INTRODUCTION TO ISOTOPES AND ISOTOPE APPLICATIONS TO LAKE STUDIES

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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 number of neutrons (N) but same number of protons or electrons are called isotopes. For example, hydrogen has three isotopes (fig. 1) 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.

$_1^2H_1$ -   one neutron added to the nucleus of $_1^1H_0$ atom.

$_2^3H_2$ -   one more neutron added to the nucleus of $_1^2H_0$.

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.

Name : (Nucleus)	Protium (1p)	Deuterium (1p +1n)	Tritium (1 p+ 2n)
Schematic:			
Characerstic:	Light (Stable)	Heavy (Stable)	Still Heavy (Radioactive)
Abundance:	99.985%	0.015%	"decays" to 3He

Fig. 1. Isotopes of hydrogen

In water resource applications most widely used isotopes are that of oxygen (^{16}O, ^{17}O, ^{18}O),

hydrogen (^{2}H, ^{1}H) and carbon (^{12}C, ^{13}C and ^{14}C). It may be noted that naturally occurring elements in waters contain about 1700 stable and unstable (radioactive) isotopes, commonly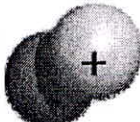 referred to as environmental isotopes. While nuclear configuration of stable isotope do not change with time the unstable isotopes decay with time and gets transformed to another type of atom (daughter element) with emission of radiations alpha (α), beta (β) particles and/or gamma (Υ) radiation etc. The decay of parent isotope activity (related to radiation emission rate) takes place at a systematic rate governed by equation:

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

$$\ldots\ldots\ldots(1)$$

Where, Ao and A are the initial and final activity and λ is the decay constant which is characteristic of an isotope and is defined in terms of its *half life* (denoted by $t_{1/2}$ and is defined as the time in which the radioactive element decays to one half (1/2) of its initial strength) as;

$$\lambda = 0.693/\, t_{1/2}$$

In the equation (1), A is determined experimentally through measurement of sample activity, A_0, the initial activity is estimated from combination of measured data and field data. On solving the equation (1) the time 't'(age) can be calculated which is nothing but the time elapsed to decay the parent activity from A_0 to A. For the case of ^{14}C and ^{3}H the equation (1) reduces to age equations as:

$$^{14}\text{C age (years)} = 8270\ \ln A_0/A$$
$$^3\text{H age (years)} = \ln A_0/A$$

Fig. 2., provides conceptual diagram of relation between age increase with the decrease in activity of parent isotopes (tritium and carbon-14) and corresponding growth of daughter isotope concentration. The parent activity at start is normalized to 1 ($A_0 = 1$).
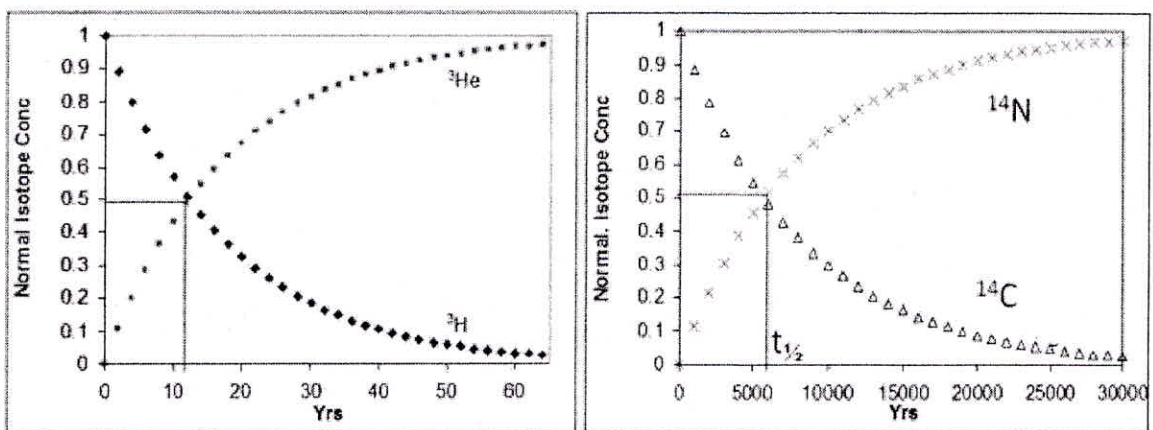

Fig 2. Radioactive decay of tritium (^{3}H) and ^{14}C isotopes, growth of their respective daughter isotopes and concept of half life ($t_{1/2}$)

In the hydrological studies, the main environmental isotopes of interest are the stable isotopes

deuterium (hydrogen-2), carbon-13, oxygen-18, and the radioactive isotopes tritium (hydrogen-3) and carbon-14. Isotopes of hydrogen and oxygen are ideal geochemical tracers of water because their concentrations are usually not subject to change by interaction with the aquifer material. Unlike radioactive isotopes, the stable isotopes do not decay with time. The variations of the isotopic ratios D/H and $^{18}O/^{16}O$ in water samples are expressed in terms of per mille deviation (δ‰) from the isotope ratios of mean ocean water, which constitutes the reference standard SMOW and is defined as;

$$\delta(\text{in }‰) = \left[\frac{R_{Sample}}{R_{Standard}} - 1 \right] \times 1000 \qquad \ldots\ldots\ldots(2)$$

Where, R = D/H or $^{18}O/^{16}O$ etc.

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.

Relative values can be converted to mg/L after Becker and Coplen (2001) using equation:

$$^2H_{conc} = 34.82 \cdot (1000 + \delta^2H_{V\text{-SMOW}})/1000$$

or absolute concentrations in parts per million as described by Rodhe (1998) by the equation:

$$^2H_{conc} = \left[\left(\frac{\delta^2H}{1000} + 1 \right) \cdot 157.6 \right]$$

2H_{conc} denotes the deuterium concentration (ppm) and δ^2H denotes the relative concentration (‰ V-SMOW).

