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SYSTEMATICS OF STABLE ISOTOPES AND RADIONUCLIDES IN PRECIPITATION AT KALAMAZOO, MICHIGAN, USA

by

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SYSTEMATICS OF STABLE ISOTOPES AND RADIONUCLIDES IN PRECIPITATION AT KALAMAZOO, MICHIGAN, USA

Madhav V. Machavaram, Ph.D.

Western Michigan University, 1997

Precipitation samples were collected at Kalamazoo from June 1992 to March 1995. The samples were analyzed for their δD and $\delta^{18}O$ values. The δD - $\delta^{18}O$ relationship is comparable to that of Meteoric Water Line (MWL). The monthly mean isotopic values in precipitation exhibited strong seasonality, being higher in summer and lower in winter months. This behavior is apparently a direct consequence of the temperature effect on isotope fractionation.

The summer precipitation at Kalamazoo is derived predominantly from the water vapor originated in the Gulf of Mexico. A box model calculation showed that a Rayleigh type distillation with Gulf moisture as the source would explain the bulk of the observed isotopic ratios in summer precipitation. Additional factors such as Gulf vapor divergence, Atlantic moisture and convective precipitation appear to account for the rest of the isotope data. The summer precipitation is characterized by a higher *d*-excess than that of the precipitation defined by the MWL. This is probably due to the contribution of evaporated moisture from Lake Michigan. The contribution of lake-evaporated moisture to summer precipitation was estimated by using the Craig - Gordon model. When compared over a three year period, the percent contribution of lake-evaporated moisture to summer precipitation is positively correlated to mean summer temperatures.

The isotopic ratios in winter precipitation reflect multiple moisture sources with significant 'Lake Effect' component. The isotopic signature of lake effect precipitation was shown to be the result of thermodynamically controlled condensation from a cloud super saturated with respect to ice.

Precipitation samples collected separately from January to December 1994 were analyzed for ^{7}Be and ^{210}Pb concentrations in addition to the stable isotopes. The concentrations of these nuclides in precipitation are strongly correlated. The precipitation during warmer months is characterized by higher ^{7}Be and lower ^{210}Pb concentrations. Based on meteorological and stable isotope data it was shown that ^{210}Pb concentrations are controlled mainly by the nature of precipitation whereas the concentrations of ^{7}Be are influenced by the vertical mixing in troposphere and tropopause folding.

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O death, rock me asleep, Bring me to quiet rest...
My Pains who can express? Alas, they are so strong...
Farewell, my pleasures past, Welcome my present pain
I feel my torments so increase, That life cannot remain....

Oh! Mother!!

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Madhav. V. Machavaram

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CHAPTER I

INTRODUCTION

The term 'isotope' was introduced by Soddy (1913) for atoms with the same number of protons but different number of neutrons. The isotopes of any atom occupy same position in the periodic table due to their same atomic number, but differ in their nuclear properties due to their different atomic weight. The 92 naturally occurring elements have more than 1000 isotopes. Though most of these isotopes occur in trace amounts in the atmosphere and terrestrial compounds, some are sufficiently abundant to be measured quantitatively. The distribution of isotopes of any element is not uniform in geological systems due to their different physical and chemical properties such as density, vapor pressure, mass and energy contents, equilibrium reaction rates, etc. These differences produce an "isotopic effect" in natural systems and are of significant geochemical interest.

The isotopes of any element may be categorized into radioactive and stable isotopes. Radioactive isotopes decay by losing energy in the form of α, β and γ particles and electron capture. Stable isotopes on the other hand, do not undergo radioactive decay. The concentrations of radioactive isotopes in any system depend on their initial concentration and decay rates whereas the abundances of stable isotopes are governed by the various physico-chemical processes. Thus, the variation in abundances of radioactive and stable isotopes in any natural system offer valuable information about its physical and chemical behavior. The distribution of stable and radioactive isotopes in natural systems, and technological advances in their measurement capabilities has laid the foundation for their wide spread use in hydrology, geochemistry, cosmochemistry, oceanography and other environmental studies.

The present work involves the study of isotope systematics in precipitation, an important component of hydrogeology in any given region. A systematic study of stable oxygen and hydrogen isotopes in sampled precipitation yields valuable information about the atmospheric processes that affect precipitation at any region, and the influence of climatic factors such as temperature, humidity and any secondary moisture sources. The study of radioactive isotopes of beryllium and lead in precipitation is extremely useful to understand the processes that affect the abundances of these nuclides in precipitation and to understand the processes that operate in tropospheric and stratospheric regions of the atmosphere. Coupled with meteorological information, these studies will give a fuller understanding about the hydrogeological and atmospheric processes at a given region. Apart from studying the stable isotopes of oxygen and hydrogen, which are inherently present in water, the current study also involves the study of ^{7}Be and ^{210}Pb, two radioactive isotopes which originate differently in the atmosphere, but are scavenged by precipitation in an identical process. Though independently used, the information obtained from the study of these isotopes proved valuable in understanding the atmospheric influence on hydrogeology in the study area. To the best of our knowledge, the current study, by using both stable and radioactive isotopic systematics in precipitation, is the first of its kind and yielded encouraging results which are presented in the following chapters. To better understand the impact of these studies in a wide variety of applications, a detailed understanding of the geochemistry of these isotopes is essential and hence is provided in the following sections.

Stable Isotopes in Precipitation

The partitioning of two isotopes of an element between two substances or phases leading to difference in isotopic ratios (heavy isotope content/light isotope content) is termed isotopic fractionation. The two main processes which cause fractionation (Hoefs, 1973) are:

1. Equilibrium exchange reactions: These reactions are not accompanied by any changes in the chemical species, but involve only isotopic exchange. For example, in a reaction,

$$A^{*} + B \rightleftharpoons A + B^{*}$$

where the asteric indicates the species containing the heavier isotope. In nature, such reactions are numerous and the following is an example involving the oxygen isotope exchange between water and carbon dioxide.

$$C^{16}O^{16}O + H_2{}^{18}O \rightleftharpoons C^{16}O^{18}O + H_2{}^{16}O$$

2. Kinetic fractionation process : Unlike equilibrium reactions, kinetic fractionation

occurs in irreversible processes. This is caused mainly by the difference in the reaction rates of isotopic molecules. When a gas diffuses, for example, the gas molecules containing the lighter isotopes diffuse more rapidly than the molecules with heavier isotopes due to their higher diffusive coefficients. These kinetic fractionation effects are generally larger than equilibrium fractionation effects and decrease with increasing temperature. The effect of kinetic fractionation has been quantitatively expressed by 'absolute reaction rate theory' derived by Glasston et al (1941). According to this theory, the kinetic effects depend on the mechanistic pathways of the reaction, especially when the breaking of covalent or semi-covalent bonds, which connect the isotope to the molecule, is involved. Biochemical processes such as photosynthesis and physical processes such as sublimation of water vapor to ice in clouds are good examples of reactions leading to kinetic fractionation. Fractionation can also be caused by physico-chemical factors such as evaporation/condensation, absorption/desorption, and crystallization.

Isotopic Fractionation (α)

The ratio of heavy isotopes to lighter isotopes of two substances or two phases of the same substance which are involved in reaction, is called the fractionation factor. This is denoted by the letter α. In a reaction of the type $A \rightleftharpoons B$, the fractionation factor is defined as:

$$\alpha_{A\text{-}B} = R_A / R_B$$

where R denotes the ratio of heavy isotope over lighter isotope (D/H, $^{13}C/^{12}C$, $^{18}O/^{16}O$ etc.) in phases A and B respectively. The α values typically are of the form 1.00XY. Since in general the α value is close to unity, the equilibrium fractionation factor 'ϵ' has been defined, which expresses the fractionation factor in per mil units. Mathematically, the equilibrium fractionation factor is defined as:

$$\epsilon_{A\text{-}B} = (\alpha_{A\text{-}B} - 1)10^3$$

In equilibrium processes the fractionation factor is related to the equilibrium constant 'K' for the isotopic exchange reaction, by the relation

$$\alpha = K^{1/n}$$

where n is the number of atoms that are being exchanged in the reaction (Fritz and Fontes, 1980).

The δ - Notation

The growth of stable isotope applications in various environmental studies disclosed the necessity of an internationally accepted nomenclature and set of standard notations for expressing the isotopic values of any element. The nomenclature is used worldwide as a standard procedure for reporting the isotopic data.

Since it is easier to measure the isotopic ratios relative to two substances rather than the absolute ratio, in isotope geochemistry, the practice is to compare the isotope ratio with respect to an international standard. The results are expressed in the δ - notation. This notation makes data presentation more convenient and conveys as much information as an absolute ratio. The δ in per mil., is given by

$$\delta‰ = [(R_{sample}/R_{standard}) - 1]\ 10^3$$

where R denotes the ratio of heavy to light isotopes of any element such as D/H, $^{18}O/^{16}O$, etc. in the sample and the standard respectively.

From further calculations the relation between α and δ can be derived as follows. For reaction (1), the fractionation factor α (2) is defined as:

$$A \rightleftharpoons B \qquad (1)$$

$$\alpha = R_B / R_A \qquad (2)$$

by substituting δ values for A and B in (2) one obtains

$$\delta_A = [(R_A / R_{std}) - 1]\ 10^3 \quad (3)$$

$$\delta_B = [(R_B / R_{std}) - 1]\ 10^3) \quad (4)$$

re-arranging (3) and (4)

$$R_A/R_{std} = \delta_A/10^3 + 1$$

$$R_B / R_{std} = \delta_B/10^3 + 1$$

$$\alpha_{(A-B)} = R_A / R_B = (R_B/R_{std}) / (R_A/R_{std})$$

$$\alpha_{(A-B)} = (1000 + \delta_A) / (1000 + \delta_B)$$

The International Standards

International standards are used to interpret δ values and to make inter-laboratory comparisons. The δ value of any sample is reported with respect to international standards. The criteria for a suitable standard include, homogeneity of composition, stability over long periods of time, availability in large quantities and the δ value of the standard should be intermediate between the range of all naturally occurring isotopes.

The international standard for comparing the isotope ratios of oxygen and hydrogen is SMOW(Standard Mean Ocean Water) which was originally prepared by Craig (1961). The international standards are prepared, calibrated and distributed by the International Atomic Energy Agency (IAEA). The preparation and cross calibrations of standards are discussed in detail by Coplen, et al., (1982, 83), Blattner and Hulston (1978) and Gonfiantini (1978).

The standard practice in routine measurements for any laboratory is to prepare what is known as secondary standards. These samples are frequently calibrated against the international standards, such as Standard Mean Ocean Water (SMOW), Pee Dee Belemnite (PDB), National Bureau of Standards no. 19 (NBS-19) etc. For the present study a large batch of distilled water (designated LAB-1) from the distillation plant in the laboratory was used. It was collected in March 1992 and stored in an air tight bottle. This was calibrated against SMOW in the Isotope Geochemistry Laboratory at Institute for Water Sciences (Western Michigan University) and all the samples were measured with respect to LAB-1 and the final conversion with respect to SMOW was achieved by the following relation.

$$\delta_{\text{sample-SMOW}} = \delta_1 + \delta_2 + \delta_1\delta_2\ 10^{-3}$$

where,

$$\delta_1 = \delta_{\text{sample-LAB-1}}$$

$$\delta_2 = \delta_{\text{LAB-1-SMOW}}$$

After repeated calibration, the δ values of oxygen and hydrogen for the LAB-1 standard with respect to SMOW are found to be -10.4±0.1 and -65.7±1.5 respectively. The calibration and comparison for LAB-1 with other international standards such as SMOW, Standard Light Arctic Precipitation (SLAP) and Greenland Ice Sheet Precipitation (GISP) was discussed in detail by Machavaram (1993).

Fractionation Effects in Precipitation

The behavior of oxygen and hydrogen isotopes in precipitation is closely related to the prevailing mechanism during various stages of the precipitation process. The process of precipitation, in general, involves three stages, namely, evaporation from source, cloud condensation and subsequent precipitation in the form of rain or snow. Isotopic fractionation which occurs during all these stages is controlled by various physico-chemical factors such as temperature, physical characteristics of the cloud and the climatological factors such as humidity, temperature etc. The isotopic signature of any precipitation event, at a given region, is thus governed by the fractionation effects which are brought about by afore mentioned physico-chemical factors. Fractionation which occurs in various stages of the precipitation process is discussed below.

The phenomenon of isotope fractionation during evaporation and condensation of water is due to the differences in the vapor pressure of molecules with different isotopic species. For example, let ${}^{16}X_l$ and ${}^{18}X_l$ represent the mole fractions of the species $H_2{}^{16}O$ and $H_2{}^{18}O$, respectively. The vapor pressure pV due to $H_2{}^{16}O$ and $H_2{}^{18}O$ is given by the following equations:

$$pV^{16} = {}^{16}X_l\, p^{16*} \quad \text{and} \quad pV^{18} = {}^{18}X_l\, p^{18*}$$

where p* represents the vapor pressure in the pure state.

From simple gas laws, it can be deduced that pV^{16} is directly proportional to nV^{16} and pV^{18} to nV^{18} where 'n' stands for the number of molecules.

$$pV^{18}/\,pV^{16} = nV^{18}/\,nV^{16} = {}^{18}X_l\ p^{18*16}/\,X_l\ p^{16*}$$

by definition $nV^{18}/nV^{16} = R_V$ and ${}^{18}X_l\,/\,{}^{16}X_l = R_l$

therefore $R_V = R_l\, p^{18*}\,/\,p^{16*}$

and also $R_l\,/\,R_V = \alpha$ = fractionation factor.

That is, α is the ratio of vapor pressure of the liquid containing the isotopic species in the pure state. For example, the vapor pressure ratio of $HD^{16}O$ and $H_2{}^{18}O$ with respect to $H_2{}^{16}O$ is 1.085 and 1.010 respectively at 20°C (Majoube, 1971). Thus, during evaporation, isotopic fractionation results in the depletion of D and ${}^{18}O$ in the vapor which is in equilibrium with the liquid at 20°C by 85‰ and 10‰, respectively. The opposite effect takes place during condensation, in which the liquid phase becomes enriched in heavier isotopes.

The distribution of stable isotopes in precipitation in a given region are governed by other effects which are superimposed on the fractionation effect. These processes are described below.

The Rayleigh Distillation Process

In the precipitation process, continuous removal of moisture in the form of condensate, takes place during the transit of an air mass which carries the evaporated moisture from the source. Since condensation isotopically enriches the precipitate, thus leaving the remaining vapor phase in the air mass relatively depleted with respect to heavier isotopes, subsequent condensates from that air mass will be progressively depleted in their δD and $\delta^{18}O$, as it moves pole wards. This effect which is known as 'continental effect' can be quantitatively expressed as a function of the isotopic composition of the condensate, fraction of the residual vapor left over in the cloud and the temperature at which condensation occurs. This expression is termed as 'Rayleigh distillation' and the equation that governs the distribution of isotopic species can be written as

$$R = R_0 \, f^{(\alpha-1)}$$

and can be derived as follows.

Let A and B represent the amounts of $H_2{}^{16}O$ and $H_2{}^{18}O$ respectively in a vapor flux and d_A and d_B are the condensate fractions from the flux. Then

$$\alpha = \frac{(\frac{d_B}{d_A})}{(\frac{B}{A})} = \frac{d_B}{B} = \alpha\frac{d_A}{A}$$

integration of this yields

$$\int_{B_o}^{B} \frac{d_B}{B} = \alpha\int_{A_o}^{A} \frac{d_A}{A}$$

$$\ln\frac{B}{B_o} = \alpha \ln\frac{A}{A_o} \; ; \quad \frac{B}{B_o} = [\frac{A}{A_o}]^{\alpha}$$

dividing both sides by A/A_O

$$\frac{(\frac{B}{B_o})}{(\frac{A}{A_o})} = (\frac{A}{A_o})^{\alpha-1} ; \quad \frac{B}{A} = \frac{B_o}{A_o}(\frac{A}{A_o})^{\alpha-1}$$

$B \ll A$, *then* $\frac{A}{A_o} = f$ *(fraction remaining)*

$$\frac{B}{A} = R \; ; \quad R = R_o f^{\alpha-1}$$

$$R = R_0 f^{(\alpha-1)}$$

where R is the isotopic ratio of the vapor at some stage of the process when the residual fraction of vapor left is f; R_0 is the isotopic ratio at the beginning of the process and α is the fractionation factor. This equation can then be expressed in δ values, which is,

$$\delta_{vapor} = 1000\,(f^{(\alpha-1)}-1)$$

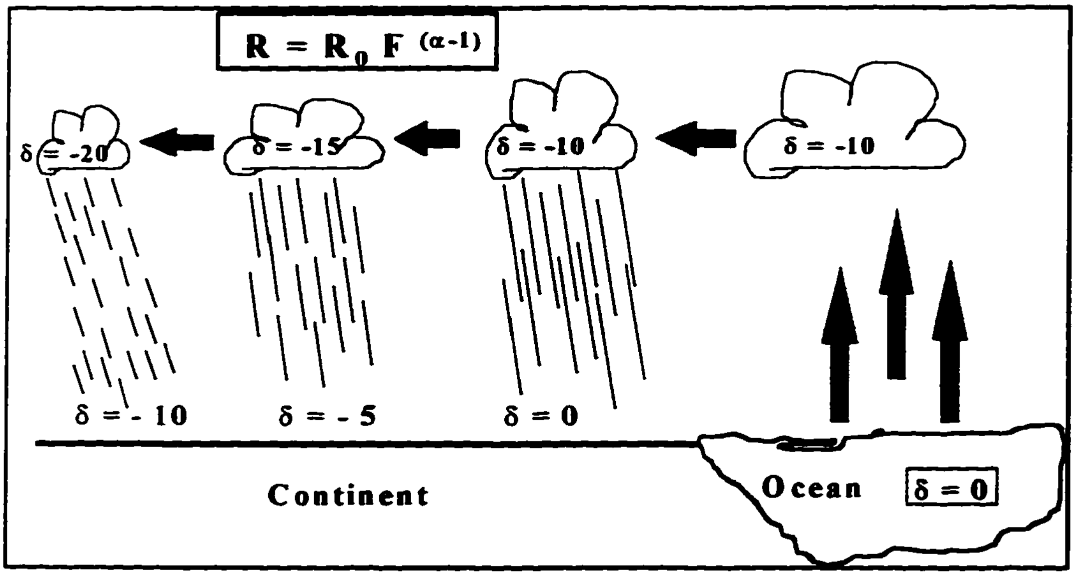

Figure 1. Rayleigh Distillation Process in Precipitation.

It can be shown that as a marine water vapor enters the continent and undergoes increased loss of vapor by continuous condensation, the “Rayleigh process” makes the vapor increasingly depleted in the heavier isotopic species. In the case of precipitation the following expression can be written for the isotopic distribution between the vapor and liquid phases.

$$R_L = \alpha R_0 f^{(\alpha-1)}$$

where, R_L represents the isotopic ratio of the liquid phase at any instance and R_0 represents the initial isotopic ratio of the vapor. Figure 1 is a schematic representation of the Rayleigh distillation process for oxygen that operates in the evaporation condensation cycle in precipitation.

It implies from the above discussion that most of the isotopic distributions in precipitation could be explained by viewing the precipitation process in a simple Rayleigh model. However, this model fails to take into account some of the secondary processes, such as addition of secondary moisture sources, evaporation of the condensate and nature of co-existing phases of water (ice, liquid and vapor) which also affect the isotopic signature of precipitation in a given region. Some modified Rayleigh models have been reported (Gat, 1980; Gedzelman and Arnold, 1994; Ciais and Jouzel, 1994). A detailed discussion of these modified models and their influence on the current study are presented in the following chapter. In addition, some other geographical and local parameters, which affect the isotopic ratios in precipitation are presented here.

Temperature Effect

At any given region, the isotopic ratios in precipitation are observed to exhibit a positive linear correlation with the ambient surface air temperature of that region. From the monthly mean data collected by IAEA for over 300 stations worldwide Yurtsever (1975), by multiple regression analysis, developed a relationship expressed as

$$\delta^{18}O‰ = 0.521T_a - 14.96$$

where $\delta^{18}O$ is the oxygen isotope ratio expressed in per mil notation and T_a is the mean annual surface air temperature expressed in degrees Celsius. Daansgard (1964) gave a similar relationship, which is expressed as

$$\delta^{18}O‰ = 0.69T_a - 13.6$$

and also found that this effect can be explained by the assumption that the condensation part of the precipitation obeys a simple Rayleigh process, where the fractionation factor governing the condensation was calculated by taking surface air temperature.

Amount Effect

The amount effect refers to a negative correlation between the amount of monthly precipitation and the corresponding monthly mean isotopic values in precipitation. This effect is predominantly observed in tropical regions and in mid latitudes during summer months. The effect becomes negligible in polar areas where temperature effect predominates relative to other effects. Due to the preponderance of complex convective precipitation in mid latitudes and tropical regions, no satisfactory explanation was offered for this effect. Evaporation and exchange of falling rain drops might be an important factor which controls this effect (Daansgard, 1964). In continental regions variations in humidity may also play an important role (Ehhalt et al., 1963).

Altitude Effect

Altitude effect is another important geographical factor that affects the isotope ratios in precipitation, which is observed in mountainous region. This effect results mainly from the orographic ascent of the air mass, during which progressive rain-out of the heavy isotopes takes place, especially on the windward side of the mountain range, thus resulting in a negative correlation with increasing altitude (Freidman and Smith, 1970; Dincer, et al., 1970; Moser and Stichler, 1971).

In spite of such local and regional effects that are to be considered while interpreting the isotopic ratios in precipitation, it was shown that on a global scale, and to a large extent on a regional scale, a simple Rayleigh model could be used to explain most of the observations (Epstein, et al 1965; Krishnamurthy and Bhattacharya, 1991; Machavaram and Krishnamurthy, 1994).

The δD - $\delta^{18}O$ Relationship

The initial attempts at interpreting the isotopic distribution in atmospheric waters considered the system globally, where evaporated moisture is fed by the ocean, with condensation of moisture as a result of adiabatic cooling of the air mass at higher latitudes and altitudes. Provided that an isotopic equilibrium exists between the water vapor and the condensate throughout the process, then the condensate should exhibit a correlation in the degree of depletion with respect to the heavy isotopic species of oxygen and hydrogen, thus resulting in a linear relationship between the isotopic signature of hydrogen to that of oxygen in precipitation.

Like many atmospheric properties, the isotopic compositions of atmospheric liquid water, water vapor and precipitation are quite varied. Therefore, individual precipitation events leave little impression on most hydrologic systems because of the latter's size and inertia. It is necessary to have long-term averages of the isotopic compositions of the precipitation for data inputs into hydrologic systems. The global precipitation network designed by IAEA/WMO (World Meteorological Organization) provides such information. The IAEA, in co-operation with WMO, has conducted a world-wide survey of hydrogen and oxygen isotopes in precipitation since 1961, in order to provide basic data for hydrological applications of environmental isotopes. The network consisted of a total of 144 stations. From these stations monthly composite samples are collected and analyzed at IAEA. The early data were discussed in detail by Dansgaard (1964). The linear relationship observed between δD and $\delta^{18}O$ in precipitation by Freidman (1953), and which was later defined by Craig (1961b) as the Meteoric Water Line (MWL), obtained by considering the weighted average isotopic composition for all the precipitation obtained from IAEA network was given as

$$\delta D = (8.167 \pm 0.079)\,\delta^{18}O + (10.55 \pm 0.64)$$

and may be regarded as the locus of the isotopic composition of world-wide fresh water bodies. The slope of approx. 8 can be considered to be arising from the fact that, since the Rayleigh process is operative with respect to both D and ^{18}O, the derivative d $\delta D/d\,\delta^{18}O$ is given by

$$d\,\delta D/d\,\delta^{18}O = (\alpha_D - 1)\,/\,(\alpha_{18} - 1)$$

where the α values are the respective fractionation factors. Since the α values are temperature dependent, this ratio is also temperature sensitive. For example, the ratio varies from 8.22 to 9.59 for a temperature range of 30°C to 0°C. The expression for the slope, according to the two phase model is given by

$$d\,\delta D/d\,\delta_{18}O = (1+\alpha_{18}L)\ /\ (1+\alpha_D\,L)$$

where L is the liquid water content. For the same temperature range, i.e., 0 - 30°C and when L = 1, the ratio yields values of 7.96 to 8.13.

All these models assume an equilibrium condensation process. However, when a non-equilibrium process is involved, the slope can deviate considerably from the value 8. For example, for most arid and semi arid regions the slope is much less than 8, typically between 5 and 6, obviously due to the evaporative processes which modify the MWL relation. In such cases waters are said to fall on the "evaporation line" (Gat, 1971; Stewart, 1975).

