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Distinguishing seasonal recharge to groundwater by deuterium analysis in southern Arizona

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ABSTRACT: The Tucson Groundwater Basin in southern Arizona covers an area in excess of 600 square miles and contains fill that averages more than 1,000 feet thick. The apparent age of groundwater as determined by C-14 analyses ranges from zero (near recharge areas) to about 6,000 years. Average annual precipitation is about 11 inches, slightly more than half of which occurs during the summer as convective storms and most of the remainder during the winter as frontal storms. Summer moisture mostly originates in the Gulf of Mexico and winter moisture mostly comes from the Pacific Ocean. All streams in the basin are intermittent. Our current research attempts to estimate the relative importance of winter versus summer precipitation in recharging the Basin by studing the distribution of deuterium in rainfall, snowmelt, stream flow and groundwater. Seventeen summer storms in 1968 show a weighted average deuterium value of −4.2 percent (relative to SMOW), and 14 winter storms in 1968-69 show a weighted average value of −6.1 percent. Two groundwater samples from wells near a recharge area show −6.6 and −6.3 percent values. Two other wells in widely separated parts of the valley, tapping much older water, show values of −5.8 percent each. The deuterium values for most snowfall and snowmelt in the surrounding mountains range from about −6 to −11 percent. The greater isotopic similarity between winter precipitation and groundwater gives strong reason to suspect that winter runoff is the dominant factor in producing recharge to the Basin. A program is planned to provide sufficient data for a more precise statistical analysis of this hypothesis. It is hoped that an analysis of deuterium distribution in groundwater combined with C-14 ages, will provide a means for detecting past climatic changes.

INTRODUCTION

This paper reports the results of a one-year exploratory study of the distribution of deuterium in rainfall, snow, stream runoff, and groundwater in and near the city of Tucson in southern Arizona. The original impetus to make the study arose from a desire to find a way to distinguish between recharge to groundwater in basin alluvium that occurred as a result of summer precipitation from that resulting from winter precipitation. The regional weather pattern is such that most summer moisture is advected from the Gulf of Mexico and sub-tropical Atlantic Ocean, whereas most winter moisture is advected from

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the Pacific Ocean. It was therefore suspected that the deuterium content of summer precipitation is significantly different from that of winter precipitation. The first-year results show that a difference does occur and that there is reason to believe that continued and careful sampling will provide information on the history of groundwater accumulation. In addition, although beyond the scope of this report, it appears that useful information can also be obtained on snowmelt-runoff relationships and on the ageing of snow (Judy, Meiman and Friedman, 1970).

In southern Arizona, as in many other arid and semi-arid regions, the groundwater now in storage accumulated over past centuries and millenia, and the volume in storage is immense compared to the amount annually recharged. Furthermore, the areas of recharge are small compared with the total area of exposed alluvium.

Areas of natural recharge may be divided into two kinds: (1) channel bottom areas which provide recharge only during periods of stream runoff, and (2) mountainfront areas which provides ubsurface recharge by groundwater flowing from fractures in rocks of the mountain mass to pores of the basin alluvium, more or less continuously. In each case, the particular conditions of the local watershed, rock type, depth to the water table, vegetative cover, etc., impose a specific chemical and isotopic character to the recharged water. In recent years, attempts have been made to define source areas of recharge by studying the areal distribution of the minerals dissolved in groundwater (Smoor, 1967; Laney, 1970) and the age of groundwater by C-14 analysis (Bennett, 1965). These studies represent a beginning in the Tucson area to relate chemistry with hydrogeology, mainly in terms of identifying source areas for particular water types. It is possible that closer analysis will yield information on magnitude of recharge as well.