The values of abundance ratios ($^2H/^1H$ and $^{18}O/^{16}O$) some reference standards are given in given in Table 1.

Table 1. Measured abundance ratios in international standard reference material

Isotopes	Standard	Abundance Ratio
$^2H/^1H$	SMOW	0.000158 [158($\pm$2) $\times 10^{-6}$]
$^{18}O/^{16}O$	SMOW	0.0019934 [1993.4($\pm$2.5) $\times 10^{-6}$]
$^2H/^1H$	SMOW	0.00015575 [155.75($\pm$0.45) $\times 10^{-6}$]
$^{18}O/^{16}O$	VSMOW	0.0020052 [2005.2($\pm$0.05) $\times 10^{-6}$]

The relative isotopic values of standard light water SLAP and GISP with respect to VSMOW are:

$\delta^{18}O$ SLAP = –55.50‰ VSMOW; δD SLAP = –428.0‰ VSMOW
$\delta^{18}O$ GISP = –24.76‰ VSMO W; δD GISP = –189.5‰ VSMOW

STABLE ISOTOPE SYSTEMATICS IN HYDROLOGICAL CYCLE

Environmental isotope hydrology deals with hydrological investigations based on isotopic variations observed in natural waters established due to natural processes over a broad scale in space and time. The observed variations are interpreted to gain valuable regional information on the origin, turnover and transit time of water in the system which often is difficult to obtain by other techniques. The cost of such investigations is usually relatively small in comparison with the cost of classical hydrological studies.
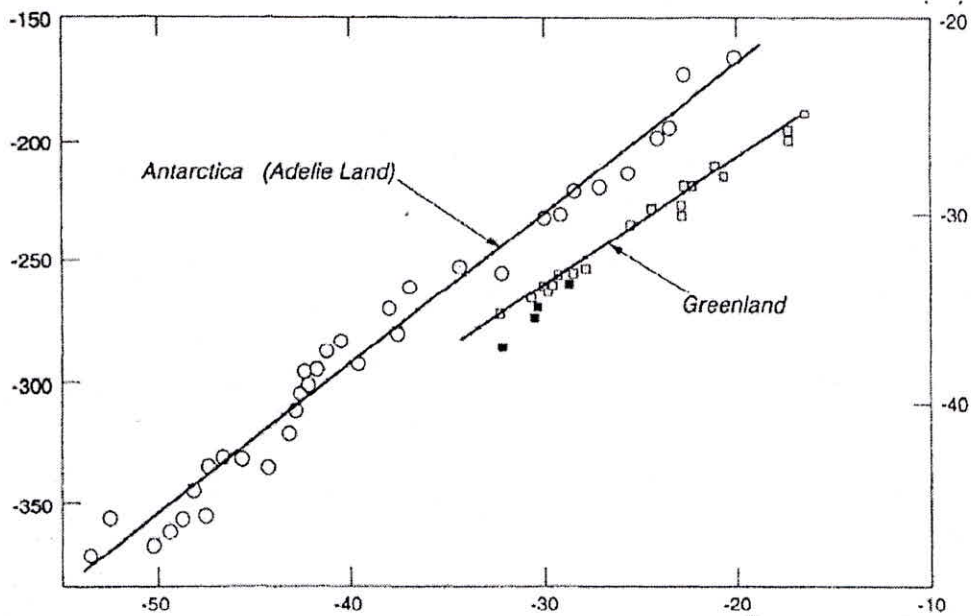

Fig. 3: Effect of temperature of condensation on isotopic composition of precipitation (after Jouzel et al., JGR, 1997)

The most important natural processes that cause variations of the stable isotopic composition of natural waters are evaporation and condensation. The light molecules of water, $H_2^{16}O$, are more volatile than the heavier ones, so on cooling of atmospheric moisture the heavy molecules condense preferentially, leaving a residual vapour more and more depleted in heavy isotopes. Such sequential condensation occurs as air masses move inland from the sea or rise to higher altitudes. Because the residual vapour requires a lower and lower temperature for further condensation, a relationship between temperature of condensation and isotopic composition of precipitation is observed; as the condensation temperature decreases, the heavy isotope content of the precipitation is lower (fig 3). This dependency on temperature produces (i) seasonal isotope variations of precipitation (winter precipitation is depleted in heavy isotopes with respect to summer precipitation, Fig. 5), (ii) latitude variations (high latitude precipitation is depleted with respect to low latitude precipitation) and (iii) altitude variations (the heavy isotope content of precipitation decreases with increasing altitude: Fig. 4). The last effect is especially important in regional hydrological studies, where for instance groundwaters deriving from recharge areas at different elevations may be differentiated.
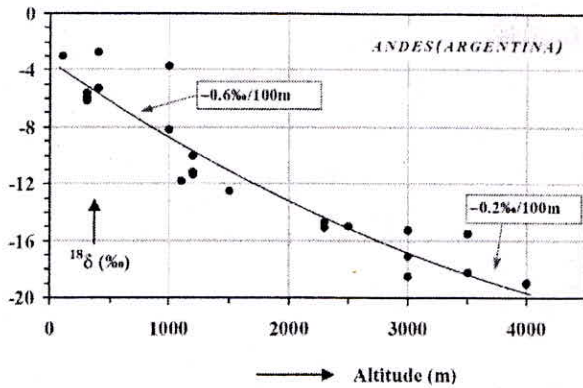
Fig 4: Altitude effect on precipitation for the eastern slopes of the Andes mountains, as deduced from samples of undeep groundwater/soilwater, collected from springs (Vogel et al., 1975).
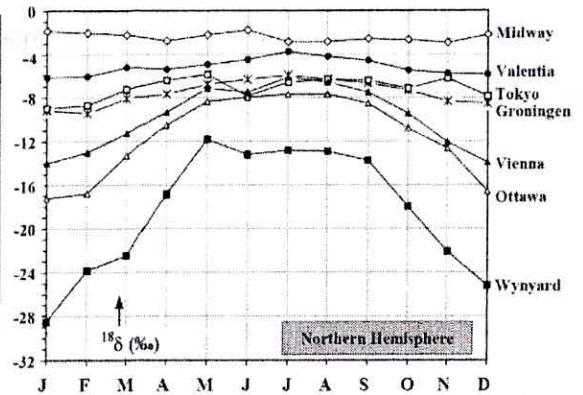
Fig 5. Seasonal variations in $^{18}\delta$ shown by weighted averages of monthly precipitation samples (pcpt) collected in some typical locations in Northern Hemispere.

