastic bottles, which were oven dried and capped before sampling.

Four surface water locations were sampled for stable isotopes - Grand Traverse Bay, south Lake Leelanau, Lake Michigan and a small creek which discharges to south Lake Leelanau. A composite sample of about 0.3 meters of snow was sampled from the Northwest Michigan Agricultural Extension Station, south of Bingham. All sampling locations are shown in Figure 10.

Tritiated Sample Preparation

Samples to be analyzed for tritium activity were prepared for decay measurement by the U.S.G.S. electrolytic enrichment method (Thatcher et al., 1977) of pre-distillation, electrolysis, and post-distillation. The

method is also described in detail by Wyerman (1976). Other descriptions can be found in Offer (1982), Slayton (1983) and Delcore (1985).

Pre-distillations are run with a small quantity of powdered copper, which ensures that any sulfur present is sequestered. The radioisotope of sulfur, like tritium, is a beta - emitter, whose energy emission spectrum overlaps that of tritium.

Electrolyses were run in sets of six to eight samples. Each set was run with one standard and one blank consisting of dead water, which is taken from a 500-meter deep well at the fish hatchery in Thompson, Michigan. Electrolysis reduces the sample volume from 200 ml to between 5 - 10 ml, thereby enriching the sample with respect to tritium.

Post-distillations were run using liquid nitrogen as the coolant. Such extreme temperatures are necessary due to the small mass of sample at this point. Upon completion, approximately 5 to 6 ml of sample is delivered to a 20 ml borosilicate glass vial, and mixed with a liquid scintillation counting cocktail.

Analysis

Tritium activities were measured by means of liquid scintillation spectroscopy, which is an indirect process. The liquid scintillation spectrometer counts not the actual decay events, but rather, detects photons produced by the bombardment of the cocktail by beta radiation from the

tritiated water molecules. Produced at a rate proportional to the frequency of decay, the detectable photons are photo-multiplied and recorded electronically as decay events. For a thorough treatment of the liquid scintillation technique and theory, the reader is referred to Long (1978) and Florkowski (1981).

All samples were counted for at least 270 minutes. Several of the deeper well samples were counted for over 1000 minutes or longer. The deeper samples require longer counting times in order to reduce their 2-sigma errors to the point where they can be distinguished as dead or bomb-tritiated waters. All tritium counting data is presented in Appendices A and B. The method for calculating tritium activities is presented as Appendix C.

Stable isotopic ratios were measured by means of mass spectroscopy, at the Isotope Research Laboratory of the University of Waterloo in Waterloo, Ontario.

RESULTS

Tritium

A plot of tritium activity as a function of depth is shown in Figure 11. Depths are given in meters from the water table to the bottom of the well screen.

Assuming any activity over 5 TU indicates the presence of bomb tritium, the deepest penetration of bomb-tritium lies between 25 and 25.5 meters. The average depth of all screens, however, is about 0.7 m less, since they are about

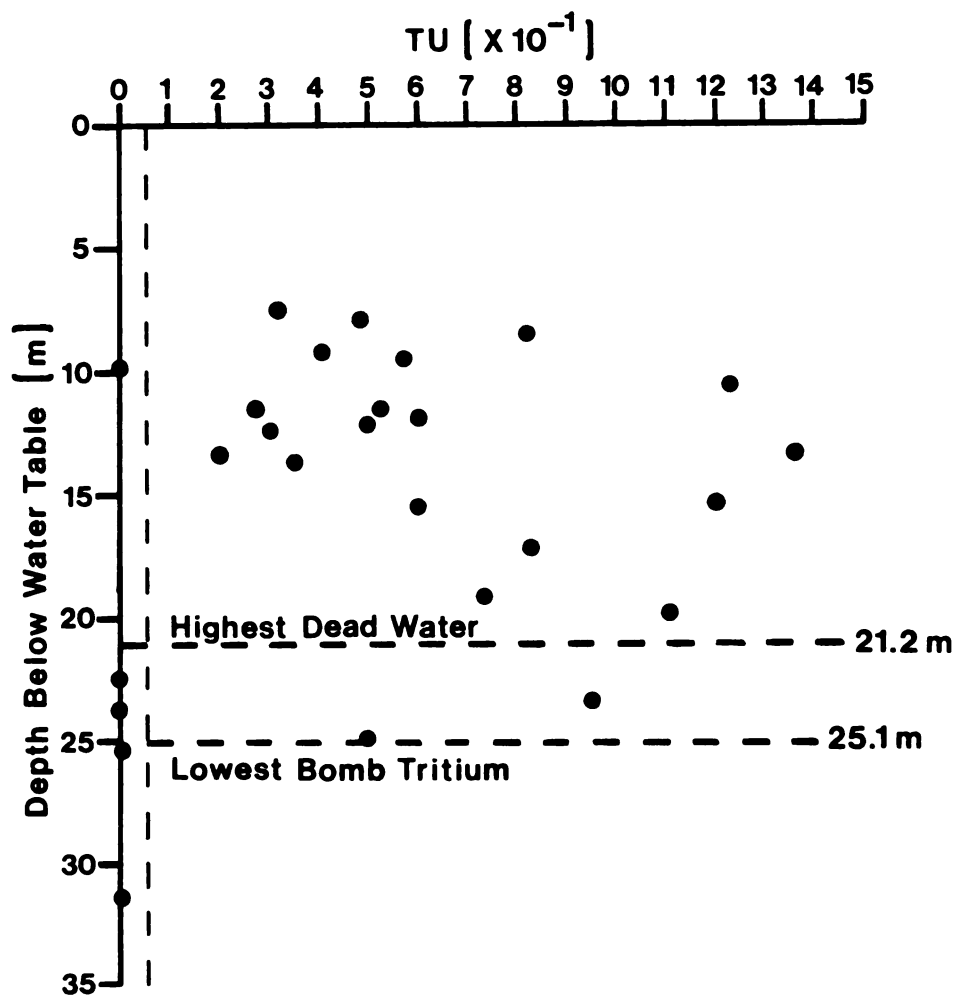


Figure 11. Plot of tritium concentration vs. sample depth.

1.2 meters long. This places the deepest bomb-tritium at an average depth of 25.2 m. The shallowest dead water (less than 5 TU), on the other hand, is found between average depths of 19.2 and 22 m (again, accounting for screen lengths), or an average depth of 20.6 m. The dead water sampled at a depth of about 10 m is not used to define the depth of the interface, for the well from which this sample

was taken falls about 2 km laterally off the groundwater divide in the northern part of the peninsula. It is believed that at this location the groundwater flow is being strongly affected by horizontal and perhaps upward flow components.

