ASSESSMENT OF THE SEASONAL FLUCTUATIONS IN RELATIVE ISOTOPIC ABUNDANCES OF OXYGEN-18 AND DEUTERIUM IN RAIN WATER FROM THE TUCSON BASIN, ARIZONA

by

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TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF ILLUSTRATIONS

LIST OF TABLES

ABSTRACT

Rainfall in the Tucson Basin, located in southeastern Arizona, averages about 30 centimeters annually and is distributed unevenly between the summer and winter rainy seasons. Additionally, both the source of water vapor and the meteorological conditions differ during summer and winter storms. Previous investigations in the Tucson Basin and elsewhere have noted seasonal variations in the relative isotopic abundance ratios of oxygen-18 and deuterium and have attributed this variation in part to the meteorological conditions that prevailed during each storm. The purpose of this study was to use simple statistical tools to evaluate variations in isotopic abundance ratios in terms of ground level meteorological conditions, specifically, rainfall amount, air temperature, cloud ceiling elevation, rainfall intensity, and relative humidity. When evaluated individually, the amount of storm precipitation had the largest effect on summer and winter storm sets, whereas, temperature had the greatest effect when compared with the combined or yearly storm set.

CHAPTER 1

INTRODUCTION

Scope of Research

In a recent ground water study by Simpson et al. (1970), the stable isotopic composition of ground water in the Tucson Basin was reported to be isotopically heavier in the central portions of the basin as compared to near the mountain front boundaries. In an attempt to utilize this spatial variability in oxygen-18 and deuterium in ground water as a geochemical tool to evaluate the temporal and spatial distribution of recharge, a basin wide study of the stable isotopic composition of rainfall, runoff and ground water, including spring water from the higher elevations of the basin, was initiated at the University of Arizona.

As part of the basin wide study, this paper presents the results of the rainfall portion of the study, specifically, those results describing the stable isotopic composition of rainwater collected during 1978 and 1979. In addition to reporting the stable isotopic compositions of rainfall, the local weather conditions present at the time samples were collected are also reported here in an attempt to identify those factors most influential in controlling the seasonal isotopic fluctuations in the semi-arid Tucson Basin. Statistical methods were used to formulate predictive equations based on the

correlation between the stable isotopic composition of a bulk rain sample and its contemporaneously measured climatological parameters.

Location

The Tucson Basin is an approximately 1000-square kilometer alluvial-filled graben located within the basin and range physiographic province of southeastern Arizona. The elevation of the University of Arizona, located near the center of the basin, is about 800 meters. Mountains bordering the basin have peaks exceeding 3000 meters in elevation.

Seasonal Rainfall Patterns

Rainfall in Tucson, Arizona, averages less than 30 centimeters annually and is distributed unevenly between two rainy seasons. The best defined of these is the summer season, particularly July, August and September, when almost half the precipitation falls. A second wet season usually starts in December and ends the following March and accounts for about 30 percent of the annual total precipitation. Relatively dry conditions prevail during the late spring and fall, between the two rainy seasons.

Both the source of precipitable water vapor and the rainfall characteristics such as intensity, duration and spatial distribution are different for the two rainy seasons. Summer rainfall is characteristically high intensity, short duration, usually less than an hour, and small areal extent, usually less than 5 kilometers in diameter. Summer storms are almost always convective, resulting from the flow of moist air from the Gulf of Mexico and the Atlantic Ocean.

Winter precipitation differs in that it is characteristically low intensity, long duration, often lasting one or more days, and of large areal extent, sometimes covering the entire Tucson Basin. Winter rainfall is of frontal origin, resulting from the flow of moist air from the North Pacific (Sellers, 1975).

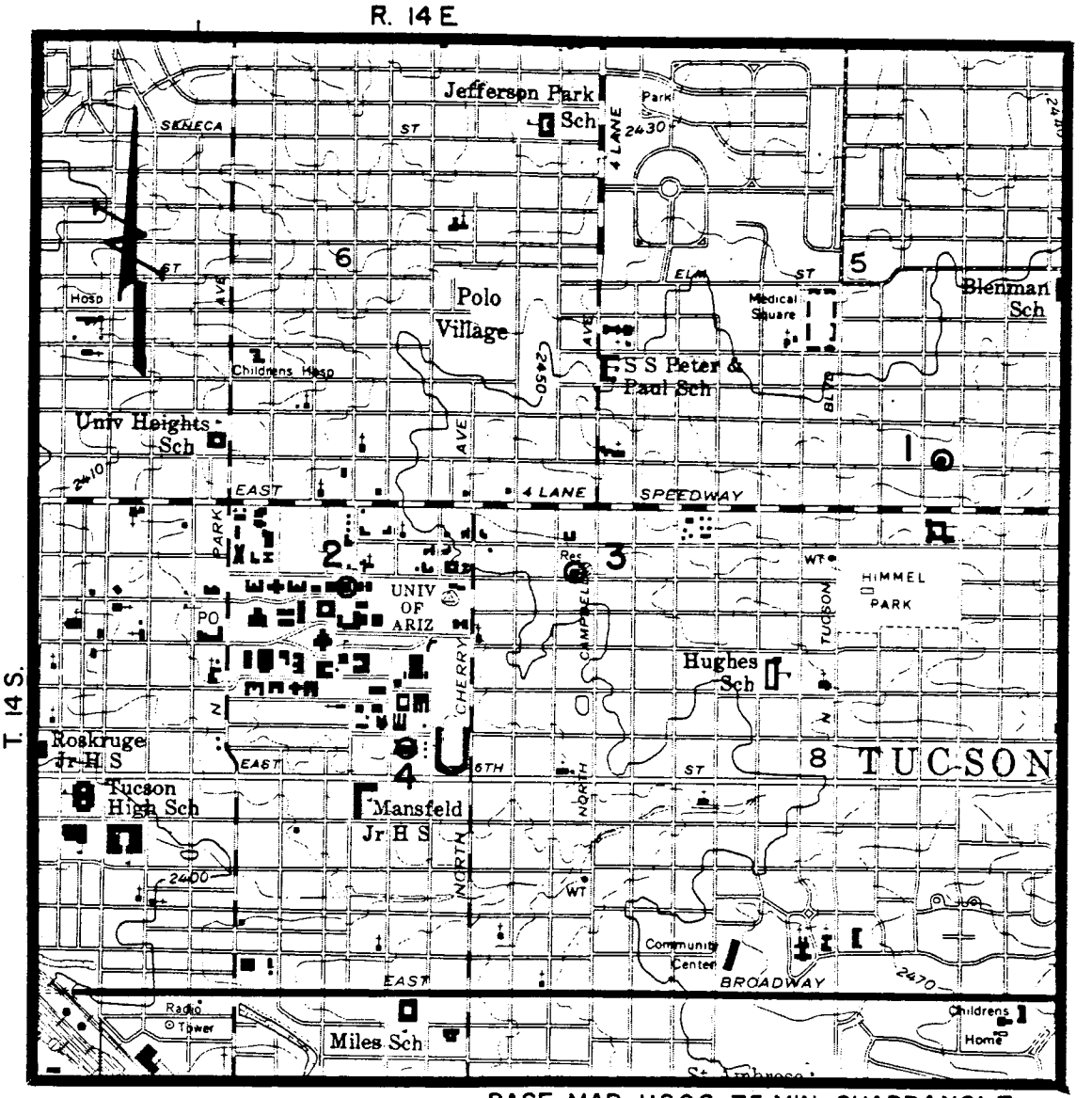
Collection and Analysis of Rain and Meteorological Data

Rain samples were systematically collected for isotopic analyses at two locations within the central basin where the effects of orographic cooling from surrounding mountains were considered minimal. These two sample collection sites are identified on Figure 1.

The bulk rain samples were collected at a private residence by Dr. Austin Long. Each of the 78 separate rainfall events during 1978 and 1979 were sampled. Forty samples were from summer storms and 38 samples were from winter storms. Each of these bulk rain samples were stored in 2 ounce amber glass bottles with paraffin sealed lids. These samples were later analyzed by the author and the results used to evaluate seasonal trends in isotopic concentration.

Samples from a single summer thunderstorm on August 10, 1980 were collected at the Laboratory of Isotope Geochemistry by the author. These 8 samples collected were used to evaluate the variations in isotopic concentration during a single storm.

Weather measurements at the time of rainfall were also collected. These measurements included rainfall amount, rainfall intensity, air temperature, relative humidity, and cloud ceiling elevation. Because there were no weather instruments at either of the



SITE DESCRIPTION

BASE MAP: U.S.G.S. 7.5 MIN. QUADRANGLE
TUCSON, ARIZONA

1. BULK RAIN SAMPLE COLLECTION SITE
2. FRACTIONAL RAIN SAMPLE COLLECTION SITE
3. RAINGAGE R-52 SITE
4. HYGROTHERMOGRAPH SITE

1000 0 1000 2000 3000 4000 5000 FEET

1 0.5 0 1 METER

GRAPHIC SCALE

MAP LOCATION

Figure 1. Rain sample collection site map.

two rainfall sampling sites, meteorological data were obtained from weather stations located nearby.

Ground-level measurements of rainfall intensity were recorded by the Arizona Water Resources Research Center using a Belfort weighing-type rainfall recorder. These measurements were made at gaging station R-52 located about 1.3 kilometers southeast of the bulk rain sampling location (see Figure 1). The rainfall amount, intensity, time of day, and duration were obtained from the hyetograph recorded on a continuous-strip chart. Storm intensity was expressed as an average by taking the ratio of total rainfall amount and storm duration.

Air temperature and relative humidity measurements were collected by the Institute of Atmospheric Physics. These measurements were made with a hygrothermograph on the fifth floor of the Physics/Math building at the University of Arizona located about 2.2 kilometers southwest of the bulk rain collection site (see Figure 1). The values of air temperature and relative humidity were summarized from the continuous-strip chart records as time-averaged quantities. Unfortunately, the hygrothermograph was malfunctioning for much of 1979 resulting in an absence of data for that period.

Cloud ceiling elevation was monitored by the National Oceanic and Atmospheric Administration (NOAA) at the Tucson International Airport located about 15 kilometers south of the bulk rain sampling site. Summaries of these data were in terms of the average cloud ceiling elevation at the time rainfall was recorded at rain gage R-52.

The rain samples were analyzed by the author for their relative oxygen and hydrogen isotopic compositions using a Micromass 602C mass

spectrometer and standard techniques of sample preparation described in the early papers by Friedman (1953) and Epstein and Mayeda (1953).

Relative abundances of oxygen-18 and deuterium were expressed in terms of their per mil difference with respect to the isotopic ratios of Standard Mean Ocean Water, SMOW (Craig, 1961). This is generally given by the equation:

$$\delta = ((R_{sample}/ R_{SMOW}) - 1) * 1000 \quad (1)$$

where R is the absolute abundance ratio $^{18}O/^{16}O$ or D/H, and δ is given in parts per thousand or per mil (o/oo) (Friedman and O'Neil, 1977).

Analytical precision was routinely and systematically monitored by including known and replicate samples with each batch of unknown samples prepared and analyzed. In general, the distribution of unknown, known and replicate samples were, 80 percent, 10 percent and 10 percent, respectively. Precision for these analyses was plus or minus 0.2 per mil for oxygen-18 and plus or minus 2 per mil for deuterium.

Linear and multilinear regression analyses were performed on the isotope and weather data in order to evaluate correlations and to develop predictive equations. These analyses were performed with the help of SPSS (Nie et al., 1975), a statistical software package.