The spatial variations of the stable isotopes due to the above mentioned factors based on the precipitation data collected from IAEA/ WMO network provides a characteristic linear relation between $\delta^{18}O$ and δ^2H called as Global Meteoric Water Line (GMWL), as a consequence of the fact that both oxygen and hydrogen isotopes are equally gets affected due to above mentioned effect (Craig, 1961). The relation between these two is given by:

$$\delta^2H = 8\delta^{18}O + 10 \qquad \ldots\ldots\ldots(3)$$

This equation was further refined by including longer data range and from more number of stations (219 stations). The refined relationship between 18O and D in global precipitation (*Figure 6*) is given by (Rozanski et al 1993):

$$\delta D = 8.17 \, (\pm 0.07) \times \delta^{18}O + 11.27 \, (\pm 0.65) \, (‰ \text{ SMOW}) \qquad \ldots\ldots\ldots(4)$$

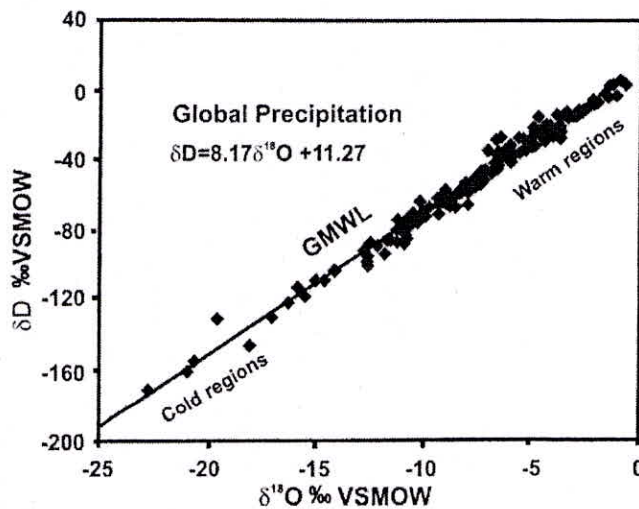The equation (3) was based on fresh surface water samples while (4) is based on actual precipitation data.

Fig 6: 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).

It should also be noted that, while the equation given (3) & (4) above are valid as a global average relation, it may however have different characteristic values in different climatic regions, particularly with respect to the intercept (often referred to as deuterium excess) of the line. The GMWL is of practical interest to explain various hydrological processes as shown in fig. 7. It provides original isotopic composition of precipitation that has not undergone evaporation during infiltration (intersection point of evaporation line with meteoric line)
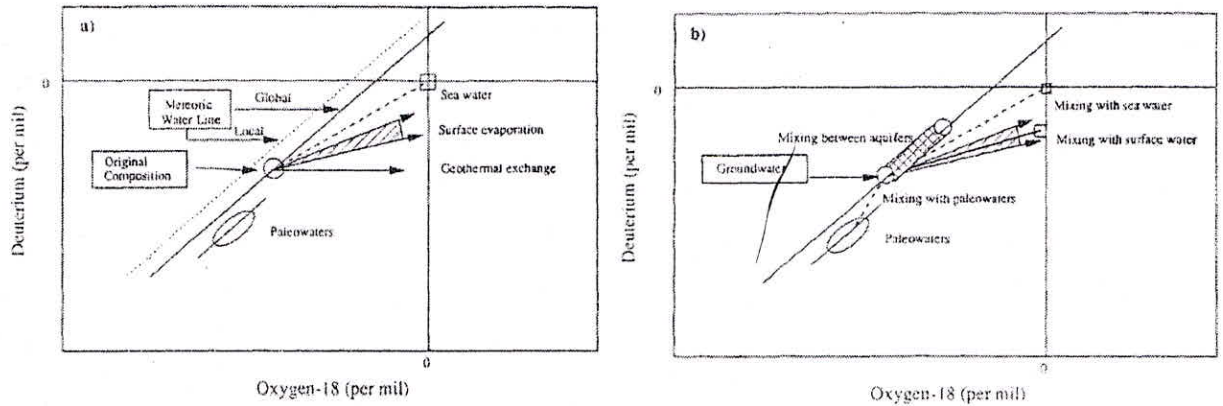

Fig. 7. Characteristic $\delta^{18}O/\delta D$ relations for different processes a) Related to processes b) Related to hydrological applications.

