

**Isotope Techniques for Estimating Natural and Artificial Recharge to
Groundwater
(Semi-Arid/Arid Regions)**

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1.0 Introduction

The total amount of water on this earth is virtually constant but its distribution over time and space varies to a great extent. Wherever people live, they must have a clean and continuous water supply as a primary requirement to the human beings. The assessment of quality, supply, and renewal of resources of water is a well known problem, particularly in semiarid and arid regions, but it is becoming critical with increasing demand of fresh water due to alarming growth of population and rapid industrialization.

In the past few decades, sophisticated nuclear-hydrological instruments have been developed to measure accurately both radioactive as well as stable isotopes and accordingly various nuclear methods have been evolved. It is therefore, now very easy to solve many hydrological problems related to planning of water resources, agriculture, industry, and habitation using isotope techniques which were very difficult, sometimes impossible to tackle in the past.

Isotopes can be used to study the different facets of hydrologic cycle. However, the use of different types of isotopes, i.e., radioactive (artificial) -sealed or tracers, radioactive (environmental) or stable isotopes depends upon the type and requirement of the study to be carried out. The major applications of isotopes in Groundwater Hydrology are listed below.

- Soil moisture variation, movement and recharge
- Origin
- Mixing and distribution
- Occurrence and recharge mechanism
- Groundwater flow velocity and direction
- Interconnections between groundwater bodies
- Identification of recharge sources and areas of deeper aquifers and springs
- Effectiveness of artificial recharge measures
- Groundwater and surface water interaction
- Data on lithology, porosity and permeability of aquifers
- Pollution source and mechanism

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The information on aquifer dynamics can be used to understand the availability of groundwater/replenishment, origin and source of groundwater, artificial measures to increase groundwater recharge, and sustainability of springs etc. In the present lecture only techniques useful for estimating natural and artificial recharge have been discussed.

As isotope hydrology may be a new subject to many readers, therefore, before giving details of isotopic investigations required for watershed management, the basics of isotopes are discussed below.

2.0 ISOTOPES - BASICS

There are three important terms i.e., isotopes, isobars and isotones that are used to differentiate and distinguish the atoms of a same element and atoms of different elements showing similarities in physical and chemical properties. 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 having the same atomic number of 1 but different atomic masses or weights of 1, 2 and 3 respectively i.e.,





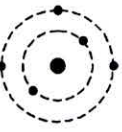
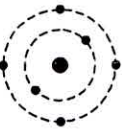




1_1H_0 - only one proton in nucleus & one electron revolving around the nucleus in an orbit.

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_1 .

Similarly oxygen has eleven isotopes, ${}^{12}O$, ${}^{13}O$, ${}^{14}O$, ${}^{15}O$, ${}^{16}O$, ${}^{17}O$, ${}^{18}O$, ${}^{19}O$, ${}^{20}O$, ${}^{21}O$ and ${}^{22}O$, 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 femo 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 ${}^{14}C$.

Table -2.1: Electronic configurations of atoms of various light elements.

1_1H 							2_2He 
3_3Li 	4_4Be 	5_5B 	6_6C 	7_7N 	8_8O 	9_9F 	${}^{10}_{10}Ne$ 
${}^{11}_{11}Na$	${}^{12}_{12}Mg$	${}^{13}_{13}Al$	${}^{14}_{14}Si$	${}^{15}_{15}P$	${}^{16}_{16}S$	${}^{17}_{17}Cl$	${}^{18}_{18}Ar$

Isobars are the atoms of different elements having same atomic weight (A) but different atomic number (A). For example, ${}^3_1\text{H}$ and ${}^3_2\text{He}$ are isobars. On the other hand atoms having same number of neutrons but different atomic number (Z) and atomic weight (A) are called isotones. For examples, ${}^2_1\text{H}_1$ and ${}^3_2\text{He}_1$ are the isotones.

2.2 Classification of Isotopes

Isotopes can be classified in two important categories, (i) stable isotopes and (ii) unstable isotopes.

Stable isotopes are the atoms of an element, which are satisfied with the present arrangement of proton, neutron and electron. On the other hand, unstable isotopes are the atoms of an element which do not satisfy with the present arrangement of atomic particles and disintegrate by giving out alpha (α), beta (β) particles and/or gamma (γ) radiation etc. and transform into an another type of atom. This process continued till the stable nuclide (element) is formed. Because of disintegration or the property of giving out radiation, the unstable isotopes are also called radioactive isotopes. For example, ${}^1\text{H}$ and ${}^2\text{H}$ are stable isotopes while ${}^3\text{H}$ is unstable. Similarly ${}^{12}\text{C}$ and ${}^{13}\text{C}$ are stable isotopes while ${}^{14}\text{C}$ is unstable. On the other hand, isotopes of oxygen (${}^{16}\text{O}$, ${}^{17}\text{O}$ and ${}^{18}\text{O}$) are stable.

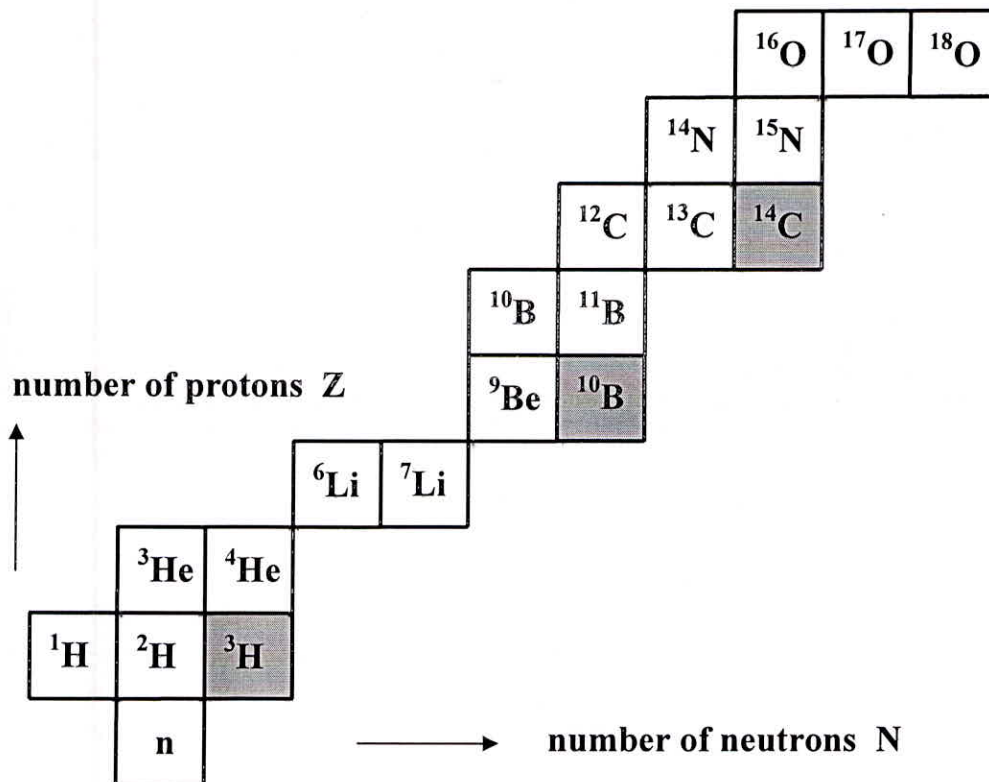
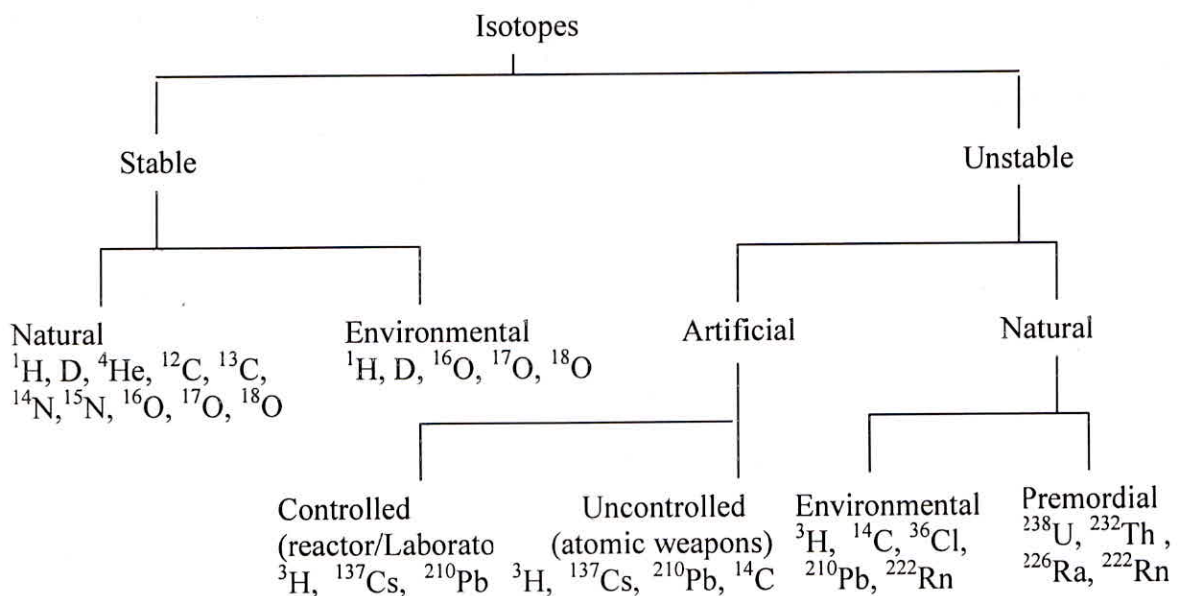


Fig. 2.2.1: The isotopes of an element (equal Z) are found in a horizontal row, isobars (equal A) along diagonal lines, isotones (equal N) in vertical columns. The natural radioactive isotopes of H, Be, and C are marked grey.

Isotopes can also be classified as natural and artificial isotopes, i.e., the isotopes that occur naturally are called natural isotopes while those produced in a reactor or laboratory under controlled conditions are known as artificial isotopes. Normally the artificially produced isotopes are radioactive while stable and radioactive, both types of isotopes occur naturally.

Another category of isotopes has been devised that is called environmental isotopes. These isotopes have different types of categories i.e. naturally occurring stable and radioactive isotopes and radioisotopes introduced into the atmosphere due to anthropogenic activities etc. The environmental radioisotopes whether naturally occurring due to cosmic ray interaction with various gaseous molecules or anthropogenically produced and become the part of hydrological cycle are safe in normal conditions and do not pose any threat to human health.

The following diagram gives a clear picture about the classification of various isotopes



Stable Isotopes

As described earlier, the atoms of an element which do not decay with time or take infinite time to decay are called stable isotopes of that element. Over 2000 isotopes of 92 naturally occurring elements have been identified out of which several hundred are stable isotopes.

The stable isotopes commonly used in hydrology as water tracers are,

- Deuterium
- Oxygen-18
- Carbon-13

But in general we talk much about hydrogen and oxygen stable isotopes. As we know water molecule is made up of two hydrogen atoms and one oxygen atom therefore, many combinations (18) are possible out of which $^1\text{H}^1\text{H}^{16}\text{O}$, $^1\text{H}^1\text{H}^{16}\text{O}$, $^1\text{H}^2\text{H}^{16}\text{O}$, $^2\text{H}^1\text{H}^{16}\text{O}$, $^1\text{H}^1\text{H}^{17}\text{O}$ and $^1\text{H}^2\text{H}^{17}\text{O}$ are important. The natural occurrence of few very important types of water molecules is given below:

$\text{H}_2^{16}\text{O} \sim 999680$ ppm (99.9680 %)

$\text{HD}^{16}\text{O} \sim 320$ ppm (0.032 %)

$\text{H}_2^{18}\text{O} \sim 2040$ ppm (0.204 %)

Carbon-13

The universally accepted Carbon-13 standard is PDB. The PDB originates from the calcium carbonate of the rostrum of a cretaceous belemnite collected from Pee Dee formation of South Carolina in USA.

The chemistry of groundwater is strongly dependent on Carbonate geochemistry. The $\delta^{13}\text{C}$ of soil CO_2 in most temperate and humid climates fall between -21 to -26. In arid areas, enriched values can be found because of special plant assemblages and increased importance of atmospheric CO_2 which has a $\delta^{13}\text{C}$ of -7. Water which passes through unsaturated zone towards the water table will become saturated with this CO_2 and the $\delta^{13}\text{C}$ of dissolved inorganic carbon will reflect the composition of recharging waters.

Modification of ^{13}C contents of aqueous carbonate after infiltration could occur through a number of processes, the most important of which are carbonate mineral dissolution or precipitation reaction and biological processes.

Marine carbonates have $\delta^{13}\text{C}$ values close to 0. Similarly the $\delta^{13}\text{C}$ of metamorphic carbonate sequences are close to 0, unless magmatic CO_2 played a role in its formation. In such cases ^{13}C values between -5 to -2 could be expected. These values are considerably enriched compared to soil CO_2 . As a result carbonate dissolution will bring about an enrichment in ^{13}C in the dissolved aqueous carbon.

There are few other stable isotopes (^3He , ^6Li , ^{11}B , ^{15}N , ^{34}S , ^{37}Cl , ^{81}Br and ^{87}Sr) which have been found useful in many hydrological studies. These stable isotopes are popularly called environmental stable isotopes as they are available in the environment and introduced in the hydrological cycle naturally. Thus the investigator does not require them to either purchase or inject into the system for carrying out hydrological studies. The use of stable isotopes in hydrology depends on their variation in natural waters. The details of these isotopes with other useful information are given in table-2.2.1

Isotope fractionation

Stable isotope variations result from isotope fractionation which occurs during physical and chemical processes. Examples of physical processes which could lead to isotopic fractionation are evaporation of water or condensation of vapor.

During evaporation, the residual liquid is enriched in the heavier isotope molecule because the lighter molecules move rapidly and hence has a greater tendency to escape from the liquid phase – there is a difference in the volatility between the two molecular species.

Chemical fractionation occurs because a chemical bond involving a heavy isotope is stronger than that with light isotope.

Fractionation may occur during both equilibrium and non-equilibrium conditions. Condensation is predominantly an equilibrium process whereas evaporation occurs under non-equilibrium conditions.

Table-2.2.1: Stable isotopes with their natural abundance and reference standards used for ratio measurements.