In order to evaluate seasonal trends, the data were divided into two groups representing the summer and winter rainy seasons. The summer season included storms in May through October, whereas the winter season included rain during the months of November through the following April. Division was based on ground observations and

synoptic maps of southern Arizona available at the University of Arizona's Institute of Atmospheric Science.

Isotopic Fractionation

Equilibrium isotopic fractionation of water results from the fact that at constant temperature the vapor pressure of the $H_2{}^{16}O$ molecule is greater than that of the molecule containing the heavier isotopic components. This results in a larger vapor pressure for the common molecule. The hydrometeorological implication of this is that during a change in state, such as evaporation or condensation, there is a small yet detectable fractionation or change in the isotopic abundance ratio of meteoric waters as they move through the hydrologic cycle (Friedman et al., 1963).

Condensation of atmospheric water vapor is a natural example of Rayleigh distillation utilizing an equilibrium process (Hoefs, 1980; Craig et al., 1963).

Evaporation of water droplets is a non-equilibrium process where the degree of kinetic fractionation is governed by the size of droplets, the rate of evaporation, the relative humidity, and the diffusion rate of the interior water molecules within the droplets (Stuart, 1975). Craig et al. (1963) demonstrated that water undergoing nonequilibrium evaporation (i.e., rain drops evaporating in an atmosphere with a relative humidity of less than 100%) will generally do so along a δD versus $\delta^{18}O$ trajectory with a slope of less than 8. Thus, evaporation will cause the isotopic composition of evaporated

water to be displaced to the right of Craig's meteoric line on a plot of δD versus $\delta^{18}O$.

At the beginning of the basin wide study of stable isotopes of the Tucson Basin waters, the abundance ratios of rain water were expected to vary seasonally in response to the annual change in the local meteorological conditions. Dansgaard (1961), among others, reported that winter precipitation in the northern hemisphere is depleted in heavy isotopes with respect to the summer precipitation. Furthermore, the anticipated seasonal isotopic change was expected to be affected by the difference in air temperature and/or sea surface temperature at the source of atmospheric water vapor common to the Tucson Basin. The isotopic relationship between oxygen-18 and deuterium was anticipated to correspond to the linear correlation reported by Craig (1961) as $\delta D = 8\,\delta^{18}O + 10$, except that a deviation from the Craig meteoric line could be expected for summer rains when evaporation of the falling raindrop would result in kinetic fractionation.

Stuart (1975) reported an equation that describes the changes in the isotopic abundance ratios for a reservoir of diminishing volume, such as a falling raindrop, with equilibrium fractionation taking place during condensation and kinetic fractionation taking place during evaporation. The equation was developed from an isotope and mass balance and expressed in terms of meteorologic parameters. The change in abundance ratios for a reservoir of diminishing volume is given by:

$$\delta = \delta_{end}\,(1 - f^{\beta}) \qquad (2)$$

where,

δ = relative abundance ratio. Here, δ differs from Equation 1 by a factor of 1000, as shown below,

$$= (R - R_o)/R_o \quad (3)$$

R = Absolute isotopic abundance ratio, defined as the ratio of the number of moles of the heavy (rare) isotope to that of the light (common) isotope.

R_o = Absolute abundance ratio for the initial raindrop.

$$\delta_{end} = (\gamma(R_b - R_o))/R_o \quad (4)$$

R_b = Absolute abundance ratio for the bulk atmospheric vapor.

$$\gamma = (\alpha_p\, h)/\ ((1 - \alpha_p)\ (D/D')^n(1 - h) \quad (5)$$

$$\beta = \frac{((1 - \alpha_p)\ (D/D')^n(1 - h))}{(\alpha_p)(D/D')^n(1 - h)} \quad (6)$$

f = Residual fraction. Defined as the ratio of the remaining mass to the initial mass.

α_p = Equilibrium fractionation factor, R/R_o.

n = An empirical exponent found by Stuart (1975) to be 0.58.

h = Atmospheric relative humidity expressed as a decimal quantity ($h = 1$ at saturation).

$(D/D')^n$ = Kinetic fraction factor.

The purpose in presenting the Stuart Model is not to demonstrate its use; rather, it is given here in an attempt to show those meteorological and geochemical parameters that affect the relative isotopic abundance ratios of oxygen-18 and deuterium in bulk rain samples. See the following section of this thesis for a more thorough discussion of individual meteorological factors.

From Equations 2, 4 and 5, it can be seen that raindrop temperature controls δ values through a linear function of the equilibrium fractionation factor, α_p. Temperature also affects relative humidity identified in Equation 5 and 6. By knowing the wet adiabatic lapse rate and the wet-bulb depression using psychrometric charts, it is possible to evaluate the effect of temperature on the equilibrium fractionation factor. Average air temperature measured during each of the sampled storm events was used in this study as a statistical index rather than the actual raindrop surface temperature.

From Equation 4, it is apparent that the isotopic abundance ratio of the initial water vapor is a controlling factor. Therefore, both the sea surface temperature at the source of precipitable water vapor as well as the possible difference between the isotopic abundance of the vapor in the cloud and that immediately below the cloud are theoretically significant.

If the vapor beneath the cloud differs substantially from that in the cloud, then the amount of time available for the drop to equilibrate would also be significant. Cloud ceiling elevation would be a measure of this travel time. Similarly, the greater the rainfall intensity (i.e., the larger the drops), the faster the rate of fall and

the less time available for equilibration during descent of the individual drops.

Stuart (1975) showed that Equation 2 reduces to the Rayleigh Equation, and therefore, the amount of precipitation during any single storm is also a controlling factor.

The next section deals with the individual meteorological factors and their influence on isotopic abundance ratios of bulk rain samples.

CHAPTER 2

METEOROLOGICAL FACTORS INFLUENCING ISOTOPIC ABUNDANCE RATIOS

The rain samples collected by Dr. Long were analyzed by the author for their relative abundance ratios of oxygen-18 and deuterium at the University of Arizona Laboratory of Isotope Geochemistry. The results of these analyses, listed on Tables 1 and 2 and plotted on Figure 2, reveal the anticipated annual fluctuation of oxygen-18, with the isotopically lighter rain found in the winter. A similar fluctuation was seen in the measured deuterium concentrations, and therefore, not presented here.

Tables 1 and 2 contain the $\delta^{18}O$ and δD values for each of the rain samples collected in 1978 and 1979. These tables also include a tabulation of the contemporaneously measured meteorologic parameters used in the subsequent statistical analysis.

The amount-weighted average precipitation δ values for oxygen-18 and deuterium for summer were found to be -4 o/oo and -30 o/oo, respectively, and for winter the averages were -10 o/oo and -70 o/oo, respectively. The scatter of the data points suggests that the isotopic history of the atmospheric water vapor along its trajectory from its oceanic source and the local meteorologic condition are important in regulating the final isotopic composition of bulk samples of Tucson rain water.

Table 1. Oxygen-18 and deuterium concentrations and their corresponding meteorologic conditions for rain in 1978.

Event Date	Season *	$\delta^{18}O$ (o/oo)	δD (o/oo)	Amount (mm)	Intensity (mm/hr)	Relative Humidity (%)	Temperature (°C)	Elevation ($x10^3$m)
January								
10	-1	-12.4	-86	18.5	5.88	65	4.4	14.0
11	-1	- 5.7	-37	2.4	1.38	85	0.6	16.1
15	-1	- 9.4	-58	21.2	2.34	71	5.6	16.5
16-17	-1	- 4.3	-21	14.0	5.58	72	5.6	46.6
20	-1	-10.5	-57	8.8	1.44	71	3.3	19.8
30	-1	- 8.4	-67	5.4	1.68	75	10.0	22.9
February								
1	-1	-14.3	-90	8.6	21.60	88	6.1	
5-6	-1	- 6.6	-53	4.6	6.60	56	5.6	18.3
8	-1	+ 0.2	- 2	3.0	1.26	88	5.6	14.0
12	-1	-11.3	-64	28.0	2.16	79	3.9	10.7
13-14	-1	-10.2	-61	5.4	3.12	71	0.0	21.4
14	-1	- 8.5	-43	5.1	7.62	71	0.0	7.0
28	-1	-11.7	-87	13.0	4.74	63	11.1	15.2
March								
1-2	-1	- 7.2	-33	12.4	9.66			14.6
6		- 3.6	-16	6.0	2.88			12.5
10	-1	- 4.5	-33	3.2	3.96	84	5.0	14.0
12	-1	-12.4	-73	10.0	5.22	84	3.3	7.6
April								
8	-1	- 5.7	-14	4.2	3.06	55	6.7	22.9
May								
1	1	+ 1.8	+ 6	6.0	5.88			15.2
6	1	- 2.5	- 4	16.4	4.26			12.8
June								
4	1	- 6.2	-37	3.5				
27	1	- 0.9	+ 3	9.6	26.16	60	18.3	23.5
July								
8	1	+ 0.4	+ 7	7.8	15.78	69	25.0	27.4
25	1	- 5.7	-30	9.0	26.22			39.6
30	1	- 0.7	+ 1	25.3	17.53	88	22.8	24.4

Table 1--Continued.

Event Date	Season *	$\delta^{18}O$ (o/oo)	δD (o/oo)	Amount (mm)	Intensity (mm/hr)	Relative Humidity (%)	Temperature (°C)	Elevation ($x10^3$m)
August								
4	1	- 2.1	-14	3.8	8.70	82	21.7	27.4
7	1	- 1.9	-16	2.6	15.24	46	22.2	24.4
8	1	- 1.1	- 4	2.4	9.96	59	23.3	33.5
11	1	- 1.2	- 5	15.4	9.66	78	23.3	24.4
12	1	+ 2.5	+16	1.9	1.14	52	24.4	
17	1	- 3.4	-20	11.0	46.74	61	25.0	27.4
17	1	- 3.6	-23	8.0	47.88	65	23.3	27.4
September								
21	1	- 5.1	-34	1.5	22.86	54	22.8	7.6
October								
20-21	1	-17.3	-93	41.0	12.60			9.1
23-24	1	- 8.6	-53	15.6	12.42			13.4
November								
12	-1	- 3.0	-12	4.4	3.36			13.7
14-15	-1		-11	10.2	6.78			10.0
23-24	-1	-10.3	-63	33.4	3.78			14.0
December								
6	-1	- 7.6	-45	7.6	4.08		2.2	8.2
17-18	-1	-12.8	-102	39.0	4.38		10.6	11.6
19	-1	- 4.1	-10	1.5	3.06			7.6
29-31	-1	-20.1	-146	35.4	2.40	66	11.1	7.6

* -1 = Winter, 1 = Summer

Table 2. Oxygen-18 and deuterium concentrations and their corresponding meteorologic conditions for rain in 1979.