In the case of evaporative enrichment, Geyh and Ploethner (1997) provided a procedure to correct the observed $\delta^{18}O$. The corrected values indicate the isotopic composition without enrichment by evaporation. As the corrected value marks the intersection of the evaporation line with the Global MeteoricWater Line, it is defined by:

$$\delta^{18}O_{corrected} = \frac{\delta^2 H_{measured} - e*\delta^{18}O_{measured} - d}{8 - e}$$

where e corresponds to the slope of the evaporation line determined, for example, as 4.5, and d is the deuterium excess of global precipitation, with d = +10‰. Once the $\delta 18O$ has been corrected for evaporation, the corresponding deuterium value can be obtained by solving the equation for the global meteoric water line. This method is extremely useful in studying flow paths of surface and groundwater that have been affected by evaporation. Once the evaporation effect has been corrected for, it can be analysed whether the original water type is prevailing or whether mixing with another source of water (resulting in different $\delta 18O$ values) takes place. It is important to note that only conditions where (a) kinetic fractionation takes place and where (b) a reservoir is partially depleted result in evaporation effects.

ISOTOPIC FINGERPRINTING METHODS TO EXAMINE HYDROLOGICAL PROCESSES

Due to their conservative nature stable isotopes are used in tracing hydrological system, groundwater and surface waters interaction, for estimating mixing proportions of different sources, evaporation loss, component flows (component-tracing); and or between different aquifer units within a given groundwater system. Qualitative interpretation of data is usually

very simple and cost effective. Principles and techniques commonly used in interpreting the data is described below.

Inter-relation between multiple springs: The relationship between δH and $\delta^{18}O$ can be used to identify spring waters that have similar histories, such as source, flow paths, and mixing. If δH and $\delta^{18}O$ values plot near or next to one another, the samples have a similar history. Samples that are separated have different values and therefore have different histories.

Hydrograph Separation: Isotope hydrograph separation is based on the assumption that the isotopic compositions (e.g. $\delta^{18}O$) of both new water and old water (water existing in the watershed prior to the event) at a given instant in time are known and that the stream water is a mixture of the two (Taylor et al., 2002). The simplest form is a two-component system, where the $\delta^{18}O$ of the pre-event base flow is used as the composition of the old water ($\delta^{18}O$ Old) and the $\delta^{18}O$ of the bulk precipitation (or snowmelt) is used as the composition of new water ($\delta^{18}O$ New). Then the stream water $\delta^{18}O$ ($\delta^{18}O$ Str) can be expressed as
$\delta^{18}O_{Str} = x\delta^{18}O_{New} + (1-x)\delta^{18}O_{Old}$
where x is the fraction of new water at a given instant in time during the event. Therefore,

$$x = \frac{\delta^{18}O_{Str} - \delta^{18}O_{Old}}{\delta^{18}O_{New} - \delta^{18}O_{Old}}$$

For the equations to be valid along an event hydrograph, it is necessary that both $\delta^{18}O_{Old}$ and $\delta^{18}O_{New}$ are temporally invariant, and so a change in $\delta^{18}O_{Str}$ can be attributed only to a change in x.

In case of separation hydrograph components in springs for their discharge formed from combination of surface water (say from lake) and groundwater can be computed if isotopic composition of groundwater, surface water and spring water is known. This is given by:

$$f_g.K_G + (1-f_g)K_L = K_s$$

Where,

f = fraction of groundwater present in the sample.
K = isotopic composition of the groundwater
K_L = Isotopic composition of the lake water
K_S = Isotopic composition of the emerging water.

If all the three waters have different chloride or EC values then the similar equation of mass balance can be used to resolve the components.

Lake water-well water interaction: Water in reservoir, lake, surface ponds usually show enrichment in isotopic composition due to evaporation with respect to local meteoric water especially if their turnover time is very slow. This fact is used in several studies to identify surface water intrusion in the groundwater pumping wells. Natural tritium of water can provide similar information due to difference in time of arrival of surface water and

groundwater at the point of sampling.

Evaporation from water bodies : The evaporation of water from lakes can be estimated from water and isotope mass balances. The water balance of a lake is:

$$\frac{dV}{dt} = Q_{in} + P - Q_{out} - E$$

where V is the volume of the lake, Qin and $Qout$ are in- and outflow, P precipitation and E evaporation. The general water and isotope balance approach is given by the equation below. Additional terms can be added for different types of inflow (surface, groundwater). The balance equation writes:

$$\frac{d(V^*\delta_V)}{dt} = Q_{in}{}^*\delta_{Q_{in}} + P^*\delta_P - Q_{out}{}^*\delta_{Q_{out}} - E^*\delta_E$$

where δi represent the respective isotopic composition of the hydrological component identified by the subscript i. Difficulties arise from the fact, that the lake volume is not fully mixed. The isotopic composition of the lake can be determined by adequate sampling. The isotopic composition of rainfall, inflow and outflow need to be determined in the field. The major difficulty is the determination of δE which depends on transport processes through the boundary layer and on atmospheric conditions such as wind speed and relative humidity. For well-mixed steady state systems Gibson *et al.* (1993) proposed an estimation based on a two-component mixing approach according to:

$$\frac{E}{P} = \frac{(\delta_P - \delta_V)}{(\delta_E - \delta_V)}$$

where the subscripts P, V and E represent the mean weighted local isotopic composition of precipitation, lake water and evaporating moisture. While the isotopic composition of lake water and precipitation can be obtained by sampling, the isotopic composition of evaporating moisture needs to be determined by field experiments, for example with evaporation pan experiments or through calibration for lakes with known water balance or based on theoretical relationships. This approach works only for steady-state systems as long as evaporation does not affect the lake volume significantly.