Isotope	Ratio	% natural Abundance	Reference (abundance ratio)	Commonly measured phases
² H	² H/ ¹ H	0.015	VSMOW (1.5575 . 10 ⁻⁴)	H ₂ O, CH ₂ O, CH ₄ , H ₂ , OH ⁻ minerals
³ He	³ He/ ⁴ He	0.000138	Atmospheric He (1.3 . 10 ⁻⁶)	He in water or gas, crustal fluids, basalt
⁶ Li	⁶ Li/ ⁷ Li	7.5	L-SVEC (8.32 . 10 ⁻²)	Saline waters, rocks
¹¹ B	¹¹ B/ ¹⁰ B	80.1	NBS 951 (4.04362)	Saline waters, clays, borate, rocks
¹³ C	¹³ C/ ¹² C	1.11	VPDB (1.1237 . 10 ⁻²)	CO ₂ , carbonate, DIC, CH ₄ , organics
¹⁵ N	¹⁵ N/ ¹⁴ N	0.366	AIR N ₂ (3.677.10 ⁻³)	N ₂ , NH ₄ ⁺ , NO ₃ ⁻ , N-organics
¹⁸ O	¹⁸ O/ ¹⁶ O	0.204	VSMOW (2.0052 . 10 ⁻³) VPDB (2.0672 . 10 ⁻³)	H ₂ O,CH ₂ O,CO ₂ , sulphates NO ₃ ⁻ , carbonates,silicates OH ⁻ minerals
³⁴ S	³⁴ S/ ³² S	4.21	CDT (4.5005 . 10 ⁻³)	Sulphates, sulphides, H ₂ S, S-organics
³⁷ Cl	³⁷ Cl/ ³⁵ Cl	24.23	SMOC (0.324)	Saline waters, rocks, evaporites, solvents
⁸¹ Br	⁸¹ Br/ ⁷⁹ Br	49.31	SMOB	Developmental for saline waters
⁸⁷ Sr	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr=7.0 ⁸⁶ Sr=9.86	Absolute ratio measured	Water, carbonates, sulphates, feldspar

Isotopic Notations and Measurements

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. For example heavy water

$^2\text{H}_2^{16}\text{O}$ (D_2^{16}O) has a mass of 20 compared to normal water $^1\text{H}_2^{16}\text{O}$ which has a mass of 18. Similarly heavier stable molecule of water D_2^{18}O has a mass 22. This is because of the variation in the number of neutrons. However, the absolute abundance ratio of isotopes is not usually measured in natural waters and in other components. Only the relative difference in the ratio of the heavy isotopes to the more abundant light isotope of the sample with respect to a reference is determined. The difference is designated by a Greek letter δ and is defined as follows:

$$\delta = (R_{\text{sample}} - R_{\text{reference}}) / R_{\text{reference}}$$

Where R's are the ratios of the $^{18}\text{O}/^{16}\text{O}$ and D/H isotopes in case of water.

The difference between samples and references are usually quite small, δ values are therefore, expressed in per mille differences (‰) i.e. per thousand, δ (‰) = $\delta \times 1000$.

$$\delta$$
 (‰) = $[(R_s - R_r) / R_r] \times 10^3 = [(R_s / R_r) - 1] \times 10^3$

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 Oceanic Water) and VSMOW (Vienna Standard Mean Ocean Water)

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

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

Craig evaluated the isotopic ratios of SMOW as;

$$^{18}\text{O}/^{16}\text{O} = (1993.4 \pm 2.5) \times 10^{-6} \text{ and } \text{D}/\text{H} = (158 \pm 2) \times 10^{-6}$$

VSMOW has the same ^{18}O content as defined in SMOW but its D-content is 0.2 ‰ lower.

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 SLAP (Standard light antarctic precipitation), NBS-1 and NBS-1A (National Bureau of Standard) and GISP (Greenland ice sheet precipitation).

Global Meteoric Water Line:

The relation between δD and $\delta^{18}\text{O}$ can be written in a standard form (equation for straight line) i.e.;

$$\delta\text{D}\text{‰} = A \delta^{18}\text{O} + d$$

Where A is the slope and d is the intercept of $\delta D - \delta^{18}O$ line of fresh global meteoric waters.

One can develop regional and local meteoric water lines on the pattern of standard relationship between δD and $\delta^{18}O$ valid on regional or local levels.

- For northern hemisphere: $\delta D = 8\delta^{18}O + 10$
- For southern hemisphere: $\delta D = 8\delta^{18}O + 22$
- New relationship, Rozonski (1993): $\delta D = 8.13\delta^{18}O + 10.8$

δD and $\delta^{18}O$ in water vapours at low altitudes in the atmosphere differs considerably than the isotopic composition in clouds or precipitation

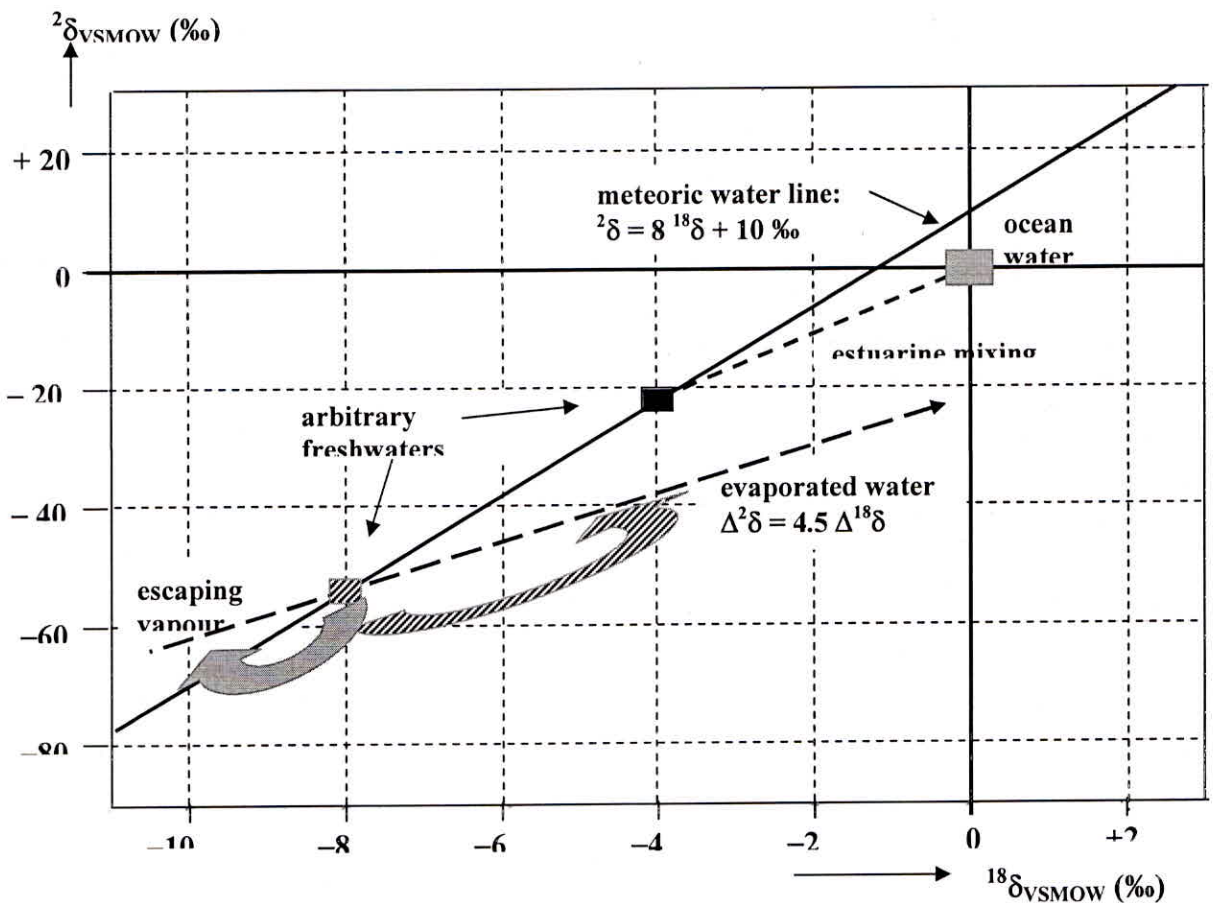


Fig. 2.3: Relation between $^{18}\delta$ and $^{2}\delta$ for estuarine mixing and for evaporating surface water. Because the evaporation is a non-equilibrium process, isotope fractionations involved are not necessarily related by a factor of 8, as is the equilibrium condensation process.

Isotope Effects

Variation of isotopic composition in atmosphere is also governed by various factors like, latitude, altitude, distance from sea, amount of rain, etc. These are called as isotope effects and described below.

Latitude Effect:

Relations established by Daansgard in 1964 and later by Yurtsever and Gat (1981) using annual average and monthly average temperatures:

$$\delta^{18}\text{O} = 0.695 T_{\text{annual}} - 13.6^{\text{TM}} \text{ SMOW} ; \delta\text{D} = 5.6 T_{\text{annual}} - 100^{\text{TM}} \text{ SMOW}$$

$$\delta^{18}\text{O} = (0.338 \pm 0.028) T_{\text{monthly}} - 11.99^{\text{TM}} \text{ VSMOW}$$

On average there is a 1TM decrease in average $\delta^{18}\text{O}$ corresponding to the average annual temperature. As latitude increases, the temperature decreases, therefore isotopic composition depleted in precipitation. Polar Regions are located at the highest latitudes and also at the end of Rayleigh rainout process, thus precipitation has maximum depleted values in heavier isotopic composition

Thus, water vapours or precipitation depletes in heavier isotopes with the increase in latitude. In low latitudes water vapours depletes very less in heavier isotope species of water molecule. $\delta^{18}\text{O}$ varies 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.

Continental Effect:

Precipitation depletes in heavier isotopes of water molecules as clouds move away from the coastal parts.

On average, $\delta^{18}\text{O}$ depletes about -2 ‰ per 1000km from seacoast.

Global T- $\delta^{18}\text{O}$ relationship - $\delta^{18}\text{O} = 0.695T_{\text{annual}} - 13.6 \text{ ‰ SMOW}$ changes significantly due to continental effect.

Altitude or Elevation effect:

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, $\delta^{18}\text{O}$ varies between -0.15 to 0.5 ‰ per 100m rise in altitude δD depleted 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:

Variation of δD and $\delta^{18}O$ due to change in season is called seasonal effects. Mainly two factors are responsible for the seasonal effects

- (i) Variation in temperature with respect to seasons and
- (ii) Change in amount of precipitation.

Evaporation and evapotranspiration increases with increase in temperature. Local or regional water vapours mixes with the water vapours originated from the sea and enriches the precipitation in ^{18}O and D. Increase in temperature increases the effect of evaporation in the falling raindrops and enriches the precipitation in D and ^{18}O . This effect is least when precipitation occurs in large amount or with high intensity.

Radioisotopes:

In early days, the use of radioisotopes was in vogue. Mostly, the radioisotopes, artificially produced in reactor/laboratory, were used as tracers. The radioisotope of hydrogen (tritium) in the form of water molecule (3H_2O) and denoted by symbol 3H or T is still widely used for various hydrological studies. There are other variety of artificially produced radioisotopes like ^{60}Co , ^{82}Br , ^{131}I , ^{137}Cs , ^{198}Au , ^{226}Ra / ^{241}Am etc. that are used for various hydrological investigations.

However, with the introduction of sophisticated instrumentation, the radioisotopes that occur in traces in the environment and past and parcel of hydrological cycle are used. This has reduced the use of artificial radioisotopes tremendously which may have an unwanted impact of health hazards in the mind of users as well as in the public. The most widely used radioisotopes are given in Table -2.2 with their half life, decay mode, principal sources and commonly measured phases while other categories of radioisotopes are shown in tables 4 & 5.

Radioactivity

The phenomenon of disintegration of unstable atoms to the stable form is called radioactivity. The unit of radioactivity is denoted by Curie (Ci) and one Curie is equal to 3.7×10^{10} disintegrations per second. In case of very low activity, it is also denoted by Becquerel (Bq) and one Becquerel is equal to one disintegration per second (1 dps). The activity per unit gram is known as specific activity and it is denoted by Curies/milli Curies/micro Curies per gram. The energy of disintegration or radiation is denoted by KeV or MeV.

Table-2.2: Details of various radioisotopes with their half lives, decay mode, principal sources and commonly measured phase.

Isotope	Half-life (years)	Decay mode	Principal Sources	Commonly measured phases
^3H	12.43	β^-	Cosmogenic, weapons testing	H_2O , CH_2O
^{14}C	5730	β^-	Cosmogenic, weapons testing,	DIC, DOC, CO_2 , C_aCO_3 CH_2O
^{36}Cl	301,000	β^-	Cosmogenic and subsurface	Cl^- , surface Cl-salts
^{39}Ar	269	β^-	Cosmogenic and subsurface	Ar
^{85}Kr	10.72	β^-	Nuclear fuel processing	Kr
^{81}Kr	2,10,000	ec	Cosmogenic and subsurface	Kr
^{129}I	1.6×10^7	β^-	Cosmogenic, subsurface, nuclear reactors	I and I in organics
^{222}Rn	3.8 days	α	Daughter of ^{226}Rn in ^{238}U decay series	Rn gas
^{226}Ra	1600	α	Daughter of ^{230}Th in ^{238}U decay series	Ra^{2+} , carbonate, clays
^{230}Th	75,400	α	Daughter of ^{234}U in ^{238}U decay series	Carbonate, organics
^{234}U	2,46,000	α	Daughter of ^{234}Pa in ^{238}U decay series	UO_2^{2+} , carbonate, organics
^{238}U	4.47×10^9	α	Primordial	UO_2^{2+} , carbonate, organics

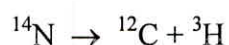
β^- - beta emission.; α - alpha emission.; ec - electron capture.

Half Life

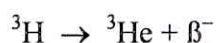
The time in which the radioactive element decays to one half (1/2) of its initial strength is known as half life. Different radioisotopes have different half lives and the decay rate is a characteristic property of an atom.

Radioactive Isotope of Hydrogen

Radioactive isotope of hydrogen, ^3H (tritium or T), originates (as does ^{14}C) from a nuclear reaction between atmospheric nitrogen and thermal neutrons (Libby, 1946):



^3H enters the hydrologic cycle after oxidation to $^1\text{H}^3\text{HO}$ and finally decays according to:



with $E_{\beta\max} = 18 \text{ keV}$ and a half-life of 12.430 years (Unterweger et al., 1980).

According to a recent re-evaluation, a more preferable value is 4500 ± 8 days (equivalent to 12.32 year).

Under undisturbed natural conditions the ^3H concentration in precipitation was probably about 5 TU, which is equivalent to a specific activity of about 0.6 Bq/L (Roether, 1967).

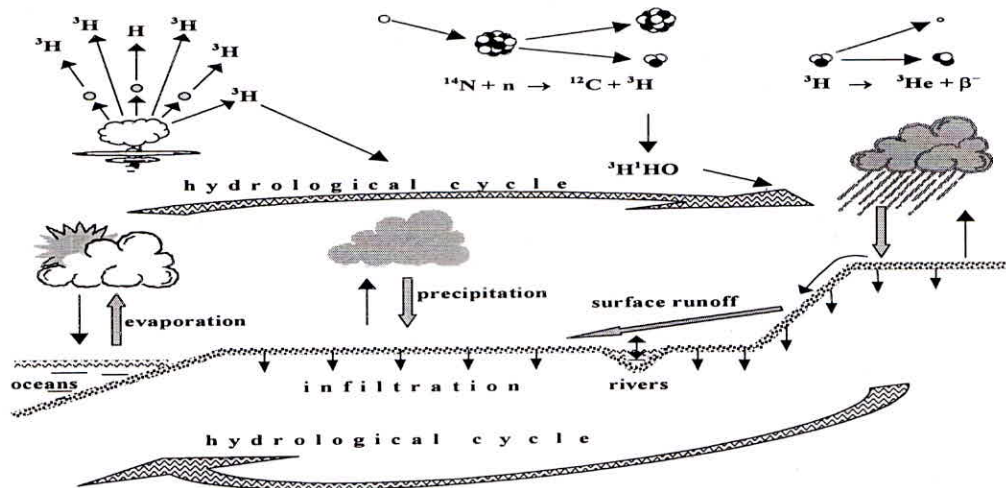


Fig.-2.4. Origin and distribution of ^3H in nature. Contrary to ^{14}C , the turnover of ^3H is very fast, except where it is fixed in glacier ice or groundwater.