The intercept of 10 stems from the fact that the initial evaporation from the ocean is kinetically controlled so that the water vapor over the ocean has an initial composition of -94‰ for δD and -13‰ for $\delta^{18}O$, whereas equilibrium water vapor would have -80‰ and -10‰ respectively at 20°C. Condensation is assumed to proceed under equilibrium conditions, so that the first condensate will have a δD value of -14‰ and $\delta^{18}O$ of -3‰. Here again, secondary processes exert a modifying effect on the intercept of later rains, as has been seen for arid and semi arid regions (Gat, 1971).

Craig and Gordon (1965), Gat and Craig (1966), Gat (1971) and Merlivat and Coantic (1975) have discussed the δD-$\delta^{18}O$ relationship extensively, taking into account the humidity and aerodynamic factors at the liquid-vapor interface. Merlivat and Jouzel (1984), assumed steady -state regimes for the evaporation of water at the ocean surface and the subsequent formation of precipitation, and have explained the linear relationship between δD and $\delta^{18}O$. In particular, they have argued that the intercept is primarily dependent on the humidity of the air masses above the ocean surface.

The *d*-excess Parameter

This was defined by Dansgaard(1964) as:

$$d = \delta D - 8\delta^{18}O$$

in order to relate the available information on the δD- $\delta^{18}O$ relationship of any water sample to that of Meteoric Water Line, whose *d*-parameter is 10‰. The *d*-parameter can provide valuable geophysical information on the composition of air mass from which the precipitation derives, provided the slope is close to 8. For example, Merlivat and Jouzel (1979) showed that the *d*-parameter value can be linearly correlated to the relative humidity over the oceanic surface. The *d*-value has little significance when the slopes are less than 8 or for waters that are subjected to non-equilibrium processes (Yurtsever and Gat, 1981). But where the slopes are close to 8 the *d*-parameter can be used as a valuable tool to understand the source flux of precipitation in a given region and to identify and estimate secondary sources of importance.

Radionuclides of ^{7}Be and ^{210}Pb in Precipitation

The presence of radioisotopes in atmosphere can be attributed to two sources, namely, naturally produced and bomb produced. Once produced, these radio nuclides, being highly particle reactive, get attached to aerosols and are brought down in precipitation. Since the concentrations of these radio nuclides in atmosphere depend primarily on their production mechanism and the scavenging properties of the aerosols, the study of radio nuclide concentrations in precipitation has become an important source of information pertaining to the processes that operate in atmosphere. The use of these nuclides in understanding atmospheric mixing and transport processes is well documented in literature (Lal, et al., 1958; Wogman, et al., 1968; Young and Silver, 1974, Benninger, et al., 1979; Turekian, et al, 1983; Todd, et al., 1989; Baskaran et al., 1993).

Naturally produced radio isotopes in the atmosphere can be classified into two categories based on their production mechanism. One type of nuclides occur in nature while the others are produced cosmogenically. Terrestrially produced radio nuclides are useful in the study of tropospheric wash out processes, while the other type of nuclides are beneficial for the understanding of upper atmospheric processes, such as troposphere-stratosphere interactions. Moreover, when analyzed in the same precipitation, these two kinds of radio nuclides with their different source functions are useful in studies designed to understand mechanisms and rates of aerosol removal from the atmosphere. This in turn helps in understanding the behavior of environmentally sensitive chemical species that are injected into the atmosphere, and also aids in meteorological information which could be used in General Circulation Model(GCM) studies. Thus, a coupled study of both cosmogenic and terrigenous radionuclides in precipitation would be of immense scientific importance in addressing questions related to atmospheric and meteorological importance. The present study, realizing the importance of such studies in the Great Lakes region where no similar studies exist, proceeded to analyze the cosmogenic radio nuclide concentrations of ^{7}Be and terrigenously produced ^{210}Pb concentrations in precipitation. The production mechanisms of ^{7}Be and ^{210}Pb in detail are as follows.

Production of ^{210}Pb

The uranium and thorium present in the earth's crust account for much of the radioactivity observed on earth. The decay of uranium and thorium to the stable isotopes of lead(Figure 2) is the basis of several important methods of dating. Uranium has three naturally occurring isotopes: ^{238}U, ^{235}U and ^{234}U. All three isotopes are radioactive. The decay chain of uranium to its daughter products starts by a β particle emission from ^{238}U thereby losing some of its energy to form ^{234}U among other daughter products. These daughter products in turn decay radioactively to other daughter products. The activity of any radio nuclide is measured in disintegrations per minute (dpm) and is dependent on the half life of that particular radio nuclide. A half life of any nuclide could be explained qualitatively as "the time required for a radioactive element to become half of the number of atoms initially present in a system" and can be deduced from the equation that describes radioactive decay process:

$$A = A_0 e^{-\lambda t}$$

the above equation gives the number of radioactive parent atoms(A) that remain at any time t of an original number of atoms(A_0) that were present when t = 0. λ is the decay constant. The half life ($T_{1/2}$) is the time required for one-half of a given number of a radionuclide to decay. Thus it follows that, when $t = T_{1/2}$, $A = \frac{1}{2}A_0$. Substituting these values into the radioactive decay equation given above, the half life of any nuclide can be determined by using the equation:

$$T_{1/2} = \ln 2/\lambda = 0.693/\lambda$$

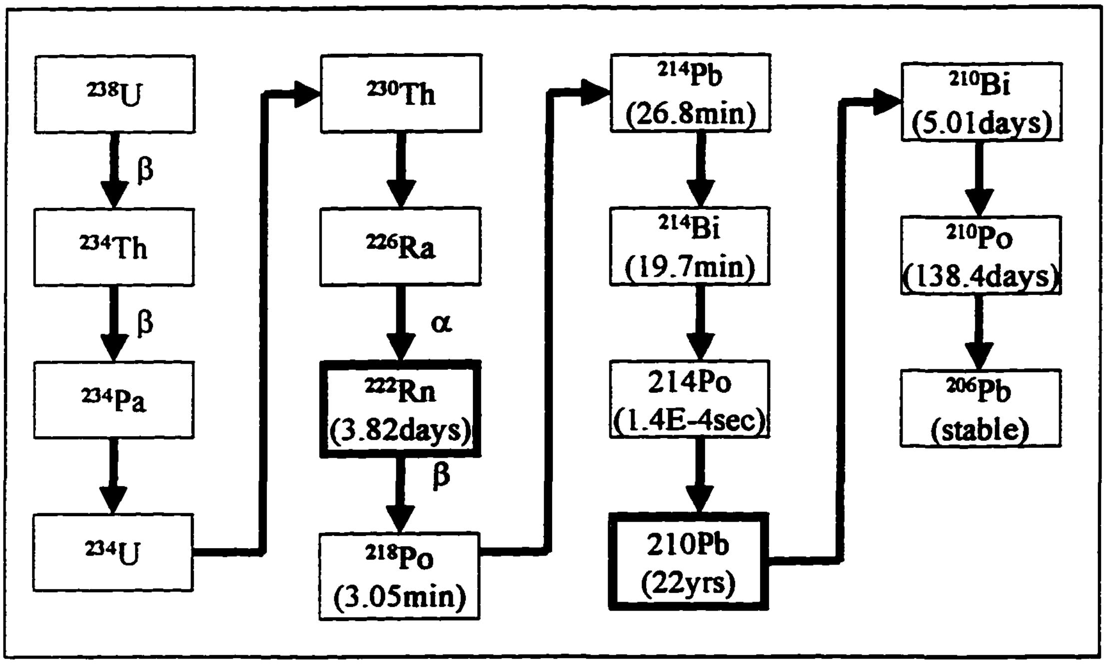

Figure 2. **The Decay of ^{238}U to ^{206}Pb. The Numbers in Parentheses Are Half-Lives of the Daughter Products.**

For example, the half life of ^{238}U is 4.468X10^{9} years which means that this will be the time taken for *n* number of ^{238}U atoms to become *n*/2 by decay. During the decay ^{238}U produces ^{226}Ra which has a half life of 1622 yrs. The decay of ^{226}Ra produces ^{222}Rn, which is a rare gas. Being a gas, it escapes from the lithosphere into atmosphere. The radon gas thus escaped, with a half life of 3.82 days, decays to produce ^{210}Pb with a half life of 22 years through a series of reactions which involve production of daughter nuclides with half lives of not more than few minutes. In essence, the radon gas emanating from earth's surface produces ^{210}Pb in three days. Since the half life of ^{210}Pb is comparatively long with respect to other daughter products, it remains for some time in the atmosphere. The ^{210}Pb nuclide, being highly particle reactive easily gets attached to the aerosol particles and is brought down to the earth's surface. The principle of continuity (what goes up must come down again) means that on the global scale there should be an atomic balance between the radon gas flux from the earth's surface and the removal of its longest lived daughter ^{210}Pb from the atmosphere by wet scavenging processes. Thus, measuring the ^{210}Pb flux in precipitation will yield information on the global production of radon gas and also about the mean residence times of the nuclides in the atmosphere.

Production of ^{7}Be

The cosmogenic radio nuclide ^{7}Be with a half life of 53.3 days is produced by the spallation reactions of protons produced by Galactic and Solar Cosmic rays(GCR & SCR) with Nitrogen and Oxygen. Two-thirds of the production of ^{7}Be takes place in the stratosphere and one-thirds in the troposphere. Much like ^{210}Pb, the ^{7}Be is highly particle reactive and readily gets attached to aerosols and other precipitating nuclei and is brought down by precipitation.

In order to understand the production rates and behavior of these nuclides in atmosphere the mean residence times were calculated. The mean residence time is the number of days any nuclide stays in the atmosphere before they are scavenged by precipitation. Thus, using the intensity of cosmic rays and the cosmic production rates the residence times of ^{7}Be are calculated to be around one year in stratosphere and few days (~ 60 days) in troposphere. The mean residence time for ^{210}Pb is calculated to be around 30 - 40 days. This is due to the much turbulent nature of the troposphere.

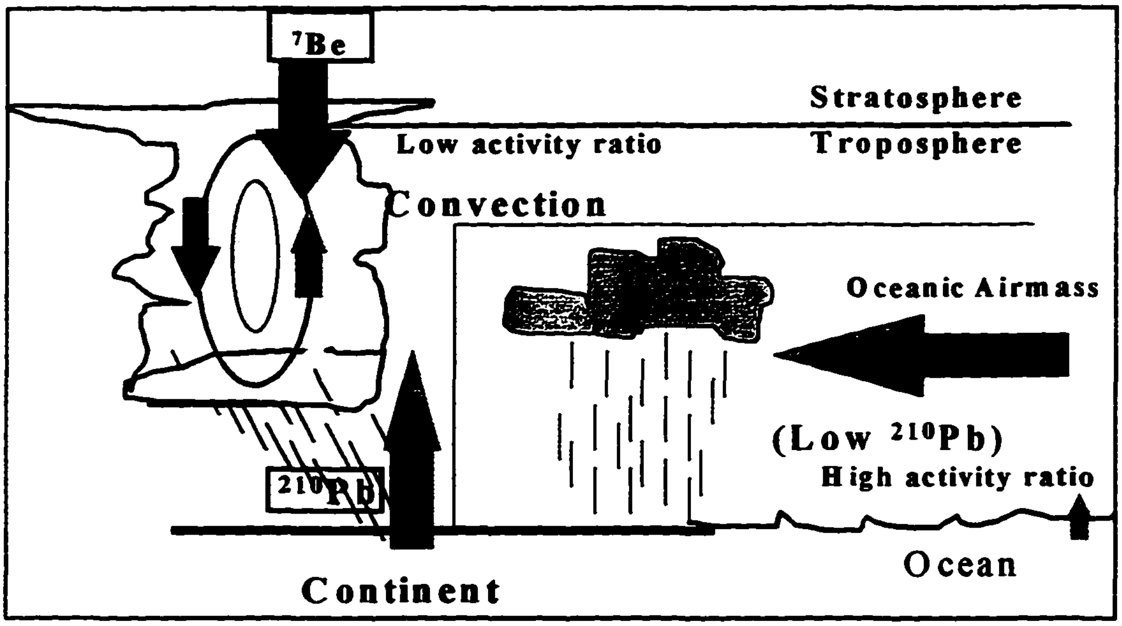

Figure 3. Systematics of ^{7}Be and ^{210}Pb Radionuclides in the Atmosphere.

Systematics of ^{210}Pb and ^{7}Be in Precipitation

An understanding of the production mechanism of these radio nuclides reveals some salient features of their systematics in the atmosphere. Figure 3 summarizes the mechanism by which the concentrations of these nuclides are controlled in the atmosphere. Since ^{210}Pb is produced on the surface of earth, the concentration of ^{210}Pb decreases with increasing altitude, due to decrease in the concentration of ^{222}Rn (Moore et al., 1973). Concentration of ^{210}Pb is higher on the continents than on the oceans, since its progenitor ^{222}Rn emanates primarily from the land surface. As a consequence, the ^{222}Rn flux is 100 times higher on the continents than the oceanic flux. Therefore the concentration of ^{210}Pb in the atmosphere strongly depends on the longitude, and on whether it is above ocean or continent (Wilkening, et al., 1975).

On the other hand, ^{7}Be concentrations increase with increasing altitude owing to its stratospheric production. Due to its short half life and longer residence times in the stratosphere, most of the stratospheric ^{7}Be does not readily reach the troposphere. However, during spring, in mid latitudes, exchange between stratosphere and troposphere due to tropopause thinning will result in some stratospheric input of ^{7}Be into the troposphere. Since ^{7}Be is of cosmogenic origin, its flux to the earth surface has a latitudinal dependence, and is independent of whether it is located over continents or oceans. The reason is that the intensity of protons in the stratosphere depends primarily on the intensity of galactic cosmic rays. On the earth such intensities are observed only near the polar stratosphere. The protons, similar to solar radiation, whose intensity depends upon angle of incidence, geo-magnetic co-ordinates and the magnetic rigidity of these particles, are strongly influenced by the geomagnetic field. Thus towards equatorial regions, the concentrations of nuclides decrease, due to the restriction imposed by geo-magnetic field (Lal and Peters, 1967). Thus, it is evident that an air mass originating or traversing across a continent should scavenge higher ^{210}Pb fluxes through precipitation than an airmass of oceanic origin. A local convective process such as a thunderstorm event should result in higher ^{210}Pb and ^{7}Be fluxes because the convection cell mixes the circulates and mixes the air masses of upper and lower troposphere. On the other hand, a regional precipitation event resulting from the high altitude clouds should have higher fluxes of ^{7}Be than ^{210}Pb flux. In higher altitudes, the presence of various global air currents causes the cosmogenic nuclides to distribute evenly throughout the atmosphere. Thus the differences in the depositional fluxes of ^{210}Pb and ^{7}Be could be best utilized for the understanding of the atmospheric processes.

In recent years, most of the research was focused on the understanding of atmospheric processes by studying the fallout concentrations of ^{7}Be and ^{210}Pb (Baskaran, 1995; Baskaran, et al., 1993; Kritz, et al., 1991; Todd, et al., 1989; Feely, et al., 1989, Nevissi, 1985; Turekian, et al., 1983; Young and Silver, 1980; Perkins, et al., 1970). Some of the salient features observed so far can be categorized as follows.

1. The depositional fluxes of ^{7}Be and ^{210}Pb are generally linearly correlated with the amount of precipitation. Since more than 90% of the radio nuclides deposit through precipitation, the amount of precipitation controls the depositional fluxes.

2. Another important and still debatable aspect is seasonality in fluxes. The extent to which seasonality could be observed depends on the geographical locality of the station at which these nuclide fluxes are measured. For example, it has been shown that during Spring and Summer there is a maxima in ^{210}Pb and ^{7}Be fluxes measured in the precipitation samples at Galveston and College Station, Texas (Baskaran, 1993). In coastal regions of tropical and mid-latitudes climatic regimes experience the maximum amount of

precipitation during Spring and Summer due to convection. But the maxima of fallout could not be explained by this simple process since the annual flux being constant, an increase in one season should result in the minimal deposition in another season of the same year. Baskaran (1993) has shown that there is a constant minimum production during the Fall season and a maximal production during Spring. Such seasonal differences were observed from various stations at mid latitudes. Such a variation is seemed to be effective for both the cosmogenically produced ^{7}Be and terrestrially produced ^{210}Pb.

There are various arguments to explain the seasonality observed in the radio nuclide fluxes in precipitation. The major hypothesis is the vertical mixing of stratospheric and tropospheric air. It is believed that during warmer months of spring and summer airmass mixing between stratosphere and troposphere results in additional ^{7}Be source (Todd, et al., 1989; Olsen, et al., 1985; Young, et al., 1970). This is apparently important at mid latitudes (38^0-51^{0}N) since the folding of tropopause is significant here. But some workers have shown that stratospheric contribution to the ^{7}Be flux is negligible on a seasonal basis, and attributed the increase of ^{7}Be to several meteorological variables, such as variability in the amounts of precipitation, and vertical mixing of lower and upper troposphere(Feely, et al., 1981 and 1989, Baskaran 1995). This is based on the hypothesis that ^{7}Be increase in precipitation due to stratospheric input by mixing should not increase the ^{210}Pb concentrations(Baskaran, 1995). And also, mid latitude stations appear to show no spring maxima. However, the ^{210}Pb flux maximum, wherever observed during spring, was attributed to the increase in amount and frequency of precipitation, and also to the warming of frozen soils, or drying out of saturated soils. But the prominent feature in all studies seems to be the minimal flux during fall season. Balkanski, et al., (1993), based on a global three dimensional simulation model, predicted that ^{210}Pb concentrations in the free troposphere are much higher than expected. This prediction was based on the observation of frequent convective pumping of ^{222}Rn to high latitudes in the tropics and mid latitudes. This should result in a lesser flux in the mid latitude belt during other seasons when the updrafts are not dominant. However, a seasonal increase of ^{210}Pb observed at various geographic locations, needs further explanation.

The Spring maxima could also be attributed to the nature of the precipitation, duration and sparsity of individual precipitation events. For example, a single thunderstorm event after a long dry spell would result in a higher flux. The so called pulse rain events with a precipitation of more than 5 cm in a day were observed to bring down higher concentrations of ^{7}Be and ^{210}Pb (Olsen, et al., 1985). Convective updrafts are another source for higher fluxes where the turbulent vertical mixing of atmosphere takes place. Such convective updrafts are supposed to increase the ^{210}Pb flux rather than the ^{7}Be flux. But the reasons for a constant minima of fluxes during fall season are not clear. At the present stage, it is assumed that a combination of atmospheric processes affect the fluxes rather than a single dominant process.

It is evident from the above discussion that understanding the depositional behavior of radio nuclides is mainly dependent upon understanding the atmospheric processes. Most of the differences in interpretation of these studies clearly indicate a lack of meteorologically supported assumptions. For example, it has been assumed that a convective updraft or a thunderstorm should increase the concentration of ^{210}Pb but not

^{7}Be. However, a convective updraft mechanism shows formation and growth of cumulonimbus clouds during convective updraft which extend well up to stratospheric heights. Such an extensive cloud formation mechanism then may scavenge some of the stratospheric aerosols also. This could result in the increase of not only the ^{210}Pb flux but also the ^{7}Be flux. Thus a strong need exists to understand the relation between the precipitation mechanism and the fluxes.

Study Area and Sampling Methods

Samples were collected in Kalamazoo, located in southwestern Michigan at approximately 42^{0} N latitude and 86^{0} W longitude (Figure 4). Michigan's latitude is the major climatic control, determining the amounts and seasonal contrasts of the incoming solar radiation. This accounts for the marked seasonality of Michigan's climate. However, the dynamic and changing character of Michigan's weather on a day to day basis is a result of the upper air circulation which occurs over the mid-latitude portion of North America. Kalamazoo, within 40 miles of Lake Michigan, reflects typical Michigan's weather patterns. Kalamazoo's average annual precipitation is 85.75 cm. Mean Summer (April to October) temperatures are in the range of 14.4 to 22.7^{0}C. Mean Winter (November to March) temperatures decline by almost 20^{0}C reflecting a high seasonal contrast. The average relative humidity values are moderate, substantially lower than they might be at oceanic coastal locations.

Stable Isotope Analyses

Precipitation samples for stable isotope analyses were collected using a commercially available glass jar. The jar was cleaned and kept in the open atmosphere prior to any precipitation. The collected rain or snow sample was immediately transferred to air tight scintillation vials and stored for analysis. The time of duration, date and nature of precipitation were recorded along with meteorological information such as temperature, humidity and the amount of precipitation. The samples were analyzed for their hydrogen and oxygen isotopic values at the Stable Isotope Geochemistry Laboratory, of Western Michigan University.

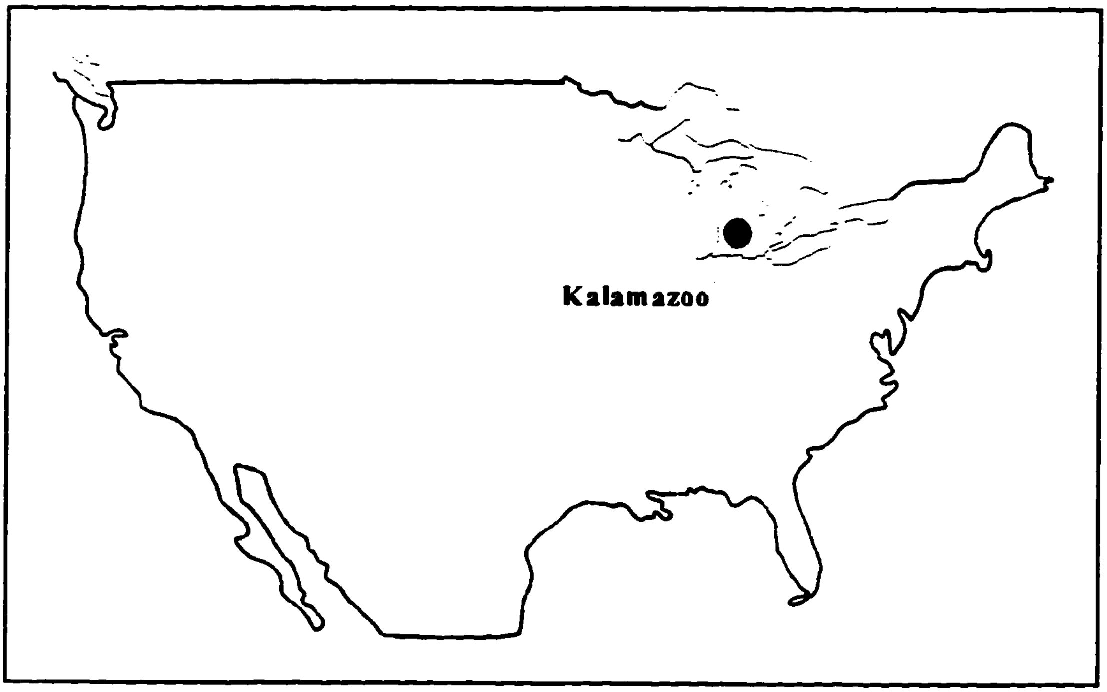

Figure 4. Map Showing the Study Area.

For deuterium analyses the samples were quantitatively reduced over uranium at 800^{0}C under vacuum (Bigeleisen et al., 1952) according to the reaction

$$2H_2O + U \xrightarrow{800^0} UO_2 + 2H_2$$

For oxygen isotope analyses a modified CO_2 - H_2O equilibration technique was used. This method, first proposed by Cohn and Urey (1938) was used later by Epstein and Mayeda (1953), who first reported accurate oxygen isotopic analyses of natural waters. This method is based on the principle that the equilibrium isotope exchange reaction between CO_2 and water occurs with a fractionation factor which is constant at a particular temperature. The equilibration takes place via hydration of CO_2, along the following steps:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) \rightleftharpoons HCO_3^- + H^+$$

The isotopic exchange reaction is:

$$C^{16}O_2 + H_2{}^{18}O \rightleftharpoons C^{16}O^{18}O + H_2{}^{16}O$$

Two ml. of each sample were loaded into evacuated septum tubes (Vacutainer brand) along with known amount of CO_2 from a commercially available tank. With each batch of sample LAB-1 standard was also loaded and the samples were allowed to equilibrate at 25^{0}C for approximately 26 hours. Then the CO_2 from the septum tubes was collected cryogenically into sample tubes for isotopic analyses. The samples were analyzed using an Optima isotope ratio mass-spectrometer, manufactured by Micromass. The reproducibility of the analyses was within 1‰ for hydrogen and 0.1‰ for oxygen.

The procedure in detail for sample analyses has been documented by Machavaram (1993).