Estimates of the magnitude of recharge through channel bottoms have been made by (1) measuring channel losses and deducting estimated evapo-transpiration losses (Burkham, 1970), (2) making an overall water balance wherein recharge is the solved for unknown variable; this kind of analysis makes no distinction between channel bottom recharge and mountain-front recharge (Schwalen and Shaw, 1961), and (3) assuming an aquifer response model and calculating the recharge (input) from measurements of water level response (output) in wells located near the recharging stream channel (Foster, 1969). Very recently, a method for estimating both channel bottom and mountain-front recharge by their effect on geothermal heat flux has been developed (Supkow, 1970).

Where storage is large compared to annual recharge, it is perhaps more important to know long-term average rates of recharge, than to know its value for a particular year, and in the end it may be easier to develop methods for determining long-term averages than year-to-year values. Moreover, knowledge of long-term seasonal distribution of recharge provides a more perfect understanding of water balance from the scientific point of view, and is important to water management in the design of structures to increase recharge by artificial means. It is especially important to be able to detect changes in recharge resulting from such things as lowering of the water table, urbanization, and other effects of man's activity. Notwithstanding the attention given to the problem, great uncertainty exists. In a recent discussion of a paper by Sorey and Matlock (1969), K.G. Renard (1969), Director of the Southwest Watershed Research Center, U.S.D.A., stated that: "For this reason [uncertainty of amount of water transpired by riparian vegetation] estimates of the distribution of transmission-loss water between groundwater recharge, evaporation, and transpiration are at best 'guesstimates' by trained scientists or technicians."

THEORY

The concentration of deuterium in a water sample is measured relative to its concentration in standard mean ocean water (SMOW) available to laboratories performing stable

isotope analyses. In SMOW there is approximately 1 atom of deuterium to 6500 atoms of hydrogen; or, in other terms, the concentration by weight of HDO in H_2O is about 300 p.p.m. The deuterium content is expressed as a percent difference between the sample and SMOW, denoted by δ, where

$$\delta = \frac{(D/H)\text{ sample} - (D/H)\text{ SMOW}}{(D/H)\text{ SMOW}} \times 100$$

Near-surface ocean water from equatorial and mid-latitudes, from whence most atmospheric water vapour originates, is slightly heavier in deuterium than SMOW. In the Pacific, the maximum delta value is about +1 percent and in the Atlantic Ocean, the maximum delta value is about +0.5 percent (Friedman, *et al.*, 1964).

During the processes of evaporation and condensation a fractionation occurs because the vapour pressure of HDO is different from that of H_2O. Under equilibrium conditions, the fractionation coefficient is equal to the ratio of vapour pressures (Friedman, *et al.*, 1964). For example, the fractionation coefficient for evaporation at 20°C is about 0.93. Hence, water vapour at 20°C will contain about 7 percent less deuterium than that of the water from which it was evaporated. In the process of condensation, the fractionation coefficient is the inverse of that for evaporation, or about 1.07. Hence, water at 20°C will contain about 7 percent more deuterium than the vapour from which it was condensed. As temperature increases, the difference between the vapour pressure of HDO and H_2O decreases, and the fractionation coefficient nears a value of 1.0.

When this process is applied to evaporation from the ocean and subsequent precipitation of the vapour on land, the ocean may be regarded as an infinite source of constant deuterium concentration (at least to a first approximation), whereas the atmospheric vapour is finite. That is, all the vapour arising from ocean water in mid-latitudes will have a delta value of about −5 to −7 percent. However, when this vapour precipitates only the first portion of the condensate will have a delta value close to that of the original ocean water. The remaining vapour, after each precipitation event, becomes progressively poorer in deuterium.

In a general way, the further a vapour mass travels from its region of origin, the more precipitation events will have occurred within it, and the poorer the remaining vapour becomes in deuterium content (see, for example, Thatcher, 1967). Furthermore, since condensation and freezing occur progressively with increasing altitude, there is a tendency for precipitation at high altitude to be poorer in deuterium than precipitation at low altitude. Another mechanism producing the same result, is that of evaporation from raindrops as they fall. If a portion of a raindrop evaporates between the time of condensation and the time of arrival at the land surface, the remaining water in the drop will be enriched in deuterium.