However, as tritium is also produced in the atmosphere due to testing of atomic devices similar to cosmogenic tritium. Its present environmental concentration is normally considered 10 TU, but it may be different depending upon the local conditions. It is also produced artificially under controlled conditions in laboratory/ reactor. The variation of environmental tritium in the northern hemisphere is shown in the figure given below.

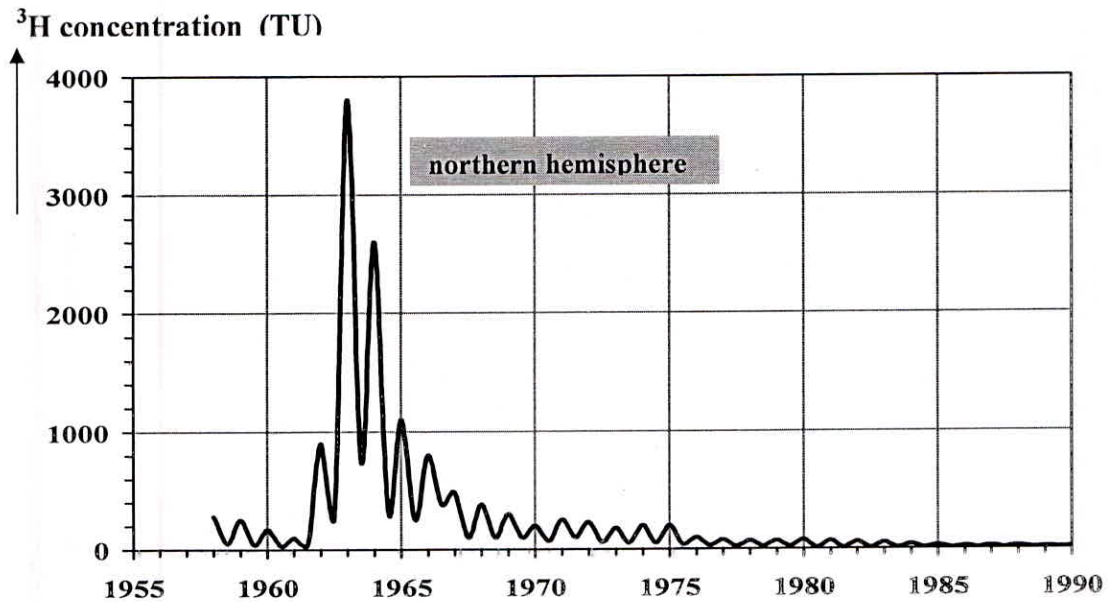
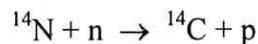


Fig-2.5. Smoothed curve representing the average ³H content of precipitation over the continental surface of the Northern hemisphere.

Radioactive Isotope of Carbon

Carbon-14 is produced in the atmosphere primarily due to interaction of cosmic rays with nitrogen gas molecule. It is also produced due to various anthropogenic activities like burning of fossil fuel etc..



Thermal neutrons required are produced by reactions between very high-energy primary cosmic ray protons and molecules of the atmosphere. ¹⁴C thus formed very soon oxidises to ¹⁴CO, and ultimately to ¹⁴CO₂ which mixes with the inactive atmospheric CO₂ and becomes part of the atmospheric CO₂ reservoir. Like tritium, carbon-14 has also been added to the atmosphere since 1952 as a result of testing thermonuclear devices. The ¹⁴C concentration before the thermonuclear tests was about 100% modern carbon (pmc). This corresponds to 13.56 dpm/g of carbon. The thermonuclear tests increased the atmospheric ¹⁴C concentrations in the northern hemisphere from 100 pmc to nearly twice that value. The atmospheric ¹⁴C peaked in 1963 and decreased subsequently due to moratorium of tests. ¹⁴C decays according to: ¹⁴C → ¹⁴N + β⁻ with a maximum β⁻ energy of 156 keV and a half-life of 5730 ± 40 years (Godwin, 1962).

Originally the half-life was thought to be 5568 years correct. But, because of the natural variations in the ¹⁴C content of atmospheric CO₂ during geologic times and deviating from the present, the errors were found even larger. Nowadays, the ¹⁴C calibration, based on the known ¹⁴C content of tree rings with exactly known age, removes both errors at once.

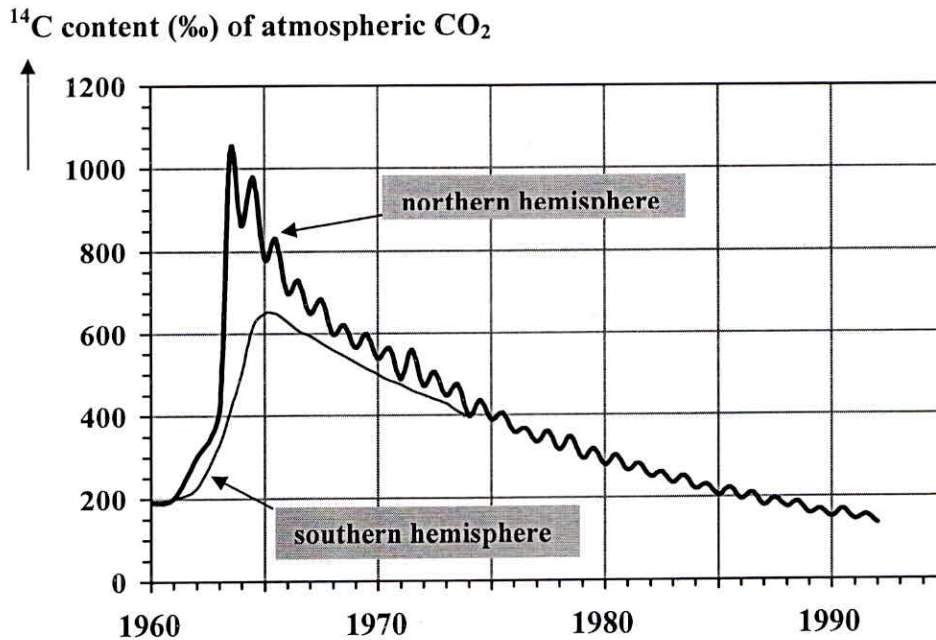
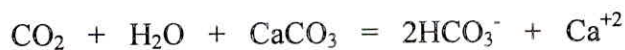


Fig.-2.6: Curve representing the natural ^{14}C northern hemisphere content of atmospheric CO_2 (data for Nordkapp, Norway, representative for the northern hemisphere).

Carbon-14 is not an isotopic tracer of water molecule and like ^{13}C occurs in water as various species of DIC. The non conservative nature of Carbon-14 as a tracer for water molecule demands the use of complete water chemistry as well as measurement of $\delta^{13}\text{C}$ of DIC for proper interpretation of ^{14}C data.

Atmospheric CO_2 exchanges with oceanic dissolved carbon (primarily bicarbonate) and most $^{14}\text{CO}_2$ molecules enter the oceans and living marine organisms. Some are also assimilated by land plants, so that all living organisms, vegetable as well as animal, contain ^{14}C in concentrations about equal to that of atmospheric CO_2 . The principal input of ^{14}C to the groundwater occurs in the unsaturated zone where the partial pressure of CO_2 , as a result of root respiration and decay of organic matter, is normally higher than CO_2 dissolved in precipitation. Commonly the CO_2 pressure in soil reaches or exceeds 10^{-2} atmosphere. The biogenic CO_2 or soil CO_2 then gives the dissolved carbon according to several processes depending on the geological conditions encountered as depicted below. For example reaction of carbonic acid with solid carbonate



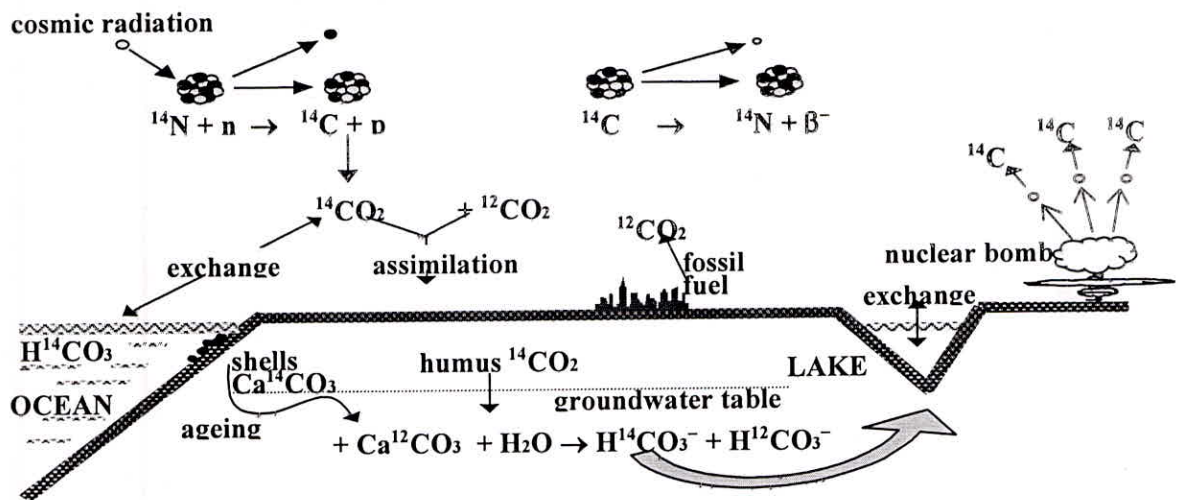


Fig.-2.7 Origin and distribution of ^{14}C in nature

These processes produce large amount of HCO_3^- (or CO_3^{2-} depending on the pH). In the above reaction the dissolved carbon comes from both biogenic as well as solid carbonate. Hence the carbon-14 activity of biogenic CO_2 will be diluted by carbon coming from leaching of carbonate which could be very old and hence carbon-14 free. This leads to dilution of the initial carbon-14 content. The use of ^{14}C as a dating tool of groundwater has been proved very useful in understanding the aquifer dynamics and age of available groundwater.

2.3 Environmental Isotopes

Environmental isotopes, both stable and radioactive (unstable), occur in the Earth's environment in varying concentrations with respect to location and time over which the investigator has no direct control. Environmental isotopes are neither required to be purchased nor to be injected as these are freely available and automatically injected in the hydrological cycle. Earlier only artificially produced radioactive isotopes were used but with the better instrumentation facilities, now a days environmental isotopes are used more and more except in few cases where artificial radioisotopes can only be useful. The most commonly used environmental stable isotopes are Deuterium (D), Oxygen-18 (^{18}O), Carbon-13 (^{13}C) and radioisotopes Tritium (^3H) and Carbon-14 (^{14}C), Nitrogen-15 (^{15}N), Chlorine-36 etc. Silicon-32 (^{32}Si), Caesium-137 (^{137}Cs) and Lead-210 (^{210}Pb) etc. are also used as environmental radioisotopes for few specific studies in Hydrology. Silicon-32 (^{32}Si) is potentially attractive because, its half life (100 yr) is between that of ^3H and ^{14}C . A number of measurements have been made in India but, it has not been used widely. Argon-39 (^{39}Ar) has also been investigated and research is still in progress, but the disadvantage of using both ^{32}Si and ^{39}Ar is that large amount of water (a few tons) is required to provide required amount of sample for measurement.

3. Estimation of Natural Groundwater Recharge

Groundwater recharge can be determined from water balance computations, from pumping over very long periods, from mass balance of different artificial or environmental tracers, or from hydraulic interpretations of the soil moisture movement below the active roots in the unsaturated zone. The hydraulically based methods, though highly developed in theory and practice, are hampered by the complex relationship between hydraulic conductivity and hydraulic gradient in the unsaturated zone. Tracer techniques have the advantage that old soil water can be differentiated from relatively fresh water. A rather new way of estimating groundwater recharge is to use isotopes as tracers. The methodology of using artificial as well as environmental isotope tracers for estimating percolation rate and groundwater recharge is discussed here.

Mostly water table fluctuation approach is used to evaluate recharge to groundwater. But as the water table fluctuation may occur due to many processes like, vertically downward percolation of precipitation water, irrigation return flow, percolation/seepage from surface water bodies/ pondings, draft of groundwater for irrigation, drinking, industrial and similar other purposes, flow of groundwater to river or vice-versa, leakage from shallow aquifers to deeper aquifers etc therefore, the water table fluctuation approach may lead to wrong predictions, if the information about the effect of individual parameter is not known. In such conditions, isotopes can be used to estimate the vertically downward component of recharge to groundwater without being influenced by any of the above said process.

Artificial Radioactive Isotope Tracers for Estimating Groundwater Recharge

Radioactive isotopes that are produced artificially either in laboratory or in a reactor are known as artificial radioactive isotopes. These artificial radioactive isotopes can be used as water tracers. The artificial tracers have the advantage over environmental tracers that they are injected in a controlled way and that the concentrations are high enough to be easily detected. The disadvantage is that it is non-natural, which mean environmental hazard and that experiments can only be made at specific points and at specific times. The choice of artificial tracer should take into account that the tracer travels with the water and does not adsorb to the soil particles; in-situ detection is preferable and the tracer should be least toxic. Artificial tracer isotopes, which have been found useful as tracers in groundwater studies in a broad perspective include ^3H , ^{24}Na , ^{32}P , ^{36}Cl , ^{51}Cr , ^{60}Co , ^{82}Br , ^{86}Rb , ^{106}Ru , ^{131}I and ^{198}Au . The most commonly used artificial tracer isotope for groundwater studies is tritium (^3H) as HTO, which is applied below the root zone or in the groundwater depending on the purpose of the study. It was found by, for example Blume et al (1967) and Zimmermann et al (1967b) that the tracer should not be introduced at the surface because of the tracer losses by evapotranspiration. Among other radio isotopes that have been tried, ^{60}Co as $\text{K}_3\text{Co}(\text{CN})_6$ should be mentioned. Nair et al (1979) found no significant differences in the behaviour of the mentioned ^{60}Co complex and tritiated water in terms of retardation due to adsorption or molecular exchange with the interstitial water in the soil profile. However, ^{60}Co -EDTA (Ethylene Diamine Tetra Acetic Acid) complex was strongly retarded in comparison with the cyanide complex. On the other hand, Knutsson and Forsberg (1967) reported ^{51}Cr -EDTA to behave as an ideal tracer in soils free from montmorillonite. Still, the method of gamma-emitting tracers has to show its versatility in different geological settings.

Therefore, ^3H as HTO is the only artificial tracer whose applicability is treated in more detail in this chapter.

