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TRITIUM IN PRECIPITATION FROM LOWER MICHIGAN

By

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ABSTRACT

TRITIUM IN PRECIPITATION FROM LOWER MICHIGAN

by

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Precipitation samples were collected at 15 stations in lower Michigan to determine the distribution of and factors affecting tritium concentrations in precipitation for the period of July through December 1989. The data show that tritium concentrations increase in a west to east direction (16 to 36 TU) within the southern part of lower Michigan and generally increase in a south to north direction (22-32 TU) within the northern part of lower Michigan. In the area separating the southern and northern part of lower Michigan tritium concentrations tend to be low (16-20 TU).

The distribution of tritium in precipitation in the southern and the northern part of lower Michigan is most likely controlled by the type and origin of air masses flowing across lower Michigan. The major air masses include maritime tropical and continental polar and are associated with a particular climatic regime. In the south the climatic regime is the Southern Lower Peninsula Transitional Province and in the north the climatic regime is the Northern Lower Peninsula Province. Water vapor from Lake Michigan does not seem to be significantly affecting the concentration of tritium in precipitation across southern lower Michigan.

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INTRODUCTION

Tritium has been used extensively in measuring the pathways and rates of recharge to natural waters. For example, Dincer et al (1974), Andersen and Sevel (1974) and Delcore and Larson (1987) have utilized tritium produced by thermonuclear testing to assess infiltration and recharge rates to groundwater. While in another study Egboka et al (1983) used 'bomb' tritium to investigate migration of contaminants in groundwater at a landfill. Tritium has also been used in lake studies, for determining mixing rates between stratified layers (Gonfiantini et al, 1979) and in assessing evaporation rates from lakes (Brown and Barry, 1979; Gat, 1970 and Prantl, 1974). While these lake studies yielded much information on lake dynamics, none of them looked at how large lakes have affected the concentration of tritium in precipitation falling on their lee shores.

Prerequisites required for the hydrological application of tritium generally rely on a detailed record of the areal and temporal distribution of tritium in precipitation falling on the area of study. Within lower Michigan however, this information is generally not available, since there has been no systematic monitoring of tritium in precipitation within the state. In fact, the only way to estimate the concentration of tritium in precipitation falling on Michigan has been to extrapolate from the record of tritium in precipitation of Ottawa and Chicago (Regalbuto, 1987 and Delcore, 1985).

The purpose of this survey is to closely examine the distribution of tritium in precipitation falling on lower Michigan in the hope that this will provide useful information for tritium's continued application as a hydrologic tool.

CLIMATOLOGY OF LOWER MICHIGAN

The Great Lakes region experience a continental climate modified by maritime influences. Changnon and Jones (1972) and Eichenlaub (1979) identified that the type of weather conditions observed are a function of:

1) depth of the lakes - The depth will affect the heating and cooling rates, degree of interaction with air masses and the amount of ice cover on the lake surface in winter.
2) orientation of the lake and areal extent - These factors will result in modification of weather of the surrounding region (lake effect).
3) origin and type of air mass which dominate the area - The air mass influence varies according to the season (Figure 1).
4) latitude - Because of the latitude winter temperatures are cold enough that some precipitation falls as snow.
5) position of the lake region in the belt of westerlies - This is a region of west to east air flow.

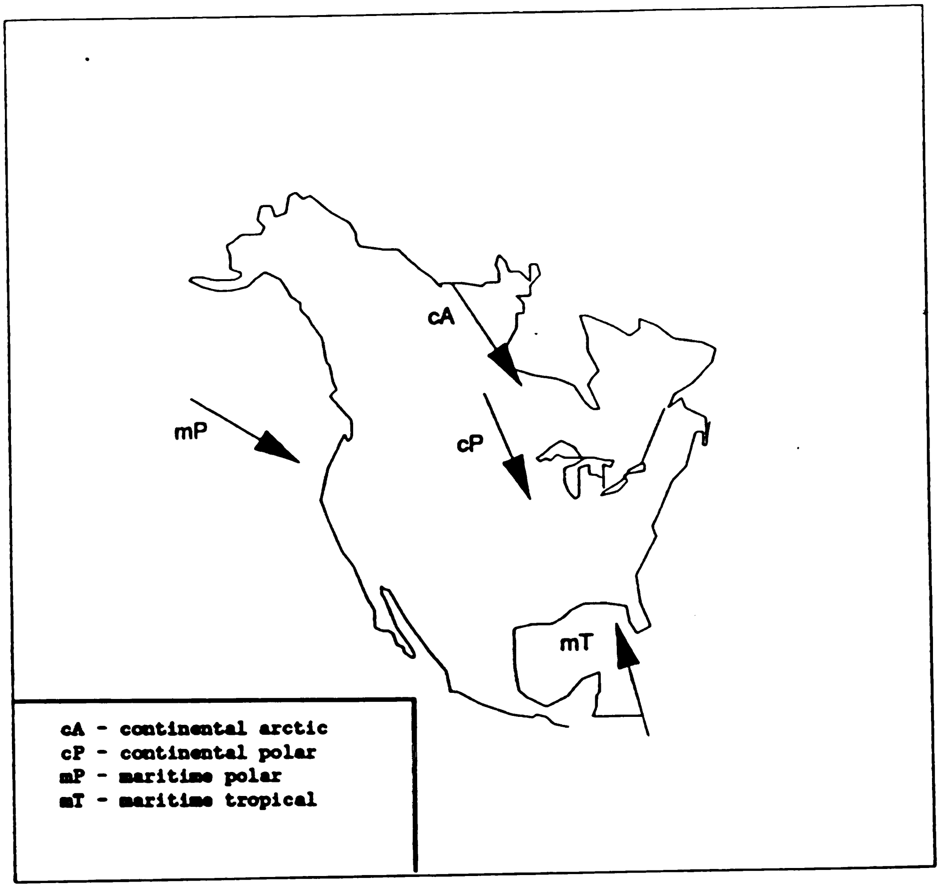

Figure 1. Air masses affecting the Great Lakes region.

LAKE EFFECT

The modifying effect of lakes on weather and climate in the Great Lakes region is known as the lake effect. This effect is primarily due to the difference in temperature between lake and land surfaces and, also the area of lake surface which is exposed to the atmosphere and available for evaporation (Eichenlaub, 1979). In general, large lake surfaces react slowly to temperature changes and therefore are cooler than the land during the warm months and warmer during the cold months. Air masses which pass over large lakes will therefore be affected by the water's modifying temperature.

Lake Michigan which lies in the Great Lakes area provides conditions favorable for the formation of thunderstorms, hailstorms and snow by providing heat and occasionally moisture to overlying air masses. This heating of air masses helps to create convective currents and uplifts the moisture laden air (Changnon, 1968).

Summer and Fall Effects

Thunderstorms induced by the lake occur throughout the year but the lake's influence on the production of these storms is variable, being strongest in summer and fall. The influence of the lake on thunderstorms in the summer appears to be mostly as a heat source (Changnon, 1968). Whereas in fall, the lake acts as a source of both heat and moisture for thunderstorms. About 15-17% of the average fall precipitation in Michigan is produced over the lake.

Winter and Spring Effects

Snowfall in the Great Lakes region can be induced by both cyclonic and lake inputs. Eichenlaub (1970) identified one synoptic condition which is favorable for the formation of lake effect snow. This occurs when a low pressure system (cyclone) lies east of the Great Lakes region and a high pressure system to the west. This condition allows cold Arctic air to descend on the area (Eichenlaub, 1979). The cold air is warmed by the surface waters of the lake and evaporation of lake water takes place. The air mass becomes unstable, rises and clouds can develop which may produce snow that falls in downwind areas, mostly on the eastern shores of the lake (Eichenlaub et al, 1990). This region is called the snow belt and the maximum snowfall region extends 10-25 miles inland (Changnon, 1968). The amount of lake effect snow which falls is also dependent on the fetch (length of lake over which the air mass travels). The longer the air travels across the lake the greater chance of picking up moisture (Eichenlaub, 1979). The direction and amount of fetch over which the air masses pass is a function of the relative positions of the high and low pressure systems affecting the area. Lake effect snow has less moisture content than frontal snow and therefore contributes less than these snows to total seasonal precipitation (Dayton, 1972).

