Technical Report #8
The Use of Environmental Tracers
for the Estimation of Recharge
at Yucca Mountain: A Summary

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THE USE OF ENVIRONMENTAL TRACERS FOR ESTIMATION
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1.0   INTRODUCTION

Yucca Mountain has been identified a possible site for the nation's first high level nuclear waste repository. A detailed site characterization, during which additional information on the mechanical, geological, and hydrological systems at the site will be gathered, is scheduled to begin in the near future. A conceptual model of the hydrogeology has been proposed for Yucca Mountain and the surrounding area from data collected prior to initiation of the site characterization process. Because the potential repository is located above the water table in the unsaturated zone, the majority of the work related to future data collection will be in this zone. According to the current conceptual model, the unsaturated zone at Yucca Mountain is the zone which will provide the greatest buffer against release of radionuclides to the accessible environment.

The unsaturated zone at Yucca Mountain consists of alternating layers of welded and nonwelded tuff. Because the welded tuff is highly fractured, it is considered to be a dual porosity system, with distinct fracture and tuff matrix porosities. The flow of water through a dual porosity system in the unsaturated zone is highly complex and at present is not completely understood. A portion of the upcoming site characterization program will address this problem and will hopefully obtain data which will allow the dual porosity system to be modeled.

The current conceptual model of the unsaturated zone has the flow of water occurring primarily in the welded tuff matrix of the unit containing the repository horizon. This unit, the Topopah Springs welded (TSw) unit, is highly fractured with a matrix having a very low permeability. Thus, if matrix flow does provide the major water pathway, the time for radionuclides to reach the accessible environment from the repository is probably on the order of tens of thousands of years (Sinnock, et al., 1984; Sinnock, et al., 1986; WWL, 1986). However, if fracture flow occurs to a greater extent than is currently believed, radionuclides could possibly reach the accessible environment in a relatively short time period.

The amount of water passing through the TSw unit (flux) is one of the factors which determine whether matrix flow or fracture flow dominates. This

flux of water is a function of the amount of meteoric water which infiltrates through the overlying rock. At Yucca Mountain, there is considerable uncertainty as to the actual amount of net infiltration. The net infiltration is a function of precipitation and several other factors. A long-term record of direct precipitation measurements at Yucca Mountain is not available.

Limitations in the use of conventional tools for the study of the unsaturated, low permeability, dual porosity rock may require relatively new techniques for characterization of the Yucca Mountain site. The use of naturally occurring isotopes has been proposed as one method to determine the amount of precipitation which becomes net infiltration and, ultimately, the flux passing through the repository horizon. A number of isotopes have the potential for use in site characterization studies at Yucca Mountain. Some restrictions may exist for the use of a particular isotope due to its reaction characteristics or analytical restrictions. Hydrogen and oxygen both have isotopes which have been extensively utilized in hydrogeologic studies for decades. Because of recent advances in analytical instrumentation, chlorine and other isotopes are also becoming useful in hydrologic investigations. This paper will discuss various isotopes, how they are used in hydrologic studies, and the use or possible use of these isotopes during site characterization at Yucca Mountain.

2.0 MODELS FOR ISOTOPE STUDIES

Tracers have been utilized by the petroleum and mining industries in the study of surface and ground water systems and by others to determine transport mechanisms and flow patterns in porous media. The same principles which apply to the movement of artificially injected tracers also apply to natural species. The advantage of using natural environmental tracers is that perturbations to the system are minimized. The flow of tracers through a dual porosity, porous medium is a highly complex process, which is not completely understood. The use of natural radioactive and stable tracers have great potential to provide information on the flow regimes which are occurring or have occurred in the past at Yucca Mountain. Given the assumption that natural tracers were input into Yucca Mountain at a relatively constant rate during the past centuries, then an isotope which had a significant increase in the thermonuclear age provides a tracer pulse for analysis. Information from the analysis can show the effect which two phase flow has on the transfer of water and solutes through the various hydrogeologic units within Yucca Mountain. Changes in concentration of natural tracers in a hydrogeologic system can be an indication of long term flow patterns. On the other hand, artificially injected tracers are limited, both spatially and timewise, in characterizing formations.

The movement of water in porous media is usually described by Darcy's Law which states that the flow rate is proportional to the hydraulic conductivity in the surrounding porous media and hydraulic gradient across the porous media. The average groundwater velocity of the water within the media is inversely proportional to the effective porosity. For flow in an unsaturated, single porosity medium, the hydraulic conductivity becomes a function of the saturation of the material. In dual porosity systems where the fractures and fissures have a high degree of connectivity, the flow of water through the system becomes more complicated. In the saturated zone, water may tend to flow preferentially through the fracture network. In the unsaturated zone, depending upon system characteristics, water may flow primarily in the matrix, primarily in the fractures, or simultaneously in both.

2.1 MATHEMATICAL MODELS FOR SINGLE POROSITY SYSTEMS

Although hydrologic tests performed by injection of an artificial tracer generally require the analysis of changes in concentrations in two or three dimensions, natural tracers can often be analyzed with one-dimensional

equations since the input of natural tracers can be reasonably assumed to be of extensive lateral extent. The one-dimensional form of the advection-dispersion equation, including effects due to sorption and decay, in homogeneous, isotropic media under steady state, uniform flow is:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - R\lambda C \qquad (1)$$

in which x is a coordinate direction taken along the flowline, v is the average linear groundwater velocity, D is the coefficient of longitudinal hydrodynamic dispersion along the flow path, C is the solute concentration, R is the retardation factor (≥ 1), and λ is the decay constant. The average linear groundwater velocity, or seepage velocity, is obtained by dividing the Darcy flux, q, by the volumetric water content, θ, for partially saturated systems or the effective porosity, n_e, for saturated systems.

A tracer being transported by water in a porous medium will exhibit a different velocity than will the water. An ideal tracer, one which does not interact with the rock matrix in any way and is not subject to chemical or radioactive decay, will still show a "spreading" simply due to molecular diffusion. Mechanical dispersion is an additional mechanism by which the ideal tracer will spread. Mechanical dispersion occurs due to random variations of water velocities and directions in the individual pores of the porous media (IAEA, 1983). Laboratory data usually can not be used to describe dispersion in the field, as field dispersion coefficients seem to increase with increasing distances of plume travel (IAEA, 1983). Field observation of the spreading of the tracer pulse will give an indication of the dispersion along the flow path as well as transverse to the flow path. Theoretically, the dispersion coefficient can be determined from such field experiments. For an ideal tracer, the retardation factor, R, becomes equal to one and the decay constant, λ, becomes equal to zero. The term D can be expressed in terms of two components

$$D = \alpha v + D^* \qquad (2)$$

where α, the dispersivity, is a characteristic property of the porous medium, and D^* is the effective molecular diffusion coefficient.

For a non-ideal tracer, one which interacts with the rock matrix, the degree to which the tracer is slowed relative to the water flow must be determined. This slowing, or retardation, may be due to diffusion into the pores of the solid matrix, adsorption, ion exchange, chemical reactions, or other mechanisms. The summation of all these mechanisms is usually called sorption. The retardation factor, R, which is often used to roughly describe the sorption effect on the tracer flow can be conceptualized as:

$$R = \frac{T_t}{T_f} \tag{3}$$

where T represents the time of arrival at a plane some distance from the source and the subscripts t and f indicate the tracer and the flow, respectively. The retardation factor expresses how much slower the tracer moves than the water. Under equilibrium conditions, the adsorbed and solute concentrations are normally considered to be related according to a Freundlich-type isotherm

$$S = KC^{\eta} \tag{4}$$

where K and η are empirical constants and S represents the mass of absorbed solute per unit mass of solid. For the case of a linear isotherm ($\eta = 1$), the retardation factor is generally assumed to have the form

$$R = 1 + K (\rho/\theta) \tag{5}$$

where ρ represents the bulk density of the medium and θ is the volumetric water content (for saturated conditions θ is equal to the effective porosity of the medium, n_e). In groundwater literature, the term K in Eq. 5 is often called the distribution coefficient, K_d, and the retardation factor is given the symbol R_d. For the case of a nonlinear isotherm, the following relationship for R has been suggested:

$$R = 1 + \frac{\eta K \rho}{\theta} C^{\eta-1} \tag{6}$$

If the tracer under consideration is radioactive, the concentration of the tracer in the transporting water is reduced by radioactive decay as a function

of time. Depending on the half-life of the radionuclide or the time period for which tracers are being studied, the decay of the tracer may or may not be important. For short-lived nuclides (tritium, for example) radioactive decay is an important process which cannot be neglected in an analysis. Decay can often be neglected when the half-life is very long and relatively short time periods of flow are being analyzed (for example, during injection tests using radioactive tracers). However, the analysis of flow over extremely long time periods using natural tracers usually requires accounting for radioactive decay. Indeed, radioactive decay may be the primary mechanism in many cases by which important hydrologic parameters are deduced.

Analytical solutions to Eq. 1 are available for a variety of boundary and initial conditions (van Genuchten, 1982). The resultant equations are generally valid only for solutes that partition between solutions and solid according to a linear Freundlich isotherm (Eq. 5) since for the nonlinear cases an additional concentration term must be included in both sides of Eq. 1. Under such conditions, numerical techniques are often utilized to obtain a solution to Eq. 1.

2.2 MATHEMATICAL MODELS FOR DUAL POROSITY SYSTEMS

Fractured formations are usually anisotropic due to the frequency and orientation of the fractures and fissures. Therefore, the differences between longitudinal and transverse dispersivities are functions of the fractured media. Flow of tracers through most fractured rocks cannot be adequately described by the equations for single porosity, homogeneous rock. A qualitative picture of the increased complexity which a dual porosity system adds to tracer flow is shown on Figure 1. This figure shows the effects which molecular diffusion and adsorption have on the transport of a tracer through a dual porosity system. Diffusion into the matrix from the fracture can have a significant effect on the behavior of tracers.

For a saturated, dual porosity system, the concentration of the solute is initially high, yielding large rates of mass transfer from the fracture system to the matrix. The front of the tracer profile for a dual porosity, saturated system is shown at a given time, t_1, for three cases on Figure 1a. The solute tracer travels the longest distance in a system where the matrix is impermeable, and the shortest distance in the permeable matrix where diffusion and adsorption processes occur. The situation becomes more complicated in the

Saturated Conditions

Input Contration

Input Co— ┌Penetration by Diffusion

Input Co—

t_1

t_1

t_1

Fracture

Impermeable
Matrix

Permeable
Matrix

No Adsorption

Permeable
Matrix

Adsorption

(a)

Unsaturated Conditions

Impermeable
Matrix

Permeable
Matrix

Permeable
Matrix

Adsorption
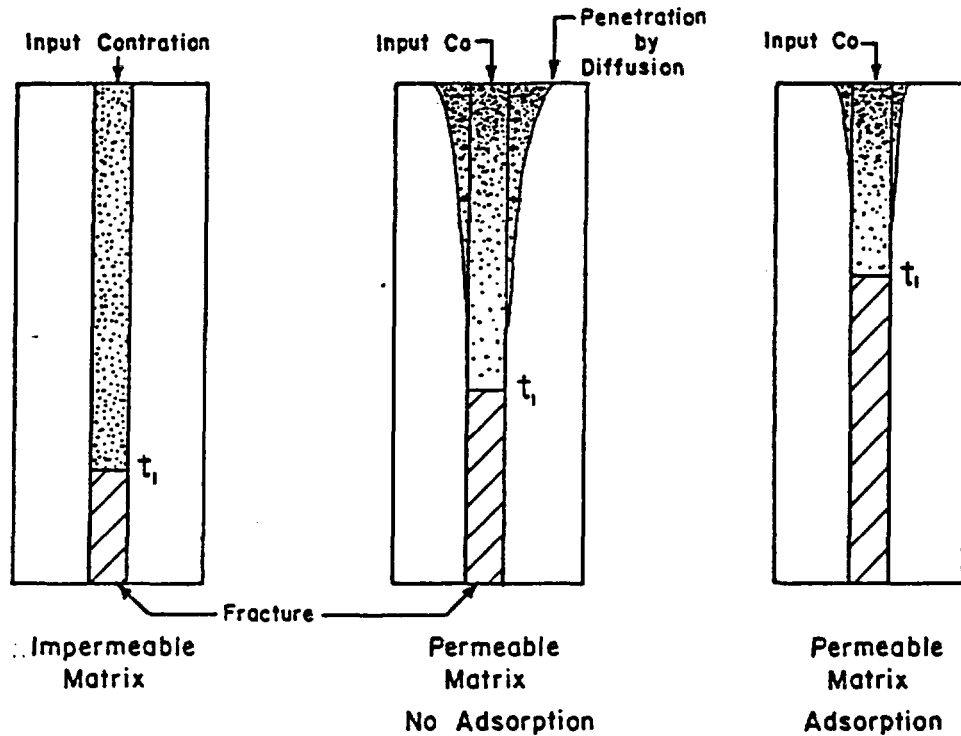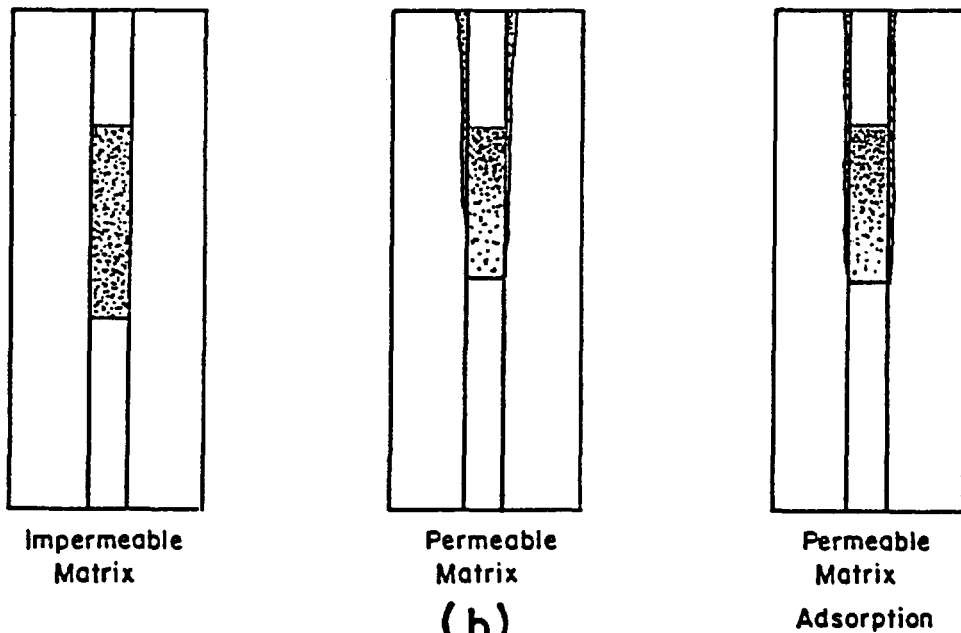
(b)

Air Phase

Water

Water with Solute
(Density of Dots Indicates Relative Concentration)

Water, Waste & Land, Inc.	Figure 1 Flow of Tracer through Dual Porosity Systems	Date: June 1987
		Project: 4001

unsaturated zone. For unsaturated conditions, two phase flow occurs not only
in the fracture but also in the matrix. For the ideal case where there is no
interaction between the fracture and an impermeable matrix, a plug of water
from an infiltration event can be represented as shown on Figure 1b. When the
matrix is permeable, solutes and fracture water can be transferred from the
fracture. This adds another degree of complexity to the system as the amount
of water from an infiltration event can vary, and thus the depth which the
water can reach is also a function of the precipitation.

An approach that has been proposed for mathematical modeling of
contaminant transport in fractured media is to couple a one-dimensional,
vertical model for transport in the fracture with a one-dimensional, horizontal
model for transport into the matrix (from the fracture). The differential
equation which describes transport in the fracture is (Tang et al., 1981):

$$\frac{\partial C'}{\partial t} + \frac{v'}{R'}\frac{\partial C'}{\partial z} - \frac{D'}{R'}\frac{\partial^2 c}{\partial z^2} + \lambda\,C' + \frac{q}{R'b} = 0 \tag{7}$$

in which C' is the concentration of solute in the fracture, v' represents the
groundwater velocity in the fracture, R' is the retardation factor for the
fracture face, D' is the hydrodynamic dispersion coefficient, λ is the decay
constant, b is the fracture width, q is the diffusive flux perpendicular to the
fracture face, and z is the coordinate axis along the axis of the fracture.
Eq. 7 is quite simply Eq. 1 written in terms of the fracture as the primary
mechanism for flow and transport. The final term on the left side of Eq. 7
represents the loss of tracer to the matrix as the solute passes through the
fracture.

By assuming that the transport within the matrix occurs primarily in
response to molecular diffusion allows Eq. 1 to be rewritten so that

$$\frac{\partial c}{\partial t} - \frac{D}{R}\frac{\partial^2 c}{\partial x^2} + \lambda\,c = 0 \tag{8}$$

where D represents the diffusion coefficient for the matrix material. In
general, it is necessary to reduce D below its free solution value, D*, to
account for tortuosity of the matrix. Eq. 7 is coupled to Eq. 8 through the

diffusive flux term which represents the diffusive mass crossing the fracture-matrix interface. This flux can be expressed according to Fick's first law as

$$q = - \theta D \left. \frac{\partial c}{\partial x} \right|_{x=b} \qquad (9)$$

where θ is the moisture content (effective porosity) of the matrix and b represents the location of the fracture-matrix interface along the x axis with x=0 located at the center of the fracture. Substituting Eq. 9 for q in Eq. 7 leads to

$$\frac{\partial C'}{\partial t} + \frac{v'}{R'} \frac{\partial C'}{\partial z} - \frac{D'}{R'} \frac{\partial^2 c}{\partial z^2} + \lambda C' - \frac{\theta D}{bR'} \left. \frac{\partial c}{\partial x} \right|_{x=b} = 0 \qquad (10)$$

which represents the coupled form of the equation for fracture transport. Appropriate boundary conditions for Eq. 10 are

$$C'(0,t) = C'_0 \qquad (11a)$$
$$C'(\infty,t) = 0 \qquad (11b)$$
$$C'(z,0) = 0 \qquad (11c)$$

where C'_0 is the source fluid concentration. Boundary conditions for Eq. 8 can be expressed as

$$c(b,z,t) = C'(z,t) \qquad (12a)$$
$$c(\infty,z,t) = 0 \qquad (12b)$$
$$c(x,z,0) = 0 \qquad (12c)$$

The coupling of the porous matrix to the fracture is provided by Eq. 12a and is based on the assumption that transverse diffusion and dispersion within the

fracture assures complete mixing across the fracture width in addition to the one dimensional nature of Eq. 10.

By assuming that the retardation coefficients, R', and R, are governed by the linear adsorption isotherm, Tang et al. (1981) and Sudicky and Frind (1982) obtained solutions for the coupled equations for a single fracture and parallel fractures, respectively. It should be noted that the fracture face retardation factor is defined as

$$R' = 1 + K_f/b \qquad\qquad\qquad\qquad (13)$$

where K_f is the fracture distribution coefficient and b is the half width of the fracture.

3.0 RADIOACTIVE ISOTOPES USED IN HYDROGEOLOGY

Isotope studies can be useful in determining the age of waters, the age gradients, the type of flow occurring, flow paths and mixing characteristics, pluvial conditions, and the amount of net flux (recharge) which is passing through the repository horizon. Therefore, isotopic studies can be used to further refine the conceptual model of flow in the unsaturated and saturated zones at Yucca Mountain and the surrounding environs. Radioactive isotopes which have been primarily used worldwide in studies of hydrogeological systems are tritium (^{3}H or usually T), carbon-14 (^{14}C), and chlorine-36 (^{36}Cl). Other radioactive isotopes also have been used or have the potential to be used in hydrogeological studies.

Many of the radioactive isotopes are produced naturally in the upper atmosphere by the interaction of gas molecules with primary or secondary cosmic radiation. After forming, the isotopes can slowly diffuse downward from the upper layers of the atmosphere and enter into the hydrologic cycle. Because of the variety of isotopes which are naturally formed, a large range of half-lives exist. This range in the decay rate is one of the principle reasons why the use of radioactive isotopes is valuable in the study of hydrogeologic systems. If the assumption is made that the flux of cosmic rays and chemical makeup of the upper atmosphere has remained relatively constant in the past, then the production of the radioactive isotopes may also be assumed to have been relatively constant. These radioactive isotopes enter into the surface and groundwater systems and because of radioactive decay, the change in the concentrations of the radioactive isotopes in the various waters can be used to estimate hydrogeologic parameters.

These parameters may be estimated by determining the age of the water, which is an indication of the travel time of water through the rock upgradient from the sampling site. The concentrations of isotopes in the groundwater are compared to the concentrations of the water where the meteoric water enters the formation. A good understanding of the mineralogy of the aquifer is necessary to account for isotope exchange and fractionation processes.

An additional amount of radioisotopes come from meteorites entering and vaporizing in the upper regions of the stratosphere. These radioisotopes eventually enter into the hydrologic cycle and fall to the surface of the Earth in rainfall. After the initiation of the thermonuclear age, large amounts of radioactive isotopes were injected into the atmosphere and hydrosphere,

primarily by weapons testing. In many of the atmospheric weapons tests significantly larger amounts of some radioactive isotopes were produced and entered the global atmosphere. Ultimately, these isotopes came down as fallout, either as particles or in rainwater. Some of the fallout entered into the surface and groundwater, thus forming a pulse tracer which can be identified in many instances by various testing techniques.

The types of measurements of radioisotopes can generally be classified according to radioisotope half-life. The radioisotopes having half-lives greater than about 10^9 years are measured by the build up of stable decay products. Radioisotopes with half-lives in the range of 10^3 to 10^8 years are difficult to measure and have until recently required large samples and long counting times. Radioisotopes with half-lives of less than a year can be measured with high sensitivity by conventional counting techniques.

For a number of radioisotopes in the 10^3 to 10^8 half-life range, a new technique has been developed to allow the measurement of these isotopes with enough sensitivity for detection at natural levels (Elmore and Phillips, 1987). The technique, called accelerator mass spectrometry (AMS) has been used to measure ^{36}Cl from one mg of total chloride with a background 10 to 100 times lower than those of conventional techniques. This can be compared to the conventional ^{36}Cl decay counting requirement of 40 g of total chloride extracted from thousands of liters of water (Elmore and Phillips, 1987). The precision of AMS varies depending upon the isotope, with natural samples usually limited in precision to about 3 to 10% by counting statistics. Elmore and Phillips (1987) concluded that AMS has been proven to have sensitive detection capability for five long-lived radioisotopes: ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, and ^{129}I.

3.1 TRITIUM

Tritium (T) is the heaviest isotope of hydrogen with an atomic mass of 3.016. Environmental tritium is introduced into atmospheric, surface and ground waters by cosmic radiation and by nuclear testing. The artificial tritium produced by nuclear testing is distributed throughout the hydrologic cycle by natural processes and therefore can serve as an environmental tracer pulse. During the past 10-20 years, tritium levels in atmospheric water have risen as much as three orders of magnitude over those in the pre-nuclear era. After entering a groundwater system, these peaks can be used to trace the flow

of water. However, because of its short half-life, 12.26 years, the time span
of tritium dating is limited to about 50 years.

3.1.1 Natural Atmospheric Production and Concentration

Tritium is naturally produced in the atmosphere by nuclear particles of
cosmic origin, mainly neutrons and protons, interacting with nitrogen and
oxygen nuclei. Only 3-5% of all the neutrons generated by cosmic rays in the
Earth's atmosphere take part in the production of tritium. The natural pre-
bomb steady state amount of tritium on the Earth formed by cosmic radiation was
estimated to vary between 3 and 10 kg (Ferronsky, 1982). Approximately 93% of
this tritium is contained in the hydrosphere and only about 7% is in the
atmosphere. Soon after production, tritium is oxidized to form molecules of
water (HTO). The stratosphere (the upper layer of the atmosphere) is the
reservoir where the bulk of the natural tritium is initially accumulated and is
the main source of the tropospheric tritiated water falling to the Earth's
surface as precipitation (Ferronsky, 1982).

Tritium is a soft beta emitter with a maximum energy of the beta particles
equal to 18 keV. The final product of tritium decay is the stable helium
isotope, ^{3}He. Because of the very small concentrations in which tritium is
usually found, it is common to express tritium concentrations in tritium units
(TU). A tritium unit corresponds to one atom of tritium per 10^{18} atoms of
hydrogen, which is equivalent to 3.2 pCi/liter. Prior to the first atmospheric
thermonuclear tests in 1952, few measurements of natural tritium on the Earth
had been performed. Therefore, pre-bomb tritium concentrations have been
estimated after studies indicated that considerable variation of tritium
concentration occurs both in time and space. The natural pre-bomb
concentration of tritium in precipitation has been estimated to range from 0.1
TU up to 10 TU. This range is based on a constant rate of atmospheric tritium
production of about 30 atoms/cm^2 min relative to the terrestrial surface
(Ferronsky, 1982).

3.1.2 Production and Global Distribution By Nuclear Tests

Thermonuclear tests in the atmosphere have provided another source of
atmospheric tritium since 1952. The amount of tritium released during
thermonuclear explosions has been estimated to be 0.7-5 kg per megaton of
thermonuclear fusion or 0.07 kg per megaton of thermonuclear fission

(Ferronsky, 1982). Beginning in August, 1958, high altitude explosions of greater than one megaton of energy were carried out. These tests continued until 1963 when the test ban treaty was signed. As a result of these tests, up to 200 kg of tritium was injected into the stratosphere (Ferronsky, 1982). A considerable amount of tritium in the environment also originates from the nuclear fuel reprocessing industries and nuclear power plants. Since most of this tritium will be collected and buried as radioactive waste, it is of negligible concern from a global distribution viewpoint as it cannot reach the stratosphere. However, on a local scale this should be taken into account when studying surface and ground water using tritium measurements.

The tritium content in atmospheric moisture reached its greatest values in 1963 following the most numerous and powerful atmospheric nuclear tests during the years 1961 -1962. Eriksson (1968) plotted the global-scale distribution of tritium in precipitation for 1963, based upon experimental data of tritium content from more than 100 meterological stations. This global distribution is shown on Figure 2. Tritium concentrations in precipitation have decreased gradually since 1963, due to fallout from the stratosphere as well as the short half-life of tritium. Figure 3 shows tritium variation in time for each of the three major bands of latitude.

