ENVIRONMENTAL ISOTOPES FOR HYDROLOGICAL INVESTIGATIONS

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INTRODUCTION

Isotopes are the atoms of an element having same atomic number (Z) but different atomic weight (A). In other words, the atoms of an element having different num ber of neutrons (N) but same number of protons or electrons are called isotopes. For example, hydrogen has three isotopes having the same atomic number of 1 but different atomic masses or weights of 1, 2 and 3 respectively i.e.,

$^1_1H_0$ - only one proton in nucleus and one electron revolving around the nucleus in an orbit.

$^2_1H_1$ - one neutron added to the nucleus of $^1_1H_0$ atom.

$^3_2H_2$ - one more neutron added to the nucleus of $^2_1H_0$.

Similarly oxygen has eleven isotopes, ^{12}O, ^{13}O, ^{14}O.. ., ^{22}O, but except ^{16}O, ^{17}O, and ^{18}O all other isotopes are radioactive and their existence in nature is very small (half life vary from 150 seconds to few femto seconds - of the order 10^{-15} seconds) therefore, we normally talk about only three isotopes of oxygen i.e., ^{16}O, ^{17}O, and ^{18}O. The carbon also has three isotopes ^{12}C, ^{13}C and ^{14}C. Isotopologues are molecules that differ only in their isotopic composition eg., $H_2^{18}O$ and $H_2^{16}O$ are oxygen related isotopologues of water. Naturally occurring elements in waters contain about 1700 stable and unstable (radioactive) isotopes, commonly referred to as environmental isotopes.

FORMAT OF PRESENTING THE STABLE ISOTOPE DATA

Measurements of stable isotopes are done in terms of abundance ratios i.e. atomic mass of heavy atom to the atomic mass of light atom of isotopologues. However, instead of the absolute abundance ratio only the relative difference with respect to a reference is determined. The difference is designated by a Greek letter δ, expressed in per mill (‰) and is defined as follows:

$$\delta(\text{in } ‰) = \left[\frac{R_{Sample}}{R_{Standard}} - 1 \right] \times 1000 \qquad (1)$$

Where R's are the ratios of the $^{18}O/^{16}O$ (for $\delta^{18}O$) and D/H isotopes (for δD) in case of water. If the δ value is positive, it refers to the enrichment of the sample in the heavy-isotope species with respect to the reference and negative value corresponds to the sample depleted in the heavy-isotope species.

The reference standards normally considered are SMOW (Standard Mean Ocean Water)/ VSMOW (Vienna Standard Mean Ocean Water), SLAP (Standard Light Antarctic Precipitation) and GISP(Greenland Ice Sheet Precipitation). Over the period of use, the old standards have been consumed. Therefore, other reference standards have been developed in

due course of time. These are and now VSMOW-2, SLAP-2 and GISP-2 (supplied by International Atomic Energy Agency, Vienna, Austria), NBS-1 and NBS-1A (supplied National Bureau of Standard, now National Institute of Standards and Technology, USA). The values of measured abundance ratios ($^2H/^1H$ and $^{18}O/^{16}O$) in SMOW and VSMOW are given in *Table 1*.

Table 1. Measured abundance ratios in international standard reference material

Isotopes	Standard	Abundance Ratio
$^2H/^1H$	SMOW	0.000158 $[158(\pm2) \times 10^{-6}]$
$^{18}O/^{16}O$	SMOW	0.0019934 $[1993.4(\pm2.5) \times 10^{-6}]$
$^2H/^1H$	SMOW	0.00015575 $[155.75(\pm0.45) \times 10^{-6}]$
$^{18}O/^{16}O$	VSMOW	0.0020052 $[2005.2(\pm0.05) \times 10^{-6}]$

$$\delta^{18}O \text{ SLAP} = -55.50‰ \text{ VSMOW}; \quad \delta DSLAP = -428.0‰ \text{ VSMOW}$$
$$\delta^{18}O \text{ GISP} = -24.76‰ \text{ VSMOW}; \quad \delta DGISP = -189.5‰ \text{ VSMOW}$$

To understand how δvalues are calculated from ratios, one can do the following simple exercise. If the $^{18}O/^{16}O$ and $^2H/^1H$ ratios in a sample are given to be 0.0020104 and 0.00015735 respectively, its oxygen and hydrogen isotopic compositions ($\delta^{18}O$ =2.59‰ and δD = 10.27‰) with respect to VSMOW can be easily calculated using Equation (1) and the isotopic ratios for VSMOW, as given in *Table 1*.

ISOTEOPE FRACTIONATION

In general, as a result of mass difference, as compared to heavier isotopologues (eg., $H_2^{18}O$ or and $HD^{16}O$), lighter isotopologues ($H_2^{16}O$) evaporate faster (during evaporation of water), condense slower (during condensation of vapour to water), reacts faster in a chemical reaction and show higher diffusivity in molecular kinetics. Due to this differential characteristic of isotopologues, during any phase change process (evaporation of surface water or condensation of vapour (eg., rainout process)) the heavier isotopologues (e.g. $H_2^{18}O$ or and $HD^{16}O$) gets enriched in the condensate phase (such as the liquid water for the case of phase transition from liquid water to its vapour) compared to and lighter ($H_2^{16}O$) isotopologues. For, example, during rainout, the precipitating water gets enriched in heavier isotopes (while the remaining vapor gets progressively depleted with heavier isotopes). This differential partitioning of isotopes between the two phases is known as the isotope fractionation.

The fractionation continues till the process of phase change continues and accordingly, the enrichment of denser phase by heavier isotopologues. On reaching the thermodynamic equilibrium fractionation process ceases and the system is said to be at equilibrium fractionation. Non-equilibrium fraction is also termed as kinetic fractionation. As a result of fractionation both $\delta^{18}O$ (for $H^{18}O$ and $H^{16}O$) and δD (for HDO and HHO) changes proportionately (approximately) in a given thermodynamic condition. Therefore, a plot between $\delta^{18}O$ and δD usually leads to a linear graph.

GLOBAL METOERIC WATERR LINE (GMWL)

Craig (1961a) for the first time showed that $\delta^{18}O$ and δD in fresh surface waters (representing precipitation on global scale) correlate linearly by equation;

$$\delta D = 8\delta^{18}O + 10 \ (\text{‰ SMOW}) \ \text{--------------------}(2)$$

The regression line between $\delta^{18}O$ and δD is referred to as Global Meteoric Water Line (GMWL).