Event Date	Season *	$\delta^{18}O$ (o/oo)	δD (o/oo)	Amount (mm)	Intensity (mm/hr)	Relative Humidity (%)	Temperature (°C)	Elevation ($x10^3$m)
January								
5	-1	- 9.5	- 36	21.4	3.00		5.0	13.1
9	-1	-10.3	- 72	1.4	3.06		1.1	7.6
14-15	-1	- 6.7	- 47	3.4	2.52		7.2	18.3
16	-1	- 8.6	- 57	27.4	10.62		7.2	15.2
24-25	-1	-19.4	-108	18.0	4.35		4.4	15.2
28-29	-1	- 8.4	- 61	14.4	2.58		-2.2	15.2
February								
4-5	-1	-10.9	-56	15.2	3.72		-0.6	9.7
22	-1	- 3.3		2.0	4.56		0.0	13.1
March								
2	-1	- 9.9	-64	2.7	10.14		-0.6	10.7
17	-1	- 6.8	-21	5.7	10.86			14.6
20-21	-1	-10.2	-51	15.2	4.56			14.6
28-29	-1	- 1.8	-14					10.7
April								
10	-1	+ 0.1	+13	1.4	5.10			11.6
May								
9	1	- 7.2	-17	4.0	3.36		12.2	10.7
19-20	1	- 5.3	-18	3.5	7.14		21.1	19.8
23	1	+ 3.2	+10	2.0	5.10		18.9	27.4
26	1	- 7.6	-25	4.2	25.92		18.3	24.4
June								
5	1	+ 0.1		2.0	7.62		25.0	22.9
30	1	+ 1.8	+ 1	1.6	15.24		22.2	36.6
July								
1	1	+ 3.6	+14	2.0	15.24		21.7	26.5
16	1	+ 3.0	+ 2	6.2	16.32		23.9	32.0
18	1	- 1.5	- 7	3.4	18.36		22.8	22.9
18	1	- 2.7	-11	5.8	11.76		21.7	16.8
20	1	- 6.0	- 23	1.6	3.84		17.2	15.2
20	1	-11.6	- 68	15.2	17.40		15.6	
29	1	- 3.9	- 20	5.0	1.02			24.4
29	1	- 4.0	- 26	5.3	9.72		17.8	36.6

Table 2--Continued.

Event Date	Season *	$\delta^{18}O$ (o/oo)	δD (o/oo)	Amount (mm)	Intensity (mm/hr)	Relative Humidity (%)	Temperature (°C)	Elevation ($x10^3$m)
August								
4	1	- 7.7	- 22	12.0	18.84		22.2	22.9
10	1	- 3.5	- 17	3.8	20.94		22.2	24.4
11-12	1	- 1.7	- 2	2.4	11.22		21.7	20.4
12	1	- 8.0	- 31	6.2	10.68		17.8	22.9
12	1	-11.4	- 75	22.1	71.70			9.1
15	1	- 3.0	- 23	3.2	3.84			15.5
16	1	- 6.2	- 42	9.6	29.70		23.3	
October								
21	1	- 2.8	- 8	2.8	15.24		15.6	11.0
November								
8	-1	- 2.6	- 9	3.4	17.52		12.8	15.2

* -1 = Winter, 1 = Summer

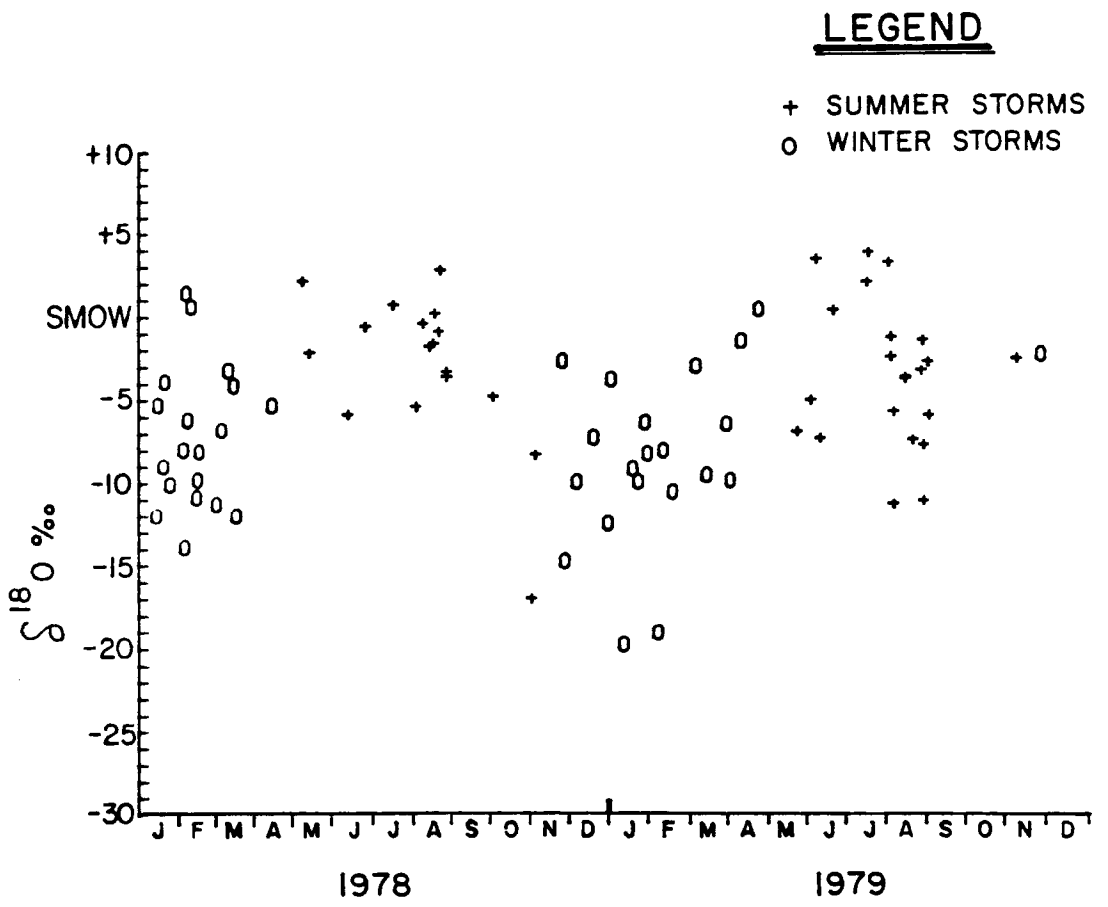


Figure 2. Seasonal fluctuation in oxygen-18 in bulk rain samples collected in 1978 and 1979.

Dansgaard (1964) reported a similar seasonal variation in δ values for monthly precipitation samples. He also reported δ values that were unusually high or low within a given rainy season which he attributed to unusually high amounts of precipitation during a given month.

Relationships Between Oxygen and Hydrogen Isotopes

A plot of δD with $\delta^{18}O$ yields information about the nonequilibrium processes taking place as the raindrop falls through the unsaturated air beneath the cloud. Evaporation, as expected, concentrates the heavier isotopes in the remaining droplets. When the rate of evaporation is less than or equal to the diffusion rate of the inner-droplet molecules, the resulting partitioning of isotopes will follow Craig's meteoric line, having a slope of eight. However, when the vaporization rate exceeds that of molecular diffusion, the resulting plot of δ deuterium with δ oxygen-18 will have a slope less than eight, indicating kinetic fractionation (Dansgaard, 1964).

Combined summer and winter rainwater samples collected in the Tucson Basin, seen plotted on Figure 3, have least-squares best-fit lines with slopes less than eight revealing the effect of kinetic fractionation. The slope for summer rain samples is 5.0. Winter samples have a slope of 7.0. These slopes suggest that fast evaporation and the resulting kinetic fractionation is more important in altering summer rain than winter rain. Similarly, this difference in slope gives an indication that rainfall is not from a homogeneous population having similar meteorological characteristics.

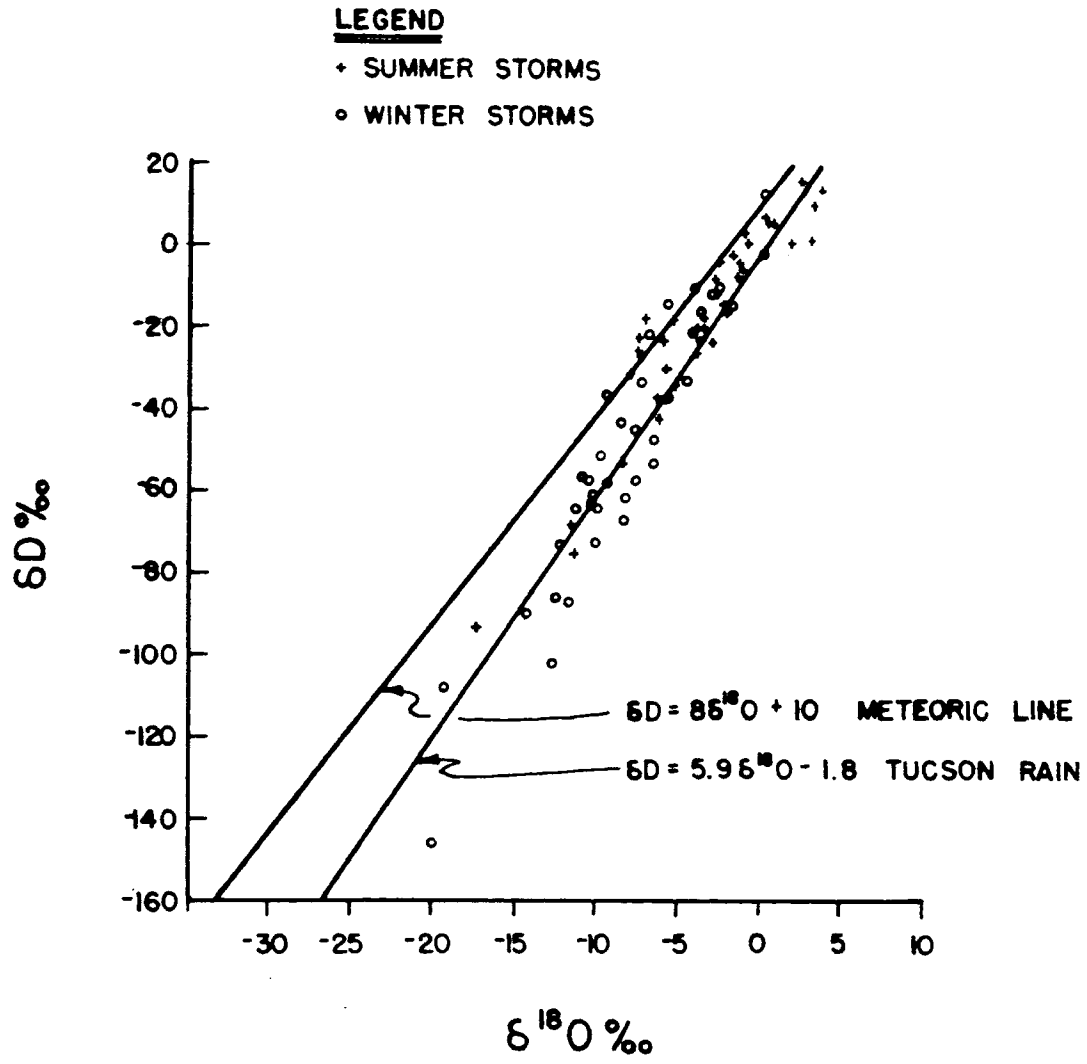


Figure 3. δD versus $\delta^{18}O$ for bulk rain samples.

Temperature

Since vaporization, condensation and isotopic fractionation are temperature dependent, then it can reasonably be expected that the isotopic abundance ratios are also temperature dependent. Dansgaard (1964), in testing this hypothesis, demonstrated a marked seasonal variation in deuterium and oxygen-18 at a given location. His reported variation in average concentration of oxygen-18 with mean annual temperature, 0.7 o/oo O-18 per degree Celsius, parallels that of air temperature such that the more depleted values are found during the cold months while the heavier values are found during the warm months. Dansgaard's linear relationship can be explained by considering the formation of precipitation by a Rayleigh process in which rainfall becomes progressively lighter due to preferential condensation and removal of the heavy molecules from the water vapor contained within the air parcel.