Tritium concentration varies with distance from oceanic source, with elevation, and with latitude. Ferronsky (1982) presented a general picture of the global tritium distribution over time and concluded that although the degree of decrease of tritium content depends upon the site, the general features of its distribution remain unchanged. A comparison of the average global distribution of tritium in precipitation in 1965 and 1969 is shown on Figure 4.

3.1.3 Removal From Atmosphere

A number of investigators, beginning in the early 1950's, realized the use of tritium as a tracer in hydrologic studies. To use the tritium fallout to determine recharge the following three factors must be considered (Thatcher, 1967):

(1) the distribution of isotope with time in the annual precipitation,

(2) the distribution of precipitation intensity throughout the year, and

Figure 2
Global Distribution of Tritium in 1963
Adapted from Ferronsky (1983)

Date: June 1987

Project: 4001

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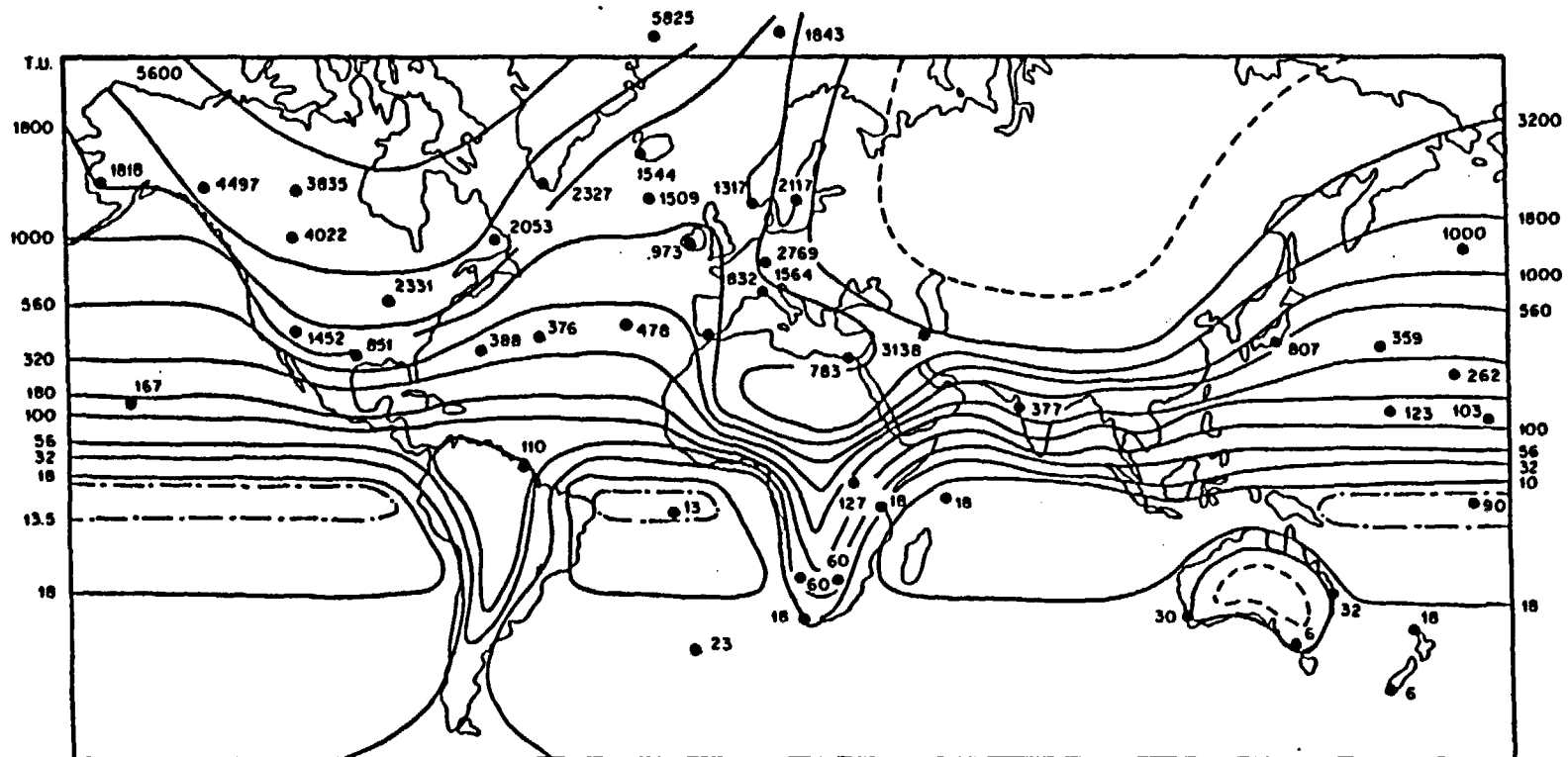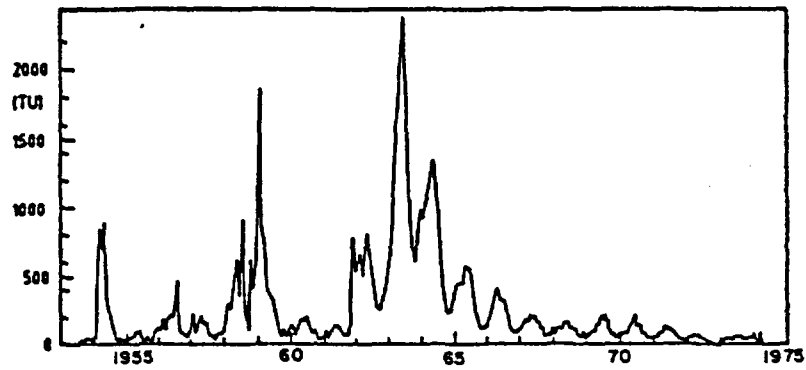
a) Northern Hemisphere
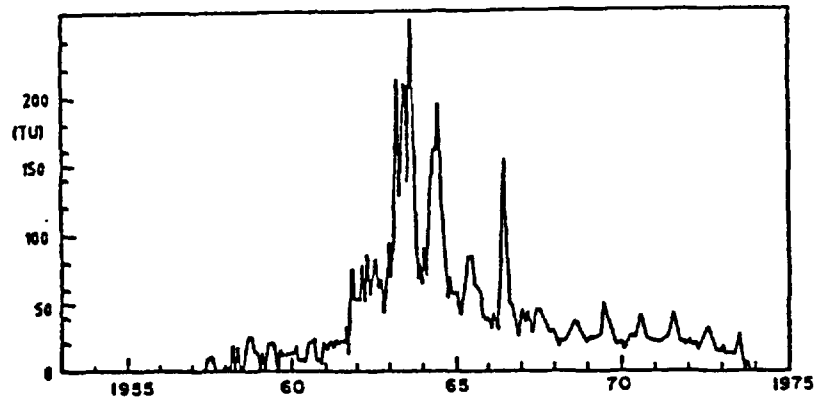
b) Tropics
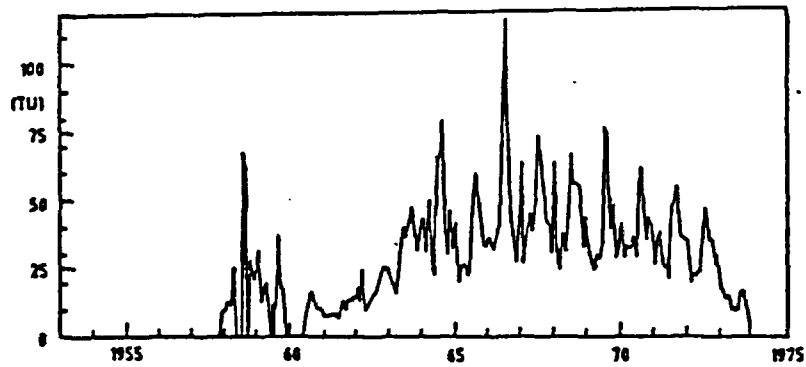
c) Southern Hemisphere

| | Figure 3 | Date: June 1987 |
| Water, Waste & Land, Inc. | Tritium Variation with Time and Latitude | Project: 4001 |
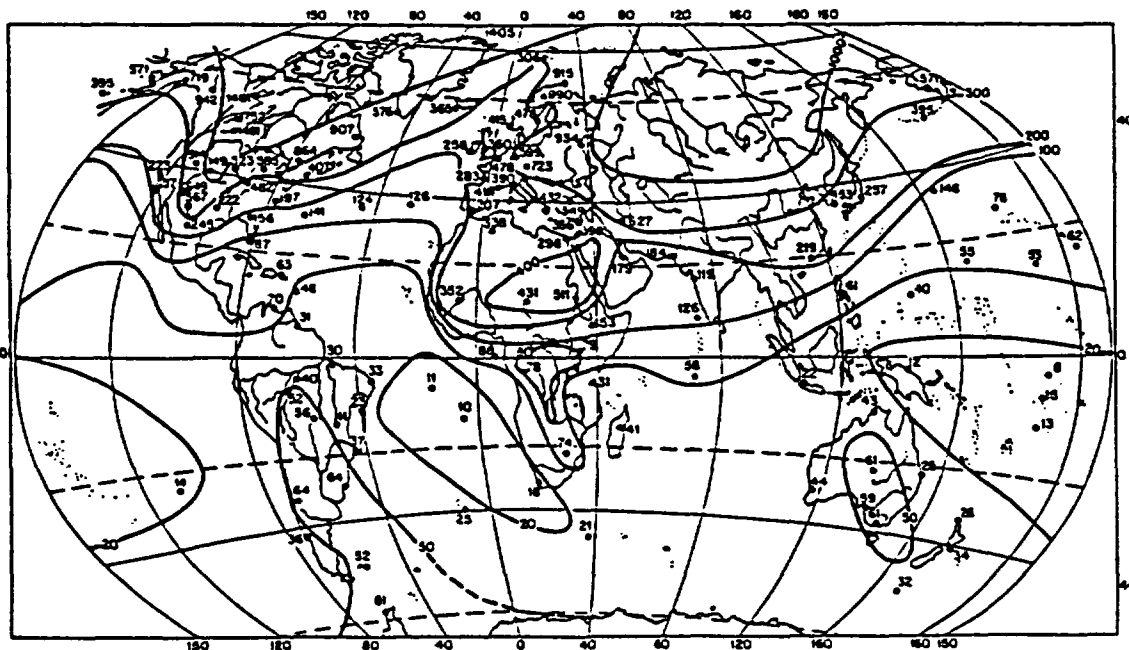
a) Global Distribution of Tritium in 1965
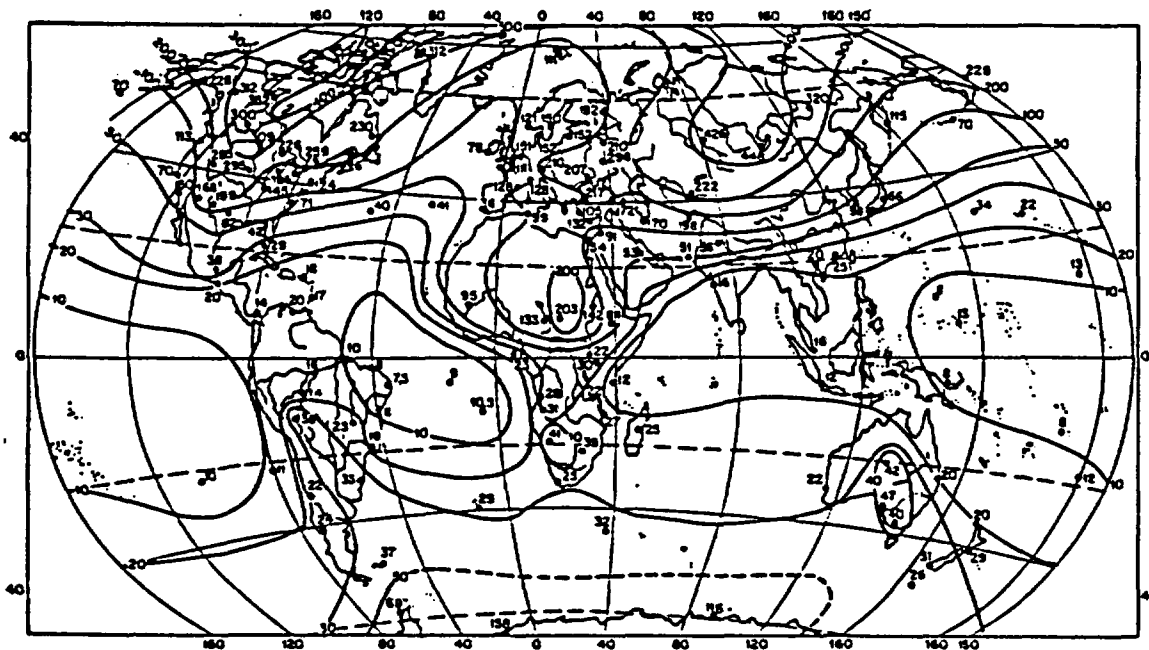
b) Global Distribution of Tritium in 1969

	Figure 4	Date:	June 1987
Water, Waste & Land, Inc.	**Global Distribution of Tritium** Adapted from Ferronsky (1983)	Project:	4001

(3)   the evapotranspiration cycle.

The only continuous record for the deposition of tritium at a site prior to the start of large atmospheric thermonuclear tests is for Ottawa, Canada. Because of the lack of data for other locations, many investigators have used the Ottawa data to estimate the thermonuclear tritium deposition at their particular sites.   The use of tritium as a tracer to determine the recharge into an aquifer was reported by Rabinowitz et al. (1977), for the Roswell Basin in New Mexico.   The basin has a semi-arid continental climate, with nearly 70% of total precipitation falling from May through September primarily in intense, but brief thunderstorms.   Orographic effects are very pronounced with precipitation patterns at the different stations around the basin showing large differences among themselves.   Tritium measurements began in October, 1956, with a number of gaps occurring after that date.

Because of the gaps in the precipitation/tritium concentration data, a correlation analysis was carried out between mean values of tritium concentrations of precipitation at New Mexico and Ottawa, Canada.   This provided a reconstructed set of average monthly tritium concentrations in the precipitation for central New Mexico from 1954 to 1969.   Correlations were also developed for the New Mexico data and two neighboring meterological stations, Flagstaff, Arizona, which is 360 miles to the west and Waco, Texas, which is 750 miles to the east.   Rabinowitz reported that the tritium concentrations in precipitation at the New Mexico site showed a remarkable similarity in magnitude and periodicity with those from Waco, Texas.   However, appreciable differences exist between the New Mexico and Flagstaff, Arizona, data.

A tritium fallout profile was constructed for the Roswell basin, where the fallout profile is the corrected monthly precipitation multiplied by the corresponding monthly average tritium concentration.   In general, the precipitation and the fallout profile curves are different since high tritium concentrations may not correspond to large precipitation amounts, and conversely, some precipitation does not have high tritium concentrations.   The tritium concentration in the precipitation is shown on Figure 5a.   The fallout profile is the corrected monthly precipitation multiplied by the corresponding monthly average tritium concentration.   The fallout profile is shown on Figure 5b.
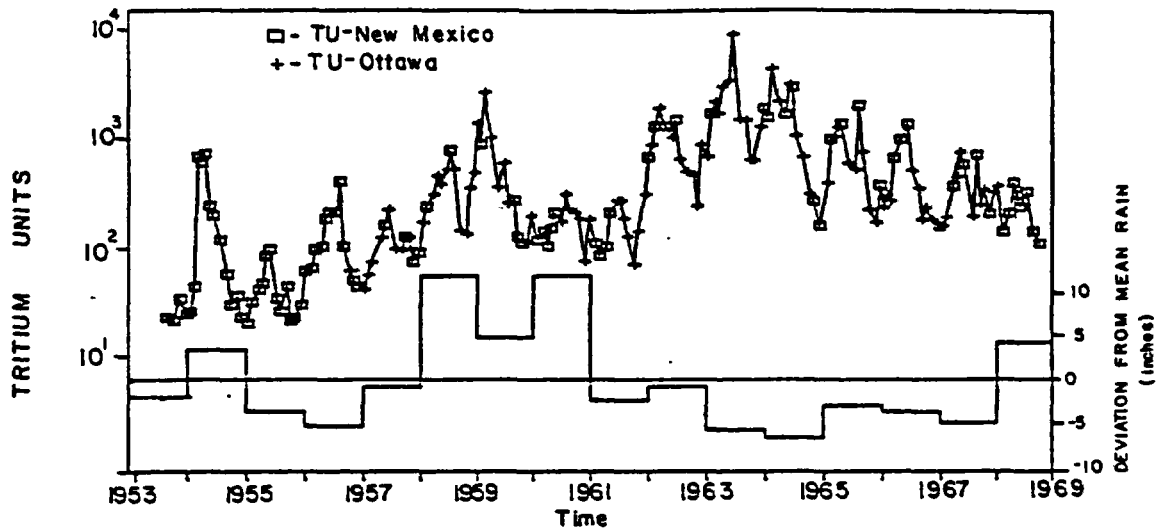
a) Tritium Concentration in Precipitation
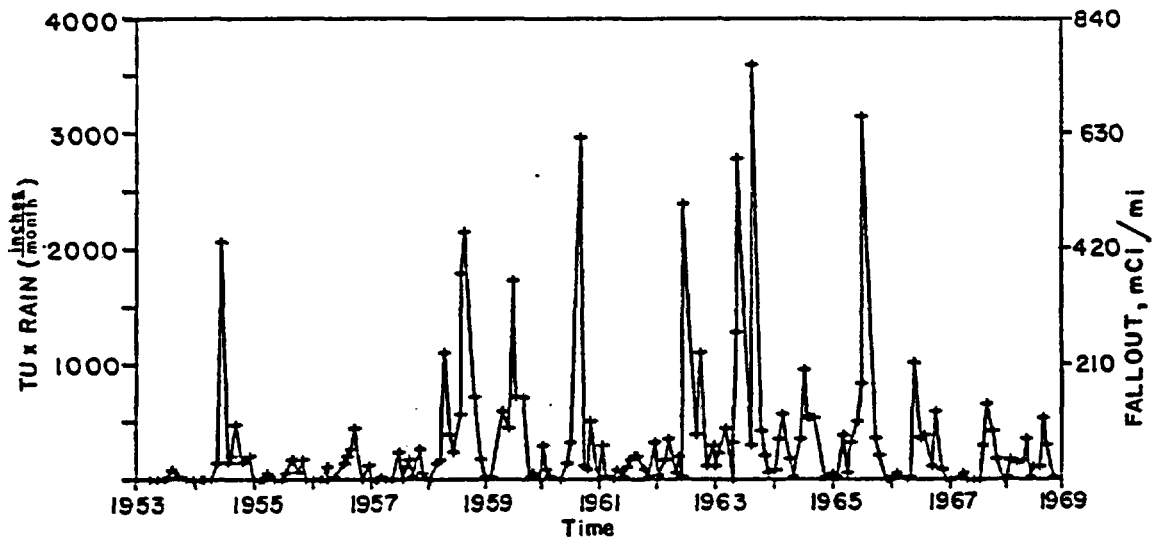
b) Tritium Fallout
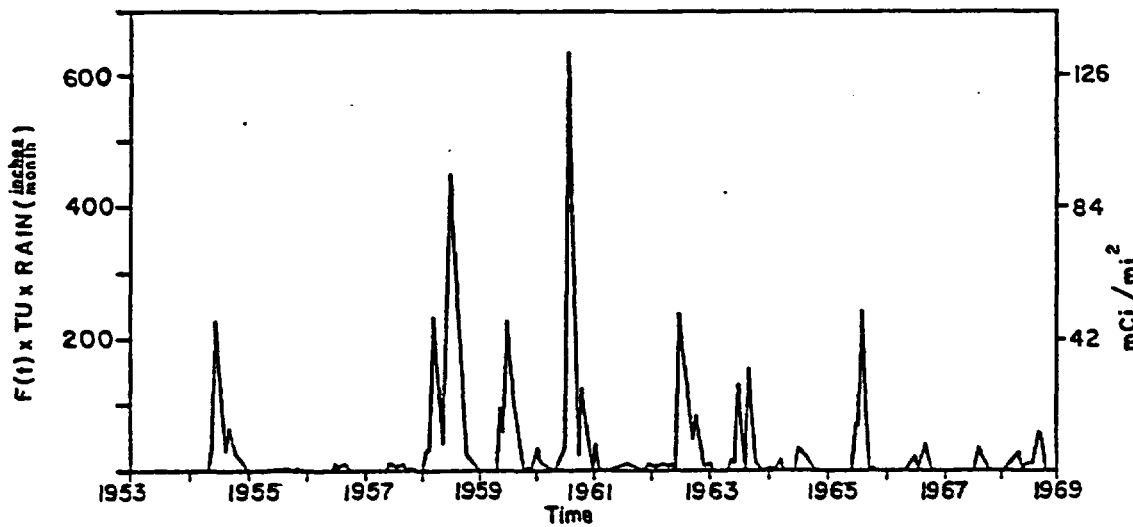
c) Tritium Input Function

Figure 5 Tritium Concentration, Fallout Profile and TIF for Central New Mexico	Date: June 1987
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Shown on Figure 5c is the Tritium Input Function (TIF), which is the amount of radiation per unit area actually reaching the groundwater system. (A fallout of 2,250 TU-in over 100 square miles is the equivalent of 47.3 Ci of tritium [Rabinowitz, et al., 1977].) The empirical TIF is constructed from the fallout profile and a relationship for estimating effective recharge as a function of precipitation amount. As defined by Rabinowitz, the TIF should be capable of predicting the observed tritium variations in groundwater. The TIF is obtained by multiplying the surface fallout of each month by a proportionality factor, f, which is the fraction of annual precipitation that becomes recharge. As shown on Figure 6c, there were seven periods where appreciable tritium amounts were injected into the aquifer. When the three graphs on Figure 5 are compared, the gap created by the first testing moratorium in 1961 is apparent. The atmospheric tritium concentration peak of 1956 disappears in the fallout profile due to very low precipitation. Significant differences exist between fallout and effective input as computed by the TIF (Rabinowitz et al., 1977).

3.1.4 Nevada Area Tritium Fallout

As part of a meterological study of the Yucca Mountain Site, Eglinton and Dreicer (1984) compiled climate data from a number of weather stations on and around the Nevada Test Site (NTS) and generated the decade precipitation trends of the 1950's and 1960's for south central and extreme south Nevada. These trends are compared with the tritium concentrations in the Ottawa precipitation during the same time period on Figures 6a and 6b. When compared with the Ottawa data, a similarity is noted between many of the high tritium fallout periods and the occurrences of mild to severe drought conditions in south central and extreme south Nevada. This indicates that the creation of a site specific TIF for Yucca Mountain may show that significant differences exist between the fallout and the effective tritium input.

At the NTS both onsite and offsite radiological monitoring programs have been ongoing for at least 30 years. Prior to 1954, an offsite surveillance program was conducted by the Los Alamos Scientific Laboratory and the U.S. Army. Radiological monitoring at or near the NTS has been performed by the Environmental Monitoring and Support Laboratory-Las Vegas (EMSL-LV) since 1954. During the period from 1954-1958, the monitoring was test-series related. Continuous monitoring has been performed since 1958, with all air sampling
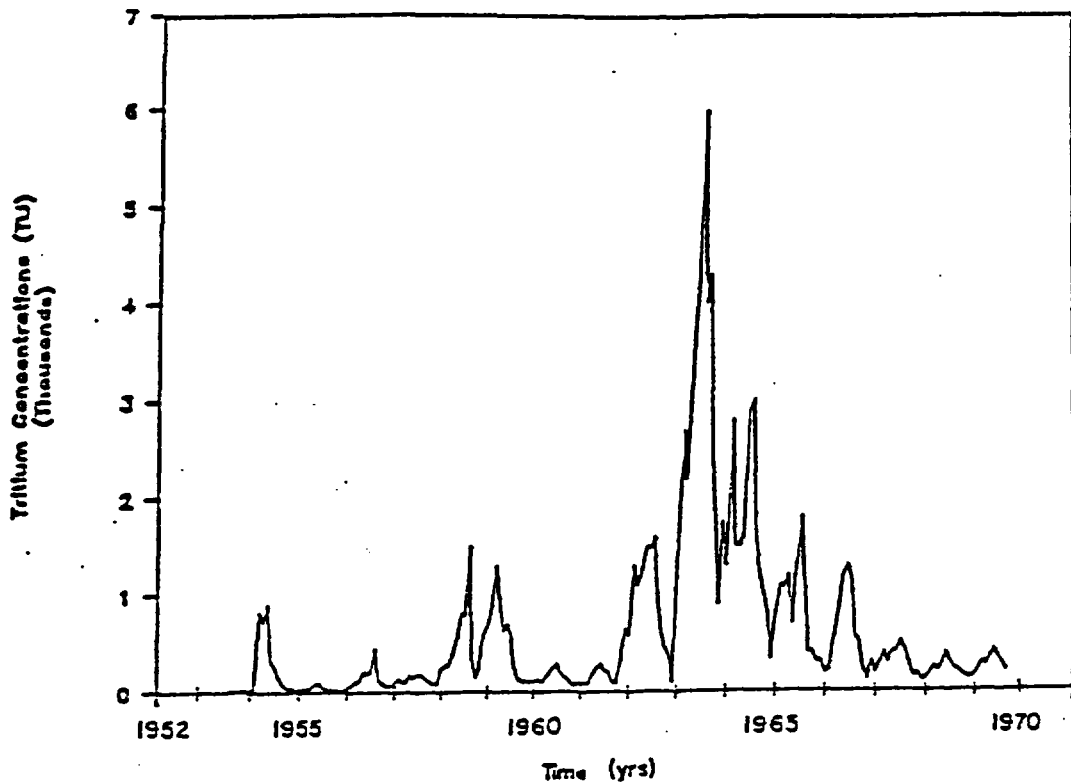
a) Tritium Fallout Curve Ottawa, Canada,
Adapted From IAEA (1983)

b) Drought Cycles For Southern Nevada
Adapted From Eglinton (1984)

Figure 6
Comparison of Ottawa Tritium
Concentration and Nevada Drought Cycles

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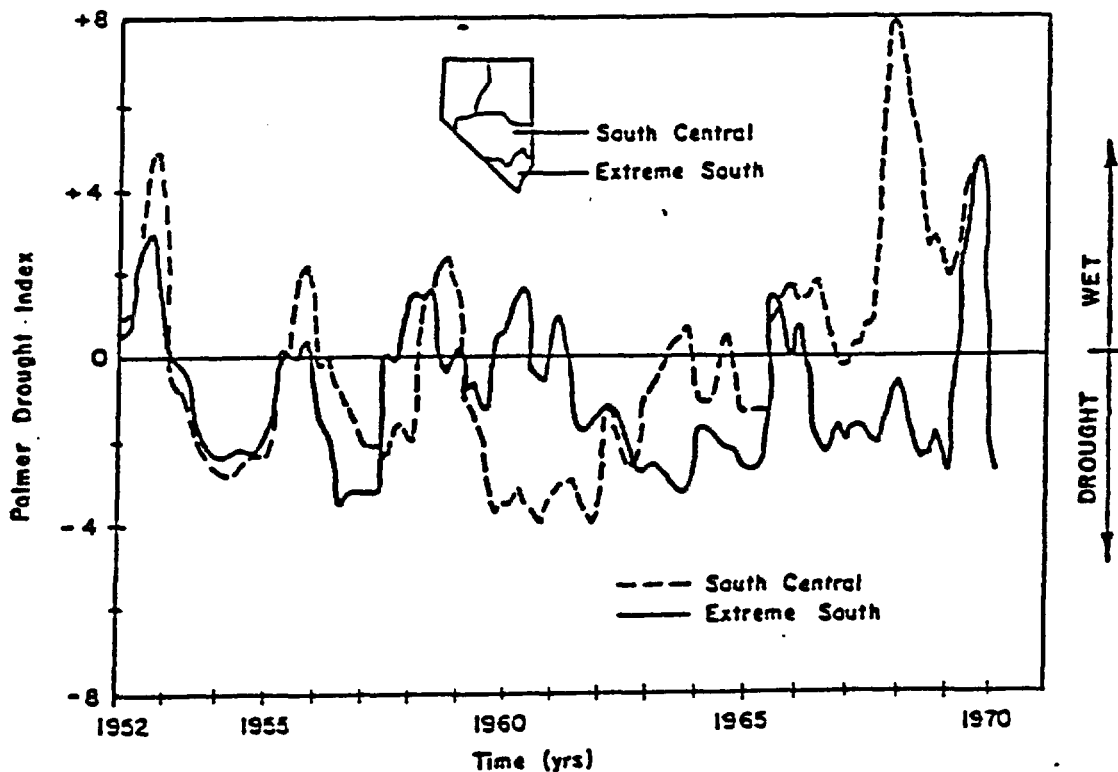
stations being operated 24 hours a day. Since the cessation of atmospheric testing, a general pattern of steadily decreasing levels of man-made radioactivity has been observed (ERDA, 1977). The surveillance networks have measured only the expected ambient levels of radioactivity, with several minor exceptions, since early 1971. Foreign nuclear testing has occasionally resulted in short-term increases in the observed airborne concentrations of radionuclides.