December marks the peak in lake related snowfall with up to 100% more snow than along the Chicago side of Lake Michigan. In January, February and March the lake affected snowfall in the southern and northern part of western lower Michigan is 33% to 66% greater than similar latitudinal sites in eastern Wisconsin (Changnon, 1968). Estimates of the contribution of lake derived snow to measurable snow in the snow belts ranges from 30-52% (Eichenlaub, 1970 and Changnon, 1968). The annual snowfall distribution shows highs in northwestern rather than southwestern lower Michigan and this is attributed to both lake and altitude effects (Changnon, 1968).

AIR MASSES AND MESOCLIMATIC REGIMES

The air masses which affect the weather in the region are shown in Figure 1. The continental polar (cP) air mass has its origin in Central Canada and the Northern Great Plains and is characterized by low moisture content (Eichenlaub, 1979). The source region for modified polar (mP) air is the Northern Pacific and thus its air is generally cold and moist. Whereas maritime tropical (mT) air originates in the Gulf of Mexico and is warm and moist. The continental Arctic (cA) air mass is from the Arctic Ice Cap and is extremely cold and dry. An important effect of the air masses because of their characteristics is their influence on the surrounding area during the different seasons. For example in Winter the lake may act as a local source of moisture for the cold and dry continental polar (cP) air and in Summer the warm maritime tropical air (mT) may actually provide moisture to the lake. Continental polar and continental arctic air are the major air masses in winter, especially on windward slopes near to the lake, whereas maritime tropical air is dominant throughout the other seasons (Niedringhaus, 1966).

Niedringhaus (1966) divided the lower peninsula into two major mesoclimatic regions: Southern Lower Peninsula Transitional Province and the Northern Lower Peninsula Province (Figure 2). Air masses in the southern province are mostly controlled by the maritime tropical source. The northern province in contrast is largely surrounded by the Great Lakes and hence air masses passing over it are generally lake modified and most frequently have a polar continental source.

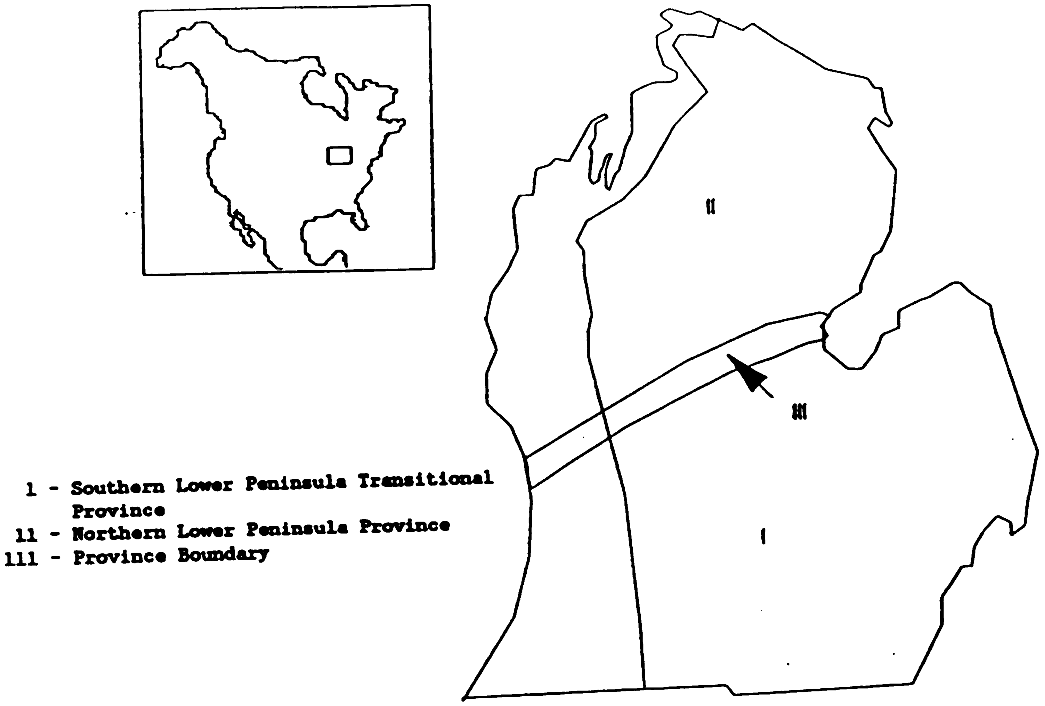

Figure 2. Location of study area and mesoclimatic regions of lower Michigan.

METHODS

SAMPLING METHOD

Precipitation samples from the lower peninsula of Michigan were obtained from the stations shown in Figure 3. For nine of the stations composite monthly samples were collected for the period July 1 through December 30, 1989. At the four remaining stations precipitation samples were collected for the period January 1 to December 30, 1989. The apparatus for collecting the samples consisted of a 17 cm diameter funnel connected to a ball valve and attached to a 1 liter reservoir tank. Precautions taken to reduce evaporation losses included placing the reservoir beneath the ground surface at <1 m, and the addition of paraffin oil to the reservoir after collection of monthly samples. Several samples of Lake Michigan surface water were also collected from the central part of the lake during September of 1989.

SAMPLE PREPARATION

Six month composite samples (July-December) were made for each precipitation station, by mixing together volume weighted samples of monthly precipitation. The samples were then transferred into separatory funnels to separate any residual oil from the samples. The six month composite samples were then filtered, mixed with hot paraffin wax to remove any oil remaining and stored in airtight containers. The samples of lake water required no preparation.

Electrolysis and post-distillation proceedures were then performed on all the samples. For an explanation of these proceedures see Appendix A.

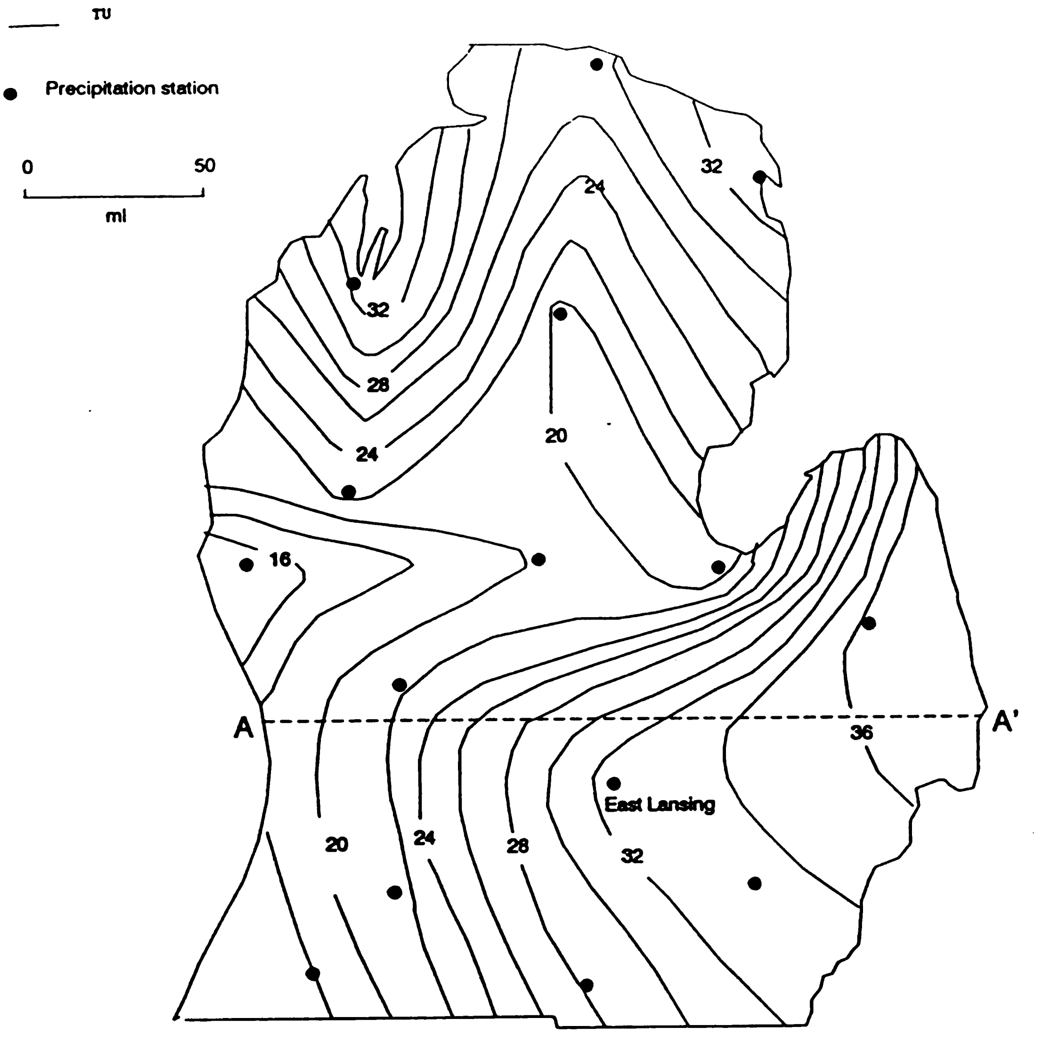

Figure 3. Location of precipitation stations and contoured tritium concentrations in precipitation.