Rozanski et al.(1993) compiled the isotope data of precipitation from 219 stations of the IAEA/WMO operated Global Network for Isotopes in Precipitation (GNIP). This refined relationship between 18O and D in global precipitation (*Figure 1*) is given by:
$$\delta D = 8.17 \ (\pm 0.07) \times \delta^{18}O + 11.27 \ (\pm 0.65) \ (\text{‰ SMOW}) \ \text{--------------------}(3)$$

The $\delta^{18}O$ - δD regression equation of *Rozanski et al.*(1993) is based on actual precipitation whereas that of *Craig* (1961) was based on fresh surface waters.
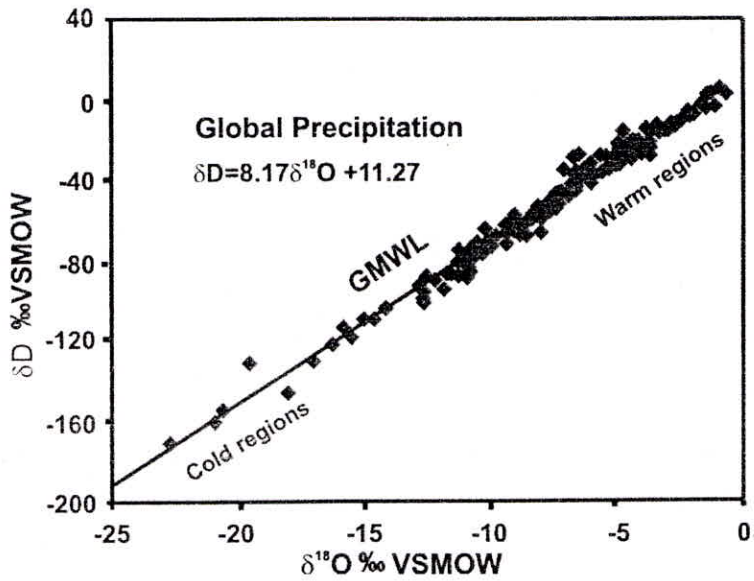

Figure1.The linear regression line between $\delta^{18}O$ &δD of global precipitation sample monitored at 219 stations of IAEA/WMO global network (after Rozanski et al 1993).

Dansgaard defined a parameter (*d*-excess), defined as;

$$d\text{-excess} = \delta D - 8 \times \delta^{18}O \ (\text{‰}) \ \text{--------------------}(4)$$

Dansgaard (1964) reviewed the global distribution pattern of stable isotope content in precipitation and related the spatial distribution of heavy isotope content to environmental parameters, such as altitude, latitude, amount of precipitation, air temperature and degree of continentality. All of these factors reflect the degree of washout from the air mass, and to some extent, the water vapor history from the source to the site of precipitation.

Latitudinal Effect: Water vapours or precipitation depletes in heavier isotopes with the increase in latitude. This is interpreted Yurtsver and Gat (1981) as due to decrease in temperature with increase in latitude from equator to pole. The tropical and subtropical oceans constitute the major source of water vapour. With the poleward transport, isotopic composition of water vapour depletes as a consequence of rainout process and decreasing water vapour content in the atmosphere and lower temperatures of condensation.

This is supported by the observed relation between annual average and monthly average temperatures as given below:

$$\delta^{18}O = 0.695\ T_{annual} - 13.6\ (VSMOW) \quad \text{------------------} \quad (5)$$
$$\delta D = 5.6\ T_{annual} - 100\ (VSMOW) \quad \text{-----------} \quad (6)$$
$$\delta^{18}O = (0.338 \pm 0.028)\ T_{monthly} - 11.99\ (VSMOW) \text{-------} \quad (7)$$

The variations in $\delta^{18}O$ are on the order of -0.6‰ per degree of latitude for continental stations of the North America, Europe and about -2‰ per degree latitude for the colder Antarctica stations. One may expect very low gradients in the low latitudes where over 60% of atmospheric water vapours originate.

Amount effect: The amount "effect" is clearly observed in areas where temperature does not show a clear seasonality during the year. On tropical islands, where the observed seasonal variation of temperature cannot account for isotopic variations, the observed variability is controlled by the amount of precipitation, indicating the degree of rain-out from the original air mass.

The continentaleffect:Represent a progressive removal of moisture from the original airmass moving from the ocean towards the continent. The preferential removal of heavyisotopes during the first stages of precipitation leads to a progressive depletion of precipitationmoving inland. Therefore, coastal precipitations are isotopically enriched while the colder inner continental regions receive isotopically depleted precipitation with strong seasonal differences. On average, there is about -2‰ depletion in $\delta^{18}O$ per 1000km from seacoast.

Altitude effects:Precipitation progressively depletes in δ-values with increase in altitude, mainly, due to two reasons:
    (i) Decrease in temperature with increase in altitude
    (ii) Rainout process increases with increase in altitude due to orographic effect.

In general, $\delta^{18}O$ varies between -0.15 to 0.5 ‰ per 100m rise in altitude and δD depletes between -1 to -4 ‰ per 100m increase in altitude. This effect is used in the identification of location/altitude and source of springs. Source of precipitation can also be identified by knowing the altitude and continental effects.

Seasonal Effects:The seasonal effect is seen in temperate and high-latitude stations (depleted values in winter and enriched in summer). This reflects the variations in temperature of condensation, to some extent differences in air mass trajectories and sources of vapour (local and regional water vapour), and change in amount of precipitation. Increase in temperature increases the effect of evaporation in the falling raindrops and enriches the precipitation in D and 18O. This effect is least when precipitation occurs in large amount or with high intensity.

In general, isotopic composition of rainfall results from superimposition of all the above effects.
    The observed temporal variations of 18-0 values of precipitation andcorresponding surface air temperatures for the station in Vienna, Austria, is shown in Fig.2 as an example.