A positive correlation between δD in rain water samples and average air temperature was found by Ehhalt et al. (1963). They also cautioned that the usual seasonal variation in δD was sometimes obscured by local meteorological conditions.

The $\delta^{18}O$ values for the seventy-eight rain samples collected in 1978 and 1979 are plotted on Figure 4 along with their corresponding temperature values. The slope of the best-fit line through these data is 0.36 o/oo per degree Celsius. Summer rain δ values are clearly heavier than those for winter rainfall.

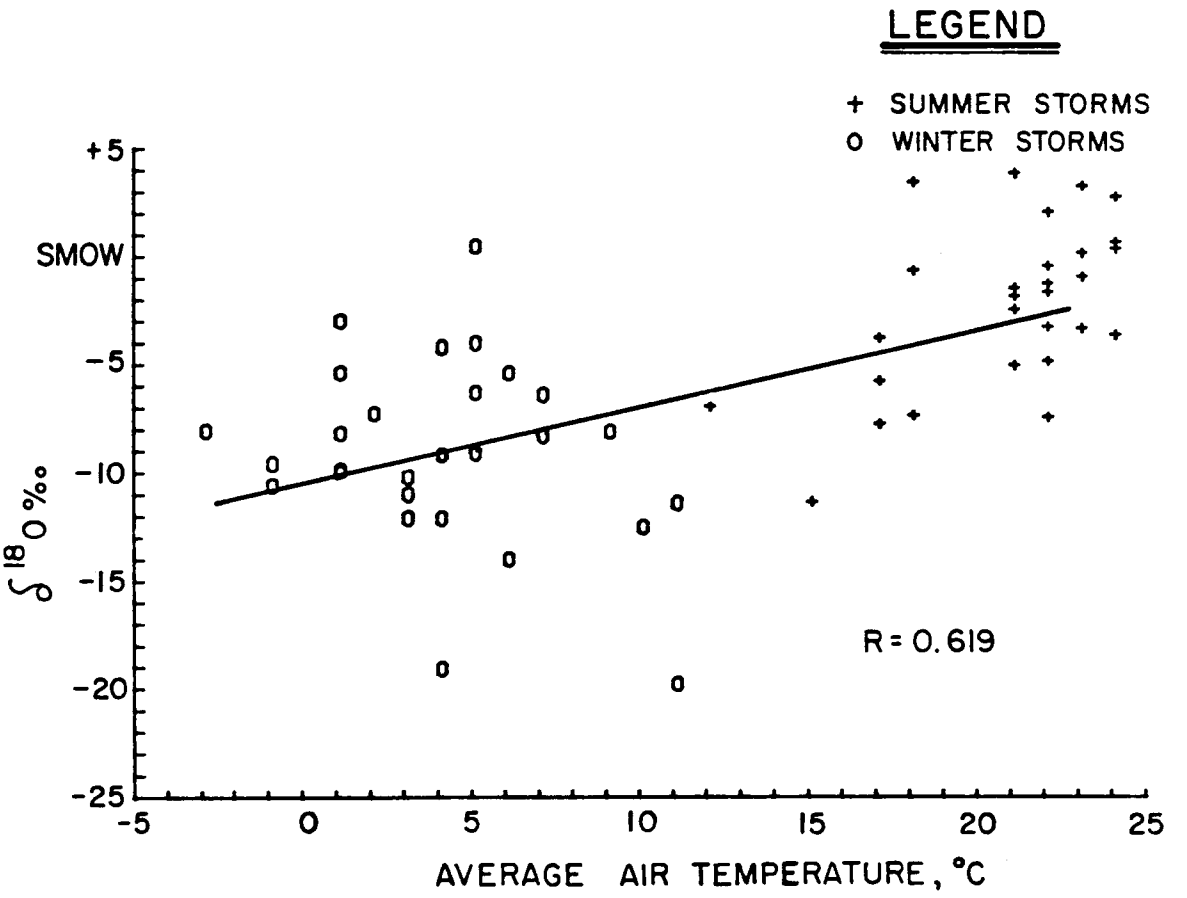


Figure 4. $\delta^{18}O$ versus average air temperature.

Precipitation Amount

If condensation of atmospheric water vapor proceeds under Rayleigh conditions, then in order to maintain a mass balance, the vapor must become progressively lighter isotopically as the heavy isotopes are preferentially precipitated. Correspondingly, the values for bulk rain samples became successively lighter as the total amount of precipitation increased. Dansgaard (1964) in describing the "amount effect" stated that fractionation by isotopic exchange between the falling rain drops and the water vapor in the air mass below the cloud base is more pronounced for light rains. This he said was in part because the low humidity below the cloud causes a relatively larger proportion of these individual raindrops to evaporate during their fall to the ground, with a corresponding enrichment of the heavy isotopes in the drops.

It can be speculated that winter rain, with smaller, more uniform-sized raindrops will exhibit more isotopic enrichment than summer rains which typically have a relatively large range in drop sizes. However, contrary to this speculation, Figure 5 shows that all three data sets (summer, winter and combined) have roughly equal tendencies towards lighter abundance ratios with larger precipitation amounts. The negative correlation seen in Figure 5 corresponds to the same trend reported by Dansgaard (1964). Here, correlation can be expected to be moderate because of the relatively large range in rainfall amount within the statistical population.

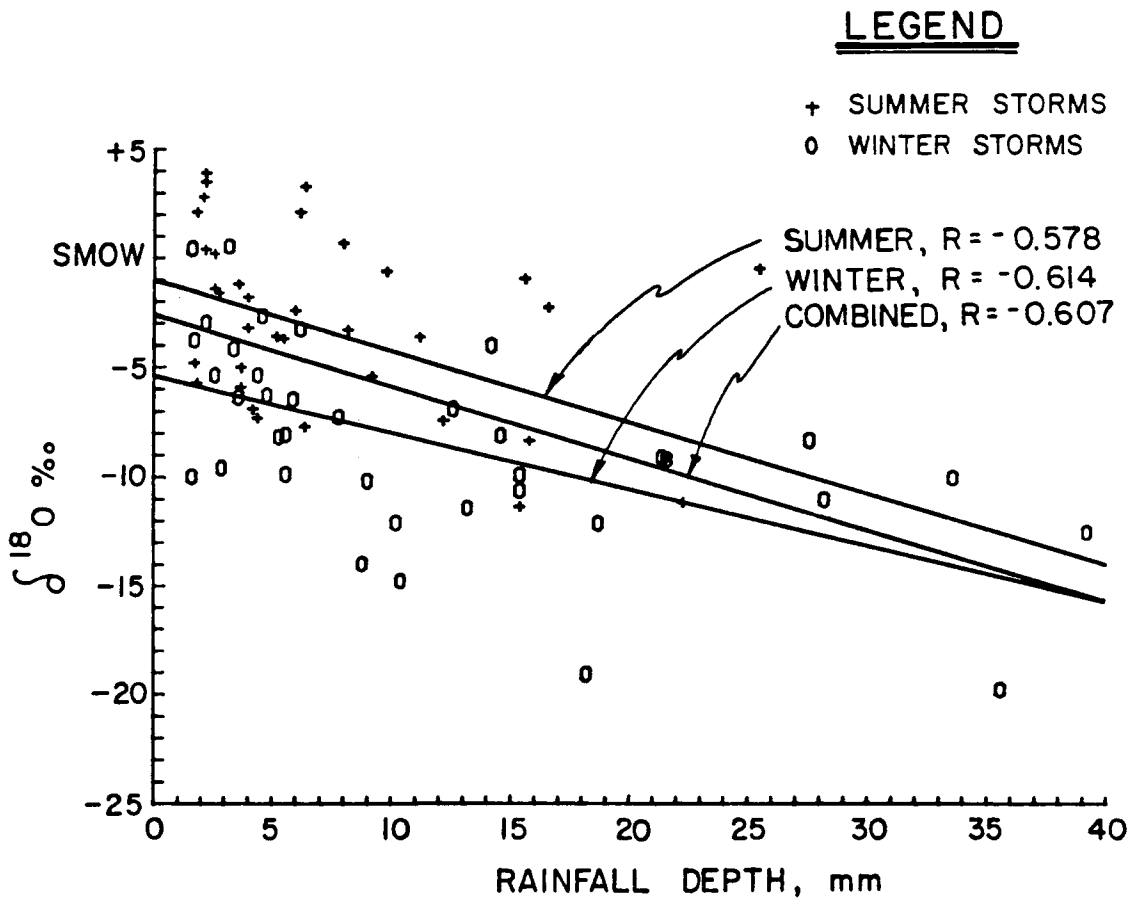


Figure 5. $\delta^{18}O$ versus precipitation amount.

Rainfall Intensity

The intensity of precipitation depends upon, among other factors, the temperature difference between the earth's surface and the overlying air. During winter months when the ground-air temperature difference is relatively small, cloudiness is widespread and rainfall is continuous and usually gentle with only slight variations in intensity. As the temperature difference becomes greater, thermal heating of the lower air creates an unstable condition which results in local updrafts and convection. During the summer months when the temperature differential is greatest, cloudiness is spotty and centered around regions of upward moving air and precipitation is intermittent and has a large variation in intensity (Sellers, 1975).

Raindrops naturally have a spectrum of sizes. The larger drops have a faster terminal velocity than smaller drops, and these larger drops also have less time in which to evaporate and to exchange isotopically (Woodcock and Friedman, 1963). Reductions in both the amount of raindrop evaporation and the duration of isotopic exchange tend to enrich the rain water in the heavier isotopes (Dansgaard, 1964). High intensity storms not only deposit large quantities of water in a short time, they are also accompanied by larger rain drops than those during less intense storms. Generally, it can be expected that rain samples collected during high intensity storms would be less enriched in the heavy isotopes than those samples collected during the more gentle storms.