Tritium Tagging Technique

Moisture Movement and Tracer Displacement

Soil water moves along a range of different pathways. Local field heterogeneity should bring about a considerable dispersion of pollutants or of a tracer. However, field experiments of Zimmermann et al. (1967a and 1967b) and Blume et al. (1967), showed "piston flow" type behaviour of soil moisture in nearly homogeneous soils; infiltrating water simply pushes the old water downward. This means that the soil moisture profile may change shape, but no newly percolated water bypasses water that has previously percolated below the root zone. In the above-mentioned experiments, the broadening of the peak of the injected tracer was of the same magnitude as expected by molecular diffusion only. Also, experiments conducted in the alluvial tracers of north India by Bahadur et al. (1977) showed broadening of the tracer peak comparable to the spread by molecular diffusion. It seems that if the flow is slow, the lateral mixing, mostly from molecular diffusion, in rather homogeneous soils between moisture packets having different flow velocities is quite effective, thus indirectly counteracting vertical dispersion.

In this context, it is necessary to distinguish between particle velocity, soil moisture flux, recharge rate and propagation rate of a disturbance. Particle velocity is the velocity of individual water molecules. The velocity depends on soil characteristics and moisture conditions. Typically the velocity is low, one to a few metres per year. In heterogeneous soils particle velocities vary within a large range. Soil moisture flux or percolation rate is related to a fixed point at a fixed time. It is the "unsaturated Darcian velocity". A typical flux value is half a metre per year or less. Below the root zone, capillary tension gradients play only a minor role. The moisture content is at or above field capacity. The soil moisture flux corresponds to the unsaturated hydraulic conductivity. Increased flux at the lower root zone is not immediately recognised as groundwater recharge. The increased flux propagates down-wards with a propagation rate that depends on the moisture conditions in the soil profile. A typical propagation rate is a few metres per month, but it may be lower as well as higher. If the soil is initially dry the propagation rate is close to the particle velocity value, but if the initial soil moisture conditions correspond closely to the flux at root zone level, the propagation rate is fast giving a fast groundwater response to infiltration.

In the course of water infiltration, an injected or environmental tracer is carried along with the soil water. The position of the peak tracer concentration can be monitored in the soil profile; from the temporal displacement of the tracer a percolation rate or a moisture flux, and for certain conditions the groundwater recharge, can be estimated provided the measurements are taken below the root zone so that all water movements are directed downwards. Zimmermann and co-workers used deuterium and tritium. They called the method of tracing the peak tracer tagging technique. The principle of how percolation rates are determined from tracer monitoring is illustrated in Fig.1. Shortly

after the tracer injection, the peak concentration is at depth z_1 and after a certain time it is found at depth z_2 . Provided no vertical mixing takes place during the downward movement, the mean moisture flux, q at the lower depth z_2 over the time period, Δt , between the two observations is,

$$q = \theta_v (z_2 - z_1) / \Delta t$$

Where, θ_v is the average volumetric moisture content between the two depths at the time of the first observation after reduction of eventual residual moisture content, i.e. interstitial water or water that adheres to the soil particles. This residual moisture content is generally believed to be negligible, except may be for very fine soils.

If the time period is a full season or full year, the moisture flux corresponds to the recharge over a season or year, although the particular soil water particles do not reach the groundwater during the particular year when the observations were made. A different technique for evaluating annual recharge when using stable environmental isotopes is to measure the soil moisture between two levels at which the soil water can be identified to originate from two events, preferably snowmelt, one year apart in time.

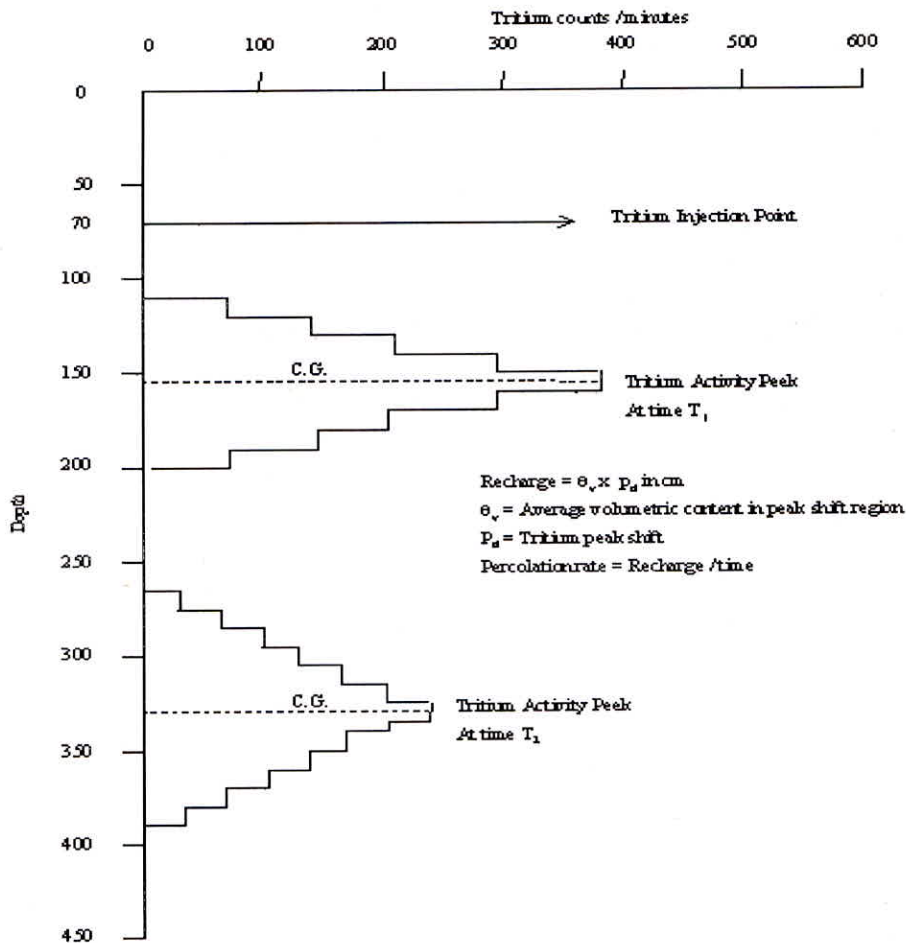


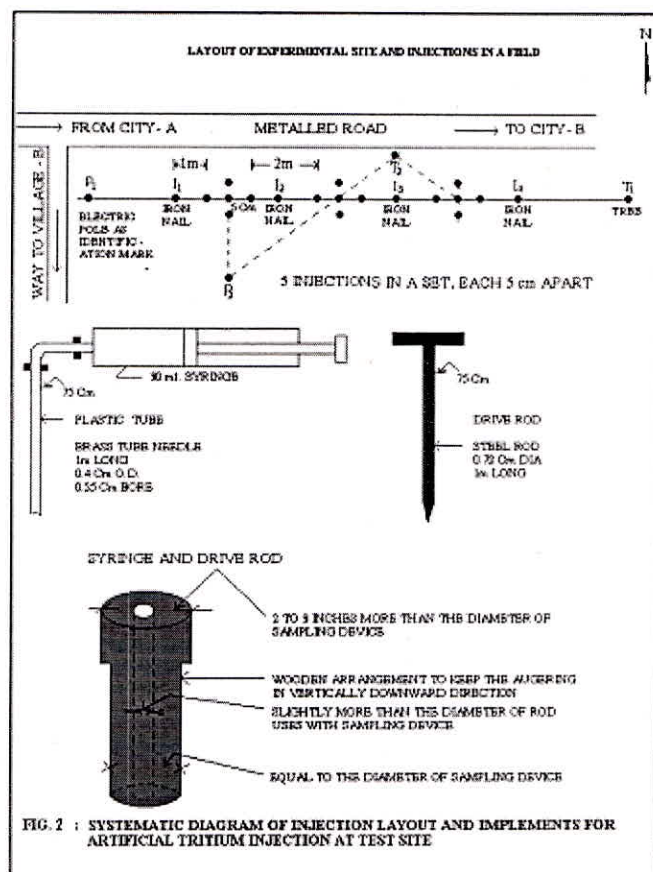
Figure 1 Shifting of injected tritium with respect to the movement of infiltrated water

Methodology

Tritium is a radioactive isotope of hydrogen having half-life 12.32 years. Being a part of water molecule, tritium is commonly used as an artificial tracer for hydrological studies. Although, the analysis of tritium activity requires some costly laboratory facilities but, keeping in view the low health hazard possibilities and accuracy in water tracing studies, its use is increasing in developing countries.

Tritium tagging technique was developed by Zimmermann et al (1967a,b), Blume et al (1967) and Munnich (1968a,b) with 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. Although, it can be well understood that in case of unsaturated flow where air and water are found, which have entirely different properties, the movement of soil moisture can not be a piston type flow. Therefore, a number of questions have been raised by the various researchers (Datta *et al.*,1990; Mookerjee, 1990; Singh and Kumar, 1993) on the assumption of piston flow movement and some evidences have been reported where the soil moisture flow does not follow the piston type movement. At the same time, it has also been mentioned that the results of recharge to groundwater determined using tritium tagging technique are comparable to those determined using gravimetric soil-moisture method. Therefore, there is no doubt about the validity and results obtained by using this technique.

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 tritium injection site is left open for agricultural and other activities including natural variations. 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 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. It has been noticed that the tritium peak obtained after the chosen period broadens due to diffusion, streamline dispersion and input water irregularities (Fig. 1). Therefore, the center of gravity of the broad tritium peak is considered to calculate the recharge to groundwater (Zimmermann *et al.*, 1967b). The recharge to groundwater is calculated by multiplying the tritium peak shift with the average volumetric moisture content obtained in the tritium peak shift region. The layout of the tritium injections is shown in Fig.- 2.



Zimmermann et al (1967a, b) and Blume et al (1967) found the downward moisture displacement for central European soils and climates, to occur at a rate of about 1 m/y, and the groundwater recharge to be about 200 mm/y. They considered the error in the recharge estimate to be less than 10%. Similar studies were carried out in India in the alluvial deposits of the Indo-Gangetic plain by Datta et al (1973), by Bahadur et al (1977) in the semi-arid regions around New Delhi and Athawale et al (1980) in the Maner basin. These studies showed the applicability of tritium when the surface inputs come in heavy impulses, i.e., the monsoons. According to Datta et al, the annual recharge for the area around Delhi region for 1971-72 was about 215 mm, which,

however, is far from the estimated 33 mm/y by Eridsson (1976) based on chloride concentration in groundwater in Delhi. The poor agreement between the two different methods refutes, at least when monsoon rains are present, that recharge can be estimated with an accuracy of 10%. Bahadur et al (1977) studied only the seasonal recharge due to the monsoon, but their data when extrapolated to yield annual recharge gave a value ranging from roughly 15 to 25 mm/y for 1973-1975.

The method described, using tracer input impulses, requires that the tracer is not retarded on its downward movement, or that the physics of the retardation is known. It is generally accepted that tritium moves with the water, not being adsorbed and not being affected by any physical fractionation. In laboratory soil-column studies Knutsson and Forsberg (1967) found no significant adsorption or retardation of HTO in soils dominant in illite and kaolinite. However, tracer losses were found in bentonite and montmorillonite dominant soils.

Environmental Isotope Tracers for Estimating Groundwater Recharge

Isotopes found in the atmosphere are known as environmental isotopes. These may be radioactive as well as stable in nature and both types can be used as water tracers. An environmental tracer has the advantage over an artificial tracer as it does not need to be injected and it is already a part of the environment. Environmental tracers can be used over large areas, but the concentrations are low and difficult to detect. Environmental

isotope techniques are based on isotopic variations in time and space in natural water systems. These variations can be observed to gain information about the origin of water and about mixing conditions. The most commonly used environmental isotopic tracers in groundwater investigations are the radioactive carbon-14 and tritium, and the stable ones deuterium and oxygen-18. Carbon-14 is used for determining the age of very old groundwater.

Environmental Tritium Technique

The radioactive isotope of hydrogen, i.e. tritium, released from thermonuclear explosions in the atmosphere made possible a way of estimating groundwater recharge. The cosmogenically produced tritium is found entirely in atmospheric vapour and is brought down to earth's surface by precipitation. Before 1952, the tritium concentration in precipitation was low. When thermonuclear tests in the atmosphere began in 1952, tritium concentrations in precipitation suddenly increased and reached a record-high concentration in 1963-64 in the northern hemisphere. In India, the peak concentration of bomb derived tritium in 1963 was more than 1000 TU: in Sweden 2100 TU : (1 TU is equal to 1 atom of tritium in 10^{18} H atoms, or 0.12 Bq/l water). The fact that water originating from precipitation which has fallen before 1952 has lower tritium concentration than water contributed by more recent precipitation can be used when tracing groundwater.

Assuming that more recent infiltrating water pushes previously infiltrated water, the bomb tritium of the infiltrated precipitation of a particular year can be found in a soil profile. The tritium concentrations in the soil profile will be moderated due to dispersion and molecular diffusion. Among others, Munnich et al(1967), Sukhija and Shah (1976) in India, and Andersen and Sevel (1974) in Europe have used bomb-released tritium for the evaluation of groundwater recharge in Europe and India, respectively.

In this method, it is assumed that the amount of water from the soil surface to the soil depth, where the 1963-64 tritium peak is located, is the measure of recharge from that time until the time of investigation. In the other method, the tritium concentration of the water lost as evaporation of surface runoff as well as of the water percolating below the root zone is, at any time, assumed to equal the concentration of the precipitation. The accumulated percolation, R , which will contribute to groundwater recharge, is simply given by,

$$R = P (M_s / M_p)$$

Where, 'P' is accumulated rainfall since the beginning of the bomb tests, M_p is the total amount (per unit area) of tritium in the precipitation, and M_s is the amount of tritium found in the soil above the depth where the tritium concentration is at pre-1952 level. The method can be adjusted to be applied from the peak concentration time instead of from 1952, i. e., from 1964.

Stable Isotopes Technique

The stable isotopes oxygen-18 and deuterium in precipitation have long been known as potential tracers for natural waters yet they have been little exploited for measuring percolation. The flux of HDO and H₂¹⁸O from an open water body to the atmosphere is reduced relative to the flux of the lighter H₂¹⁶O because of the lower vapour pressure of the former species, which causes fractionation in evaporation and condensation processes. In cold climates seasonal stable isotopic composition of precipitation is rather well reflected in soil moisture. In semi-arids however, the isotope picture of soils is rather complex due to strong fractionation caused by high evaporation rates from the soil.

Soil water infiltrated during two periods with a time span of a year can be identified within a soil profile on the basis of stable isotopic composition of either deuterium (²H or D) or oxygen-18 (Fig. 3). Therefore, the total amount of percolated water during the year can be estimated simply by totalling the amount of soil water between the two depths where the soil water from the two periods is found. Reduction should be made for eventual residual water. Mathematically expressed, the annual percolation, R, which will later contribute to groundwater recharge, is

$$R = \int_{z_1}^{z_2} \theta_v dt$$

Where z_1 and z_2 are the identified depths and θ_v is the volumetric soil moisture content after reduction of eventual residual water. The method cannot be applied in areas where the groundwater level is shallow during some periods of the year.

The first attempt was made for estimating recharge to groundwater in sand dunes with depth fluctuations in deuterium in soil moisture profiles (Thoma et al, 1979). The seasonal variations of oxygen-18 in precipitation have been traced in the soil moisture and estimates of groundwater recharge and rates of moisture movement were estimated for Swedish glacio-fluvial deposits and moraine formations (Saxena, 1984). Now, this technique is used wherever the measurement of stable isotopes is possible.