Hansen (1978) reported on the investigation of tritium distributions in the unsaturated zone of various valley fill sediments at the Nevada Test Site. The tritium concentrations for surface sediments on Yucca Flat ranged from 250 to 900 TU, dropping to 100 TU at 1.0' in depth. Surface concentrations at Frenchman Flat ranged from 80 to 550 TU. Hansen (1978) concluded that meteoric precipitation in the Frenchman, Yucca, and Jackass Flats high fan, mid-fan, and playa regions of the NTS did not infiltrate beyond 1.5 feet before it was evaporated to the atmosphere. The infiltration depth was not governed by the geomorphic settings of the valley fill sediments. Silt and clay matrix in high and mid fan regions, combined with caliche at 1.5 to 2.0 feet in Frenchman, Yucca, and Jackass Flats limited the downward movement of soil moisture.

3.1.5 Detection/Analyses

As reported by the IAEA (1983), water samples for tritium analysis are collected in 500 ml sealed bottles, taking care not to expose the samples to the atmosphere. The samples are then measured by liquid scintillation or gas proportional counting giving detection limits of 10 and 2 TU, respectively. To increase the detection sensitivity, water samples are usually enriched by electrolysis, thermal diffusion, or gas chromatography. The detection limit for the enriched samples is below 0.1 TU with a routine precision of about 0.2 TU. The above techniques are similar to the recommended analysis for tritium by the Standard Methods Committee, (1981):

> A sample is treated by alkaline permanganate distillation to hold back most quenching materials, as well as radioiodine and radiocarbon. Complete transfer of tritiated water is assured by distillation to near dryness. A subsample of distillate is mixed with scintillation solution and the beta activity is counted on a coincidence-type liquid scintillation spectrometer. Samples with tritium activity above 200 pCi/mL can be analyzed with precision of less than ± 6% at the 95% confidence level and those with 1 pCi/ml can be analyzed with a precision of less than ± 10% (Franson, 1985).

In the study of the dual porosity unsaturated zone of the Chalk aquifer in Great Britain, Foster (1975,1980) reported on the investigation methods used to obtain water containing tritium. Three sampling methods were used to obtain unsaturated zone water:

(1) Mechanically excavated trenches were used to obtain samples at shallow depths.

(2) A 0.45 m long, 100-mm diameter, drive core barrel was used with dry percussion drilling.

(3) From the harder and more cemented Chalk, air flush rotary drilling with a lined double core barrel was used.

Foster (1980) reported that a comparison of laboratory results between the three sampling methods showed good agreement. The actual determination of the tritium content involved

(1) Extraction of water from the cores by distillation to complete dryness,

(2) electrolytic enrichment,

(3) conversion to ethane, and

(4) measurement in a proportional counter.

The accuracy of the TU determinations was $\pm$ 10 % (Foster and Smith-Carrington, 1980). This is the same overall accuracy which Rabinowitz et al. (1977) reported in their tritium study in New Mexico.

3.1.6 Hydrologic Studies

A number of hydrogeologic studies have been performed using tritium as a tracer to determine a variety of aquifer characteristics. The majority of the studies were for single porosity flow systems; however, some monitoring and analyses of tritium has occurred in dual porosity systems.

3.1.6.1 Single Porosity

In the study of the central New Mexico aquifer, Rabinowitz et al., (1977) concluded that:

1. The records of tritium in precipitation at Socorro showed a remarkable similarity in magnitude and periodicity with those from Ottawa, Canada, and a similarity in periodicity with those from Waco, Texas. However, appreciable differences exist between the Socorro data and that from Flagstaff, Arizona.

2. Tritium fallout in the recharge area of the Roswell basin is extremely sensitive to the detailed precipitation space and time patterns, which must be worked out separately for each portion of the basin. This conclusion is probably valid for other basins in semi-arid climates and critically affects recharge calculations.

3. Recharge is not a linear function of precipitation. This non-linearity amplifies the fluctuations of tritium input. The tritium concentration peaks in precipitation do not show a one to one correspondence with those in recharge. Thus, the construction of the correct tritium input function is the key to computations of recharge.

A field study at the Nevada Test Site (NTS) for the distribution of radionuclides around an underground nuclear explosion cavity was initiated in 1974, about nine years after detonation. The goals of the project were to determine the rates of underground migration in various media at the NTS and to determine the potential for movement of radioactivity from underground nuclear explosions both on and off the NTS. The nuclides measured were produced in the Cambric test, which was detonated in NTS tuffaceous alluvium on May 14, 1965, with a yield of 0.75 kiloton (Coles, 1981). During April, 1974, a satellite well was drilled 91 m south of the explosion point coordinates to enable the study of migration rates of the radionuclides present in the cavity water. A pump was placed in the well at the same depth as the explosion point. Pumping induced an artificial ground water gradient between the explosion point and the well. Assuming that the tritium is not retarded, the relative movement of observed radionuclides can be compared to tritium movement, and an in situ retardation factor can be determined (Coles, 1981).

Ruthenium-106 (^{106}Ru) was observed to migrate at the same velocity as tritium in ground water from the site of an underground nuclear explosion to a pumped satellite well. This finding contradicted laboratory sorption studies using material from this site that indicated ^{106}Ru should migrate at a much slower rate than tritium.

3.1.6.2 Dual Porosity

A dual porosity system in Great Britain has been studied (Foster et al., 1975, 1980) using bomb pulse tritium as a tracer. The Chalk aquifer matrix has a permeability of 10^{-3} to 10^{-4} m/d (10^{-6} to 10^{-7} cm/sec) and a porosity range from 0.15 to 0.40 with a specific yield less than 0.01. The Chalk is described as a very pure, fine-grained carbonate with some horizons having significant proportions of clay minerals and occasional thin marl bands. The fracture system consists of frequent high angle joints and numerous horizontal discontinuities associated with bedding and secondary structures. The fracture apertures are typically small or microscopic with every meter of Chalk traversed by at least one high angle joint with an opening of 0.1 mm.

Significant surface run-off does not develop even after prolonged or high intensity rainfall. This observation coupled with the relatively low matrix permeability indicates that fracture flow provides a major flow path for water transversing the unsaturated zone. However, there is a low level of thermonuclear tritium in groundwater in the saturated zone of the Chalk aquifer throughout much of its intake area and clearly defined tritium profiles from thermonuclear testing exist in the unsaturated zone matrix. A model was developed which could explain the low levels of HTO in the saturated zone, high levels in the matrix, and at the same time be compatible with relatively-rapid flow down joints and fissures in the unsaturated zone.

The model proposed the existence of large HTO concentration gradients present between the fracture water and the matrix pore water causing some diffusion of HTO into the pore water. This process would continue as long as a favorable concentration gradient existed. The HTO would tend to pass through the unsaturated zone more freely as the concentration in the unsaturated zone pore waters built up. Foster (1975) concluded that:

(1) The volume of pore water available to take part in a diffusion process will in general be a number of times greater than the total infiltration to date containing thermonuclear tritium, due to the high porosity and specific retention of the Chalk.

(2) The role of diffusion needed to be further investigated before tritium determinations can be interpreted with confidence in studies of groundwater movement in dual porosity systems.

Foster and Smith-Carrington (1980) updated the conceptual model of the flow of water in the Chalk unsaturated zone by performing a mass balance on the

pore-water tritium. In the mass balance, the tritium content of the pore-water profiles are compared with the tritium input from infiltration (TIF). The pore water tritium content of the matrix down to some depth was assumed to have been derived from infiltration during a known period. In addition, it was assumed that the flow can be described as piston flow. This apparent piston flow is caused by the retardation of the tritium in the fractures by molecular diffusion between the mobile fissure water and the relatively static pore water. Examples of some of the Chalk matrix tritium profiles and their analyses are shown on Figure 7. The mass balance showed that the previous tritium input function (TIF) was not sufficient to account for the corresponding amount of tritium (TU-m) in the pore water profiles. Infiltration volumes estimated with the previous model were not capable of displacing the main tritium peak to the observed depth. The revised model considered some tritium from summer rainfall, which possesses the highest tritium concentration in Great Britain each year, to be retained in the soil moisture and enters infiltration in the subsequent autumn-winter.

The revised model indicated that the tritium observed in the Chalk pore water profiles represented a smaller proportion of the total input in post 1962 infiltration than previously estimated. The new model suggested up to 20% of the tritium is transported by fractures to the groundwater. Foster and Smith-Carrington (1980) concluded that

1. Individual profiles cannot be interpreted with sufficient precision to question or to qualify the standard hydrometeorological models for the calibration of excess rainfall.

2. Long-term investigation of the temporal changes in pore-water tritium profiles at individual sites will be required before unsaturated zone models to predict solute movement can be adequately calibrated.

Foster and Smith-Carrington (1980) also pointed out that there is substantial uncertainty in the tritium concentration in the rainfall at the site during the critical period from 1962-1964 due to the lack of close meteorological stations monitoring precipitation/tritium values.

Other studies in fractured rock have given somewhat different results than the Chalk. A study by Fontes is described in the IAEA (1983) for the Mont Blanc area in France. Water samples were taken from fissures in fractured granite along a 12 km tunnel under the mountain. Thermonuclear produced tritium was observed along the entire tunnel. The tritium values indicated

a) Individual Profile Concentrations

b) Calculated Average Profile Concentration

Legend for plot a):
— NOIX, Feb 1976
····· NO2X, Mar 1976
—·— N11A, Feb 1977
— — N50A, Mar 1977
——— N60A, Apr 1977
—▼— N06A, Oct 1977

Legend for plot b):
A: tritium in soil zone (1u m low and estimation difficult)
A: tritium from post-1961 rainfall
Error in subdivision of profile due to variable tritium concentration in rainfall and vertical diffusion
B: tritium from 1954-1961 rainfall (mostly post-1958)

	Figure 7	Date: June 1987
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that rain water had vertically penetrated 100 m of glacier and 2000 m of rock within a few months to a few years. Tritium studies performed in the Vedavati river basin of India to determine recharge conditions by Sukhija (1983) showed post-thermonuclear rain in the aquifers. The water bearing zones are described as gneissic complex, granites, and metamorphic rocks. The groundwater movement is controlled by fractures, fissures, a weathered zone, and surficial mantle. In these studies, the majority of the tritium was not adsorbed by the matrix, but passed through the unsaturated zone.

3.2 CHLORINE-36

Chlorine is naturally present in the atmosphere and arises from ocean spray (Bentley et al., 1979) and consists primarily of two stable isotopes. Chlorine-35 (^{35}Cl) has a natural abundance of 75.53% of the total chlorine on earth, with the remaining chlorine consisting almost entirely of Chlorine-37 (^{37}Cl). Atmospheric chlorine-36 (^{36}Cl) is continuously being produced by interactions of cosmic rays and their secondaries with Argon-40 (^{40}Ar) and ^{35}Cl with an additional small influx of ^{36}Cl possibly originating from meteoric dust. Chlorine-36 is the longest lived radioactive isotope of chlorine with a half life of about 310,000 years.

3.2.1 Natural Atmospheric Concentration

Natural pre-bomb concentrations of ^{36}Cl were initially determined by Elmore et al. (1979) from water obtained from two wells in Arizona. Subsequent analysis on other water samples were performed by Bentley et al., (1982). In an attempt to exclude the bomb input source, a sample was obtained from a deep well near Tucson, Arizona. Waters from that well had been estimated by means of tritium and ^{14}C analyses to be more than 2,000 years old. As dilution from old salt deposits was also expected to be low, the ^{36}Cl/Cl ratio in this sample was thought to provide a direct indication of the cosmic ray production rate in the atmosphere - the most important result required for establishing a ^{36}Cl chronology (Elmore, et al., 1979). The results of their testing are shown in Table 1.

This pre-bomb water was confirmed as such by tritium and carbon-14 dating, but is young enough so that measurable ^{36}Cl decay should not have occurred. The data presented in Table 1 conforms to the geographical distribution of naturally produced ^{36}Cl fallout predicted by Bentley and Davis (Bentley et al.,

TABLE 1

PRE-BOMB ^{36}Cl BACKGROUND CONCENTRATIONS AND FALLOUT

Location	Precipitation/ Evapotranspiration (mm/%)	Measured Concentration $\dfrac{\text{atoms}^{36}\text{Cl}}{\text{liter}} \times 10^{-7}$	Calculated Fallout $\dfrac{\text{atoms }^{36}\text{Cl}}{\text{m}^2 \text{ sec}}$
Arizona			
Tucson City Wells			
B8	300/98%	11.7	23
C13	300/98%	9.6	18
A31	300/98%	6.6	12
Monkey Springs	300/98%	8.1	15
Benson Well	300/98%	7.4	14
St. David Well	300/98%	6.5	12
MEAN		8.4	16

1982). Ferronsky (1982) summarized the results of several investigations relating to the production rates and steady-state abundances of various cosmogonic radioisotopes. He reports a production rate of ^{36}Cl of 11 atoms per m^2 sec, which is in good agreement with the mean calculated fallout presented in Table 2. Elmore et al. (1982) determined an upper limit for the pre-bomb ^{36}Cl fallout of 80 atoms per m^2 sec.

3.2.2 Production and Global Distribution by Nuclear Tests

Because ^{36}Cl is neither a product of direct fission nor of fusion, virtually all anthropogenic ^{36}Cl originates from thermal activation of ^{35}Cl. Only when nuclear explosions are detonated near seawater is sufficient chloride (^{35}Cl) present to produce measurable global thermonuclear ^{36}Cl fallout. Therefore, only explosions on barges or islands, and of sufficient yield, were capable of producing the bomb pulse ^{36}Cl (Bentley et al., 1982).

An atmospheric box model was calibrated against ^{36}Cl concentrations measured in rainfall at Long Island, New York, during the time period of nuclear testing in the Pacific. The calibrated calculated fallout at Long Island was converted to global fallout according to a latitude-fallout dependence published by Peterson (Bentley et al., 1982). In the mid-latitudes, the bomb pulse peak height was about 1,000 times the natural background level. The results of tests on water containing thermonuclear ^{36}Cl fallout are shown in Table 2. Elmore et al. (1982) reported peak values of ^{36}Cl fallout at Ontario, Canada, of 48,000 atoms/m^2sec and 5,000 atoms/m^2sec at Greenland. The calculated global ^{36}Cl bomb pulse has been used as the input function for a number of hydrologic studies. The ^{36}Cl fallout pulse is compared with the precipitation trends of southern Nevada on Figures 8a and 8b.

Bentley et al. (1982) determined that precipitation and groundwater data obtained thus far are consistent with the ^{36}Cl fallout predictions and that the pulse lasted from 1953 to 1964. The ^{36}Cl fallout rates have returned to levels existing before thermonuclear testing, in contrast with ^{14}C and tritium (Bentley et al., 1982). The ^{36}Cl leaves the atmosphere in rain and enters the hydrosphere directly whereas ^{14}C forms a large atmospheric reservoir as gaseous CO_2 (Elmore et al., 1979). As of yet, information on the effects which French thermonuclear testing in the Pacific Ocean have had on ^{36}Cl fallout rates are unavailable.

TABLE 2

BOMB PRODUCED ^{36}Cl CONCENTRATIONS AND FALLOUT

Location	Date Collected	Measured Concentration $\dfrac{\text{atoms}\,^{36}Cl}{\text{liter}} \times 10^{-7}$	Calculated Fallout $\dfrac{\text{atoms}\,^{36}Cl}{m^2\ \text{sec}}$
New York			
Long Island	Aug. 1957	77	28,000
	Sept. 1957	183	67,500
	Apr. 1959	24	8,900
	May 1959	1.02	370
	Feb. 1960	26.3	9,600
MEAN		62	23,000
Shallow Well	Aug. 1957	64	25,500
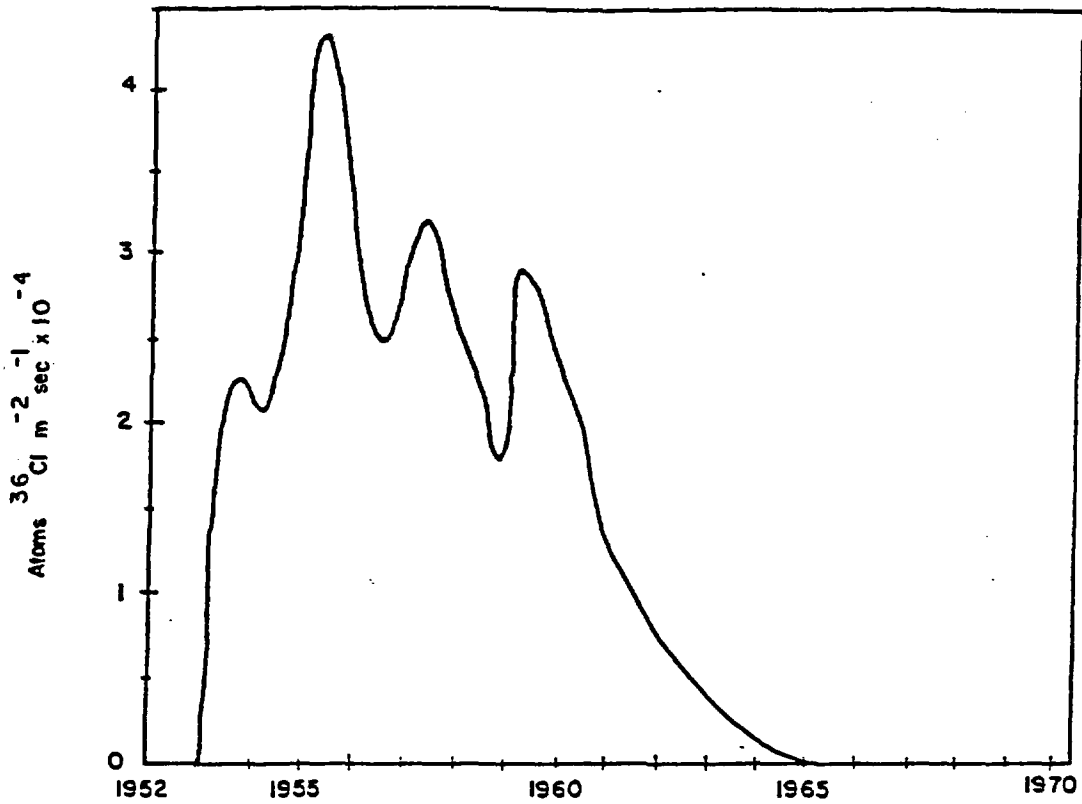
a) Global ^{36}Cl Fallout Curve
Adapted from Bentley et al.(1982)
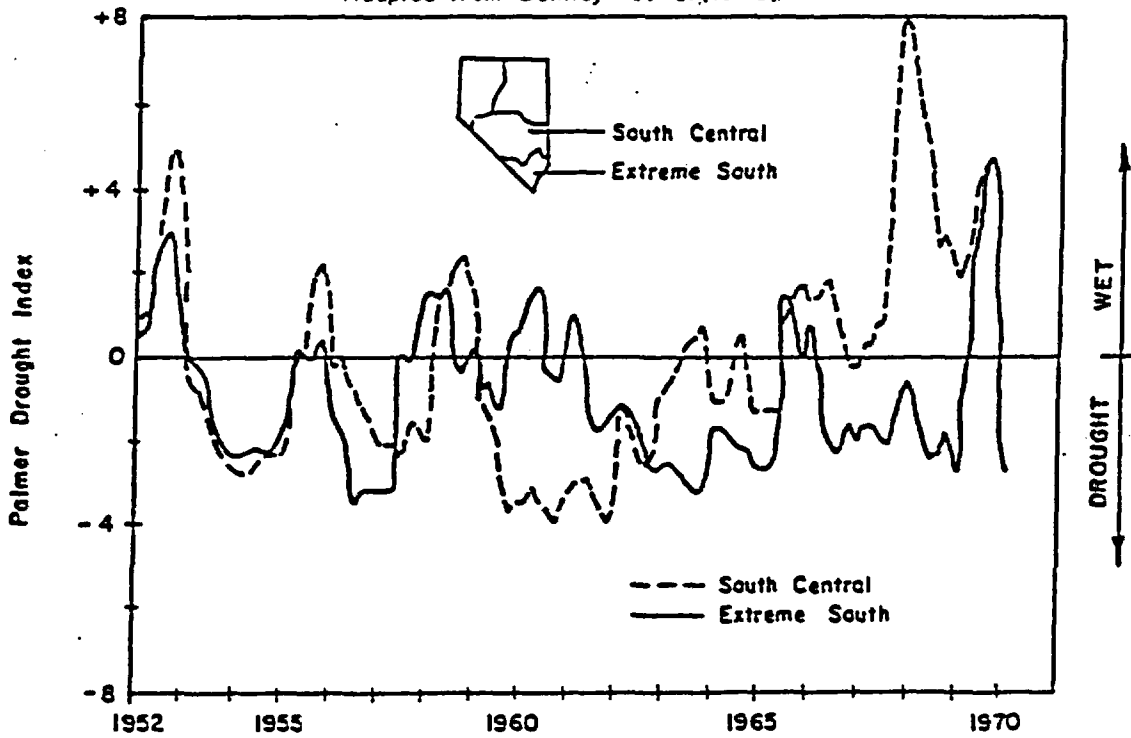
b) Drought Cycles for Southern Nevada
Adapted from Eglinton (1984)

	Figure 8	Date: June 1987
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3.2.3 Detection/Analyses

The collection technique as described by Bentley et al. (1986) for chloride and ^{36}Cl analysis of water from the Great Artesian Basin in Australia is given as follows. Chloride was collected by field precipitation. Sufficient water to obtain several hundred milligrams of chloride (usually 1-5 liters) was introduced into a clean container at the well head. The water was acidified to an approximate pH of 3 with nitric acid. The chloride was then precipitated as AgCl (silver chloride) by the addition of excess AgNO$_3$ (silver nitrate). The supernatent was decanted and the AgCl transferred to small, dark glass bottles. An additional 250-ml sample was collected in a polyethylene bottle for chloride analysis in the laboratory. The AgCl was refined by washing in distilled water, dissolution in purified NH$_4$OH (ammonium hydroxide), precipitation by evaporation of the NH$_4$OH, rewashing, and repetition of the entire procedure. The purified AgCl was oven dried and stored in sealed bottles. All ^{36}Cl determinations were performed at the Nuclear Structure Research Laboratory, University of Rochester, New York. The water samples for chloride determination were analyzed using the mercuric nitrate method (Franson, 1985).