Radionuclide Analyses

The sampling site chosen for the collection of precipitation samples for radio nuclide analyses was the roof of Rood Hall (~15 meters above ground level) located at Western Michigan University campus at Kalamazoo. A 200 liter polyethylene drum was deployed on the roof for the collection of rain and snow samples. Bulk depositional samples were collected from January 1994 to January 1995. Prior to deployment, the inside of the drum was thoroughly rinsed with 6M HCl, to prevent the adsorption of Pb and Be isotopes to the drum surface. Each sampling period was based on the amount collected in the drum, which is a minimum 6 liters. Once the sample collected exceeded the required amount, the sample was transferred into a smaller container. The drum collector was then rinsed thoroughly with 1liter of 6M HCl and the rinse was added to the sample. After further rinsing with acid the drum was redeployed for further sample collection.

The collected sample was spiked with 1 mg of stable Pb and Be in 100 ml of 6M HCl. Then the sample was stirred vigorously following the addition of 2cc of ferric chloride solution, and the ferric hydroxide was precipitated directly by adding ammonium hydroxide. Then the sample was let to equilibrate for 10 to 14 hours, until the precipitate settled to the bottom of the container. The precipitate was collected by filtering the decant through a Whatman 42 filter paper. The residue retained on the filter paper was washed with filter water and re-dissolved in a minimum amount of 6M HCl. The solution was then dried on a hot plate. The completely dried residue was packed immediately in to 10-ml gamma ray counting vials. The samples were then sent to Texas A&M University for measurement of radio nuclide concentrations. The Gamma counting was done on a high-purity Ge well detector coupled to a Canberra S-100 multichannel analyzer. The samples were typically counted for about 6-24 hours depending on the activity of ^{210}Pb in the sample since all the samples have relatively high concentrations of ^{7}Be. The final concentrations and depositional fluxes for ^{7}Be were corrected for radioactive decay from the end of sample collection to the mid-time of counting, as well as for the decay during deployment period. The overall error in the value of final concentrations and fluxes is estimated to be less than 5% for ^{7}Be and less than 10% for ^{210}Pb (Baskaran, 1993).

Objectives of the Study

Kalamazoo, lying in the vicinity of the Great Lakes (Figure 4), offers a unique opportunity to study issues concerning earth surface hydrologic process, in view of its proximity to Lake Michigan and contrasting airmass trajectories that bring precipitation during summer and winter months. One of the means to conduct these studies is by using naturally available isotope tracers. This project measured the ^{18}O/^{16}O, D/H, ^{7}Be and ^{210}Pb concentrations in direct precipitation (rain and snow) with a view to understand the factors that control their distribution in precipitation. This is an important task since the isotopic ratios in precipitation are controlled by climatic factors such as temperature, humidity, amount of precipitation etc. Once a quantitative relationship between the isotope ratios and these climatic variables is established, it then becomes feasible to understand the hydrogeology and past climate record of a given region. This capability is provided by proxy recorders of isotope ratio of precipitation such as tree rings, lake sediments, old groundwater etc. Added to this, radio nuclide concentrations are measured for the first time in a Great Lakes region, the results of which will yield valuable information regarding the role of Great Lakes and the atmospheric factors that influence this climatologically complex region.

The objectives of this project are summarized as follows:

1. Address fundamental questions regarding the factors that control the distribution of stable and radio nuclides in precipitation in the study area.

2. Make Inter-annual and seasonal comparison of isotopic data obtained between 1992 and 1995, from the climatic view point i.e., to study the effect of intra and inter seasonal variations on the isotopic systematics.

3. Coupling of stable and radio isotopes in precipitation to examine if there are common underlying factors that affect their distribution in precipitation and also to further the understanding of climatological aspects of the Great Lakes region.

4. Synthesis of all the isotopic data in terms of climatic and atmospheric forcing factors. This has implications also for the interpretation of isotopic data from proxy climatic indicators for the reconstruction of paleoclimate.

CHAPTER II

ANALYSIS OF STABLE ISOTOPE DATA

The present study utilized precipitation samples that were collected between June 1992 and March 1995. A total of 235 individual rain and snow samples were collected and analyzed for their δD and $\delta^{18}O$ values. It was seen that the individual samples exhibit considerable scatter, when plotted against the day of the event (Machavaram, 1993). This scatter arises from the complexities involved in the precipitation process, when isolated events are considered (Yurtsever and Gat, 1981). However, much of this 'isotopic noise' can be eliminated by appropriate weighting methods. The weighting procedure adopted for this study is the 'Bulk Rainfall Method' and results in weighted isotopic values of a precipitation event, which are normalized to the amount of precipitation. The total amount of precipitation, which was continuous during the period of sample collection is defined as an event and a time of more than 48 hours is used to separate events of precipitation. In cases where more than one sample was collected during a single event, only those sets of samples were weighted using the following expression.

$$\delta(\mathrm{D\ or\ }^{18}\mathrm{O}) = \Sigma P_i\delta_i \,/\, \Sigma P_i$$

where P_i and δ_i denote the fraction of the precipitation collected and its isotopic value for the i^{th} sample. In cases where one precipitation event was collected as a single sample, the isotopic values of such samples were not affected by weighting since, the single isotopic value represented the entire precipitation event. A total of 72 weighted isotopic values were obtained for the duration of sampling. The weighted isotopic values of oxygen and hydrogen isotopes and the corresponding mean humidity and temperature values during the precipitation event are presented in appendix-A. Monthly mean isotopic values were calculated using these weighted averages. The meteorological history of each event is recorded in appendix-B, where the nature of precipitation and the source of moisture for the event are presented. The methods and procedures used to interpret the weighted isotopic data are presented in the following sections.

Data Analysis and Discussion

As explained in the earlier chapter, in order to understand the hydrological implications of stable isotope investigations in precipitation, a climate - isotope relationship and the nature of precipitation process must be evaluated. This can be achieved by analyzing the δD - $\delta^{18}O$ relationship, and the isotope - temperature relationship. To discern regional climatological information, the analyzed data should be compared with that of global data and the deviations must be explained based on the regional climate. The weighted isotopic values obtained were divided based on a seasonal scale where each year represents a complete season of summer and winter, in order to preserve continuity of the seasonal isotopic signal. Thus the sampling period was divided into three yearly data sets namely, June 92 - March 93, April 93 - March 94 and April 94 - March 95, and were analyzed accordingly. The following δD - $\delta^{18}O$ and $\delta^{18}O$ -

temperature relationships were obtained.

$\delta D = 7.43\ \delta^{18}O + 12.3\ (r^2 = 0.98)$ for 1992 - 93, (Figure 5),

$\delta D = 7.84\ \delta^{18}O + 18.4\ (r^2 = 0.98)$ for 1993 - 94, (Figure 6),

$\delta D = 7.47\ \delta^{18}O + 18.6\ (r^2 = 0.95)$ for 1994 - 95, (Figure 7) and

$\delta D = 7.49\ \delta^{18}O + 13.9\ (r^2 = 0.96)$ for 1992 - 95, (Figure 8).

The $\delta^{18}O$ - temperature relationships are

$\delta^{18}O = 0.4326\ t^0C - 13.876\ (r^2 = 0.62)$ for 1992 - 95, (Figure 9),

$\delta^{18}O = 0.5786\ t^0C - 15.059\ (r^2 = 0.69)$ for 1992 - 93,

$\delta^{18}O = 0.3812\ t^0C - 13.42\ (r^2 = 0.70)$ for 1993 - 94 and

$\delta^{18}O = 0.3329\ t^0C - 12.723\ (r^2 = 0.54)$ for 1994 - 95.

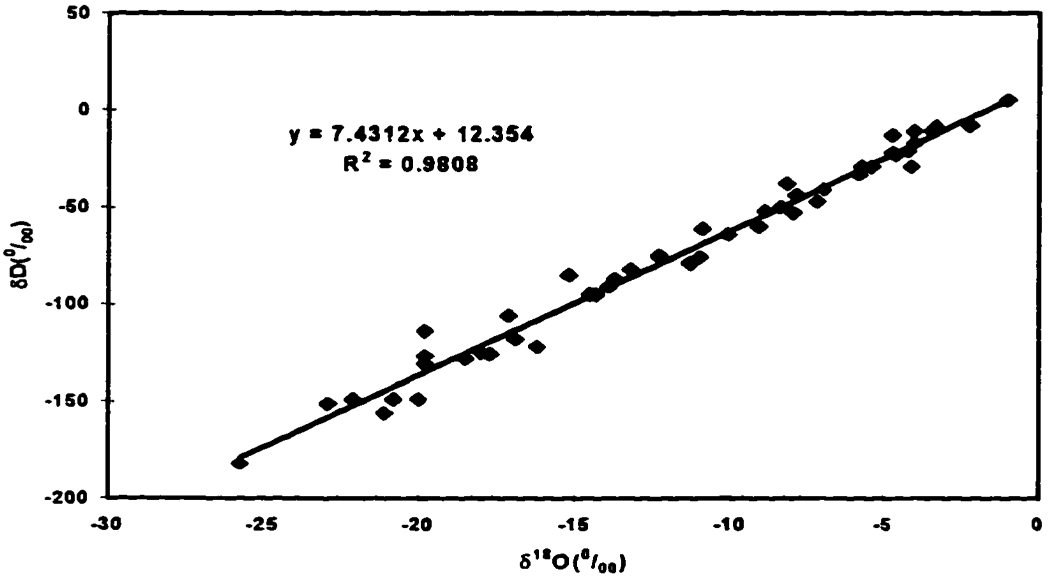

Figure 5. The δD - $\delta^{18}O$ Relationship in Precipitation of 1992 - 93.

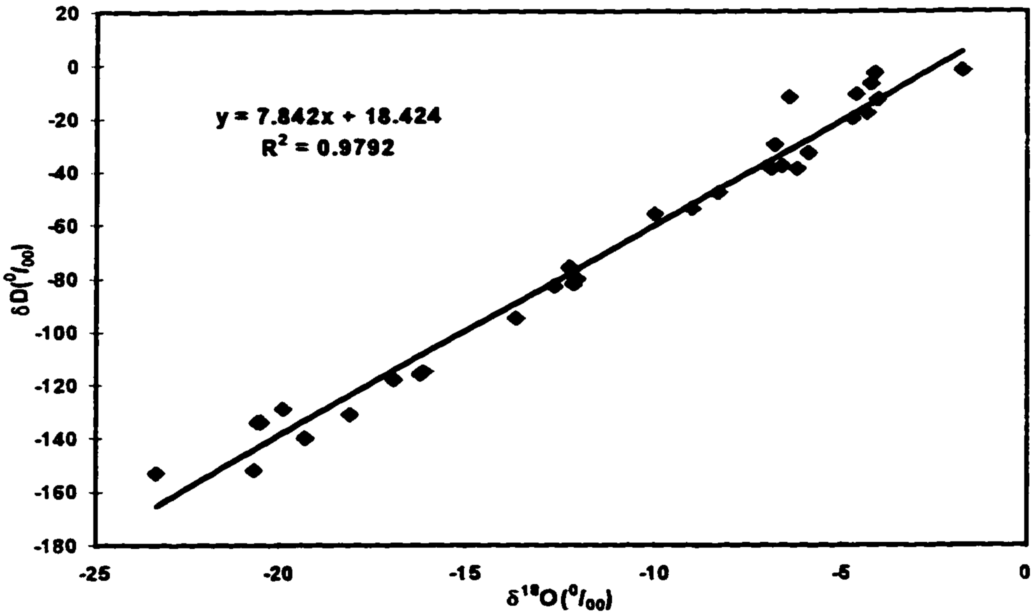

Figure 6. The δD - $\delta^{18}O$ Relationship in Precipitation of 1993 - 94.

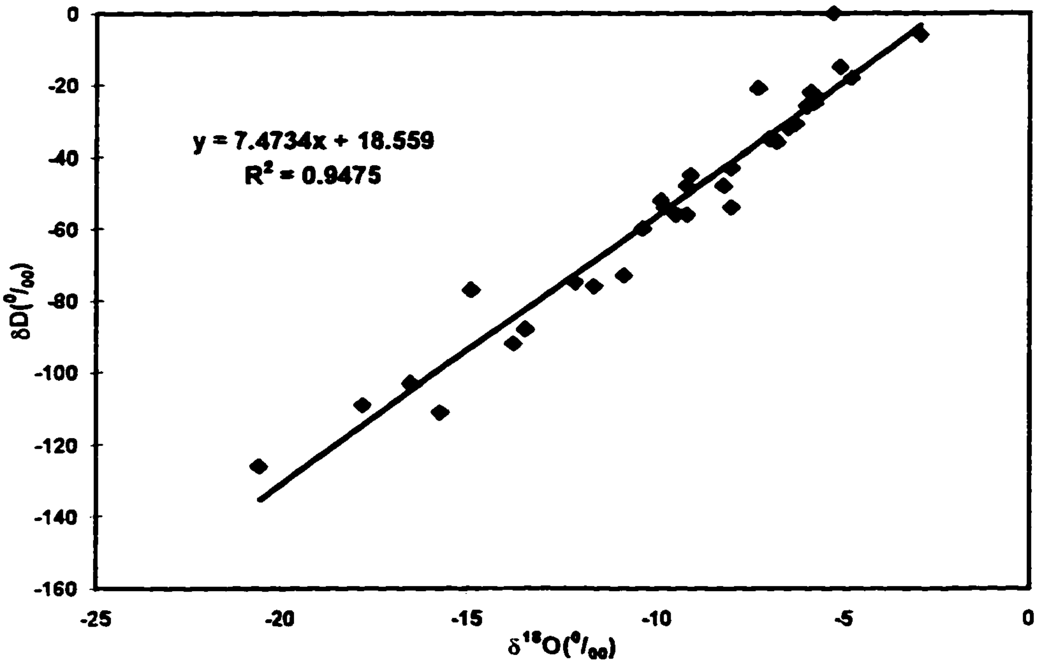

Figure 7. The δD - $\delta^{18}O$ Relationship in Precipitation of 1994 - 95.

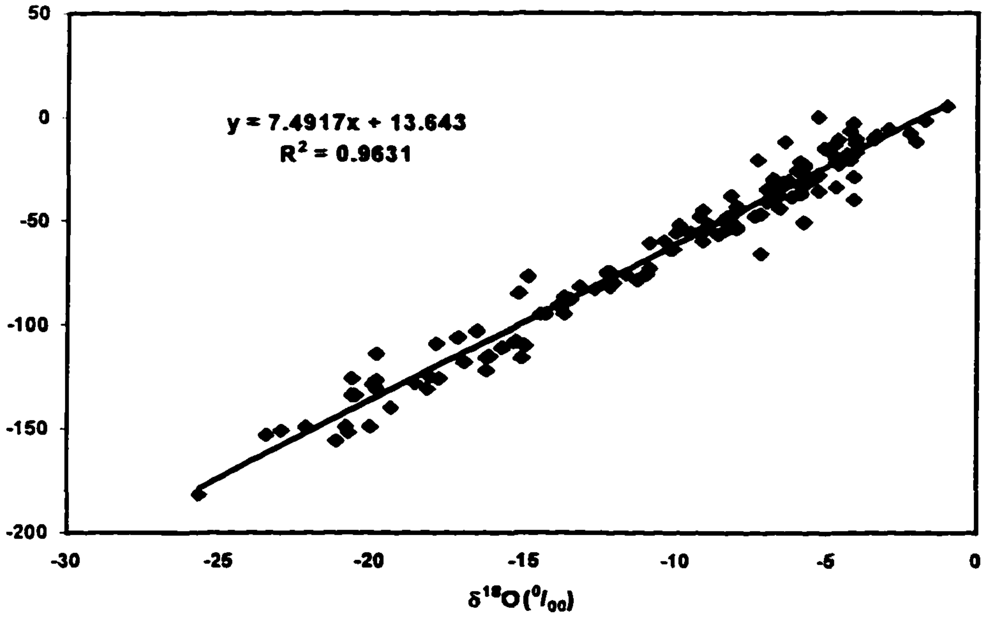

Figure 8. The δD - $\delta^{18}O$ Relationship in Precipitation of 1992 - 95.

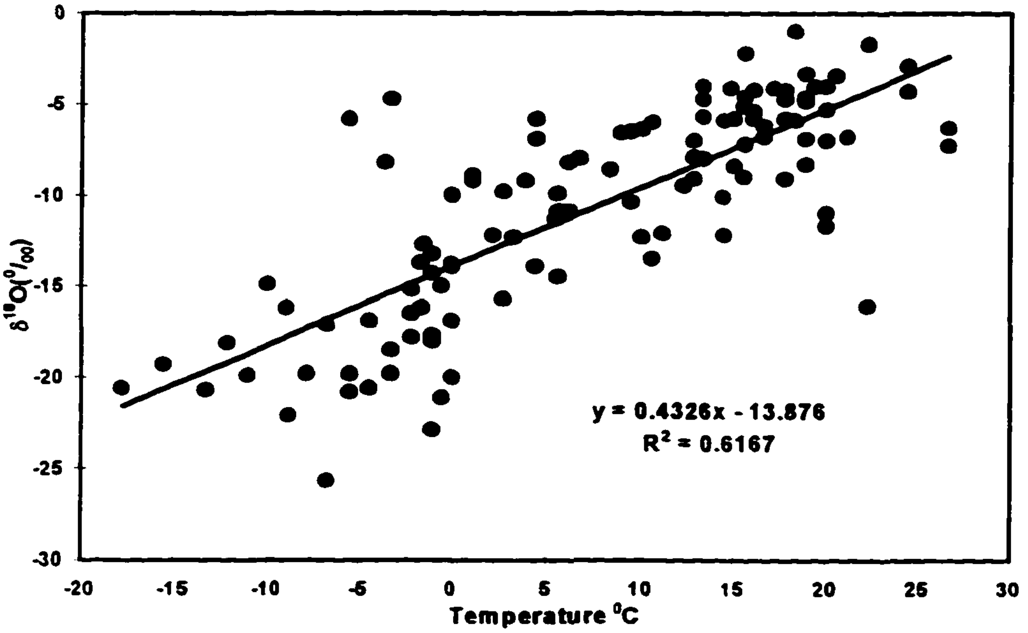

Figure 9. The $\delta^{18}O$ - Temperature Relationship in Precipitation of 1992 - 95.

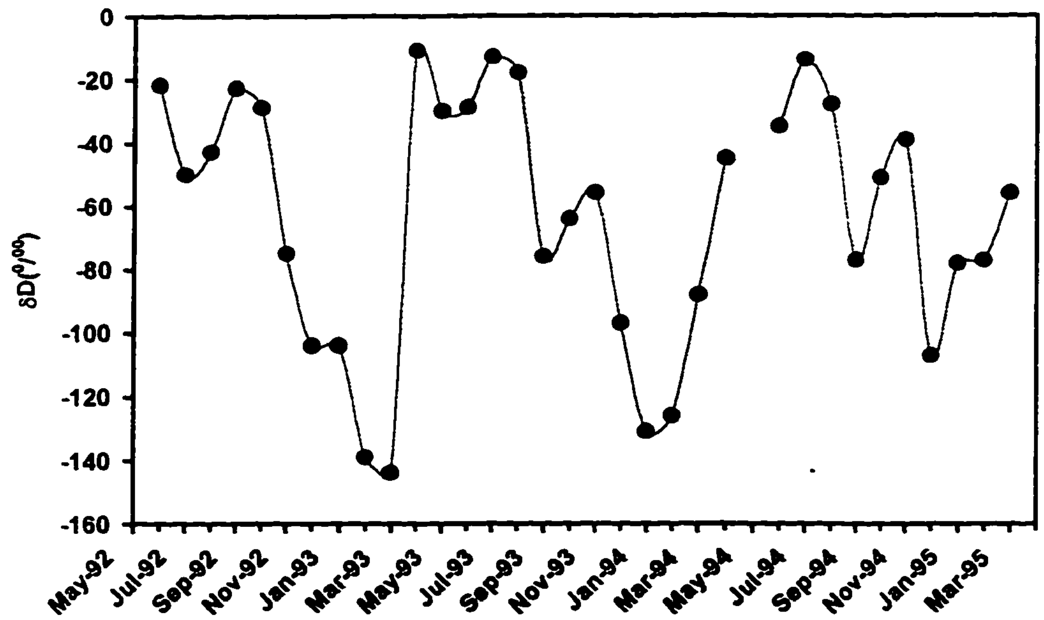

Figure 10. Monthly Mean δD Values in Precipitation.

The δD - $\delta^{18}O$ relationships obtained for the precipitation at Kalamazoo are comparable to that of Meteoric Water Line (MWL) ($\delta D = 8\ \delta^{18}O + 10$) with slopes close to 8 (refer Chapter I for a detailed discussion on Meteoric Water Line). As explained earlier, a slope of 8 results from an equilibrium condensation process. Thus, the condensation component of precipitation at Kalamazoo can be assumed to have occurred under equilibrium conditions and no secondary processes such as evaporation of falling raindrops influenced the isotopic ratios in precipitation. The intercept of greater than 10 obtained from these relationships supports this assumption, since any secondary evaporation process would result in deuterium deficit along with deviation from the slope of 8. However, when compared to the MWL obtained by the IAEA for the north American continent(Yurtsever and Gat, 1981), whose relationship is given as

$$\delta D = 7.95\ \delta^{18}O + 6.03$$

the relationships obtained from this study show an intercept of greater than 10. This intercept, also known as *d*-excess indicates admixture of a secondary evaporated moisture source and is of great geophysical importance. The significance of this *d*-excess in Kalamazoo precipitation is dealt in detail separately for summer and winter precipitations later in this chapter.

The $\delta^{18}O$ - temperature relationships obtained from this study are comparable to the relationship found by Dansgaard(1964) and Yurtsever(1975) which are:

$\delta^{18}O = 0.69\ t^0C - 13.6$ and

$\delta^{18}O = 0.521\ t^0C - 14.96$ respectively.

It was also found that the so called temperature effect can be explained by the assuming that the condensation phase of precipitation cycle follows a Rayleigh distillation process (Dansgaard 1964). Since in a Rayleigh process condensation is considered to be under equilibrium conditions, the $\delta^{18}O$ - temperature relationships obtained in this study appears to support the assumption that the precipitation at Kalamazoo occurs under equilibrium conditions. However, the relationships obtained for the years 1993 -94 and 1994 - 95 slightly deviate from the relationships observed by Yurtsever(1975) and the 1992 - 93 relationship found in this study. A more detailed discussion on the implications of this deviation for the later years is presented later in this chapter.

The mean annual δD values of precipitation at Kalamazoo are -74‰, -70‰ and

-51‰ and the $\delta^{18}O$ values are -11.7, -11.2 and -9.3 for the years 1992-93, 1993-94 and 1994-95 respectively. The mean δD and $\delta^{18}O$ values for the study period are -65‰ and -10.7‰ respectively. The progressively positive isotopic values observed in precipitation are in agreement with the increasing mean annual temperature during the study period.

Since isotopic ratios in precipitation are controlled mainly by temperature, a plot was constructed using monthly mean isotopic values of precipitation, to reflect the strong seasonal contrast in temperature observed in the study area. The monthly mean isotopic values were calculated by re-weighting the weighted precipitation events, using the same 'Bulk Rainfall Method' employed in initial weighting of individual precipitation samples. The monthly mean weighted data are presented in Appendix C. Based on the contrast observed (Figure 10) for the years 1992 - 93, precipitation events were divided into Summer and Winter precipitations, where Summer was defined by precipitation events from April to October and Winter from November to March. The same classification was then extended to years 1993 - 94 and 1994 - 95.

It is evident from Figure 10 that, isotopic ratios in precipitation strongly reflect the temperature contrast between summer and winter seasons. The mean δD and $\delta^{18}O$ values for summer and winter precipitation for the study period are:

Summer precipitation	δD = -37‰, $\delta^{18}O$ = -6.9‰;
Winter precipitation	δD = -98‰, $\delta^{18}O$ = -15.1‰.

The weighted isotopic ratios show a general depletion in the winter season compared to those of summer precipitation as expected. The isotopic ratios in condensation are governed by fractionation factors which in turn are temperature dependent. The temperature at which condensation takes place controls the fractionation, i.e., the lower the temperature the higher the fractionation and lighter resultant isotopic ratios. This mechanism explains the depletion of isotopic values in the winter season compared to those observed in the summer season.

During Summer months, the precipitation at Kalamazoo is heavily influenced by the moisture from Gulf of Mexico brought by the Maritime-Tropical airmass. Due to the southward movement of upper level jet stream during Winter months, the influence of Gulf moisture on Winter precipitation is reduced and Pacific moisture and the Polar-Continental airmass influence the Winter precipitation to a greater extent. Owing to the differences in the sources of precipitation and also the nature of precipitation viz., rain and snow, the summer and winter precipitation events are treated separately for a better understanding of the factors that influence precipitation on a seasonal basis.