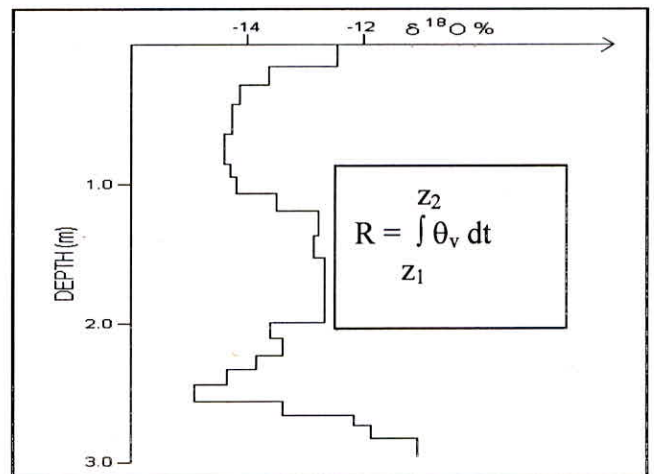


Figure 3: Oxygen-18 profiles in soil moisture patterns indicating of infiltrated water in different years

Application of any of the two methods is restricted to sites where the water of peak tritium concentration has not yet reached the groundwater table. In fact the environmental tritium method was relatively more useful only until mid 1970s. Most of the bomb tritium has by now mixed with the groundwaters and the soil profiles have more or less a constant concentration of tritium.

CASE STUDIES:

Recharge to Groundwater in Bundelkhand Region of U. P., India Using Tritium

Tagging Technique

The Bundelkhand region in India comprises 12 districts out of which 5 falls in Uttar Pradesh and 7 falls in Madhya Pradesh. The study area comprises of four districts, namely Jalaun, Banda, Hamirpur and Jhansi, covering an area of approximately 24079 km². Bundelkhand region of India falls in subtropical region characterized by hot and prolonged summer followed by rainy season and cold winter. The distribution of rainfall is not only erratic in the region but the same situation persists even in a small area, causing occasional drought conditions. District Jalaun, Banda and parts of Hamirpur (60%) and Jhansi (10%) are underlain by indo-gangetic marginal alluvium of quaternary age and comprise mainly sand of various grades, clay and clay mixed with kankar while the major parts of district Jhansi and about 40% area of district Hamirpur fall under rocky formation therefore, the surface soil is more compact in comparison to that in other two districts.

Bundelkhand region in India faces acute water deficiency due to higher losses of rain and surface waters. Although, the rainfall in this region is less in comparison to the surrounding region but it is much higher in comparison to the rainfall in semi arid regions. The groundwater reserves have been found very limited and groundwater level is also deep at number of places. Hence, it is treated as an undeclared semi-arid region in India. Keeping in view the prevailing conditions in Bundelkhand region, it is necessary to estimate the correct value of recharge to groundwater due to monsoon rains, which is the main source.

Tritium was injected at 25 sites before the start of monsoon rains. Soil samples were collected from the injected sites in the month of November and recharge percentages were determined. Since, sampling was carried out in November; the water input for the irrigation was also taken into account while determining the percentage of recharge. It is clear from the results obtained (Table- 3) that there is a wide variation in the values of recharge to groundwater. This variation may be due to different type of soil, topography, hydrogeology, groundwater level conditions, cropping pattern, rainfall pattern, evapotranspiration and several other local factors which are very difficult to account for. A sample plot of shifting of tritium activity and variation of soil moisture with depth are shown in Fig. 4.

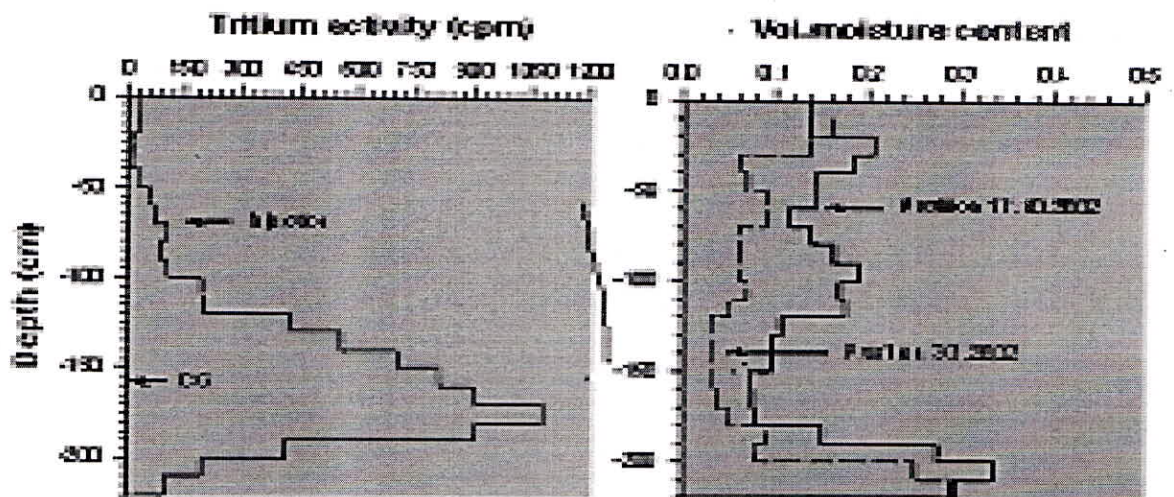


Fig.4. Tritium and soil moisture profiles

MATHEMATICAL APPROACH

Although large area can be covered at a time by using tritium tagging technique but, it is very difficult to carry out the field experiments every time for the evaluation of recharge to groundwater using this technique. Therefore, it is necessary to develop some mathematical formulation to calculate the recharge due to monsoon rains, if only the information on rainfall is available. But, it is also not advisable to develop an empirical relation using only one or more of those hydrological parameters, which act as constants but affect the rainfall- recharge process. The authors have given emphasis to study the recharge to groundwater due to monsoon rains as major recharge to groundwater takes place during this season, otherwise, the method suggested here can also be applied for estimating recharge to groundwater during other seasons.

Groundwater recharge by rainfall is very complex process influenced by numerous surface and sub surface parameters including rainfall intensity, its frequency and several other local factors (e.g. vegetation cover, soil properties, etc.). Therefore, it is advisable that once, the recharge to groundwater due to rains and/or irrigation is determined using tritium tagging technique, a partly suitable mathematical approach can be developed which will be accounting for all the known and unknown factors affecting the rainfall-recharge process. However, the authors are not of the opinion that one should only follow this procedure, therefore, if the correct information of all the processes and parameters which affect the rainfall- recharge process are possible to obtain, a suitable mathematical model can be developed.

Table 3: Rainfall + Irrigation and estimated recharge at different stations in the Bundelkhand region, U.P., India for the period from June, 1980 to November, 1980

Co de	Station	Distri ct	Rain fall + Irrigati on (cm)	Estim ated Recha rge (cm)	Co de	Station	District	Rain fall + Irrigati on (cm)	Estim ated Recha rge (cm)
1B	Bania Ka Purwa	Band a	72.16	13.12	2J A	Kadaura	Jalaun	164.70	17.86
2B	Murwal	Band a	64.38	11.25	4J A	Jalaun	Jalaun	106.20	13.00
3B	Padmai	Band a	79.76	14.64	5J A	Rampur a	Jalaun	134.30	34.00
4B	Tara	Band a	81.99	12.81	6J A	Konch	Jalaun	103.70	10.19
5B	Mrigha ni	Band a	91.99	19.87	1H	Muskar a	Hamirp ur	81.21	21.95
1J	Khillar a	Jhans i	81.20	8.05	2H	Lalpura	Hamirp ur	95.18	22.04
2J	Siyoni Khurd	Jhans i	104.06	8.29	3H	Kuchch echa	Hamirp ur	95.18	22.78
3J	Khirak	Jhans i	79.32	23.48	4H	Rewai	Hamirp ur	111.77	11.60
4J	Khilli	Jhans i	88.05	16.15	5H	Engohta	Hamirp ur	71.90	6.09
5J	Baruw a Sagar	Jhans i	95.30	10.97	6H	Gatak Nahar	Hamirp ur	81.20	7.31
6J	Pandu wah	Jhans i	86.85	10.69	7H	Khanna	Hamirp ur	81.21	15.50
7J	Manip ur Moitra	Jhans i	99.40	6.35	8H	Bharwar a	Hamirp ur	76.21	18.98
8J	Mando ri	Jhans i	92.50	11.78					

The recharge values were analyzed with respect to clay percentage, clay/sand ratio, water table fluctuation and rainfall data. It has been observed that the recharge values follow a unique logarithmic relationship with rainfall, for similar site conditions, while different relation is observed for the other set of sites. The plots of recharge values obtained at 25 sites in four said districts are shown in Fig. 5. The following two mathematical formulations fairly satisfy the variation of recharge values.

$$\text{Group A} \quad R_g = 29.316 \ln(P) - 111.259 \quad (r = 0.83) \quad (1)$$

$$\text{Group B} \quad R_g = 12.861 \ln(P) - 48.757 \quad (r = 0.85) \quad (2)$$

Where,

R_g - is recharge to groundwater in cm.

P - is rainfall/precipitation in cm.

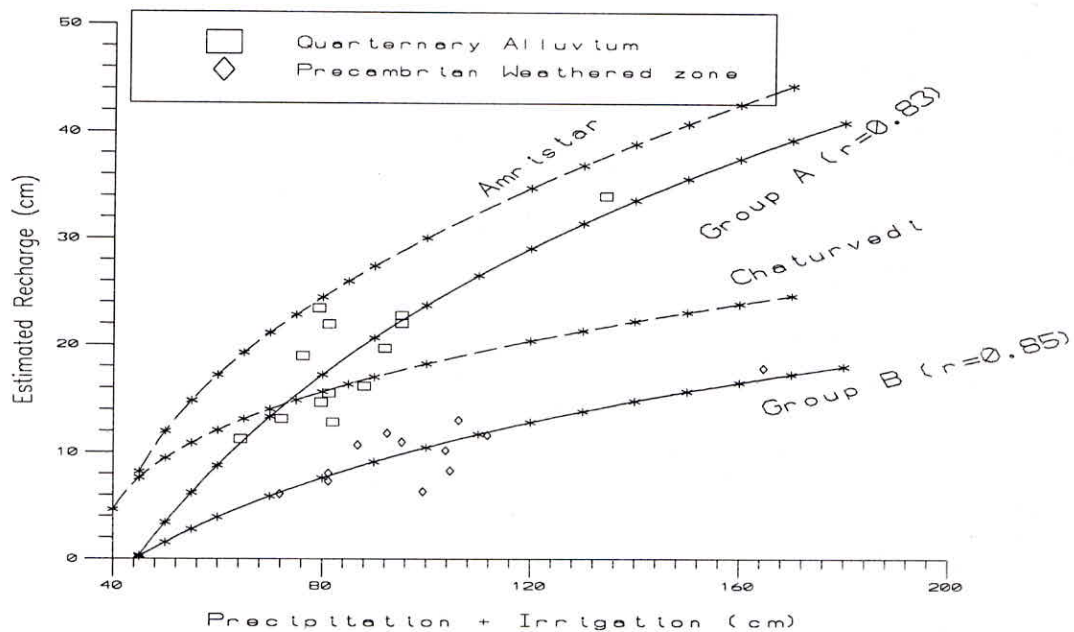


Figure 5- Correlation of estimated recharge (cm) with precipitation

It is interesting to note that when the two different trends of variation were correlated with hydrogeological conditions, it has been found that recharge values for the sites which fall in the marginal alluvium region follow equation (1) and those which fall in the hard rock region follow equation (2). The plots of recharge values, calculated using Chaturvedi (Chaturvedi, 1973) and Amritsar formulae (Sehgal, 1973) and shown in Fig. 5, clearly indicate that Amritsar formula gives consistently higher estimates while the Chaturvedi formula seems to be partly applicable.

In addition, the mathematical approach has also been applied for Sabarmati basin and Mahi Command Area in Gujarat State for which Bhandari *et al.* (1986) have studied recharge to groundwater using tritium tagging technique. These investigators have developed empirical relation using precipitation and in some cases type of soil approaches. The equations for three trends that hold good as per the experimental data for Sabarmati basin are as follows:

$$\text{Group A} \quad R_g = 20.469 \ln(P) - 60.568 \quad (r = 0.80) \quad (3)$$

$$\text{Group B} \quad R_g = 14.345 \ln(P) - 42.376 \quad (r = 0.94) \quad (4)$$

$$\text{Group C} \quad R_g = 15.681 \ln(P) - 58.174 \quad (r = 0.92) \quad (5)$$

The above two examples of Bundelkhand region and Sabarmati basin are indicative of the fact that, the net result is better if the area under question is subdivided

on the basis of observed variations in the precipitation - recharge plots and equations are developed, than to treat them as one single unit and try to relate the recharge with other factors with poor statistical parameters. These mathematical formulations can be used to determine recharge to groundwater with respect to precipitation and irrigation during monsoon seasons in future.

Discussion

From the results presented under the section 'mathematical approach' using tritium tagging technique, the following points emerged out.

- i) It is clearly seen from the plots of recharge to groundwater with respect to rainfall for Bundelkhand region of Uttar Pradesh State and Sabarmati basin and Mahi Command Area in Gujarat State, India that a single empirical relation may not hold good for the whole region. Therefore, in order to explain the wide variations in the experimental results, it is advisable to consider the area under study in small sub-regions on the basis of observed trends in plots. Subsequently it may be verified in the field for the influencing parameters viz. hydrogeology, physiography and other local factors.
- ii) The author is of the opinion that if reliable information on recharge to groundwater is required for any area, neither water table fluctuation approach nor empirical relation that has been developed for another area should be used. Instead tritium tagging technique which is simple and fairly accurate should be used to develop a separate empirical relation between rainfall and recharge for the area under question, to be used to estimate groundwater recharge in future.

b) Recharge to Groundwater in Uppsala, Sweden Using Oxygen-18

Percolation rates in an Esker (glacio-fluvial formation) in Uppsala, Sweden have been estimated using the environmental isotope oxygen-18. Winter precipitation being depleted in oxygen-18 differs from summer precipitation in their oxygen-18 contents. Thus, melt water is of relatively light isotopic composition. This oxygen-18 depleted water can be considered as a tracer of infiltrating melt water in the soil. After the melt period, water originating from rains of relatively high oxygen-18 content that eventually penetrates below the root zone "pushes" down the oxygen-18 depleted melt water, which in turn further pushes down the older moisture (having high oxygen-18 content) contributed by the previous year's summer and autumn rains. Ideally, the infiltration an esker in Uppsala, where the depth to the groundwater table is about 4m, infiltrated melt water from two consecutive melt periods was traced in the unsaturated zone providing estimates of annual recharge. The measured oxygen-18 profiles are shown in Fig3.

In Fig.3, the melt periods of 1981 and 1982 can be distinguished in the soil moisture profile observed in May 1982. The first oxygen-18 depleted layer (average depth 65 cm and the front at 115 cm) represents snowmelt 1982, and the second depleted layer (average depth 235 cm and the front at about 265 cm) is due to contribution from the 1981 melt period. The total water present in between these two oxygen-18 depleted layers is the water, which has percolated below the root zone during one year. Soil

moisture measurements showed the total soil water between the average depths of the two depleted layers to be 280 mm. This value agrees fairly well with the mean annual recharge arrived at by regional water balance studies (Eriksson, 1980).