Tandem accelerator mass spectrometry allows the detection of one ^{36}Cl atom in 10^{16} Cl atoms, extracted from samples of less than one liter. A comparable resolution can also be obtained by the liquid scintillation method when sufficient counting time is taken. This method requires the ^{36}Cl as a tetrachloride in a toluene cocktail (IAEA, 1983). The basic limitation in measuring small concentrations of ^{36}Cl with mass spectrometers is due to the necessity of separating ^{36}Cl from the argon and sulfur isobars (^{36}Ar and ^{36}S) and from mass 36 molecules (Elmore, et al., 1979). The information presented in Table 3 is available (Elmore and Phillips, 1987) for ^{36}Cl measured routinely at natural levels with AMS. The sample size listed in Table 3 is for the element only and not the compound, and is the size required for less than 10% precision. A carrier material of the same element, Cl, containing negligible radioisotope, can be added (if needed) to bring the sample weight up to that given in the table. Sample sizes larger than that listed are easier to handle and may result in better precision. The background value listed in Table 3 is the radioisotope ratio obtained for a blank sample with a negligible radioisotope content. The blank sample is prepared identically to the unknown sample. The run time is the time necessary to count 100 radioisotope events in

TABLE 3

^{36}Cl ISOTOPE ANALYSIS PARAMETERS

Half Life(years)	3.0×10^5
Stable Isotopes	^{35}Cl, ^{37}Cl
Stable Isobars	^{36}Ar, ^{36}S
Chemical Form	AgCl
Sample Size (mg)	2
Background ($\times 10^{-15}$)	2
Run Time (minutes)	30
Atoms per sample	5×10^5
Decay Counting Interval (years)	86

==

the detector of a sample that has an isotope ratio several times the background value. Additional counting time is sometimes needed to obtain 10% precision since uncertainties in the background and standard must be included. The atoms per sample is the number of atoms of ^{36}Cl in the original sample needed for 10% precision. The decay counting interval is the time required to count 100 radioactive decay events for the same number of atoms placed in a detector that is 100% efficient.

3.2.4 Hydrologic Studies

The application of ^{36}Cl tracing to the movement of soil water in arid climates was tested at a site in central New Mexico, near Socorro. The site has a typical high-desert climate, with an annual precipitation of about 200 mm and an annual potential evapotranspiration of about 1800 mm (Phillips et al., 1984). Soil samples were collected from a vertical auger hole and analyzed for chloride and ^{36}Cl. The $^{36}Cl/Cl$ ratio of the soil water as a function of depth is illustrated on Figure 9. The bomb pulse may easily be distinguished between 0 and 2 m (Phillips et al., 1984).

The average $^{36}Cl/Cl$ ratio below 2 m is 717 x 10^{-15} and compares quite favorably with the natural background ratio of 640 x 10^{-15} as predicted by Bentley et al. (1982). The maximum bomb-fallout $^{36}Cl/Cl$ ratio measured at the site, 5890 x 10^{-15}, was about one order of magnitude less than the ratio which the authors had calculated. They attributed this difference to the effects of hydrodynamic dispersion.

Preliminary work has been performed at the Yucca Mountain site using the ^{36}Cl isotope. The purpose of this work was to determine the contributions to hydrologic flow through Yucca Mountain from surface infiltration where different surficial soil characteristics or runoff effects may be important. The measurements of the bomb pulse ^{36}Cl in two types of surficial material at Yucca Mountain were performed to obtain information about potential recharge. The material types are relatively flat-lying alluvial sediment and fractured tuff that is either exposed at the surface or thinly covered by soil or loose rock (Ogard and Vaniman, 1985). Samples were collected from the following sites:

1. Yucca Crest - Four soil samples and one tuff sample for chloride analyses, plus one surface sample for Cesium-137 analysis.
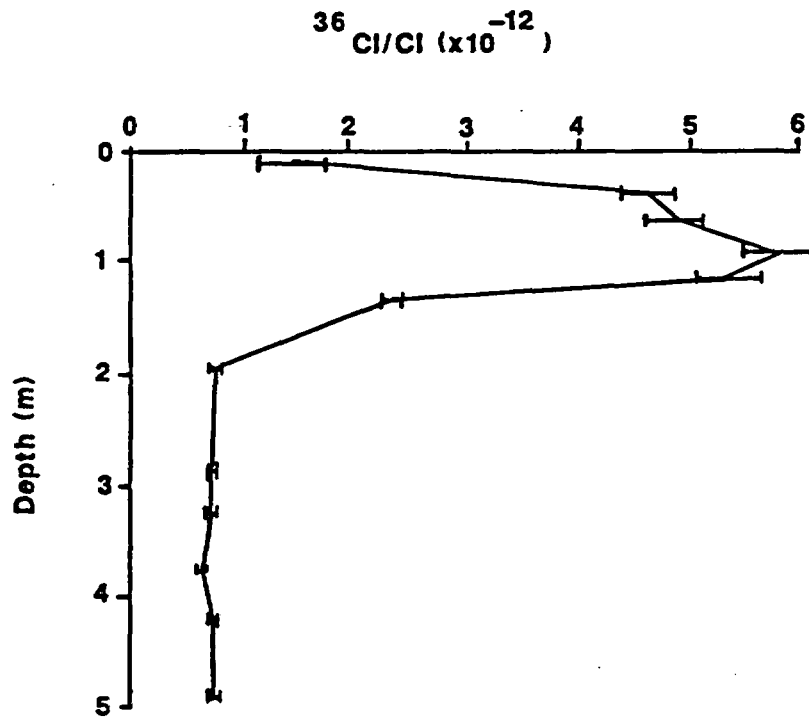
Figure 9
New Mexico Chlorine-36 Study Results
Adapted from Phillips (1984)

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2. Coyote Wash - Thirteen soil samples from a trench located a few
    hundred meters northwest of the Exploratory Shaft site.

3. Yucca Wash - Thirteen soil samples from trench YW6 and one surface
    sample for Cesium-137 analysis.

4. Fortymile Wash - Seven soil samples from trench FW3.

The two ^{137}Cs samples were shipped to Los Alamos to determine whether
local fallout, indicated by the presence of ^{137}Cs, might have been deposited.
Locally formed ^{36}Cl could affect the hydrologic interpretation of any observed
^{36}Cl infiltration. Preliminary data from the Yucca Wash sample indicate a
^{137}Cs activity of about one disintegration per minute (dpm) per gram of dry
soil. Ogard and Vaniman (1985) concluded that this low level of activity is
more likely to result from global fallout than from NTS activities. Of the
four sites that were sampled, Yucca Wash, YW6, appears to be the only one where
the ^{36}Cl infiltration should be undisturbed by water flow on the surface, which
is a desirable characteristic with respect to sample collection. However, the
Yucca Wash trench is four kilometers from the Exploratory Shaft location.

An additional field trip investigated whether the ^{36}Cl technique might
permit measurement of rainfall infiltration into the fractured tuffs of Yucca
Mountain. A backhoe and a pneumatic hammer were used to excavate a hole about
0.8 m deep and four soil samples and two tuff samples were collected. Holes
were drilled to permit blasting to deeper levels, but heavy rains resulted in a
pool of standing water in the excavation. Water from this pool could have
carried chloride and ^{36}Cl to deeper levels than it might have moved during the
past 25 years, thus compromising the interpretation of the data if sampling and
analysis had continued (Ogard and Vaniman, 1985).

The preliminary conclusions were that both the low chloride concentrations
in the samples taken from the crest of Yucca Mountain and the maximum chloride
concentration for the data set, which occurs at the bedrock surface, are what
one would expect from recent leaching. The shallow depth to bedrock (0.46 m)
is such that even a moderate precipitation event could flush the section. The
low chloride content at the bedrock surface indicates that a drain exists for
infiltrating water (Rundberg et al., 1985).

Other conclusions reached by Ogard and Vaniman (1985) and Rundberg et al.
(1985) are summarized in the following. The chloride data from the Coyote Wash
samples can be interpreted in terms of active, but not recent, flushing of

chlorides. There may be a significant horizontal component to recharge at the location sampled, which is not unexpected for a wash such as this one. The relatively high chloride concentrations at the surface may be attributable to surface vegetation, which holds rainfall infiltration within the shallow root zone. The soil unit boundary at 2.5 m may help to limit the downward leaching of chloride. However, the low chloride concentrations at the bottom of the bulldozer cut indicate that chloride leaching is not stopped at that point. The highest chloride concentrations were observed in soil samples from the Yucca Wash trench. Recent leaching appears to have moved the chloride down from the surface about 0.16 m, but subsequent leaching appears to be very slow. The data from the Fortymile Canyon trench can be interpreted in terms of chloride leaching within the past 20 years that has decreased the concentrations of chloride in the top 0.8 m of the trench. This postulated flushing may have resulted from water flowing in the flood plain that includes the FW-3 trench site (Rundberg et al., 1985).

3.3 CARBON-14

The use of radiocarbon (^{14}C) for dating materials has been common in the latter part of this century, especially in archeology. Radiocarbon dating of groundwater has been performed for the past 30 years. Radiocarbon dating can be used to identify the age of waters up to several tens of thousands of years.

3.3.1 Radiocarbon Production

Radiocarbon, with a half life of 5730 $\pm$ 30 years, is produced naturally in the upper atmosphere due to cosmic ray interaction with ^{14}N. The newly formed ^{14}C atom rapidly reacts with O_2 molecules to form radioactive carbon dioxide ($^{14}CO_2$), thus entering the carbon cycle. Radiogenic CO_2 is mixed throughout the atmosphere and eventually is incorporated into the biosphere. This incorporation occurs through photosynthesis and exchange with the hydrosphere.

Anthropogenic effects on the ^{14}C content of the atmosphere, biosphere, and hydrosphere have been caused by two distinctly different mechanisms. The first mechanism noted worldwide was due to the increased CO_2 production from fossil fuel combustion. The CO_2 from this combustion contains essentially no radiocarbon. Therefore an increase in the content of CO_2 in the atmosphere because of this combustion has caused the relative ^{14}C concentration to

decrease. This mechanism has been attributed to the decrease in the ^{14}C noted around the beginning of this century (IAEA, 1983).

The other mechanism caused a significant increase in atmospheric radiocarbon and was due to the atmospheric thermonuclear testing during the 1950's, 60's and 70's. The northern hemisphere middle latitude ^{14}C content increased by 100 percent with the tropospheric content peaking in 1963. The radiocarbon concentration has decreased since. However, Chinese and French thermonuclear testing from 1963 to 1976 inhibited the decrease.

A reconstructed radiocarbon content of the atmosphere has been determined for the past 8,000 years from the ^{14}C analysis of annual tree rings. The individual rings have incorporated radiocarbon from CO_2 respired during the growing season. By dendochronologically dating bristlecone pine and giant sequoia tree rings, the ^{14}C concentration in each ring was related to the historical time scale. Both short-term (decades and centuries) and long-term (millennia) fluctuations of natural radiocarbon concentrations have been shown to occur. These fluctuations range from about one or two percent for the short events and about 10 percent for the long-term events.

The ^{14}C content of a sample is usually reported using percent modern carbon (pmc) units. A 100 pmc value is the approximate mean atmospheric ^{14}C activity before thermonuclear age radiocarbon was introduced and corresponds to 13.56 disintegrations per minute per gram of carbon. Usually, values of pmc will range from 100 for carbon in equilibrium with the atmosphere to 0 pmc for carbon that has been isolated from sources of ^{14}C for a long time. Values of pmc greater than 100 percent are also found because the standard represents ^{14}C contents before atmospheric nuclear testing increased the ^{14}C content (Kerrisk, 1987).

3.3.2 Radiocarbon Dating Methods

The use of radiocarbon for dating can be described most readily by using an idealized, simple model. This model assumes that the radiogenic CO_2 in the atmosphere is uniformly mixed and is exchanged with the biosphere and hydrosphere in a global equilibrium. Members of the biosphere incorporate this carbon into their physical structures. Once a lifeform dies, theoretically, no additional radiocarbon can be added to the physical structure and the initial activity present at death will begin to decrease. The activity of the ^{14}C in a

sample of a structure can be determined, and based upon this activity the age of the sample can be calculated.

The validity of the simple model depends upon a number of assumptions. The most important of these are:

1. The atmospheric production of radiocarbon has been constant for the last 100,000 years.

2. The mixing and uptake of CO_2 have been uniform and rapid.

3. No "young" or "old" carbon has been added to the sample since it was isolated from the global equilibrium state, and

4. No isotopic fractionation has occurred to alter the standard carbon-14, carbon-13, and carbon-12 ratios in the samples (see Section 4.6.1).

Unfortunately, the simplifying assumptions stated above are rarely satisfied in nature. The concentration of ^{14}C in the atmosphere has changed through time, with the causes, magnitudes, and possible cycles of the natural ^{14}C fluctuations still the object of active research.

3.3.3 Problems Associated with Carbon-14 Dating

While the use of ^{14}C dating has provided invaluable information, some problems remain with the technique in hydrologic systems. According to Terrasmae (1984) and Davis and Murphy (1987) some of these problems are:

1. Secular fluctuations of radiocarbon,

2. Reconstruction of the carbonate geochemistry,

3. Subsurface production of ^{14}C, and

4. Correction and evaluation of radiocarbon dates.

Secular fluctuations of radiocarbon was discussed in Section 3.3.1. Carbonate geochemistry is important in an aquifer because the carbonate minerals are in a state of near equilibrium with ground water. When slight changes occur in the water temperature or chemistry, dissolution or precipitation of carbonate ions can occur. This can cause isotope fractionation and the addition of "old" carbon into the system. Isotope fractionation of carbon isotopes can also occur during the growth processes of all organic materials, with the isotope

ratios varying between species and also between different parts of the same organism (Terasmae, 1984).

3.3.4 Sampling and Measurement

Radiocarbon dating is conventionally performed by the accurate measurement of the beta rays emitted during the decay of ^{14}C. The direct determination of ^{14}C atoms can be accomplished using tandem accelerator mass spectrometry. For contemporary carbon, the specific activity is about 15 disintegrations per minute per gram.

Gas samples were obtained from the unsaturated zone at USW UZ-1 by two sampling methods (Yang, 1985). The potassium hydroxide (KOH) method of CO_2 sampling consisted of pumping formation gas through KOH solution, with the CO_2 being absorbed in the solution. The CO_2 collected in the KOH solution was released by acidification and then converted into benzene for ^{14}C analysis by scintillation counting. Smaller size samples were measured for ^{14}C concentrations by tandem accelerator mass spectrometry.

The other method, the molecular sieve, required sample gas to be pumped through a stainless steel cylinder containing molecular sieve pellets. Both CO_2 and H_2O vapor were trapped in the molecular sieve. A system was designed to separate the two components, however, this required the molecular sieve to be heated to 350° in a vacuum system. Because of this high temperature an exchange of oxygen atoms between the water and the molecular sieve occurred during degassing and affected the oxygen isotope values. The hydrogen-isotopic data seemed to be unaffected by the exchange process. Thus, deuterium and possibly tritium data can be obtained by the molecular sieve method simultaneously with CO_2 samples. The KOH method cannot be used to collect both samples at the same time.

3.3.5 Carbon-14 in Yucca Mountain Ground Water

Until the exploratory shaft is constructed, the only water available for analyses of ^{14}C activity has come from the saturated zone, primarily deep wells on and near Yucca Mountain. Kerrisk (1987) reported the ^{14}C concentrations from samples of the saturated zone at Yucca Mountain. These values are shown in Table 4. Also shown in Table 4 are the total carbonate, pH, carbon-13 (^{13}C), and the apparent age of each sample. The units for ^{13}C are described in Section 4.6.1. Note that some of the wells had more than one sample taken

TABLE 4

CARBONATE SYSTEM DATA

Well #	Total Carbonate mmoles/liter	pH	$\delta^{13}C$ (mil)	PMC %	Apparent Age (years)
J-12	1.95027	7.1	-7.9	32.2	9,139
J-13	2.03222	7.2	-7.3	29.2	9,927
UE-25B#1	2.83527	7.1	-10.7	----	-----
UE-25B#1	2.27805	7.5	-10.4	16.7	14,433
UE-25B#1	2.17972	7.1	-8.6	18.9	13,436
UE-25C#1	2.47472	7.6	-7.1	15.0	15,300
UE-25C#2	2.27805	7.7	-7.0	16.6	14,480
UE-25C#3	2.24527	7.7	-7.5	15.7	14,931
UE-25P#1	4.62166	6.8	-4.2	3.5	27,035
UE-25P#1	9.32525	6.6	-2.3	2.3	30,421
UE-29A#1	1.75361	7.2	-13.0	62.3	3,816
UE-29A#2	1.75361	7.0	-13.1	60.0	4,119
USW G-4	2.27805	7.7	-9.1	22.0	12,210
USW H-1	1.88472	7.7	----	19.9	13,019
USW H-1	1.99944	7.5	-11.4	23.9	11,543
USW H-3	4.49054	9.2	-4.9	10.5	18,175
USW H-4	2.83527	7.4	-7.4	11.8	17,234
USW H-5	2.06499	7.8	-10.3	18.2	13,740
USW H-5	2.08138	7.9	-10.3	21.4	12,434
USW H-6	2.98277	8.1	-7.5	16.3	14,629
USW H-6	3.55638	8.3	-7.3	10.0	18,569
USW H-6	3.83499	8.3	-7.1	12.4	16,834
USW VH-1	2.73694	7.9	----	----	------
USW VH-1	2.70416	7.5	----	----	------
USW VH-1	2.65499	7.5	-8.5	12.2	16,966

during tests. The location of the wells relative to the Exploration Block and Fortymile Wash are shown on Figure 10. The apparent ages of the water from those wells are shown on Figure 11. Where more than one test was performed, the youngest apparent age is listed.

The wells with water which exhibit the youngest ages are located along the Fortymile Wash drainage system, (UE-29a#2, J-13, and J-12). Well UE-29a#2, located at the head of the wash, has water with the youngest apparent age of any of the wells tested in the Yucca Mountain area. An abandoned well, UE-29a#1 was located nearby and also had high pmc values in water samples. The DOE (1987) reported that the ^{14}C content ranged from 75.3 to 60.0 pmc depending on the well and the interval. Based on these high PMC values and by the high tritium content of the shallower water (62 TU), the wash appears to receive occasional rapid bottom recharge from intermittent (rain storm water) flow in the Fortymile Canyon. Because the high tritium value could only be derived from precipitation recharging the aquifer since the 1960's and the ^{14}C activity is below 100 pmc, appreciable dilution of the recent recharge waters must have occurred (DOE, 1987). This indicates that the recharging water must have had an even higher tritium concentration.

All but one of the wells (UE-25p#1) were completed in the tuffaceous aquifer around Yucca Mountain. Well UE-25p#1 has a total depth of 1800 m with the bottom 500 m being completed in the carbonate aquifer. The pmc of water samples taken from this well are significantly lower than the other Yucca Mountain wells. This is indicative of the carbonate aquifer adding older, ^{14}C free carbon to the sampled water. Most circulating ground waters can potentially come into contact with carbonate sources and dissolve certain amounts. However, Classen (1985) stated that little or no ^{14}C dilution occurred during the evolution of water in tuff or tuffaceous valley fill. He investigated the effect of caliche on the carbon isotope composition of ground water and concluded that the Fortymile Canyon floor probably does not contain caliche. Caliche, therefore, can be considered a minor factor in the determination of groundwater chemistry for the tuff aquifers. Claassen (1985) did not consider that a correction was necessary for the ground water ages in tuff and tuffaceous valley fill. Hence, the apparent ages should represent the true ground water age.

Claassen (1985) considered the southern portion of Yucca Mountain south of Death Valley as his study area. Wells completed in tuff or tuffaceous valley

USW H-1
USW H-5
USW G-4
USW H-6
UE 25b#1
USW H-4
Exploration
Block
UE-25c#1,2,3
USW H-3
UE-25p#1
USW VH-1
UE-29a#2
Fortymile
Wash
J-13
J-12

1 0 1 2
Miles

1 0 1 2 3 4
Kilometers

N
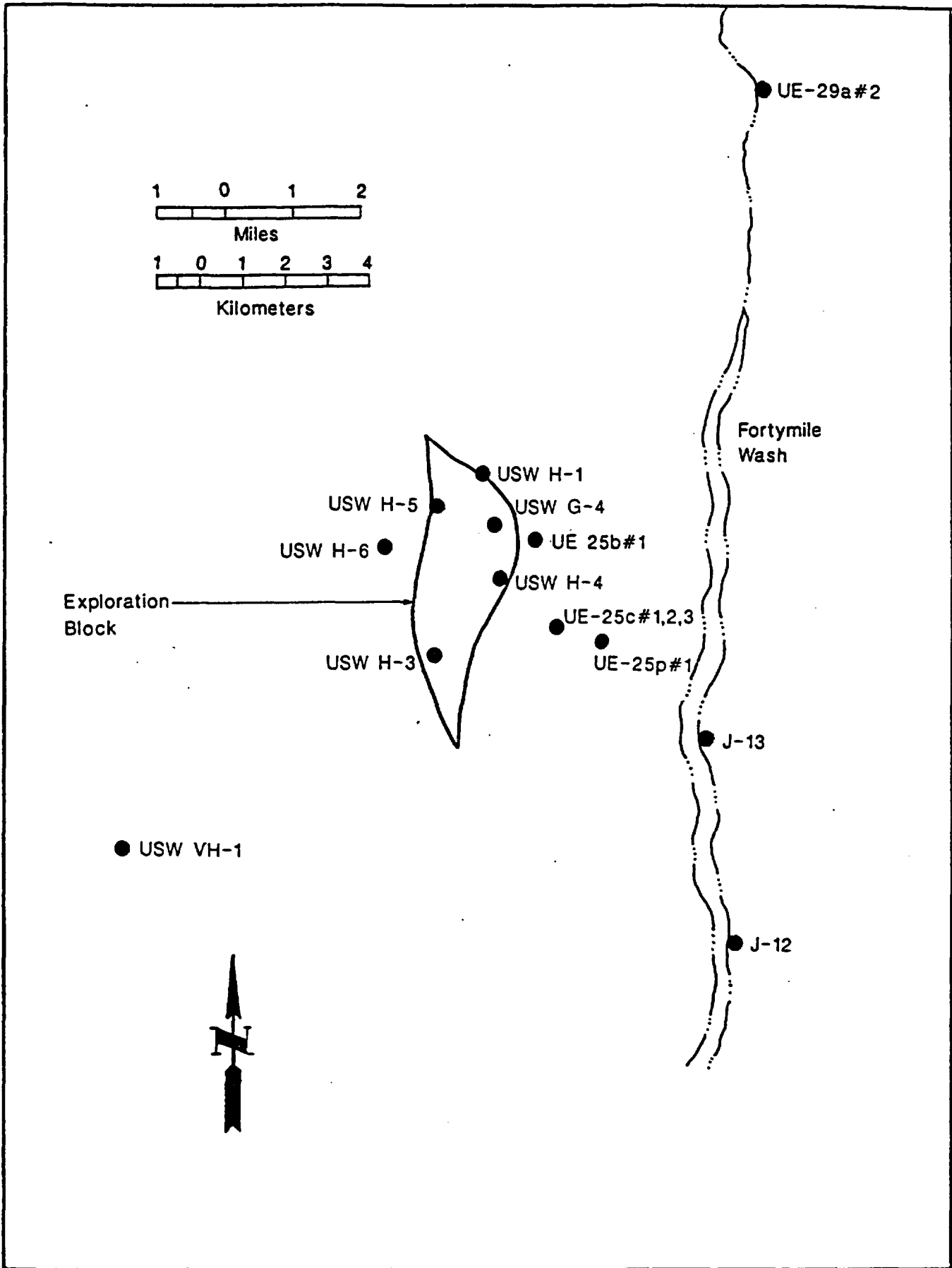
	Figure 10	Date: Nov. 1987
Water, Waste & Land, Inc.	Yucca Mountain Area Wells Having ^{14}C Analysis	Project 4001

1 0 1 2
Miles

1 0 1 2 3 4
Kilometers

Exploration Block

(3,967 yrs)

Fortymile Wash

(11,543 yrs)

(12,434 yrs)

(12,210 yrs)

(14,629 yrs)

(13,436 yrs)

(17,234 yrs)

(14,480 yrs)

(28,728 yrs)

(18,175 yrs)

(9,927 yrs)

(16,966 yrs)

(9,139 yrs)

N

Water, Wastes & Land, Inc.

Figure 11
Apparent Ages Based on ^{14}C Analysis

Date: Nov. 1987

Project 4001

fill are shown on Figure 12. He gave the following three explanations for the absence of water older than 17,000 years:

1. The absence of ages greater than 17,000 years is an artifact of location and completion.

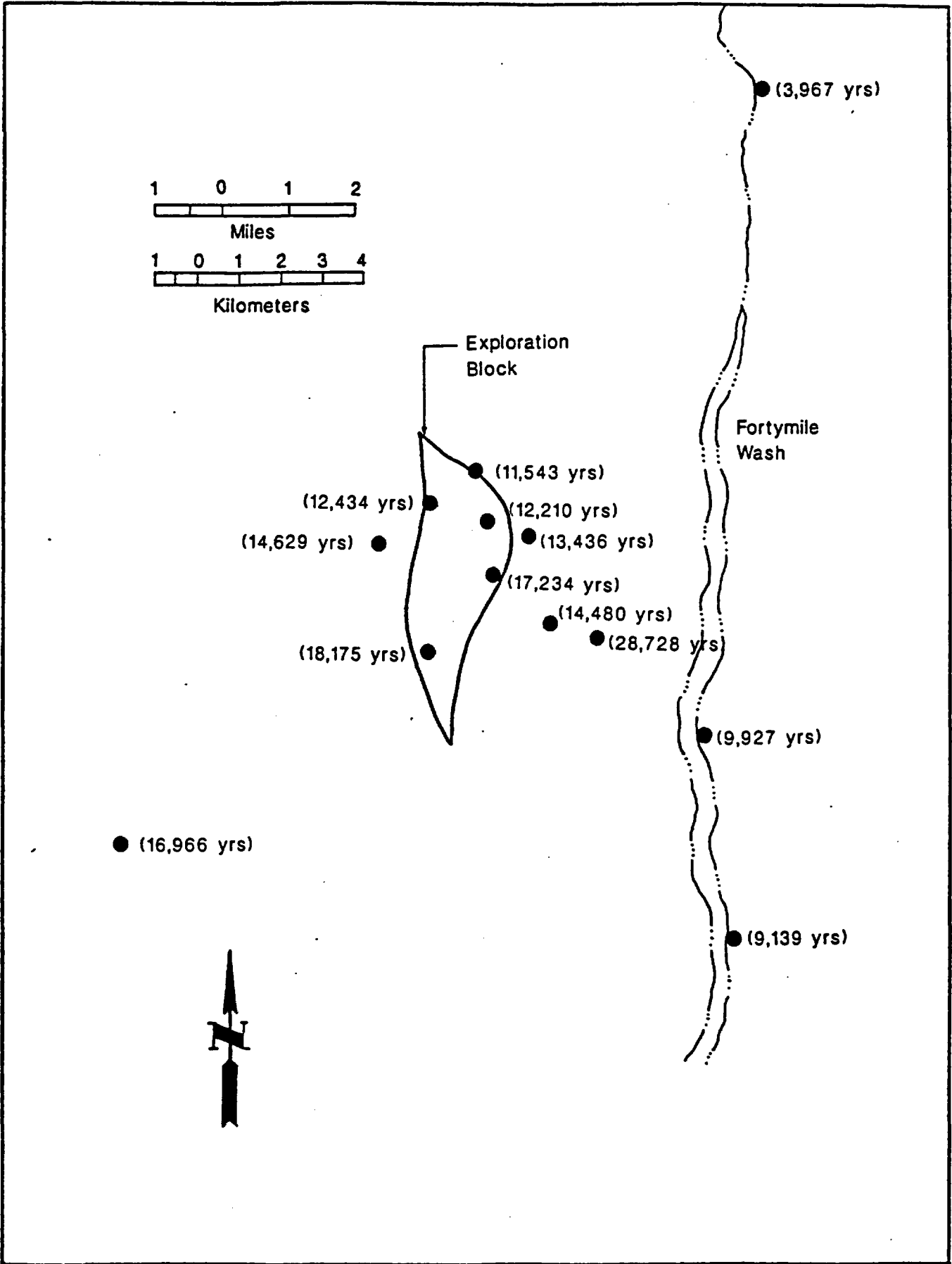2. Permeability characteristics of the aquifers sampled are such that the older ground water has moved beyond the study area. If it is assumed that significant recharge also occurred from 17,000 to about 27,000 years ago (the end of the next nearest significant interstade), then those ground waters may have left the region that was sampled in his study.