It is evident that the deuterium content of a given sample of rainfall or snowfall results from a combination of many factors. The most important of these are: (1) the deuterium concentration and temperature of the water from which the vapour mass came, (2) the mixing of that vapour mass with vapour from other sources, (3) precipation from the vapour mass occurring earlier along its path, (4) temperature at which the given sample was precipitated, (5) exchange between the raindrop or snowflake and the water vapour in the air through which they fall, (6) evaporation from the drop or flake into the air through wich they fall, and (7) evaporation of the sample between the time of accumulation in a rain gage or other collecting device, and the time the sample is bottled.

In southern Arizona, it would appear that factors 3, 4, and 6 of the preceding paragraph are particularly important in producing a different deuterium content in winter than in summer precipitation. The path of winter vapour from the Pacific to southern Arizona is longer and undergoes more prior precipitation events than that of summer vapour from the Gulf of Mexico; the average temperature of precipitation is colder in winter than in

summer; winter (frontal) storms are more widespread, longer lasting, and less intense than summer (convective) storms, minimizing evaporation from raindrops as they fall. These factors singly and in combination, should produce precipitation in winter containing a lower concentration of deuterium than in summer.

In this paper, it is not our purpose to explore in detail the mechanisms that could produce a seasonal distribution of deuterium concentration. Rather we wish to determine whether or not a distribution exists and, if so, whether or not it can be applied to the solution of problems related to recharge and water balance in the Tucson basin. The set of data collected during 1968-69 does show a seasonal distribution of deuterium. The sample is too small, both in space and time to draw more than tentative conclusions, given in the following sections. A closer analysis of mechanisms no doubt will be required consistent with the accumulation of additional data. In particular, the question of "stationarity" of the time series, represented by seasonal deuterium pulses over the past several thousand years, will have to be examined. Analysis of carbonate fractions in lake marls and mollusks indicates that the mean oxygen-18 content of atmospheric precipitation probably has been stable during the past 9,000 years in northeastern United States (Stuiver, 1968). If so, it may be inferred that the mean content of deuterium in atmospheric precipitation also was stable. A figure given by Epstein, *et al.* (1970), indicates that the delta value for deuterium in Antarctic ice fluctuated in a random manner within a range of about 2 percent over the past 9,000 years. No similar data are available for southwestern United States at the present time. An examination also should be made of possible fractionation within the unsaturated zone, through which recharge water passes. Evapo-transpiration mechanisms in this zone could remove part of the water being recharged; this effect, if significant, would tend to enrich the remaining water in deuterium.

THE TUCSON BASIN AQUIFER

The alluvium that underlies the valley of the Santa Cruz River in Pima and Santa Cruz counties of southern Arizona, constitutes one of the most important aquifers of that region (Davidson, 1970). For purposes of this paper, the Tucson Basin Aquifer is regarded as that part of the Santa Cruz Valley alluvium utilized in the City of Tucson and its environs as a source for municipal, industrial and irrigation water supply. So defined, the aquifer covers about 600 square miles. All of the water utilized for these purposes is pumped from wells. Average annual consumption is about 125,000 acre-feet (about 110 million gallons per day), of which about 75,000 acre-feet are for municipal and industrial use and the remainder for irrigation. Currently, the amount of water withdrawn exceeds the amount of average natural replenishment by a factor of 2 or there abouts. The average thickness of the alluvium is on the order of a few thousand feet, but almost all of the water is pumped from the upper 500 feet. The future utilisation of water from the deeper horizons is uncertain because they are, in general, of low permeability and contain water of poor chemical quality.

The surface elevation of the Tucson Basin aquifer ranges from about 2400 feet to 3000 feet above mean sea level. Mountains to the east and to the north rise to elevations of 8,000 feet and 9,000 feet. Hills of volcanic origin to the west rise to elevations of about 4,000 feet. Drainage of both surface and subsurface water is to the north and northwest. Except in the higher mountains, all streamflow is intermittent, and rarely is runoff of sufficient magnitude to carry surface flow out of the basin. Rainfall in the basin averages about 11 inches per year, more than half of which occurs during the summer months July through September, most of the remaining precipitation occurs during the winter months December through March. The magitude of precipitation increases with elevation in the mountains. Near the summit of the mountains bordering the basin to the north, annual prnecipitation (much of which falls as snow) averages about 25 inches.