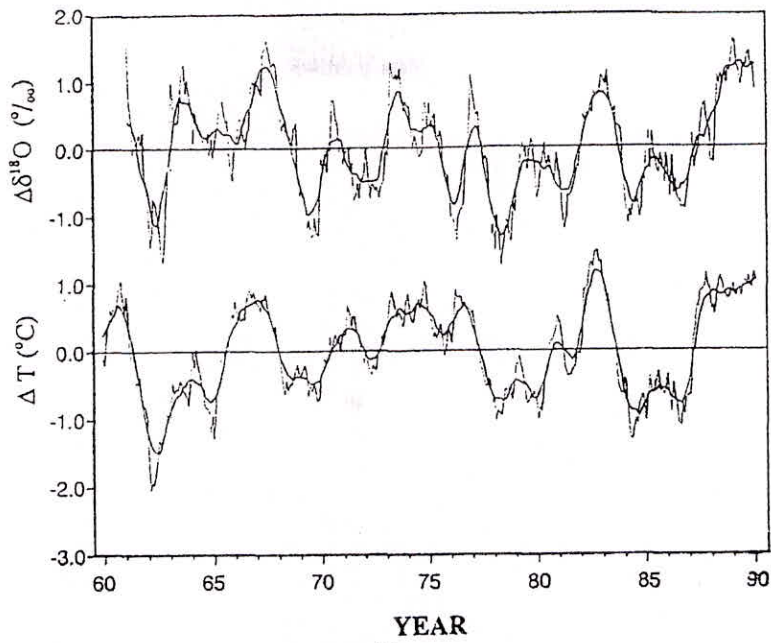**Figure2. Smoothed temporal variation of$\delta^{18}O$ data of monthly precipitationand temperature at the station Vienna, Austria.**

The possible ^{18}O-^2H linear relations expected for various processes of practical interest in hydrology are shown in Fig. 3.
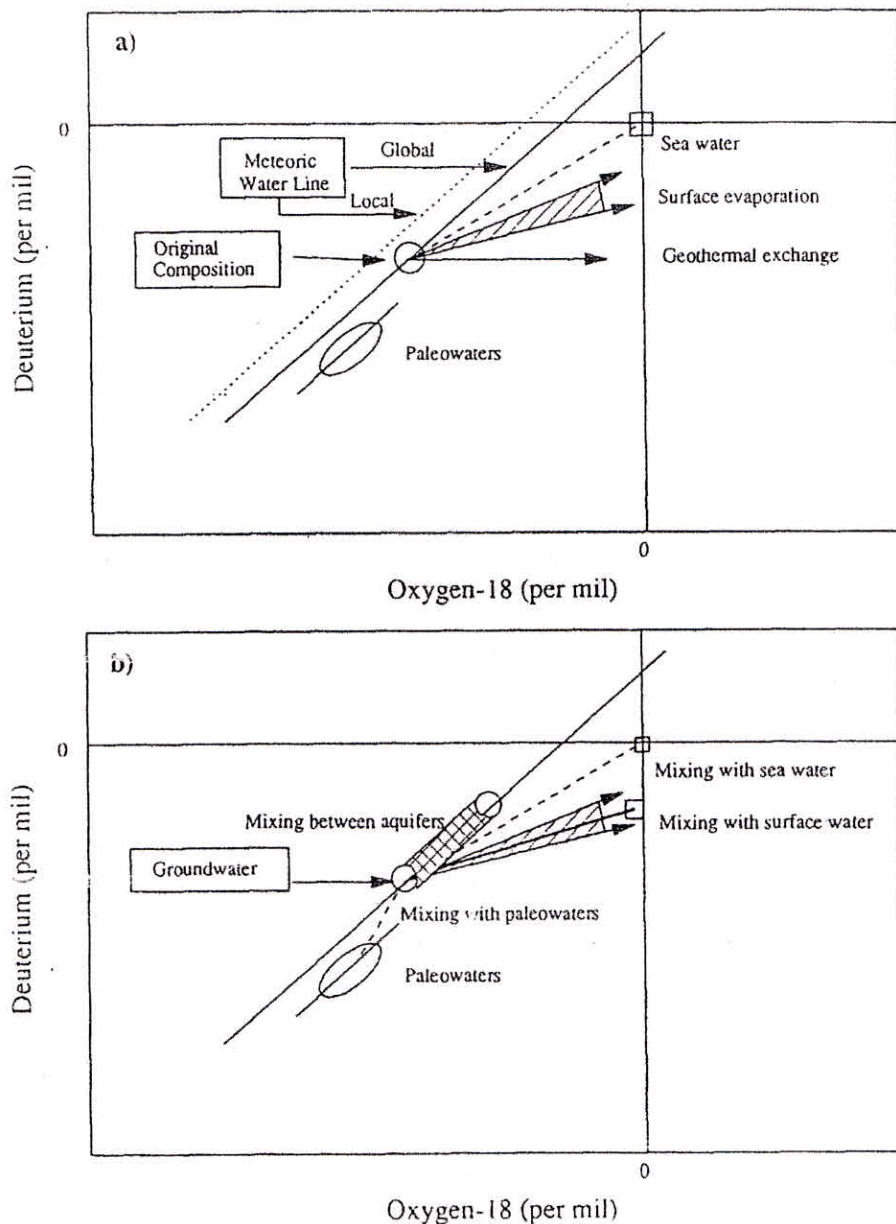
Figure3. Characteristic $\delta^{18}O$ -δD relations for different processes a) Related to processes b) Related to hydrological applications

APPLICATIONS

Due to their conservative nature stable isotopes are used in tracing hydrological system. In groundwater system these are used to finger-print history of the processes involved in formation and circulation of .Stable isotopes are commonly employed in studying hydraulic relations between groundwater and surface waters, for estimating mixing proportions of different sources, evaporation loss, component flows (component-tracing); and or between different aquifer units within a given groundwater system.

Recharge zones: The variations induced in stable isotopic composition of precipitation due to altitude effect provide label for the recharge to the groundwaters at different elevations, thus enabling assessment to be made of the replenishment areas.

Base flow study: The isotopic composition of river waters draining higher altitude precipitation often have significantly different isotopic content than the adjacent aquifer, providing the basis for study of hydraulic relations between river-aquifer system, or assessing the recharge to the adjacent aquifer through such line-sources.

Lake water Groundwater Interaction: The enrichment of the ^{18}O and ^2H isotopic contents of surface water bodies in lakes or reservoirs due to direct surface evaporation provides a natural label for them, so that hydraulic inter-relations between such water bodies with groundwater can be investigated.

Rainfall-runoff processes: The component flows involved in the runoff process such as baseflow and overland flow within a given basin can effectively be quantified through simple mass balance considerations of the stable isotopic composition of the river water prior to and during the individual rainfall events. The results of hydrograph separation based on such observations in different sizes of surface catchment basins indicate that the contribution of the groundwater to the total hydrograph of the basin can be substantially higher than that envisaged through classical concepts so far applied (Hino & Hasebe, 1986; Hooper & Shoemaker, 1986). These studies are also important contributions to delineation of the fluxes and their pathways in the basin, which is most relevant to understanding of the processes involved in stream acidification and pollution due to diffused sources.