RESULTS

TRITIUM IN PRECIPITATION

Time Variation

Fluctuations in the amount of tritium in East Lansing precipitation for the 12 month period of 1989 are shown in Table 1. The data indicate a high concentration of 51 and 128 TU in June and July, respectively, and a low concentration of 5 TU in November. The tritium concentration in precipitation during the other months of the year varied from approximately 26 to 48 TU. The average tritium concentration for the period January through December is 34 TU and for the period July through December is 33 TU (Table 2).

Spatial Variation

The concentration of tritium in precipitation collected at 15 stations in Michigan for the period from July 1989 to December 1989 is shown in Table 1 and Figure 3. The data show a range of tritium concentrations from 14.97 TU at the westernmost station (Shelby) to 36.43 TU at the easternmost station (Marlette) and an average tritium concentration of 24.9 TU. Figure 3 also shows that the concentration of tritium tends to increase from west to east (16-36 TU) in the southern part of lower Michigan whereas in the northern part the concentration of tritium tends to increase (22-32 TU) from south to north. In the region separating these two areas there is also an east-west belt where tritium concentrations tend to be low (16-20 TU).

Table 1. Tritium Results

SMPL	CPM	CE	EE	β	TU	+/-TU
STD.	39.03	0.13	0.66	5.29	3462.70	76.86
BKG.	3.50	0.13		-0.19		
el1	5.97	0.13	0.64		31.04	2.04
el2	6.34	0.12	0.64		39.06	2.68
el3	6.28	0.13	0.64		34.96	2.44
el4	6.11	0.12	0.66		40.11	2.96
el5	5.09	0.12	0.58		26.05	2.97
el6	7.63	0.14	0.64		51.50	2.59
el7	11.46	0.14	0.67		128.22	4.11
el8	6.10	0.13	0.65		35.04	2.59
el9	6.24	0.13	0.62		29.60	2.09
STD	45.84	0.10	0.85	16.63	5411.69	121.04
r2tr	8.52	0.13	0.85		33.63	1.87
r2an	7.45	0.13	0.84		33.72	2.43
r2hi	7.56	0.13	0.86		28.46	1.98
r2ch	6.97	0.11	0.85		27.50	2.30
r2pl	6.09	0.14	0.84		20.37	2.50
r2kz	6.78	0.12	0.85		21.55	1.93
r2ba	5.94	0.14	0.83		22.02	2.95
STD	71.26	0.14	0.76	9.40	6297.59	134.11
r311	10.18	0.12	0.75		57.80	2.45
r334	8.45	0.12	0.73		47.90	2.98
r337	15.42	0.13	0.75		101.35	1.98
r3sn	7.54	0.13	0.74		31.91	2.35
r3gr	5.92	0.12	0.74		21.72	1.25
STD	59.87	0.12	0.90	24.55	5806.66	123.40
r4oc	11.69	0.13	0.90		47.98	1.48
r4no	4.61	0.12	0.89		4.63	0.61
r4gr	7.76	0.13	0.90		19.66	0.92
r4ed	7.50	0.12	0.90		17.96	0.88
r4ba	7.56	0.13	0.89		19.71	0.96
r4al	9.27	0.12	0.90		31.63	1.18
r4sh	5.85	0.13	0.88		14.97	1.11
r4ma	9.23	0.12	0.90		36.43	1.37

Table 2. Tritium Data for East Lansing

Month	Mthly pptn(ins)	Avg mthly T.U.	T.U.- ins
Jan	1.15	31.04	41.05
Feb	0.67	39.06	26.17
Mar	2.13	34.96	74.46
Apr	1.44	40.11	57.76
May	6.57	26.05	171.15
Jun	3.61	51.5	185.92
Jul	0.93	128.22	119.24
Aug	4.9	35.04	171.70
Sep	3.49	29.6	103.30
Oct	1.29	47.98	61.89
Nov	3.65	4.63	16.90
Dec	0.86	31.91	27.44
Total	30.69		1,056.98
T.U. (12 mth)			34.44
T.U. (Jul-Dec)			222.79

INTERPRETATION OF TRITIUM DATA

General

Tritium is produced naturally in the atmosphere by bombardment of nitrogen by solar radiation (Faure, 1986). It is also produced anthropogenically, especially by thermonuclear testing in the 1950's and 1960's, when very large amounts of tritium were introduced into the stratosphere (Michael, 1989). Eventually the tritium generated is oxidized and becomes part of the water molecule as HTO (Michael, 1989). Vertical exchange processes bring this tritium into the troposphere. Tritium is eventually removed from the troposphere by precipitation and direct molecular exchange over both land and oceans (Eriksson, 1967).

There are certain controls on the amount of tritium in precipitation. These include seasonal, continental, and latitudinal effects. The seasonality of tritium concentrations in precipitation occurs because transference of tritium from the stratosphere to the upper troposphere takes place in winter to early spring (Thatcher, 1967). However, downward mixing into the lower troposphere is delayed and results in a tritium maxima in May-June for the Northern Hemisphere, and a minima in the fall and winter, generally around October to December (Eriksson, 1967).

Tritium concentrations in air masses that pass over the oceans is significantly diluted by exchange with ocean water vapor (Gat, 1962). As vapor flows inland it picks up tropospheric tritium and therefore the concentration of tritium in precipitation increases inland (Eriksson, 1967). This is known as the continental effect. Increasing tritium concentrations in precipitation with increasing latitude is known as the latitudinal effect and is the result of the fact that the major input of tritium from the troposphere appears to be above 50°N and 50°S latitude (Thatcher, 1967). Figure 4 illustrates for the continental United States the prevailing pattern of tritium in precipitation which generally increases from southwest to northeast (Michael, 1989). The tritium distribution is a function of both the latitudinal and continental effects.

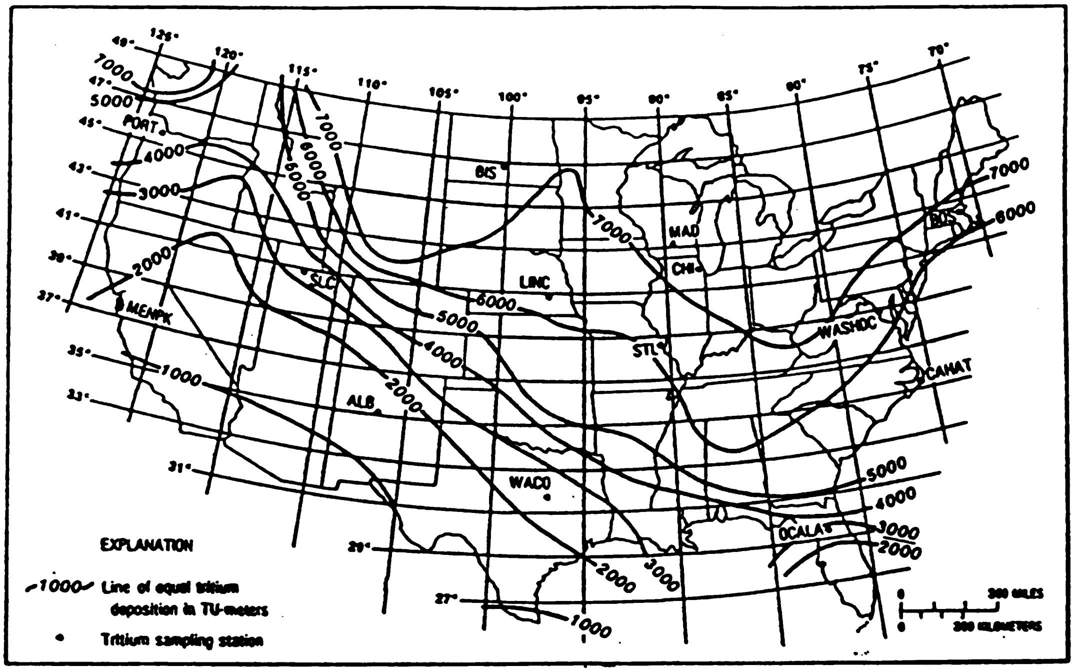

Figure 4. Tritium deposition in the continental United States (Michael, 1989).