DEUTERIUM ANALYSES: RAINFALL

Rainfall samples for measurement of deuterium were collected at a private residence about a mile east of the University of Arizona. A can was placed under a 3-foot diameter galvanized iron collecting funnel and, in order to minimize evaporation, the sample in the can was bottled and sealed as soon as possible following each rainstorm. Rainfall amount was measured in a wedge-type rain gage, attached to a post about six feet above ground, adjacent to the funnel. Although this gage did not conform in all respects with standard U.S. Weather Bureau practice, it undoubtedly provided a much better estimate of rainfall amount at the sampling site than the nearest standard gage located at the University. Table 1 gives the results of sampling from April 1968 through May 1969. These data are also plotted on Figure 1.

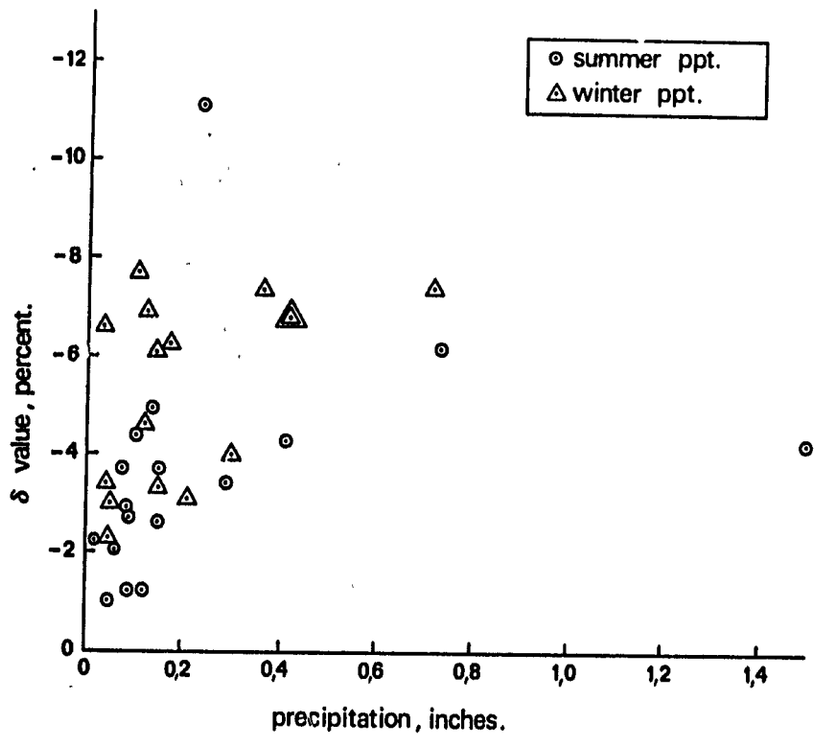

FIGURE 1. *Deuterium content of summer and winter precipitation in the Tucson Basin, Arizona, July 1968 through March 1969.*

During 1968-69 the distribution of deuterium in rainfall indicates: (1) winter rainfall contained less deuterium than did summer rainfall, and (2) there is a tendency, both in summer and winter, for deuterium concentration to decrease with an increase in amount of precipitation per storm.