CASE STUDIES

Groundwater mixing

Unlike most goechemical tracers, ^2H and ^{18}O are inert and conservative in mixing relationships. Therefore, stable isotopes can serve to quantify groundwater mixing at the local to watershed scale where mixing between groundwaters of different recharge origins, from different aquifers, and flow systems, can take place. Mixing between two distinct groundwaters (end-members) is quantified by simple linear algebra using δD or $\delta^{18}O$. Figure 4, for example, shows the fraction (X) of groundwater A in a mixture of two groundwaters A (δ_A) and B (δ_B). in a mixture of A and B. The proportion of mixing for a given sample in a two-component mixing system will then relate directly to its position on the mixing line, according to:

$$\delta_{sample} = X \cdot \delta_A + (1-X) \cdot \delta_B \qquad \text{-----------------(8)}$$

An example of two-component groundwater mixing is given in Fig. 5. Two mineral springs, the Hamei Zohar and Hamei Yesha springs, are seen to lie on a fresh water-Dead Sea mixing line, indicating these springs are formed by intermixing of Dead Sea water (brine) brought to the surface with the emerging local fresh water recharged at the Judean Mountains (Gat et al., 1969).
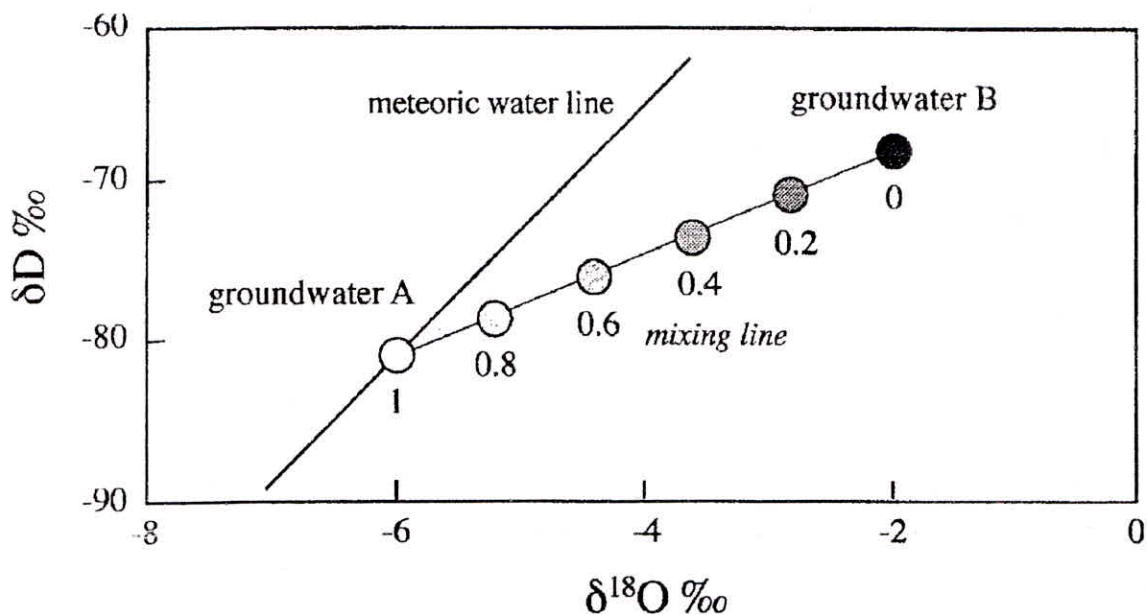
Figure4.Fractional mixing of two groundwaters quantified on the basis of their isotopic composition, and it is shown as the fraction of groundwater A
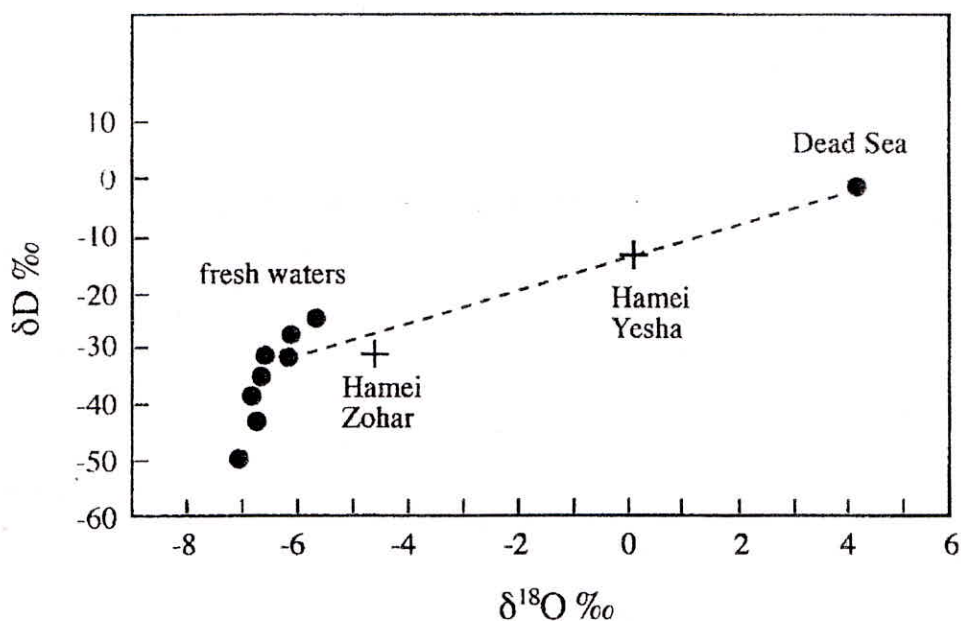

Figure5.Isotopic composition of two mineral springs on the Dead Sea shores,indicating these springs are formed by intermixing of Dead Sea brinewith local fresh water (Gat et al., 1969)