In Figure 6, $\delta^{18}O$ values are plotted against their corresponding time averaged rainfall intensity. It is visually

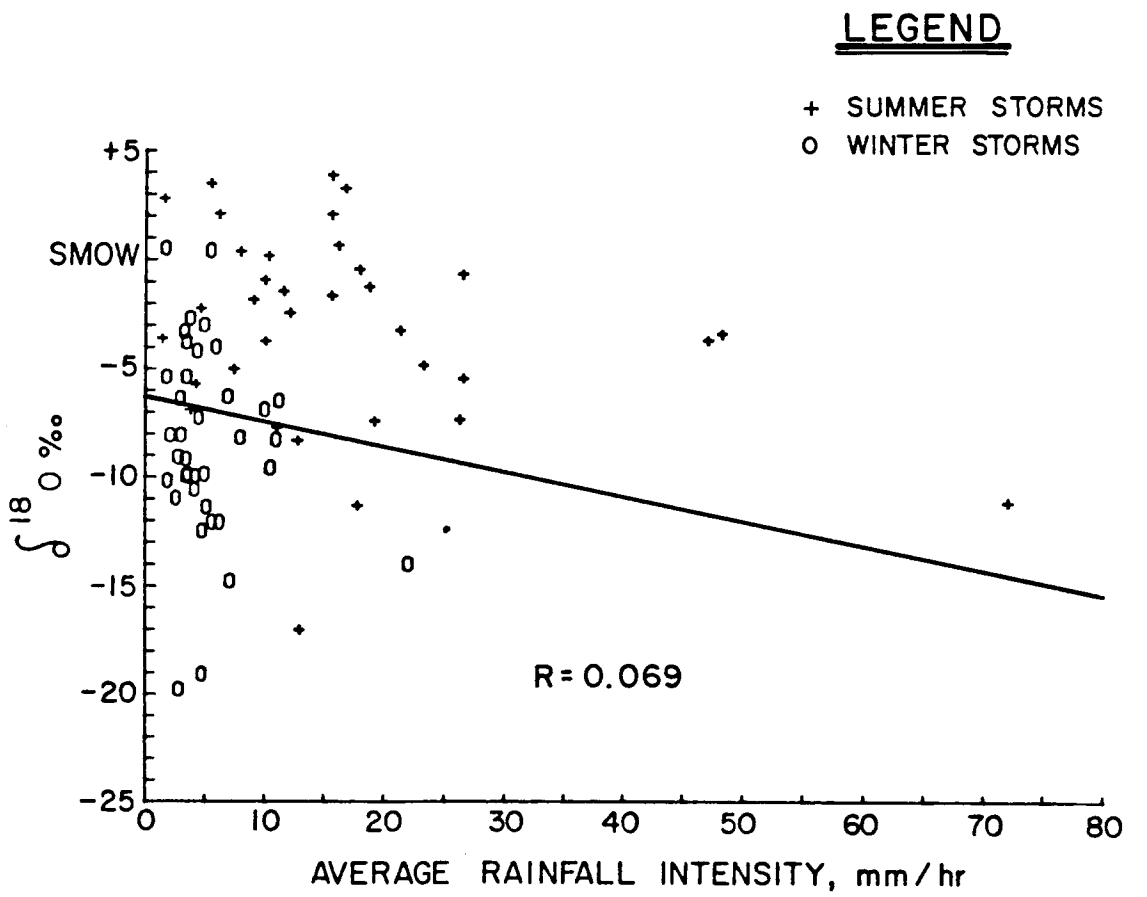


Figure 6. $\delta^{18}O$ versus precipitation intensity.

apparent from this figure that correlation between the variables in lacking.

This lack of correlation is perhaps in part due to the reduction of data in terms of time averaged quantities or to the small number of high intensity samples collected.

Yapp (1982) demonstrated that rainfall from geographical regions which exhibit little seasonal temperature or humidity fluctuations and whose precipitation originates from air masses with a constant initial isotopic composition, there exists an observed negative correlation between δD of bulk rainfall samples and rainfall intensity. However, Yapp (1982) continued by stating that this correlation would not be apparent from data sites where weather conditions were not relatively constant.

Relative Humidity

The effect of relative humidity in controlling abundance ratios is the same for very high values as it is for very low values. When the relative humidity is 100 percent, vaporization equals condensation and the net evaporation is zero. Raindrops in this humid environment exchange with the surrounding isotopically lighter vapor.

Dansgaard (1964) reported that relative humidity was more important than rainfall amount or intensity in determining the isotopic composition of bulk rain samples collected at continental stations.

The time averaged relative humidities for the subject rain samples were plotted on Figure 7 along with their measured $\delta^{18}O$ values. The hygrometer used in this study malfunctioned during most 1979 which

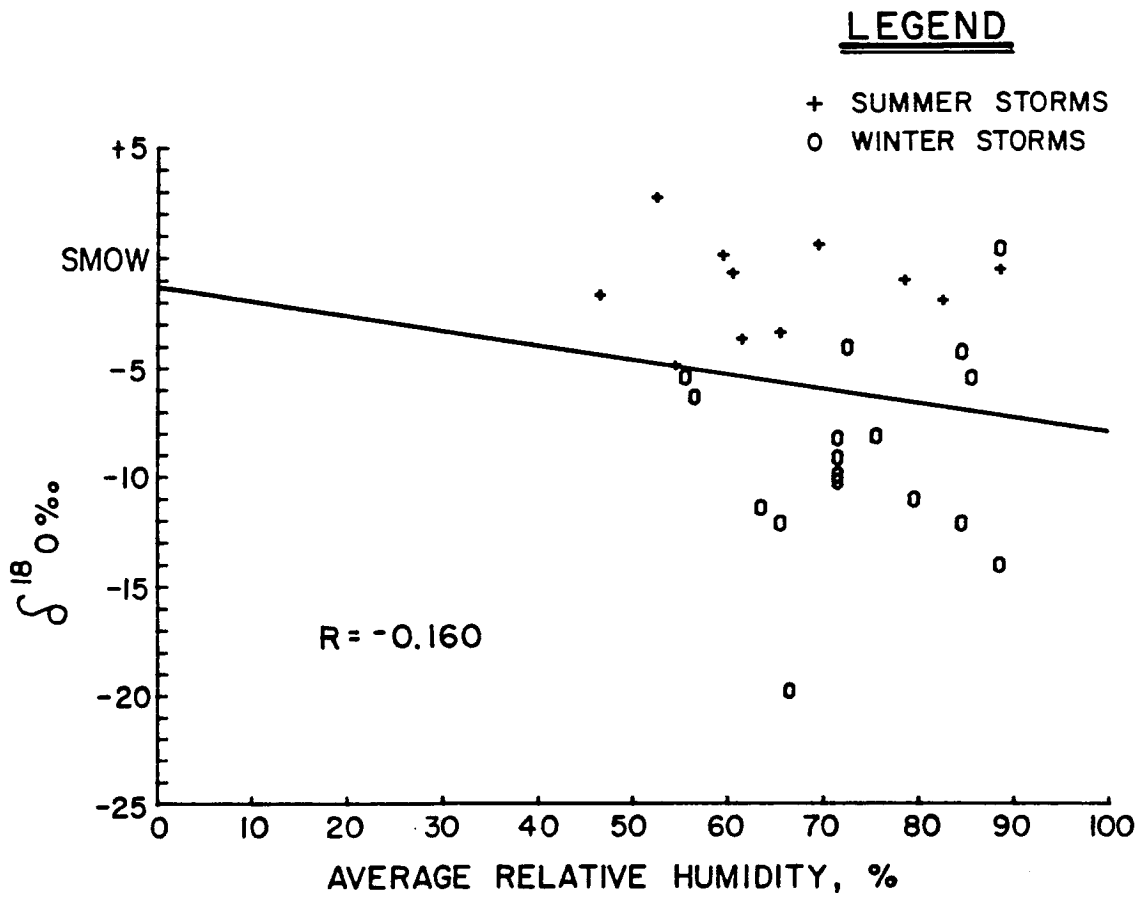


Figure 7. $\delta^{18}O$ versus average relative humidity.

substantially reduced the total number of data pairs. The average summer and winter relative humidity for the available data varied equally from about 50 to 95 percent.

As seen on Figure 7, the correlation is poor for the data set.

Cloud Ceiling Elevation

The types of clouds present during the two wet seasons are generally different. Winter storms are frontal type and are associated with low-lying stratoform clouds. Summer storms differ in that they are of convective origin and are associated with cumulonimbus clouds developed at higher altitude.

Because of this general elevation difference, the distance and time available for individual rain drops to fall is greater for drops formed during summer storms. Similarly, the amount of isotopic enrichment resulting from rain drop evaporation and exchange would also be greater for the longer fall paths found during summer thunderstorms (Woodcock and Friedman, 1963).

To test this hypothesis, the author collected cloud ceiling elevation measurements taken by NOAA at the Tucson International Airport located about 15 kilometers south of the bulk rain sample collection site. Because of the large distance separating the two data collection sites and the uneven rainfall distribution, only those elevation measurements taken when rainfall was recorded at the W.R.R.C. gage R-52 were used in the statistical analysis.

A plot of cloud ceiling elevation and $\delta^{18}O$ seen in Figure 8 clearly shows the expected proportionality between increased fall path and a greater isotopic enrichment of rain.

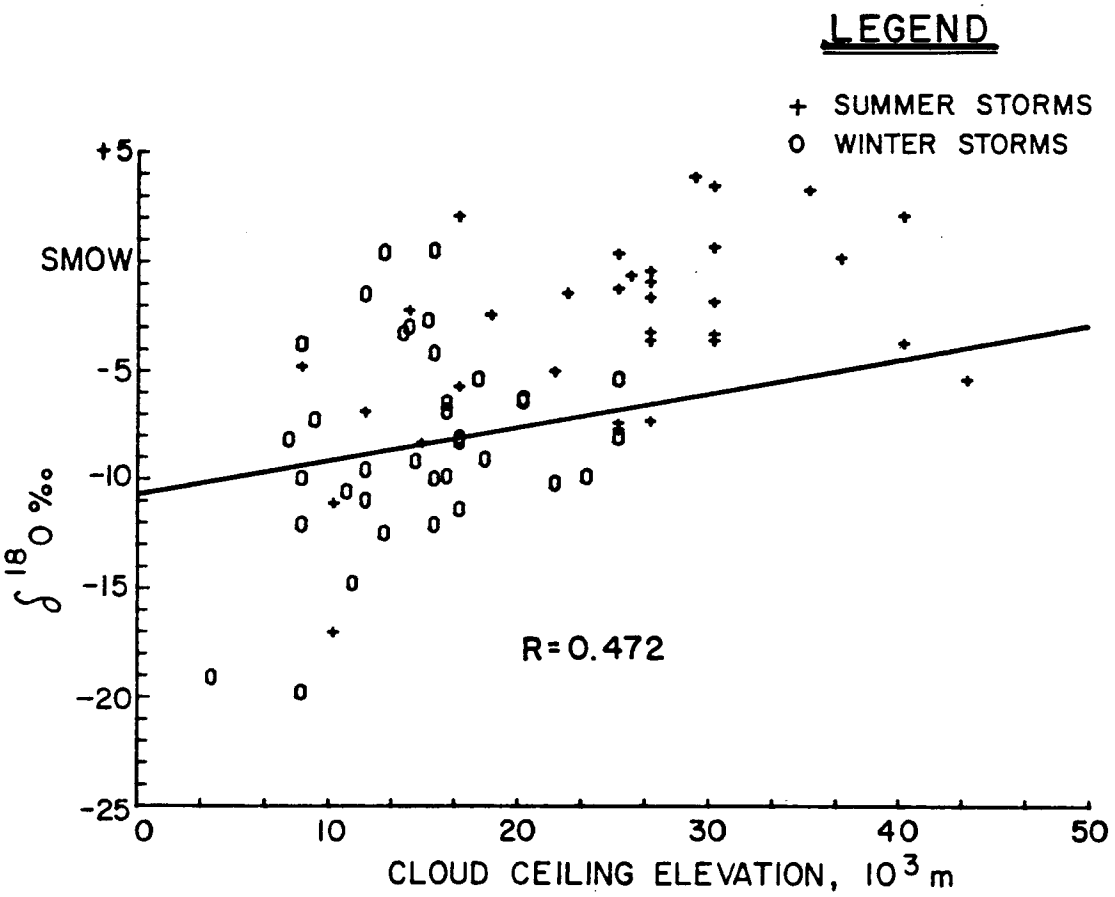


Figure 8. $\delta^{18}O$ versus cloud ceiling elevation.

CHAPTER 3

METEOROLOGICAL FACTORS INFLUENCING ISOTOPIC ABUNDANCE RATIOS OF RAIN SAMPLES COLLECTED DURING A SINGLE SUMMER THUNDERSTORM

In the previous section of this report, it was shown that correlation exists between some climatological factors and measured $\delta^{18}O$ values. If these factors influence annual behavior, then these same climatological factors should also be expected to correlate with the isotopic content of incrementally collected samples collected during a single rain storm.