An analysis of weather patterns associated with the summer storms from 4 July 1968 through 31 August 1968 was made by G.J. Nibler, graduate student in hydrology at the University of Arizona, for which work we make grateful acknowledgement. Mr. Nibler found that all storms, except those of 4 July 1968 and 19-20 August 1968, were associated with synoptic patterns typical of the summer type. However, he found no peculiarities in

TABLE 1. The deuterium content (percent departure, δ, from SMOW) and amount of precipitation collected at a site in the Tucson Basin (a)

Date	Amount (inches)	δ	δ × inches	
4 July 1968	0.23	−11.1	(b)	
18	.08	− 2.9	−.232	
19	.06	− 2.1	.126	
22	.09	− 2.8	.252	
25	.02	− 2.2	.044	
27	.13	− 4.9	.636	
30	.15	− 2.6	.390	
31	.29	− 3.4	.986	
3 Aug 1968	.05	− 1.0	.050	
4	.15	− 3.7	.555	
6	.41	− 4.3	1.760	
10	1.50	− 4.3	6.450	
19-20	.73	− 6.2	4.520	
30	.07	− 3.7	.259	
31	.10	− 4.4	.440	
2 Oct 1968	.12	− 1.2	.144	
3	.09	− 1.2	.108	
Totals	4.04		−16.952	Weighted mean = −4.2
13 Oct 1968	0.71	− 7.4	−5.250	
14	.41	− 6.8	2.790	
14 Nov 1968	.17	− 6.3	1.070	
20 Dec 1968	.10	− 7.7	.770	
26	.30	− 4.0	1.200	
27	.21	− 3.1	.651	
14 Jan 1969	.36	− 7.4	2.660	
15	.41	− 6.8	2.790	
22	.05	− 3.0	.150	
26	.03	− 6.6	.198	
7 Feb 1969	.15	− 3.3	.495	
20	.11	− 4.6	.506	
22	.12	− 6.9	.829	
7 Mar 1969	.04	− 2.2	.088	
11	.04	− 3.4	.136	
22	.14	− 6.1	.855	
Totals	3.35		−20.438	Weighted mean = −6.1

(a) Collection site located about one mile east of University of Arizona in Tucson (lat. 32°14′ N; long. 110°56′ W); land surface elevation about 2475 feet above mean sea level.
(b) This record not included in computing weighted mean (see text).

the weather charts for the typical summer storms of this period that might account for the observed range in delta values from −1.0 to −4.4.

The storm of 4 July 1968 provided the first rainfall in the area since the preceding April when sampling began. The weather patterns preceding the onset of this storm, even though of a summer type, indicate that the storm's moisture possibly orginated in the Pacific Ocean and that its trajectory was unusually long. Making the tentative assumption that this storm was a rare event, it was not included in the weighted mean delta value for summer precipitation. The storm of 19-20 August was associated with synoptic patterns similar to the winter type. A more extended investigation will be made to deter-

mine the frequency of this type of event. For the time being, we assume it is not a rare event and include it in computing the weighted mean. Synoptic maps were not studied beyond August 1968. In lieu of direct evidence, we assume that the change in delta values which occurred between the rain of 3 October 1968 and 13 October 1968 represents the shift from summer to winter type of atmospheric circulation in the region.

The total summer rainfall at the sampling site (including the storm of 4 July 1968) was 4.27 inches, which is about one inch below normal. The Weather Bureau record for the same summer season, gaged at the Tucson Airport, some 8 miles to the south, was 3.09 inches, and at the Univeristy of Arizona it was 4.23 inches.

DEUTERIUM ANALYSES: STREAM FLOW

During 1968-69, seventeen samples were collected from some half-dozen small streams whose watersheds are mostly at middle and high altitudes in the Santa Catalina Mountains to the north of Tucson. Our most complete record is for Sabino Canyon Creek (table 2). The delta values for this creek are similar to all the others. The record for Sabino Canyon creek shows that: (1) the deuterium content is least in early spring during periods of maximum snowmelt, and (2) the spring runoff in 1968 contained a lower concentration of deuterium than did the spring runoff in 1969. The deuterium content in snow sampled during the two winters showed about the same deuterium content, except for a late snowfall in March 1968 that was exceptionally low in deuterium (table 3).