Summer Precipitation

The mean summer isotopic values in precipitation for 1992 (June -October), 1993 and 1994 (April - October), are -34‰, -38‰ and -40‰ for δD and -6.1‰, -7.2‰ and -7.7‰ for $\delta^{18}O$ respectively. The mean summer δD and $\delta^{18}O$ for the study period are found to be -37‰ and -6.9‰ respectively. The δD - $\delta^{18}O$ relationships for summer precipitation are as follows:

$\delta D = 7.82\ \delta^{18}O + 13.2\ (r^2 = 0.97)$ for 1992,

$\delta D = 8.34\ \delta^{18}O + 22.2\ (r^2 = 0.95)$ for 1993,

$\delta D = 8.56\ \delta^{18}O + 26.4\ (r^2 = 0.91)$ for 1994 and

$\delta D = 7.91\ \delta^{18}O + 18.1\ (r^2 = 0.93)$ for 1992 - 94, (Figure 11).

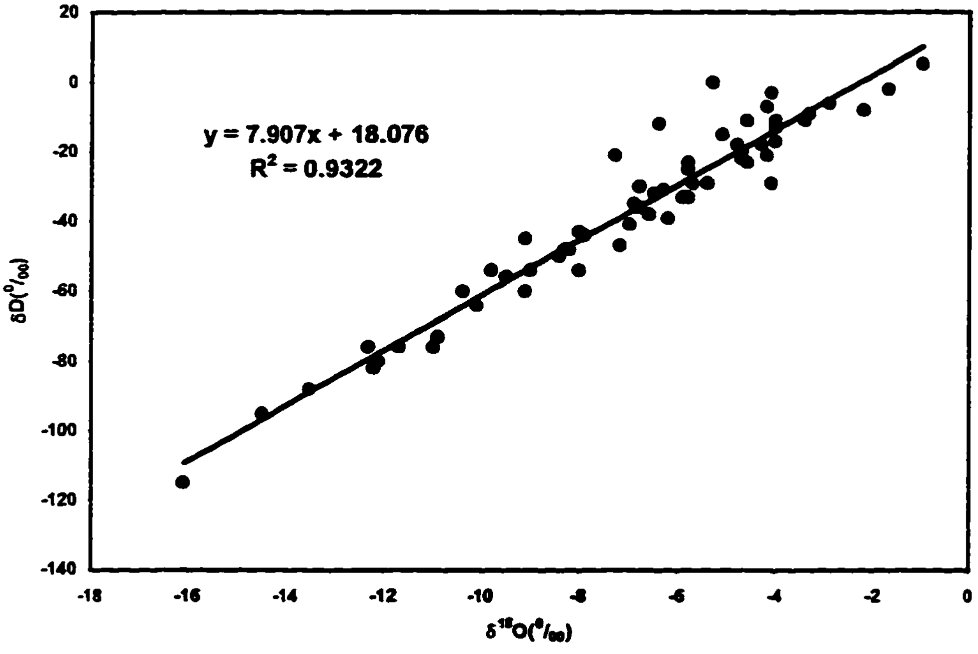

Figure 11. **The δD - $\delta^{18}O$ Relationship in 1992 - 94 Summer Precipitation.**

As explained earlier, the predominant source of moisture for Summer precipitation at Kalamazoo is the Gulf of Mexico, due to the strong influence of maritime-tropical airmasses flowing through the North American continent from the equatorial regions. In a study of moisture flux movements across the continent, Rasmusson (1967) has shown that during summer months, most of the Gulf moisture moves towards the North Pole and is the main source of moisture for precipitation in the eastern half of the United States. Based on the δD - $\delta^{18}O$ and $\delta^{18}O$ - temperature relationships the condensation at Kalamazoo was assumed to be under equilibrium conditions and to obey a Rayleigh process as explained earlier. For a fuller understanding of the summer precipitation at Kalamazoo, the isotopic values observed in precipitation at Kalamazoo were analyzed as follows:

Firstly, a box model calculation was performed to understand whether the summer precipitation at Kalamazoo, which is mostly derived from the vapor flux originating from the Gulf of Mexico, follows a first order Rayleigh distillation process. The validity of this model was then tested against meteorological data obtained for all the precipitation events.

Secondly, the sources and nature of secondary moisture that influences the isotopic ratios in summer precipitation at Kalamazoo were considered in order to explain the intercept of greater than 10 obtained from the above listed δD - $\delta^{18}O$ relationships.

In view of the linear relationship observed between δD and $\delta^{18}O$, we use only the $\delta^{18}O$ values for all the calculations in the following sections. It is evident that use of either δ values yield similar results.

A Rayleigh Distillation Model

In Chapter I it was shown that, in the precipitation process, a continuous removal of the vapor phase occurs through rain-out or condensation. The condensate can not re-equilibrate with the vapor reservoir and the isotopic composition of both the condensate and the vapor change as a function of the residual vapor left and of the isotopic fractionation factors. This effect is termed as `Rayleigh distillation' as it was first derived by Lord Rayleigh for the case of fractional distillation of mixed liquids. The equation that governs the distribution of isotopic species in vapor in such a process is:

$$R = R_0 f^{(\alpha-1)}$$

where R is the isotopic ratio of the vapor, R_0 is the initial isotopic ratio of the vapor flux. The fraction of the vapor remaining in the vapor is f and α is the fractionation factor during condensation. When the isotopic species removed at every instance are in thermodynamic equilibrium with those remaining in the system, then the Rayleigh equation can be applied to that system.

In order to understand whether the summer precipitation at Kalamazoo follows a Rayleigh distillation process, the moisture from which the precipitation derived has to be treated as explained in the above paragraph. Since most of the summer precipitation at Kalamazoo is derived from the moisture originating in the Gulf of Mexico, the Rayleigh process was applied to the Gulf moisture by adopting a box model (Rozanski et al., 1982; Krishnamurthy and Bhattacharya, 1991). According to this model, the Gulf moisture during its traverse across the continent towards the Great Lakes region losses moisture by successive condensations, each of which obey the Rayleigh process. Thus, by taking the amount of moisture condensed at every instance and the mean surface air temperature of the area in which condensation occurred, it is feasible to calculate the isotopic ratios of the vapor that remains in the flux after each successive condensation. The procedure for such calculations is as follows.

A box was constructed to encompass the area between the Gulf of Mexico and Kalamazoo by dividing the continent into 10 equal gridcells, with grid numbers progressively increasing towards Kalamazoo (Figure 12). The area of each grid was 125708.2 km^2. From each gridcell, three stations were selected which represent typical monthly mean precipitation and temperature values. The stations in each grid for which mean precipitation and temperature data available are given in Appendix D. The mean values from all stations within each geographical divisions were taken instead of the individual station values to provide a better average for the summer months. Using the mean temperature, the fractionation factor - α, was calculated for each grid by the equation (Majoube, 1971):

$$\ln \alpha\,(\delta^{18}O) = (1.137/T^2)10^3 - (0.4156/T) - (2.0667 \times 10^{-3})$$

where T is the absolute temperature in degrees Kelvin.

The total water vapor flux which enters the North American continent across the Gulf of Mexico was taken from the data of Rassmusson(1967) as 2.65 X 10^{15} kg/(Jun - Oct). This is the mean value obtained from data collected over two years. The fractions of the vapor flux which is condensed over each grid and the amount of vapor left over in the flux(f) are calculated by using the area of each grid and the mean precipitation values. The $\delta^{18}O$ values of the condensate in each grid were obtained by the equations

$$R_p = \alpha_i R_0 f_i^{(\alpha i-1)}$$

$$\delta_p{}^0/_{00} = [(R_p/R_{std}) - 1]\ 10^3$$

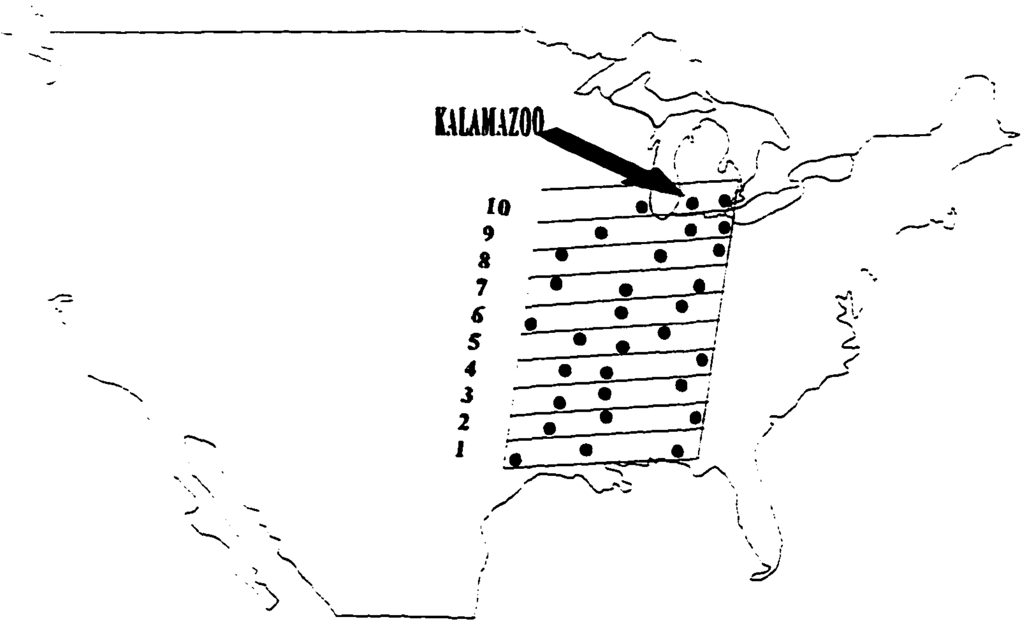

Figure 12. The Box Model Constructed to Model the $\delta^{18}O$ in Summer Precipitation in Terms of Rayleigh Distillation Process.

where R_p is the isotopic ratio of the condensate in the ith grid, R_0 is the isotopic ratio of the initial vapor flux, α_i is the fractionation factor for the ith grid and f_i is the fraction that remains in the vapor above the ith grid (Rozanski, et al., 1982; Krishnamurthy and Bhattacharya, 1991). δ_p is the isotopic value of the condensate in the ith box expressed in δ‰ with respect to SMOW. The isotopic ratio of SMOW used in this calculations was that of Yurtsever and Gat (1980)(2005.2×10^{-6}). The results of the calculations done for the years 1992, 93 and 94 were summarized in Tables 1, 2 and 3 respectively.

Under equilibrium conditions and without addition of any evapotranspirated vapor from the continent to the initial flux, the precipitation in the 10th grid i.e., Kalamazoo

Table 1

Calculated α, Σ, f and $\delta^{18}O$ Values for Gulf Moisture Flux Undergoing Rayleigh Distillation Process, Where α = the Fractionation Factor, Σ = Cumulative Amount of Condensate in Each Grid and f = the Fraction Remaining in Vapor. 1992 Summer Precipitation
Total Flux = 2.65 X 10^{15} Kg/(Jun - Oct)

Grid No.	α	Σ (Kg/Jun-Oct)	f	$\delta^{18}O$(‰)
1	1.009342	7.547E+13	0.971521	-2.27
2	1.009458	1.511E+14	0.942987	-2.44
3	1.009488	2.241E+14	0.915426	-2.69
4	1.009635	2.922E+14	0.889735	-2.83
5	1.009650	3.617E+14	0.863515	-3.11
6	1.009739	4.294E+14	0.837958	-3.32
7	1.009792	4.842E+14	0.817279	-3.52
8	1.009908	5.521E+14	0.791659	-3.75
9	1.010014	6.201E+14	0.765984	-4.00
10	1.010078	6.779E+14	0.744171	-4.24

should have $\delta^{18}O$ values of -4.24‰, -4.23‰ and -4.08‰ for precipitation derived from the Gulf moisture for the years 1992, 93 and 94 respectively. The $\delta^{18}O$ values change to -3.76‰ and -3.63‰ for 1993 and 94 respectively, when the summer season is taken from April to October. Similar calculations performed for a minimal initial flux of 1.18 X 10^{15}

Table 2

Calculated α, Σ, *f* and $\delta^{18}O$ Values for Gulf Moisture Flux Undergoing Rayleigh Distillation Process, Where α = the Fractionation Factor, Σ = Cumulative Amount of Condensate in Each Grid and *f* = the Fraction Remaining in Vapor. 1993 Summer Precipitation
Total Flux = 2.65 X 10^{15} Kg/(Jun - Oct)

Grid No.	α	Σ (Kg/Jun-Oct)	*f*	$\delta^{18}O$(‰)
1	1.009125	6.842E+13	0.974082	-2.45
2	1.009356	1.282E+14	0.951432	-2.46
3	1.009389	1.807E+14	0.931569	-2.62
4	1.009532	2.346E+14	0.911125	-2.70
5	1.009550	2.890E+14	0.890547	-2.90
6	1.009635	3.557E+14	0.865270	-3.10
7	1.009745	4.307E+14	0.836867	-3.33
8	1.009828	5.120E+14	0.806071	-3.63
9	1.009922	5.870E+14	0.777659	-3.91
10	1.009973	6.583E+14	0.750657	-4.23

Kg/Jun-Oct (Rasmusson 1967) gave a $\delta^{18}O$ value of -5.98‰ for the precipitation in the 10th grid. Thus it can be shown that, when moisture flux from the Gulf of Mexico undergoes a Rayleigh type condensation, during its traverse across the continent, the precipitation at Kalamazoo can have $\delta^{18}O$ values ranging from -3‰ to -6‰.

Table 3

Calculated α, Σ, *f* and $\delta^{18}O$ Values for Gulf Moisture Flux Undergoing Rayleigh Distillation Process, Where α = the Fractionation Factor, Σ = Cumulative Amount of Condensate in Each Grid and *f* = the Fraction Remaining in Vapor. 1994 Summer Precipitation
Total Flux = 2.65 X 10^{15} Kg/(Jun - Oct)

Grid No.	α	Σ (Kg/Jun-Oct)	*f*	$\delta^{18}O$(‰)
1	1.009340	8.826E+13	0.966569	-2.32
2	1.009418	1.715E+14	0.935023	-2.55
3	1.009438	2.496E+14	0.905465	-2.84
4	1.009576	3.187E+14	0.879276	-3.00
5	1.009576	3.807E+14	0.855801	-3.25
6	1.009650	4.301E+14	0.837096	-3.41
7	1.009697	4.751E+14	0.820025	-3.57
8	1.009803	5.194E+14	0.803268	-3.68
9	1.009878	5.651E+14	0.785951	-3.84
10	1.009913	6.203E+14	0.765051	-4.08

The frequency distribution of oxygen isotopic values in summer precipitation is shown in Figure 13. In light of the above box model and from Figure 13, it can be shown that most of the summer precipitation which is derived from the Gulf moisture source, follows a Rayleigh process. Thus, according to the Rayleigh model, Gulf moisture contributed

55%, 43% and 31% to the summer precipitation for the years 1992, 93 and 94 respectively. The -9‰ to -12‰ range can be attributed to the moisture source originating from the Atlantic ocean. In a study of oxygen isotopic variation in rain storms, Pionke and Dewalle(1992) have shown that the precipitation at Pennsylvania resulting from Atlantic moisture is more depleted (-10.9‰) than that of Gulf moisture(-6.2‰). The fractions with 0‰ to -3‰ range is attributed to thunderstorms and other precipitation which result from locally derived moisture. A detailed discussion on the nature of locally derived moisture sources is presented later in this chapter.

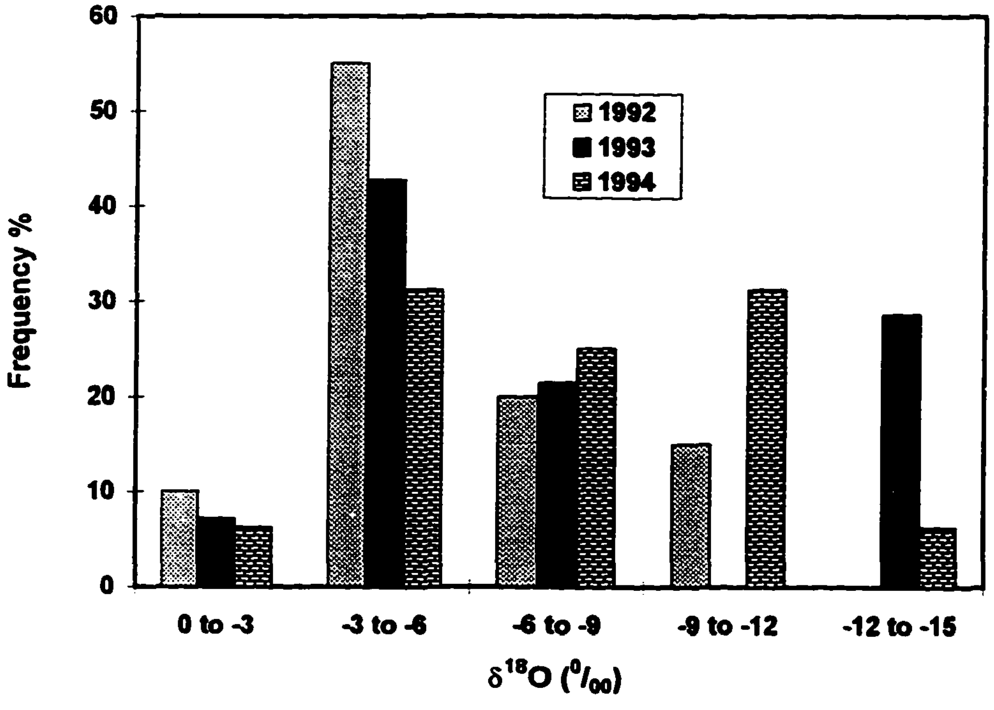

Figure 13. Frequency Distribution of $\delta^{18}O$ in Summer Precipitation Events.

Thus, based on Figure 13 it can be assumed that less than 10% of summer precipitation at Kalamazoo, is a result of locally derived moisture. It can also be noted from the Figure 13 that there is an overall shift towards more negative isotopic values from 1992 to 1994. One reason for this shift might be due to the increasing influence of secondary evaporated moisture, which is isotopically depleted, on the atmospheric moisture in this region. A more detailed discussion on the source and nature of this secondary evaporated moisture is presented later in this chapter.

Though a Rayleigh model as described above seems to explain the systematics of isotopic ratios in precipitation satisfactorily, few important issues related to the distribution of D and ^{18}O in precipitation need further discussion. These include the evapotranspirational effect, moisture flux divergence and the nature of the precipitation itself. The model described above inherently assumes a stratiform type precipitation without taking into consideration the nature of clouds from which precipitation occurs and also the complex processes that operate within the cloud. This necessitates a detailed meteorological investigation of the sources and nature of precipitation in order to fully understand the effect of the afore mentioned processes. Such an effort made in the present study is presented here. A meteorological database (Appendix B) was constructed by interpreting surface weather maps and 500mb upper air circulation charts, published by the National Oceanic and Atmospheric Administration (NOAA), for all the days during which precipitation samples were collected at Kalamazoo. The evaluation of the Rayleigh model in light of this meteorological information is presented below.

Of all the processes mentioned above, the effect of evapotranspiration on the

Rayleigh model is ignored due to lack of precise evapotranspirational data. In order to take evapotranspiration in to account, the isotopic composition of precipitation in each gridcell is required (Rozanski, et al, 1982; Krishnamurthy and Bhattacharya, 1991). Only by comparing the isotopic composition of precipitation in each gridcell with that of the Rayleigh model results, the evapotranspirational effect can be satisfactorily explained. Evapotranspiration affects the Rayleigh model in two ways. If the evapotranspirated moisture has the same isotopic signature as that of the vapor from which last condensation took place, then there will be no net isotopic change. However, this added moisture will affect the fraction remaining in the atmospheric vapor and changes the isotopic composition of further condensates by shifting them towards more positive isotopic values. On the other hand, if there is fractionation associated with evaporation as well as transpiration, the net evapotranspirated moisture is isotopically more depleted than the atmospheric moisture. The addition of this isotopically depleted moisture shifts the isotopic ratios of further condensates towards more negative values. Thus, the addition of evapotranspirated moisture can have two distinctly opposite effects on the atmospheric vapor. However, this explanation was not experimentally tested due to the reasons cited above.

During its transit over the continent, some of the Gulf moisture moves north-east towards the Atlantic coast of North America. This divergence reduces the amount of total flux that moves towards the America - Canada border. This results in the reduction of amount of moisture in the flux that condenses in the midwest region of North America. The resultant precipitation from this flux would invariably result in lighter isotopic signatures. Due to the lack of necessary data a precise estimation of flux divergence could not be made. However, based on the moisture flux movements in Atlantic, Pacific and mid-United States region, which interact with the Gulf flux, a preliminary estimate was made. Based on this estimate the amount of Gulf moisture that reaches the Great Lakes region after flux divergence is in the order of ~1 X 10^{15} Kg/(Apr - Oct). As previous calculations indicate, for this amount of flux the condensate in the 10th grid, i.e., Kalamazoo would have $\delta^{18}O$ values in the range of -6‰ to -7‰. Another way to take the flux divergence into account would be to increase the width of grid cells so that they encompass all the area from the east coast to the central United States. Calculations with modified gridcell areas are currently under progress in order to verify this assumption.

Meteorological analysis coupled with stable isotope data in precipitation mainly serves two purposes: one, to study the stable isotope systematics in clouds during their formation and subsequent precipitation and two, to distinguish and quantify various moisture sources that contribute to precipitation in a given region. The information obtained from the first is of importance in modeling stable isotope behavior associated with cloud micro physics where as the second aids in understanding the influence of various moisture sources on the regional hydrology. Though a few previous studies analyzed meteorological data either based on moisture sources(Leguy et al., 1983) or on nature of precipitation (Gedzelman and Arnold, 1994), no combined study of these parameters was published. Such an attempt is made in the present study to discern various moisture sources and nature of precipitation from a stable isotope perspective. This attempt is hoped to evaluate the possibility of identifying a given moisture source and the type of precipitation by the stable isotopic signature of that particular precipitation. When studied on a seasonal basis such an attempt results in a better understanding of the applicability of the Rayleigh model.

The meteorological data collected for all the weighted precipitation events were divided into three categories based on the source of moisture, which are termed as Gulf source, Atlantic source and Pacific/Continental source. Since most of the Pacific moisture precipitates on the west side of the Rocky Mountains, it can be assumed for all practical purposes, that the influence of Pacific moisture on the precipitation in the Great Lakes region is negligible. The continental moisture refers to the residual atmospheric moisture and thus can also be considered as locally derived moisture. A summary of the major moisture sources, their mean oxygen isotopic values and contribution to summer precipitation both in frequency and amount is presented in Table 4.

It is evident from table 4 that more than 80% of precipitation results from a Gulf moisture source. The mean $\delta^{18}O$ values for the precipitation events derived solely from the Gulf moisture are -6.6‰, -6.6‰ and -7.3‰ for the years 1992, 93 and 94 respectively. These data seem to support the argument presented above based on the flux divergence calculation.

The nature of precipitation during summer months at Kalamazoo is more varied and various attempts to distinguish these precipitations based on stable isotope data yielded less than satisfactory results with no discernable correlation. The nature of precipitation can broadly be categorized into frontal and non frontal (local convection) precipitations (Figure 14). The frontal precipitation is more complex and quite varied since precipitation may occur at the frontal boundary or throughout the front. The nature and intensity of precipitation also changes drastically when such a front becomes stationary. When precipitation results from either a low pressure system or from a low associated with a front, the dynamics of such systems are significantly different than other frontal systems. Due to innumerable possibilities that exist in these systems the stable isotope ratios analyzed from different precipitations of similar meteorological conditions may vary significantly. Added to these complexities, the amount of moisture present in the cloud and the temperature at the cloud base also play a dominant role in governing the stable isotope ratios in any given precipitation. Yet again, the stable isotope ratios in any condensate can also be affected by the nature of previous condensates resulted from the same moisture flux.