The recharge estimates obtained from this method are not more accurate than other methods, but it is possible to tell from which rain or snowmelt event the fairly deep soil water originates, and thus during which periods infiltrated water percolates below the root zone. The measurements from Upsala Esker are used as an example. In Fig.3, melt water from the spring of 1982 is seen to be distributed from depth 15 to 115 cm. The average soil moisture content between these two depths is 0.18, giving a soil water contribution from 1982 snowmelt of 180mm. The melt water from the spring of 1981 is found between 200 and 265 cm, where the average soil moisture content is 0.17, and thus the amount of percolated 1981 melt water about 110 mm, whereas soil water between 115 and 200 cm amounting to about 120 mm is the contribution from percolation of rains.

For estimating the rate of moisture movement for relatively short periods, frequent sampling is required. Three oxygen-18 profiles observed during July, September and December 1982 are shown in Fig. 6. The infiltrated melt water from the spring was observed at the average depth 115 cm in July, in the September at 155cm and in the December at 170cm. Thus, the rate of displacement of this depleted layer was during July-September 6.5 mm/d and during September-December 1.9 mm/d. The average soil moisture content between 115 and 155 cm was 0.11 in July. The average soil moisture flux at 155cm during July-September is found to be 0.72 mm/d. Knowing the average moisture content between 155 and 170 cm in September, 0.22, the average soil moisture flux September-December at 170 cm can be estimated as 0.42 mm/d. The average soil moisture flux or percolation rate at 170cm can be found from the oxygen-18 profiles

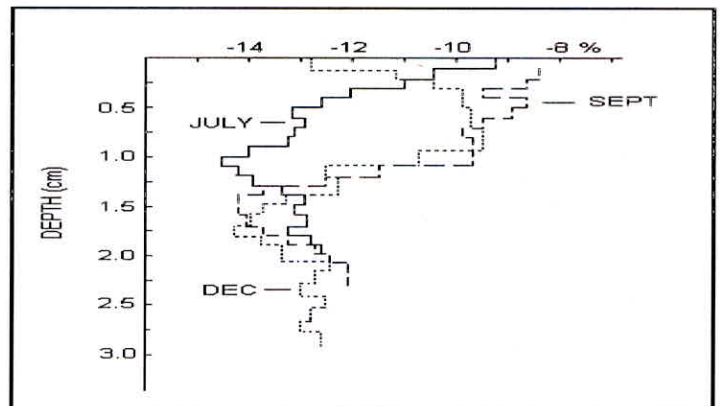


Figure-6: O-18 profiles observed during different months

for the full period i.e., July to September/ December. From the displacement rate 4.1 mm/d and the average soil moisture in July, 0.14, this percolation rate is 0.57 mm/d. Thus, the percolation rate during July-September must have been 0.77 mm/d, which is close to the percolation found at the depth of 155 cm for the same period. The computed percolation rates are summarized in Table 4.

Table 4: Percolation rates (mm/d) in Uppsala Esker, autumn 1982, estimated

from the measurement of O-18 concentrations and soil water content.

Level	July-Sept.	Sept-Dec	July-Dec.
155	0.72	-	-
170	0.77	0.42	0.57

Using the environmental tracer technique, the contribution to groundwater recharge from different seasons can be determined and the origin of recharging water can be found. The exact time when the groundwater is recharged cannot be determined. But particle velocities of individual water molecules can be determined. It is possible to estimate the time required for non-adhering conservative substances to reach the groundwater. The particle velocity below the root zone at the Uppsala Esker site as reported by Saxena (1984) varies only within a small range. The glacio-fluvial deposits are rather homogeneous. Newly percolated water does not bypass previously percolated water. The average velocity is 1.5-2 m/y, which means that it takes more than two years even for conservative non-adhering pollutants to travel with the percolating water from the ground surface to the groundwater table at about 4 m.

Recharge to Groundwater in Gujarat, India Using Environmental Tritium

The estimation of vertical component of recharge to groundwater by using environmental tritium differs in two ways from the injected tracer technique:

- i) Tritium input
- ii) Tritium measurement

As already stated that in case of environmental tritium, it is naturally injected in the soil system with precipitation while in case of injected tritium it is to be injected manually. As the activity of environmental tritium is not measurable using the system, which are used for injected tritium therefore, special equipment like, Ultra Low Level Liquid Scintillation Spectrometer is used to measure it.

In this technique, soil samples are collected from the site of interest and tritiated water is obtained by vacuum distillation. In certain cases, where the tritium activities are not measurable, the water samples are enriched in order to increase the tritium concentration. Environmental tritium activity is measured with the help of special equipment, as stated above, in the tritiated water using Ultra Low Level Liquid Scintillation Spectrometer. The tritium activity is plotted with respect to depth along with moisture content. The total tritium activity is determined from the plot using the following relation.

$$Ta = \Sigma \text{ Tritium concentration in TU} \times \text{Volumetric moisture content}$$

$$\text{Recharge to groundwater} = (Ta / Tp)$$

Where, Ta = Total tritium activity observed

Tp = total tritium input through precipitation

TU = tritium unit

$$1\text{ TU} = {}^3\text{H}/{}^1\text{H} = 10^{-18} \text{ (1 L of water with 1 TU activity emits 7.2 dpm or 0.12 Bq)}$$

Physical Research Laboratory (PRL), Ahmedabad has carried out the study of groundwater recharge using environmental tritium in different parts of Gujarat, India. Results of a study carried out by PRL, Ahmedabad at few sites are given in Table-5 while the plots of observed environmental tritium activity are shown in Fig. 6.

Table-5: Estimated values of groundwater recharge using environmental tritium

Sl. no	Name of site	Avr. P.P.(mm)	Avr.G.W. mm	Recharge % of Rainfall
1.	Varahi	450	13-18	2.9 - 4.0
2.	Sankeshwar	500	10-25	2.0 - 5.0
3.	Balol	600	25	4.2
4.	Taranga	530	50-60	9.4 - 11.3
5.	Ahmedabad	800	32-40	4.0 - 5.0

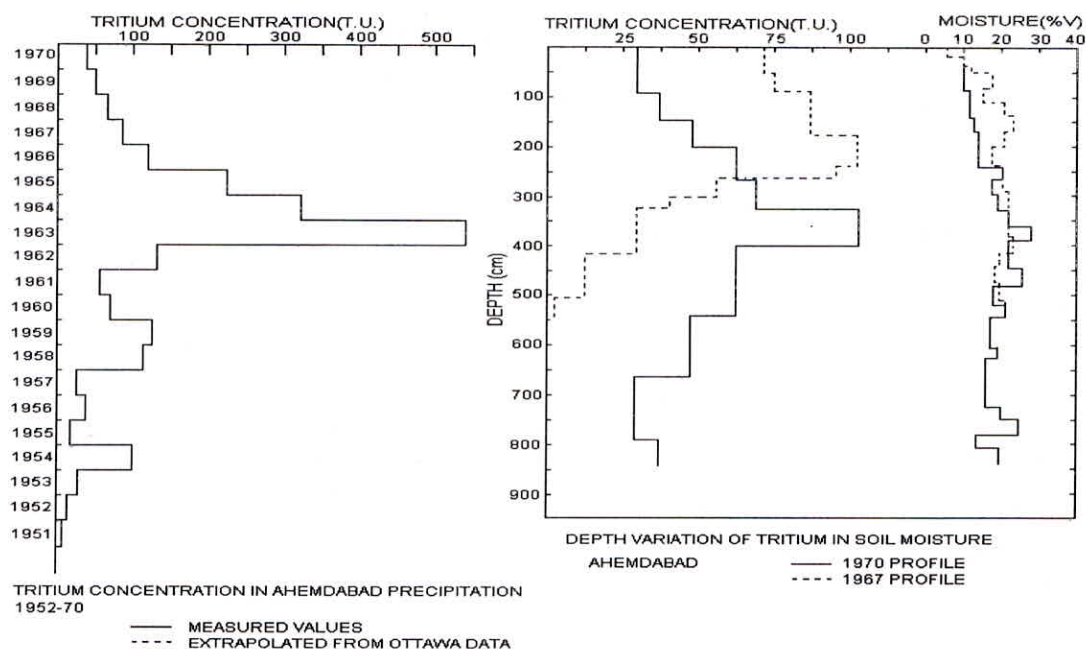


Figure 7: Environmental tritium and soil moisture profiles source (PRL 1986)

2. Origin of Groundwater

All groundwater of economic interest originates as precipitation. This means that the amount of recharge to a groundwater system related to its storage capacity determines the maximum available resources for exploitation. Under favourable conditions (that is, groundwater basins where the barrier boundaries and the inputs and outputs are well

defined) it is possible to construct a simple conceptual model of the system to obtain a water balance. Nevertheless, in many cases recharge and water flow are rather complex and more information of the actual process is desirable. Knowledge of the recharge process is also important for preventing deterioration of water quality by salinization and pollution. The environmental isotopic methods provide a valuable approach to understand these complex phenomena as well as to test the validity of the alternative hypothesis.

The application of the environmental isotope methods to understand the origin of groundwater w.r.t. its recharge is based on the spatial and temporal variability of the isotopic contents of water. The spatial variability can be grouped in four different topics

Altitude Effect

Groundwater recharge from high altitude either directly or by rivers draining high altitude catchment basins can be distinguished from recharge originating from low-altitude precipitation due to altitude effect in precipitation. This effect is most useful in regimes having orographic precipitation, where there is a regular relationship between land-surface altitude and condensation temperature of precipitation (isotopic composition of heavier isotopes depletes in precipitation with increasing altitude). When saturated air moves upward it cools, which causes condensation. Consequently heat is released which counteracts cooling. The resulting change in temperature with altitude is called adiabatic lapse rate. The wet adiabatic lapse rate varies with altitude, but a value of $0.6\text{ }^{\circ}\text{C} / 100\text{ m}$ is reasonable. For ^{18}O , the temperature dependence during wet adiabatic cooling is about $0.5\text{ }^{\circ}\text{‰} / ^{\circ}\text{C}$. The observed range of variation of $\delta^{18}\text{O}$ per 100 m is between -0.16 and $-0.7\text{ }^{\circ}\text{‰}$ with an average value of $-0.25\text{ }^{\circ}\text{‰}$ while for $\delta^2\text{D}$ per 100 m is between -1.0 and $-4.0\text{ }^{\circ}\text{‰}$ with an average value of $-2.0\text{ }^{\circ}\text{‰}$.

Latitude Effect

The stable isotope content of precipitation shows a marked dependence on latitude (depletes with increasing latitude) thus, groundwater replenished by rivers spanning significant latitude zones can be distinguished from local recharge.

Deuterium Excess

Another geographic effect on the stable isotope content that can be applied effectively is the shift in the D- ^{18}O relationship, relating to the source of atmospheric moisture. It has been noted that in the eastern Mediterranean and similar marine belts of rapid evaporation the resulting precipitation has a D - ^{18}O relation of $\delta\text{D} = 8\delta^{18}\text{O} + 22$, quite different from the general northern hemisphere precipitation in which $\delta\text{D} = 8\delta^{18}\text{O} + 10$. This difference can be used in the border areas of climatic zones, where precipitation on the coastal mountains can be of Mediterranean or oceanic origin.

Seasonal Recharge

In regions where temperature and precipitation are distinctly seasonal and groundwater flow occurs in crystalline or karstic rocks, the stable isotope content of groundwater may indicate the seasonal dependency of recharge and in some instances even the influence of specific large storm events. The stable isotope content can also be used to determine the ratio of seasonal recharge and base-flow of springs having such a composite discharge regime.

Dating of Groundwater

The dating of groundwater also helps in understanding the origin of groundwater i.e., of recent origin or old water. Many radioisotopes are produced in the environment by interaction of neutrons from cosmic rays with nitrogen. The nature of decay of these environmental radioisotopes can be used to detect the age of groundwater or other materials also. Radioisotopes mixed with water vapours in environment and enter into groundwater bodies with precipitation water.

Several groundwater dating techniques are available, but popularly, only two dating techniques are used for estimating age of groundwater.

- i) Tritium dating
- ii) Radiocarbon dating

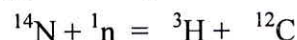
The details of groundwater dating techniques are beyond the scope of this lecture, however, a brief idea will be provided to the readers/participants in this regard.

Identifying Modern Recharge

Ground Water Dating With ^3H

Tritium is of special value in detecting recent recharge because of its short half-life of 12.32 years and because of high levels of tritium in the atmosphere since the beginning of atmospheric testing of thermonuclear devices in 1952.

- * Tritium is produced due to the interaction of the cosmic rays produced neutrons in the upper atmosphere with nitrogen atoms;



- * Man-made, principally from the detonation of thermonuclear devices;
- * Environmental concentrations of tritium in natural waters are denoted as an isotope ratio in terms of tritium unit (TU);
- * One TU has an isotopic ratio of $^3\text{H} / ^1\text{H} = 10^{-18}$
- * One litre of water with a concentration of 1 TU produces 7.2 dpm (0.12 Bq);
- * Direct age estimation using tritium is difficult due to variable input of tritium, since 1952;
- * Tritium concentration in environment is routinely measured (monthly averages) at various gauging stations fixed by IAEA/WMO since 1961;

- * Qualitative approach can be used to distinguish between old water (pre bomb) and waters containing at least a contribution of recent precipitation.

Tritium contents in the environment has reached to its normal value i.e., normally the natural level of tritium vary between 5 and 15 T.U. according to the geographical location of the area. The existence of tritium in a water sample is a definite proof of the presence of some components of modern recharge. Therefore, if tritium content is observed 10 T.U., the groundwater may be of recent origin and if we get 5 TU, then the groundwater may be 12.32 years old (uncorrected). One can measure age of groundwater up to 100 years using this technique.

In some systems, where the discharge represents a variable composite of current-year recharge and older water of low tritium content, it is possible to calculate the ratio of the two components on the basis of periodic tritium sampling.

Isotopic profiles in the unsaturated zone can help in the evaluation of the infiltrated water, although disturbances introduced in the profiles by exchange with the atmosphere need further investigation. The tritium vertical stratification study can be also extended to the saturated zone, but here disturbances introduced by the horizontal groundwater flow should be taken into account. Injection of artificial tritium or other radioisotopes should also be considered when the detection of environmental tritium peaks is difficult.

Identifying Paleowater

Paleowater is the old groundwater (> thousands of years old that does not has dynamic recharge system at present). Owing to cooler and more humid conditions during the Pleistocene glaciations, reservoirs replenished during pluvial episodes are characterised by low deuterium excess, accompanied by relatively depleted ^{18}O and D contents as compared to modern recharge. This has been found true for North Africa and Middle East arid zones. It has been shown that a D-excess of 10 ‰ (as most frequently observed in modern precipitation) is produced with 70 ‰ (as often observed in old groundwaters in Africa and parts of the Middle East) is produced with about 85% of relative atmospheric humidity. However, caution should be exercised in using stable isotopes in identifying paleowater. Care should also be taken in the discussion of ^{14}C data which has to support the hypothesis on the occurrence of paleowater.