TABLE 2. The deuterium content (percent departure, δ, from SMOW) of flow in Sabino Canyon creek; elevation of sampling site, 2720 feet; maximum elevation of watershed 9,100 feet; area of watershed above sampling point, 35.5 square miles

Date	δ
15 March 1968	−7.9
23 May 1968	−6.6
9 June 1968	−6.0
4 Sept 1968	−5.7
9 Feb 1969	−6.6
2 March 1969	−6.4
23 March 1969	−6.1

Sabino Canyon creek is a perennial stream in most of the portion of its watershed lying within the mountains, but flow out of its canyon occurs only during periods of active snowmelt or prolonged or intense rainstorms. Below the mouth of the canyon, Sabino Canyon creek flows across a dissected alluvial fan and then joins Rillito Creek which flows westerly on alluvium near the base of the Santa Catalina Mountains. Rillito Creek is known to contribute recharge to groundwater through its channel bottom.

The delta values obtained in Sabino Canyon creek in May, June, and September of 1968 (table 2) should be indicative of the delta values of groundwater in the fractured rock of the mountains. During this period there was no rainfall and only insignificant snowmelt contributing to overland runoff. Hence, the flow of the creek must have been supported by effluent groundwater seepage.

DEUTERIUM ANALYSES: SNOW

Twenty-two analyses were made of snow, sampled at various elevations in the Santa Catalina Mountains. Table 3 gives the results for the samples taken near the summit

TABLE 3. The deuterium content (percent departure, δ, from SMOW) of snow sampled near the summit of Mt. Lemmon; elevation about 9,000 feet.

Date	δ	Remarks
15 March 1968	−10.1	New snow
15 March 1968	− 7.6	Old snow
23 May 1968	− 6.5	Depth, 0 to 6 inches below snow surface
23 May 1968	− 5.1	Depth, 5 to 10 inches below snow surface
25 February 1969	− 6.1	New snow
25 February 1969	− 2.7	Second layer, 9 to 11 inches
25 February 1969	− 6.4	Third layer, 13 to 22 inches

of Mt. Lemmon, within the watershed of Sabino Canyon creek. As was the case with streamflow, the delta values for these samples are similar to those sampled at other sites on the same dates.

DEUTERIUM ANALYSES: GROUNDWATER

Four samples of groundwater were analyzed and the results are given in table 4. The wells from which water was sampled are in widely different locations. Well SC-21, about 14 miles south of the city, taps water of unknown age, but probably not extremely old since it is within a few miles of possible recharge areas. The Avra Valley well, about 14 miles west of the city, is west of the Tucson Mountains, and isolated from the water in the Tucson basin. The age of the water in this well also is unknown, but probably is quite old. The two observation wells at the University of Arizona Campbell Avenue farm, near Rillito Creek, tap water that undoubtedly is very young. Water taken from a nearby pumped well (Bennett, 1965) had an apparent C-14 age of zero years.

TABLE 4. The deuterium content (percent departure, δ, from SMOW) of groundwater

Date	δ	Remarks
26 March 1968	−5.8	Tucson City well SC-21, in Santa Cruz Valley, about 14 miles south of Tucson; depth to water, 160 feet; total depth of well, 600 feet.
May 1968	−5.8	Tucson City well, Avra Valley, about 14 miles west of Tucson.
4 Sept. 1968	−6.6	University of Arizona observation well, A-4, Campbell Avenue farm, about 50 feet from south bank of Rillito Creek; depth of well about 75 feet.
4 Sept. 1968	−6.3	University of Arizona observation well, A-6, as above except about 500 feet from bank of Rillito Creek.

The samples from observation wells A-4 and A-6 suggest some interesting possibilities. These wells tap water part of which undoubtedly was recharged from snowmelt via the channel bottom of Rillito Creek and part of which may have come from mountain front recharge coming out of the Santa Catalina Mountains. The groundwater in this area flows southward and westward away from both the channel and the mountain front. The difference in delta values either is due to deuterium differences in the annual recharge pulses, or to a mixing of water from both recharge sources in the farther well (A-6), or both. (Tritium age determinations will help here.) In either case it will be interesting

to determine how far down the flow lines a change in delta values persists. It possibly provides a means for estimating the mixing property of the aquifer.