Stable Isotopes

Plots of stable isotope ratios in the groundwater samples, as a function of depth, are shown in Figure 12. It is immediately apparent that there is no correlation between depth and deviation from SMOW for either isotopic ratio.

The plot of δD vs $\delta^{18}O$, which includes both surface and groundwater samples, is shown in Figure 13. As might be expected the snow sample gives the most negative values. Groundwater values are slightly more positive, while the creek which discharges to Lake Leelanau yields values in the same area as the groundwaters. Lake Michigan gives the most positive value; Lake Leelanau is intermediate between Lake Michigan and groundwater.

DISCUSSION

Recharge Rates

The formula used to calculate recharge rates is simply an expression of velocity:

$$R = (D \times N_e) / T$$

(Delcore, 1985; Andres, 1985; Offer, 1982), where R is the recharge rate in meters per year, D is the depth of the

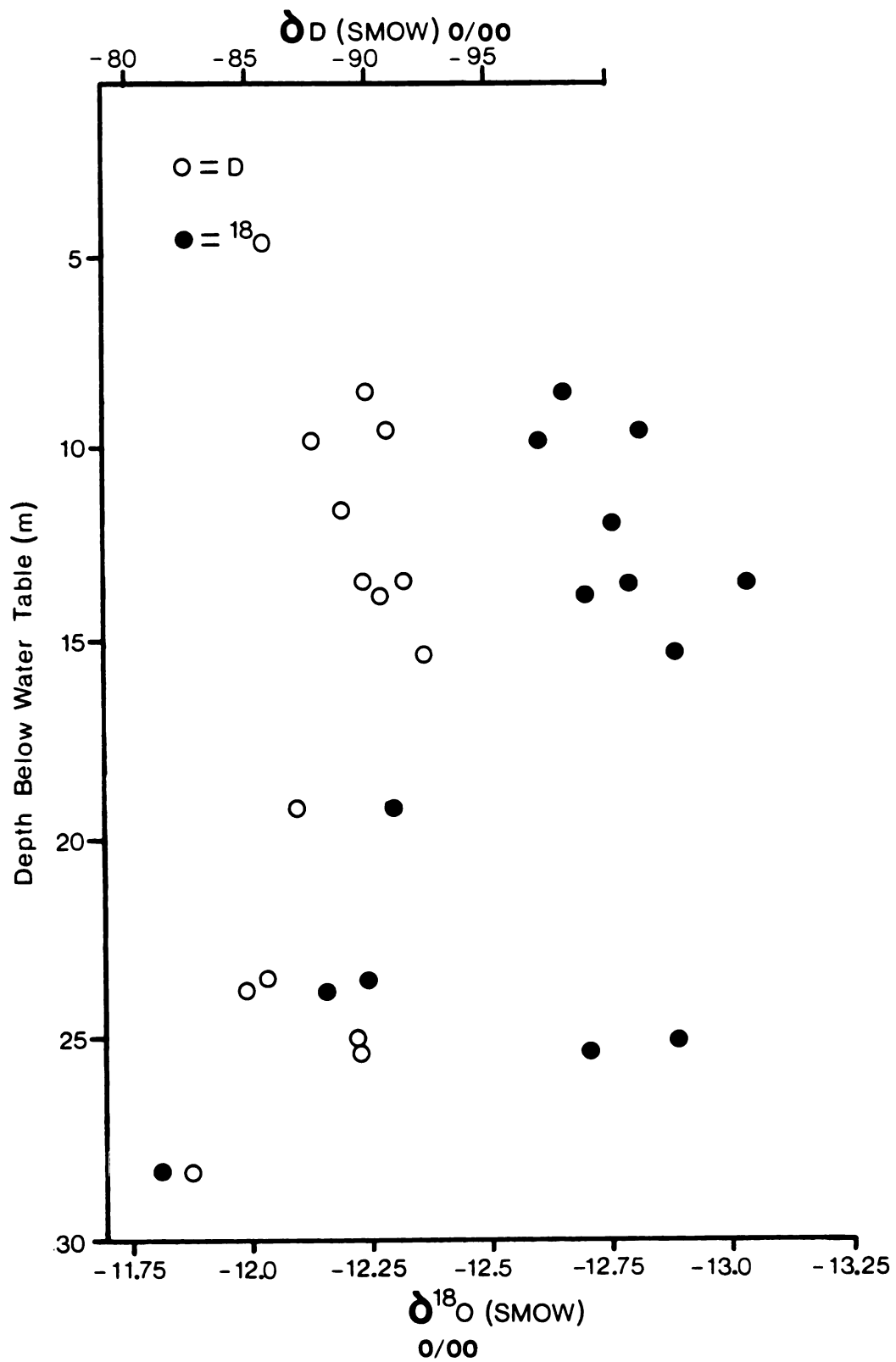


Figure 12. Plot of δD and $\delta^{18}O$ vs. sample depth.