4. Recharge Zones and Sources to Deeper Aquifers and Springs

Recharge Zones

Groundwater forms the most important resource of potable water as it is believed to be safe, free from pathogenic bacteria and from suspended matter. However, the deeper aquifers are becoming increasingly important with the increase in urban area and density of urbanization. The area of groundwater recharge varies inversely with the density of urbanization in urban areas. Thus the shallow aquifers are either drying -up or being contaminated in densely urbanized areas in the country. This leads to the more dependency on deeper aquifers which have not been given due importance so far from

investigation point of view. Our most of the observations and investigations are limited to the shallow aquifers. Thus, the deeper aquifers for which recharge zones are located in remote areas may be suffered adversely by the various anthropological activities that may either reduce the recharge area or contaminate the recharge source. It has increased the concern on groundwater resource mapping and its management that requires the identification of recharge-zones to deeper aquifers. In fact, the deeper aquifers not only cater the maximum need of fresh water at present but these will also be the potential source of fresh water in future when the shallow aquifers will either be dried up or contaminated in densely populated areas and metropolitan cities. Once the recharge zones are identified, these can be protected from the anthropogenic activities.

Environmental isotopes like ^3H (tritium-3), ^{14}C (carbon-14), ^2H (deuterium-D), and ^{18}O (oxygen-18) are used to identify the recharge zones and recharge sources to aquifers and springs. Geohydrological details like groundwater level conditions, geological cross sections etc., and water quality data like major and minor ion chemistry, physico-chemical parameters etc., are used as supporting tools. Groundwater samples are collected from different aquifers for the measurement of ^3H , ^{14}C , ^2H , and ^{18}O . The dating of groundwater using Tritium and Carbon-14 provide information of recharge zones, groundwater flow velocity and flow pattern while the D and O-18 (δD and $\delta^{18}\text{O}$) analysis help in understanding the contribution of different recharge sources and also to pinpoint the most important recharge source.

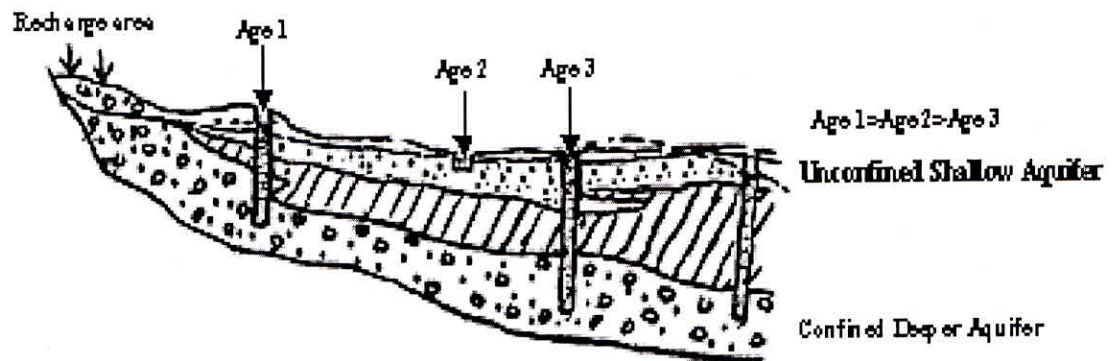


Fig. 8: Representation of recharge and discharge zones in confined aquifers

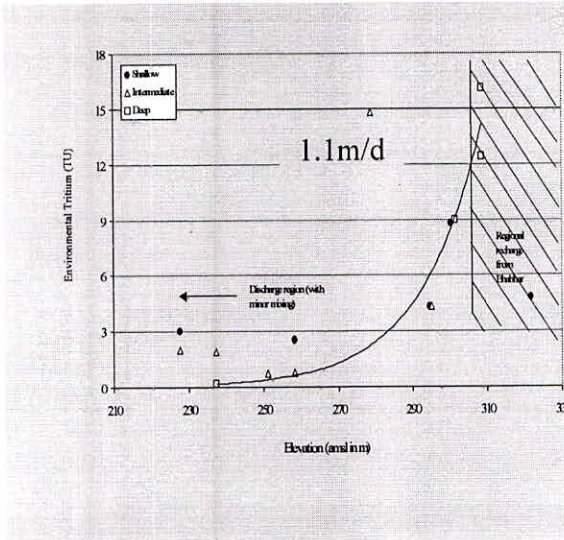


Fig. 9a: Variation of environmental tritium concentrations with elevation in Solani-Ganga Interfluvium

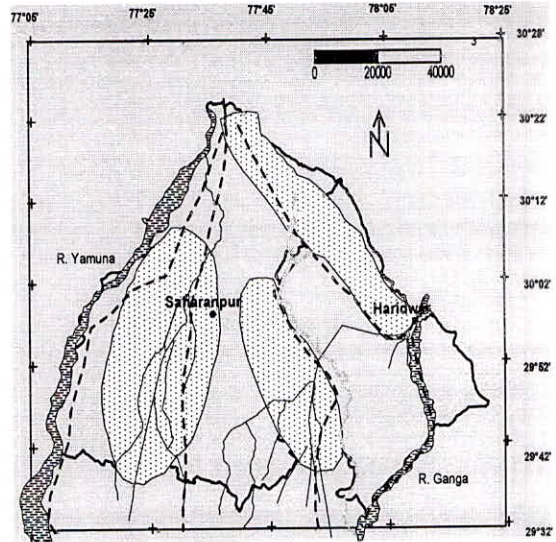


Fig. 9b: Map showing different recharge zones identified on the basis of environmental tritium concentrations.

Recharge Sources

Change in oxygen and hydrogen isotopes composition in precipitation with change in altitude (altitude effect) enables to determine the average elevation of recharge zone for a spring or aquifer. In regions where direct and rapid infiltration of rain occurs, the composition of the groundwater will have isotope ratio as that of the precipitation or slightly enriched due to evaporation effect during the process of infiltration as when evaporation precedes, the heavier isotope gets enriched in water phase. The analyses of stable isotopic composition together with that of dating using radioisotopes gives a reliable 'fingerprint' whereby to identify each group of water of different sources. Water infiltrated at higher altitude and is transmitted over long distances will show depleted $\delta^{18}O$ and low tritium compared to water infiltrated from local precipitation.

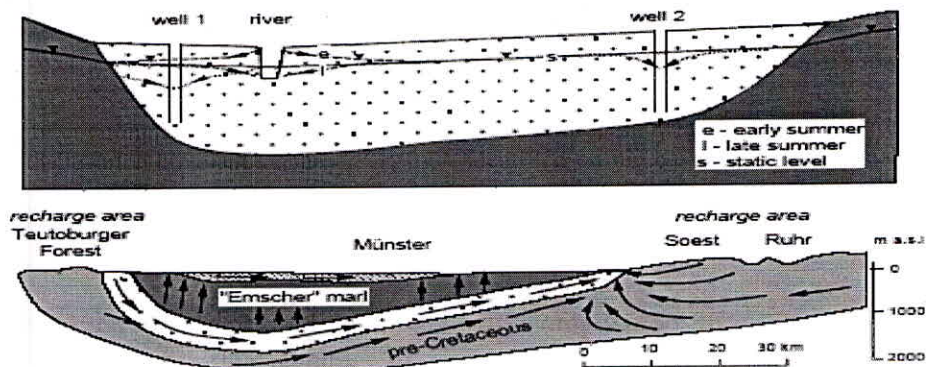


Fig. 10. Mixing and movement of waters from different sources

The isotopic index of different possible sources is determined and then using two or three box model $[m_p = (\square^{18}O_{gw} - \square^{18}O_p) / (\square^{18}O_{ch} - \square^{18}O_p)]$, the proportion of different

sources are identified. Based on the maximum contribution, the important source to be protected is finalized.

Table 6: Isotope characterization of Shallow Aquifers: an example for sources characterization

Area type	Site name & height above mean sea level (m)	$\delta^{18}O$ (‰)		TU	Interfluve type	Possible recharge sources
		Local rainfall (*)	Ground water			
Tarai-Plains Away from rivers and canal network.	Chhutmal-pur (295)	-6.8	-5.8	<i>Intermediate aquifer</i> TU= 17.8)	Solani-Yamuna	100% local precipitation recharge. Enrichment due to evaporation.
Plains, Close to Canal	Roorkee (265)	-6.7	-7.6	--		Rainfall - 73% & Canal Seepage 27%
Plain region. Away from rivers and canal system	Gagalhedi (280)	-6.7	-5.3	7.2		100% local precipitation recharge.
	Nakud (263)	-6.7	-5.5	11.7		100% Local precipitation recharge.
Plains, near river Yamuna	Toda (247)	-6.6	-6.7	--		Rainfall - 96% & Canal seepage 4%
Plains, Close to River Ganga	Chandpuri Kalan (228)	-6.5	-7.8	3.0	Solani-Ganga	87% from Middle Siwalik (~700m) & 13% from local precipitation

Table 7: Isotopic characterization of deeper aquifers in Solani-Yamuna Interfluve

Region	Site name and height above msl (m)	$\delta^{18}\text{O}$		TU	Recharge source
		Local rainfall (*)	Ground-water		
Siwalik foot hills	Nagal Kothari (417)	-7.1	-9.0	11.1	100% precipitation recharge at Upper Siwalik (~1000m msl).
	Timli (550)	-7.7	-8.0	10.4	100% recharge from Middle/Upper Siwalik (~700m)
Tarai-Plain interfringe	Chhutmalpur (295)	-6.8	-7.3	1.8	100% recharge at Lower Siwalik (~450m)
Plains near Upper Ganga Canal	Roorkee (265),	-6.7	-8.8	5.0	14% recharge from shallow aquifer ($\delta^{18}\text{O} = -7.6$) + 86% from Upper Siwalik (~1000m)
	Purkazi (232)	-6.5	-7.1	10.7	83% local precipitation ($\delta^{18}\text{O} = -6.5$) + 17% canal ($\delta^{18}\text{O} = -10$)
Plains, near the river Yamuna	Nakud (263)	-6.7	-7.3	ND	100% precipitation recharge from Lower Siwalik (450m).

(*) - Isotope index in precipitation is estimated by considering an altitude effect of 0.31‰ decrease per increase in altitude of 100 meters in $\delta^{18}\text{O}$.

Groundwater Dating with ^{14}C :

- * Carbon-14 is a radioactive isotope of carbon.
- * Its half life is 5730 years.
- * Environmental C-14 produced in the upper atmosphere

$$^{14}\text{N} + ^1_0\text{n} = ^1_1\text{H} + ^{14}_6\text{C}$$
- * C-14 is oxidized to CO_2 and becomes part of the atmospheric CO_2 reservoir.
- * The activity of radiocarbon is measured in PMC (Percent Modern Carbon) corresponds to the activity of carbon-14 which is equal to 13.56 dpm/gm and is treated as 100 PMC).
- * For practical purposes, the activity of MC is 0.95 of the sp. activity of the carbon of oxalic acid (NBS)
- * CO_2 enters into the water cycle by two main processes (neglecting direct dissolution)
 - (i) By pure chemical process of dissolution buffered by solid carbonate
 - (ii) By biochemical production of CO_2 and bicarbonate

The use of ^{14}C as a dating tool of groundwater is based on the following decay equation

$$A = A_0 e^{-\lambda t} \quad \text{and hence}$$
$$t = 8270 \ln A_0/A_t$$

where, A_0 and A_t are the initial and final ^{14}C activities respectively.

In routine ^{14}C dating, initial ^{14}C content is known by analysis of tree rings. However in hydrology the situation is much more complicated, the origin of C in water is less certain than that it is for plant and animal carbon.

By knowing the PMC value(also referred as pMC), one can calculate the age of the water sample. For example, if we get C-14 activity as 100 pMC, the groundwater is of recent origin or has direct contact with natural C-14 reservoir and if we get 50 pMC, the groundwater is 5730 years (uncorrected) old. One can measure age of groundwater up to 40,000 years using C-14 dating technique. However, groundwater age calculation using C-14 dating is neither simple nor very accurate as several corrections are to be done before arriving at any conclusion. Therefore, while dating groundwater using C-14 dating techniques, the factors like chemical (dilution) and isotopic (exchange), dissolved carbon of pure biogenic origin and dissolved carbon of mixed origin should be taken into account. Many different models have been suggested in the literature for predicting the initial ^{14}C activity. The carbon-14 method can be used for dating groundwater in the range 3000 to 40,000 a.

Case Study-I (Springs)

A study was conducted in the Uttarakhand state along the Bhagirathi River by the National Institute of Hydrology, Roorkee (Uttarakhand) to identify the recharge areas and source of the springs. The groundwater (hand pump), rainwater and spring water samples were collected (Fig. 10) and the spatial distribution of $\delta^{18}\text{O}$ for river water, groundwater was plotted from Goumukh to Devprayag.

The local meteoric water line (LMWL) was developed for Bhagirathi river catchment as shown in Figure-2 using the monthly weighted average isotopic values of precipitation. The equation for LMWL is given by:

$$\delta D = 8.0 \delta^{18}\text{O} + 11.5$$

The altitude effect in isotopic composition of precipitation was established by plotting the yearly weighted average $\delta^{18}\text{O}$ values of precipitation with respect to altitude (Fig. 12). The altitude effect of $-0.004 \text{‰} / 100\text{m}$ was found in $\delta^{18}\text{O}$ in the study area. The $\delta^{18}\text{O}$ and δD values of spring water were plotted along with the LMWL for the study area (Fig. 11).

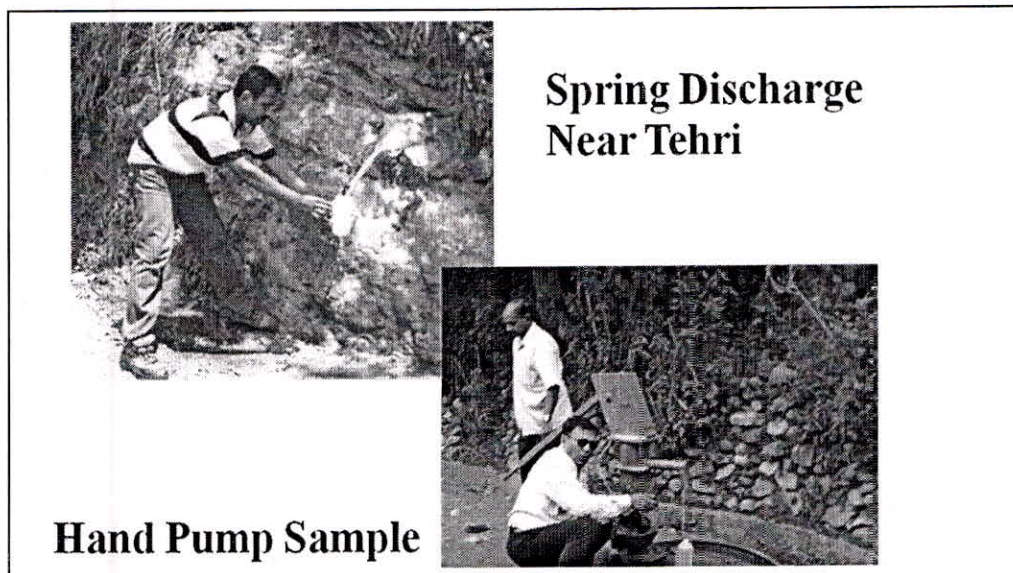


Fig. 10. Collection of water samples from a spring and a hand pump

Isotopic values of some of the springs fall on the LMWL indicating no evaporation effect. Therefore, altitudes of recharge areas were estimated directly applying the altitude effect as given in Table-1, while the isotopic values for those springs which fall on the evaporation lines (EVP1 & EVP2) were determined by extending the line towards the LMWL. After getting the real values of $\delta^{18}\text{O}$ for such springs, the altitude of recharge area has been determined as given in Table-8.