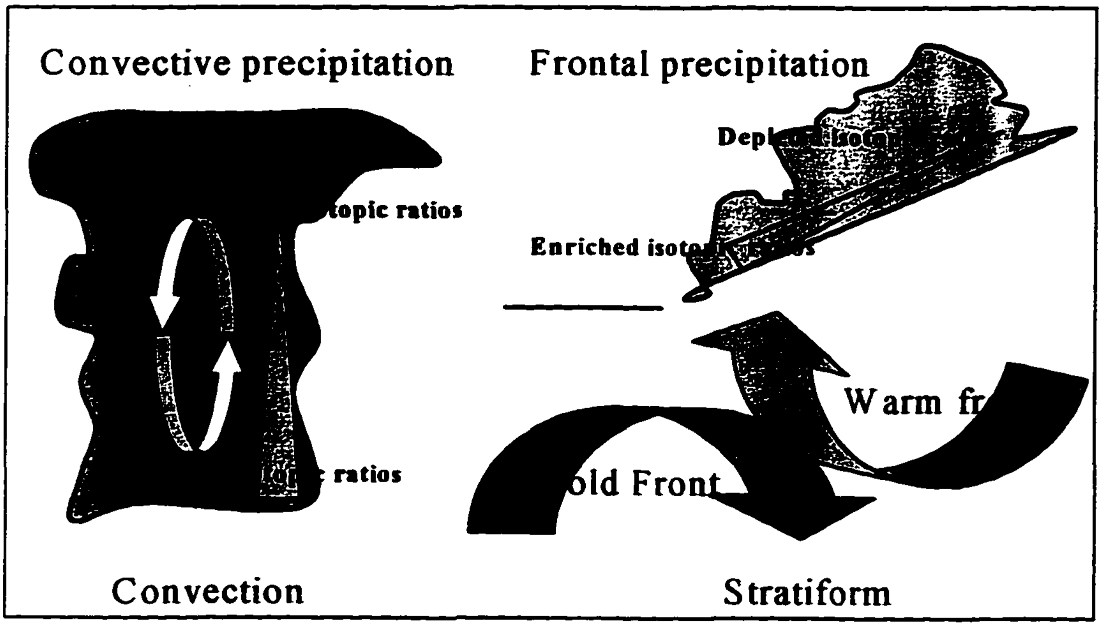

Figure 14. Schematic Showing the Nature of Convective and Frontal Precipitation.

Table 4

Contributions of Major Moisture Sources to Summer Precipitation at Kalamazoo and Their Representative Oxygen Isotopic Values

	Gulf		Atlantic		Continental	
Year	Frequency	Amount	Frequency	Amount	Frequency	Amount
1992	81%	86%	4%	1%	15%	13%
1993	88%	97%	6%	1%	6%	2%
1994	85%	81%	10%	3%	5%	14%
Mean $\delta^{18}O$	-6.8‰		-11.4‰		-4.6‰	

On the other hand, non frontal or convective precipitations (defined in general as thunderstorms) are varied only in the extent of the intensity of the updraft. In a convective precipitation, the surface moisture is swept aloft almost vertically and is allowed to fall without much sorting. Thus, the isotopic ratios of the source water vapor (which is locally derived) forms the lower bound for the resulting precipitation. This source water vapor for thunderstorms is often confined to the humid air which is present in the lowest kilometer of the atmosphere, which typically has higher δ values. Due to rapid equilibrium the isotopic ratios of the precipitation resulting from such near vertical updrafts is usually higher than that of the source vapor from which it is derived (Gedzelman and Arnold, 1994).

Another possible explanation for higher isotopic ratios in thunderstorms could be derived from the vertical profile of a convective cloud. In a well developed convective cloud, the top portion is usually glaciated (i.e., dominated by ice and snow pellets) due to deposition of convecting source vapor (water vapor condenses directly to ice at sub freezing temperatures). This partial condensation leaves the remaining moisture in its vapor and liquid phases isotopically enriched , which dominate the lower and warmer part of the cloud. Since precipitation results from the bottom of the convective cloud, the condensate can be expected to have higher isotopic values.

In exceptional cases of severe thunderstorms where there is a significant tilt in the updraft or when hail or snow approaches the ground, the condensate may not be enriched in heavy isotopes. Since the existing measurements of isotopic ratios from convective precipitation are entire storm samples, it is not yet possible to relate details of thunderstorm structure to changes of isotopic content of its precipitation. However, it is well documented that convective precipitation in general, is isotopically heavier than a stratiform or frontal precipitation (Federer et al., 1982; Gedzelman et al., 1987).

Due to the lack of any significant relationship between frontal precipitation events and their corresponding isotopic ratios, further meteorological analysis was concentrated on non frontal precipitation events. These non frontal precipitation events include thunderstorms, showers, precipitation from low level moisture sources and other precipitation events associated with convective clouds. The oxygen isotopic values for most of these events range from -1‰ to -4.3‰ with majority of the values falling between -2‰ and -3‰.This is encouraging since it not only supports the above discussion but also enables us to differentiate convective precipitation events based on the isotopic signatures. The implication of these results in understanding the interaction between troposphere and stratosphere are presented in Chapter III.

From the above discussion, it can be concluded that the Summer precipitation at Kalamazoo is mostly dominated by the precipitation resulting from the Gulf moisture source and other non Gulf sources only account for a very small fraction. The summer precipitation, for the most part, can be explained by a first order Rayleigh model. Most of the limitations of the model can be overcome, by precise flux measurements and modification of the box model such that all the areas influenced by the Gulf flux are accounted for. The fraction where correlation between the results of this model and the meteorological data are not significant, must be viewed as due to the difference in temporal scale and hence no individual precipitation event can be expected to simulate a Rayleigh type distillation. Each of the frontal precipitation events is independently governed by the atmospheric conditions during the time of its condensation, where as the Rayleigh model, applied on a seasonal scale, inherently masks all the complexities associated with precipitation. Thus, a Rayleigh model as described above could be used for understanding precipitation on a seasonal basis. However, as noted from the meteorological data, the range of isotopic values for summer precipitation at Kalamazoo predicted by this model, could also result from moisture sources other than the Gulf. In areas where a single moisture source predominates, as in the case of this study, this may not affect the model significantly. In areas where precipitation is influenced by multiple sources of moisture this model should be applied with utmost caution.

The *d*-excess Parameter

The *d*-excess or deuterium excess results from the fact that during evaporation process there is a preferential removal of HDO over $H_2{}^{18}O$ which results in measurable excess of deuterium in the vapor. The composition of moisture in the marine atmosphere is controlled by the air-sea interaction processes (Craig and Gordon, 1965) and the *d*-excess value is fixed by these processes. As described in Chapter II, the *d*-parameter was defined by Dansgaard (1964) as

$$d = \delta D - 8\delta^{18}O$$

The vapor flux from a marine source moves across the continent and loses moisture by successive condensations thus getting depleted in the heavy isotopes. This has no effect on the *d*-excess and the δD-$\delta^{18}O$ relation will maintain its initial *d*-excess value. When part of the rained-out moisture is returned to the atmosphere by means of evaporation, then the effect of the evaporation flux on the isotopic composition of the atmospheric moisture and precipitation depends on the details of the evapotranspiration process. Transpiration from dense vegetation and evaporation from open water bodies fractionates the isotopes of hydrogen and oxygen in a manner which depends on a number of environmental factors. The most important factor which influences the extent of fractionation due to evaporation is ambient humidity.

The evaporated vapor is usually depleted in the heavy isotopic species and is actually closer to the composition of atmospheric moisture. The most interesting difference is the high *d*-excess values of evaporated flux compared to atmospheric moisture. The admixture of the evaporated flux into the original moisture flux thus results in a larger *d*-excess value and hence, the precipitation from such an admixed flux reflects this higher *d*-excess. Because of this characteristic, it is possible to apply the "*d*-excess" value as a diagnostic tool for recognizing the admixture of evaporated moisture into the continental atmosphere (Gat and Matsui, 1991).

The isotopic composition of the evaporated moisture can be calculated using an equation given for evaporating water bodies(Craig and Gordon, 1965). This is given as

$$\delta_E = (\delta_W - h\delta_a - \epsilon)/(1-h)$$

where δ_E, δ_W and δ_a are the isotopic compositions of the evaporated moisture, surface water and the atmospheric moisture respectively. The relative humidity, h, is normalized to the saturated vapor pressure at the temperature of the surface water.

ϵ is defined as $\epsilon_{eq} + \epsilon_k$ where ϵ_{eq} is the equilibrium fractionation factor and ϵ_k, the diffusive (kinetic) isotope fractionation factor, both expressed in permil. According to the Craig-Gordon model ϵ_k has the form $\epsilon_k = (1-h)\,\Theta\, C_k$, where C_k is a model dependent kinetic constant and Θ a weighting factor: $\Theta = P_{mol}/P_{total}$, P_{mol} being part of the total resistance to vapor transport in the atmosphere above the liquid surface in which molecular diffusivities are expressed (Gat et al., 1994).

The summer precipitation at Kalamazoo is characterized by a *d*-excess of greater than 10. It is clear from the above discussion that this higher d-excess results from evaporation of large water bodies. Given its proximity to the study area, the most likely source is Lake Michigan. Also, if the d-excess of the evaporated flux is known, it should be possible to estimate the fraction of secondary evaporated moisture in the mixed vapor mass assuming that the primary vapor has a d-excess of ≤ 10. An effort is made based on the isotopic values in the precipitation on the west side of the Lake Michigan, isotopic values of precipitation at the study area and the Lake Michigan to estimate the contribution of Lake derived moisture to the summer precipitation. The details of this calculation are as follows.

The contribution of Lake Michigan evaporated flux to the atmospheric moisture was calculated using the above mentioned Craig-Gordon evaporation model. The values taken were: δ_W = -5.9‰ and -45‰ which are the measured values of Lake Michigan water; δ_a = -18.05‰ and -145‰ for $\delta^{18}O$ and δD respectively. The δ_a values were calculated using the mean lake surface temperatures and precipitation data at Milwaukee, WI. This is the only station for which isotopic values for precipitation could be obtained that is in the pathway of the vapor flux which moves towards the Great Lakes region. The stations which are further north are neglected. ϵ_{eq} is expressed in the form of $(1-\alpha)10^3$ and, by using the mean summer surface water temperatures of Lake Michigan, the value obtained was 10.22‰ for $\delta^{18}O$ and 90.96‰ for δD. ϵ_k values are calculated (assuming that $\Theta = 1$, $h = 0.80$ and C_k = 15‰($\delta^{18}O$); 13‰(δD)) to be 3 and 2 per mil. respectively for oxygen and hydrogen. Thus the δ_E values and the corresponding *d*-excess parameter values calculated for humidities of 0.80, 0.75 and 0.85 are as follows:

for h = 0.75 δD = -119‰ and $\delta^{18}O$ = -22.3, d-excess = 59.6‰

for h = 0.80 δD = -113‰ and $\delta^{18}O$ = -23.4, d-excess = 74.4‰

for h = 0.85 δD = -102‰ and $\delta^{18}O$ = -25.2, d-excess = 99.4‰

The mean d-excess in summer precipitation at Kalamazoo was calculated according to the relationship given above and by taking the mean δD and $\delta^{18}O$ values of the weighted precipitation events. The percent contribution of Lake Michigan evaporated moisture was calculated using a simple mass balance equation(Machavaram and Krishnamurthy, 1995) as follows:

$$L\% = [1-\{(d_K - d_E)/(d_X - d_E)\}]\ 100$$

where $L\%$ = The contribution of Lake Michigan derived moisture, d_K = the *d*-excess value for Kalamazoo precipitation, d_E = the *d*-excess values of evaporated Lake moisture and d_X = the *d*-excess value in Milwaukee precipitation. The d-excess value in Milwaukee precipitation was calculated [δD (-57‰) and $\delta^{18}O$ (-8.0‰)] to be 7‰. The results of this calculation were presented in Table 5.

Based on above calculations it was found that evaporated moisture from Lake Michigan has contributed 12%, 19% and 22% to the Summer precipitation for the years 1992, 93 and 94 respectively. This is consistent with the increasing mean Summer temperatures for these three years (Table 5), since evaporation rates are directly related to the ambient air temperatures. Since the mean Summer humidities observed in this study represent a value closer to 0.80, the Summer contribution from the lake evaporation can be suggested to be about 18 - 20%. The significantly lower contributions calculated for the summer of 1992 might be due to the smaller sampling period (Jun - Oct) as opposed to the sampling periods (Apr -Oct) of the later years.

Table 5

Contribution of Lake Michigan Evaporated Moisture to Summer Precipitation

Year	Temp(°C)	Humidity(%)	*d*-excess	Lake Contribution
		0.75		15%
1992	15.76	0.80	15‰	12%
		0.85		9%
		0.75		25%
1993	17.71	0.80	20‰	19%
		0.85		14%
		0.75		29%
1994	18.86	0.80	22‰	22%
		0.85		16%

It must be recalled that the mean Summer isotopic values in precipitation for the years 1992, 93 and 94 showed a depleting trend, which is contrary to what one would expect given the increasing mean summer temperatures. As is noted earlier, the evaporated moisture is highly depleted in its heavy isotope content. The increasing admixture of this evaporated moisture with the atmospheric moisture seems to shift the isotopic values towards more negative numbers, thus superceding the effect of temperature. The increasing trend in the slopes of δD - $\delta^{18}O$ relationships in summer precipitation during the study period also supports this argument.

It should be noted that the influence of lake evaporated moisture on the atmospheric water content described above, differs from the so called "lake effect precipitation" a frequent phenomenon that occurs during Winters in areas which lie in the vicinity of the Great Lakes. This is a process that is engendered mainly by aerodynamic effects rather than changes in the atmospheric water content. A more detailed discussion on this lake effect and its influence on winter precipitation is discussed in the following section.

Winter Precipitation

The mean Winter (November - March) isotopic values in precipitation for 1992 - 93, 1993 - 94 and 1994 - 95, are -105‰, -114‰ and -68‰ for δD and -15.9‰, -16.8‰ and -11.7‰ for $\delta^{18}O$ respectively. The mean Winter δD and $\delta^{18}O$ for the entire study period are found to be -98‰ and -15.1‰ respectively. The δD - $\delta^{18}O$ relationships for Winter precipitation are as follows:

$\delta D = 7.73\ \delta^{18}O + 18\ (r^2 = 0.96)$ for 1992 - 93,

$\delta D = 7.3\ \delta^{18}O + 9.1\ (r^2 = 0.96)$ for 1993 - 94,

$\delta D = 7.2\ \delta^{18}O + 16\ (r^2 = 0.96)$ for 1994 - 95 and

$\delta D = 7.7\ \delta^{18}O + 18.4\ (r^2 = 0.96)$ for 1992 - 94, (Figure 15).

The weighted mean isotopic ratios in winter precipitation show a general depletion compared to those of Summer precipitation as expected. The isotopic ratios in condensation are governed by fractionation factors which are temperature dependent. The temperature at which condensation takes place controls the fractionation i.e., the lower the temperature the higher the fractionation and lighter resultant isotopic ratios. Added to this, there exists a kinetic fractionation effect associated with vapor deposition leading to snow formation. These two factors explain the depletion of isotope values in the winter season.

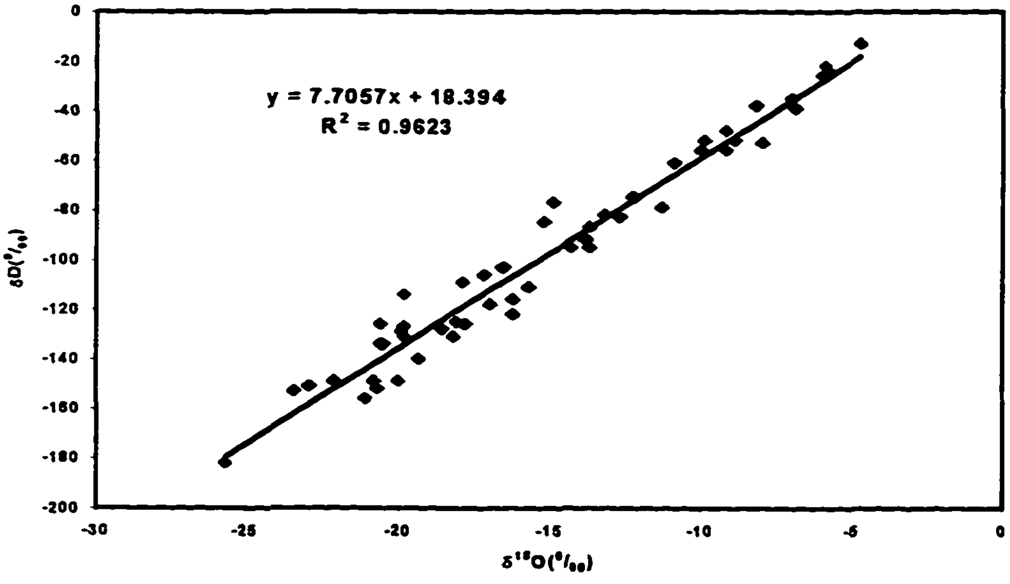

Figure 15. The δD and $\delta^{18}O$ Relationship in Winter Precipitation.

The recorded mean Winter temperatures are 0.62°C, -2.21°C and 1.03°C for 1992 - 93, 1993 - 94 and 1994 - 95 respectively. The congruent relationship observed between the mean seasonal temperatures and the mean isotopic values in winter precipitation seems to support the explanation offered above i.e., the lower the temperature the lower the resultant δ values.

The frequency distribution of oxygen isotope values in the Winter precipitation (Figure 16) is much varied than that of summer. As explained earlier, due to the southward shift of upper level jet stream which blocks Gulf moisture, the influence of Gulf moisture on the Winter precipitation is reduced. This shift of jet stream facilitates Pacific moisture and Polar - Continental air masses to play a greater role in the Winter precipitation. Unlike Summer, the condensation process in winter is more complicated due to complex in-cloud phenomena. At colder temperatures the moisture in the cloud exists in solid, liquid and vapor phases. The supersaturation of any one of these phases with respect to the other two in the cloud defines the resultant isotopic ratios in the condensate. Usually at colder temperatures, when both liquid water and ice co-exist in the cloud, the cloud is always supersaturated with ice which results in a non-equilibrium process between the liquid and the ice crystals. This is the so-called "Bergeron - Findesein process" which formulates (As stated in Mason, 1971) that "the vapor tension in the cloud will adjust to itself to a value in between the saturation values over ice and water. The effect of this must then be that condensation will take place continually until the liquid phase is entirely consumed." Thus in mixed clouds, i.e. clouds containing both liquid water and ice, the environment should always be over saturated with respect to solid phase. In such an environment, the liquid droplets tend to evaporate causing a two phase transition to the formation of ice. One is direct deposition of vapor onto the existing crystals by inverse sublimation and the other is freezing of super cooled liquid droplets (Ciais and Jouzel, 1994). This disequilibrium between vapor-liquid-ice transition leads to a kinetic fractionation effect, which varies over a range of temperatures (approximately between -15°C to -40°C).

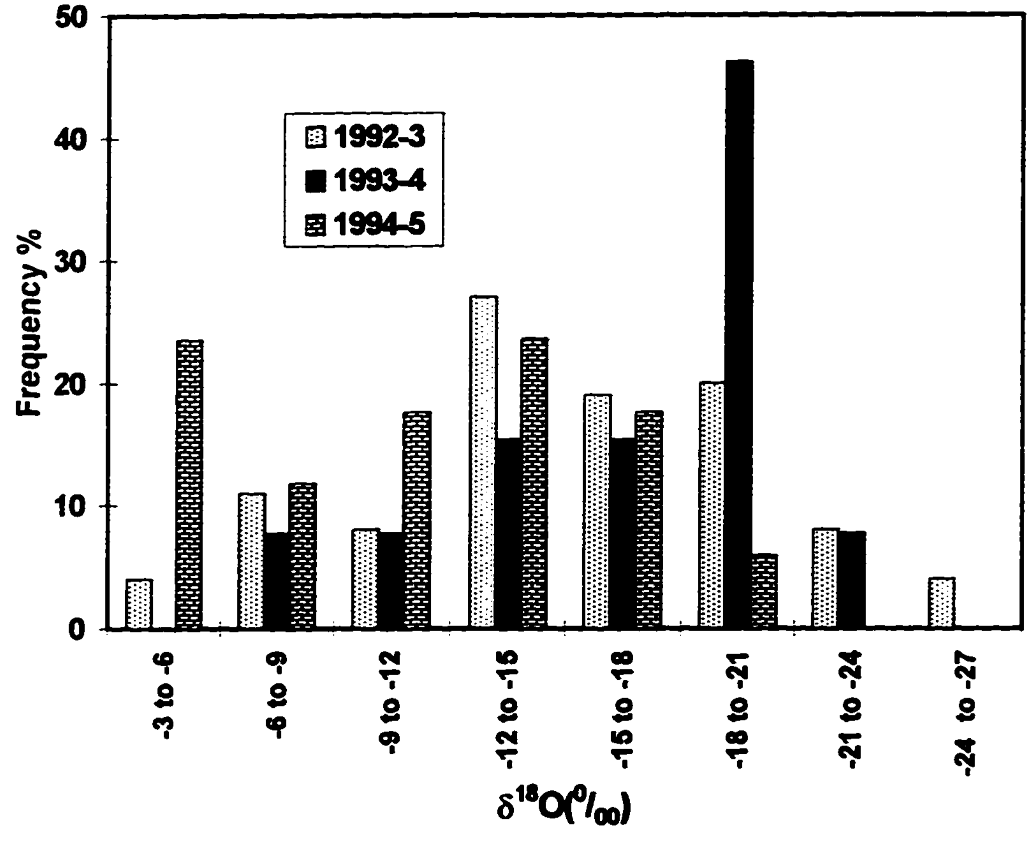

Figure 16. The Frequency Distribution of $\delta^{18}O$ in Winter Precipitation.

Thus the scatter of isotopic values in Winter precipitation can be attributed to multiple sources of moisture and kinetic fractionation associated with colder temperatures and mixed cloud formation. Due to the large isotopic variability of the atmospheric moisture and complexity of the in-cloud processes, a precise estimation of the influence of any single moisture source on the winter precipitation is not possible. For the same reason, a simple Rayleigh model cannot be applied to winter precipitation. However, when the isotopic ratios of atmospheric moisture from which condensation occurs can be measured with reasonable certainty, a model can be applied by including the kinetic fractionation factor. Lake effect precipitation, which is an important source of precipitation during Fall and Winter months in the Great lakes region offers such a possibility. A detailed discussion on the lake effect precipitation and the kinetic model is given below.

Lake Effect Precipitation

The Great Lakes which surround Michigan have a great impact on the climatology of this region. These water bodies strongly modify the climate of Michigan and give rise to what is called a "lake effect". The lakes warm more slowly than the land in spring season and cool more slowly in fall causing a strong thermal gradient. This is due to the fact that lakes require more solar energy than the land to warm as they transmit energy to greater depths. During Spring warming the cool and dense surface waters sink and are replaced by warmer waters from depth. During Winter seasons, when the surface waters cool they become more dense and sink, being replaced by warmer subsurface waters. Surface cooling is retarded and the immense heat storage of the lake keeps temperatures above those of the surrounding area during most of winter months. When cold and relatively dry air passes over the relatively warm waters of the lakes, as during Fall and Winter, the evaporated moisture of the lakes is adiabatically lifted and forms clouds which condense on the down wind side of the lakes. Thus, the evaporated moisture of the lakes become a dominant source to the Winter precipitation. In Michigan, the cold polar-Continental air mass which moves into Michigan from the west of the Lake Michigan generates lake effect precipitation on the east side of the lake. Since the lake effect precipitation completely comprises lake evaporated moisture, by calculating the isotopic ratios in the evaporated moisture and in the subsequent condensation, it might be possible to quantify the contribution of lake effect to the Winter precipitation.

Taking the nature of lake effect precipitation into consideration, a model is constructed in which the lake effect is assumed to be a one step evaporation - condensation process. In this model the condensation is assumed to occur from a cloud which is supersaturated with respect to ice and which contains negligible amount of liquid water. The isotopic ratios in the evaporated moisture were calculated using the isotope values of Lake Michigan water, and the mean lake surface temperature for the months of December, January and February (the months during which lake effect is dominant). The isotopic ratios in the condensate were calculated by taking both equilibrium and kinetic fractionation factors (Ciais and Jouzel, 1994, Gedzelman and Arnold, 1994), which were derived as follows.

The δD and $\delta^{18}O$ values for Lake Michigan water are -45‰ and -5.9‰ respectively. The fractionation factor for evaporation, α_W, was calculated using the mean lake surface temperature of 4.4°C and the equation derived by Majoube (1971), which was given earlier in this chapter. The δD and $\delta^{18}O$ values for the evaporated moisture of Lake Michigan, using a calculated α_W of 1.105216 for δD and 1.011258 for $\delta^{18}O$ were

-136‰ and -16.9‰ respectively. These values were assumed to represent the isotopic composition of the moisture in the cloud. Since this cloud is assumed to be super saturated with ice and condensation proceeds under disequilibrium conditions fractionation factors for condensation had to be calculated differently. The equilibrium fractionation factor for condensation of ice, α_I, was calculated for a temperature range of -10°C to -50°C, using the following equation given by Majoube(1971)as

$$\ln(\alpha_I) = (16288/T^2) - 0.0934 \text{ for } \delta D \text{ and}$$

$$\ln(\alpha_I) = (11.839/T) - 0.028224 \text{ for } \delta^{18}O$$

where T is the mean seasonal temperature expressed in degrees Kelvin. The kinetic fractionation factor, α_K, was determined for the same temperature range mentioned above, by the equation given below, which was derived by Jouzel and Merlivat (1984) for air in clouds supersaturated with ice over vapor.

$$\alpha_K = (\alpha_I S_I)/ \alpha_I (S_I - 1)\Psi + 1$$

where, S_I = saturation ratio with respect to ice and Ψ= the diffusion coefficient of light isotope over heavy isotope. The Ψ values used in the above equation are 1.0251 and 1.0289 for D and ^{18}O isotopes respectively (Jouzel and Merlivat, 1984). The values for S_I are chosen from 1.1 to 1.4 representing various levels of super saturation with respect to ice. The isotopic ratios in the condensate were then calculated by multiplying the δD and $\delta^{18}O$ values of the moisture in the cloud with α_{KI} which is a product of both equilibrium and kinetic fractionation factors. Table 6 summarizes the resultant isotopic values in the condensate for the range of temperatures and saturation indices mentioned above. It is evident from the results presented in Table 6 that, for a representative saturation ratio of 1.2, the lake effect precipitation should have a value of -135‰ and -17.1‰ for δD and $\delta^{18}O$ respectively. It should also be noted that the variation in isotopic values of the condensate is very minimal over the range of temperatures used in the calculation. This is understandable since most of the parameters were taken to be constant and the variation in the kinetic fractionation factor is relatively small. Thus the lake effect precipitation can be assumed to exhibit a very narrow and defined range in its isotopic signature.