Time Variation

East Lansing vs. Ottawa and Chicago - The record of tritium in precipitation for East Lansing during 1989 is presented in Figure 5a and b together with the record of tritium in precipitation for Chicago and Ottawa for a total of 10 years. The record for East Lansing is normalized against the highest monthly value recorded for the year (Table 2), whereas the records for Chicago and Ottawa are 10 year averages of the normalized monthly values for each year.

The tritium record for both Chicago and Ottawa show that the concentration of tritium in precipitation is generally greatest during the months of May through August and least during the months of October through December. This variation of tritium in precipitation clearly reflects the seasonal transference of tritium from the stratosphere to the troposphere. With respect to the East Lansing data, it too shows a similar variation of tritium in precipitation and is also related to the seasonal transference of tritium from the stratosphere to the troposphere. However, the maximum concentration of tritium occurs only during the months of June and July as opposed to May through August.

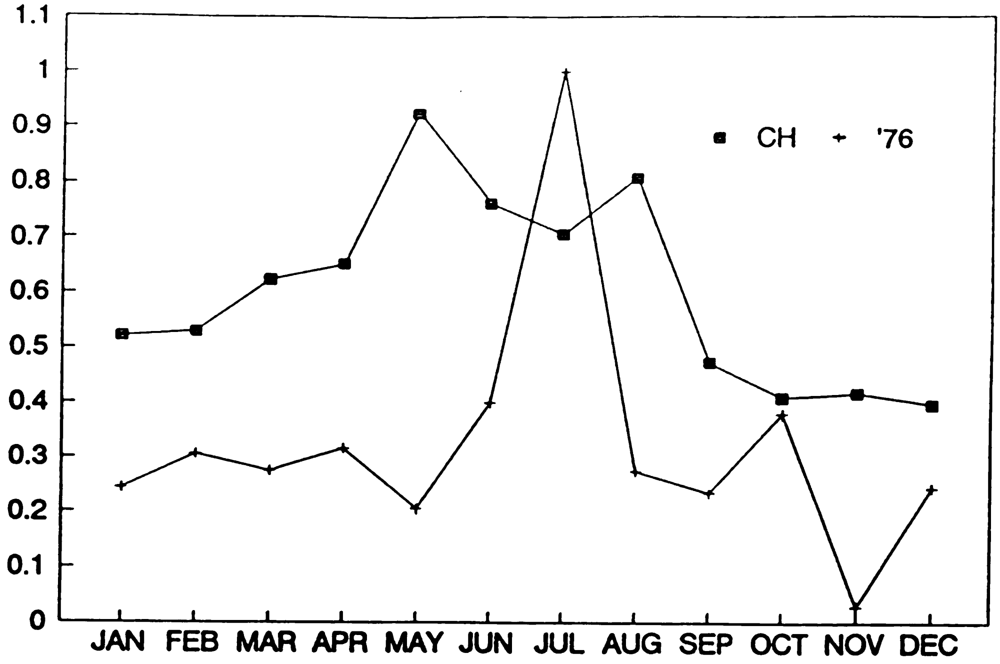

Figure 5a. Normalized tritium data for East Lansing (1989) and Chicago (1967-1977).

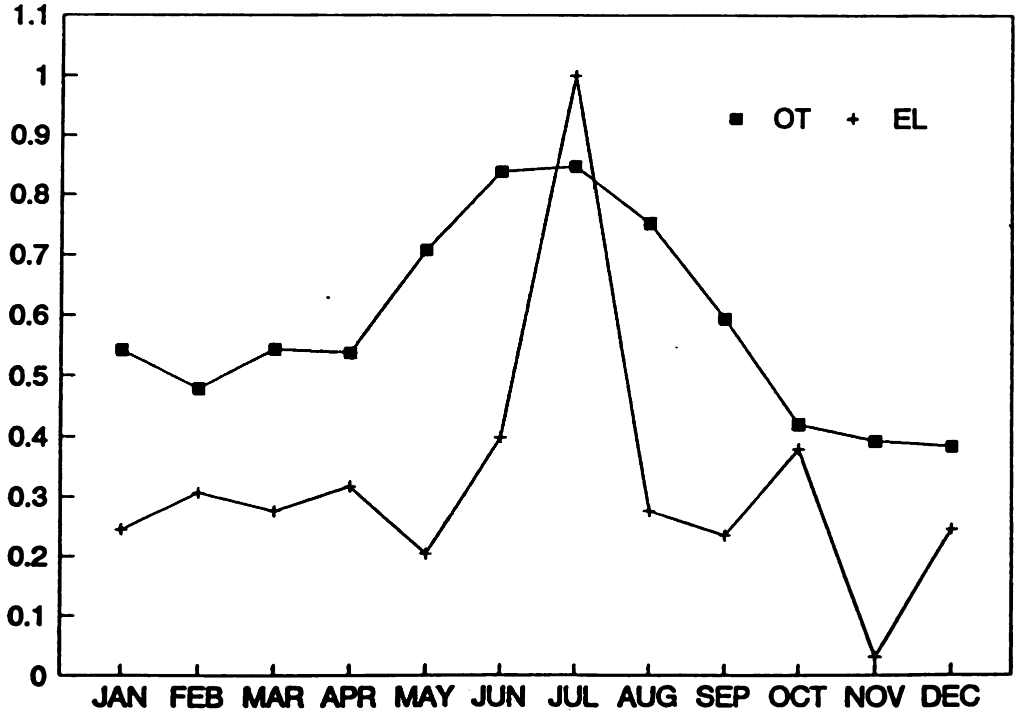

Figure 5b. Normalized tritium data for East Lansing (1989) and Ottawa (1972-1983).

Spatial Variation

Interstation differences for tritium in precipitation may be the result of a combination of meteorological factors which include the source region and pathways of air masses crossing the region and reflect the mesoclimatic provinces of lower Michigan. This is supported by Brown (1974) who cites that isotope concentrations in Ottawa are greatly affected by the origin and trajectories of air masses which enter the area. It is possible that the above factors also affect the isotope concentrations of tritium in precipitation in lower Michigan because of its location in the path of air masses affecting Ottawa.

The prevailing wind direction and its relationship with the distribution of tritium in precipitation for lower Michigan is illustrated in Figure 6. The southern part of lower Michigan is characterized by southerly and southwesterly prevailing winds as well as a southwesterly to northeasterly gradient in tritium concentrations. This part of the state is related climatically to the Southern Lower Peninsula Transitional Province of Niedringhaus (1966) which is shown in Figure 6. The source of the major air mass associated with the winds in this province is the Gulf of Mexico. This air mass, called the maritime tropical (mT), flows from the Gulf across the continent and towards the northeast. The tritium concentrations recorded in precipitation related to this air mass also tends to increase along this path, due to the continental effect previously discussed and shown in Figure 4