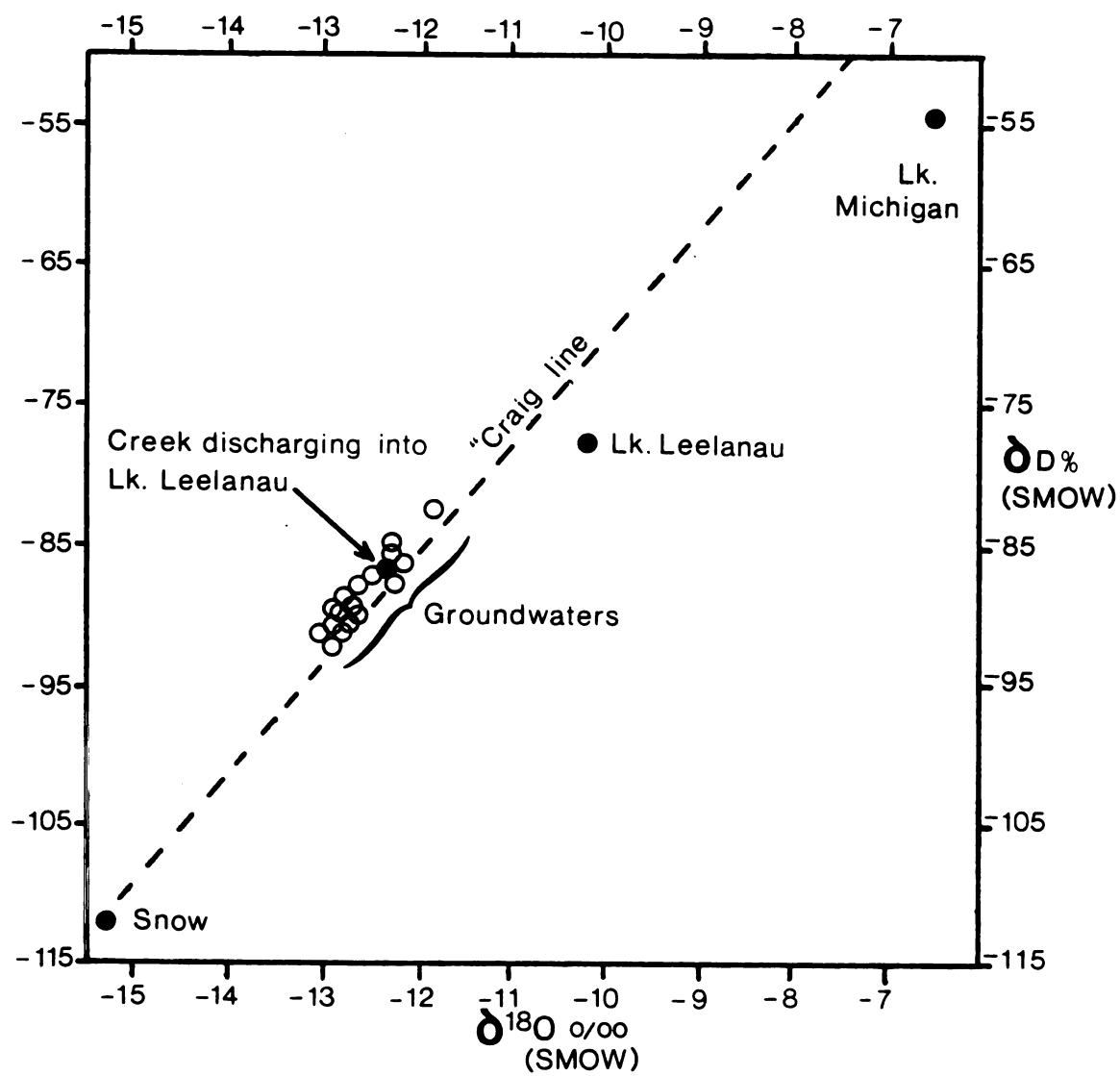


Figure 13. Plot of δD vs. $\delta^{18}O$.

bomb-tritium interface in meters below the water table, N_e is the effective porosity of the aquifer and T is the amount of time, in years, between the first input of bomb-tritium into the aquifer system (1953) and the date of groundwater sampling (1985).

When solving for R , the two values for depth, 20.6 and 25.2 m must be used, since the lowest depth of bomb-tritium, shown in Figure 11, does not coincide with the highest dead water. Porosity of drift materials was measured on a total of six samples, whose locations are shown in Figure 10. The samples were collected in undisturbed till about one meter below the land surface. The average porosity measured in these is 31.5% (+/- 3.5%). The effective porosity, however is estimated to be near a nominal value of 25%.

The recharge rates to the aquifer system are calculated to be a minimum of:

$$\begin{aligned} R &= (20.6 \text{ m})(0.25) / 33 \text{ yrs} \\ &= 0.16 \text{ m/yr} \end{aligned}$$

and a maximum of:

$$\begin{aligned} R &= (25.2)(0.25) / 33 \text{ yrs} \\ &= 0.19 \text{ m/yr.} \end{aligned}$$

The average recharge rate would thus be 0.17 meters per year, or about 17 cm (6.5 inches). That this value is only 60% of the depth of baseflow for the Boardman River Basin (30.0 cm), for the same 33-year interval, raises the question of how realistic the calculated recharge rates are, and hence if the interface method is applicable to a heterogeneous aquifer system.

A number of arguments can be made to account for the apparently low values for R calculated above. First of all is the difference in drift textures. The drift on the Leelanau Peninsula, while being predominantly sandy, contains much more clay than the outwash system underlying much of the Boardman River basin. This results in a lower infiltration capacity, which increases surface runoff on the peninsula. The relief on the Leelanau peninsula must also be considered. Much of the peninsula is underlain by slopes exceeding 25% (Weber, 1973). Dunne and Black (1971) and Price and Hendrie (1983) demonstrated that over 50% of the equivalent water depth of a snowpack can be lost as surface runoff, even over sandy soils, during a snowmelt period when soils are still frozen. Petrie (1985) demonstrated within the greater Grand River drainage basin in south-central Michigan that relief exerts a greater influence in reducing baseflow than does infiltration capacity. It is suggested by the author, then, that an average recharge rate of 6.5 inches per year is realistic for the study area, given the nature of the drift and the relief developed on the peninsula due to drumlins and the Manistee moraine.

The value of 17.5 centimeters per year is close to the nominal value of 20.3 cm (8 inches) per year which is commonly used by the USGS in Michigan, for recharge to till plains when calibrating groundwater flow models (Granneman, 1987, personal communication).

Stable Isotope Ratios

Values for D in groundwater samples range from a low of -92.2 to a high of -82.4. For $\delta^{18}\text{O}$, the minimum and maximum are -13.03 and -11.81, respectively. These "light" waters are indicative of recharge during cool temperatures, as ratios for δD in precipitation during the summer months are normally 30 to 50 ‰ more positive than the observed ratios. Values for $\delta^{18}\text{O}$ in summertime precipitation are commonly 4 to 6 ‰ more positive than the observed values (IAEA, 1953-1986). The snow sample from the study area yielded values of -15.29 and -112.0 for $\delta^{18}\text{O}$ and δD , respectively. It is suggested, then, that the source of groundwater in the study area is local precipitation, being a combination of rainfall and snowmelt. This conclusion corroborates measurements of evapotranspiration from northern lower peninsula and the eastern upper peninsula, where it is found that ET exceeds precipitation from May to August (Nurnberger, 1982).

From Figure 13 it is seen that there is no systematic decrease in isotopic ratios with depth, contrary to the proposed stable isotope input function (Figure 4). This is one piece of evidence that none of the groundwater samples reflect recharge during the Little Ice Age. Besides the stable isotopic ratios, the average vertical displacement of the tritium interface - 22.6 meters in 33 years - would place water 300 years old at a depth of more than 200 m below the water table. This would make it impossible to sample the isotopically lightest water, recharged during the

height of this cool period, with the existing well coverage.

The Possible Effect of Lake Michigan Water on Tritium Activities in Groundwater

According to the tritium input function (Figure 2), some of the deeper samples from the Leelanau Peninsula should have activities over 200 TU, even exceeding 400 TU. The highest activity found in this study, however, is only 136 TU; in fact only four wells yielded water of 100 TU's or more.