A three-component mixing system was identified by Kawanabe et al.(1999) for groundwaters from the seepage caldera lake district in thesouthernmost part of Japan. The evaporative enrichment in δD and $\delta^{18}O$ of theLake Ikeda water, that is the departure of the isotopic composition from themeteoric water line, permits the recognition of the contribution of lake waterto the shallow aquifer and to the discharge of springs and rivers locateddown-gradient the lake. In their study, mixing between lake water, rain water,and sea water was quantified based on the δD vs. $\delta^{18}O$ diagram (Fig. 6) and$\delta^{18}O$ vs. Cl- diagram (Fig. 7).
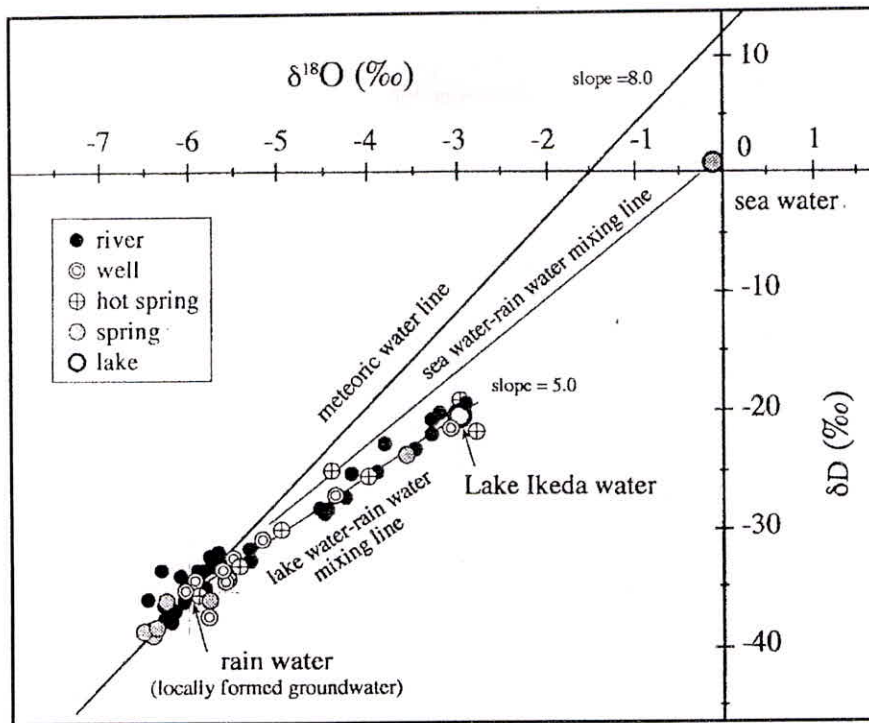
Figure6.Plot of $\delta^{18}O$ and δD for waters around Lake Ikeda, a seepagecaldera lake in the southernmost part of Japan (Kawanabeet al., 1999)

In Fig. 6, three end-members of recharge to the groundwater system areisotopically distinct: (1) lake water; (2) rain water; and (3) sea water. Theisotopic composition of samples from the lake and also from many rivers, hotsprings, wells, and springs, are seen to lie on a straight line distinctly differentfrom the local meteoric water line. A regression carried out on these samplesresults in a line with a slope of about 5.0, which is characteristic of open water bodies subjected to evaporation. A point for the rain water, which is apotential source of recharge to the groundwater system, is marked in Fig. 6on the extension of the line at the intersection with the local meteoric waterline. The values of -36‰ δD and -6.0‰ $\delta^{18}O$ are considered to berepresentative of the local rain water. The alignment of data points on thislake water-rain water mixing line (LRL) is explained by simple mixing, invarying proportions, of the isotopically depleted local rain water and enrichedlake water which leaks from Lake Ikeda. On the other hand, data points forsome rivers, wells, and hot springs do not align on the LRL (Fig. 6). Theyexhibit a positive δD shift of 2-3‰ and scatter between the LRL and the seawater-rain water mixing line (SRL). This is indicative of contribution of seawater to these waters. Figure 7 illustrates the variation of $\delta^{18}O$ against theCl concentration of samples which plot on the LRL or those of partial seawater origin (Fig. 6). From Fig. 7, it is obvious that the Cl- concentrationis a result of mixing of lake water (Lake Ikeda; -3.0‰ $\delta^{18}O$; 0.3 mmol l^{-1} Cl),rain water (-6.0‰$\delta^{18}O$; 0.2 mmol l^{-1} Cl), and sea water (-0.1‰$\delta^{18}O$; 544mmol l^{-1}l Cl).Based on Fig. 7, mixing proportion of each end-member is calculatedby applying a three-component mixing model, which is fundamentally in thesame manner as determined for a two-component mixing system.
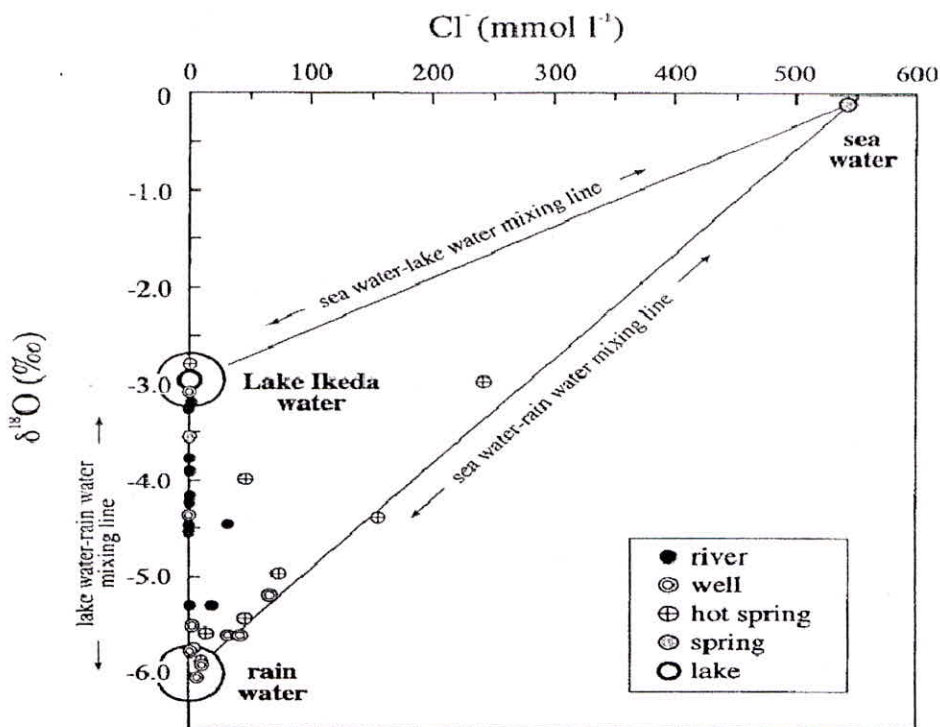
Figure 7. Plot of $\delta^{18}O$ and Cl⁻ concentration for waters in the LakeIkeda district (Kawanabe et al., 1999)

Paleo-hydrological Studies

Stable isotopes are effectively used for paleo-hydrological studies through delineating the origin of groundwaters replenished mainly during the earlier pluvial periods, which is relevant particularly to the occurrence of groundwater in arid regions. Such paleowaters are often characterized by the relatively low deuterium excess values in addition to their identification through age-dating. A typical example of the use of stable isotopes of ^{18}O and ^{2}H in studying groundwater genesis is shown in Fig. 8 (Gat, 1983), where groundwaters replenished through recent precipitation and paleowaters in different aquifer systems are identified. The major regional aquifer systems in arid regions of the Middle East and northern Africa, such as Dammam Formation and Umm Er Rhaduma aquifers in the Saudi Arabian peninsula; Nubian Sandstone and Continental Intercalaire aquifer systems in north Africa; have been found to contain paleowaters mainly replenished during earlier pluvial periods.