To test this hypothesis, a single summer thunderstorm on August 10, 1980, was sampled sequentially. In addition to these eight sequential samples and a single bulk sample collected by the author, two additional bulk rain samples were collected by others for analysis. One bulk sample was collected by Dr. Austin Long at the usual bulk sampling location. The second bulk sample was collected by Dr. Anthony Mueller at a private residence located about 7.0 kilometers east of the discrete sampling location.

Results presented in this section are essentially qualitative.

Thunderstorm of August 10, 1980

The rainfall on August 10th was a typical summer convective thunderstorm with a measured rainfall depth of 13.1 mm. The duration of this storm was approximately 3.5 hours with about 70 percent of the total precipitation falling in the first half-hour. The air

temperature, relative humidity, and rainfall intensity, seen plotted on Figure 9, changed as the storm progressed.

The small sample volume, particularly for the later samples, precluded the analysis of oxygen isotopes. Instead, deuterium was the isotopic constituent analyzed.

Results for these analyses, given on Figure 10, show that measured deuterium concentrations tend to be lower for those samples collected while the rainfall intensity and air temperature were high. Conversely, the δ values increased for those samples taken while the relative humidity was high. These trends can be seen on Figures 11, 12 and 13.

Visually, the best correlation appears to be with rainfall intensity. Samples collected while rainfall intensity was low (and the drops size was small) tended to be isotopically heavier than samples collected during the high intensity portion of the storm. This trend suggests that a large fraction of small drops evaporated even though the relative humidity was high. Again, this visual correlation between deuterium and rainfall intensity supports the "amount effect" hypothesis described earlier.

In order to test the so-called amount effect, the three bulk samples were analyzed and the results plotted on Figure 14 along with their corresponding distance from the University of Arizona. Each of these three samples contained about the same equivalent depth of rainfall (13.1 mm, 9.2 mm, and 19.1 mm, going west to east, respectively) suggesting that each sampling location experienced the same storm characteristics as the thunderstorm moved westward across

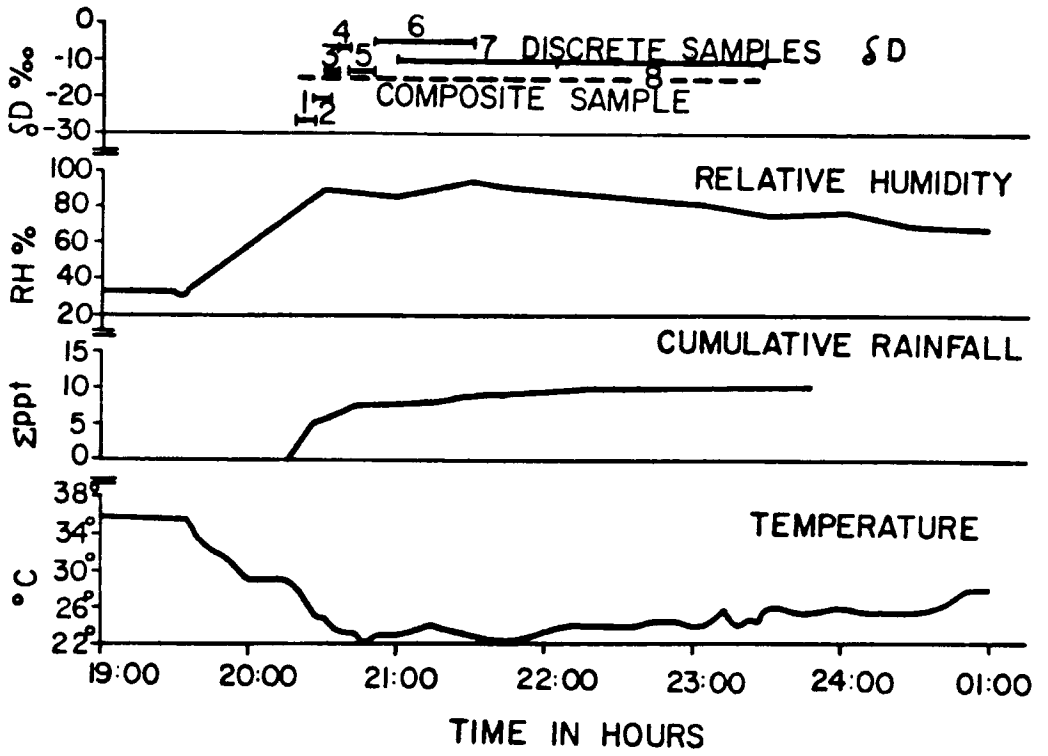


Figure 9. Temporal distribution of δD, relative humidity, rainfall amount, and temperature during the storm of August 10, 1980. The numbers one (1) through eight (8) plotted in the top portion of this figure (seen again enlarged in Figure 10) represent the individual samples collected.

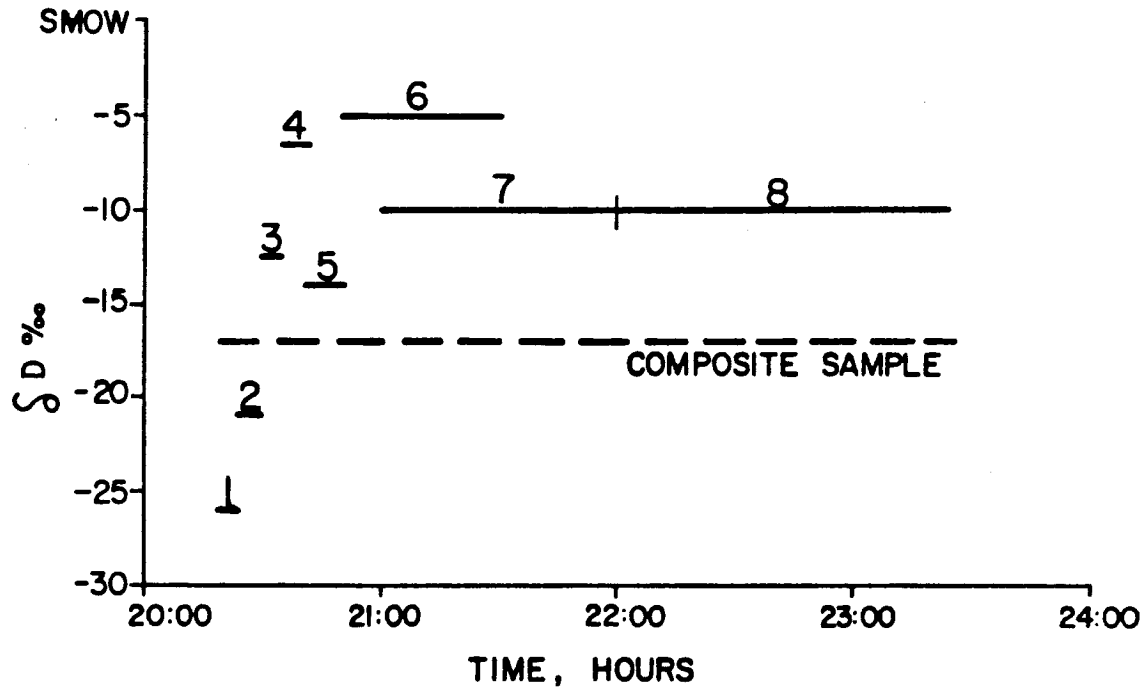


Figure 10. δD versus time during the storm of August 10, 1980.

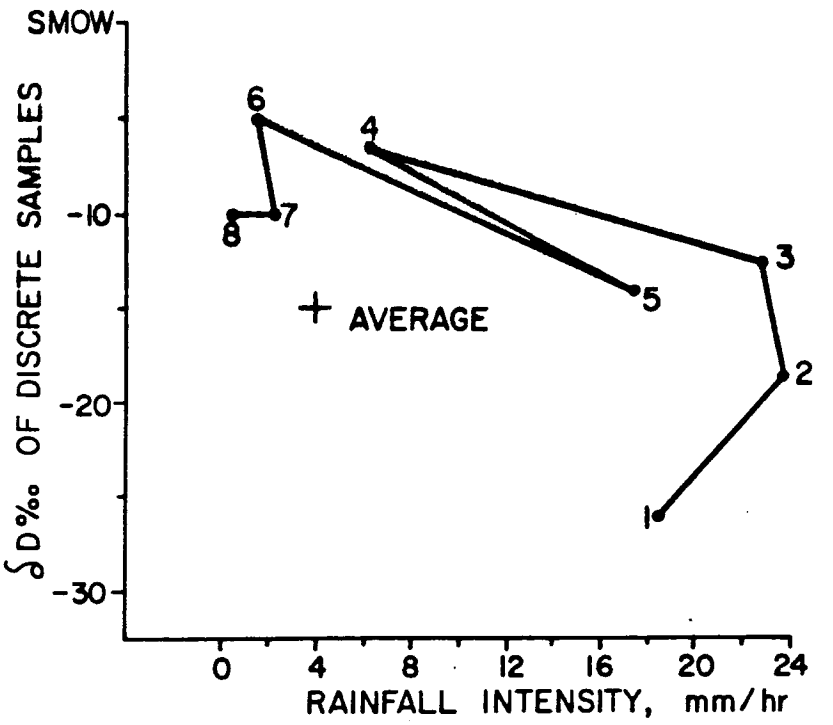


Figure 11. δD versus rainfall intensity during the storm of August 10, 1980.

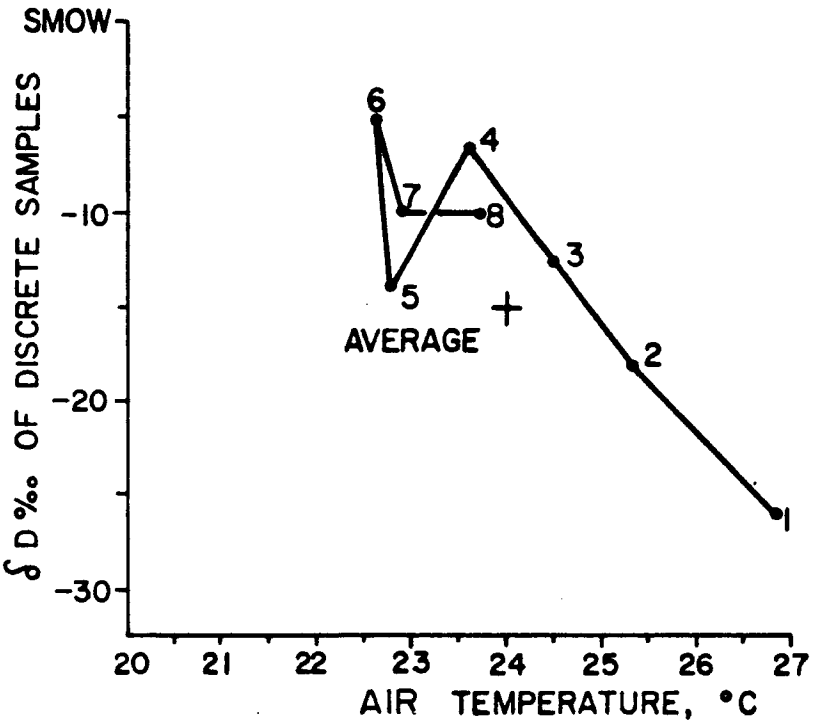


Figure 12. δD versus air temperature during the storm of August 10, 1980.