There are a number of possible explanations for this. It may be that the zone of highly tritiated water, recharged from 1962 - 1965, was not sampled, for well screen coverage in the bomb-tritiated zone is not complete. This notion is rejected, however, because at an average seepage velocity of 22.6 m/33 yrs, the highest value used in the input function (426 TU in 1964) should occur where there is adequate well screen coverage (14.4 m). It can be argued that the low measures values are a result of averaging values over the length of a well screen. This explanation, too, is rejected, for at an average recharge rate of 16.7 cm/yr and an effective porosity of 25%, the vertical displacement in the four years time mentioned above exceeds the length of any four or five-foot well screen by a factor of nearly two.

A third possibility is that that original tritium activities, upon entering the aquifer, have been altered by dispersion. The input function does not account for hydrodynamic dispersion, for it assumes piston flow in the

saturated zone. Hydrodynamic dispersion would result in decreased maximum values, for it causes mixing due to variations in groundwater pore velocities (Ogata, 1970). Piston flow, as described by Nir (1964), assumes that essentially no mixing occurs as a recharge event (rainfall or snowmelt) adds a discrete increment of water to a groundwater column which is continuously translated downward, as is the case on a groundwater divide (Figure 9).

To test the influence of hydrodynamic dispersion, the values of tritium activities from the input function were modeled in the groundwater flow regime in the study area. The transport model used (Javandel et al., 1984) is one-dimensional; it was modified to account for decay, retardation, hydrodynamic dispersion, and exchange of the solute (tritium). Exchange, in this case, refers to the additional input of nearly dead water, in the form of lake-effect snow, derived from Lake Michigan.

Hydrodynamic dispersion also causes a solute front (in this case the first bomb-tritium from the autumn of 1952) to advance faster than the average groundwater seepage velocity. It was suspected, though, that the effect of dispersion would be minimal, for two reasons. First of all, hydrodynamic, or mechanical, dispersion is proportional to groundwater seepage velocity. The average downward velocity in the sampled area, 0.68 m/yr, in terms of meters per day, is 1.87×10^{-3} . This is relatively small in comparison to other field studies of dispersion (Sudicky et al., 1983;

Fried, 1975). Secondly, dispersion is a scale-dependent parameter (Anderson, 1979); dispersion coefficients tend to increase as a function of distance from the solute source. In a comprehensive review of dispersion coefficients measured in field studies, Gelhar et al. (1983) found that for distances of several to a few tens of meters, dispersion coefficients rarely exceed one meter, and are commonly on the order of centimeters.

In Figure 14 are plotted two curves of simulated tritium activities. One assumes no dispersion and no exchange, the other assumes no exchange but uses a dispersivity of $10E-4$ m²/day. When dividing this value of dispersivity by the seepage velocity of $1.87 \times 10E-3$ m/day, the dispersion coefficient is 0.05 m, or 5 cm, which is a

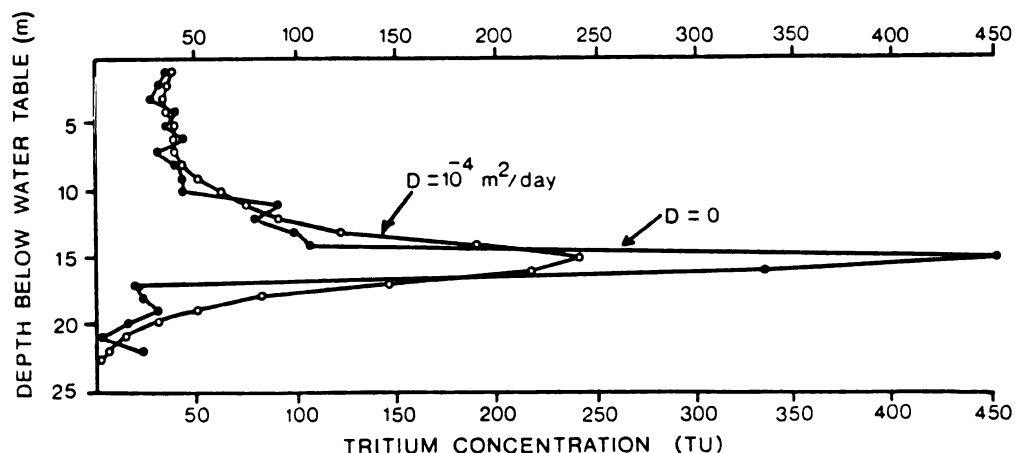


Figure 14. Comparison of simulated tritium concentrations when $D=0$ and $D=10E-4$ m²/day.

realistic value for such a shallow penetration of the tritium front. As seen in Figure 14, there is little difference in the depth of the tritium front between the two curves.

The other remaining possibility is that input of relatively dead water, from Lake Michigan, is entering the aquifer system during recharge events. The proposed additional input is, of course, in the form of lake effect snowfall. The influence of the Great Lakes on increased snow depths along their lee borderlands is well documented (Eichenlaub, 1970). Chagnon et al. (1972) estimate that the lake effect increases winter precipitation in lee areas by as much as 45%, compared to areas outside of the lake effect. As the tritium activity of Lake Michigan is around 10 TU (Begemann and Libby, 1957), lake snow is thought to decrease values predicted by the input function. This is not accounted for by the input function, since the tritium values used are from Ottawa, which does not experience such a pronounced lake effect as the Leelanau Peninsula.

Using a value of $10E-4$ m²/day for dispersivity, a number of simulations were run, using values for exchange ranging from 50 to 75%. An exchange factor of 75% means that 25% of the input water is being replaced by dead water. The results are plotted in Figure 15, along with the measured values. It is observed that at an exchange value of about 55%, the maximum simulated value matches the maximum measured activity of 136 TU. This is not considered to be an