3. Based on Spaulding's (1983) studies of past climates, until about 23,000 years ago, the average annual precipitation was only about 20 percent greater than current precipitation, although much of the increase was during the winter months. During the late Wisconsin, however, average annual precipitation increased to about 40 percent greater than the current precipitation, with 70 percent increases for the winter component. Snowfall earlier than about 20,000 years ago was insufficient to result in snowmelt recharge, while subsequent climatic conditions caused such recharge.

3.3.6 Carbon-14 in Yucca Mountain Gas Phase

As previously described, samples of the gas phase have been obtained from the unsaturated zone at Yucca Mountain. Gas samples were collected from the borehole of USW UZ-1 to a depth of 368 meters in 1984 and 1985. The gas samples were then analyzed for CO_2 and water vapor content. During the CO_2 analysis the content of the ^{14}C and ^{13}C isotopes was also determined. Two different collection techniques were used to obtain the CO_2 and water vapor from the formation (see Section 3.3.4). The concentrations determined by the two methods were not consistent (Yang, et al., 1985). General agreement between the molecular sieve and KOH methods was indicated for the ^{14}C data.

The data presented by Yang et al. (1985) was considered to be preliminary as the gas concentrations were continuing to change at the site and changes in the ^{14}C content were probably occurring. The report concluded that the $^{14}CO_2$ in the unsaturated zone gas phase was significantly higher at probe number 1 (12.8 meters deep) than at either the surface or at greater depths. This large $^{14}CO_2$ value (121.8 pmc) was presumed to be the result of the thermonuclear testing conducted in the early 1960's. Therefore, this peak concentration is a good indication of the penetration of gaseous CO_2 from the early 1960's to that

USW H-1
11,543 •
13,436 • UE 25b #1

USW VH-1 • 16,966   J-13 • 9,927

J-12 • 9,139

Fortymile Wash

• 13,200

14,900 •
14,200 •
10,400 •   • 10,100
                • 12,800
                13,200
• 13,600

• 10,300

• 15,900

0   5   10 Miles
0   5   10 Kilometers

NEVADA
CALIFORNIA
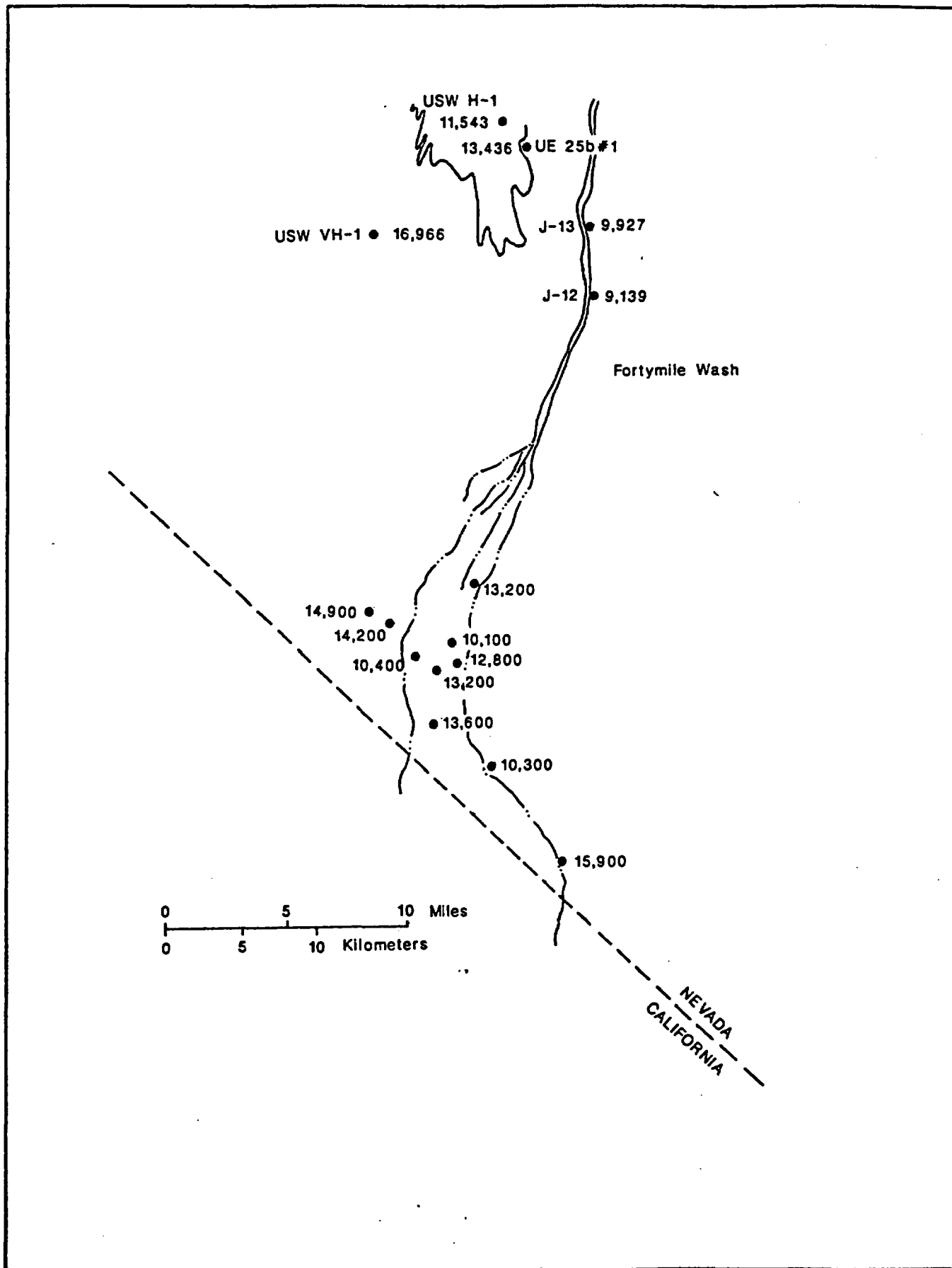
Water, Waste & Land, Inc.	Figure 12 Apparent Ages of Tuff or Tuffaceous Valley Fill	Date: Nov. 1987
		Project: 4001

depth. Table 5 shows the data obtained by the molecular sieve method (Yang, et al., 1985).

3.4 OTHER ISOTOPES

Several other isotopes have the potential to be used to help characterize the recharge at Yucca Mountain. The use of AMS allows significantly smaller water samples for some of these isotopes thus making them extremely attractive in characterizing the unsaturated zone.

3.4.1 Silicon-32

Silicon-32 (^{32}Si) is of interest for use as a hydrogeologic tracer as its half-life lies between those of tritium and ^{14}C. It is cosmic ray produced by spallation reactions with atmospheric argon-40 (^{40}Ar) and introduced into the hydrologic cycle by dissolving into atmospheric water. The deposition rate depends upon latitude. A study was performed by Lal, et al. (1970) to determine concentrations of ^{32}Si in precipitation, streams, rivers, lakes, and subsurface waters. They concluded:

1. The mean annual weighted concentration of ^{32}Si in precipitation over the Indian sub-continent is 0.3 disintegrations per minute per cubic meter (dpm/m^3).

2. Apparent ^{32}Si ages for ground water (500-2000 years old) in arid to semi-arid and semi-arid to wet regions of India are found to be in good general agreement with ^{14}C ages with the ^{32}Si ages usually lower by a few hundred years.

As reported by the IAEA (1983), the determinable specific ^{32}Si activity is about 0.01 dpm/m^3 of water. It requires the extraction of the ^{32}Si from several cubic meters of water. Two methods are used for extraction, scavenging with iron hydroxide, Fe(OH)$_3$, and extraction by ion exchange. The extracted silica is radiochemically purified and stored allowing the daughter product phosphorous-32 (^{32}P) to grow in near secular equilibrium with ^{32}Si decay. The ^{32}P is then counted by anti-coincidence gas or semiconductor detectors allowing a determination of ^{32}Si concentration. Elmore (1987) reports that AMS has been demonstrated for ^{32}Si, which could make the use of the isotope as a hydrologic tracer more attractive as smaller samples would be required.

TABLE 5

UNSATURATED ZONE GAS PHASE CARBON

Probe No.	Depth (m)	Collection Dates in 1985	CO_2 % Vol.	$\delta\ ^{13}C$ (mil)	^{14}C PMC
1	12.8	4/30-5/2	0.789	-22.3	121.8 ± 1.8
2	20.3	4/30-5/4	0.043	-26.2	99.3 ± 1.7
3	28.3	4/30-5/6	0.014	-25.0	85.3 ± 2.3
5	61.3	4/30-5/4	0.024	-23.8	70.3 ± 3.3
6	81.1	3/26-3/28	0.030	-19.2	85.1 ± 4.0
8	128.3	3/25-3/27	0.059	-23.3	88.3 ± 2.5
10	189.3	3/27-3/28	0.024	-15.8	----------
11	227.7	5/1-5/4	0.045	-20.1	61.7 ± 1.8
12	265.5	3/19-3/22	0.013	-25.4	----------
13	304.2	?	0.003	-11.0	----------
14	335.3	3/19-3/25	0.011	-21.6	----------
15	367.9	3/19-3/22	0.039	-21.0	34.2 ± 1.5

3.4.2 Argon-39

The Argon-39 (^{39}Ar) isotope has the advantage that its half-life period of 269 years allows dating of water samples characterized by ages ranging from 50 to 1000 years, filling the gap in dating using the tritium and ^{14}C isotopes. And because ^{39}Ar is a noble gas, it does not come into interaction with the water bearing formations. However, its specific activity is very low (0.1 dpm per liter of Argon) and large volumes of water are required for analyses. In the atmosphere, the ^{39}Ar atoms are produced by cosmic ray interactions with ^{40}Ar. In ground water, ^{39}Ar can be produced by neutrons reacting with potassium-39 (^{39}K). Thus, ^{39}Ar concentration in ground water depends on the content of radioactive elements (uranium, thorium) and potassium in the water bearing rocks. According to Ferronsky (1982) the maximum contribution of ^{39}Ar from thermonuclear tests and ejections of the atomic industry does not exceed 12% of its cosmogenic content. Therefore, manmade contributions can be neglected (IAEA, 1983).

The IAEA (1983) summarized the results of comparing ^{39}Ar age dating with ^{14}C age dating methods. A parallel trend of ^{14}C and ^{39}Ar activities was observed with concentration levels decreasing in the flow direction. However, the ^{14}C ages are usually higher. To explain the results, the IAEA provided the following conclusions. ^{39}Ar and ^{14}C data can more readily be brought to agreement in some cases, if one assumes that the collected water is a mixing of different components (old and young water). In deep or well-confined aquifers gas exchange between the atmosphere and the groundwater though an aquitard can be excluded. Where ^{39}Ar is produced underground, the diffusion of the ^{39}Ar out of the grains into the water in these types of rock is rapid enough to produce the measured ^{39}Ar excess of up to 600% modern. Time information for these types of water by the ^{39}Ar method can therefore not be obtained. However, underground production rates of radioisotopes can be estimated, which may be especially important for the interpretation of ^{36}Cl and ^{14}C results.

Ferronsky (1982) reported that in order to obtain 3 liters of Argon required for its activity measurement, at least 20 tons of water has to be processed. The processing procedure consists of (1) extraction of gases from water, (2) separation of argon from the gaseous mixture (during which special attention should be paid to the separation of the krypton-85 (^{85}Kr) admixture), and (3) measurement of the ^{39}Ar activity with the help of the proportional counter. A high ^{85}Kr activity can indicate recent contamination since the

atmospheric ^{85}Kr activity is quite high at the present time (IAEA, 1983). Smaller high-pressure proportional counters have been developed for ocean water dating using ^{39}Ar. These counters need about 0.2 liters of argon which can be obtained from the degassing of 1-1.5 m^3 of water.

3.4.3 Iodine-129

Iodine-129 (^{129}I) is a long lived isotope with a half-life of about 1.6 X 10^7 years. The ^{129}I atom is produced by the action of cosmic rays on stable elements in the upper atmosphere and from fission of heavy elements within the earth. Additional ^{129}I is produced from fallout of nuclear weapons testing and from gaseous effluents from nuclear reactors and reprocessing. A limiting factor in the use of ^{129}I in hydrogeologic studies previously was the lack of capability for measurement of very low isotope ratios. This problem has been resolved by the use of AMS for detection of the atom.

The reporting of ^{129}I is usually as its ratio to the stable ^{127}I atom, as the ^{127}I atom is fairly conservative in groundwater. Fabryka-Martin et al. (1985) calculated a total steady-state ^{129}I inventory of 1.2 X 10^{27} atoms in the hydrosphere. They compared this value with the total hydrospheric inventory of ^{127}I, which makes up nearly 100% of the total iodine, and determined a predicted average hydrospheric ratio of 5.5 x 10^{-13}. The authors concluded that on a global scale, ^{129}I/I ratios throughout the hydrosphere should be essentially constant over time. The starting isotope ratio in recharged ground water is expected to have been both spatially and temporally constant and approximately equal to 6.4 x 10^{-13}. Interpretation of the ^{129}I/I ratios requires possible sources of the ^{129}I and iodine to be identified, a difficult process in the subsurface environment.

Fabryko-Martin et al. (1985) reported on the behavior of ^{129}I in ground water from two field studies. Some of their conclusions were:

1. The pre-bomb atmospheric equilibrium ratio is 5.7 x 10^{-13} based on a sample collected from the Great Artesian Basin, Australia.

2. Subsurface production of ^{129}I can be significant.

The studies demonstrated the capability of AMS to measure as few as 10^7 atoms of ^{129}I in a sample containing 10 mg I with 10% precision, which corresponds to an isotope ratio of 8 x 10^{-13}. The detection limit is about 10^6 atoms, or a ratio of 1 x 10^{-13}.

3.4.4 Krypton-81 and Krypton-85

Krypton-81 (^{81}Kr) has a long half life of 210,000 years and thus can be used to date waters older than can be dated using ^{14}C. Krypton-81 is produced naturally in the upper atmosphere by cosmic radiation and has a measured atmospheric concentration range of between 0.067 to 0.10 disintegrations per minute per liter for pre-bomb krypton (IAEA, 1983). Because the natural concentrations of ^{81}Kr from atmospheric sources are very small, very large water sample sizes are required for conventional counting. However, Davis and Murphy (1987) reported that new methods using laser beam excitation techniques (resonance ionization spectroscopy) may enable smaller samples to be analyzed with increased accuracy. Because krypton is inert against chemical reactions, the geochemical interpretation of ^{81}Kr in ground waters may be simplified. However, very little information is currently available on the use of ^{81}Kr in groundwater studies.

Krypton-85 (^{85}Kr) is also produced in the atmosphere by interactions of cosmic rays with ^{84}Kr. The present atmospheric concentrations of ^{85}Kr are almost entirely from artificial nuclear fission (Davis and Murphy, 1987). The half life of ^{85}Kr is 10.7 years, similar to that of tritium. However, the ^{85}Kr atmospheric concentrations have been increasing at a steady rate for the past 35 years resulting in a simpler input function to groundwater than tritium. Concentrations of ^{85}Kr in ground waters is extremely low and large samples are still required for analysis.

3.5 CONCLUSIONS

Isotope measurements can be used to help interpret the rate of groundwater flow along flow paths between the repository site and the accessible environment. Isotope studies may also help establish the history of climatic and geomorphological processes which might affect a repository or alter radionuclide migration rates to the accessible environment. Tritium is an indication of recent water, either by contamination or infiltration. For older waters, ^{36}Cl might prove valuable in determining rates of water movement in the unsaturated zone.

Isotope concentration can be influenced by exchange between isotopes in solution and in the formation rock and differential sorption or desorption. The fission of uranium in the formation produces neutrons which may create active isotopes such as ^{14}C or ^{36}Cl, raising their concentrations. Therefore

it is important that age dating by isotope techniques be integrated with the study of the mineralogy and stratigraphy of the formation. It is useful to compare the ages derived from various isotopes. When done with consideration for the mineralogy of the formation, corrections can be made for deviations due to isotope exchange or differential processes.

The meteoric fallout of the ^{36}Cl provides a steady source of solutes to the land surface. If recharge rates are rapid, these solutes are carried to the water table in quite dilute form. However, under arid conditions other mechanisms occur which can alter the chloride concentration profile. Where recharge rates are very low these meteoric solutes are concentrated by evapotranspiration. However, Phillips et al. (1983) concluded that due to the approximate square-wave shape of the pulse and the hydrophilic nature of chloride, the pulse can be used as an excellent tracer in the hydrologic cycle.

Bomb-produced ^{36}Cl will usefully supplement bomb-tritium as an environmental tracer, and as the bomb-tritium pulse decays to background levels, ^{36}Cl will eventually replace it (Bentley, et al., 1982). The ^{36}Cl tracing method has significant advantages over alternative techniques for measuring net infiltration through desert soils. Bomb ^{36}Cl tracing also demonstrates significant advantages over bomb-tritium tracing. These include:

1. simpler sampling,

2. smaller contamination problems,

3. an approximate square-wave input function simplifies interpretation and calculation of dispersion, and

4. the longer half-life avoids the pulse-detection problem now beginning to affect tritium and avoids confusion of decay with dispersion.

Based on the ^{36}Cl results, Phillips et al., (1983) concluded that blanket assumptions that the net flux is negligibly small in arid regions are not justified, and that present methods are capable of measuring the net soil-water flux in arid environments only with considerable difficulty and uncertainty.

The use of radioactive isotopes has been shown to be a useful tool in investigating hydrologic systems with information about water velocity, dispersion, recharge, and other parameters being obtained from carefully designed studies. The added complexity of flow through an unsaturated dual porosity system makes the planning and interpretation of tracer studies more

difficult. As described in previous dual porosity tracer studies, a wide range of tracer behavior can exist. The behavior of the tracer in the hydrologic system is a function of the tracer properties, the flux of water moving in the system, the fracture properties, the matrix properties, and the physical and chemical interaction between the rock and tracer.

For a hydrologic system similar to the one at Yucca Mountain, a number of scenarios are possible for the study of radioactive tracers and their movement in the unsaturated zone. A natural radioactive tracer falling on the surface of Yucca Mountain in precipitation will contact the Tiva Canyon welded unit (TCw) and alluvial material. If the precipitation event is large, a significant portion of the water may enter into the TCw fracture system. Radioactive tracers which are in the water will therefore be carried into the TCw fractures. Several possibilities exist for the tracers at this point:

1. A particular tracer may pass through the fracture system with the downward flowing water and enter the non-welded Paintbrush tuff (PTn) hydrogeologic unit,

2. A portion of the tracer in the flowing water may be adsorbed onto the fracture face,

3. Diffusion of the tracer into the matrix may occur as the water pulse moves downward, or

4. A combination of the above events may occur. The degree to which any of the possibilities is realized may also be a function of the precipitation event, where the amount of water entering into the fracture system determines the depth to which the tracer is carried (WWL, 1986b).

After a water pulse has passed through or has been attenuated by the TCw unit, secondary processes can occur which can alter the tracer distribution (if any) in the TCw unit. Two phase flow is presumed to occur in this unit, and as such, the air phase will allow evaporation to take place, not only in the fracture system but also between the matrix and the fractures. Evaporation can cause redistribution of the isotopes to occur, leaving an altered concentration profile in the matrix and fracture. Thus, interpretation of natural tracer data may be possible only with great difficulty. Certainly bounds on the processes which are taking place may be realized. If high tritium concentrations are found in the TCw unit, then a welded tuff's ability to retard the hydrogen isotope may be confirmed. However, as indicated by the

Chalk study in Great Britain, the finding of tritium within the matrix does not rule out the possibility that transport due to fracture flow can occur, in spite of considerable attenuation through diffusion into matrix pore water.

The current hydrogeologic conceptual model for flow at Yucca Mountain has any water passing through the TCw unit entering into the matrix of the PTn (DOE, 1986). Again, a bound on the water flow may be determined from the radioactive tracers. For example, if tritium is found above background levels in the PTn, a mass balance may indicate the minimum amount of water passing through the TCw and entering the PTn. This approach would require a development of a TIF for the Yucca Mountain Site. Longer lived radioisotopes will also be important tracers in this unit. Presumably, water which enters the PTn is transmitted laterally to large faults where it can drain to the regional ground water surface. Therefore, if tritium and other radioisotopes are not found in the TCw but are found in the PTn, the single porosity flow present in the PTn would make analysis of the concentration profiles much more amenable. A tracer profile present in the PTn should allow a determination of net infiltration into that unit.

Below the PTn is the Topopah Springs welded tuff (TSw), a highly fractured dual porosity hydrologic system. Again, analysis of radioisotope data collected during site characterization will be influenced due to the fracture/matrix flow interaction. However, if bomb pulse isotope concentrations are found in either matrix or fracture water, the travel times and ultimately the conceptual model may have to be re-evaluated. On the other hand, the lack of bomb pulse concentrations of isotopes in the TSw unit does not provide conclusive proof that matrix flow is occurring.

3.6 RECOMMENDATIONS

A number of isotopes have been or have the potential to be used in the study of hydrogeologic systems. Advances over the past decade in AMS has significantly increased the detection capability for a number of long-lived radioisotopes. This increased detection capability has also been accompanied by a tremendous reduction in sample size as compared with the conventional decay-counting methods. In particular, anthropogenic ^{36}Cl has become an important radioisotope tracer in the hydrologic cycle, primarily due to the development of AMS.

Because of the complexity of flow in the dual porosity systems currently being considered at Yucca Mountain and the possible interactions of the radioisotope tracers, it would seem prudent to analyze for a number of tracers during the site characterization process. Radioisotope tracers which can be analyzed for by AMS are excellent candidates for studying the unsaturated zone as small water samples are required. For any perched water zones encountered, other isotopes may also be considered for analysis as sufficient water may be available.

Differences in radioisotope concentrations in the matrix as a function of distance from the fracture face would yield valuable information for the diffusion and adsorption characteristics of radionuclides in tuff. Care would have to be taken during the sampling as differential slices of the matrix would need to be analyzed independently.

4.0 STABLE ISOTOPES USED IN HYDROGEOLOGY

Hydrogen and oxygen are two natural stable elements which have been used in a large number of hydrologic studies. The two stable isotopes of hydrogen are protium (H) and deuterium (^{2}H or D) which have average abundances of 99.985 and 0.015 percent, respectively. Oxygen has three stable isotopes, oxygen-16 (^{16}O), oxygen-17 (^{17}O), and oxygen-18 (^{18}O), with abundances of 99.01, .01, and .08 percent, respectively. The concentrations of the isotopes in nature are dependent upon evaporation, condensation, and exchange reactions.

Stable isotopes of interest in the circulation of water in nature are deuterium (D) and ^{18}O both of which are found in water molecules as HDO and H_2 ^{18}O. Because of the higher masses, both have slightly lower saturation vapor pressures than the ordinary water molecule H_2 ^{16}O. Therefore, a fractionation of the HDO and H_2 ^{18}O will occur during evaporation and condensation processes with the molecules becoming enriched in the liquid phase and depleted in the vapor phase.

As water evaporates from the ocean surface the vapor becomes enriched with ^{16}O and H relative to ^{18}O and D in the ocean surface water. As ocean water accounts for the vast majority of the total water in the hydrosphere, Craig (1961) proposed it as a standard for reporting concentrations of D and ^{18}O content in natural water. The isotopic composition of the ocean appears to remain constant despite the fact that great amounts of water are constantly evaporated from the ocean surface. This constancy can be explained by the fact that the evaporated water ultimately returns to the ocean.

The water vapor in the atmosphere represents only a minuscule amount of the water in the hydrosphere, but is responsible for the relationship between the ocean, continental surface, and ground waters. In 1961, the IAEA and World Meterological Organization (WMO) initiated a worldwide survey of hydrogen and oxygen isotopes in precipitation. One of the aims of the project was to deduce some characteristics of the circulation patterns and mechanisms of the global and local movements of water (Dansgaard, 1964). Since then a number of investigators have used the isotopic variations in vapor, precipitation, and groundwater for the study of hydrologic and geologic systems.

Changes in the heavy isotope content of water in an aquifer at depth or distance from a recharge area may be indications that the waters formed under different climatic conditions or of other processes which can alter the isotopic composition of rainwater. Some of these other processes are

evaporation in the unsaturated zone, exchange with oxygen bearing minerals, and a difference in altitude between the recharge area and the area where the water was sampled.