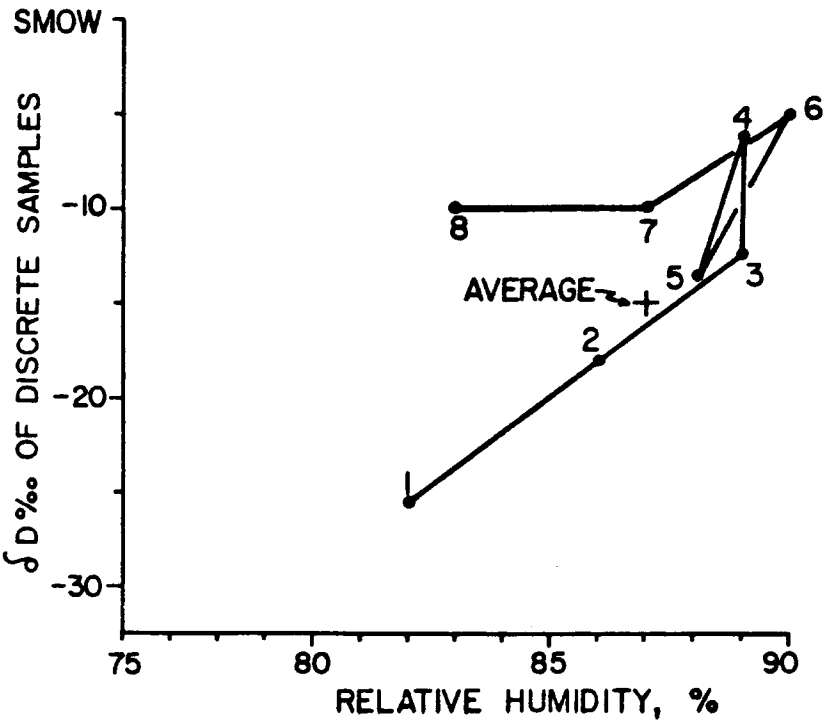


Figure 13. δD versus relative humidity during the storm of August 10, 1980.

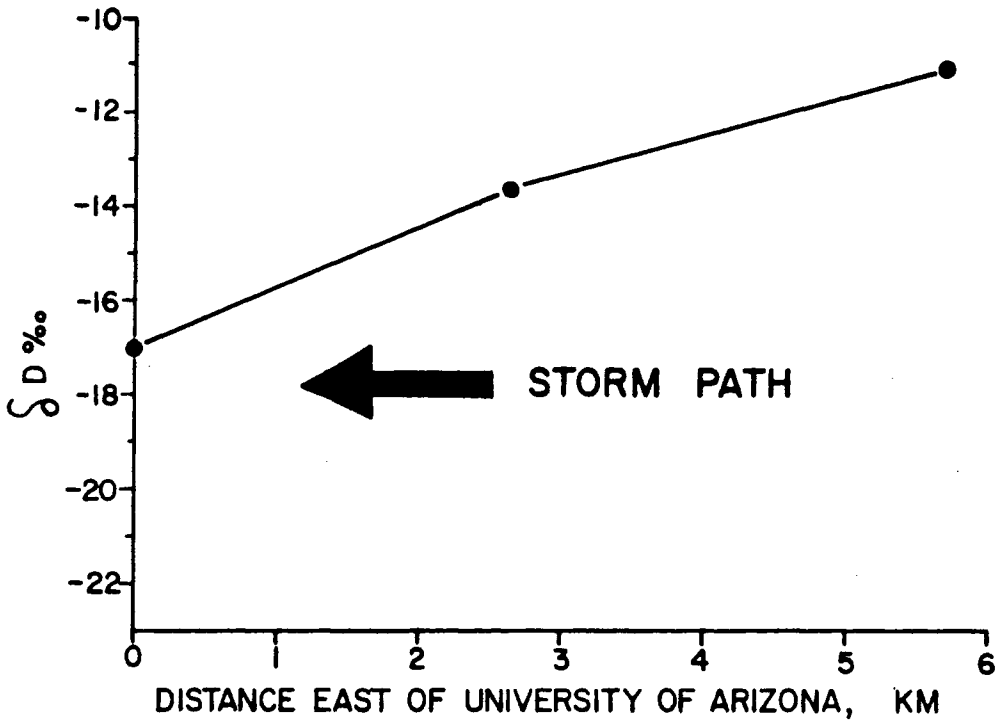


Figure 14. δD versus length of storm travel measured as the distance east of the University of Arizona.

the City. The plot of distance versus deuterium does suggest that Rayleigh distillation was in part responsible for the progressive decrease in deuterium.

CHAPTER 4

PREDICTIVE EQUATIONS BASED ON LINEAR AND MULTILINEAR REGRESSION ANALYSIS

In the previous chapters it was shown that the measured meteorologic parameters were moderately correlated with the δD and $\delta^{18}O$ values for bulk and discretely collected rain samples. Using the correlation coefficient as basis for determining causality, rainfall amount and ambient air temperature each had correlation coefficients greater than 0.5, whereas rainfall intensity, relative humidity and cloud ceiling elevation had coefficients less than 0.5 suggesting less significant effect.

Perhaps the combined effect of the climatological factors tend to obscure any simple pattern that describes their influence on the seasonal variability in isotopic abundance ratios. In order to elucidate any patterns or causal relationships, linear and multilinear regression analyses were performed. Results from these statistical analyses were used to formulate predictive equations. Similarly, these results were used to evaluate which of the many meteorological parameters were most influential in determining the measured annual variation in relative isotopic abundance ratios. The focus was primarily on the formulation of predictive equations.

Linear Regression Analysis

The first step in developing equations to describe the annual fluctuation in isotopic abundance ratios was to re-examine the individual meteorologic factors and to compute the linear equations that best predict the expected value of the isotopic abundance ratios. The outcome of this was the development of three sets of linear equations for each of the six measured meteorologic parameters. A set was determined for each of the sample populations that represented the summer, the winter and the whole year.

These linear equations are of the standard form $Y = BX + A$. A correlation coefficient also was calculated so that the individual equations could be ranked on the basis of the strength of their statistical relationship.

Generally, the closer the data cluster about the regression line that best summarizes their relationship, the stronger the correlation between the variables. Where there is a perfect fit, the correlation coefficient, R, takes on values of +1 or -1, where the sign is the same as the sign of the slope of the best fit line. When the line is a poor fit to the measured data, R will tend toward zero.

The first statistical relationship examined in this study was that for oxygen-18 and deuterium. The rainfall data for the two year period of record were placed into three sets representing winter, summer and year. The three resulting equations, given in Table 3, each had slopes less than eight.

The summer data produced a regression line with the shallowest slope of the three populations. The implication of a shallow slope is

Table 3. δD versus $\delta^{18}O$ for winter, summer and combined rainfall populations.

Season	Equation	Correlation Coefficient
Summer	$\delta D = 5.05\ \delta^{18}O - 0.25$	0.938
Winter	$\delta D = 6.68\ \delta^{18}O - 6.45$	0.928
Combined	$\delta D = 5.98\ \delta^{18}O - 1.73$	0.939

that kinetic or fast evaporation was responsible for preventing equilibrium between the atmospheric water vapor and the falling raindrop. Based on slope, the summer population exhibited greater nonequilibrium evaporation than the other two populations.

The next statistical relationship examined was that between the meteorologic parameters and $\delta^{18}O$ and δD. Tables 4 and 5 contain sets of ranked linear equations. Average rainfall amount consistently has the largest correlation coefficient.

Table 6 contains a set of equations predicting δ values for the combined rain population. Temperature, in degrees Celsius, and rainfall amount in millimeters, show favorable correlation ($R > 0.5$).

Multiple Regression Analysis

A multiple regression analysis was performed on the data presented in Tables 1 and 2 in order to statistically evaluate the best combination of meteorologic parameters to describe the variation in oxygen-18 and deuterium values of bulk rain samples on an annual or seasonal basis. The primary goal was to produce a set of equations that were a linear combination of independent meteorologic variables that could be used to predict isotopic abundance ratios in Tucson rain water. The secondary goal of the multiple regression analysis was to rank each of the meteorologic parameters in terms of their importance in determining δ values.

The order in which independent variables were introduced into the regression equations by the SPSS subroutine REGRESSION/STEPWISE was based on the statistical F-test which measured the relative

Table 4. Linear equations of $\delta^{18}O$ and δD versus ground level meteorological conditions for summer rainfall events.

Equation	Correlation Coefficient
$\delta^{18}O$ = - 0.320 Amount (mm) - 1.043	- 0.578
$\delta^{18}O$ = 0.592 Temperature (°C) - 15.214	0.507
$\delta^{18}O$ = 0.249 Elevation (10^3m) - 8.892	0.477
$\delta^{18}O$ = - 0.093 Intensity (mm/hr) - 1.950	- 0.293
$\delta^{18}O$ = 0.010 Relative Humidity (%) - 2.241	0.065
δD = - 1.790 Amount (mm) - 4.690	- 0.588
δD = 1.149 Elevation (10^3m) - 42.555	0.427
δD = - 0.659 Intensity (mm/hr) - 7.190	- 0.388
δD = 1.960 Temperature (°C) - 54.189	0.345
δD = 0.173 Relative Humidity (%) - 19.300	0.154

Table 5. Linear equations of $\delta^{18}O$ and δD versus ground level meteorological conditions for winter rainfall events.

Equation	Correlation Coefficient
$\delta^{18}O$ = - 0.266 Amount (mm) - 5.336	- 0.614
$\delta^{18}O$ = 0.117 Elevation (10^3m) - 9.786	0.177
$\delta^{18}O$ = 0.076 Relative Humidity (%) - 14.713	0.169
$\delta^{18}O$ = - 0.109 Temperature (°C) - 8.663	- 0.097
$\delta^{18}O$ = - 0.046 Intensity (mm/hr) - 8.167	- 0.044
δD = - 1.253 Amount (mm) - 31.412	- 0.398
δD = 1.003 Temperature (°C) - 56.089	0.161
δD = - 0.512 Intensity (mm/hr) - 41.299	- 0.085
δD = 0.216 Elevation (10^3m) - 44.998	0.059
δD = 0.115 Relative Humidity (%) - 61.316	0.046

Table 6. Linear equations of $\delta^{18}O$ and δD versus ground level meteorological conditions for combined summer and winter rainfall events.

Equation	Correlation Coefficient
$\delta^{18}O = 0.358$ Temperature (°C) - 10.550	0.621
$\delta^{18}O = -0.328$ Amount (mm) - 2.754	- 0.607
$\delta^{18}O = 0.283$ Elevation (10^3m) - 10.966	0.477
$\delta^{18}O = -0.069$ Relative Humidity (%) - 1.329	- 0.156
$\delta^{18}O = 0.031$ Intensity (mm/hr) - 6.248	0.072
$\delta D = 2.197$ Temperature (°C) - 60.148	0.703
$\delta D = -1.680$ Amount (mm) - 15.569	- 0.492
$\delta D = 1.261$ Elevation (10^3m) - 52.775	0.398
$\delta D = -0.528$ Relative Humidity (%) + 2.386	- 0.206
$\delta D = 0.005$ Intensity (mm/hr) - 30.586	0.002

contribution of each dependent variable in explaining variance. The subroutine would enter and delete variables with each new iteration, provided that the new equation explained a greater amount of variance in the dependent variables.