Seepage During Tunneling for Salal Hydropower Project

During construction of Tail Race Tunnel for the Salal Hydropower Project in Jammuseveral seepages were encountered. The tunneling was through a dolomite rock which is highly jointed and often crumbly and sheared. The total length of the tunnel was 2.4 km long & 11 m in dia. The purpose of the tunnel construction was to carry the tail waters from the power house and to put them back into the river (Chenab). Samples for the analysis were collected from neaby springs, nallahs , river Chenab and the seeping water. The isotopic results clearly indicated that the seepage water that has isotopic composition ($\delta^{18}O$ –7.7 ‰)all along the tunnel is different from isotopic composition of Chenab river (~-12 ‰). 3H and EC profile of seepage waters showed a good correlation along the length of the tunne and was different from the Chenab river water. Using Piston Flow model the age of seepage water is estimated

to be 10-15 years. It was concluded that the seepage water is old precipitation water stored or percolating in the fractured dolomite.
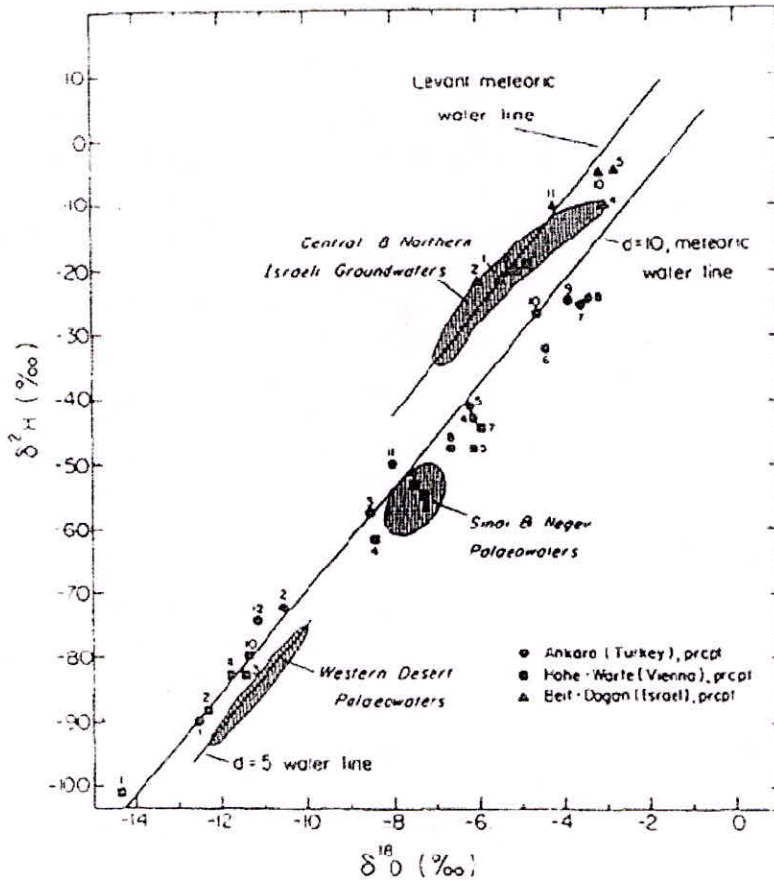

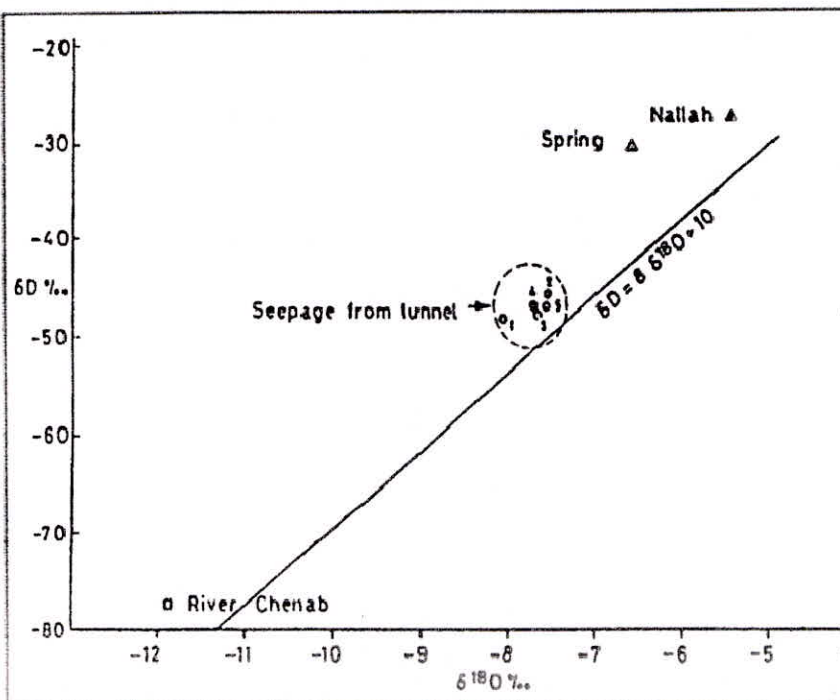Figure8. Isotopic composition of precipitation and groundwater in the East-Mediterranean region (Gat, 1983)

Figure 9. Isotopic composition of samplewaters collected in Salal H.P. Project

GROUNDWATER DATING

Groundwater age is defined as the amount of time that has elapsed since a particular water molecule of interest was recharged into the subsurface environment system until this molecule reaches a specific location in the system where it is either sampled physically or studied theoretically for age-dating. On the other hand, groundwater residence time is the time it takes for particles of water to travel from the recharge area to the discharge area of the aquifer (Modica et al., 1998). It is the time interval between infiltrating into, and exfiltrating out of, the subsurface media. It is impossible to find a single molecule of groundwater that has no age. As soon as a water molecule enters the subsurface, it becomes groundwater and it has an age. In groundwater sample there are billions of water molecules. In a well-mixed groundwater system, any one of these molecules may have its own distinct particular age. Mean age or the age measured by isotopic and chemical methods, is practically the average of ages of all molecules in the sample.