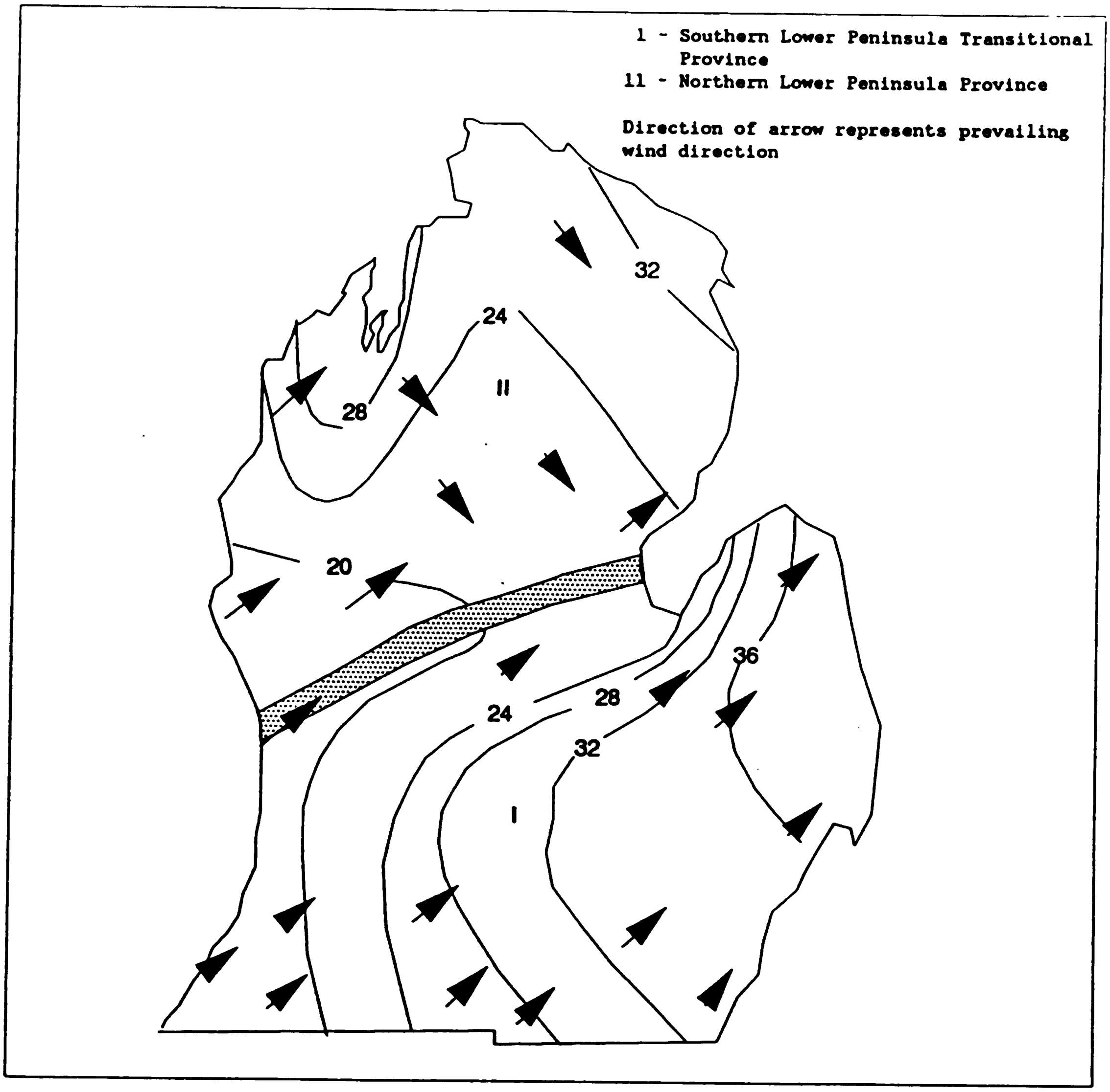

Figure 6. Prevailing wind direction, contoured tritium concentrations in precipitation and mesoclimatic regions.

(Eriksson, 1967). The distribution of tritium in precipitation for southern lower Michigan closely resembles this pattern and is probably a continuation of this regional trend.

The northern part of lower Michigan is typified by southwesterly and northwesterly prevailing winds and by a general north to south gradient of decreasing tritium concentrations. This portion of the state forms part of the Northern Lower Peninsula Province (Niedringhaus, 1966) and is illustrated in Figure 6. The origins of the major air mass for the prevailing winds in this region are Central Canada and the Northern Great Plains and is called the continental polar (cP). Tritium concentrations in precipitation associated with this air mass tend to decrease in a southerly direction, probably due to the latitudinal effect which was described previously. The tritium pattern in precipitation for northern lower Michigan is possibly a continuation of this latitudinal trend, except for a west to east zone of low tritium concentrations that lies immediately to the south.

The prevailing winds in the west to east zone are southwesterlies and northwesterlies and therefore the major air masses affecting the zone probably originate in the Gulf of Mexico and Central Canada. In fact during fall and Spring the front separating these two air masses, known as the Polar front, lies directly over Michigan (Niedringhaus, 1966). The polar front is an east to west trending boundary zone, which is normally associated with cold fronts, as these occur more frequently in Michigan than warm ones (Niedringhaus, 1966).

A cold front occurs when cold air masses advance into areas previously occupied by warm air masses (Eichenlaub, 1979). In the case of lower Michigan warm maritime tropical air is displaced by cold continental polar air along the front (Figure 7). The warm air becomes unstable, rises and can produce precipitation over the area of the boundary zone of the front (Figure 7). This precipitation is relatively depleted with respect to tritium compared to continental polar derived precipitation. This most likely produced the east-west zone of low tritium concentrations that is located between the Southern Lower Peninsula Transitional Province and the Northern Lower Peninsula Province.

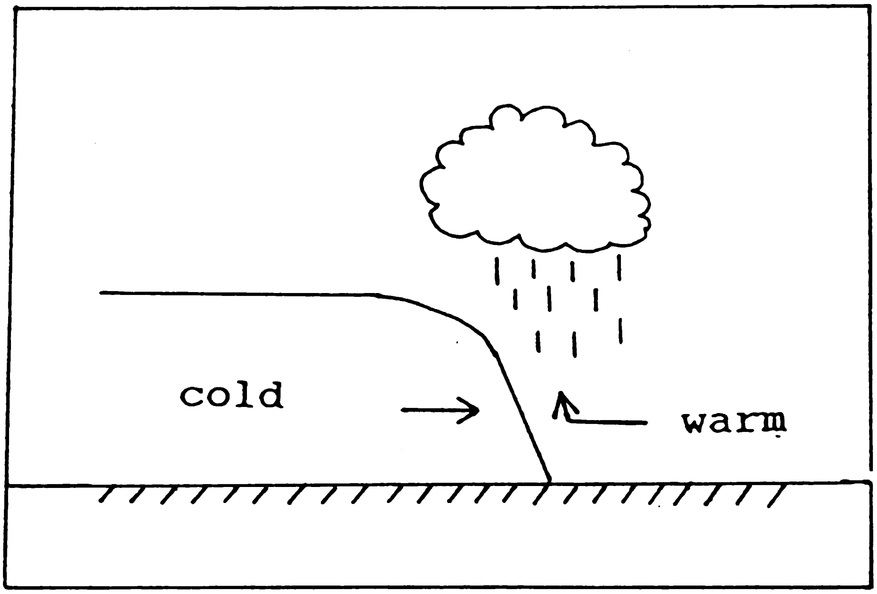

Figure 7. Cold front in vertical representation (Eichenlaub, 1979).

Lake Effect

Tritium concentrations in precipitation along oceanic coastlines are influenced by the low TU concentrations in the oceans (<1TU). These low values are due to the large volume of the oceans. The same dynamics probably also apply to coastal regions of lower Michigan despite the fact that the volume of the Great Lakes is less than the oceans.

Tritium in Lake Michigan - In this study the tritium concentration observed for 2 samples of Lake Michigan water ranged from 57.8+/2.45 TU to 47.9+/2.98 TU and averaged 52.85 TU. These concentrations are significantly greater than the value of 28 +/- 3 TU measured in February 1960 (Libby, 1962). The reason that the concentration of tritium in Lake Michigan has increased since 1960 is because the lake has acted as a reservoir for "bomb" derived tritium that entered the lake since 1952 via direct precipitation, molecular exchange and drainage from the catchment area (Begemann and Libby, 1957; Libby, 1962). This is particularly true during the late 1950's and early 1960's when the concentration of bomb tritium in precipitation exceeded thousands of TU's (Egboka et al, 1983). However, since 1952 some bomb tritium also has been removed from the lake via discharge outlets, evaporation and decay.

Fractionation of Tritium in Precipitation - Evaporation from the surface of Lake Michigan is the major means by which the lake may influence tritium concentrations in precipitation falling inland from the eastern shore of Lake Michigan. Therefore, it is of interest to model the fractionation process associated with evaporation and condensation of tritiated water derived from Lake Michigan and to compare the results of the model with observed tritium concentrations in precipitation.