Well SC-21 and the Avra Valley well are in regions of the aquifer that receive a much smaller fraction of snowmelt recharge than does the area near Rillito Creek. It is not surprising, therefore, that the deuterium content of this water is higher than that near Rillito Creek. However, the two wells are about 20 miles apart, and it is surprising that they show exactly the same delta value. The identity may be fortuitous or it may indicate a very small range in delta values over a large portion of the aquifer.

The groundwater data, though meager, are consistent with what is know concerning groundwater flow patterns in the area.

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DISCUSSION

Groundwater moves and mixes slowly. To the extent that it remains unmixed and can be sampled in small unmixed volumes, a groundwater system may be regarded as a slowly moving assemblage of discrete small volumes of water. In principle, for each such volume, we can identify its point of recharge into, pathway through, and point of discharge from the aquifer. On entering the aquifer, each small volume has certain chemical and physical

characteristics; specifically, temperature, concentrations of various gases and minerals dissolved in water, and radio-active and stable isotopes of elements in the water molecule itself.

For groundwater systems in steady-state flow we can, in principle, continuously describe the changes in chemical and physical cahracteristics of each small volume from recharge to discharge. This description requires the assumption that at any instant in time the changes in space, meaning the assemblage of small volumes along any flow path, would be repeated by changes with time in any individual small volume moving along the same flow path.

As a first approximation we assume that such changes are not random, but dependent on the sum of determinable antecedent conditions experienced by the small volume of water prior to its analysis. The main difficulty lies in the phrase "determinable antecedent conditions." Inputs to the systems that occurred tens, hundreds or even thousands of years ago are no longer directly measurable, but must be estimated by indirect methods. The individual physical and chemical peculiarities of each small volume as determined by analysis, may therefore be regarded as a kind of memory of its previous history.

The amount of information contained in any small volume is an inverse function of its degree of mixing with other small volumes of a different kind. As previously mentioned, such mixing may occur within the aquifer or in the sampling procedure, or by both mechanisms. Groundwater occupies a position somewhere between relatively mixed systems such as the lower atmosphere, streams, and shallow lakes and relatively unmixed systems such as tree rings, lake varves and snow layers. Hence, to decipher the "memory" of a small sample of groundwater, one must utilize chemical theory, a map of flow paths, and an estimate of mixing.

Our objective is to use the deuterium concentration to detect seasonal differences in recharge to groundwater. Winter precipitation appears to have less deuterium than summer precipitation, based on one year of record. If this record is representative of all previous years of input to the groundwater system, and if the four samples of groundwater are representative of all groundwater in the basin, then winter precipitation is clearly more important to recharge than summer precipitation.

Any fractionation due to evaporation or transpiration at the land surface or in channel bottoms, will tend to increase the deuterium concentration of water reaching the water table. Such fractionation undoubtedly occurs, especially during the simmer and has the effect of shifting the mean value of the input toward the value typical of winter precipitation and snowmelt. Once the recharged water is beyond the reach of evapo-transpiration processes, there should be little or no further fractionation. In this sense, the concentration of deuterium is conservative, since it is not subject to change either in time or space within the aquifer, except by mixing of waters having different concentrations.

Further work is required to adequately test the hypothesis that little or no summer runoff recharges groundwater. Streams will be sampled at or near one or more zones of recharge along arroyos during each flood event. Groundwater will also be sampled in observation wells to obtain, insofar as possible, unmixed samples from different depths. These data, collected over a period of years, will help determine the extent to which individual pulses of deuterium may be identified in moving through the aquifer, and also relative seasonal contributions.

deuterium in rainfall, snow, stream runoff, and groundwater in and near the city of Tucson and the time of arrival at the land surface, the remaining water in the drop will be enriched in deuterium.