Table 7 contains two equations that predict $\delta^{18}O$ and δD in summer rain samples based on measured ground level meteorological conditions. These two equations have rainfall amount and temperature as their primary terms.

Table 8 contains equations for winter rainfall data. Rainfall amount and temperature are still the dominant factors.

Table 9 has two sets of regression equations for the total or combined rainfall population. As in the equations for summer and winter populations, both temperature and rainfall amount are the most important parameters in explaining annual isotopic variation.

As a visual demonstration of the ability of the regression equations to predict oxygen-18 and deuterium concentrations, Figures 15 and 16 were prepared using the two equations presented in Table 9. As seen on Figure 15, the regression equation for predicting oxygen-18 has a good correlation ($R = 0.78$) with measured values of $\delta^{18}O$. Correlation between measured and predicted δD was fair ($R = 0.56$) as shown on Figure 16.

Table 7. Multiple regression equations of $\delta^{18}O$ and δD based on ground level meteorological conditions for summer rainfall events.

Equation / Correlation Coefficient
$\delta^{18}O$ = - 0.283 Amount (mm) + 0.836 Temperature (°C) - 0.101 Intensity (mm/hr) + 0.043 Elevation (10^3m) - 18.280
R = 0.856
δD = -1.446 Amount (mm) + 3.329 Temperature (°C) - 0.633 Intensity (mm/hr) + 0.316 Elevation (10^3m) - 74.353
R = 0.795

Table 8. Multiple regression equations of $\delta^{18}O$ and δD based on ground level meteorological conditions for winter rainfall events.

Equation / Correlation Coefficient
$\delta^{18}O$ = -0.293 Amount (mm) + 0.232 Temperature (°C)
- 0.193 Intensity (mm/hr) + 0.070 Relative Humidity (%)
+ 0.075 Elevation (10^3 m) - 11.106
R = 0.666
δD = - 1.652 Amount (mm) + 2.144 Temperature (°C)
- 1.441 Intensity (mm/hr) - 0.173 Relative Humidity (%) - 40.995
R = 0.579

Table 9. Multiple regression equations of $\delta^{18}O$ and δD based on ground level meteorological conditions for combined summer and winter rainfall events.

Equations / Correlation Coefficient
$\delta^{18}O = 0.413$ Temperature (°C) - 0.248 Amount (mm) - 0.137 Intensity (mm/hr) + 0.066 Relative Humidity (%) - 0.032 Elevation (10^3 m) - 12.555
$R = 0.845$
$\delta D = 3.361$ Temperature (°C) - 1.337 Intensity (mm/hr) - 0.891 Amount (mm) + 0.299 Relative Humidity (%) - 0.430 Elevation (10^3 m) - 64.140
$R = 0.912$

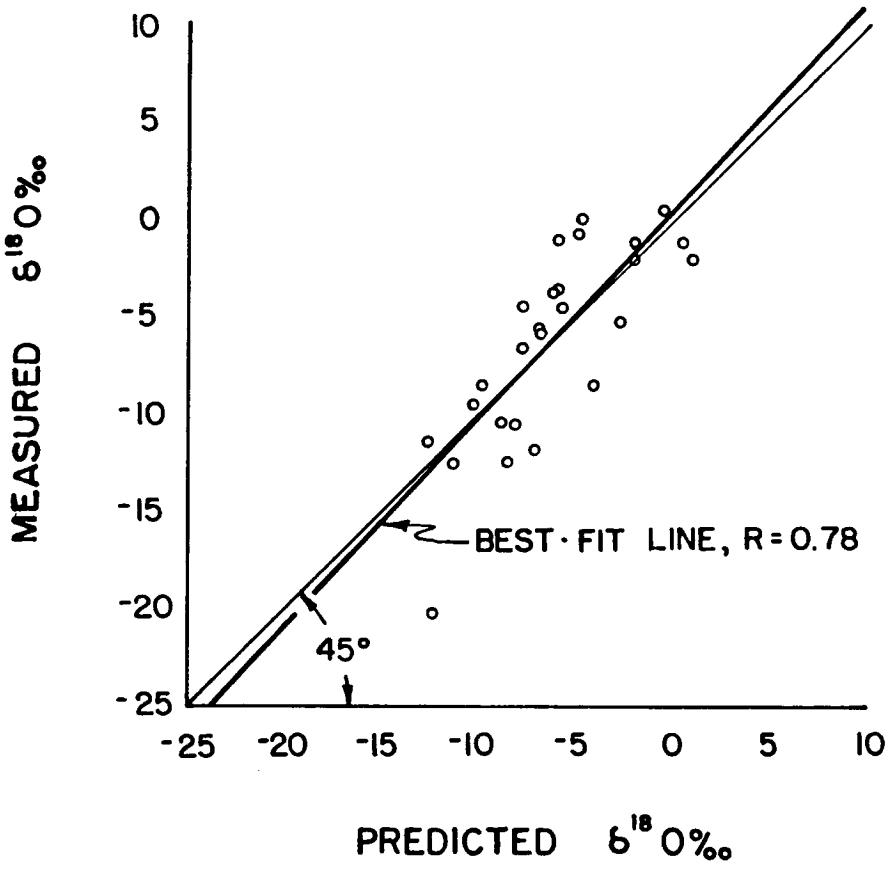


Figure 15. Measured versus predicted $\delta^{18}O$.

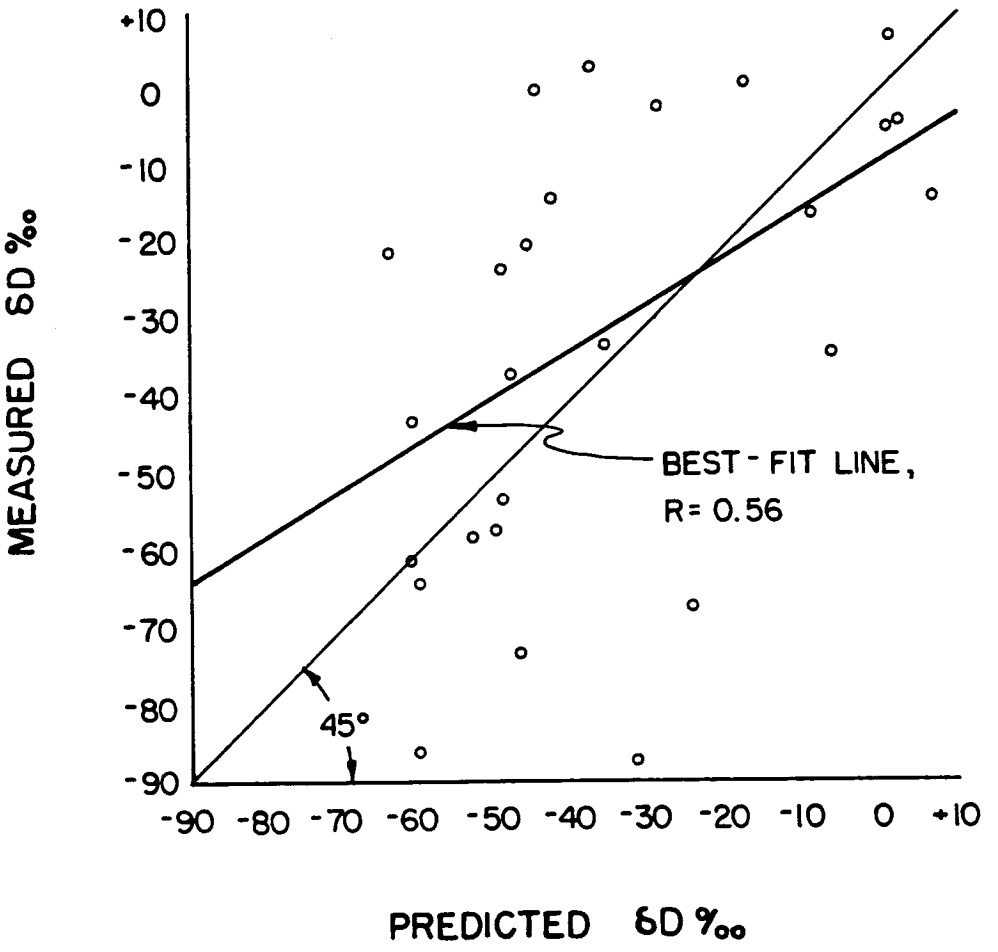


Figure 16. Measured versus predicted δD.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR ADDITIONAL RESEARCH

This final chapter contains a set of conclusions and recommendations based on a reflection of the four parts of this investigation. These four parts were (1) the collection and storage of representative rain samples, (2) the laboratory preparation and mass spectrometric analysis of the water samples, (3) the evaluation and synthesis of the available meteorologic records, and (4) the statistical analysis and interpretation of the data base.

Conclusions

Rain water collected during 1978 and 1979 in the Tucson Basin exhibited a large seasonal variation in the abundance ratios of oxygen and hydrogen isotopes. A simple statistical analysis showed that there were two distinct groups of δ values for the two rainfall seasons. The seasonal isotopic fluctuation reported here corroborated results presented earlier by Simpson (1970) and White (1976).

The regression equation of δD and $\delta^{18}O$ was shown to have a slope less than eight for each of the three statistical populations. The obtained slopes, 5.0, 7.0 and 5.9, for summer, winter and combined populations, respectively, suggest that kinetic or fast evaporation was responsible for the shift from the equilibrium slope of eight.

A set of predictive equations, based on multiple regression analysis, was presented. These equations had moderate to good correlation between the meteorologic parameters and the measured values of $\delta^{18}O$ and δD. Rainfall amount was found to be the most significant factor in predicting summer and winter δ values. Because of the large difference in summer and winter rainfall temperatures, this parameter became the best indicator of seasonal variations in $\delta^{18}O$ and δD.

Ground level measurements of rainfall amount, rainfall intensity, ambient air temperature, relative humidity and cloud ceiling elevation were collected in conjunction with bulk and fractional rain samples. These individual meteoric parameters demonstrated a moderate to very poor statistical correlation with the measured δ values. Rainfall amount had the largest individual correlation coefficient for both the summer and winter populations. Temperature had very poor correlation with summer and winter populations, whereas, for the combined population, temperature had the largest correlation coefficient of the meteorologic parameters tested.

Recommendations

The following is a set of suggested recommendations to be considered by future researchers involved in the study of the variation in isotopic abundance ratios of rainfall from arid environments.

1. Collect discrete or fractional samples of sufficient volume to facilitate analysis of both hydrogen and oxygen isotopes. The set of samples for the individual storms would, after isotopic analysis, reveal any tendency for kinetic evaporation. This

tendency would be illustrated by a shallow slope of the best-fit line through the data points when $\delta^{18}O$ is plotted against δD. Discrete rain samples could easily be collected with the hermetically self-sealing rain sampler developed and tested by Adar and others (1980) in the Negev Desert in Israel.

2. Install and monitor the recording raingage and hydrothermograph at the rainfall collection site. This would permit greater confidence in the degree to which measurements are representative of conditions affecting the raindrops, particularly those falling during summer thunderstorms of limited areal extent.
3. Collection of rain by airplane at or just below cloud height in order to better examine elevational differences in isotopic abundance ratios.
4. It is recommended that a more detailed investigation of the theoretical fractionation models be implemented by future researchers. This additional work should shed light on the question of the validity of the linear models presented in this preliminary paper.
5. Collection of rain samples and subsequent analysis of these samples should be continued in order to increase the statistical population and reduce the uncertainty in any newly formulated predictive equations.

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