Evaporation from the surface of Lake Michigan involves a change of phase from liquid to vapor. Because of mass and bond strength differences between tritium and protium the relative concentration of these will be different in the two phases. This is known as the fractionation effect and under equilibrium conditions can be represented by the fractionation factor α which is defined by the equation:

$$\alpha = \delta_l + 10^3/\delta_v + 10^3 \qquad \text{(i)}$$

α = isotope fractionation factor for water vapor (v) in isotopic equilibrium with the lake water (l)

$$\delta_l \text{ and } \delta_v = ((R_{spl} - R_{std})/R_{std}) * 10^3 \qquad \text{(ii)}$$

where R = ratio of tritium to protium for the sample (spl) and a standard (std) which in this case is modern Lake Michigan water (MLMW).

The equilibrium fractionation factor α is temperature dependant and can be calculated from the following equation:

$$\ln \alpha = 46480/\Gamma^2 - 103.87/\Gamma \qquad \text{(iii)}$$

where Γ is in degrees Kelvin (Koster et al (1989)). Table 3 shows the values of α for different temperatures.

Table 3. Values of the fractionation factor at different temperatures

Temperature °C	α
0	1.27
6	1.25
10	1.24
20	1.21

In this study, modern Lake Michigan water will be assigned a relative value of 0.0. Also, kinetic fractionation effects associated with evaporation will be neglected as these are small for hydrogen isotopes compared to oxygen isotopes (Zimmermann and Ehhalt, 1970).

The model used for predicting the fractionation process associated with evaporation and condensation of tritiated water is a simple two phase Rayleigh distillation. It assumes that as precipitation forms in the cloud it is immediately removed thus reducing the amount of water left in the cloud (Jouzel, 1979). The concentration of tritium in the remaining vapor is calculated from the following equation:

$$\delta v = (\delta v^{o} + 10^{3}) * f^{(\alpha-1)} - 10^{3} \qquad \text{(iv)}$$

f = fraction of water remaining in the cloud

Predicted vs. Observed Concentrations of Tritium in Precipitation - The tritium concentrations in lake-derived water vapor and the successive condensate calculated from equations (i) and (iv) are shown in Figure 8. The results indicate that the first condensate has the same tritium concentration as water from Lake Michigan (MLMW) and that as the amount of water remaining in the cloud is reduced the tritium concentrations in the condensate become depleted with respect to water from Lake Michigan (MLMW). Also, during any rainfall the condensate is relatively more enriched in tritium than the vapor from which it originated.

Figure 8 also shows that the difference between the first condensate (f=1) and the final condensate (f=0.1) is approximately 43 to 46 TU for 20°C and 0°C respectively. This difference is the maximum fractionation that can be expected between vapor derived from Lake Michigan and the resultant condensate. However, the predicted fractionation of tritium represents only concentrations derived from a single storm or rain event where vapor is derived exclusively from Lake Michigan. Obviously, the predictions do not take into account multiple storm events or mixing with vapor derived from alternative sources.

Based on the above model, precipitation derived from Lake Michigan and falling on the western part of Michigan should exhibit decreasing concentrations of tritium inland from the lake shore. In order to test this the contoured values of observed tritium concentrations in precipitation intersecting

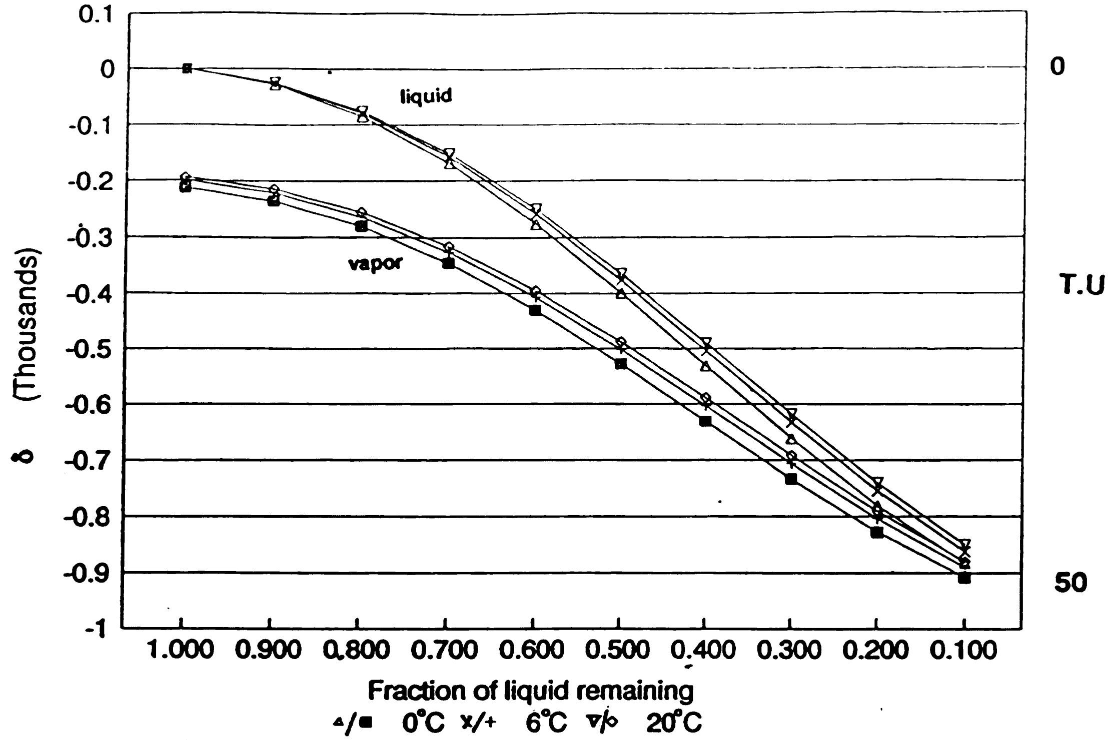

Figure 8a. Evolution of tritium in condensate and vapor.

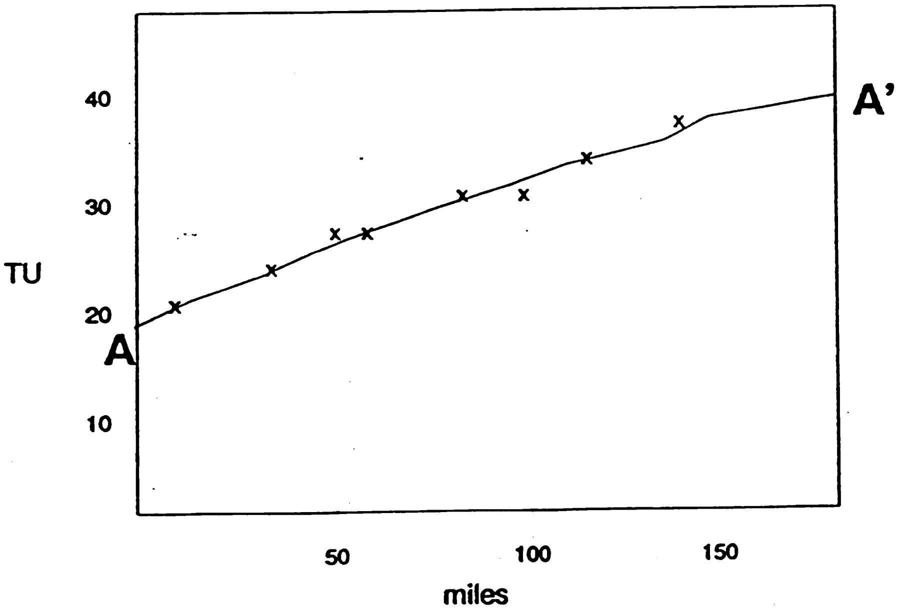

Figure 8b. Profile of contoured tritium concentrations.

line A-A' in Figure 3 are presented along with predicted tritium concentrations in Figure 8. The values range from 20-36 TU and show an increasing concentration inland whereas the predicted range from 0-46 TU and indicate a decreasing concentration. The difference in the contoured and predicted trends suggests that water vapor from Lake Michigan is not significantly influencing the concentration of tritium in precipitation across southern lower Michigan. However, it is possible that water vapor from the lake is influencing the tritium concentrations in precipitation falling within 10-25 miles inland from the lake shore. Unfortunately, because of the lack of tritium data within this area this lake effect simply can not be resolved.