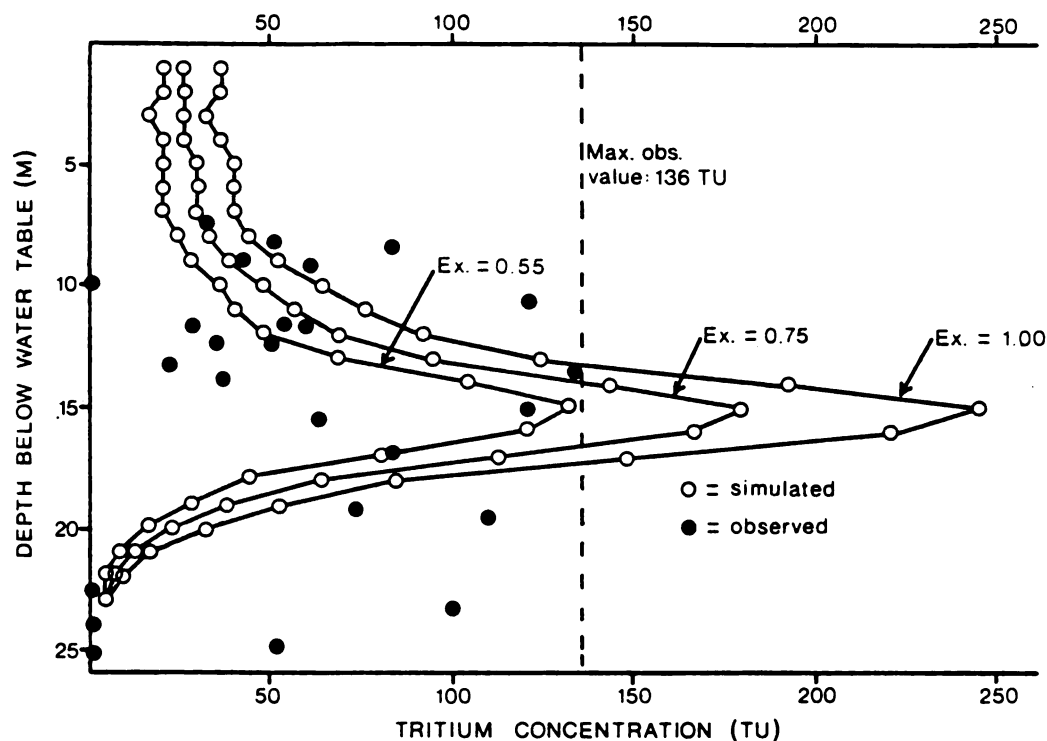


Figure 15. Comparison of maximum observed tritium concentrations with simulated values, at varying solute exchange fractions.

accurate simulation, however, because the field measurements give average values over the length of a well screen, while the 1-D transport model simulates values at points in depth, at one-meter intervals.

To achieve a more realistic match, mean values for the observed groundwater column and the simulated values were compared. Since the highest depth any well screen in this study could have sampled formation water (assuming lateral flow into a well screen) is about 6 meters, no simulated samples above 6 meters were used for averaging simulated

tritium activities. The model, as it was run, gives simulated values at one-meter intervals. Field sample means, for a given depth corresponding to the depth of a simulated value, were calculated by averaging the measured activities of each sample whose well screen lies at the same depth as a simulated value. As all well screens are at least four feet long, the same well sample could be used in determining mean measured activities corresponding to two simulated values. The method for determining mean field sample activities is demonstrated in Table 2, which includes the profile of well coverage within the bomb-tritiated interval of the groundwater column. The mean value for all field measurements is then calculated by averaging all the means which correspond to depths at which values were simulated.

Table 2 shows the plots of all tritium measurements, averaged measurements (corresponding to the depth of a simulated activity) and simulated values using the exchange values ranging from 0 to 40%. Taking the total mean of the corresponding well sample activities as 74 TU, it is seen that the more realistic value for exchange is around 20%.

CONCLUSIONS

The geological, hydrological and analytical data presented in this study, combined with the tritium and stable isotope input functions, permit the following conclusions to be drawn for the drift aquifer system underlying the study

Table 2 . Comparison of average observed tritium concentrations with average simulated values, at varying solute exchange fractions.

Simulated Depth Below Water Table (m)	Well Screen Coverage	Average TU	Simulated TU Values With Variable Exchange				
			0%	10%	20%	30%	40%
5							
6	48.3	40.1	41	37	33	29	25
7	31.8	65.0	41	37	33	29	24
8	57.3	48.8	45	40	36	31	27
9	122.6	122.6	52	47	42	36	31
10	49.5	47.3	65	59	52	45	39
11	33.1	73.0	79	71	63	55	47
12	35.3	64.0	93	83	74	65	55
13	119.8	119.8	127	115	102	89	76
14	80.4	60.4	193	174	154	135	116
15	82.5	82.5	244	219	195	171	146
16		-	-	-	-	-	-
17	73.0	92.0	150	135	120	105	80
18	111.1	-	-	-	-	-	-
19		-	-	-	-	-	-
20	0	-	-	-	-	-	-
21	0	94.7	19	17	15	13	11
22	49.5	47.5	11	10	8	7	6
MEANS:		73.7	89	80	71	62	53

area on the Leelanau Peninsula:

1) The aquifer system is completely heterogeneous; composed chiefly of a sandy stony till which is more clayey in the areas underlain by till plains than on the Manistee Moraine, and which contains many clay-rich zones. In the recharge area it is unconfined to semi-confined with depth. Confined conditions exist in the discharge areas, near the peripheries of Lake Leelanau and Grand Traverse Bay, which are underlain by lake clays.

2) Waters in the upper 90 meters of the aquifer system are less than 200 years old, based on an average vertical seepage rate of 22.6 m/ 33 yrs, as determined by average depth of the tritium interface.

3) Stable isotopic ratios also indicate that recharge is a combination of snowmelt and rainfall, being mostly snowmelt. The ratios also indicate that recharge occurs during the cooler months.

4) The lack of decrease in δD and $\delta^{18}O$ values with depth supports the above conclusion that the sampled groundwater has all been recharged since the height of the Little Ice Age in the early 1700's.

5) Recharge rates in the study area are between 0.16 and 0.19 meters per year. The average recharge rate is 0.17 m/yr, or 17 cm.

6) An average recharge rate of 17 cm per year is probably accurate for the Leelanau Peninsula, when considering the influence of relief on runoff during snowmelt over a

temporarily frozen soil surface.

7) Input of water to the system by lake effect snow results in a substantial decrease in the tritium activities of groundwater as compared to areas where a lake effect is not present.

SUGGESTIONS FOR ADDITIONAL RESEARCH

All sampling for isotopic analyses was performed using existing well coverage in the study area. This distribution of sampling points is not sufficient to thoroughly characterize the inherent heterogeneity of the aquifer system. The drawback associated with this is best seen in Figures 11 and 12.

In Figure 11 it is seen that different tritium concentrations were measured at nearly the same depth in the groundwater profile. It is likely, given the heterogeneity of the aquifer, that this is a result of differing recharge rates across the peninsula, due to the variable nature of the drift. The same effect is observed in Figure 12, where at the same depth, different isotopic ratios are observed, for the same reason mentioned above.