4.1 STANDARD MEASUREMENT

The reference standard for the measurement of D and ^{18}O is the Standard Mean Ocean Water (SMOW). The SMOW is defined in terms of the National Bureau of Standards reference sample 1 (NBS-1) (Craig, 1961), such that:

$$\frac{D}{H} \text{ (SMOW)} = 1.050 \ \frac{D}{H} \text{ (NBS-1)}$$

$$\frac{^{18}O}{^{16}O} \text{ (SMOW)} = 1.008 \ \frac{^{18}O}{^{16}O} \text{ (NBS-1)}$$

Data is reported as the relative deviation delta, δ, of the heavy isotope content of a sample from that of the standard

$$\delta = \frac{(R_{sample} - R_{standard})}{R_{standard}} \ 1000$$

where R is the concentration ratio D/H or $^{18}O/^{16}O$ of the Sample and Standard. Therefore, the value of zero is given to SMOW on the scale of differences (delta values) in parts per thousand. Samples relatively depleted in the heavy isotope species have negative δ values. Because the differences between samples and reference are usually quite small, it is convenient to define the scale in which the δ values are multiplied by one thousand. Values of δ are an intrinsic property of water (Wallick, 1984) and as such can be used in tracing and mixing computations in hydrology. Analysis of water for D and ^{18}O is done by mass spectrometry. A small water sample (~20 ml) is generally sufficient to obtain an accuracy of $\pm$ 0.1% for δ ^{18}O and $\pm$ 1% for δ D (IAEA, 1983).

4.2 ISOTOPIC COMPOSITION OF ATMOSPHERIC PRECIPITATION

As water vapor from the oceans moves through the moderately humid temperate zone, it becomes progressively lighter as the heavier isotopes preferentially precipitate out in a series of condensations and re-

evaporations. The ratio, R_L, of D and ^{18}O of the condensate obeys Rayleigh's law (IAEA, 1983):

$$R_L = R_L^0 \, f^{(\alpha-1)}$$

where R_L is governed by Q, the cumulative amount of initial vapor which condensed, and the initial R_L^0 when $Q=Q^0$. The terms f and α are the ratios Q/Q^0 and R_L/R_V, respectively, where R_V is the vapor ratio. The isotopic ratio depends much more on the fraction f, which varies between 0 and 1, than the fractionation factor α, which varies slightly with temperature. The decreasing D and ^{18}O content in precipitation with increasing distance from the oceans depends more on reservoir effects than isotope fractionation. The water with the most negative delta values is polar ice which represents the final stage of the repeated fractional distillations.

Rain-out from the vapor reservoir is temperature dependent. In areas of extreme temperature variations, such as the tropics or semi-arid regions, local influences affect the isotopic composition through evaporation. Correlations exist between average annual temperatures and δ ^{18}O (or δ D) values of the average annual precipitation. The δ values for ^{18}O may range from -5% at an oceanic measuring station, -10% some distance inland with the lowest δ ^{18}O values at the poles where δ ^{18}O values may approach -50%. Enrichment of the heavy isotopes may occur and departures from the standard distribution pattern are common.

The controlling factor in the fractionation of isotopic species in surface waters is the difference in the saturated vapor pressure between various water molecules where

$$P_{H_2^{16}O} > P_{H_2^{18}O} > P_{HDO}$$

Under equilibrium conditions, the fractionation factor, α, is determined by the ratio of the saturated vapor pressure of the light and heavy components, P and P', respectively. At a temperature of 20^0 C, the fractionation factors are 1.08 and 1.009 for HDO and $H_2^{18}O$, which means that vapor in equilibrium with water will be depleted in deuterium by 8% and in oxygen-18 by 0.9%. As

temperature increases the fractionation factors of D and ^{18}O decrease and can be expressed by

$$\alpha = A \exp (B/RT)$$

where A and B are constants for each isotope and R is the gas constant.

A cloud system can be idealized as an open or a closed system. For a closed system, condensate is not removed from the cloud. Fractionation of the D and ^{18}O between the vapor and condensate occurs; however, the net isotopic composition of the system remains constant. For the perfectly open system, where the liquid phase leaves the cloud as it condenses, the isotopic composition of condensate varies as a function of the amount of water previously removed from the cloud. Generally, thermodynamic and isotopic equilibrium between water and vapor does not occur. Under non-equilibrium evaporation conditions, the difference between the deuterium and ^{18}O content is limited not only by the value of the fractionation factors but also by the ratio of the diffusion rates of the molecules (Ferronsky, 1982).

The differences in the δ D and δ ^{18}O content of water are used for the solution of problems dealing with the determination of the interrelationships between surface and subsurface waters. The nonequilibrium conditions and kinetic effects determine isotopic differences between the various phases. For isotopic changes associated with evaporation from open water surfaces, this is especially important. The heavy isotope content of precipitation can be correlated to latitude, altitude, season, and palaeoprecipitation as shown on Figure 13. These relationships must be determined from analysis of precipitation and climatic data for each location. It has been shown in many studies that ground water which forms at a given recharge area is isotopically very close to the average annual isotopic composition of the precipitation.

The hydrogen and oxygen isotopes, D and ^{18}O, have an interrelationship which exists in the liquid phase. When δ ^{18}O and δ D values from precipitation are plotted as abscissa and ordinate, respectively, precipitation values lie on lines with a slope of about 8.
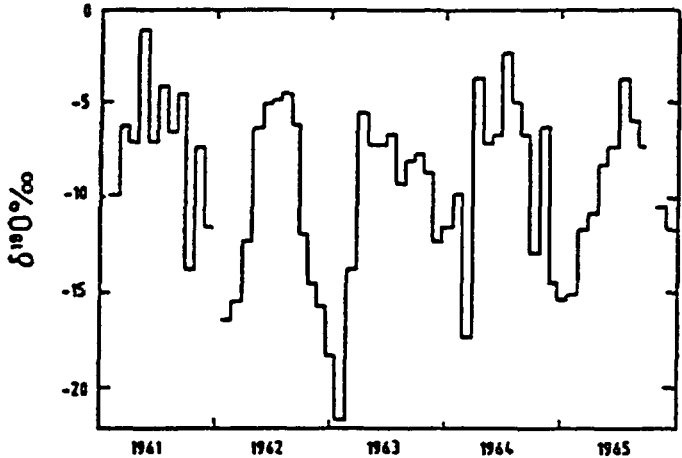
$$\delta D = 8 (\delta^{18}O) + d$$

This line is usually called the meteoric water line. The δ D intercept (d) is called the deuterium excess and varies from place to place. Across the North
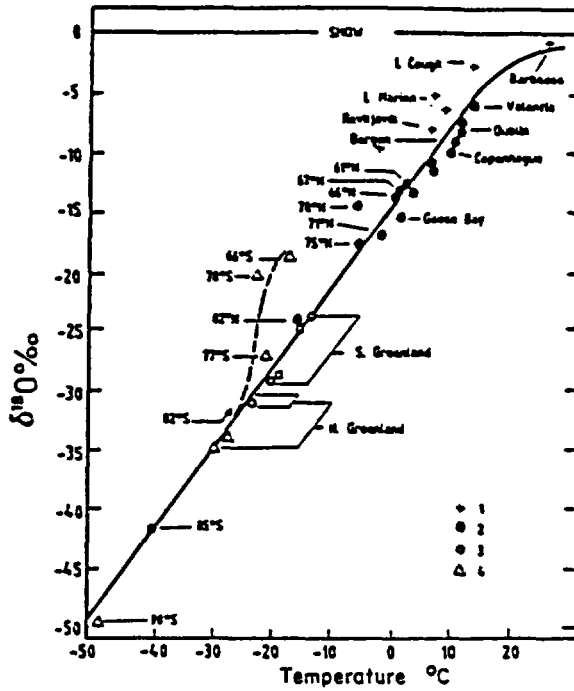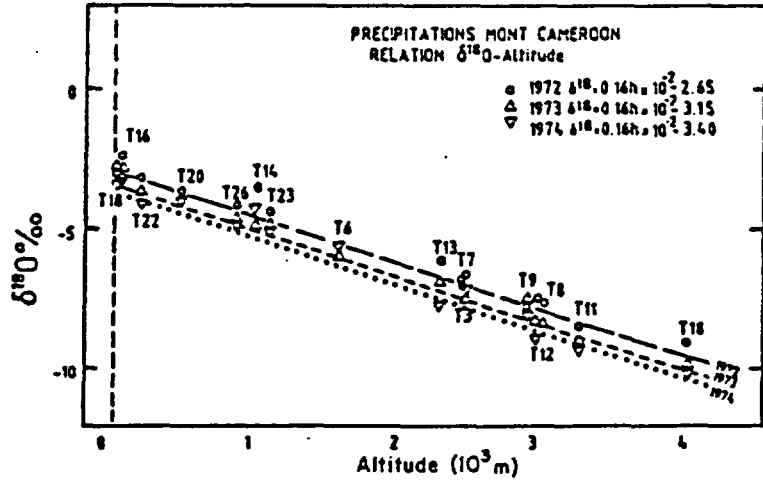
Adapted from IAEA, 1983

| | Figure 13 | Date: | June 1987 |
| Water, Waste & Land, Inc. | Effects of Temperature/Latitude, Altitude and Season on $\delta^{18}O$ | Project: | 4001 |

American continent the deuterium excess values range from about 0% to +12%
(IAEA, 1983), each area having its own meteoric water line.

4.3 ISOTOPIC COMPOSITION OF EVAPORATING WATERS

The fractionation process may be complicated by evaporation of a portion
of the water in the unsaturated zone before it becomes recharge. Evaporation
of precipitation after falling to the ground is controlled by kinetic
processes. The isotopic evolution of the liquid phase depends upon (1) the
temperature, (2) the moisture and isotopic content of the free atmosphere, (3)
the chemical activity of the liquid, and (4) the evaporated fraction. The
general pattern is that the remaining liquid becomes enriched in heavy isotopes
with respect to the initial liquid (IAEA, 1983). Some of the results of
evaporation on the isotopes can be summarized as follows (IAEA, 1983):

1. When the relative humidity of the atmosphere is above 50%, a steady-
    state value of the isotopic ratio is reached due to the exchange
    between air moisture and the liquid.

2. When the humidity is less than 50%, the isotopic enrichment proceeds
    at unsteady-state conditions towards a maximum value of isotopic
    ratio for the last molecules of the liquid.

3. For high evaporation rates, the solution may reach a high salt
    content lowering the activity of the water and the isotopic
    enrichment.

Evaporating waters also can be characterized on an δ D vs. δ ^{18}O diagram.
An evaporating body of water will exhibit a straight line with a slope which
depends upon the relative humidity. Other processes, besides evaporation, can
cause a modification to the initial groundwater composition. The effects of
these processes are shown graphically on Figure 14.

Barnes and Allison (1983) developed a mathematical model which described
the shape of the ^{18}O and D depth profiles resulting from the evaporation of
water from dry soil under quasi-steady state conditions. For most climatic
conditions the slope of the δ ^{18}O/δ D plot will lie between 4 and 6 if the soil
water has been subjected to evaporation. The δ ^{18}O/δ D enrichment process is a
function of the air temperature, relative humidity, isotopic composition of the
atmosphere, and the kinetic fractionation effect.

The kinetic fractionation effect is due to small differences in the
diffusion rates of the isotopes from the evaporation surface to the atmosphere.
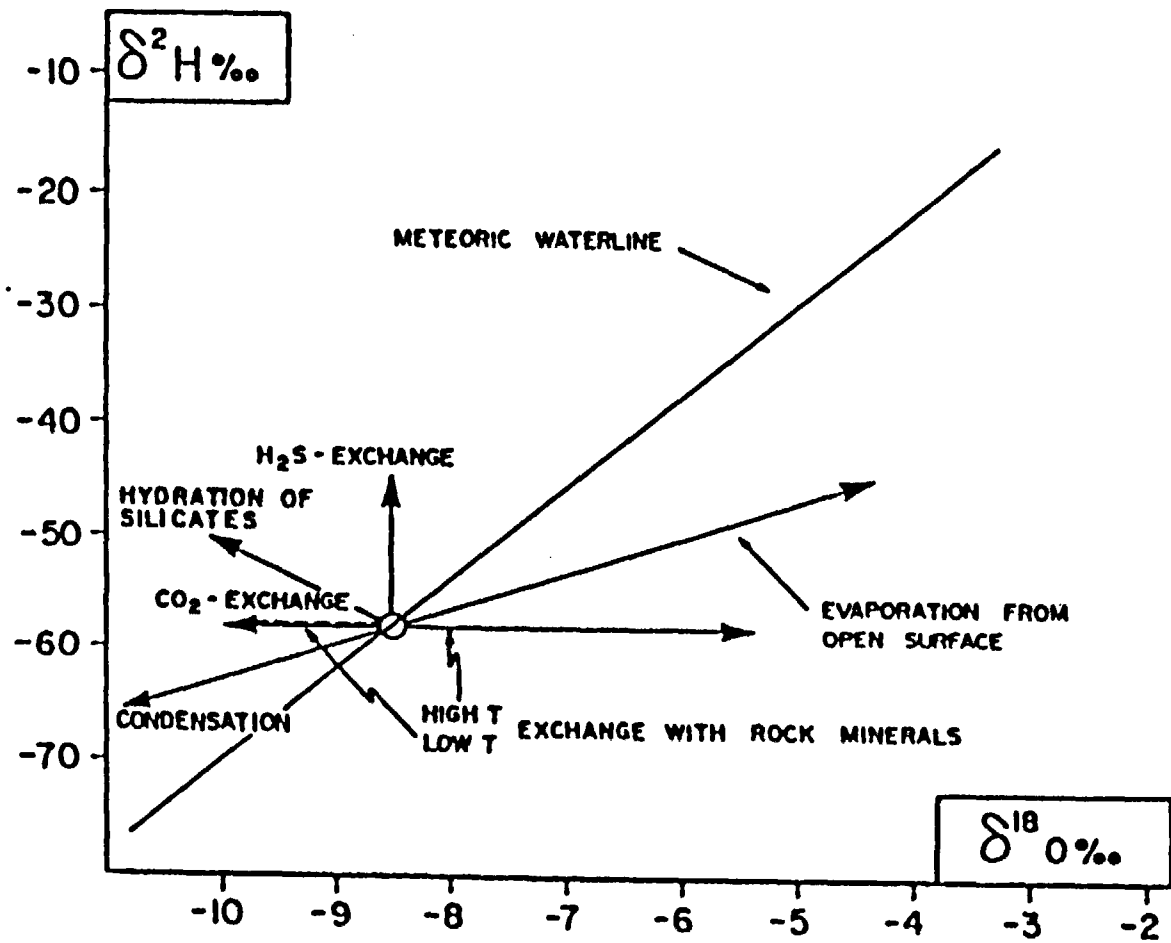
Figure 14
Processes which can Alter Groundwater Concentrations
Compared to the Meteoric Waterline

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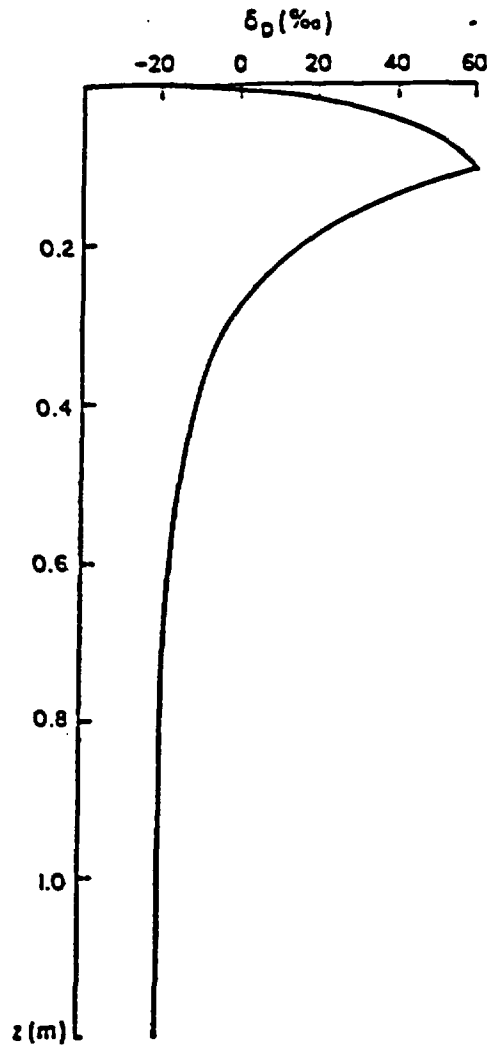Date: June 1987

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This effect on the evaporation rate was described by Barnes and Allison (1983) as being proportional to the molecular diffusivity of the isotopic species raised to a power n. The exponent n is a function of the atmospheric boundary layer above the evaporating surface ranging from 0.67 for open water bodies to 1.0 for very dry soils. The higher the value of n, the lower will be the slope of the ^{18}O versus D line, i.e. the slope of the line decreases as the soil dries out.

As described by Barnes and Allison (1983), at moderate values of the relative humidity, the δ value should rise sharply from the surface to a maximum at the bottom of the vapor transport layer. The height in the profile to which liquid movement occurs is indicated by the position of the maximum δ value. The region in which both liquid and vapor movement coexist is indicated by the broadness of the peak. A typical D δ-value profile is shown on Figure 15, where z is the depth of the soil from the surface.

4.4 ISOTOPIC COMPOSITION OF NEVADA PRECIPITATION

A stable isotope study was performed by Ingraham and Taylor (1986) to determine the history of meteoric water in hydrologic regimes in Oregon, Northern California and Nevada. Water was sampled from springs and streams across the three states and analyzed for D and ^{18}O content. Additional concentration data was obtained from other sources. The δ D values of each sample were plotted with respect to their distance from the Pacific Ocean. As Figure 16 shows, three distinct hydrologic provinces are suggested along the east-west traverse, with each province characterized by a different pattern of δ D versus distance from the ocean.

As described by Ingraham and Taylor (1986), precipitation in the first province is predominantly produced by Rayleigh distillation with water from the Pacific Ocean. In the second province, from 55 to 365 km inland, the rainwater appears to include some recycled water. The third province in the study is the Great Basin. This province is shown to be an isotopically closed system implying that all of the precipitation is returned to the atmosphere by evapotranspiration. Ingraham and Taylor (1986) concluded that the recycling of water in the Great Basin has resulted in isotopically homogeneous groundwater in a large region.
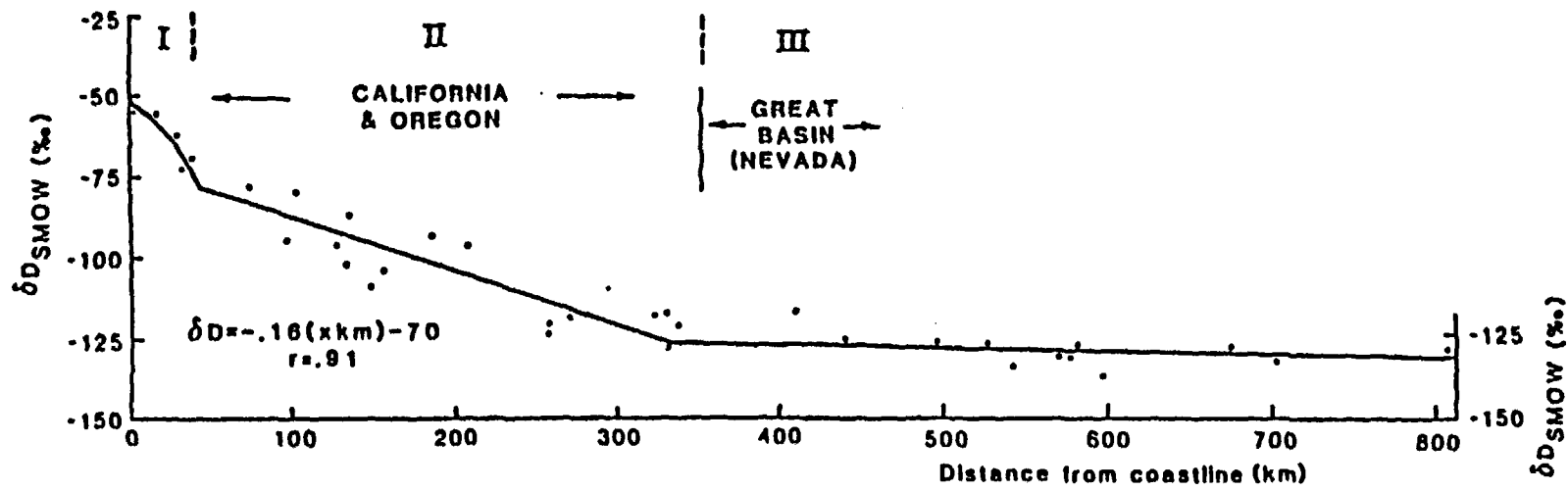
Figure 15
Effect of Evaporation of Soil Water
Adapted from Barnes (1983)

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Figure 16
δD Values as a Function of Distance from the Pacific Ocean
Adapted from Ingraham (1986)

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4.5 HYDROLOGIC STUDIES USING STABLE ISOTOPES

Allison and Hughes (1983) used ^{18}O and D concentrations in a study of land use change in southern Australia. The study area, near Walpeup, Victoria, was in a semi-arid climate with a mean annual rainfall of 335 mm. The study determined the amount of water moving through the soil beneath both native Eucalyptus scrub and cleared, cropped sites. The Eucalyptus scrub sites (mallee) are composed of trees 5-8 m apart ranging in height from 2 to 12 m. The cropped areas consist of a wheat-pasture-fallow rotation system in use since about 1910. Cores were obtained from each of these the areas with the samples being analyzed for chloride, tritium, deuterium, and ^{18}O.

The monthly rainfall D and ^{18}O concentrations during 1978/1979 and the soil water samples from virgin mallee and the cleared, cropped areas are shown on Figure 17. The meteoric line of Craig (1961) is also shown on the figure. The rainfall concentrations fall on the meteoric line. The depth profiles for the δ D and δ ^{18}O soil water concentrations are shown on Figure 18. The profiles shown on Figures 18a and 18b are for the late summer (March, 1977) and show a strong enrichment when compared to the winter rainfall. After the following winter, soil profiles for mallee and cropped areas were again obtained and are shown on Figures 18c and 18d. The winter rainfall is shown at the cropped sites as a decrease in the δ ^{18}O and δ D values of the surface areas. However, beneath the mallee a similar decrease was not noted. This was interpreted as little winter rain penetrating the mallee canopy and litter layer.

The exponential isotope profiles result from isotope enrichment due to evaporation through the soil and vapor movement from the soil to the roots. In a saturated soil, the isotopic enrichment produced at the soil surface moves downwards by diffusion against the upwards evaporative flux resulting in an exponential profile and an ^{18}O vs. D slope of from 4-6 (Allison and Hughes, 1983). The slopes of the cropped and mallee sites, 5.4 and 3.7, respectively, (see Figure 17) indicate that water loss through the dry surface soil occurs more at the mallee than the cropped sites. Allison and Hughes (1983) concluded that this was reasonable as the denser plant cover at the cropped site for most of the year made evaporation from the soil surface less likely.
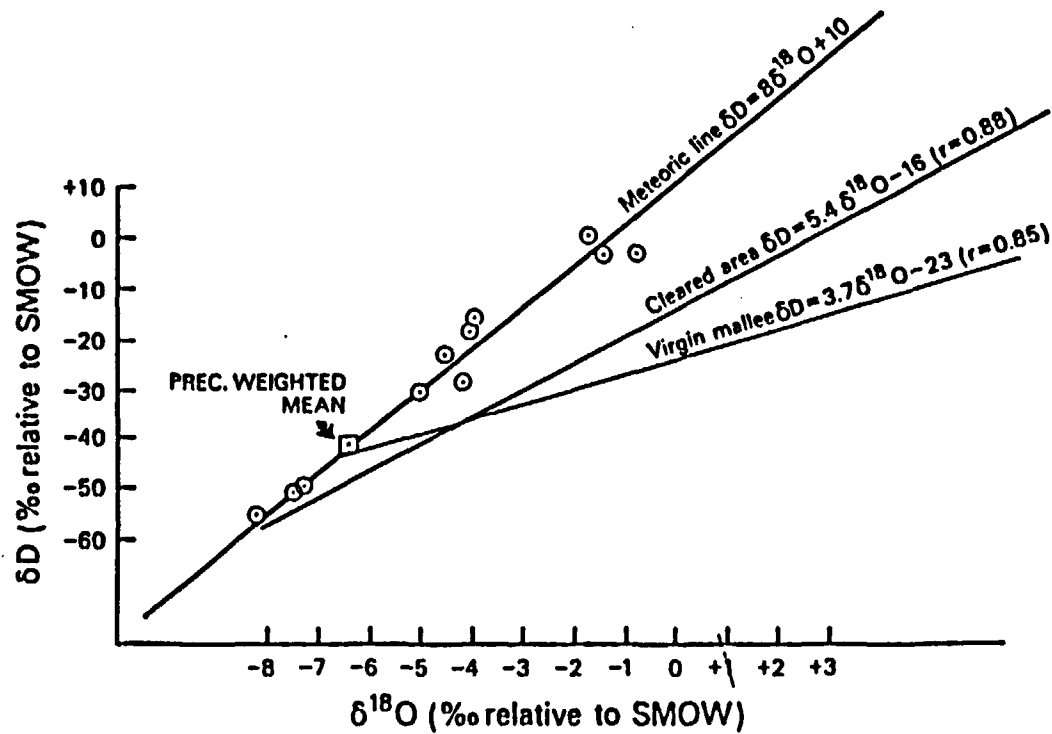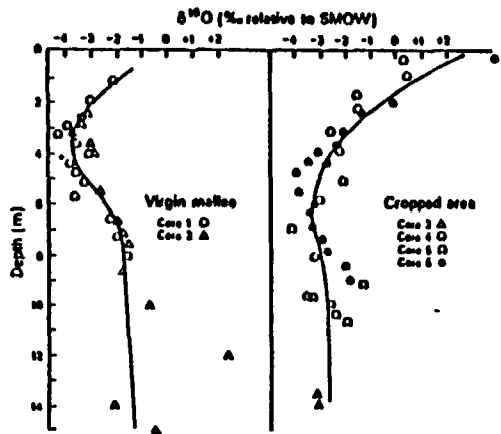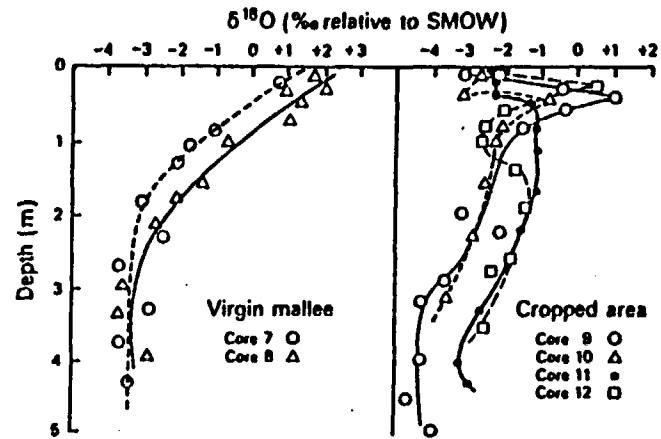
Figure 17
Soil Water Samples from Cleared Area and Virgin Mallee
Compared to Meteoric Line

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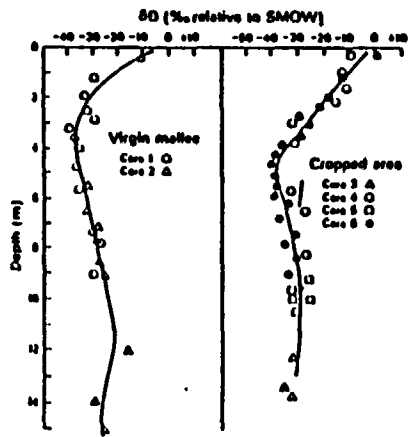
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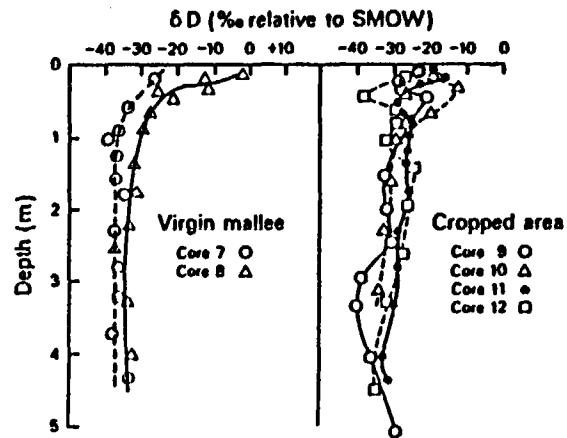
a) Depth profiles of δ^{18}O-values of soil water in March 1977.

b) Depth profiles of δD-values of soil water in March 1977.

c) Depth profiles of δ^{18}O-values of soil water in August 1978.

d) Depth profiles of δD-values of soil water in August 1978.