The validity of this model was tested by comparing the δD and $\delta^{18}O$ values of meteorologically defined lake effect precipitation samples collected during the study period. The isotopic values for these samples range from -17.1‰ to -20.7‰ for $\delta^{18}O$ and from -106‰ to -152‰, with a mean isotopic value of -18.9‰ and -129‰ for $\delta^{18}O$ and δD respectively. The rather large variation exhibited by deuterium might be due to its higher diffusion coefficient compared to that of ^{18}O. The relatively minor difference in isotopic values obtained from the samples and the model are assumed to be the result of admixture of resident atmospheric vapor on the west side of the lake brought by the Polar - Continental airmass, with the lake derived moisture.

The mean *d*-excess values observed in the winter precipitation were 22‰, 20‰ and 26‰ for 1992 - 93, 1993 - 94 and 1994 - 95 winter seasons respectively. Since Lake Michigan is the only possible source for the secondary evaporated moisture, it is logical to assume that these d-excess values may reflect the percent contribution of Lake

Table 6

Calculated Equilibrium and Kinetic Fractionation Factors for Lake Effect precipitation. S_I = Saturation Ratio With Respect to Ice in the Cloud, α_E = Equilibrium Fractionation Factor, α_K = Kinetic Fractionation Factor. The δD and $\delta^{18}O$ Values Reported Are of Lake Effect Precipitation

Temp(^{0}C)	S_I	α_E	α_K	$\delta^{18}O$	α_E	α_K	δD
-10	1.5	1.016907	0.984803	-16.92	1.152361	0.943015	-134.9
	1.4		0.989429	-17.00		1.472514	-134.3
	1.3		0.992343	-17.05		1.354386	-134.4
	1.2		0.995809	-17.11		1.236257	-134.6
	1.1		0.984803	-16.92		1.118129	-134.7
-20	1.5	1.018715	0.986428	-16.98	1.174406	1.601942	-134.7
	1.4		0.989009	-17.03		1.481553	-134.3
	1.3		0.992038	-17.08		1.361165	-134.4
	1.2		0.995641	-17.14		1.240777	-134.5
	1.1		0.984202	-16.94		1.120388	-134.7
-30	1.5	1.020676	0.985867	-17.01	1.99732	1.614923	-134.1
	1.4		0.988554	-17.05		1.491938	-134.2
	1.3		0.991707	-17.10		1.368954	-134.4
	1.2		0.995459	-17.17		1.245969	-134.5
	1.1		0.983551	-16.97		1.122985	-134.6
-40	1.5	1.022810	0.985258	-17.03	1.229045	1.629947	-134.0
	1.4		0.988059	-17.08		1.503958	-134.1
	1.3		0.991347	-17.13		1.377968	-134.3
	1.2		0.995262	-17.20		1.251979	-134.5
	1.1		0.982843	-16.99		1.125989	-134.6
-50	1.5	1.025141	0.984593	-17.06	1.263259	1.647483	-133.9
	1.4		0.987519	-17.11		1.517987	-134.1
	1.3		0.990955	-17.17		1.388490	-134.2
	1.2		0.995046	-17.24		1.258993	-134.4
	1.1		0.982071	-17.01		1.129497	-134.6

Michigan moisture to the Winter precipitation. From results obtained from the above model and Figure 14, the contribution of Lake Michigan is found to be maximum in 1993 - 94 winter season followed by the 1992 - 93 and 1994 - 95 seasons. This argument is in agreement with meteorological data in which the number of lake effect precipitation events recorded followed the same order, with highest number of events in 1993 - 94 season followed by 1992 - 93 and 1994 - 95 seasons respectively. However this is in contradiction with the mean *d*-excess values for these three seasons in that these exhibit a negative correlation with the temperature as well as amount of lake effect precipitation, the reasons for which are not understood yet.

Though it appears that the above proposed model could satisfactorily explain the isotope systematics in the so-called 'lake effect' precipitation, there is a need for further research into this interesting phenomenon for a fuller understanding. In order to achieve this objective, systematic isotopic analysis of atmospheric moisture prior to lake effect precipitation events coupled with the analysis of lake evaporated moisture and the subsequent condensation will be necessary. When combined with other meteorological information such as temperature, humidity and the nature of the clouds, it is believed that the information obtained could elucidate the nature of atmospheric processes as explained above.

CHAPTER III

ANALYSIS OF RADIONUCLIDE DATA

Precipitation samples collected between January and December of 1994 were analyzed for the concentrations of ^{7}Be and ^{210}Pb. Details of sampling and analysis were presented in Chapter I. The bulk depositional flux data along with dates of collection, number of rainy days and corresponding stable isotope and meteorological information are tabulated in Appendix E. The concentrations of ^{7}Be and ^{210}Pb in precipitation, measured in dpm/L are presented in Figures 17 and 18 respectively.

As discussed in detail in Chapter I, ^{7}Be and ^{210}Pb have different sources of production. However, the mechanism by which these nuclides are removed from the atmosphere via precipitation is very similar. Hence, any linear relationship between the depositional fluxes of these nuclides, as shown in Figure 19 suggests that these nuclides can not be used as two independent atmospheric tracers for continental and oceanic air (Baskaran, 1993).

Another useful parameter to study atmospheric processes is the activity ratio of these two nuclides. The activity ratio, defined as the ratio of ^{7}Be concentration over that of the ^{210}Pb is useful to predict the elevation at which cloud condensation took place. For example, condensation that takes place in the lower troposphere is characterized by low activity ratios, due to higher concentrations of ^{210}Pb over ^{7}Be. On the other hand,

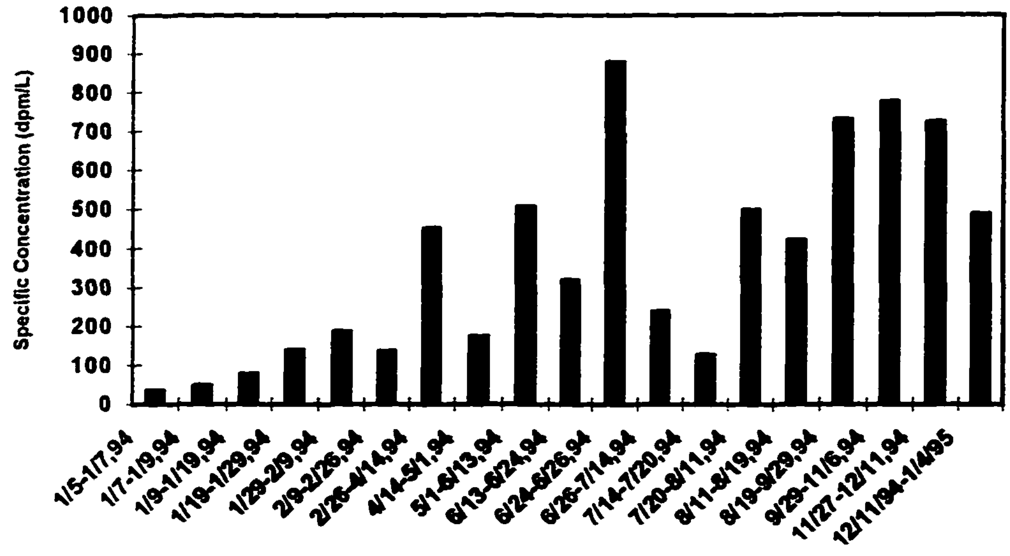

Figure 17. Specific Concentrations of ^{7}Be in Precipitation Samples.

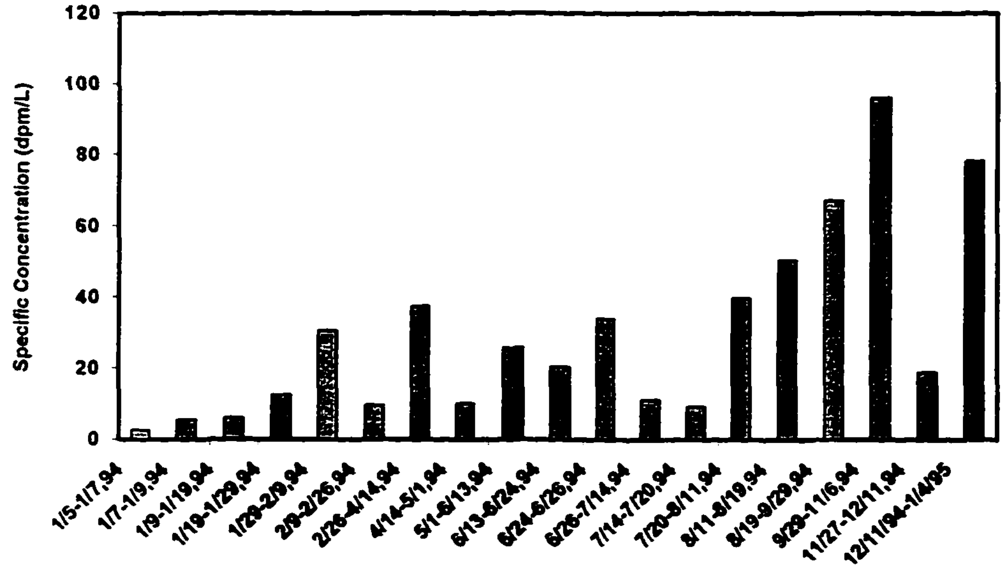

Figure 18. Specific Concentrations of ^{210}Pb in Precipitation Samples.

condensation at higher altitudes results in high activity ratio. The activity ratio parameter is also very useful in studying the physical behavior of some of the chemical species injected into atmosphere. The activity ratios and $\delta^{18}O$ values, along with the concentrations of ^{7}Be and ^{210}Pb are presented in Figure 20.

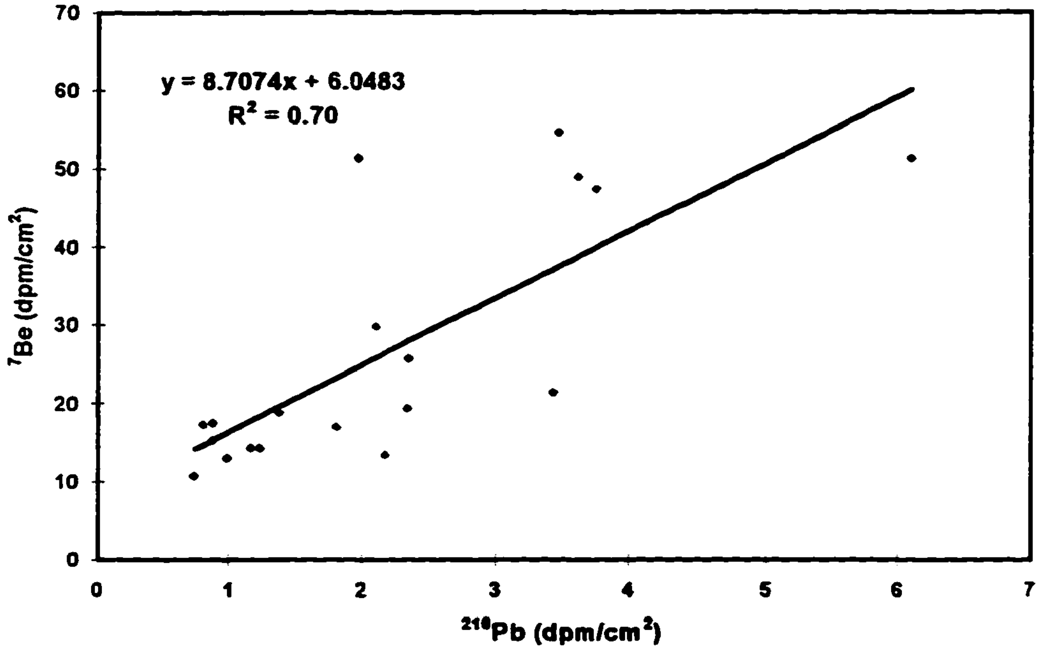

Figure 19. The ^{7}Be - ^{210}Pb Relationship in Precipitation.

There is no significant correlation between the amount of precipitation and the specific concentrations of ^{7}Be and ^{210}Pb, in individual samples. However, other studies have indicated a significant correlation between the amount of precipitation and ^{7}Be specific concentrations (Turekian et al., 1983; Olsen et al., 1985). It has been suggested that the concentration of ^{7}Be in precipitation may be higher during drier months and periods characterized by short-duration precipitation events (Canuel et al., 1990). Since smaller size cloud droplets are likely to have higher concentrations of radionuclides due to their higher affinity for aerosols, growth of these droplets by coalescence tend to keep

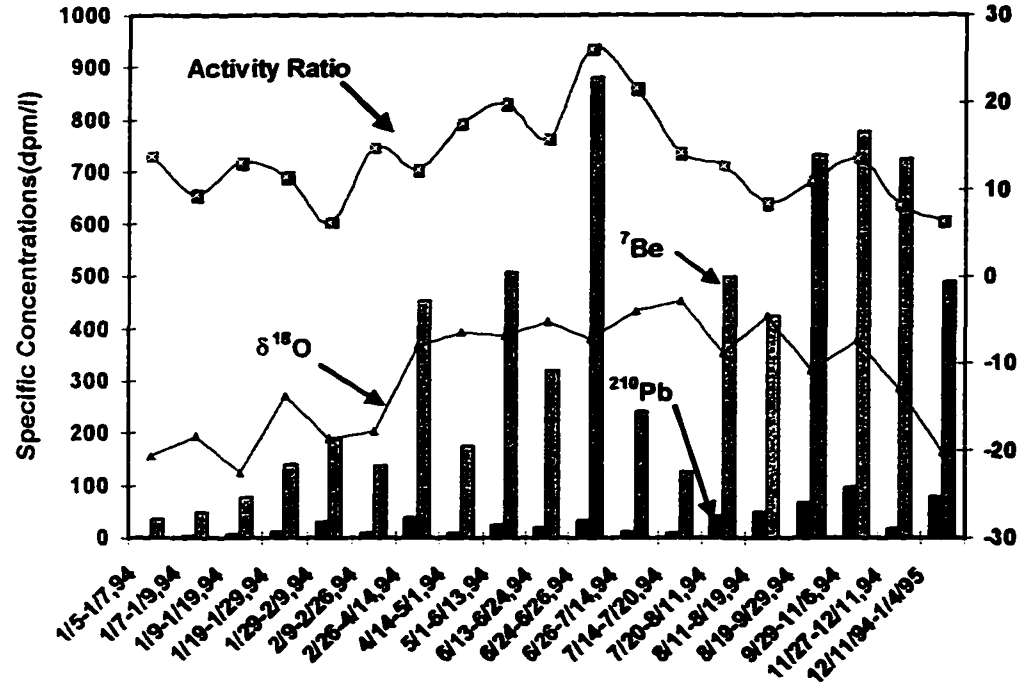

Figure 20. Plot Showing ^{7}Be, ^{210}Pb, δ^{18}O and Activity Ratios in Precipitation.

the concentrations constantly higher. On the other hand, the concentration of ^{7}Be is expected to decrease with increasing volumes of precipitation due to dilution (Wogman et al., 1968). The poor correlation ($R^2 = 0.44$, $P < 0.05$) observed between the amount of precipitation and the specific concentration of ^{7}Be and between the amount of precipitation and ^{210}Pb ($R^2 = 0.5$, $P < 0.05$) at Kalamazoo seem to indicate that ^{7}Be and

^{210}Pb concentrations are not mainly controlled by the amount of precipitation. Poor correlations were also reported by Brown et al., (1989) and Todd et al., (1989) who suggested that dilution was not the only process that controls ^{7}Be concentrations in precipitation. Owing to the nature of its production no correlation could be expected since the concentrations of ^{210}Pb in precipitation are controlled by various meteorological parameters such as, altitude of clouds, pathways, intensity of fronts etc. The weak correlation observed in Kalamazoo precipitation is in agreement with similar studies from other sites (Olsen et al., 1985; Todd et al., 1989; Hussain et al., 1990; Baskaran et al., 1993).

It is evident from Figure 20 that during Spring, Summer and early Fall months the samples are characterized by high activity ratios. The high activity ratios can result either from the enrichment of ^{7}Be concentration or by depletion of ^{210}Pb concentration. In order to explain the high activity ratios observed during spring and summer seasons a method is proposed by considering the mean concentrations of both ^{7}Be and ^{210}Pb. According to this proposed method, variation in the activity ratios are explained by taking the deviation of ^{7}Be and ^{210}Pb concentrations from the mean concentration. If a given sample exhibits higher than the mean concentration of either ^{7}Be or ^{210}Pb then the activity ratios are considered to be affected by the elevated concentration of one radionuclide over the other. Thus, high activity ratios can be explained as due to either increase in ^{7}Be concentration or decrease in ^{210}Pb concentrations.

Table 7

Specific Concentrations(dpm/L), Activity Ratios and Mean Deviation Values of ^{7}Be and ^{210}Pb in Precipitation Samples. The Mean Concentration Values Are 29.65 and 367.7 for ^{7}Be and ^{210}Pb Respectively.

Period	^{210}Pb	^{7}Be	Activity ratio	^{210}Pb Deviation	^{7}Be Deviation
1/5-1/7,94	2.65	36.4	13.7	-27	-331.3
1/7-1/9,94	5.35	50.6	9.4	-24.3	-317.1
1/9-1/19,94	6.05	79.1	13.08	-23.6	-288.6
1/19-1/29,94	12.3	140.9	11.5	-17.35	-226.8
1/29-2/9,94	30.6	189	6.15	0.95	-178.7
2/9-2/26,94	9.39	137.8	14.7	-20.26	-229.9
2/26-4/14,94	37.3	453.1	12.2	7.65	85.4
4/14-5/1,94	10	175.2	17.6	-19.65	-192.5
5/1-6/13,94	25.7	507.2	19.9	-3.95	139.5
6/13-6/24,94	20.4	321	15.8	-9.25	-46.7
6/24-6/26,94	33.8	880.1	26.1	4.15	512.4
6/26-7/14,94	11.1	240.9	21.6	-18.55	-126.8
7/14-7/20,94	9.04	127.5	14.1	-20.61	-240.2
7/20-8/11,94	39.6	500	12.6	9.95	132.3
8/11-8/19,94	50.3	423.4	8.41	20.65	55.7
8/19-9/29,94	67.1	731.8	10.9	37.45	364.1
9/29-11/6,94	96	777.5	13.5	66.35	409.8
11/27-12/11,94	18.7	725.4	8.26	-10.95	357.7
12/11-1/4,95	78.1	489.4	6.26	48.45	121.7

The mean concentrations of ^{7}Be and ^{210}Pb are 367.7dpm/L and 29.65dpm/L respectively and the deviation of ^{7}Be and ^{210}Pb from the mean are presented in Table 7 and in Figures 21 and 22. Based on the data presented in these Figures and Table 7, it can be shown that high activity ratios observed during Spring and Summer months are due to elevated ^{7}Be concentrations. Since vertical mixing of lower and upper troposphere results in increasing the concentrations of both ^{210}Pb and ^{7}Be, the increased concentrations of only ^{7}Be observed in Spring and Summer samples could not be attributed to vertical mixing. Additionally, the samples which showed higher than the mean concentrations are not convective precipitation events based on the meteorological data. It should be recalled that convective precipitation results from vertical mixing of lower and upper troposphere. The δ^{18}O values of these samples range from -7.3‰ to -8.9‰ which are typical of frontal precipitation. It should be noted that the samples are characterized by δ^{18}O values of -4‰ and -2.9‰, which are typical of convective precipitation, did not show any higher than the mean concentrations. The nature of these events was meteorologically shown to be thunderstorms. Thus, the increase in ^{7}Be concentration during spring and summer months could be regarded as due to the interaction of tropospheric and stratospheric air masses.

On the other hand, the low activity ratios observed in Fall season are primarily due to increase in both ^{210}Pb and ^{7}Be concentrations. It is not clear whether the elevated concentrations of both ^{210}Pb and ^{7}Be are due to vertical mixing of lower and upper troposphere. However, based on meteorological and stable isotope data it appears that vertical mixing might not be the causal factor for the increased concentrations. Though some of the samples collected during the fall season are affected by meteorologically proven thunderstorms and snowstorms, their effect on the overall concentrations of individual samples is not significant. This observation is based on the δ^{18}O values of these samples which are in the range of -8‰. It can be seen from Table 7 that when compared with the mean concentration, the relative increase in ^{210}Pb concentrations is significantly

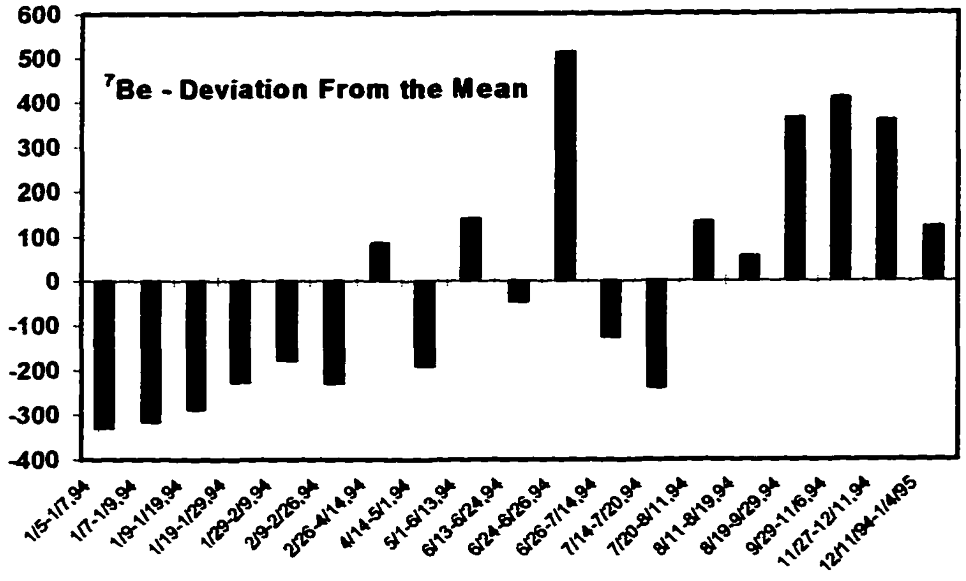

Figure 21. Deviation of ^{7}Be Concentrations From the Mean Annual Concentration.

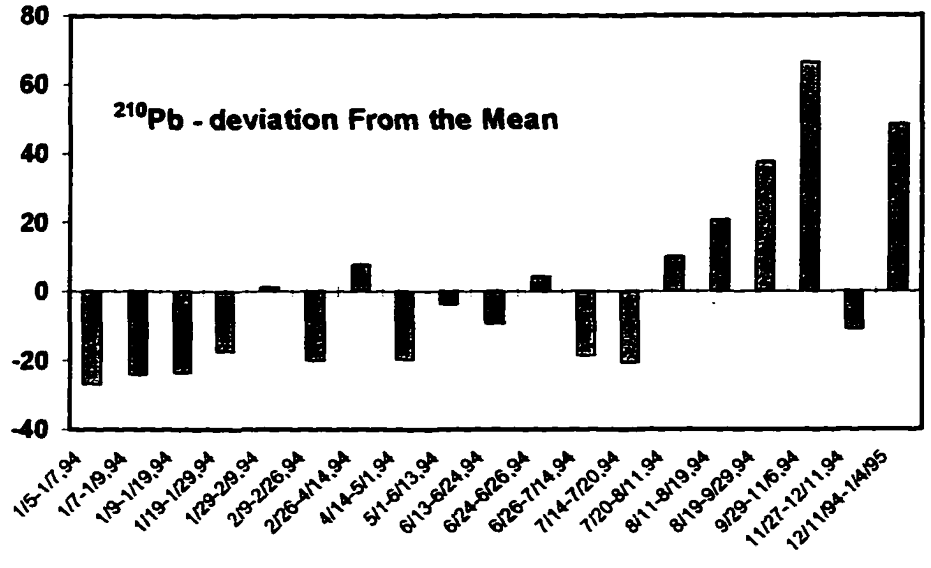

Figure 22. Deviation of ^{210}Pb Concentrations From the Mean Annual Concentration.

more compared to that of ^{7}Be concentrations. This could not be the result of spatial scavenging since the dominant air masses that bring precipitation in this area during Fall and Winter traverse for the most part on frozen earth surface which inhibits the escape of radon gas into the atmosphere. Thus, it is believed that the elevated concentrations of ^{210}Pb and ^{7}Be in the Fall and Winter precipitation samples are affected by the nature of precipitation. An in-depth meteorological analysis of individual samples is required to verify this assumption.