DATING YOUNG GROUNDWATERS

Tritium technique

^3H isotope of hydrogen has has one proton and 2 neutrons. It is radioactive with a half-life of 12.32 years. Tritium dating is used to trace water sources and to determine age of recent waters (age of ~50a). Tritium dating provides means to estimate the time since recharge to groundwater system occurred and susceptibility of the groundwater system to contamination. Sources directly fed by rainwater contain the same tritium levels as rainwater. Tritium values are reported in tritium units (TU).

$$1TU = \frac{1(^3H)}{10^{18}(^1H)} = 7.1 dpm/l \quad \text{-------------------------------} \quad (9)$$

Tritium in the recharging water starts disintegrating into ^3He when it enters the subsurface environment:

$$^3_1H \rightarrow {}^3_2He + \beta$$
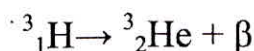
Therefore, with the passage of time, the concentration of tritium in the groundwater decreases according to the decay law.

$$C = C_0 \ln e^{-\lambda t} \quad \text{or} \quad {}^3H = {}^3H_0 C_0 \ln e^{-\lambda t} \quad \text{---------------------------------------}(10)$$

To date a groundwater sample, we have to measure the concentration of tritium in the sample (^3H), we also have to find out what was the concentration of tritium in the recharge water, or the initial value ($^3H_0$). λ is the decay constant of tritium of 0.056 year^{-1}.

Tritium dating of groundwater samples involves following procedure.

 - *Sample Collection:* For tritium analysis the quantity of natural water sample is collected as per the expected level of tritium.
 - *Pretreatment (Primary Distillation):* The samples are distilled to remove all dissolved salts that interfere with electrolysis process.

> *Sample enrichment:* After primary distillation, samples are enriched by electrolytic reduction to concentrate the tritium.
> *Distillation of enriched samples (Secondary Distillation):* Secondary distillation is carried out to remove excess Na applied during sample enrichment.
> *Liquid Scintillation Counting*

Advantages and Disadvantages

Advantages

1. Tritium is a well-established method.
2. Laboratory facilities are worldwide and the cost of analysis is relatively small.
3. Tritium can still be regarded as a supplementary dating method.
4. It is the only tracer that is part of the water molecule.

Disadvantages

1. The method is approaching its expiry date.
2. Due to the strong latitudinal variation, it would be difficult to precisely determine the initial value even if the bomb-peak tritium effects on the environment are completely reduced.

$^3H/^3He$ Technique

The technique involves 3H together with its daughter ^3He. The concentration of ^3He in the groundwater samples is reported as %δ ^3He:

$$\%\delta^3He= (Rsample-Rat)/Rat\times100 \qquad\text{------------------------------(11)}$$

where *R*sample is the $^3He/^4He$ ratio (units in cm^3 STP/g H2O) of the water sample, *R*at is the $^3He/^4He$ ratio in the atmosphere, which is 1.384×10^{-6}.

The age equation is given by;
$$^3H=(^3H + ^3Hetri) \ln e^{-\lambda} \qquad\text{------------------------------(12)}$$

The term in the bracket is the initial ^3He which is equal to un-decayed tritium (^3H) plus the decayed tritium (^3Hetri).

It is clear from the equation that in order to measure the age of a groundwater sample, we simply need to measure its tritium and ^3Hetri simultaneously.

Advantages and Disadvantages

Advantages

1. Provides high resolution age.
2. This method does not need the initial value, a parameter that is fundamental and problematic for many of the dating methods.

Disadvantages

1. Sampling and analysis are expensive and laboratory facilities are not available worldwide.
2. It is a difficult exercise to separate tritiogenic helium from the other heliums (atmospheric and insitu contaminated ^3He).

DATING OLD GROUNDWATERS (^{14}C dating)

^{14}C forms in the upper atmosphere and decays to 14N with beta emission as;

$$^{14}N + n \rightarrow {}^{14}C + p$$
$$^{14}C \rightarrow {}^{14}N + \beta^-$$
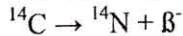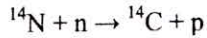
The emitted maximum energy of beta is 156 keV and half-life of ^{14}C is 5730 ± 40 years. ^{14}C activity is given in percent Modern Carbon (pMC), where as 100 pMC = 13.56 dpm/g of carbon. The age equation is given by;

$$a_t{}^{14}C = qa_0{}^{14}C\, e^{(-\lambda t)} \quad \text{---(13)}$$

where, $a_t{}^{14}C$ is ^{14}C activity of sample; $a_0{}^{14}C$ is initial activity of sample and q (varies from 0.65 to 1.0) is the dilution in initial activity due to carbon contamination (calcite, dolomite, diffusion of carbon etc.).

Advantages and Disadvantages

Advantages

1. It is well-established method.
2. Sampling and analysis for this method are now routine and cheaper than the majority of the dating methods.
3. The deficiencies, the principles, and the positive points of the methods are all well known.

Disadvantages

1. It is an extremely difficult task to determine the correct initial value due to the various processes that modify ^{14}C signature of the percolating rainwater.
2. A large number of geochemical reactions modify the concentration of ^{14}C in the groundwater. It has been tried to alleviate this problem by taking into account a large number of processes, but an appreciable amount of uncertainty surrounds the validity of this approach and the results obtained.
3. Having pointed out the above two major obstacles, it is safe to argue that the 14C method is often a semi quantitative technique.

APPLICATIONS OF GROUNDWATER AGE DATA

Groundwater age data can be used to evaluate the renewability of groundwater reservoirs, to constrain the parameters of groundwater flow and transport models, to study groundwater flow paths and vertical and horizontal flow velocities, to identify paleoclimate conditions (in combination with isotopes), to estimate groundwater recharge, to determine

fracture and matrix properties and water velocities in fractured rock environments, to help study the trend of groundwater pollution, to identify past seawater level fluctuation, to manage groundwater-driven dryland salinity, to map susceptibility of groundwater systems to contamination, and to be used in many more hydrological applications such as mixing, groundwater– surface water interaction, and seawater intrusion.

Replenishment of groundwater reservoirs

Groundwater age is, as yet, the only sound and concrete piece of scientific evidence to show that groundwater resources are recharged by modern precipitation, or else, the extracted groundwaters were accumulated in the aquifers by slow infiltration processes that happened a very long time ago. This application is more highlighted in the arid zones where due to the scarcity and periodicity of the rainfall, the question of recharge (if any) often remains open. An important fraction of young water within an extracted water sample is an indication of an actively renewable reservoir; the opposite, i.e., a considerable amount of old water in the sample, depicts a poorly recharging reservoir and/or significant internal mixing processes.