If evaporation reduces the lake volume, the Rayleigh equation can be applied to estimate the evaporated volume for progressive evaporation in a simplified way based on:

$$\frac{E}{V} = 1 - \exp\frac{(\delta_V - \delta_i)}{\frac{1}{\alpha} - 1}$$

where δV is the isotopic composition of the well-mixed water body after evaporation E took place, δi the initial isotopic composition and α the fractionation factor. This approach only holds for idealized small and well-mixed water bodies (ephemeral pans with depths <1 m)

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and does not take into account the exchange with atmospheric vapour.

Recharge zones: Isotope-altitude gradient, or altitude effect, helps to distinguish groundwaters recharged at high altitude from those at low altitude. 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 (fig. 8).
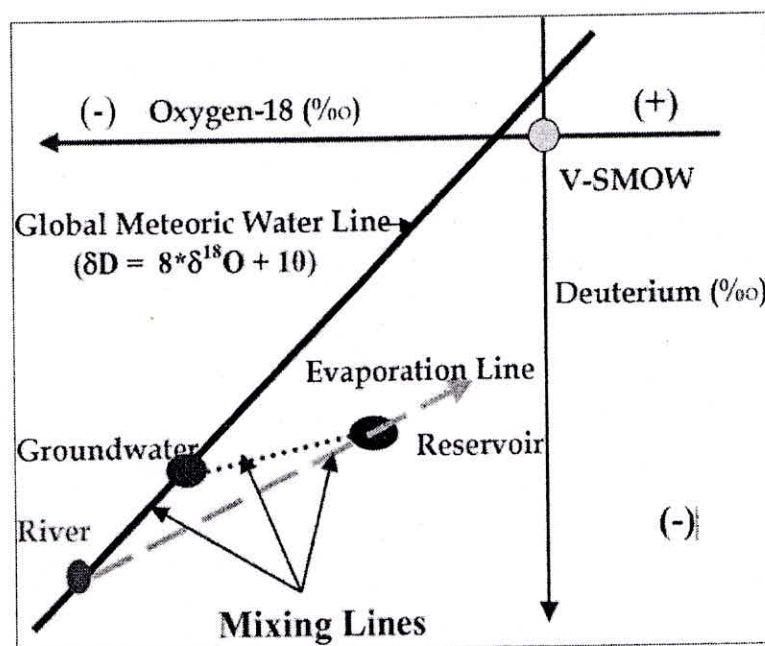
Rainfall-runoff processes: The component flows involved in the runoff process such as baseflow and overland flow within a given basin can effectively be quantified through simple mass balance considerations of the stable isotopic composition of the river water prior to and during the individual rainfall 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.

Groundwater mixing : Stable isotopes 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 9, 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:

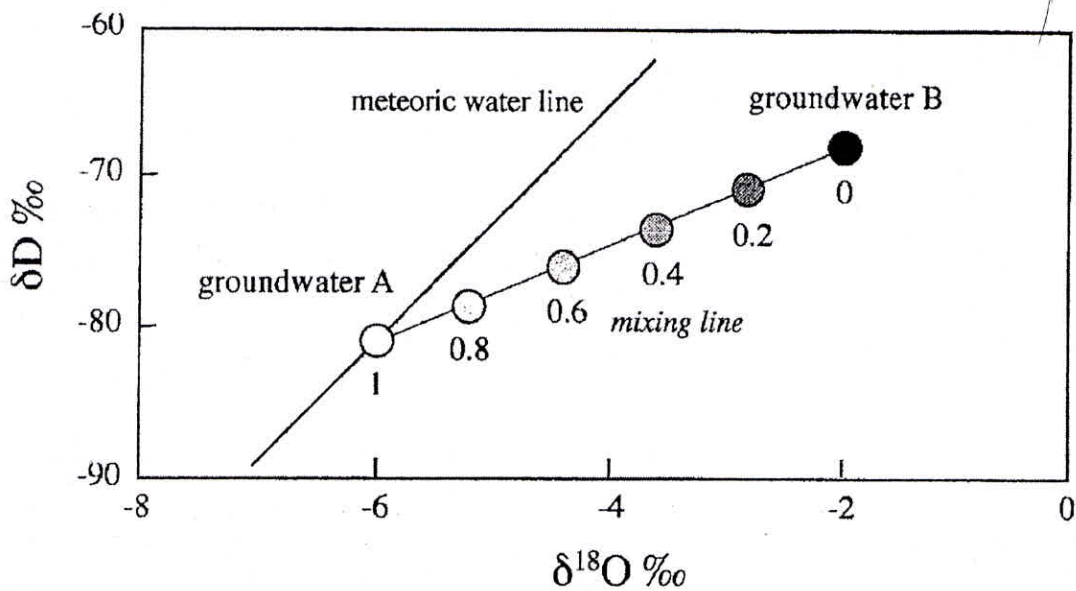$$\delta_{sample} = X \cdot \delta_A + (1-X) \cdot \delta_B \qquad \ldots\ldots\ldots/(8)$$

Fig. 9: Fractional mixing of two groundwaters quantified on the basis of their isotopic composition, and it is shown as the fraction of groundwater A