Another possibility could be the influence of aerosol concentrations during Fall season which scavenge the standing crop of ^{210}Pb and ^{7}Be more efficiently. Since the aerosols are frozen in the upper troposphere during winter months it might be a possibility that scavenging of ^{210}Pb and ^{7}Be occurs at comparatively low altitudes compared to Summer months. This in turn, would explain the relatively higher concentrations of ^{210}Pb observed during Fall and Winter months. However, due to the lack of necessary data the elevated concentrations of both ^{210}Pb and ^{7}Be during Fall season could not be verified.

It might be concluded from the above discussion that higher ^{7}Be concentrations during Spring and Summer seasons are primarily due to the interaction between troposphere and stratosphere. The higher ^{7}be and ^{210}Pb concentrations during Fall season could be dependent on the distribution of aerosols. It is not clear whether increased concentrations of both ^{7}Be and ^{210}Pb during Fall season are due to the nature of precipitation. Further analysis of meteorology associated with precipitation samples collected during Fall season will aid in better understanding the reasons behind the elevated concentrations of both ^{210}Pb and ^{7}Be. There exists a need for further sampling and analysis of precipitation samples spanning few years in order to understand he seasonal behavior of ^{7}Be and ^{210}Pb in precipitation. As the results of this study indicate the variation in ^{7}Be and ^{210}Pb concentrations in precipitation can be better understood when interpreted using meteorological and stable isotopic data.

CHAPTER IV

CONCLUSIONS

As the first study of its kind dealing with analysis of stable isotopes and radionuclides in precipitation, the main objective of this study is to understand the complex atmospheric processes that govern the distribution of these isotopes in precipitation. The salient features emerged from this study are:

1. The mean annual, summer and winter isotopic values in precipitation at Kalamazoo, for the study period are: Annual δD = -66‰ and $\delta^{18}O$ = -10.8‰; for summer, δD = -37‰ and $\delta^{18}O$ = -6.9‰, and for winter δD = -98‰ and $\delta^{18}O$ = -15.1‰.

2. The δD - $\delta^{18}O$ relationship in precipitation at Kalamazoo is comparable to that of Meteoric Water Line.

3. The monthly mean isotopic values in precipitation reflect strong seasonal contrast between summer and winter months. Variation in the magnitude of this contrast is a direct consequence of varying mean seasonal temperatures.

4. The summer precipitation at Kalamazoo is derived predominantly from the vapor flux originating in the Gulf of Mexico. A box model calculation showed that a Rayleigh type distillation with Gulf moisture as the source would explain bulk of the observed isotopic ratios in summer precipitation. Additional constraints such as Gulf vapor divergence, Atlantic moisture and Convective precipitation appear to account for

the rest of the isotope data.

5. The summer and winter precipitation at Kalamazoo is characterized by a higher *d*-excess than that defined by Meteoric Water Line. This is interpreted as due to the admixture of evaporated moisture from Lake Michigan to the atmospheric vapor flux. Calculations show that Lake Michigan contributes 12% - 23% of moisture to the summer precipitation. Over the three year period of study it is seen that the percent contribution of Lake Michigan evaporated moisture is positively correlated with mean summer temperatures.

6. The winter precipitation at Kalamazoo is characterized by multiple moisture sources including a prominent 'lake effect' component, which exhibit a distinct isotopic signature. The results of a kinetic fractionation model applied to understand this interesting phenomenon is in agreement with the meteorological data.

7. The concentrations of ^{7}Be and ^{210}Pb in precipitation are linearly correlated, which indicates that these nuclides should be used in conjunction to study atmospheric processes.

8. Precipitation during summer months was characterized by higher ^{7}Be concentrations compared to ^{210}Pb concentrations. Based on meteorological and stable isotope data, it was found that higher ^{7}Be concentrations in precipitation result from stratospheric influence. The concentrations of ^{210}Pb are controlled by the nature and intensity of precipitation.

9. The Fall and Winter precipitation samples are characterized by comparatively higher ^{210}Pb concentrations than ^{7}Be concentrations. It is believed either due to the

influence of aerosol concentrations or the nature of the precipitation. Further study is required to explain the behavior of ^{210}Pb and ^{7}Be nuclides in the atmosphere during Fall and Winter seasons.

Though this study was able to explain most of the complex atmospheric processes that effect the distribution of stable isotopes in precipitation, more future study is required in order to quantify these processes precisely. Future efforts should include precipitation analysis on west side of the Great Lakes and isotopic analysis of atmospheric moisture on a temporal scale. A better understanding of kinetic fractionation processes associated with snow formation and phase changes of vapor flux within the clouds would greatly improve the interpretation of the isotopic data in precipitation.

A systematic analysis of radionuclides in precipitation, as shown by this study, should be undertaken for few years. The information obtained can be used to understand the relationship of the radionuclides with varying amounts of precipitation, seasonal variability and variation in the atmospheric concentrations. This in turn, helps in addressing questions related to the behavior of these nuclides in atmosphere, which is of paramount importance in studies related to environmental and atmospheric sciences.

Appendix A

Weighted Isotopic Data of Precipitation Events

EVENT	δ D	$\delta^{18}O$	Temp^{0}C	Amnt(mm)
6/14/92	-22	-4.7	13.3	2.5
7/8/92	5	-1	18.3	2.5
7/13/92	-17	-4	19.4	7.5
7/14/92	-41	-7	20	26.25
7/23/92	-60	-9.1	12.8	20
7/25/92	-23	-4.6	15.6	2.5
7/28/92	-47	-7.2	15.6	2.5
7/30/92	-64	-10.1	14.4	54
8/1/92	-76	-11	20	2.5
8/8/92	-29	-4.1	17.2	15
8/27/92	-50	-8.4	15	18.7
9/2/92	-9	-3.3	18.9	2.5
9/6/92	-11	-3.4	20.5	30
9/8/92	-33	-5.8	16.1	11.25
9/9/92	-29	-5.4	16.1	45
9/15/92	-8	-2.2	15.6	2.5
9/18/92	-21	-4.2	16.1	27.5
9/26/92	-44	-7.9	12.8	6.25
10/14/92	-11	-4	13.3	23.75
10/16/92	-29	-5.7	13.3	7.5
10/20/92	-95	-14.5	5.6	6.25
11/1/92	-61	-10.9	5.6	33.75
11/13/92	-125	-18	-1.1	8.75
11/21/92	-53	-8	6.6	5
11/22/92	-75	-12.3	3.3	13.75
11/25/92	-91	-13.9	4.4	3.75
11/26/92	-82	-13.2	-1.1	3.75
11/30/92	-126	-17.7	-1.1	1.25
12/2/92	-151	-22.9	-1.1	5
12/4/92	-87	-13.7	-1.7	2.5
12/5/92	-106	-17.1	-6.7	2.5
12/9/92	-131	-19.8	-3.3	13.75
12/15/92	-52	-8.9	1.1	5
12/19/92	-95	-14.3	-1.1	5

EVENT	δ D	δ^{18}O	Temp^{0}C	Amnt(mm)
12/23/92	-127	-19.8	-5.5	6.25
12/29/92	-38	-8.2	-3.6	2.5
1/2/93	-13	-4.7	-3.3	2.5
1/4/93	-79	-11.3	5.5	8.75
1/7/93	-149	-20.8	-5.5	1.25
1/10/93	-182	-25.7	-6.7	8.75
1/12/93	-85	-15.2	-2.2	10
1/21/93	-91	-13.9	0	10
1/27/93	-118	-16.9	-4.4	2.5
2/12/93	-128	-18.5	-3.3	5
2/16/93	-149	-22.1	-8.8	11.25
2/23/93	-114	-19.8	-7.8	2.5
3/10/93	-156	-21.1	-0.6	25
3/16/93	-149	-20	0.0	20
3/19/93	-122	-16.2	-1.7	17.5
4/14/93	-38	-6.6	8.9	7.5
4/19/93	-12	-6.4	10.0	7.25
4/29/93	-3	-4.1	14.8	27.5
5/2/93	-30	-6.8	16.7	20
6/7/93	-20	-4.7	17.8	12.5
6/14/93	-48	-8.3	18.9	40
6/19/93	-11	-4.6	18.9	47.5
6/25/93	-33	-5.9	18.3	25
6/28/93	-39	-6.2	16.7	17.5
7/24/93	-13	-4	20.0	32.5
8/4/93	-115	-16.1	22.2	5
8/13/93	-2	-1.7	22.2	5
8/27/93	-18	-4.3	24.4	42.5
8/29/93	-7	-4.2	17.8	37.5
9/14/93	-82	-12.2	14.4	2.5
9/25/93	-76	-12.3	10.0	45
10/16/93	-54	-9	15.6	35
10/20/93	-80	-12.1	11.1	22.5
11/26/93	-56	-10	0.0	27.5

EVENT	δ D	δ^{18}O	Temp^{0}C	Amnt(mm)
12/4/93	-83	-12.7	-1.6	5
12/18/93	-131	-18.1	-12.2	27
12/29/93	-129	-19.9	-11.1	10
1/5/94	-152	-20.7	-13.3	32.5
1/8/94	-134	-20.6	-17.8	10
1/10/94	-153	-23.4		20
1/17/94	-134	-20.5		7.5
1/27/94	-95	-13.7		32.5
2/8/94	-140	-19.3	-15.6	7.5
2/22/94	-116	-16.2	-8.9	10
3/20/94	-39	-6.9	4.4	7.5
3/26/94	-118	-16.9	0.0	12.5
4/11/94	-48	-8.2	6.1	55
4/26/94	-32	-6.5	9.4	12.5
6/13/94	-35	-6.9	18.9	85
6/23/94	-31	-6.3	26.7	2.5
6/24/94	-21	-7.3	26.7	2.5
7/5/94	0	-5.3	20.0	52.5
7/14/94	-36	-6.8	21.1	45
7/20/94	-6	-2.9	24.4	35
8/4/94	-76	-11.7	20.0	30
8/10/94	-23	-5.8	17.8	85
8/19/94	-18	-4.8	18.9	82.5
8/30/94	-15	-5.1	15.6	7.5
9/25/94	-45	-9.1	17.8	12.5
9/27/94	-88	-13.5	10.6	45
9/30/94	-60	-10.4	9.4	7.5
10/1/94	-43	-8	13.3	2.5
10/4/94	-54	-8	6.7	2.5
10/8/94	-56	-9.5	12.2	40
10/18/94	-25	-5.8	15.0	30
10/23/94	-73	-10.9	6.1	12.5
10/31/94	-54	-9.8	2.8	80
11/3/94	-35	-7	12.8	52.5

EVENT	δ D	$\delta^{18}O$	Temp°C	Amnt(mm)
11/8/94	-52	-9.9	5.6	2.5
11/14/94	-22	-5.9	14.4	2.5
11/21/94	-26	-6	10.6	15
11/27/94	-48	-9.2	3.9	45
12/5/94	-111	-15.7	2.8	26.25
12/9/94	-92	-13.8	0.0	7.5
12/11/94	-109	-17.8	-2.2	1.25
1/1/95	-126	-20.6	-4.4	17.5
1/13/95	-24	-5.8	4.4	20
1/19/95	-75	-12.2	2.2	16.25
1/22/95	-103	-16.5	-2.2	12.5
2/5/95	-77	-14.9	-10.0	2.5
3/27/95	-56	-9.2	1.1	8.75

Appendix B

Meteorological Data Associated With Precipitation Events

Meteorology Associated with Precipitation Events at Kalamazoo, MI. June 1992 - March 1995

EVENT	δD	$\delta^{18}O$	Meteorology of Precipitation Event
6/14/92	-22	-4.7	Along non convective frontal boundary. Atlantic moisture, precipitating all the way from the Atlantic source
7/8/92	5	-1	Pre warm frontal boundary/possibly convective. Low pressure system bring pacific moisture,
			precipitation in plain states.
7/13/92	-17	-4	Stationary frontal boundary showers and T.storms.boundary stationary on SWMichigan. Gulf moisture.
7/14/92	-41	-7	Same as 7/13/92. Precipitation continues from Gulf moisture.
7/23/92	-60	-9.1	Stationary front/ showers. Gulf moisture. Precip only on stalled front, Not all the way from Gulf.
7/25/92	-23	-4.6	Same stationary front of 7/23/92.Moves closer to Mich producing showers, Gulf source, continuous precip.
7/28/92	-47	-7.2	Pacific low moves through/showers. Pacific moisture precipitates along its path to michigan.
7/30/92	-64	-10.1	Stationary frontal boundary to south of Mich precip on north front, focused on boundary.Gulf moisture
8/1/92	-76	-11	Airmass Tstorms, no fronts. Afternoon convection.Weak south wind/probably Gulf moisture.
8/8/92	-29	-4.1	Low pressure system moves in with rain pulling up gulf moisture on advancing side.
8/27/92	-50	-8.4	Frontal boundarybecomes stationary causing significant rainGulf moisture/remnants of Andrew
9/2/92	-9	-3.3	Warm frontal boundary. Gulf moisture falls out over Michigan.
9/6/92	-11	-3.4	Low associated with cold front. Pacific low interacting with Gulf moisture.
9/8/92	-33	-5.8	Same storm system as 9/6/92.
9/9/92	-29	-5.4	Pacific low and warm frontal boundary, scattered showers. Mostly Gulf moisture, local showers in Michigan
9/15/92	-8	-2.2	Cold front from Canada. Combination of midlevel pacific and low level gulf moistures.
9/18/92	-21	-4.2	Cold front with pacific low.local precip, mostly mid level pacific with some low level gulf moisture
9/26/92	-44	-7.9	Upper level disturbance with steady rain in SWMich. Mid level Gulf moisture.Precip area extends from Gulf.
10/14/92	-11	-4	Low pressure system brings showers. Gulf moisture.
10/16/92	-29	-5.7	Same system as 10/14/92. Some possible lake moisture.
10/20/92	-95	-14.5	Approaching warm fron w/rain-snow showers. Gulf moisture, with lake enhancement.
11/1/92	-61	-10.9	Large low moves with rain showers. Primarily Atlantic moisture.
11/13/92	-125	-18	Large low moves with rain showers. Gulf moisture with some continental/pacific moisture.
11/21/92	-53	-8	Low moves through with showers. Gulf moisture.
11/22/92	-75	-12.3	Second low pushes thorugh with rain. Gulf moisture/ Lake Mich influence.
11/25/92	-91	-13.9	Low moves into area with more rain showers/ Gulf moisture. Some Lake enhancement?
11/26/92	-82	-13.2	Same system/moisture source as 11/25/92.
11/30/92	-126	-17.7	Cold front with snow showers. Pacific/continental airmass.
12/2/92	-151	-22.9	Low drops through area with snow showers. Pacific/continental and interacting with gulf moisture.

Meteorology Associated with Precipitation Events at Kalamazoo, MI. June 1992 - March 1995

EVENT	δD	$\delta^{18}O$	Meteorology of Precipitation Event
12/4/92	-87	-13.7	Low pushes through with steady steady snow. Gulf moisture. Some lake enhancement.
12/5/92	-106	-17.1	**Lake Efftect snow event**
12/9/92	-131	-19.8	Large low pushes into area with large snow area. Gulf moisture.
12/15/92	-52	-8.9	Frontal boundary pushes through with steady rain. Gulf moisture.
12/19/92	-95	-14.3	Cold front passes through with snow showers. Gulf/Lake moisture.
12/23/92	-127	-19.8	**Lake effect snow event**
12/29/92	-38	-8.2	Large low moves in with rain. Gulf moisture.
1/2/93	-13	-4.7	NO DATA
1/4/93	-79	-11.3	Frontal boundary pushes through with rain showers. Gulf moisture.
1/7/93	-149	-20.8	Cold front with scattered snow showers. **Lake moisture**
1/10/93	-182	-25.7	Large low moves through with steady snow. Gulf/Atlantic moisture.
1/12/93	-85	-15.2	Low with snow showers moves through area. Atlantic moisture.
1/21/93	-91	-13.9	Low with rains moves through. Gulf moisture.
1/27/93	-118	-16.9	Low with snow showers moves through area. Pacific/continental moisture. Some lake enhancement.
2/12/93	-128	-18.5	Large low moves south of area. Birngs steady snow. Atlantic moisture.
2/16/93	-149	-22.1	The same low moves through area with snow. Atlantic moisture.
2/23/93	-114	-19.8	Upper level disturbance brings snow showers. Mostly Lake michigan/some Atlantic.
3/10/93	-156	-21.1	Low moves through with steady snow. Gulf moisture.
3/16/93	-149	-20	Cold front with rain showers moves thorugh area. Gulf moisture.
3/19/93	-122	-16.2	Cold front with snow showers pushes through area. Gulf moisture.
4/14/93	-38	-6.6	Large low moves through with steady rain. Gulf moisture.
4/19/93	-12	-6.4	Low moves through with scattered showers. Gulf moisture.
4/29/93	-3	-4.1	Low moves through with scattered showers. Gulf moisture.
5/2/93	-30	-6.8	Warm front pushes through with rain/scattered showers. Gulf moisture.
6/7/93	-20	-4.7	Stationary frontal boundary sparks showers/Tstorms. Gulf moisture/may be some lake moisture.
6/14/93	-48	-8.3	Coldfront moves through with Tstorms. Gulf moisture.
6/19/93	-11	-4.6	Warmfront pushes through with Tstorms. Gulf moisture.
6/25/93	-33	-5.9	Cold front pushes through with scattered showers/Tstorms. Gulf moisture
6/28/93	-39	-6.2	Cold front with showers moves through. Mostly Gulf/may be some pacific/continental moisture.
7/24/93	-13	-4	Warm front moves through with scattered showers and Tstorms. Gulf moisture

Meteorology Associated with Precipitation Events at Kalamazoo, MI. June 1992 - March 1995

EVENT	δD	$\delta^{18}O$	Meteorology of Precipitation Event
8/4/93	-115	-16.1	Coldfront passes with scattered showers. Lake moisture/Gulf moisture.
8/13/93	-2	-1.7	Stationary front sparks scattered showers and Tstorms. Atlantic moisture.
8/27/93	-18	-4.3	Afternoon Thunderstorms. Gulf moisture.
8/29/93	-7	-4.2	Stationary front with showers and Tstorms. Gulf moisture/may be some Lake Mich.
9/14/93	-82	-12.2	Coldfront pushes through with rain and Tstorms. Gulf moisture.
9/25/93	-76	-12.3	Low moves through with rains and Tstroms. Gulf moisture/may be some Lake influence.
10/16/93	-54	-9	Cold front pushes through with scattered showers. Gulf moisture/some lake influence.
10/20/93	-80	-12.1	Stationary front with rains/scattered showers. Gulf moisture.
11/26/93	-56	-10	Low moves through with rain. Gulf moisture.
12/4/93	-83	-12.7	Low moves through with showers. Mostly Gulf moisture/ some lake influence.
12/18/93	-131	-18.1	Low moves through with showers. Gulf/Lake Mich. Moistures.
12/29/93	-129	-19.9	Front passes with scattered snow showers. Gulf/lake Mich. Moisture.
1/5/94	-152	-20.7	**Lake effect snow event**
1/8/94	-134	-20.6	Secondary trough associated with low of atlantic coast. Steady snow event. Gulf/Atlantic. some lake enhans.
1/10/94	-153	-23.4	Cold front passage brings snow showers. Combo of Gulf and lake moistures.
1/17/94	-134	-20.5	Low pessure from plain states moves into area with steady snow.Gulf moisture with Lake enhancement.
1/27/94	-95	-13.7	Large low and associated warm front brings snow showers. Combo of Gulf/atlantic. Precip from gulf to mich.
2/8/94	-140	-19.3	Stationary frontal boundary south of state. Light snow showers. Mostly Gulf with some lake moisture.
2/22/94	-116	-16.2	Large low pressure system brings steady snow to area. Combo of Gulf/Atlantic.
3/20/94	-39	-6.9	Two lows moves thorugh area bringing rain showers. Gulf moisture for both the systems
3/26/94	-118	-16.9	Low pressure system moves htrough with light rain/snow. Gulf moisture.
4/11/94	-48	-8.2	Low pressure from plain states with rain howers. Gulf moisture.
4/26/94	-32	-6.5	Low pressure from mid section brings showers. Gulf moisture.
6/13/94	-35	-6.9	Stationary frontal boundary sparks showers/Tstorms. Gulf moisture. Local precipitation.
6/23/94	-31	-6.3	Low pressure moves through with rain. Gulf moisture out ahead of low.
6/24/94	-21	-7.3	same as 6/23/94.
7/5/94	0	-5.3	Weak frontal boundary sparks convection/Tstorms.
7/14/94	-36	-6.8	Stationary frontal boundary sparks local Tstorms. Primarily Gulf moisture.
7/20/94	-6	-2.9	Coldfront brings local showers and Tstorms. Gulf moisture.
8/4/94	-76	-11.7	Cold front focuses rain/showers over michigan. Combo of Gulf/pacific. May be some lake moisture.

Meteorology Associated with Precipitation Events at Kalamazoo, MI. June 1992 - March 1995

EVENT	δD	$\delta^{18}O$	Meteorology of Precipitation Event
8/10/94	-23	-5.8	Low pressure system brings showers. Moisture appeared to be from pacific.
8/19/94	-18	-4.8	Cold front with local scattered showers. Gulf moisture.
8/30/94	-15	-5.1	Weak low moves through with scattered showers. Mostly Gulf moisture.
9/25/94	-45	-9.1	Low moves through with local rain showers. Gulf and Atlantic moistures.
9/27/94	-88	-13.5	Same airmass system as 9/25/97.
9/30/94	-60	-10.4	Wrap around moisture from departing low pressure system. Atlantic moisture.
10/1/94	-43	-8	Stationary frontal boundary brings showers. Gulf moisture.
10/4/94	-54	-8	Upper level disturbance brings scattered showers. Mostly Lake Michigan moisture.
10/8/94	-56	-9.5	Cold front with rain and showers. Gulf moisture.
10/18/94	-25	-5.8	Large low with warm front brings rain. Gulf moisture.
10/23/94	-73	-10.9	Cold front with rain and showers. Gulf/Atlantic moisture.
10/31/94	-54	-9.8	Stationary frontal boundary with light rain. Gulf moisture.
11/3/94	-35	-7	Cold front passage with rain showers, Gulf moisture.
11/8/94	-52	-9.9	Stationary frontal boundary with steady rain event. Gulf moisture.
11/14/94	-22	-5.9	Coldfront passasge with local scattered showers. Gulf moisture.
11/21/94	-26	-6	Cold front passage with with steady rain extending from Gulf source to Michigan.
11/27/94	-48	-9.2	Low pressure system with rain showers changing to snow. Gulf/Atlantic moisture with some lake enhans.
12/3/94	-57	-8.6	Warm front moves through with scattered showers. Gulf moisture
12/5/94	-111	-15.7	Low moves through area with rain changing to snow. Atlantic moisture giving way to lake effect.
12/9/94	-92	-13.8	Scattered snow showers with low pressure systems. Gulf/lake enhancement.
12/11/94	-109	-17.8	Low pressure moves through with light snow. Gulf/some lake enhansement.
1/1/95	-126	-20.6	NO DATA
1/13/95	-24	-5.8	Stationary front with scattered rain showers in the area. Gulf moisture.
1/19/95	-75	-12.2	Large low moves through area with scattered rain showers. Gulf moisture.
1/22/95	-103	-16.5	Same as 1/19/95
2/5/95	-77	-14.9	**Lake effect snow event**
2/26/95	-51	-5.8	Stationary front with scattered snow showers. Atlantic moisture.
3/5/95	-110	-15	Low moves through area with steady rain/snow. Gulf/some lake moisture.
3/27/95	-56	-9.2	Low moves into area with showers. Gulf/Atlantic moisture.