Information about the age of groundwater is required if one is to confidently define the sustainability of groundwater resources of any particular well field. Estimates of renewable groundwater resources and an understanding of related hydrological processes are critically dependent upon determining the presence and age of modern groundwater.

Prevention of overexploitation and contamination of aquifers

By measuring the age of the water at certain time intervals within a district☐s well field (say once every five years), it would be possible to identify overexploitation before it happens. If the groundwater, being extracted, increases in age with time (becomes older and older), it means that a higher proportion of water is drawn from slow-moving storage. In contrast, if the age of groundwater being withdrawn decreases with time (becomes younger and younger), it means that a higher proportion of extracted water is derived from active present recharge. This shows that either the pumping rate has increased or the source water has changed (i.e., river recharge instead of rainfall recharge). This condition though does not imply groundwater mining, but it may not be a good sign in terms of contamination because eventually surface contaminants (if present) dissolved in very young waters (which may be contaminated) will reach the well field. Hence, regular dating of the groundwater from well fields can provides a mechanism to monitor, understand, and control exploitation and contamination of the aquifer.

Estimation of groundwater velocity

The velocity of groundwater flow can be calculated if we measure the age of groundwater at two separate points along a particular horizontal flow line. The ages should be measured at nearly the same depth and on the same flow line in order to avoid the effect of three-dimensional flows.

The important point is that groundwater flow rates for aquifers can be gained from artificial (applied) tracer experiments as well, but age data offer the only realistic alternative if time scales of years or decades have to be taken into account (Zoellmann et al., 2001). Having obtained groundwater velocity, we can also back-calculate the hydraulic conductivity of the aquifer if we have an estimation of the effective porosity of the aquifer through $V = KI/\theta$ (the assumption is that the hydraulic gradient is easily obtainable).

Identification of groundwater flow paths

Groundwater flow paths in both vertical and horizontal directions can be determined by having ages that increases along the inferred flow lines. Accurate information about the groundwater flow path is needed in many water resources projects such as in construction of dams (determining different routes that water stored in the dam lake / reservoir may escape), movement of plumes, mixing between different quality groundwaters, and study of surface water–groundwater interaction. Establishing flow directions in various parts of a deep, long regional aquifer is another example for use of groundwater age data.

Other applications include

> Confirming the parameters of groundwater flow and transport models
> Determination of mixing between various end members
> Evaluating the pollution of groundwater
> Estimating the travel time of groundwater plume to the points of interest
> Mapping of vulnerable shallow aquifers
> Assessment of radioactive waste disposal facilities
> identification of recharge areas of few springs

USE OF ARTIFICIAL TRITIUM IN GROUNDWATERR RECHARGE STUDIES

The earlier sections discussed about environmental isotopes (stable and radioactive). In the present section, use of artificial tritium water for investigation of soil moisture movement in unsaturated zone is discussed. The technique is popularly known as tritium tagging technique. The technique is based on the assumption that the movement of soil moisture in a unsaturated zone is similar to piston type flow i.e., if any amount of water is added to the ground surface due to precipitation or irrigation, it will percolate by pushing equal amount of water beneath it further down and so on such that an equal amount of the moisture of the last layer in the unsaturated zone is added to the groundwater i.e., no newly percolated water bypasses water that has previously percolated below the root zone.

In this technique, tritium is injected at a depth well below the root and sun-heating zone (70 to 100 cm) at selected site/s in the study area. . The soil samples are collected from different depths at the time of tritium injection from a nearby location for having the information of initial soil moisture conditions. The tritium injection site is left open for agricultural and other activities including natural variations. In the course of water infiltration, the injected tritium is carried along with the soil water. The injected tritium is removed by collecting the soil samples from the tritium injection points at an interval of 10 cm. depth after a chosen time interval. These soil samples are analyzed to study the soil moisture and dry/wet density. The soil samples are also subjected to distillation in order to get the tritiated water from the corresponding depths. The tritium activity is determined in the distilled water samples in order to know the movement of tritium peak (fig 1). Shortly after the tracer injection, the peak concentration is at depth z1 and after a certain time it is found at depth z2. The mean moisture flux, q at the lower depth z2 over the time period, $\Box t$, between the two observations is,

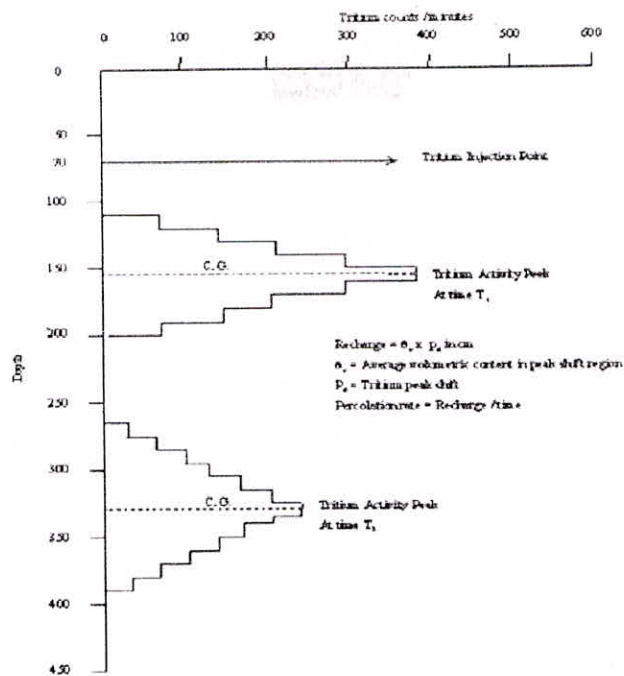$$q = \theta v \ (z2 - z1)/ \Delta t$$

Figure 10. Shifting of injected tritium with the infiltrating water

At present, isotope data collected within the framework of hydrological and hydrogeological applications are used, to a large extent, for improved understanding of processes involved in the occurrence and transport of water, and for qualitative evaluations as regards system identification. Impact of the isotope methods and quantitative information to be derived from them could be improved if proper modelling approaches are further developed. Environmental isotopes could also contribute significantly to provide improved understanding of dynamics of atmospheric circulations and employed in environmental studies related to atmosphere, and its interaction with the hydrosphere. These will be most relevant also at local, regional and global scale research being carried out in relation to the announced climatic changes.

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