Based on the conclusion that the tritium interface method has been used successfully to determine an accurate recharge rate to the study area, the method could be best applied with well control which is concentrated in a few areas where different drift types are known to exist. With sufficient vertical well screen coverage at a few locations, accurate recharge rates could be determined as a function,

in part, of drift lithology. This is, in fact, the utility of the tritium interface method, as compared to the use of a hydrologic budget, groundwater models or basin analysis. The tritium method is most valuable for determining very site specific recharge rates, while the other more traditional method are suitable on a regional scale.

APPENDICES

APPENDIX A

QUENCH MONITORING AND COUNTING EFFICIENCY

Liquid scintillation counting of tritium decay events is an inefficient process. It is a function of several parameters, including the counting window, the tritium activity itself, the ratio of sample to cocktail in the counting vial and the type of scintillation cocktail used. It is rendered even more inefficient by the presence of foreign material in the sample/cocktail mixture. Any hindrance to the liquid scintillation detection process is known as a quenching effect. Without accounting for quenching, the counting rates obtained from the liquid scintillation spectrometer may contain gross error.

Quenching is monitored on the Beckman LS 8000 by what is known as the H-number (H#), which is the instrument's indirect measure of efficiency. The H# is an expression of the extent of quench of a sample versus that of a cesium-137 standard internal to the scintillation spectrometer. The reader is referred to Long (1978) for a thorough discussion of the H# technique for quench monitoring.

A quench curve, which gives counting efficiency as a function of H#, is created by calculating the counting efficiencies of a set of tritiated standards of known activities and comparing them to the H-numbers generated by the LSC. The counting efficiency of a standard is defined as:

$$CE = [\text{CPM}(\text{qs})/\text{ml} - \text{CPM}(\text{b})] / \text{DPMo}(\text{qs})/\text{ml};$$

where:

$\text{CPM}(\text{qs})/\text{ml}$ = counting rate of the quench standard

$\text{CPM}(\text{b})$ = background counting rate

$\text{DPMo}(\text{qs})/\text{ml}$ = actual activity of quench standard.

The quench curve standards were prepared by adding varying amounts of carbon tetrachloride to the sample/cocktail mixture. The actual mass of quenching agent was very small; only a few drops from a Pasteur pipet are necessary. Quench can just as easily be manipulated by varying the amount of cocktail added to a standard.

The quench curve used for calculating counting efficiencies in this study is plotted in Figure 16. Five quench standards were counted eight times each, with a blank sample (dead water) accounting for background.

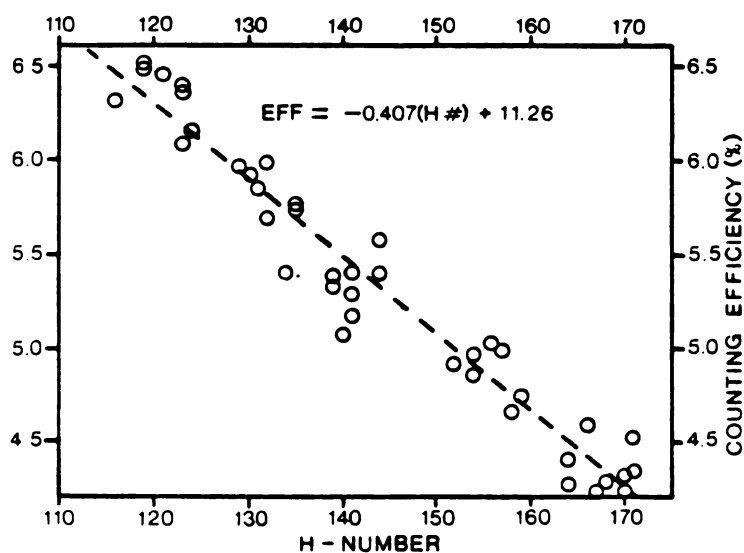


Figure 16. Quench curve for tritium counting window 170-225.

APPENDIX B

TRITIUM COUNTING DATA

Sample	H#	Eff	DPM	CPM	EE	TU	Error
ES1	124.7	11.26	0.710	10.14	0.00474	98.6	6.5
250A	132.2	5.80	0.434	7.69	0.00967	60.4	9.3
406	133.0	5.77	0.004	4.16	0.01044	0.5	3.6
188	139.7	5.49	0.356	6.71	0.00914	49.5	5.3
220	134.3	5.71	0.412	7.29	0.00797	57.3	5.2
223	135.7	5.66	0.291	6.10	0.00845	40.4	5.4
407	130.2	5.88	0.238	6.09	0.00993	33.1	4.5
ES2	114.6	6.53	0.694	8.57	0.00691	96.5	3.1
100	117.7	6.40	0.001	3.58	0.00649	0.2	2.5
362	136.7	5.61	0.356	7.69	0.01206	49.5	4.7
370	127.3	6.00	0.005	4.13	0.01293	0.7	1.7
29	123.3	6.17	-0.031	3.83	0.01176	0	4.3
146	130.7	5.86	0.254	6.59	0.00963	35.3	4.5
413	110.0	6.72	-0.085	3.55	0.00647	0	4.7
ES3	125.0	6.10	0.710	6.40	0.00761	98.6	11.4
60	117.3	6.42	-0.076	3.47	0.00178	0	9.6
248	130.0	5.89	0.378	4.98	0.00419	52.4	13.7
296	127.0	6.01	0.883	5.96	0.00239	122.6	16.8
371	127.0	6.01	0.682	6.15	0.00585	94.7	12.0
ES4	120.7	10.76	0.708	10.09	0.00437	98.4	6.6
115	131.3	10.71	0.525	6.96	0.00281	73.0	9.3
144	123.3	10.75	0.800	9.80	0.00368	111.1	7.8
213	123.0	6.18	0.587	8.47	0.00667	81.6	7.1
84	129.3	5.92	0.594	9.25	0.00787	82.5	6.6
114	140.7	5.45	0.433	7.05	0.00647	60.1	7.7
ES5	132.7	5.80	0.703	8.58	0.00836	97.6	8.7
77	129.3	5.92	0.981	10.25	0.00587	136.3	9.4
410	126.7	6.03	0.229	5.87	0.00778	31.8	6.6
58	130.0	5.89	0.147	5.34	0.00678	20.4	6.2
216	126.7	6.03	0.863	9.44	0.00586	119.8	9.3
368	130.3	5.88	0.195	5.92	0.01047	27.1	5.5

APPENDIX C

TRITIUM ACTIVITY CALCULATION

The formula used to calculate tritium activities from counting data is that used by Wyerman (1976). The counting parameters which are required for determining an activity include those obtained for electrolytic standards as well as the samples themselves. For each electrolytic standard the following values must be known:

- a) initial volume (ml).....Vo(es)
- b) final volume (ml).....Vf(es)
- c) initial activity.....DPMo(es)/ml
- d) counting rate.....CPM(es)
- e) counting efficiency.....CE(es)

For each sample, the same data must be known, except for the initial activity, of course, which is what is being measured. For the background sample (dead water), only the counting rate (CPM(b)) must be known.