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 ^2H in studying groundwater genesis is shown in Fig. 10 (Gat, 1983), where groundwaters replenished through recent precipitation and paleowaters in different aquifer systems are identified.
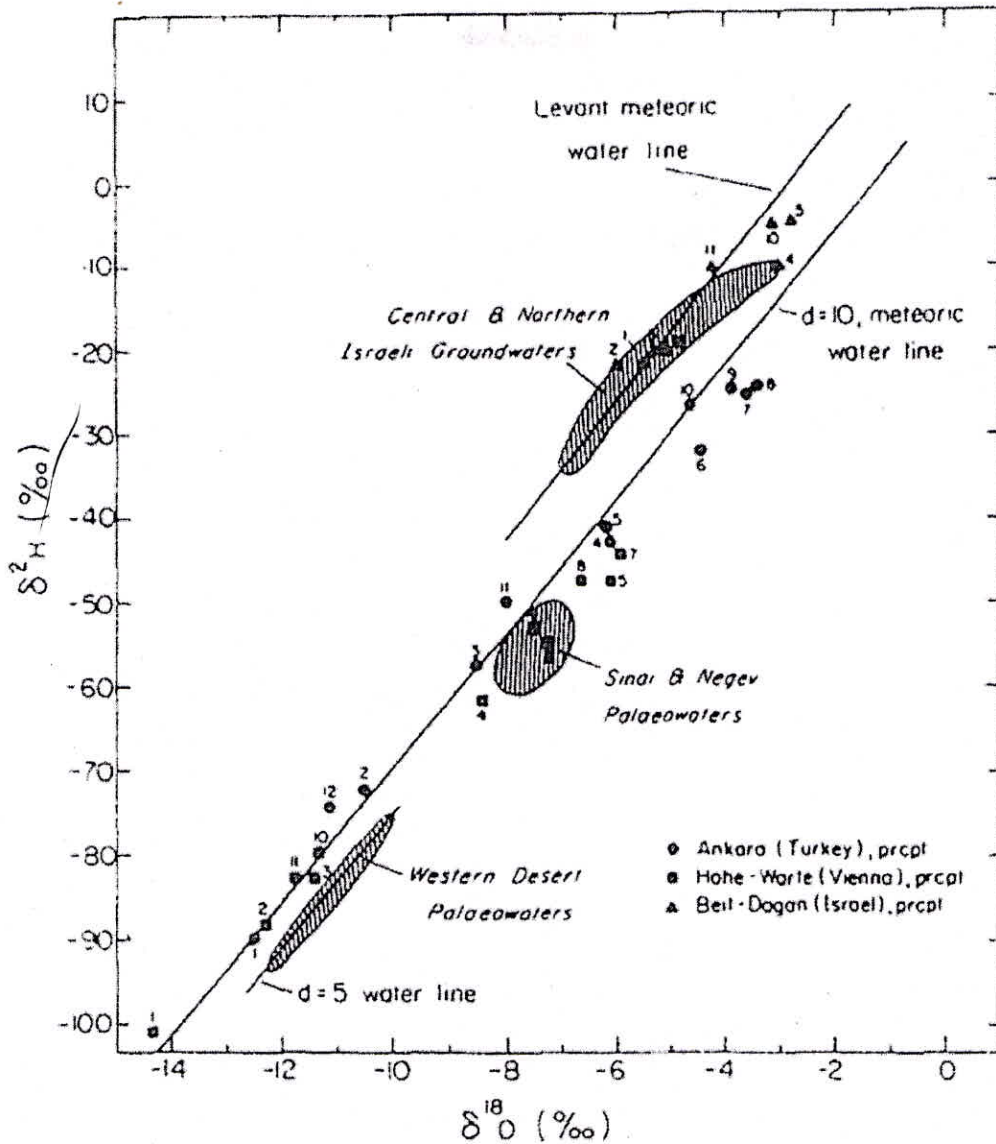
Fig. 10: Isotopic composition of precipitation and groundwater in the East-Mediterranean region (Gat, 1983).

Interlink between seepage water and nearby source: in tunnel with nearby reservoir or spring-reservoir:

Investigation of such interlink are especially important for cases like seepage in tunnel at sites close large surface water source such as reservoir or river or lake similarly; to know the interlink between a spring-water and nearby reservoir etc. Such interlink can be easily identified by comparing the isotopic characteristic of source water and seepage water. No difference between the two indicates common water source. An example of from tunnel seepage water in Salal H.P. project and nearby river Chenab is shown in the fig 11. The result clearly shows that the seepage from tunnel originates from a source which is different from the river Chenab. In addition to ^2H and ^{18}O; ^{13}C, ^3H, and chemical investigation can also be taken up to strengthen and detailed interpretation of the scenario.