Appendix C

Weighted Mean Monthly Isotopic Data of Precipitation Events

Weighted Monthly Mean δD and $\delta^{18}O$ in Precipitation

Month	δD	δO^{18}	Temp^{0}C
Jun-92	-22	-4.7	
Jul-92	-40	-6.1	20.42
Aug-92	-48	-7.8	19.01
Sep-92	-24	-3.9	16.32
Oct-92	-42	-6.6	9.75
Nov-92	-74	-14	3.72
Dec-92	-94	-14.7	-0.75
Jan-93	-105	-14	-2.80
Feb-93	-125	-19.9	-4.16
Mar-93	-144	-19.4	0.89
Apr-93	-11	-4.9	6.97
May-93	-30	-6.8	15.86
Jun-93	-30	-6.1	19.38
Jul-93	-13	-4	23.25
Aug-93	-18	-4.8	21.85
Sep-93	-79	-12.2	14.76
Oct-93	-64	-10.2	9.33
Nov-93	-56	-10	3.61
Dec-93	-125	-17.9	-1.59
Jan-94	-121	-18.2	-8.94
Feb-94	-126	-17.5	-6.13
Mar-94	-88	-13.2	2.00
Apr-94	-45	-7.9	9.99
May-94	No Rain Event		14.10
Jun-94	-29	-6.8	21.59
Jul-94	-14	-5.2	22.71
Aug-94	-28	-6.2	19.89
Sep-94	-76	-12.3	18.15
Oct-94	-50	-9	11.97
Nov-94	-38	-7.7	6.37
Dec-94	-86	-12.6	1.44
Jan-95	-78	-13.3	-2.66
Feb-95	-55	-7.3	-3.96
Mar-95	-99	-13.8	3.94
Apr-95	-61	-7.8	6.88
May-95	-58	-8.9	14.82
Jun-95	-36	-5.5	22.14

Appendix D

Precipitation and Temperature Data of the Stations Used in the Rayleigh Distillation Model

Mean seasonal Precipitation Amounts and Temperatures for the Stations Used in Rayleigh Box Model

Grid No.	Station	1992 (Jun - Oct)		1993 (Jun -Oct)		1994 (Jun - Oct)	
		Precip. Amnt(mm)	Temp0F	Precip. Amnt(mm)	Temp0F	Precip. Amnt(mm)	Temp0F
Box 1	Mobile	639.25	77.14	540.25	75.36	638.25	77.02
	Batonrouge	730.75	76.56	650.75	77.98	743.25	76.66
	Houston	432.5	79.38	442	78.78	724.75	79.5
Box 2	Jackson	592.5	73.5	471.5	75.72	749	76.7
	Montgomery	596.5	75.38	496.75	77.02	605	74.1
	Alexandria	615.5	76.56	458.75	77.24	633.5	77.22
Box 3	Birmingham	701.5	73.12	329.75	75.3	681.75	74.14
	Greensville	546.5	75	387.5	74.6	646.75	75.98
	Shreveport	495	75.36	534.25	70.74	533.75	76.62
Box 4	Chattanooga	599.25	73.06	427	74.34	535	74.44
	Little Rock	465.5	68.2	468.75	73.3	538.25	74.16
	Clarksdale	560	72.7	392.25	71.8	576.25	69.22
Box 5	Jonesboro	505	71.1	432.75	70.82	437.75	73.58
	Jackson	568.5	72.46	443.75	70.76	551.5	70.8
	Nashville	584.75	69.5	420	72.4	489.75	72.3
Box 6	Paducah	612.25	69.08	621.75	69.92	386.75	71.2
	Bowling Green	524.75	68.18	466.75	68.18	404.25	70.22
	Fayatteville	479.25	70.16	504	69.94	387.5	71.66
Box 7	St. Louis	524.75	68.18	706.75	68.92	317.25	69.98
	Louisville	432.5	68.1	524.75	68.18	404.25	70.22
	Evansville	350.5	67.82	558	69.94	354	69.88
Box 8	Columbus	524.75	68.18	879.75	68.92	317.25	69.98
	Indinapolis	577.5	64.42	594	66.16	359.25	66.98
	Columbia	523	64.3	466.5	66.74	379.25	66.44
Box 9	Peoria	595.75	62.22	454.25	64.7	424	64.82
	Fort Wayne	520.75	62.72	807.25	66.52	328.25	66.02
	Akron	507.25	65.46	528.5	64.8	338.75	67.9
Box 10	Detroit	408.75	63.1	627.25	64.98	404.25	66.34
	Kalamazoo	491	62.04	429.25	64.34	402.75	65.24
	Chicago	479.75	61.36	644.75	63.54	509.75	65

Appendix E

Details of Precipitation Samples Collected for Radionuclide Analysis

Collection period	Amnt (Lit)	Rainy Days	^{210}Pb	^{7}Be	^{7}Be/^{210}Pb	δO^{18}	Remarks
1/5-1/7,1994	8	1	2.65	36.4	13.7	-20.6	surface scoop added(~20%)
1/7-1/9,1994	6.2	1	5.35	50.6	9.4	-18.3	surface scoop added(~20%)
1/9-1/19,1994	13.2	5	6.05	79.1	13.08	-22.6	surface scoope added(~25%)
1/19-1/29,1994	6.5	1	12.3	140.9	11.5	-13.8	Mixture of snow and Freezing rain
1/29-2/9,1994	6	2	30.6	189	6.15	-18.6	Collection of many rain events
2/9-2/26,1994	8.5	4	9.39	137.8	14.7	-17.8	Various rain events
2/26-4/14,1994	9.5	5	37.3	453.1	12.2	-8	contirbuted mostly by rain of 11-13 of April94
4/14-5/1,1994	9.5	7	10	175.2	17.6	-6.5	mostly contributed by the rain of 4/31/94
5/1-6/13,1994	9.5	1	25.7	507.2	19.9	-6.9	Single rain event on 6/13/94, 3am-9am
6/13-6/24,1994	12	1	20.4	321	15.8	-5.2	heavy rain on 6/23/94. Sample has to be sepa
							rated in to A & B
6/24-6/26,1994	7.5	1	33.8	880.1	26.1	-7.3	Single rain event on 6/26/94
6/26-7/14,1994	8.3	3	11.1	240.9	21.6	-4	Mostly contributed from T-storm on 7/14/94
7/14-7/20,1994	9	1	9.04	127.5	14.1	-2.9	Single T-storm on 7/20/94
7/20-8/11,1994	14	2	39.6	500	12.6	-8.9	contributed by rain on 8/4 and 8/11-12, 1994
8/11-8/19,1994	14	2	50.3	423.4	8.41	-4.6	contributed by rain on 8/13 and 8/19, 1994
8/19-9/29,1994	9.25	5	67.1	731.8	10.9	-10.7	Rain events from 9/24-9/28, 1994
9/29-11/6,1994	10	1	96	777.5	13.5	-7.4	Collected by Kevin, numerous showers and
							t-storm on 11/4/94. sample separated A&B
11/27-12/11,1994	11.25	11	18.7	725.4	8.26	-13	Kevin collected. No details at all!
12/11/94-1/4/95	7.75	4	78.1	489.4	6.26	-20.3	lake effect snow(~15% scoop added)

BIBLIOGRAPHY

Baertschi, P. "Absolute ^{18}O content of standard Mean Ocean Water", Earth Planet.Sci.Lett.,V.31, p.341, 1976.

Balkanski, Y. L., Jacob, D. J., Gardner, G. M., Graustein, W. C. and Turekian, K. K. "Transport and residence times of tropospheric aerosols inferred from a global three dimensional simulation of ^{210}Pb", Jour. Geophys. Res., V. 98, p. 20573 - 20586, 1993.

Baskaran, M. "A search for seasonal variability on the depositional fluxes of ^{7}Be and ^{210}Pb", Jour. Geophys. Res., V. 100, no. D2, p. 2833 - 2840, 1995.

Baskaran, M. and Coleman, C. H. and Santchi, P. H. "Atmospheric depositional fluxes of ^{7}Be and ^{210}Pb at Galveston and College Station, Texas", Jour. Geophys. Res., V. 98, no. D11, p. 20555 - 20571, 1993.

Beninger, L. K., Aller, C. K., Cochran, J. K. and Turekian, K. K. "Effects of biological sediment mixing on the ^{210}Pb chronology and trace metal distribution in a Long island Sound sediment core", Earth. Planet. Sci. Lett., V. 43, p. 241 - 259, 1979.

Bigeleisen, J., Periman, M.L. and Prosser, H.O. "Conversion of hydrogenic materials to hydrogen for isotopic analysis", Anal. Chem., V.24, p.1356, 1952.

Blattner, P. "Oxygen from liquids for isotopic analysis, and a new determination of $\alpha_{CO2-H2O}$ at 250°C", Geochim. Cosmochim. Acta, V.37, p.2691, 1973.

Blattner, P. and Hulston, J. R. "Proportional variations of geochemical ^{18}O scales. An inter-laboratory comparison", Geochim. Cosmochim. Acta, V.42, p.59, 1978.

Bottinga, Y. and Craig, H. "Oxygen isotope fractionation between CO_2 and water and the isotopic composition of marine atmosphere", Earth. Planet. Sci. Lett., V.5, p.285, 1969.

Brown, L., Stensland, G. J., Klein, J. and Middleton, R. "Atmospheric deposition of ^{7}Be and ^{10}Be", Geochim. Cosmochim. Acta, V. 53, p. 135 - 142, 1989.

Canuel, E. A., Martens, C. S., Beninger, L. K. "Seasonal variations in the ^{7}Be activity in the sediments of Cape Lookout Bight, North carolina, Geochim. Cosmochim. Acta, V. 54, p. 237 - 245, 1990.

Ciais, P. and Jouzel, J. "Deuterium and oxygen 18 in precipitation: isotopic model, including mixed cloud processes", Jour. Geophys. Res., V. 99, no. D8, p. 16793 - 16803, 1994.

Coleman, M.L., Shepherd, T., Durham, J. J., Rouse, J. E. and Moore, R .G. "Reduction of water with zinc for hydrogen isotopic analysis", Anal. Chem., V.54, p.993, 1982.

Coplen, B. T. and Kendall, C. "Preparation and stable isotope determination of NBS-16 and NBS-17 carbon dioxide reference gas", Anal. Chem., V.54, p.2611, 1982.

Coplen, B.T., Kendall, C. and Hopple, J. "Comparison of stable isotopic reference sample", Nature, V.302, p.5905, 1983.

Craig, H. "Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of Carbon dioxide", Geochim. Cosmochim. Acta, V.12, p.133, 1957.

Craig, H. "Standard for reporting concentrations of deuterium and oxygen-18 in natural waters", Science, V.133, p.1833, 1961a.

Craig, H. "Isotopic variations in meteoric waters", Science, V.133, p.1702, 1961b.

Craig, H. and Gordon, C.I. "Deuterium and oxygen-18 variations in the ocean and the marine atmosphere", Stable isotopes in oceanographic studies and paleotemperatures, Ed. Tongiorgi, E., p.9, 1965.

Dansgaard, W. "Stable isotopes in precipitation", Tellus, V.16, p.436, 1964.

Dansgaard, W. "Oxygen-18 analysis of water", Medd. Gronland, V.177, p.33, 1969.

De Wit, J. C., Vanderstraten, C.M. and Mook, W.G. "Determination of the absolute isotopic ratio of V-SMOW and SLAP", Geost. Newslett., V.4, p.33, 1980.

Dincer, T., Martinee, J., Payne B. R. and Yen, C. K., Isotope hydrology, IAEA, Vienna, p.23, 1970.

Ehhalt, D., Knott, K., Nagel, J. F. and Vogel, J. C. Deuterium and oxygen-18 in rainwater", Jour. Geophys. Res., V.68, no.13, p.3775, 1963.

Epstein, S. and Krishnamurthy, R.V. "Environmental information in the isotopic record of trees", Phil. Trans. R. Soc. Lond., V.A330, p.427, 1990.

Epstein, S. and Mayeda, T. "Variation of oxygen-18 content of waters from natural sources", Geochim. Cosmochim. Acta, V.4, p.213, 1953.

Epstein, S., Sharp, R. and Gow, A. J. "Six year record of oxygen and hydrogen isotope variations in the south pole firn', Jour. Geophys. Res., V 70, p. 1809 - 1814, 1965.

Federer, B., Brichet, N. and Jouzel, J. "Stable isotopes in hailstones, 1, the isotopic cloud model, Jour. Atmos. Sci., V. 39(6), p. 1323 - 1336, 1982.

Feely, H. W., Larsen, R. J. and Sanderson, C. G. "Factors that cause seasonal variations in beryllium-7 concentrations in the surface air", Jour. Environ. Radioact., V. 9, p. 223 - 249, 1989.

Feely, H. W., Toonkel, L. and Larsen, R. J. " Radionuclides and trace elements in surface air" Environ. Rep., EML-395, Appendix - C, U. S. Dept. Of energy, new York, 1981.

Friedman, I. "Deuterium content of natural waters and other substances", Geochim. Cosmochim. Acta, V.4, p.89 - 103, 1953.

Friedman, I and Smith, J. "Deuterium content of snow cores from Sierra Nevada area", Science, V.169, p.469, 1970.

Fritz, P., Drimmie, R. J., Frappe, S. K. and O'Shea, K. "The isotopic composition of precipitation in groundwater in Canada", in Isotope techniques in water resources development, IAEA, p.539, 1987.

Fritz, P. and Fontes, J. Ch. "Handbook of environmental geochemistry, Vol-1. The terrestrial environment", Elsevier, Amsterdam, 1980.

Gat, J. R. "Comments on the stable isotope method in regional ground water investigations", Water. Res. Res., V.7, p.980, 1971.

Gat, J. R. "The isotopes of hydrogen and oxygen", in Handbook of environmental isotope geochemistry, (Eds) Fritz, P. and Fontes, J. Ch., Elsevier, Amsterdam, 1980.

Gat, J. R., Bowser, C. J. and Kendall, C. "The contribution of evaporation from the Great Lakes of North America to the continental atmospheric moisture: detection by means of stable isotopic signature of the evaporated waters", Geophys. Res. Lett, V. 21, p. 557 - 560, 1994.

Gat, J. R. and Craig, H. Characteristics of the air-sea interface determined from isotope transport studies", Trans. Am. Geophys. Union, V.47, p.115, 1966.

Gat, J. R. and Matsui, E. "Atmospheric water balance in Amazon basin: an isotopic evapo-transpiration model", Jour. Geophy. Res., V.96, p.13179, 1991.

Gedzelman, S. D. and Arnold, A. " Modeling the isotopic composition of precipitation", Jour. Geophys. Res., V. 99, no. D5, p. 10455 - 10471, 1994.

Gedzelman, S. D., Lawrence, J. R., White, J. W. C. and Smiley, D. "The isotopic composition of precipitation at Mohonk Lake, New York: the amount effect", Jour. Geophys. Res., V. 92, p. 1033 - 1040, 1987.

Gonfiantini, R. "Standards for stable isotope measurements in natural compounds", Nature, V.271, no.5645, p.534, 1978.

Haegman, R., Hief, G. and Roth, E. "Absolute isotopic scale for deuterium analysis of natural waters. absolute D/H ratio for SMOW", Tellus, V.22, p.712, 1970.

Hoefs, J. "Stable Isotope Geochemistry", Springer-Verlag, 1973.

Horibe, Y. and Kobayabawa, M. "Deuterium abundance of natural waters", Geochim. Cosmochim. Acta, V.20, p.273, 1960.

Hussain, N., Church, T., Anderson, R. and Biscaye, P. " Radon daughters (^{210}Pb and ^{210}Po): Atmospheric fallout and oceanic removal in coastal waters of the mid-Atlantic", Eos trans., abstract, AGU, V. 71(17), p. 537, 1990.

IAEA. " Statistical treatment of environmental isotope data in precipitation", Technical reports series no.206, IAEA, Vienna, 1981.

Jouzel, J. and Merlivat, L. " Deuterium and oxygen-18 in precipitation: Modeling of the isotopic effects during snow formation", Jour. Geophys. Res, V. 89, p. 11749 - 11757, 1984.

Krabbenhoft, D., Bowser, C.J., Anderson, M.P. and Valley, J. "Estimating groundwater exchange with lakes: I: The stable isotope mass-balance method", Water. Res. Res., V.26, p.2445, 1990.

Krishnamurthy, R.V. "Stable isotope studies on sedimentary deposits and ground waters and their climatic implications' Ph.D. thesis, Physical Research Laboratory, India, 1984.

Krishnamurthy, R.V. and Bhattacharya, S.K. "Stable oxygen and Hydrogen isotope ratios in shallow ground waters from India and a study of the role of the evapotranspiration in the Indian monsoon", in Stable Isotope Geochemistry: A tribute to Samuel Epstein, The Geochemical society spl. Publ., no.3, (Eds) Taylor, H.P., O'Neil, J. R. and Kaplan, R., p.187, 1991.

Krishnamurthy, R.V. and Epstein, S. "Tree ring D/H ratio from Kenya, East Africa and its paleoclimatic significance", Nature, V.317, no.6033, p.160, 1985.

Kritz, M. A., Rosner, S. W., Danielson, E. F. and Selkirk, H. B. "Airmass origins and troposphere to stratosphere exchange associated with mid-latitude cyclogenesis and tropopause folding inferred from ^{7}Be measurements", Jour. Geophys. Res., V. 96, p. 17405 - 17414, 1991.

Lal, D., Malhotra, P. K. and Peters, B. "on the production of radioisotopes in the atmosphere by cosmic radiation and their application to meteorology", Jour. Atmos. Terr. Phys., V. 12, p. 306 - 328, 1958.

Lal, D. and Peters, B. "Cosmic ray produced activity on earth" in Handbuch der Physic, V. 46(2), p. 551 - 612, Springer Verlag, New York, 1967.

LeGuy, C., Rindsberger, M., Zangwil, A., Issar, A. and Gat, J. R. "The relation between the 18O and deuterium contents of rain water in the Negev desert and airmass trajectories', Isot. Geosci., V. 1, p. 205 - 218, 1983.

Machavaram, M. "Precipitation dynamics at Kalamazoo, SW Michigan: A stable isotope perspective" M. S. Thesis, Western Michigan University, Kalamazoo, MI, 1993.

Machavaram, M. and Krishnamurthy, R. V. "Survey of factors controlling the stable isotope ratios in precipitation in the Great Lakes region, USA", Isr. J. Earth. Sci, V. 43, p. 195-202, 1994.

Machavaram, M. and Krishnamurthy, R. V. "Earth surface evaporative process: Acase study from the great Lakes region of the United States based on deuterium excess in precipitation", Geochim. Cosmochim. Acta, V. 59, no. 20, p. 4279 - 4283, 1995.

Majoube, M. "Fractionnment en oxygene-18 et en deutirium entre l'ean et sa vapeur", Jour. Chim. Phys., V.68, p.1423, 1971.

Mason, B. J. "The physics of clouds", 2nd edition, Clarendon, Oxford, 1971.

McDonell, J. J., Bonell, M., Stewart, M. K. and Pearce, A. J. "Deuterium variations in storm rainfall: implications for stream hydrograph separation", Water. Res. Res, V.26, p.455, 1990.

Merlivat, L. and Coantic, M. "Study of mass transfer at air-water interface by an isotopic method", Jour. Geophys. Res., V.80, p.3445, 1975.

Merlivat, L. and Joujel, J. "Global climatic interpretation of deutirium-oxygen relationship for precipitation", Jour. Geophys. Res., V.84, p.5029, 1979.

Mook, W.G. and Grootes, P.M. "The measuring procedure and corrections for the high precision mass-spectrometric analysis of isotope abundance ratios, especially referring to carbon, oxygen and nitrogen", Int. Jour. Mass spec. Ion. Phys., V.12, p.273, 1973.

Moore, H. E., Poet, S. E. and martell, E. A. "^{222}Rn, ^{210}Pb, ^{210}Bi and ^{210}Po profiles and aerosol residence times versus altitude", Jour. Geophys. Res., V. 78, p. 7065 - 7075, 1973.

Moser, H. and Stichler, W. "Environmental isotopes in ice and snow", in Handbook of environmental isotope geochemistry, (Eds) Fritz, P. and Fontes, J. Ch., Elsevier, New York, p.148, 1980.

NOAA, "Climates of the states II", Department of Commerce, NOAA, Washington D.C., 1974.

Olsen, C. R., Larsen, I. L., Lowry, P. D., Cutshall, N. H., Todd, G. F., Wong, G. T. F. and case, W. H. "Atmospheric fluxes and and marsh soil inventories of ^{7}Be and ^{210}Pb", Jour. Geophys. Res., V. 90, p. 10487 - 10495, 1985.

O'Neil, J. R., Adami, L.H. and Epstein, S. "Revised value for the ^{18}O fractionation between CO_2 and H_2O at 25°C", Jour. Res. U. S. Geol. Surv., V.3, p.623, 1975.

O'Neil, J. R. and Epstein, S. "A method for oxygen isotope analysis of milligram quantities of water and some of its applications", Jour. Geophys. Res., V.71, p.4955, 1966.

Perkins, R. W., Thomas, C. W. and Young, J. A. "Application of short-lived cosmogenic radionuclides as tracers of in-cloud scavenging processes", Jour. Geophys. Res., V. 75, p. 3076 - 3086, 1970.

Pionke, H. B. and Dewalle, D. R. "Intra and inter storm ^{18}O trends for selected rain storms in Pennsylvania", Jour. Hydrol., V.138, p.131, 1992.

Rasmusson, E.M. "Atmospheric water vapor transport and the water balance of North

America, Part I", Mon. Weather. Rev., V.96, p.720, 1967.

Rozanski, K. and Sonntag, C. "Vertical distribution of deuterium in atmospheric water vapors", Tellus, V.34. p.142, 1982.

Rozanski, K., Sonntag, C. and Munnich, K. O. "Factors controlling stable isotope composition of European precipitation", Tellus, V.34, p.142, 1982.

Stahl, W. and Dounas, A.H. in Isotope techniques in groundwater hydrology, IAEA, V.1, p.317, 1974.

Stewart, M. K. "Stable isotope fractionation due to evaporation and isotopic exchange of falling water drops, applications to atmospheric processes and evaporation of lakes", Jour. Geophy. Res., V.80, p.1133, 1975.

Taylor, C.B. "Measurement of oxygen-18 ratios in environmental waters using the Epstien - Mayeda technique. Part I, Theory and details of the equilibration technique", Contribution no.556 of the Inst. Nucl. Sci., D. S. I. R., New Zealand, 1973.

Todd, J. F., Wong, G. T. F., Olsen, C. R. and larsen, I. L. "Atmospheric depositional characteristics of beryllium 7 and lead 210 along southeastern Virginia coast", Jour. Geophys. Res., V. 94, p. 11106 - 11116, 1989.

Turekian, K. K., Beninger, L. K. and Dion, E. P. "^{7}Be and ^{210}Pb total depositional fluxes at new Haven, Connecticut and Bermuda", Jour. Geophys. Res., V. 88, p. 5411 - 5415, 1983.

VG Isotech "Reference manual for Optima software", Fisons Instruments, England, 1992.

Wilkening, M. H., Clemens, H. E. and Stanley, D. " Radon-222 flux in widely separated regions" in Natural radiation environment II, ed. Adams, J. A. S., U. S. energy Research and development Administration, p. 717 - 730, Oak Ridge, Tenn., 1975.

Wilson, J. W. and Pollock, D. M. "Precipitation over the great lakes", IFYGL-The International Field Year for the Great Lakes, (Eds) Aubert, T. J. and Richard, T.L., NOAA, Ann Arbor, p.51, 1981.

Wogman, N. A., Thomas, C. W., Cooper, J. A. and Engelmann, R. J. "Cosmic ray produced radionuclides as tracers of atmospheric precipitation processes", Science, V. 159, p. 189 - 192, 1968.

Yurtsever, Y. "Worldwide survey of stable isotopes in precipitation", Internal. Rep., IAEA, Vienna, 1975.

Young, J. A. and Silver, W. B. "The determination of air - sea exchange and oceanic mixing rates using ^{7}Be during the BOMEX experiment", Jour. Geophys. Res., V. 79, p. 4481 - 4489, 1974.

Young, J. A. and Silver, W. B. " Aerosol depositional velocities on Pacific and Atlantic oceans calculated from ^{7}Be measurements", Earth. Planet. Sci. Lett., V. 50, p. 92 - 104, 1980.

Young, J. A., Wogman, N. A., Thomas, C.W. and Perkins, R. W. "Short lived cosmic ray produced radionuclides as tracers of atmospheric processes" in radionuclides in the Environment, Adv. Chem. Series, V. 93, ed., Frieling, E. C., p. 506 - 521, American Chemical Society, Washington D. C., 1970.

Yurtsever, Y. and Gat, J. R. "Atmospheric waters", in Stable Isotope Hydrology, deuterium and oxygen in the water cycle, Technical report no.210, IAEA, Vienna, p.103, 1981.