Calculation

Tritium activities are expressed as disintegrations per minute per milliliter (DPM/ml) in the formula used by Wyerman (1976). Calculated values are given as:

$$\text{DPM/ml} = [\text{CPM(s)}/\text{ml} - \text{CPM(b)}] / (\text{CE})(\text{EE})(\text{V}/\text{Vo}); \quad [1]$$

where:

CE = counting efficiency of the sample

EE = electrolytic efficiency of the sample

V = mass of sample used during counting

Vo = mass of sample before electrolysis

CPM(s)/ml = counting rate of sample

CPM(b) = counting rate of background

Electrolytic efficiency is a measure of the fraction of tritium remaining in the liquid phase of a sample upon completion of electrolysis. It is defined as:

$$EE = (V_o/V)^{-(1/B)}; \quad [2]$$

where:

B = fractionation factor of the sample.

The fractionation factor for all samples within an electrolytic set are assumed to be equal, for B, in turn, is a function of the electrolytic efficiency of the electrolytic standard.

The fractionation factor, B, is defined as:

$$B = -\log [V_o(es)/V(es)] / \log EE(es); \quad [3]$$

where the electrolytic efficiency of the standard (of an electrolytic set), EE(es), is defined as:

$$EE(es) = [DPM(es)/ml] [V(es)] / [DPMo(es)/ml] [V_o(es)]. \quad [4]$$

The unknown in equation [4] is DPM(es)/ml, which is the final activity of the electrolytic standard. It is defined as:

$$\text{DPM(es)/ml} = [\text{CPM(es)/ml} - \text{CPM(b)}] / \text{CE(es)}.$$

The counting efficiency, CE, of the standard, as well that of individual samples, are calculated from the empirically derived quench curve function previously discussed in Appendix A.

To convert values of DPM/ml to tritium units (TU), the following relationship is used:

$$1 \text{ TU} = 0.0071 \text{ DPM/ml.} \quad [5]$$

BIBLIOGRAPHY

BIBLIOGRAPHY

Anderson, M. P., 1979. Using models to simulate the movement of contaminants through groundwater flow systems. C.R.C. Critical Reviews in Environmental Control, 9:97-156.

Andres, G. and Egger, R., 1985. A new tritium interface method for determining the rate of recharge of deep groundwater in the Bavarian Molasse Basin. Journal of Hydrology, 82:27-38.

Begeman, F. and Libby, W. F., 1957. Continental water balance, groundwater inventory and storage times, surface ocean mixing rates and world-wide water circulation patterns from cosmic ray and bomb-tritium. Geochimica et Cosmochimica Acta, 12:277-296.

Bernabo, J. C., 1981. Quantitative estimates of temperature changes over the last 2700 years in Michigan based on pollen data. Quaternary Research, 15:143-159.

Bredenkamp, D., Schutte, J. and Dutoit, G., 1974. Recharge of a dolomitic aquifer as determined from tritium profiles, In Proceedings of a symposium, Vienna, International Atomic Energy Agency, p. 73-94.

Brown, R. M., 1961. Hydrology of tritium in the Ottawa Valley. Geochimica et Cosmochimica Acta, 21:199-216.

Chagnon, S. A. and Jones, D. M. A., 1972. Review of the influences of the Great Lakes on weather. Water Resources Research, 8:360-371.

Clayton, R. N., 1961. Oxygen isotope fractionation between calcium carbonate and water. Journal of Chemistry and Physics, 34:724-726.

Clayton, R.N., Friedman, I., Graf, D.L., Mayeda, T.K., Meents, W.F. and Shimp, N.F., 1966. The origin of saline formation waters. 1. Isotopic composition. Journal of Geophysical Research, 71:3869-3882.

Craig, H., 1961a. Isotopic variation in meteoric waters. Science, 133:1702-1703.

Craig, H., 1961b. Standard for reporting concentration of deuterium and oxygen-18 in natural waters. Science, 133:1883-1884.

Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus*, 16:436-468.

Delcore, M.R., 1985. Rate of recharge to a heterogeneous drift aquifer: a test of the bomb-tritium method. M.S. thesis, Michigan State University.

Delcore, M.R. and Larson, G.J., 1987. Application of the tritium interface method for determining recharge rates to unconfined drift aquifers. II. Non-homogeneous case. *Journal of Hydrology* (in press).

Desaulniers, D.E., Cherry, J.A. and Fritz, P., 1981. Origin, age and movement of pore water in argillaceous Quaternary deposits at four sites in southwestern Ontario. *Journal of Hydrology*, 68:231-257.

Dincer, T., Al-Mugrin, A. and Zimmerman, U., 1974. Study of the infiltration and recharge through the sand dunes in arid zones with special reference to the stable isotopes and thermonuclear tritium. *Journal of Hydrology*, 23:79-109.

Dunne, T. and Black, R.D., 1971. Runoff processes during snowmelt. *Water Resources Research*, 7:1160-1172.

Egboka, B.C.E., Cherry, J.A., Farvolden, R.N. and Frind, E.O., 1983. Migration of contaminants in groundwater at a landfill: a case study. 3. Tritium as an indicator of dispersion and recharge. *Journal of Hydrology*, 63:51-80.

Eichenlaub, V., 1970. Lake effect snowfall to the lee of the Great Lakes: its role in Michigan. *American Meteorological Society Bulletin*, 51:403-412.

Evenson, E.B., Farrand, W.R., Eschman, D.F., Mickelson, D.M. and Maher, L.J., 1976. Greatlakean Substage - a replacement for Valderan Substage in the Lake Michigan basin. *Quaternary Research*, 6:411-24.

Ferronsky, V.I. and Polyakov, V.A., 1982. Environmental isotopes in the hydrosphere. Translated by S.V. Ferronsky. Wiley, New York, 466 pp.

Florkowski, T., 1981. Low-level tritium assay in water samples by electrolytic enrichment and liquid scintillation counting in the International Atomic Energy Agency laboratory. In: *Methods of low level counting and spectrometry. Proceedings of a symposium, International Atomic Energy Agency*, p. 335-351.