Vertical Mixing of Lake Water: Lake water gets mixed due to turbulence created from winds, inflow and outgoing water and diurnal and seasonal temperature fluctuation. Poor mixing leads to stratification of lakes. This is also due to change in water density trend above and below 4^0C. The stratification is a usually seen in very deep lakes and high altitude lakes. From the analysis of depth dependent changes in stable and ^3H content it is possible to analysis unfixed old water, average turn over time and mixing cycle (Gonfinatini et al., 1977).
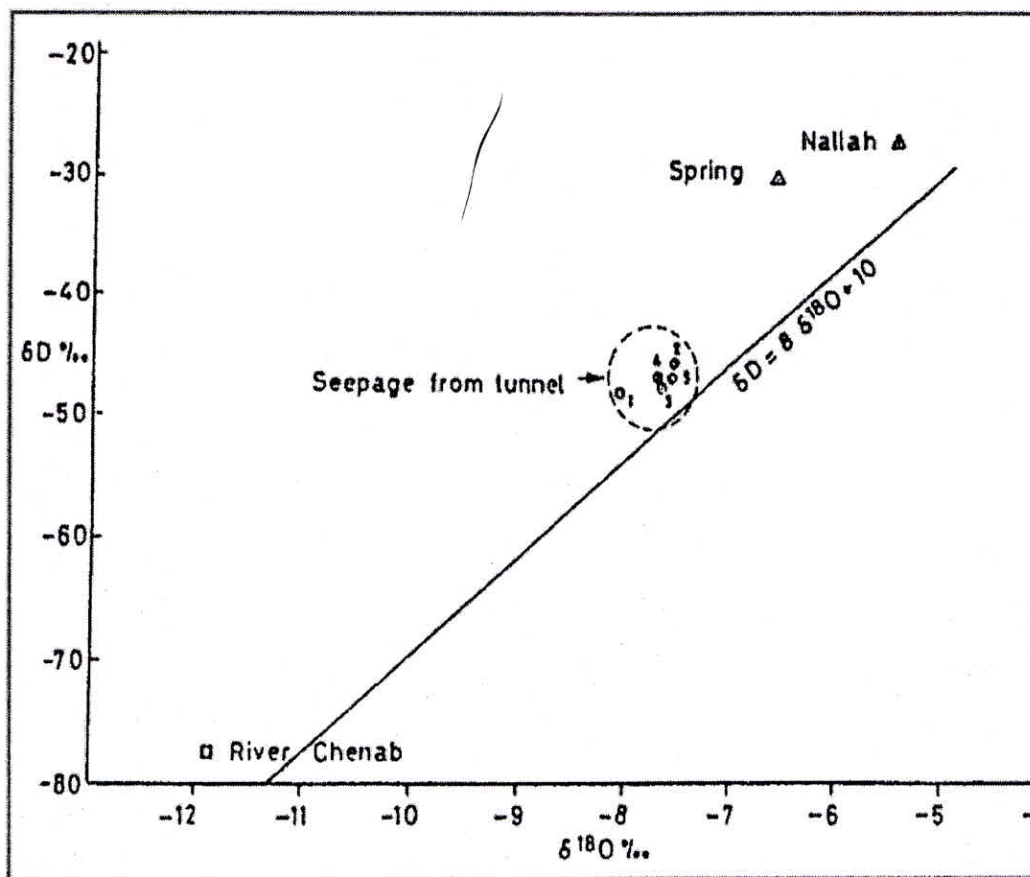

Fig.11. Isotopic composition of sample waters collected in Salal H.P. Project

Climate impact on Catchment Hydrology: Long-term records of stable isotopes in precipitation, lakes and rivers provides climate change effect on catchment hydrology and surface water system (fig.12). Such temporal record can be used to determine the mean residential time (age) of water in the system, base flow and its temporal variation. Such studies provide immnse information at basin scale hydrological changes.
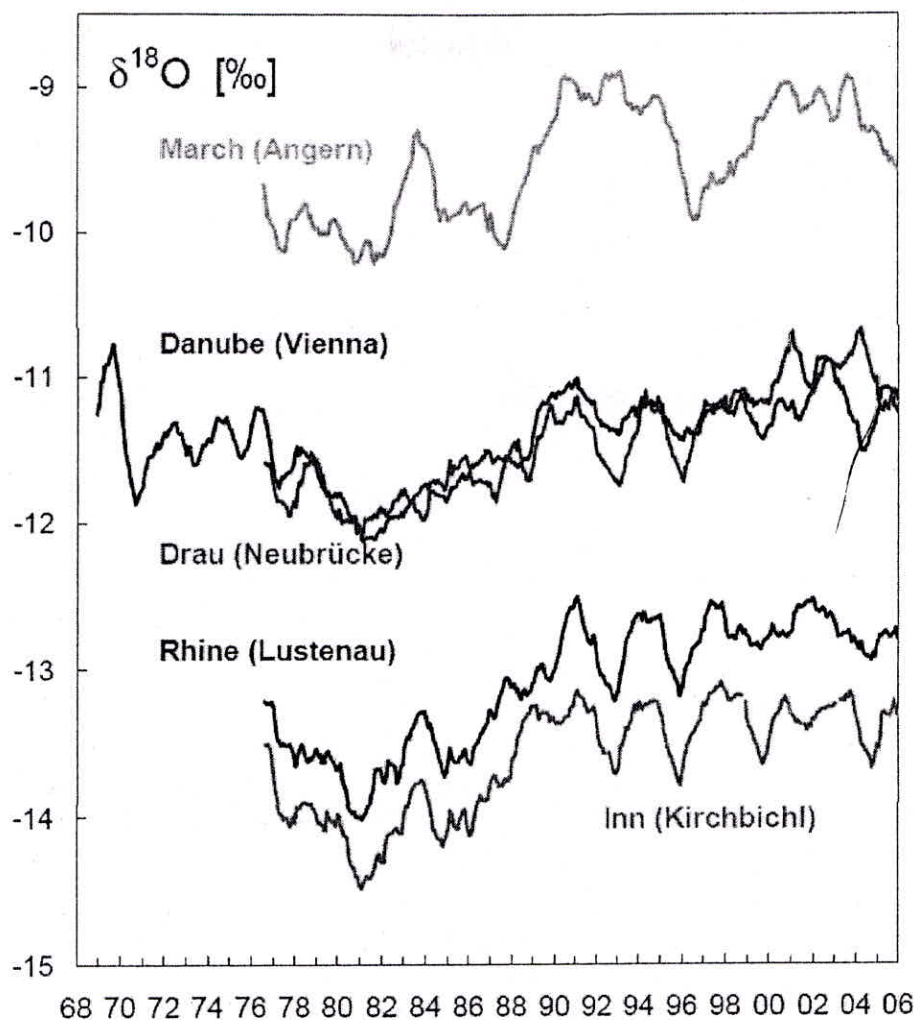
Fig. 12: 12-month running average $\delta^{18}O$ time series of some Austrian rivers (Rank & Wolfgang, 2010)

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.

Groundwater dating is usually done using tritium, helium-tritium, radiocarbon dating

techniques. Difficulties in determining the correct initial concentration of these radioactive isotopes usually creates problem in exact estimation of age. Therefore, the estimated dates even after applying a suitable model calculation are usually interpreted in 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.