CONCLUSIONS

Tritium concentration in precipitation for East Lansing, Michigan were measured for the year 1989. In addition tritium concentrations were also measured at 14 other stations in lower Michigan for the period July through December 1989. The maximum tritium concentrations observed for the East Lansing station were recorded in June and July and ranged from 51 to 128 TU. The minimum tritium concentration was recorded in November and was approximately 5 TU. The average concentration of tritium for the year was 34 TU. With respect to the other stations they show an increasing tritium concentration in a west to east direction (16 to 36 TU) within the southern part of lower Michigan and general increasing trend (22-32 TU) in a south to north direction within the northern part of lower Michigan. In the area separating the southern and northern part of lower Michigan tritium concentrations tend to be low (16-20 TU).

The measured concentrations of tritium in precipitation in lower Michigan indicate that

1) the East Lansing data is reflective of the annual transfer of tritium from the stratosphere

2) the distribution of tritium in precipitation in the southern part of lower Michigan is most likely controlled by the continental effect and reflects the Southern Lower Peninsula Transitional Province (Niedringhaus, 1966) where the most prevalent air

mass is maritime tropical which originates in the Gulf of Mexico.

3) the distribution of tritium in precipitation in the northern part of lower Michigan is probably brought about by the latitudinal effect and is associated with the Northern Lower Peninsula Province (Niedringhaus, 1966), where the dominant air mass is continental polar which has its origins in the higher latitudes.

4) the area of low tritium concentrations between the above two provinces may coincide with the polar front which separates the continental polar and maritime tropical air masses

5) water vapor from Lake Michigan does not seem to be significantly affecting the concentration of tritium in precipitation across southern lower Michigan although it is possible that it may affect the concentration of tritium in precipitation falling within 10-25 miles from the lake shore.

APPENDICES

APPENDIX A

SAMPLE PREPARATION

Electrolysis

Today, tritium concentrations in natural waters are relatively low. For this reason samples for tritium analysis were enriched by the process of electrolysis. In this study the electrolysis system used consisted of 12 iron/nickel cells, a freezer with 12 holes to accommodate the cells, fan (to ensure even circulation of air), power supply and gas exhaust lines (Figure 9). The cells were fitted with gas outlets to allow H_2 and O_2 produced during the process to be released via the exhaust lines. The reactions which occur at the electrodes are

Anode : $2H_2O \rightarrow 4H^+ + O_2 + 4e-$

Cathode : $2H^+ + 2e- \rightarrow H_2$ (Hoffman and Stewart,1966)

where H may be protium (H^1), deuterium (H^2) or tritium (H^3).

During each electrolysis run, ten of the electrolysis cells were used for unknown samples, the remaining two cells however contained standards: one a known tritium standard and the other a blank. The blank is 'dead' or 'pre-bomb' distilled water which serves as a measure of background radiation. Five ml of a 4 M NaOH solution was also added to the cells. The cells were then connected electrically in series to the power supply and placed in the freezer at -9°C. A current of 5.8A was maintained (University of Waterloo, 1992) for approximately 69 hours or when a residual volume of 11-15 ml remained in each cell.

The reasons for maintaining the freezer at a cold temperature include :

a) Evaporation loss is reduced. Evaporation can lower the recovery yield of the tritium during electrolysis (Ostlund and Werner, 1962).

b) Warm NaOH electrolyte can attack the anodes (Taylor, 1981).

c) The cold temperature increases the separation efficiency of the hydrogen isotopes (Hoffman and Stewart, 1966).

Post-Distillation

In order to separate the electrolyte from the electrolyzed sample post-distillation was carried out after electrolysis was completed. The system for post-distillation consists of glass test tubes capped by modified distillation heads and encased in heating coils, weighing bulbs, liquid nitrogen baths, and pressure compensators as shown in Figure 10 (Delcore, 1985 and Regalbuto, 1987). A vacuum was also connected to the weighing bulbs. The weight of the bulbs and distilled samples were determined before and after each distillation step.

All electrolyzed samples between 11-15 ml were transferred to the glass test tubes. Vacuum was then applied to ensure that the post-distillation system was airtight.

Prior to turning on heat, liquid nitrogen was applied to the bath surrounding the weighing bottle. Heat then was applied to the test tubes until dryness, which takes approximately 3-4 hours. Eleven ml of distillant was then pipetted into a plastic vial and stored in the dark in preparation for liquid scintillation analysis.

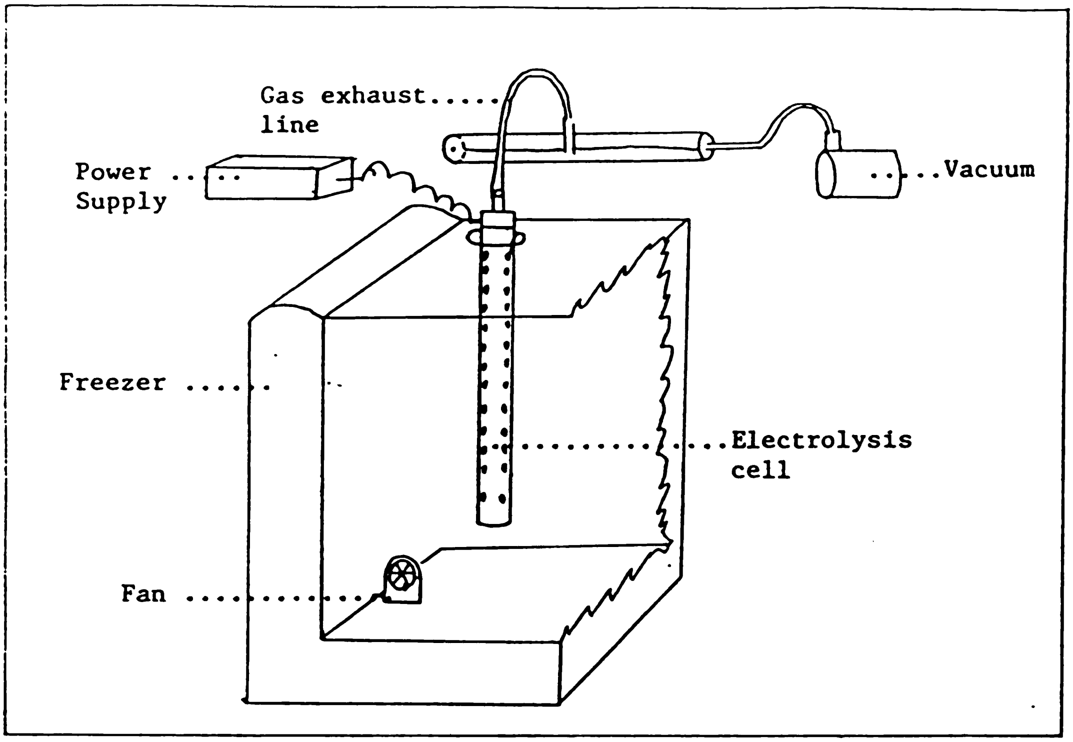

Figure 9. Simplified electrolysis apparatus.