Fried, J.J., 1975. Groundwater pollution. Elsevier Scientific, 330 p.

Friedman, I., Redfield, A.C., Schoen, B. and Harris, J., 1964. The variation of the deuterium content of natural waters in the hydrologic cycle. *Review of Geophysics*, 2:177-224.

Gelhar, L.W., Mantoglou, A., Welty, C. and Rehfelt, K.R., 1985. A review of field scale physical solute transport processes in saturated and unsaturated porous media. Rpt. RP-2485-05, Elect. Power Res. Institute, Palo Alto, Calif.

Graf, D.L., Friedman, I. and Meents, W.F., 1965. The origin of saline formation waters. 2. Isotopic fractionation by shale micropore systems. *Illinois Geologic Survey Circular* 393, p. 32.

Hitchon, B. and Friedman, I., 1969. Geochemistry and origin of formation waters in the western Canada sedimentary basin. 1. Stable isotopes of hydrogen and oxygen. *Geochimica et Cosmochimica Acta*, 33:1321-1349.

International Atomic Energy Agency, 1953-1986. Environmental isotope data nos. 1, 2, 3, 4, 5, 6, 7. Worldwide survey of isotope concentrations in precipitation. Technical report series 96, 117, 129, 147, 165, 192, 260.

Javandel, I., Doughty, C. and Tsang, 1984. Groundwater transport: Handbook of applied models. American Geophysical Union Water Resources Monograph No. 10. 228 p.

Kondoh, A., 1986. Study on the groundwater flow system by environmental tritium in Ichihara region, Chiba prefecture. *Environmental Research Center Bulletin*, Ibaraki, Japan.

Lamb, H.H., 1966. The changing climate. Methuen, London.

Larson, G.J., Delcore, M.R. and Offer, S.A., 1987. Application of the tritium interface method for determining recharge rates to unconfined drift aquifers. I. Homogeneous case.

Long, D.L., Rezabek, D.H., Takacs, M.J. and Wilson, T.P., 1986. Geochemistry of groundwater in Bay County, Michigan. Michigan Dept. of Public Health Research Rpt. ORD38553, 3 volumes.

Long, E., 1978. Liquid scintillation counting theory and techniques. Beckman Instruments, Irvine, California.

Maloszewski, P., Rauert, W., Stichler, W. and Herrman, A., 1983. Application of flow models in an alpine catchment area using tritium and deuterium data. *Journal of Hydrology*, 66:319-330.

- Martin, H., 1957. Outline of the Geologic History of the Grand Traverse Region. Michigan Dept. of Conservation, Geological Survey Division Publication 49.
- Nir, A., 1964. On the interpretation of tritium "age" measurements of groundwater. Journal of Geophysical Research, 69: 2589-2595.
- Nurnberger, F., State Climatologist, 1953 - 1985. Precipitation records for Northport - Sutton's Bay station. Michigan Dept. of Agriculture, Climatology Division, Michigan State University.
- Nurnberger, F., State Climatologist, 1982. Summary of evaporation in Michigan. Michigan Dept. of Agriculture, Climatology Division, Michigan State University.
- Offer, S.A., 1982. Determination of recharge rates to a drift aquifer using bomb-tritium in the saturated zone. M.S. thesis, Michigan State University.
- Ogata, A., 1970. Theory of dispersion in a granular medium. U.S. Geological Survey Professional Paper 411-A.
- Petrie, M.A., 1984. Morphologic and Lithologic influences on recharge in a glaciated basin. M.S. thesis, Michigan State University.
- Price, A.G. and Hendrie, L.K., 1983. Water motion in a deciduous forest during snowmelt. Journal of Hydrology, 64:339-356.
- Rabinowitz, D., Gross, G. and Holmes, C., 1977b. Environmental tritium as a hydrometeorologic tool in the Roswell Basin, New Mexico. III. Hydrologic parameters. Journal of Hydrology, 32:35-46.
- Sklash, M., Mason, S., Scott, S. and Pugsley, C., 1986. An investigation of the quantity, quality and sources of groundwater seepage into the St. Clair River near Sarnia, Ontario, Canada. Water Poll. Res. J. Canada, 21:351-367.
- Smith, D., Wearn, P., Rowe, P. and Richards, H., 1970. Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. In: Isotope Hydrology; proceedings of a symposium, Vienna, International Atomic Energy Agency, p. 73-85.
- Sudicky, E.A., Cherry, J.A. and Frind, E.O., 1983. Migration of contaminants in groundwater at a landfill: a case study. 4. A natural-gradient dispersion test. Journal of Hydrology, 63:83-108.

- Sukhiya, B.S. and Shaw, C.R., 1976. Conformity of groundwater recharge by tritium method and mathematical modeling. *Journal of Hydrology*, 30:167-178.
- Thatcher, L.L., Janzer, V.J. and Edwards, K.W., 1977. Methods for determination of radioactive substances in water and fluvial sediments, Chapter A5. In: *Techniques of water-resources investigations of the U.S. Geological Survey*.
- Toth, J., 1962. A theory of groundwater motion in small drainage basins in central Alberta, Canada. *Journal of Geophysical Research*, 67:4375-4387.
- Toth, J. 1963. A theoretical analysis of groundwater flow in small drainage basins. *Journal of Geophysical Research*, 68:4795-4811.
- U.S. Geological Survey, Water Resources Division, Lansing, Michigan. *Streamflow data for Michigan, 1953-1985*.
- Weber, H.L., 1973. Soil surey of Leelanau County, Michigan. U.S. Dept. of Agriculture, Soil Conservation Service.
- Webb, T. and Clark, D.R., 1977. Calibrating micropaleontological data in climatic terms: A critical review. *Annals of the New York Academy of Science*, 288:93-118.
- Williams, L.D. and Wigley, T.M.L., 1983. A comparison of evidence for late Holocene summer temperature variations in the northern Hemisphere. *Quaternary Research*, 20:286-307.
- Wurzel, P., 1983. Updated radioisotope studies in Zimbabwean ground waters. *Groundwater*, 21:597-605.
- Wyerman, T., 1976. Laboratory facility of the analysis of natural levels of tritium in water. U.S.G.S. Open File Report.
- Zimmerman, U., Munnich, K.O. and Roether, W., 1967. Downward movement of soil moisture by means of hydrogen isotopes. In: *Isotope techniques in the hydrologic cycle*. American Geophysical Union Monograph No. 11: 28-36.

MICHIGAN STATE UNIV. LIBRARIES



31293001003650