Recharge estimation: Recharge to groundwater using environmental radioactive isotopes is usually done using mass balance approach corrected for its decay. The input to the system is estimated from its concentration in variation in long term precipitation data. Gyeh and Ploethern (1995) computed this using the water column height in the well, h [cm], the measured ^3H value of groundwater, c [TU] and the porosity, n. Then the deep rate of percolation (groundwater recharge), r [cm year'1], is given by:

$$r = [(chn)/c_{accuml}]$$

where, C_{accum} is the total accumulated tritium, in Pakistan estimated to be 600 [TU year] for the last 40 years. For a water column of 1 m in the dug wells, a porosity of 0.4 and a tritium value of < 1.2 TU this gives a recharge rate of <0.8 mm year"1 which makes up < 0.4 % of the mean annual rainfall.

Other applications of groundwater dating:

- 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 13). 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,

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

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.
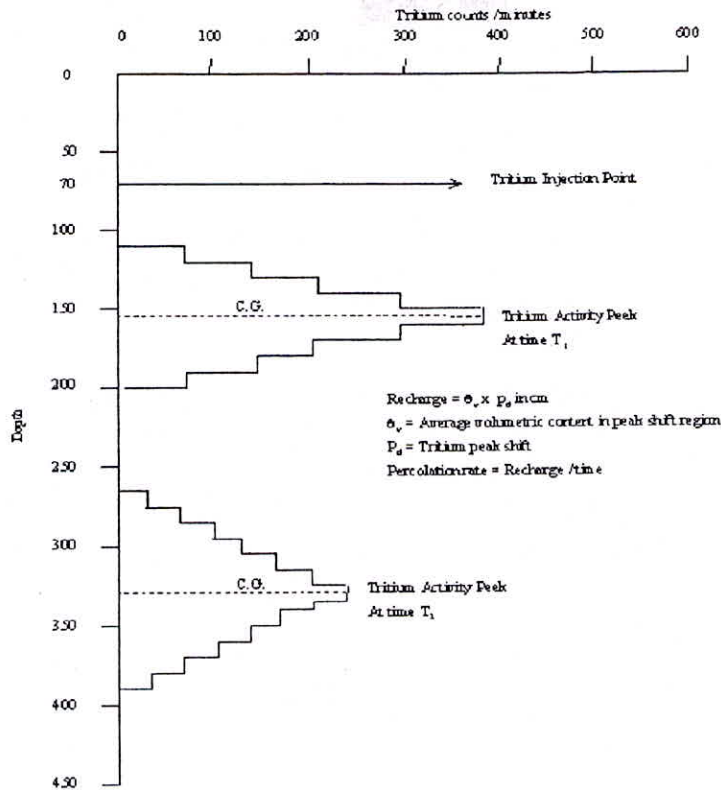
Fig 13: Shifting of injected tritium with the infiltrating water.

REFERENCES

Gat, J.R. (1983). Precipitation, groundwater and surface waters: control of climate parameters on their isotopic composition and their utilization as palaeoclimatological tools. In: Palaeoclimates and Palaeowaters: A collection of environmental Isotope Studies, IAEA, Vienna, 3-12.

Geyh M. A. & D. Ploethner (1995). An applied palaeohydrological study in Cholistan, Thar Desert, Pakistan In, Application of Tracers in Arid Zone Hydrology (Proceedings of the Vienna Symposium, August 1994). IAHS Publ. no. 232,1995. 119

Gibson, J.J., Edwards, T.W.D., Bursey, G.G., and Prowse, T.D., (1993). Estimating evaporation using stable isotopes: quantitative results and sensitivity analysis for two catchments in northern Canada, Nordic Hydrology, 24, pp. 79-94.

Gonfiantini R., G. M. Zuppi and W. Ferro (1977). Isotopic Investigation of Lake Malawi. In, Isotopes in Lake Studies, IAEA, Vienna

Jouzel, J., et al. (1997), Validity of the temperature reconstruction from water isotopes in ice cores, J. Geophys. Res., 102(C12), 26,471–26,487.

Modica, E., Buxton, H.T. and Plummer, L.N. (1998). Evaluating the source and residence times of groundwater seepage to streams, New Jersey Coastal Plain. Water Resour. Res., 34, 2792–2810.

Rank D & Wolfgang Papesch (2010). Mean residence time (MRT) of baseflow water in the Upper Danube Basin derived from decadal climatic signals in long-term isotope

records of river water

Rozanski K, Araguas-Araguas L, Giofiantini R. (1993). Isotopic patterns in modern global precipitation, Geophysical Monograph, 78: 1–36.

Taylor S, Xiahong Feng, Mark Williams and James McNamara (2002). How isotopic fractionation of snowmelt affects hydrograph separation Hydrological Process . 16, 3683–3690 (2002);

Turner J. V., M. R. Rosen, L. K. Itfteld & G. L. Allan (1995). Chlorine-36 in hypersaline palaeochannel groundwaters of Western Australia, in, Application of Tracers in Arid Zone Hydrology (Proceedings of the Vienna Symposium, August 1994). IAHS Publ, no. 232, TECDOC 1990

Vogel, J. C., Lerman J. C. & Mook, W. G. (1975). Natural isotopes in surface and groundwater from Argentina, Hydrol. Sc. Bull., 20: 203-221

Zoellmann, K.P., Kinzelbach, W., Fulda, C.,(2001). Environmental tracer transport (3H and SF6) in the saturated and unsaturated zones and its use in nitrate pollution management. J. Hydrol. 240, 187±205.