4.6 YUCCA MOUNTAIN AREA HYDROLOGY BASED ON ISOTOPE DATA

Section 3.3 described the use of radiocarbon and some possible flow scenarios for groundwater at Yucca Mountain when only radiocarbon water ages were considered. The following sections will consider the stable isotopes of carbon, along with other isotopes, to show that alternative groundwater ages at Yucca Mountain are possible.

4.6.1 Carbon System

Two extremes can be described when using the ^{14}C method to date water (Davis and Murphy, 1987). One occurs when water is recharged into an aquifer that does not contribute additional carbonate to the ground water. The total carbonate in the water is derived entirely from the CO_2 in the atmosphere and the soil horizon. The other extreme occurs when all or virtually all of the carbonate is derived from an "old" subsurface source, such as a dolomite or CO_2 from a volcanic vent. The key to successfully using the ^{14}C dating method is to determine the amount of "old" carbon that was introduced into the water sample after the water has been isolated from the atmosphere. Insight into correctly dating a groundwater can be accomplished by investigating the concentrations of the stable carbon isotope, ^{13}C.

The isotopic composition of the CO_2 in equilibrium with a given water can be determined through isotopic and chemical mass balance considerations. The isotopic composition of the various species in a ground water can help to define the recharge environment. Carbon dioxide gas dissolving in a water can be transformed into several aqueous species including carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}), and carbonate complexes. The dominant chemical forms and the mass distribution among species are strongly pH dependent. The dissolved inorganic carbon (DIC) in ground water is the sum of all the carbonate species. Different carbon isotope ratios can exist in the various aqueous species. Therefore, the isotopic composition of the DIC is determined by the amount of (and the isotopic composition of) each species present in a sample.

Variations in $^{13}C/^{12}C$ ratios are measured as $\delta\ ^{13}C$ which is defined as follows:

$$\delta\ ^{13}C\ =\ \frac{^{13}C/^{12}C_{SAMPLE}}{^{13}C/^{12}C_{STANDARD}}\ -\ 1\ *\ 1000$$

The $^{13}C/^{12}C$ standard is the ratio of the carbon isotopes in the PDB reference standard. The δ value is also called mil.

Water in the saturated zone can have its $\delta\ ^{13}C$ content altered by a number of processes, such as carbonate mineral dissolution/precipitation reactions and biological processes. Most circulating ground waters can come into contact with these carbonate minerals and dissolve certain amounts. This dissolution will greatly influence the geochemistry of the water but has no measurable effect on its oxygen isotopic composition (IAEA, 1983). However, the carbonate dissolution can bring about an enrichment in the ^{13}C content in the aqueous phase with the ^{13}C concentration in the DIC sometimes approaching those of the dissolving mineral. Also, because dissolving primary carbonates are usually free of ^{14}C, their dissolution can also cause a decrease in the ^{14}C activity of the DIC.

4.6.2 Deuterium and Oxygen-18 System

Claassen (1985) reported on the chemical analysis of water from wells and springs in the west-central Amargosa Desert south of Yucca Mountain. The plot of the δ D versus $\delta\ ^{18}O$ is shown on Figure 19. Claassen (1985) plotted precipitation values from Colorado and Nevada on the plot and compared these values with those of the groundwaters. He concluded that the isotopic composition of ground water in the Amargosa Desert showed appropriate shifts toward heavier oxygen-isotope content in the ground water as compared to precipitation. He, therefore, concluded that snowmelt was the source of recharge. He combined this information with carbon isotope data and determined that major recharge occurred in the area at the end of the Pleistocene and through early Holocene time.

Benson and McKinley (1985) reported on the chemical analyses of 15 wells in the Yucca Mountain area which had been sampled during 1971-1984. The δ D and $\delta\ ^{18}O$ concentrations indicated that the waters had been depleted in D and ^{18}O with the δ D values ranging from -93.0 to -106% and the $\delta\ ^{18}O$ values ranging from -12.8 to -14.2. The δ D versus $\delta\ ^{18}O$ values for the Yucca Mountain samples are also plotted on Figure 19.

Yang et al. (1985) reported on the analysis of isotopes in gas phase samples from the unsaturated zone at Yucca Mountain. Gas samples were collected at intervals to a depth of 365 meters from the borehole of USW UZ-1. The hole was completed with 15 sampling stations, including gas probes,
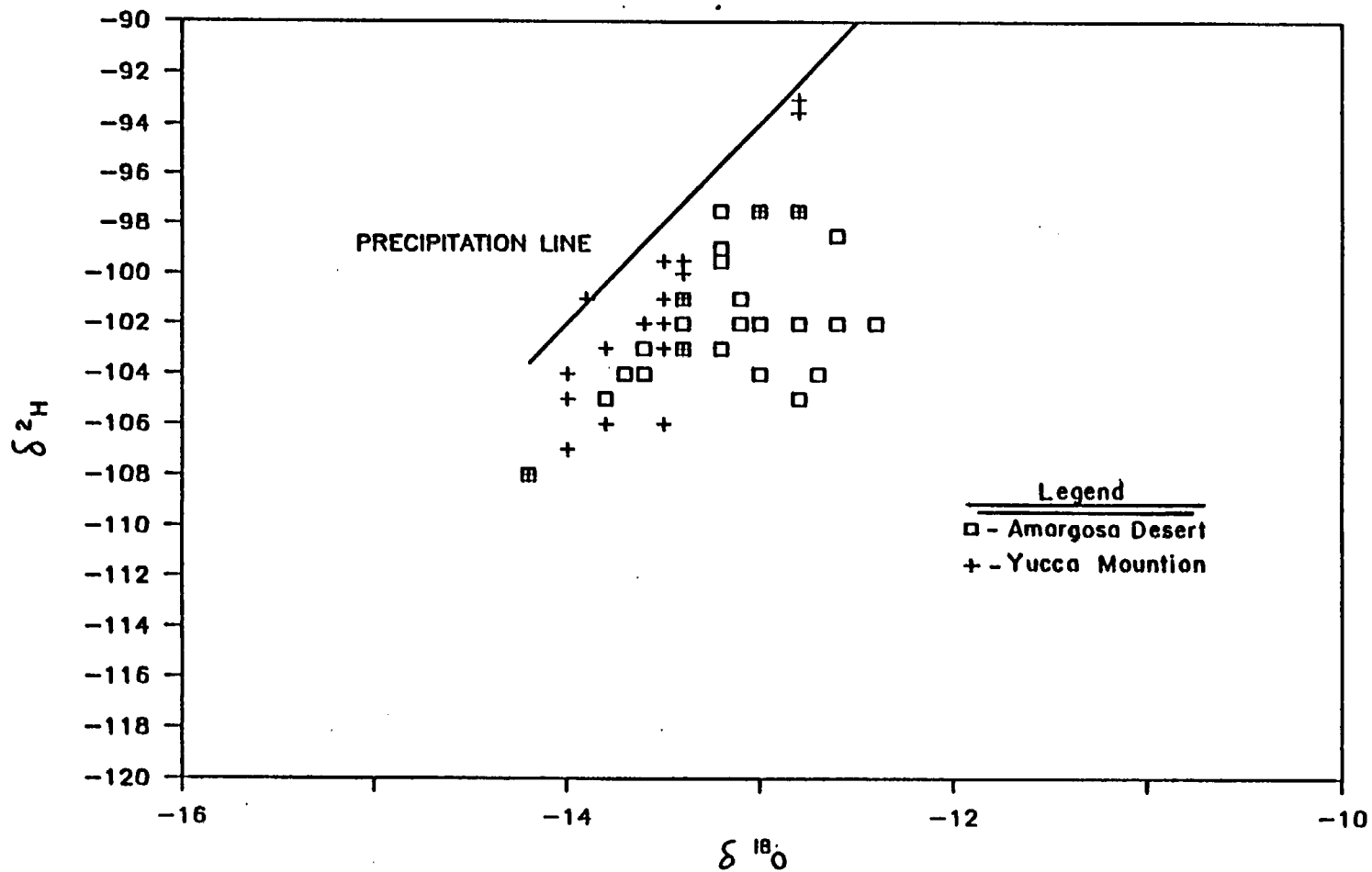
Figure 19
Composition of Water Samples from Saturated Zone Near
Yucca Mountain and in the Amargosa Desert

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isolated from each other by silica flour and cement grout. Gas samples were collected in a flow through gas collector using a peristaltic pump. Two methods were used to collect the water vapor from the collectors; the cold trap and the molecular sieve (MS). The water samples obtained were then sent to the U.S. Geological Survey laboratory for determination of the δ ^{18}O and δ D values.

The in-situ, liquid phase isotopic data was calculated assuming the vapor was in equilibrium with the water phase. The difference in isotopic ratios of the δ D in vapor samples collected by the two methods was significantly different for some of the probes. Yang et al. (1985) concluded that the differences in the two methods may be due to fractionation of vapor during pumping to the land surface through several stages of condensation and evaporation in the small probe tubes. The unsaturated zone δ ^{18}O and δ D values are shown on Figure 20 along with the data from the Yucca Mountain saturated zone and the Amargosa Desert well and spring water.

4.6.3 Hydrology Based on Synthesis of Data

Kerrisk (1987) analyzed the groundwater chemistry at Yucca Mountain and developed somewhat different scenarios for the groundwater ages than presented by Claassen (1985). Carbonate in the ground water of the tuffaceous aquifer at and near Yucca Mountain was considered to come from soil-zone CO_2. This hypothesis was generally consistent with calculated CO_2 pressures of tuffaceous water from Yucca Mountain and vicinity and with measured CO_2 pressures in the gas phase of the unsaturated zone at Yucca Mountain. Kerrisk (1987) investigated the carbonate content in the saturated zone water and concluded that it is larger than one would expect if passage through the soil zone early in the recharge cycle was the only source. There are two sources of carbon available to the saturated zone waters: (1) CO_2 from the atmosphere, soil zone, and unsaturated zone gas phase, and (2) the carbonate aquifer. Based on the available data, Kerrisk (1987) determined that CO_2 was the more likely source of the additional carbonate in the waters at Yucca Mountain for three reasons:

1. As pH increases, the equilibrium CO_2 pressure drops, creating a driving force for dissolution of CO_2 from the gas phase.
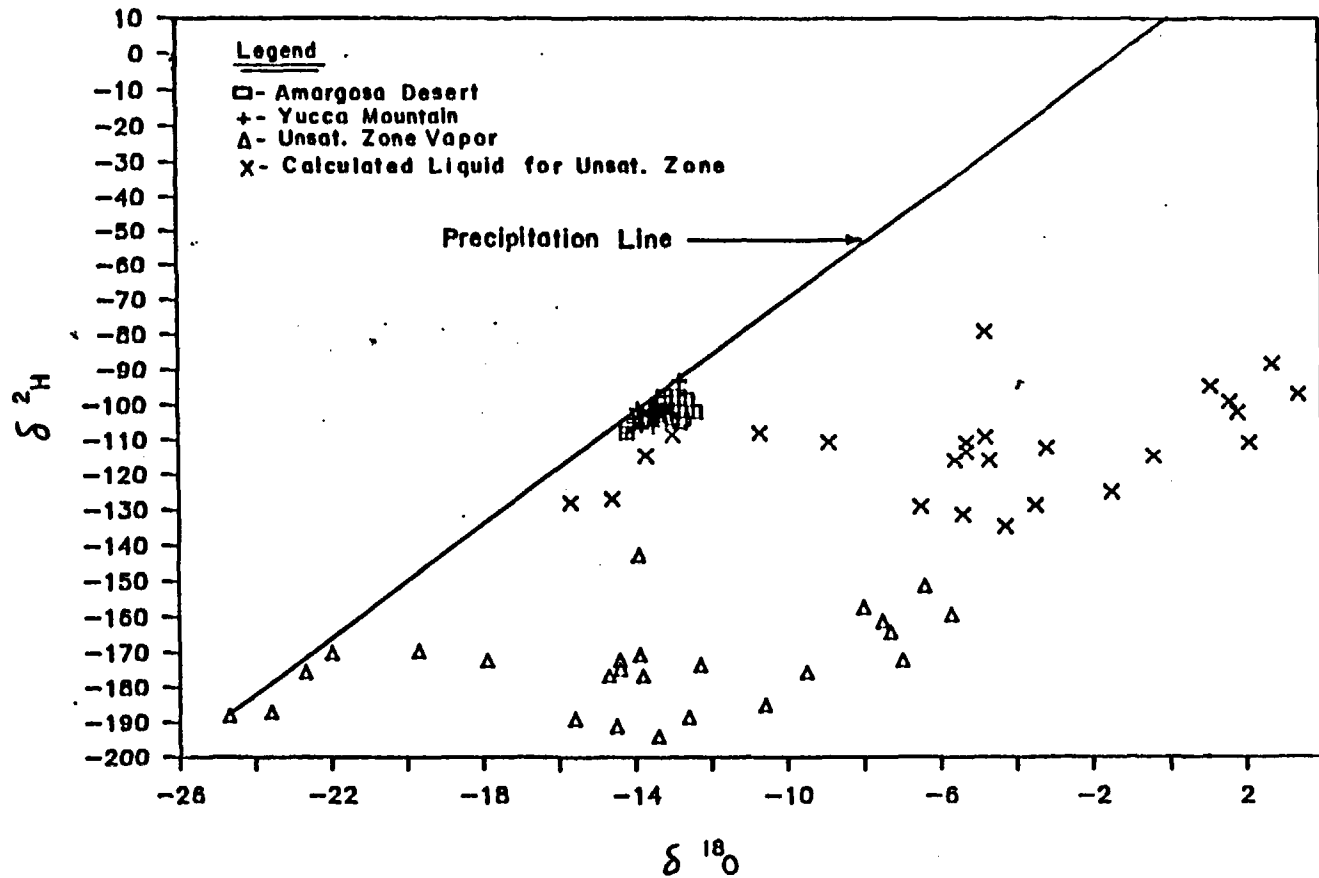
Figure 20
Water Samples from Unsaturated Zone at Well USW UZ-1
Compared with Saturated Zone Samples

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2. Carbonate in water from the carbonate aquifer would bring along
    calcium. However, where the higher-carbonate waters are generally
    located, the calcium is quite low in concentration.

3. It is unlikely that mixing the low pH water from the carbonate
    aquifer (UE-25p#1 carbonate water) would result in the high pH water
    in the tuffaceous aquifer.

The δ ^{13}C data provided additional information about the origin of the
carbonate. Paleozoic carbonates have a δ ^{13}C value of about -2 percent,
atmospheric CO_2 has a δ ^{13}C value in the range of approximately -7 to -9
percent, and soil zone CO_2 that is derived from plants has δ ^{13}C values of
approximately -12 to -25 percent. Fractionation effects occur between the
phases, thus CO_2 gas will have a different δ ^{13}C than the carbonate in an
aqueous phase in equilibrium with it. The data from Yucca Mountain and
vicinity show a slight tendency to more positive δ ^{13}C with increasing total
carbonate with the majority of the data falling between -7 and -11 mil. Only
one tuffaceous aquifer well (USW H-3) had a sample with a δ ^{13}C value above -7
mil. Therefore, Kerrisk (1987) concluded that gaseous CO_2 in the saturated
zone was the source of the additional carbonate in the saturated zone water at
Yucca Mountain.

When the pmc and δD were plotted, it indicated that water with lower
values of pmc have more negative values of δD. Lower δD (more negative)
indicates water originating as precipitation at lower temperatures or higher
elevations. Because pmc and the total carbonate content of the water from
Yucca Mountain are also related, there is also a relation between δD and total
carbonate. The results of these relations indicated that the water in the
tuffaceous formations at Yucca Mountain is an older water originating as
precipitation at lower temperatures or that it is a mixing of waters with
different values of δD. The higher pH waters in the tuff aquifer also have
higher relative sodium content. This is consistent with the process of glass
and mineral dissolution and precipitation of secondary minerals and can be
considered as mineral dissolution occurring in a system that is open with
respect to CO_2 (Kerrisk, 1987).

In an attempt to see if the model of CO_2 addition to the saturated zone
water could explain the variation of pmc and δ ^{13}C with total carbonate
content, a simplified carbon balance model was developed by Kerrisk (1987).
The model assumed that an initial charge of carbonate from the soil zone was

present in the water and that CO_2 in the gas phase of the unsaturated zone is added at some rate as time progresses. Based on this model, Kerrisk developed an alternative explanation to Claassen's (1985) conclusion that the ^{14}C determined apparent ages are representative of the water age. Kerrisk's explanation was that the apparent age of a sample (determined by ^{14}C analysis of Yucca Mountain water) with more than 2 mmoles/liter total carbonate tends to underestimate the true age. For water with less than about 2 mmoles/liter total carbonate, the age of the water is essentially the apparent age. If the carbon model ages are used, then waters older than 20,000 years are present at Yucca Mountain. This contradicts Claassen's hypothesis that snowfall earlier than about 20,000 years ago was insufficient to result in recharge.

The total carbonate in mmoles/liter is shown on Figure 21. The high carbonate value of 9.32 mmoles/liter is from UE-25p#1, completed in the carbonate aquifer. Generally, the wells with carbonate values greater than 2 are located in the south and southwest areas of Yucca Mountain. According to the carbon model of Kerrisk (1987), the apparent age in these wells underestimates the actual age of the water. This situation is the opposite to what would happen if the variation of ^{14}C content was caused by the addition of carbonate water or old carbon dioxide with a pmc of zero. For that situation, the apparent age of the mixture would overestimate the age. The ages of the samples from wells, based upon Kerrisk's carbon model, are shown on Figure 22.

The δ ^{13}C values for the wells at and around Yucca Mountain are shown on Figure 23. The values seem to generally decrease from the northeast to the southwest. The well with the most negative δ ^{13}C value, UE-29a#2, also has the smallest depth to water (about 25 m). Prior to drilling the well, the projected depth to water had been estimated to be greater than 275 m. The highest δ ^{13}C value in a non-carbonate aquifer well occurred in USW H-3. This well also had the highest total carbonate of any of the tuffaceous aquifer wells, and hence, the oldest carbon model age of the water.