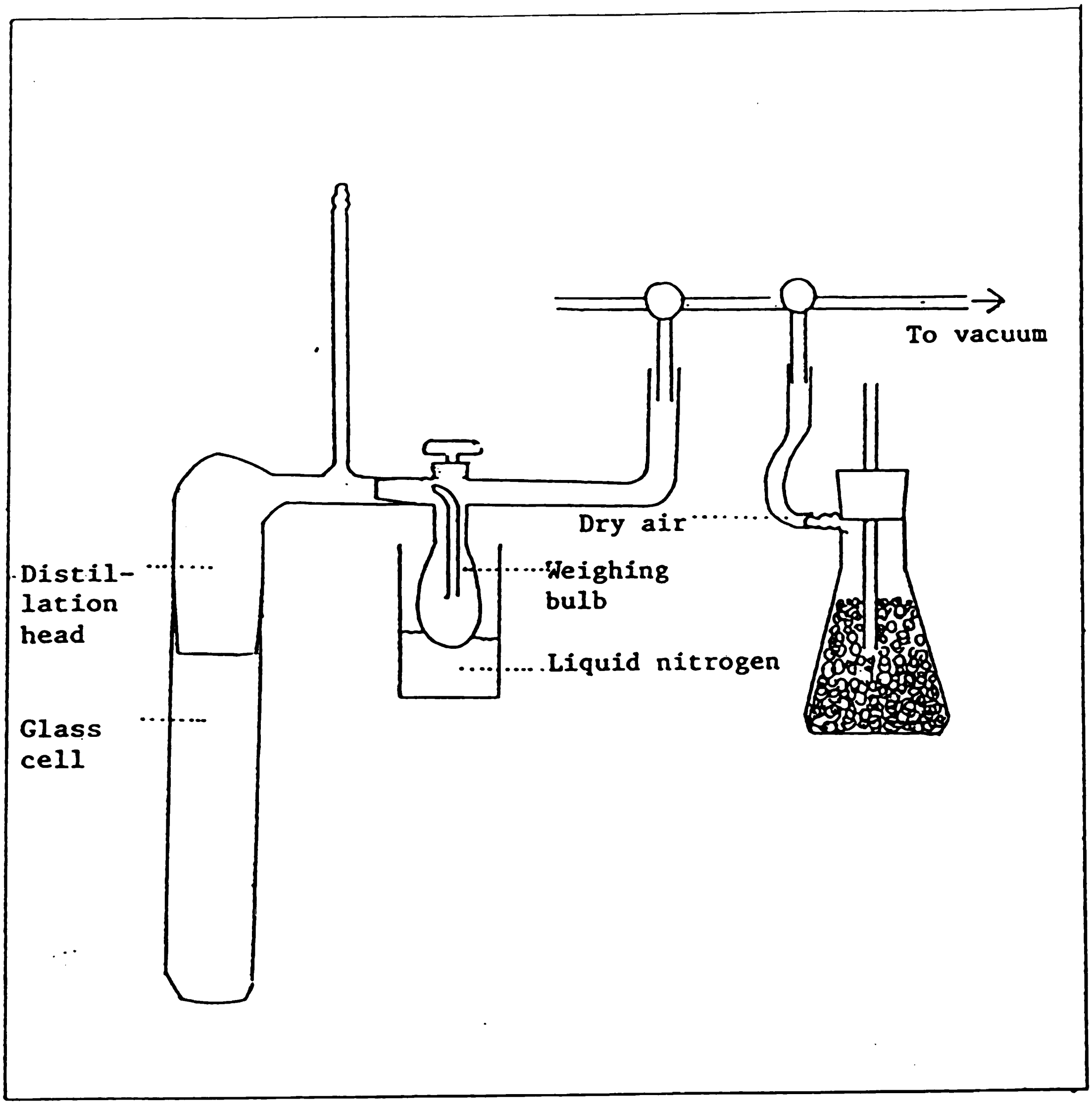

Figure 10. Post-distillation apparatus.

APPENDIX B

APPENDIX B

LIQUID SCINTILLATION COUNTING

The theory behind liquid scintillation counting (LSC) is that when radioactive particles decay within a scintillation solution photons are emitted that can be measured by the scintillation counter. In this study, Picofluor LLT was the scintillation solution chosen because of its characteristic low background and its suitability for counting low level tritium activity (Packard, 1987).

Several energy transfer steps are involved in the liquid scintillation (LS) process. The first step is radioactive decay, emission of alpha and beta particles and possibly a neutrino. The next step is transfer of the energy from the emitted particle to the solvent molecules of the solution which then fluoresce. These fluorescing molecules then pass on their energy to other molecules called fluor or solute molecules. Once the fluor molecules have accepted this energy photons are emitted (Packard, 1990). In the case of tritium decay, liquid scintillation generally measures beta particle emissions, and the number of photons or the intensity of light generated is proportional to the energy of the decaying beta particle (Long, 1978). For tritium this energy has a maximum of 18.6 KeV.

Counting Window Generation

Tritium standard and background spectrums were counted on the Packard Tri-Carb 1050 liquid scintillation analyzer and this indicated that they produce similar energy spectrums. In order to measure as many tritium disintegrations as possible but minimize the counts due to background, the standards were counted within a narrow spectrum between 0.6 to 8.0 KeV. This counting channel was chosen by recording the scintillations of the tritium and background standards in 0.5 KeV blocks and comparing the total counts. Based on these results it was determined that below 0.6 KeV the amount of tritium disintegrations detected was negligible, and similarly above 8.0 KeV the tritium counts lost would be small compared to the background.

Counting Interference

There are several problems associated with liquid scintillation counting. These include photoluminescence, wall effect, background and random noise and quenching.

Photoluminescence is the activation of cocktail and/or vial in the presence of ultraviolet light or sunlight. It can best be avoided by storing the cocktail and samples in a dark place until needed for counting. The wall effect on the other hand is caused by penetration of the walls of plastic vials by the cocktail. The walls then act as a secondary scintillator and this interferes with the counting process (Packard, 1990). Some samples were counted to test this effect and it was observed that there was a variability in the amount of scintillations detected.

With respect to background, blank standards were counted periodically over the study period to examine background fluctuations. The results showed that background does fluctuate over, time by as much as 25%. Therefore the background samples from each electrolysis run were counted for an appropriate period of time, corresponding to two standard deviations or the two sigma error (confidence limit 95.5%) to smooth any fluctuations in the spectrum. Sample counting time was usually 1000 minutes.

Quenching

Any interference with solute-solvent interactions in the LS vial which alters the detection of photons by the LSC is known as a quenching effect. There are three types of quenching : photon, color and chemical. Photon quenching causes incomplete beta energy transfer to the solvent. Color quenching is the absorption of energy by the quenching agent before it can reach the detecting system. In chemical quenching there is inefficient energy transfer from solvent to solute. This may occur when an inappropriate cocktail sample ratio is used. Too much cocktail will maximize the amount detected but lowers counting efficiency. There should be an optimum value which balances the two factors. To test this various sample to cocktail ratios, from 0.6 to 1.22 were counted. The ratio of 0.9 was chosen because while complying with the above requirements there is little fluctuation in the efficiency about this value (Figure 11). Since the sample vials used for counting hold a volume of 23 ml, 11 ml of sample to 12 ml of cocktail was used.

Quench Curve

The Packard Tri-Carb 1050 LS counter monitors the quenching effect by the transformed spectral index or TSIE value. This value is a measure of the amount of quench in a sample resulting from a Ba-133 external standard. A plot of the TSIE vs efficiency is then used to calculate the true activity for any sample. The curve is generated using twelve standards of identical activity but varying amounts of quench. The quenching agent was distilled grape juice. Prior to counting, 12 ml of cocktail was added. The activity (DPM) was calculated from the equation:

$$\text{Efficiency} = \frac{\text{counts per minute (CPM)}}{\text{disintegrations per minute (DPM)}}$$

APPENDIX C

APPENDIX C

TRITIUM ACTIVITY CALCULATIONS

The tritium activities of unknown samples were determined using the following equation (Wyerman, 1976):

DPM(s) = [CPM(s)/ml-CPM(b)/ml] / [CE*EE*(Vo/Vf)*V]

where

a) Vo(s) .... initial volume (ml)
b) Vf(s) .... final volume (ml)
c) V(s) .... volume of sample counted (ml)
d) DPMo(s)/ml ...... initial activity
e) CPM(s)/ml .... counts per minute
f) CE .... counting efficiency
g) EE .... electrolytic efficiency

These values must also be known for the electrolytic standard (es). Conversion of DPM to tritium units is based on the relationship that 1 TU = 0.0071 DPM/ml. 1 TU = 1 tritium atom per 10^{18} hydrogen atoms (Faure, 1986).

The activity of the electrolytic standard after electrolysis is determined as follows:

DPM(es)/ml = (CPM(es)/ml-CPM(b)/ml)/CE(es)

The counting efficiency is determined from the quench curve by taking the value on the y-axis which corresponds to the point where the TSIE value intersects the curve.

Next the electrolytic efficiency of the standard (EE) is calculated from the equation:

$$EE(es) = \frac{[CPM(es)/ml - CPM(b)/ml]}{[Vo(es)/Vf(es)*V*CE*DPMo(es)/ml]}$$

This is used to obtain a fractionation factor β which relates the T/H ratio to that of the evolved hydrogen (Taylor, 1981). The equation for beta is:

$$\beta = -\ln(Vo(es)/Vf(es))/\ln EE(es)$$

β is then substituted into the following equation to determine the electrolytic efficiency of the samples (EE(s)).

$$EE(s) = (Vo/Vf)^{-1/\beta}$$

The final activity of the unknown samples is then determined

$$DPM(s)/ml = \frac{[CPM(es)/ml - CPM(b)/ml]}{[Vo(es)/Vf(es)*CE*EE]}$$

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