The water table position at Yucca Mountain showing 20-meter contours of water table altitude, the location of drill holes, and the outline of the primary repository area are shown on Figure 24. Also shown on this figure are the apparent water ages based on ^{14}C analysis. The carbon model ages and the δ ^{13}C values for the wells are shown on Figure 25.
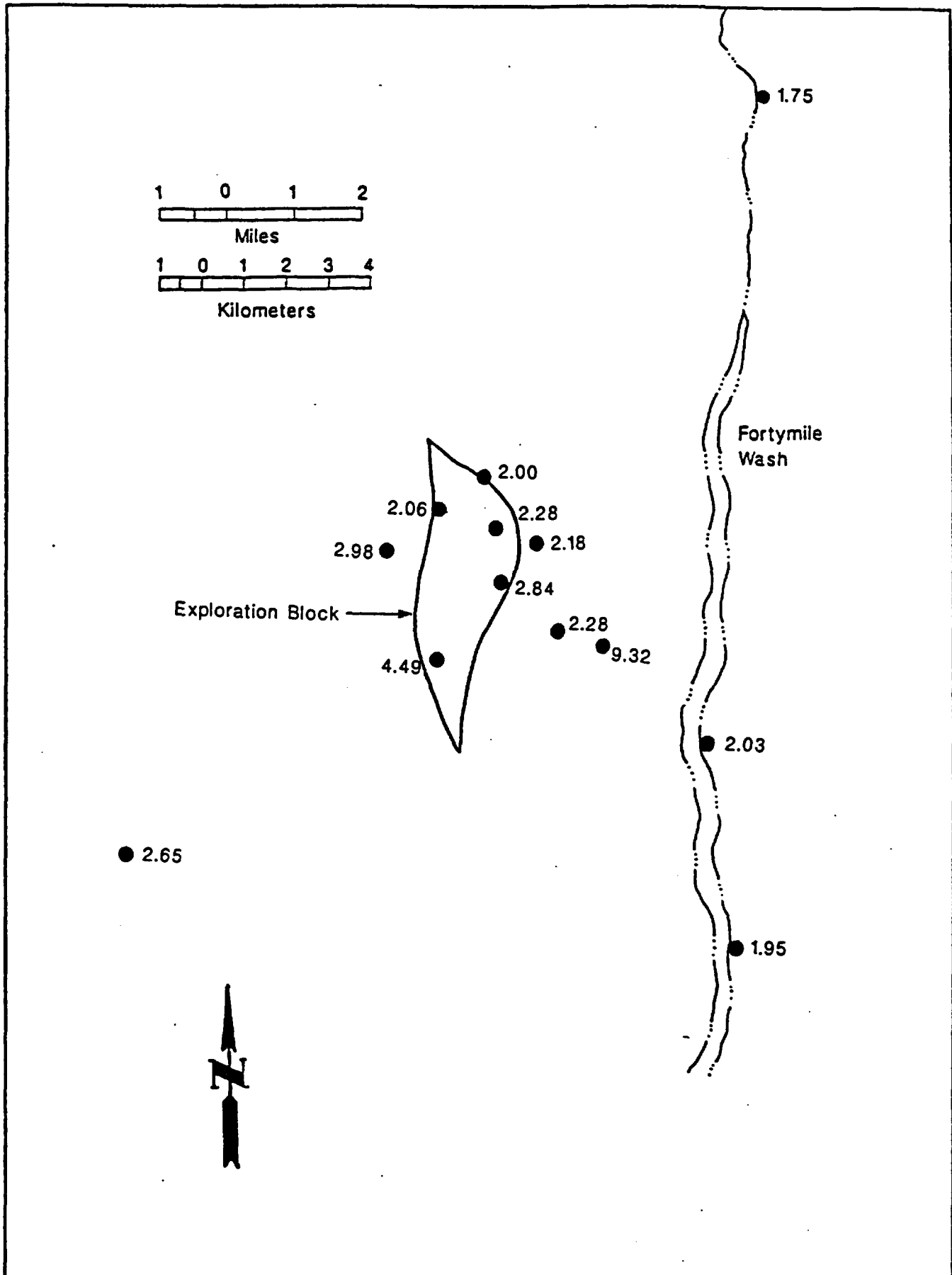
Figure 21
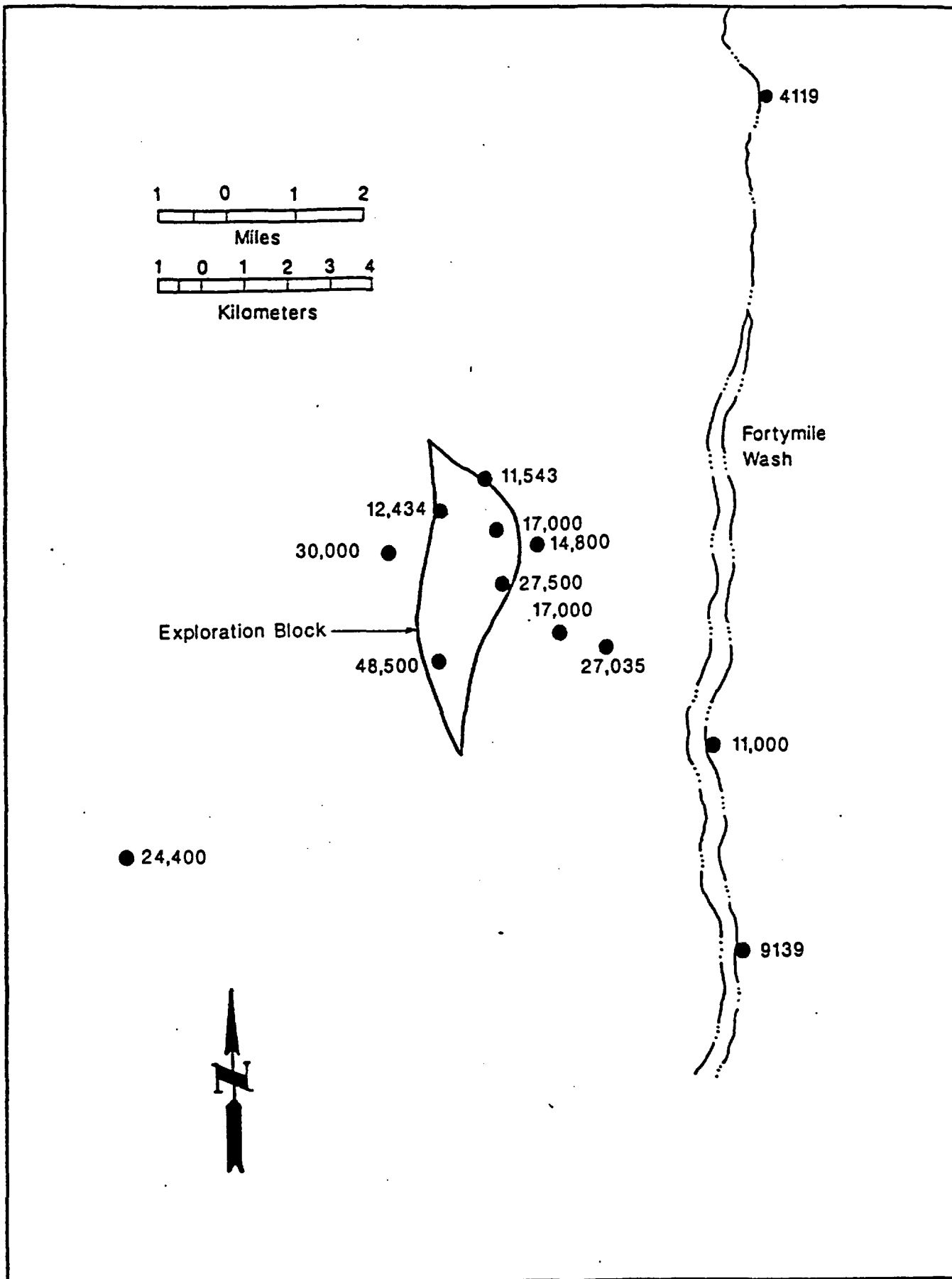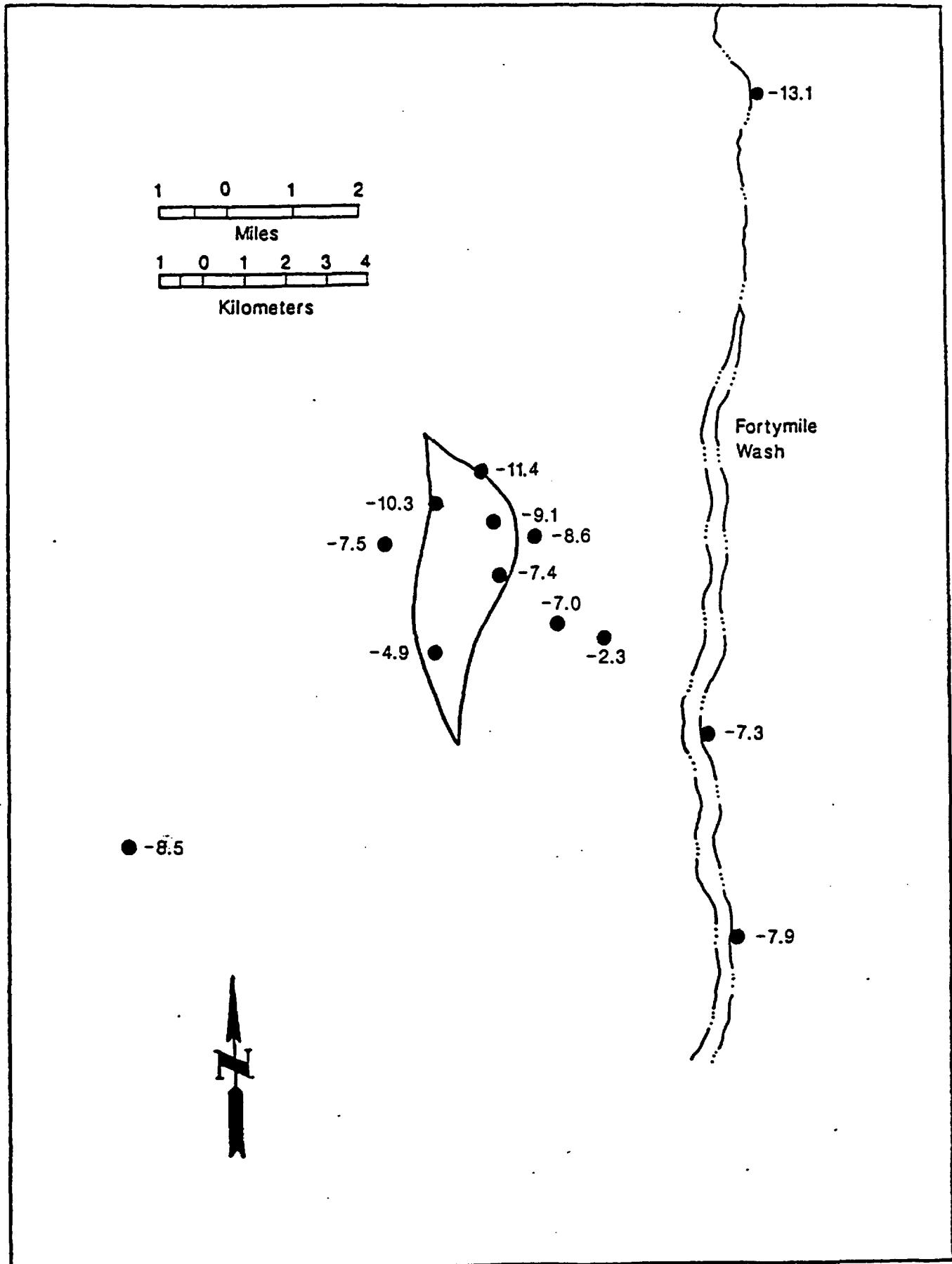**Total Carbonate in Moles/Liter**

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Figure 22
Carbon Model Age of Water

Figure 23
$\delta^{13}C$ In Wells Near Yucca Mountain

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1200m
1100m
1000m
900m
800m

● USW G-2
?

● USW H-1
11,543

● USW H-5
12,434

● USW G-4
12,210

● UE-25b#1
14,436

● USW H-6
14,629

● USW H-4
17,234

● UE-25c#1
14,480

● USW H-3
18,175

J-13 ●
9,927

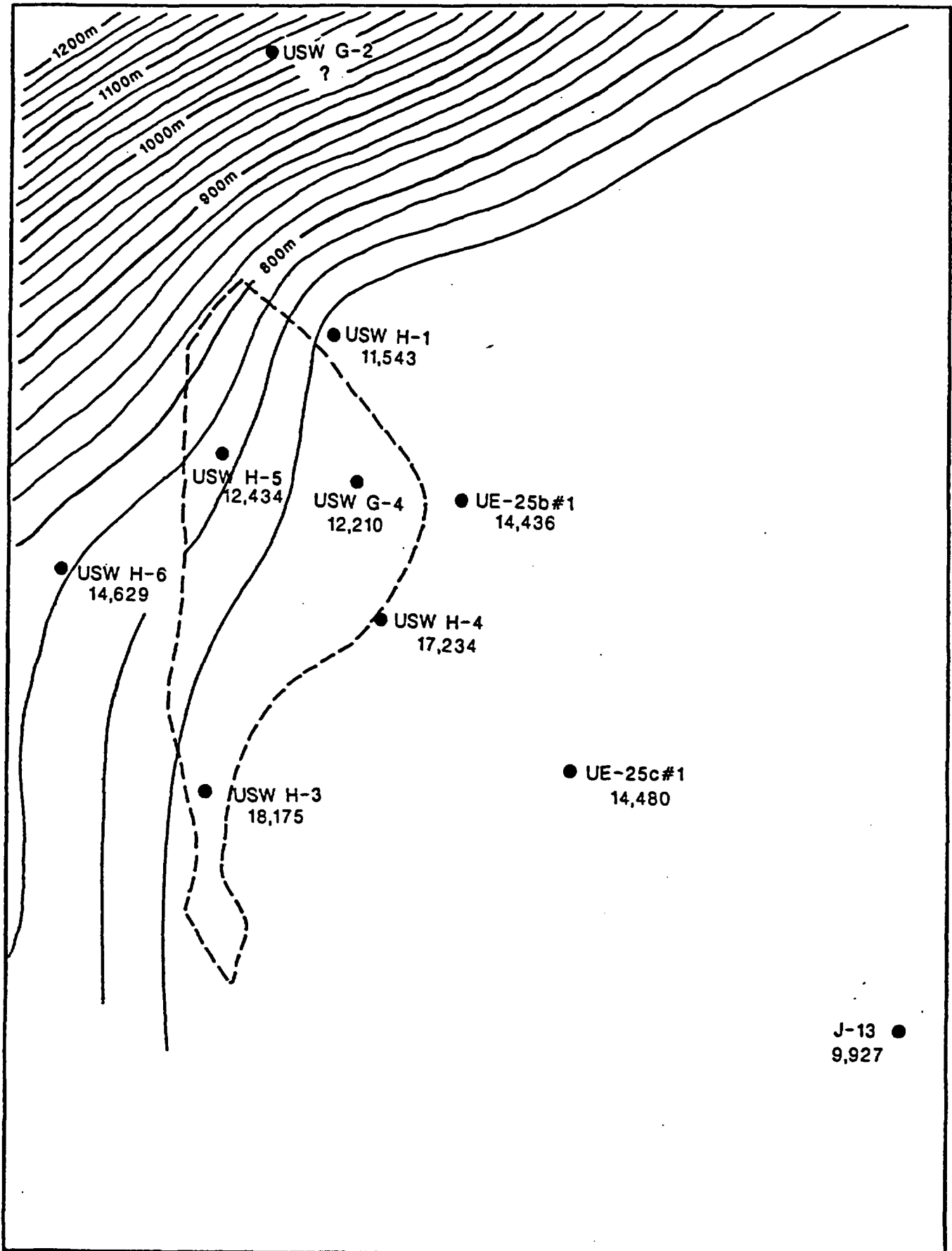Water, Waste & Land, Inc.

Figure 24
Apparent Ages and Water
Surface Elevation

Date: Nov. 1987

Project: 4001
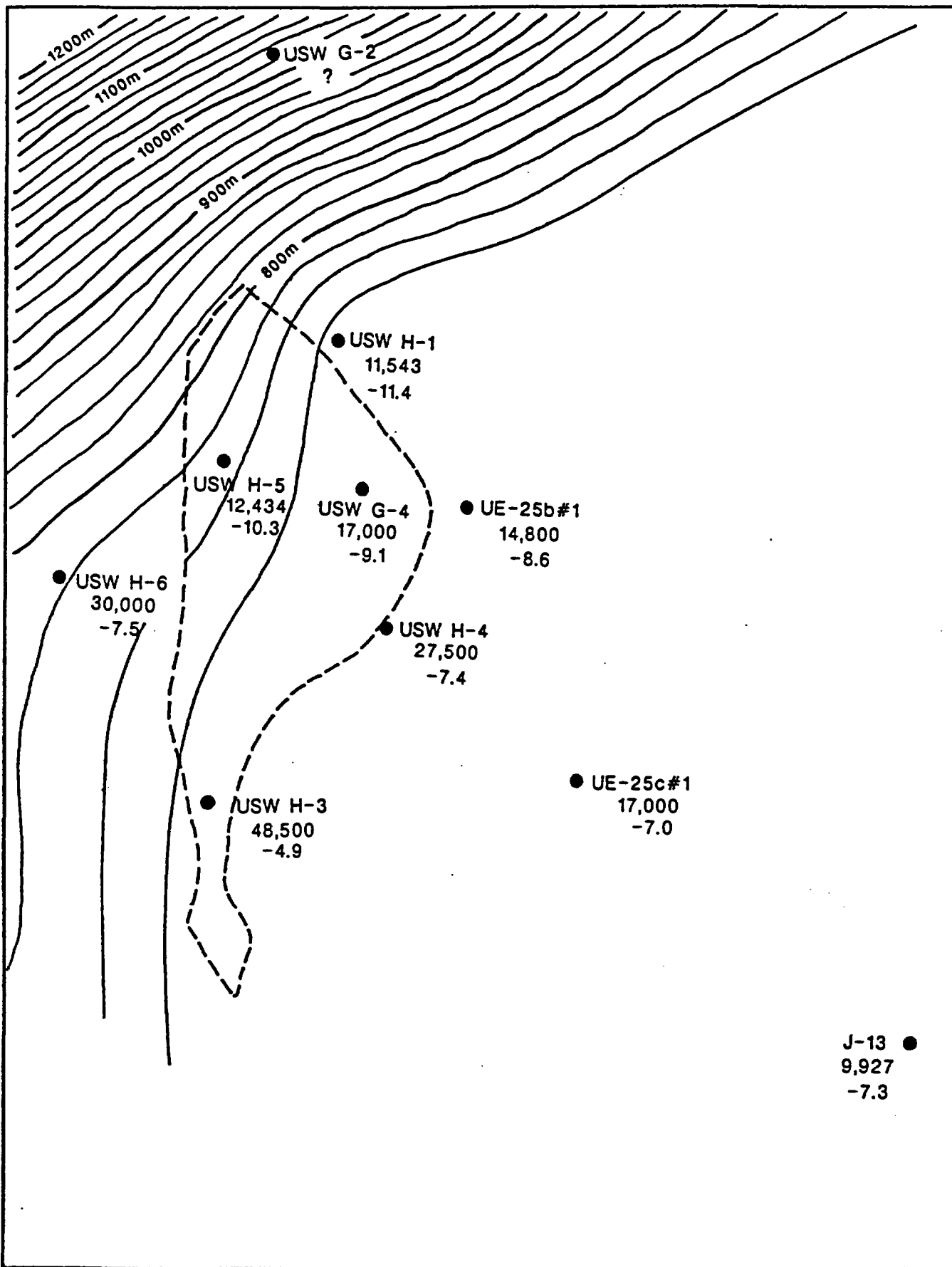
Figure 25
Carbon Model Ages and $\delta^{13}C$
Values for Tuffaceous Aquifer Wells

Water, Waste & Land, Inc.

Date: Nov. 1987

Project: 4001

4.7 CONCLUSIONS

The use of D and ^{18}O concentrations to characterize hydrogeologic systems has been demonstrated in a number of reports. In particular, the use of the isotopes in the study of arid and semi-arid regions has been shown to be particularly useful. For the Yucca Mountain site, the study of the unsaturated zone isotope concentrations may yield information on the flow mechanisms occurring through the units.

The TSw unit, as presented in the conceptual model (EA, 1986), has an extremely low flux of water passing through the potential repository horizon. In portions of the unit, it is proposed that a negative (upward) flux is occurring. The use of the D and ^{18}O concentrations obtained during the site characterization could indicate the extent by which vapor transport effects the overall flow patterns in the repository horizon and TSw unit. Changes in the matrix concentrations of D and ^{18}O with depth could be evaluated and may indicate the degree to which two phase flow has occurred or is occurring within Yucca Mountain. Additional information may be obtained from the analysis of matrix blocks along major fracture systems which could be encountered while driving the shaft. In this case, the concentrations of D and ^{18}O could be plotted not as depth, but as distance from the fracture face.

4.8 RECOMMENDATIONS

The analysis of two phase flow in the dual porosity system at Yucca Mountain will be a difficult task; however, the use of natural environmental isotopes may provide significant data to help refine interpretation of the flow system. Concentration changes across hydrogeologic units, within matrix blocks, and between matrix and fracture waters may give information as to existing and historical flow patterns. This information, when coupled with other isotopic data could provide a basis for refinement of the conceptual model of flow at Yucca Mountain, in the unsaturated and saturated zones.

5.0 BIBLIOGRAPHY

Allison, G. B., and Hughes, M. W., 1983. "The Use of Natural Tracers as
    Indicators of Soil-Water Movement in a Temperate Semi-Arid Region," Journal
    of Hydrology, vol. 60, pp 157-173.

Benson, L. V. and McKinley, P. W., 1985. "Chemical Composition of Ground Water
    in the Yucca Mountain Area, Nevada, 1971-1984," United States Geological
    Survey Open File Report-85-484.

Bentley, H. W., Phillips, F. M., Davis, S. N., Gifford, S., Elmore, D., Tubbs,
    L.E., and Gove, H.E., 1982. "Thermonuclear Cl^{36} Pulse in Natural Water."
    Nature, Vol. 300.

Bentley, H. W., Phillips, F. M., Davis, S. N., Habermahl, M. A., Airez, P. L.,
    Colf, G. E., Elmore, D., Gove, H. E., and Torgersen, T., 1986, "Chlorine 36
    Dating of Very Old Groundwater 1. The Great Artesian Basin, Australia,"
    Water Resources Research, Vol. 22, No. 13.

Binnall, E. P., Wollenberg, H. A., Benson, S. M., and Tsao, L., 1986.
    "Critical Parameters for a High Level Waste Repository Volume 2: Tuff,
    Lawrence Livermore National Laboratory.

Claassen, H. C., 1985. "Sources and Mechanisms of Recharge for Ground Water in
    the West-Central Amargosa Desert, Nevada - A Geochemical Interpretation,"
    U.S. Geological Survey Professional Paper 712-F.

Clebsch, A. Jr., 1961. "Tritium-Age of Ground Water at the Nevada Test Site
    Nye, County, Nevada," from Short Papers in the Geologic and Hydrologic
    Sciences, Articles 147-292, Geological Survey Research.

Coles, D. B. and Ramspott, L. D., 1981. "Ru-106 Migration in a Deep Tuffaceous
    Alluvium Aquifer, Nevada Test Site," UCRL-85320 Lawrence Livermore
    Laboratory.

Craig, H., 1961. "Standard for Reporting Concentrations of Deuterium and
    Oxygen-18 in Natural Waters," Science 133:1833-1834.

Crowe, B. M. and Vaniman, D. T., 1985. "Research and Development Related to
    the Nevada Nuclear Waste Storage Investigations. Jan 1 - Mar 31, 1984", LA-
    10154-PR, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

Daniels, W. R., 1981. "Laboratory and Field Studies Related to the
    Radionuclide Migration Project - Oct 1, 1979 - Sept 30, 1980", LA-8670-PR,
    Los Alamos National Laboratory, Los Alamos, New Mexico. 87545.

Dansgaard, W., 1964. "Stable Isotopes in Precipitation," in Tellus XVI, 4.

Davis, S. N., and Murphy, E., 1987, "Dating Ground Water and the Evaluation of
    Repositories for Radioactive Waste," NUREG/CR-4912.

DOE, 1986. "Environmental Assessment, Yucca Mountain site, Nevada Research and
    Development Area, Nevada," DOE/RW-0073.

Eglinton, T. W. and Dreicer, R. J., 1984. "Meteorological Design Parameters for the Candidate Site of a Radioactive-Waste Repository at Yucca Mountain, Nevada," SAND84-0440/2, Sandia National Laboratories.

Elmore, D., Fulton, B. R., Clover, M. R., Marsden, J. R., and Gove, H. E., 1979. "Analysis of Cl^{36} in Environmental Water Samples Using an Electrostatic Accelerator." Nature, Vol. 277.

Elmore, D. and Phillips, F. M., 1987. "Accelerator Mass Spectrometry for Measurement of Long-Lived Radioisotopes," Science, Vol. 236, pp 497-644.

Elmore, D., Tubbs, L. E., Newman, D., Ma, X. Z., Finkel, R., Nishiizumi, K., Beer, J., Oeschger, H., and Andree, M., 1982. "Cl^{36} Bomb Pulse Measured in a Shallow Ice Core From Dye 3, Greenland", Nature, Vol. 300. 23/30.

ERDA, Final Environmental Impact Statement, Nevada Test Site, Nye County, Nevada, Sept., 1977. ERDA-1551.

Fabryka-Martin, J., Bentley, H., Elmore, D., and Airey, P. L., 1985. "Natural Iodine-129 as an Environmental Tracer," "Geochemica et Cosmochimica Acto, Vol. 49, pp 337-347.

Ferronsky, V. I., and Polyakov, V. A. 1982. "Environmental Isotopes in the Hydrosphere.", John Wiley and Sons, Ltd.

Foster, S. S. D., 1975. "The Chalk Groundwater Tritium Anomaly - A Possible Explanation," Journal of Hydrology, Vol. 25, pp 159-165.

Foster, S. S. D. and Smith-Carrington, A., 1980. "The Interpretation of Tritium in the Chalk Unsaturated Zone," Journal of Hydrology, Vol. 46, pp 343-364.

Franson, M. A. H. (ed.), 1985. "Standard Methods For the Examination of Water and Wastewater." American Public Health Association, Washington, DC.

Freeze, R. A. and Cherry, J. A., 1979. Groundwater, Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Hansen, D. S., 1978. Tritium Movement in the Unsaturated Zone, Nevada Test Site, University of Nevada - Reno, Masters Thesis.

Heiken, J. (ed.), "Summary Report on the Geochemistry of Yucca Mountain and Environ", 1982. LA-9328-MS, Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

IAEA, Isotope Techniques in the Hydrogeological Assessment of Potential Sites for the Disposal of High Level Radioactive Waste, 1983. Vienna, Technical Report Series No. 228.

Ingraham, N. L. and Taylor, B. E., 1986. "Hydrogen Isotope Study of Large-Scale Meteoric Water Transport in Northern California and Nevada," Journal of Hydrology, vol. 85, pp 183-187.

Kerrisk, J. G., 1987, "Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity," LA-10929-MS, Los Alamos National Laboratory.

Lal, D., Nijampurkar, V. N., and Rama, S., 1970. "Silicon-32 Hydrology," Isotope Hydrology IAEA Proceedings, Vienna.

Ogard, A. E. and Vaniman, D. T., 1985. "Research and Development Related to the Nevada Nuclear Waste Storage Investigations. July 1 - Sept 30, 1984," LA-10299-PR, Los Alamos National Laboratory, Los Alamos, New Mexico.

Phillips, F. M., Trotman, K. N., Bentley, H. W., Davis, S. N., and Elmore, D., 1984. "Chlorine-36 From Atmospheric Nuclear Weapons Testing as a Hydrologic Tracer in the Zone of Aeration in Arid Climates".

Rabinowitz, D. D., Gross, G. W., and Holmes, C. R., 1977. "Environmental Tritium as a Hydrometeorological Tool in the Roswell Basin, New Mexico, I. Tritium Input Function and Precipitation-Recharge Relation," Journal of Hydrology, Vol .32, pp 3-17.

Rundberg, R. S., Ogard, A. E., and Vaniman, D. T., 1985. "Research and Development Related to the Nevada Nuclear Waste Storage Investigations Apr 1 - June 30-, 1984," LA-10297-PR, Los Alamos National Laboratory, Los Alamos, New Mexico.

Sinnock, S., Lin, Y. T., and Brannen, J. P., 1984. "Preliminary Bounds on the Expected Postclosure Performance of the Yucca Mountain Repository Site, Southern Nevada," SAND84-1492, Sandia National Laboratories.

Sinnock, S. (editor), Lin, Y. T., Tierney, M. S., and others, 1986. "Preliminary Estimates of Groundwater Travel Time and Radionuclide Transport at the Yucca Mountain Repository Site," SAND85-2701, Sandia National Laboratories.

Spaulding, W. G., 1983, "Vegetation and Climates of the Last 45,000 Years in the Vicinity of the Nevada Test Site, South-Central Nevada, USGS-OFR-83-535.

Sukhija, B. S., and Rao, A. A., 1983. "Environmental Tritium and Radiocarbon Studies in the Vedavati River Basin, Karnataka and Andhra Pradesh, India," Journal of Hydrology, Vol. 60, pp 185-196.

Tang, D. H., Frind, E. O., and Sudicky, E. A., 1981. "Contaminant Transport in Fractured Porous Media: Analytical Solution for a Single Fracture", Water Resources Research, Vol. 17, No. 3.

Terasmae, J., 1984, "Radiocarbon Dating: Some Problems and Potential Developments," in Quarterly Dating Methods - Developments in Paleontology and Stratigraphy, W. C. Mahaney (editor), Elsevier Science Publishers.

Thatcher, L. L., "Water Tracing in the Hydrologic Cycle," 1967 In: Isotope Applications in Terrestrial Waters, Geophysical Monograph Series No. 11, American Geophysical Union, pp 97-108.

van Genuchten, M. T., 1982. "One-Dimensional Analytical Transport Modeling" in
    Proceedings of the Symposium on Unsaturated Flow and Transport Modeling,
    NUREG/CP-0030.

Wallick, E. I., Krouse, H. R., and Shakur, A., 1984. "Environmental Isotopes:
    Principles and Applications in Ground Water Geochemical Studies in Alberta,
    Canada," in Proceedings-Practical Applications of Ground Water Geochemistry,
    National Water Well Association.

WWL, 1986a. "Travel Time Calculations, Yucca Mountain, Nevada."

WWL, 1986b. "Penetration and Resistance of Water in a Single Planar Fracture
    Affected by Air Flow in the Matrix."

Yang, C., Haas, H. H., Weeks, E. P., and Thorstenson, D. C., 1985. "Analysis of
    Gaseous-Phase Stable and Radioactive Isotopes in the Unsaturated Zone, Yucca
    Mountain, Nevada," in Proceedings of the NWWA Conference on Characterization
    and Monitoring of the Vadose (Unsaturated) Zone, National Water Well
    Association, Dublin, Ohio.

Yu, C., Jester, W. A., and Jarrett, A. R., 1986. "Hydrogeologic Parameter
    Identification from Nuclear Tracer Breakthrough Curve Data for Waste
    Disposal in Porous Media, "Radioactive Waste Management and the Nuclear Fuel
    Cycle, Vol. 7(1).