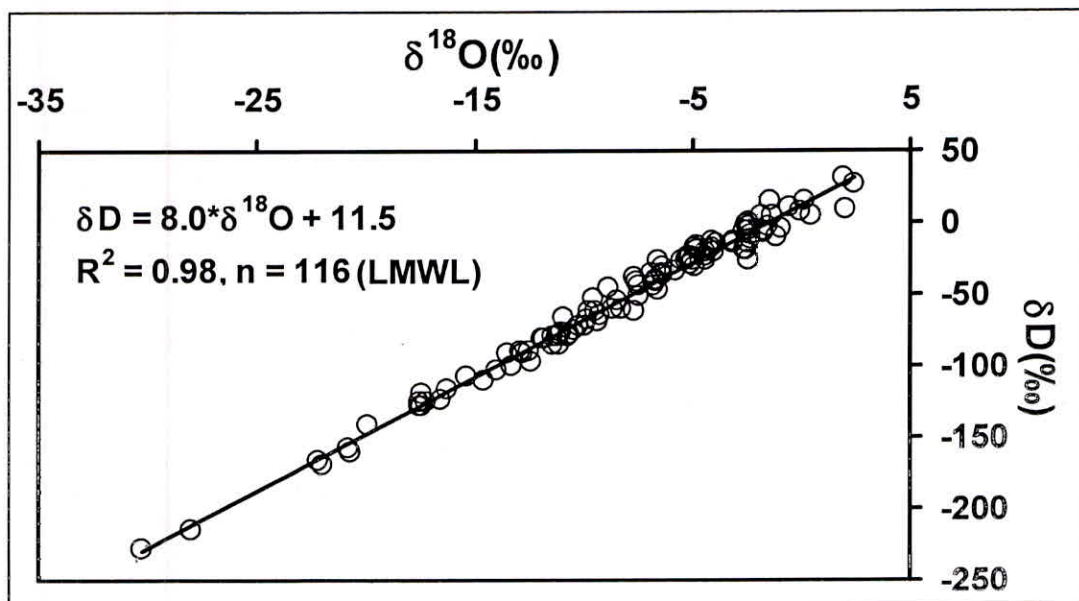


Fig. 11. Local meteoric water line (LMWL) for Bhagirathi river basin

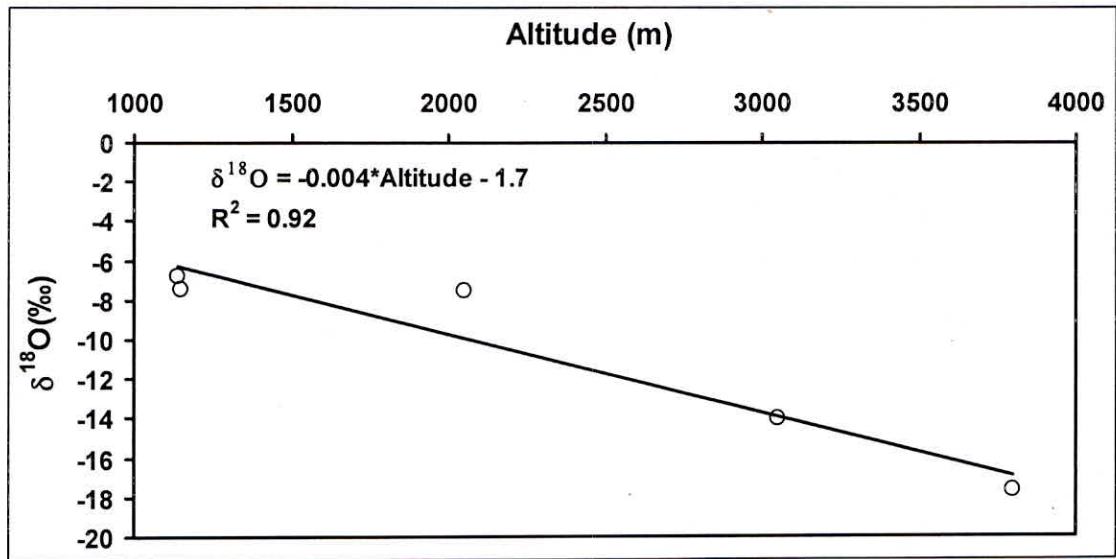


Fig. 12. Altitude effect on isotopic composition ($\delta^{18}\text{O}$) of precipitation in Bhagirathi river basin

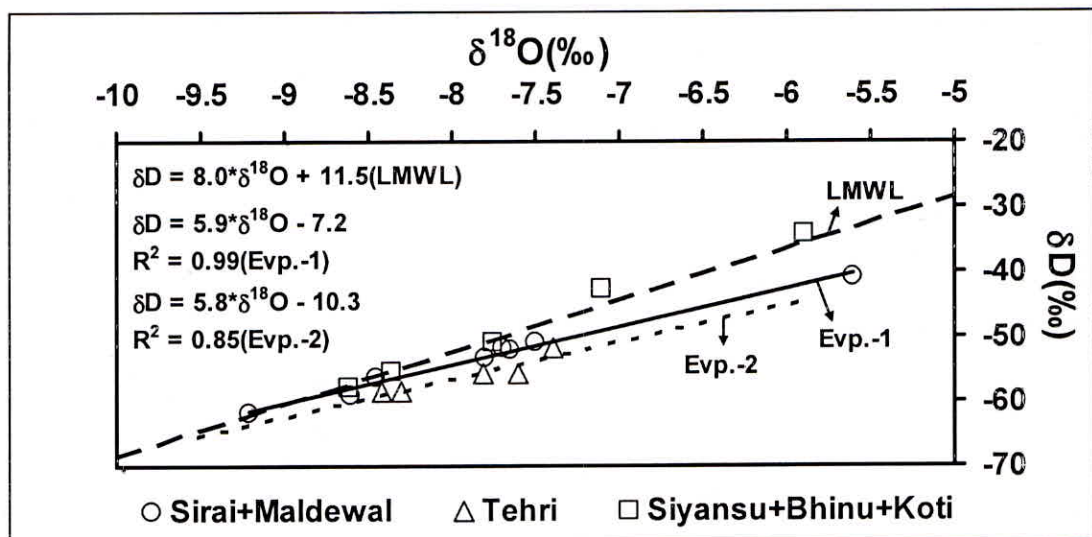


Fig. 13. Plot of isotopic values of different springs along with LMWL

Table 8. Altitude of recharge zones of springs whose isotopic values fall on LMWL

Spring name (altitude in m)	Spring $\delta^{18}\text{O}$ (‰)	Precipitation $\delta^{18}\text{O}$ (‰)	Difference $\Delta \delta^{18}\text{O}$	Projected altitude of recharge area above the location of spring (m)	Altitude of recharge area (m)
Siyansu (752)	-7.76	-4.76	-3.0	748	1500
Bhinu (1256)	-7.1	-6.78	-0.32	244	1500
Koti (1450)	-8.6	-7.55	-1.05	260	1710

Table 9. Altitude of recharge zones of springs whose isotopic values fall on Evaporation Lines (EVP1 & EVP2)

Spring name (altitude in m)	Spring $\delta^{18}\text{O}$ (‰)	Precipitation $\delta^{18}\text{O}$ (‰)	Difference $\Delta \delta^{18}\text{O}$	Projected altitude of recharge area above the location of spring (m)	Altitude of recharge area (m)
Tehri (640)	-9.3	-4.3	-5.0	1245	1885
Sirai (658)	-9.2	-4.4	-4.8	1202	1860
Maldewal (755)	-8.45	-4.8	-3.65	917	1672

The environmental tritium contents in groundwater ranges from 7.5 to 13 TU in the study area, which are almost similar to tritium contents, observed in precipitation. It reveals that the groundwater is of recent age. Because of this, most of the springs and hand pumps do not sustain the whole year (Table 10).

Table 10. Environmental tritium contents in groundwater, river and rainfall in the study area

Groundwater	Uttarkashi	Syanshu	Devprayag	Rishikesh	Range
^3H (TU)	13	10.7	12.4	7.5	7.5-13.0
River	Gangotri	Uttarkashi	Devprayag		
^3H (TU)	14	12	11		11-14
Rainfall	Uttarkashi	Devprayag			
^3H (TU)	13	12			12-13

Case study-II (Springs)

In an another study conducted jointly by Isotope Applications Division, Bhabha Atomic Research Centre, Mumbai and Himalayan Environmental Studies and Conservation Organization, Dehradun on the identification of recharge areas at Gauchar area of Chamoli (Shivanna et al., 2008).

Stable isotope data of precipitation collected from three different heights of the valleys, viz. 1180, 990 and 800 m msl, during September 2004 show that $\delta^{18}\text{O}$ varied from -10.0 to -8.2‰ and δD varied from -69.2 to -56.3‰. The isotopic composition of spring water varied from -7.7 to -7.0‰ for $\delta^{18}\text{O}$ and from -57.9 to -50.3‰ for δD . It is observed that most of the isotopic values of the precipitation samples do not fall on the GMWL. The best-fit line for the precipitation samples was plotted to construct the LMWL.

The equation for LMWL is given by:

$$\delta \text{D} = 6.8 \times \delta^{18}\text{O} + 0.3 \quad (r^2 = 0.98, n = 6)$$

Compared to GMWL, LMWL has lower slope and intercept showing evaporation effect. This is because during precipitation, the raindrops might have undergone evaporation. The samples from high-altitude springs fall on the LMWL, indicating recharge by precipitation prior to evaporation. The equation of the evaporation line (EL) is given by:

$$\delta D = 5.2 \times \delta^{18}O - 17.6 \quad (r^2 = 0.93, n = 4)$$

For estimating the altitude effect, the stable isotopic compositions of the precipitation samples were plotted against their corresponding altitudes. The altitude effect was calculated as the inverse of the slope of the best-fit line. It was found to be -0.55‰ for $\delta^{18}O$ and -3.8‰ for δD per 100 m rise in altitude. Generally, the discharge rates of springs ranged from 0.7 to 120 l/min during the monsoon season, which reduced to 0.2–99 l/min within a month after the monsoon. The discharge measurements indicated that all the springs responded instantaneously to the precipitation events.

During summer, most of the high-altitude springs dry up, whereas low-altitude springs continue to discharge with low rates. This shows that low-altitude spring discharges were a mixture of groundwater and precipitation, whereas only precipitation contributed to the high-altitude springs. This is further corroborated by hydrochemical data. The tritium content of the low-altitude springs was about 9.5 TU, whereas it was about 11.5 TU for high-altitude springs. This slight variation in tritium content can be attributed to relatively longer residence time of groundwater in low-altitude springs compared to that of high altitude springs. The enrichment in isotopic composition of high-altitude springs compared to that of precipitation during September 2004 was due to the contribution from initial rains during July 2004. Hence recharge altitude for these springs could not be estimated. Since the values of the low-altitude springs fall on an EL, their isotopic composition before evaporation was calculated by extrapolating the EL to intersect the LMWL. The corrected isotopic composition of these springs was -10.7 and -73‰ for $\delta^{18}O$ and δD , respectively. Using this corrected isotopic composition, the recharge area of the low-altitude springs was determined and it was found to be 1250 m msl. The topography and geology of the area suggests that the presence of thin, weathered, top soil cover underlain by hard and compact quartzite, phyllite and granite with a steep gradient does not allow the rainwater to percolate down, and hence the spring waters were mostly derived from seepage waters. Based on geology, geomorphology, hydrochemistry and isotope information of the study area, the possible recharge zones to the springs in valleys 1, 2 and 3 were located at altitudes of 1270, 1330 and 1020 m msl respectively. At these identified altitudes, water-conservation and artificial recharge structures like subsurface dykes (5 nos) in valley-1, check bunds (2 nos) in valley-2 and a few trenches in valley-3 were constructed for rainwater harvesting (Figure 5a). Monthly spring discharge measurements were carried out during December 2004–April 2005 before the construction of the structures and also during the same period in the following year, after the construction. The cumulative discharge rate of ten springs was found to be increased from 375 to 708 l/min during the post-monsoon period. It was found that the discharge rates had not only increased considerably, but also were sustainable even during the dry period. In addition to the existing springs, two new springs also appeared close to the subsurface dykes (Figure 14b). The cumulative

discharge rate of these new springs was about 67 l/min. The significant increase in the spring discharge rates, their longer duration and formation of new springs can be attributed to proper identification of recharge areas and implementation of artificial recharge structures.

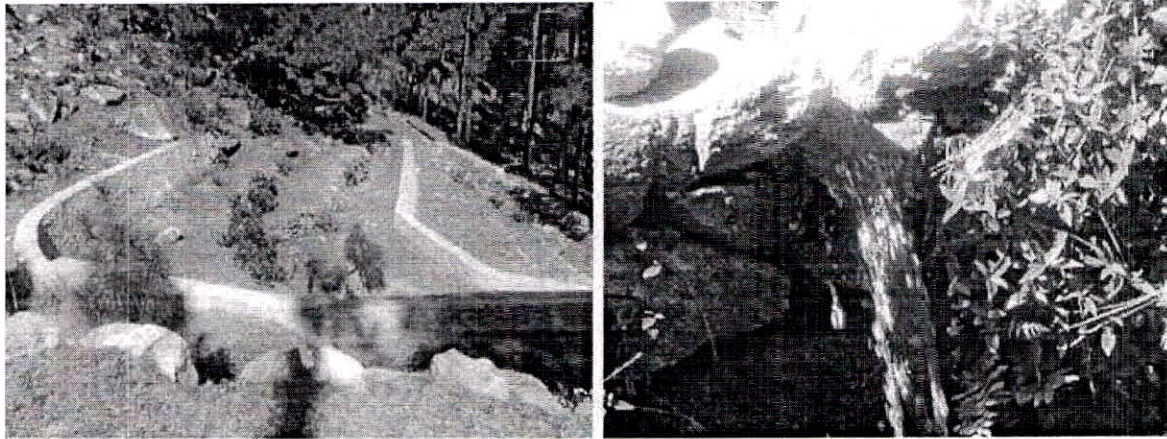


Fig . 14a, Subsurface dykes; b, New spring that appeared subsequently

5. Effectiveness of Artificial Recharge Measures

Depletion of groundwater table at a faster rate in most of the urbanized area and in semiarid/arid regions has drawn the attention of water resources managers. This situation has also arisen in areas where surface water bodies such as rivers, canals and natural or artificial lakes/ reservoirs do not exist. In order to mitigate the increasing shortage of groundwater, artificial recharge of groundwater by making earthen bunds, through injection wells or roof top rainwater harvesting programs have been given priority by the concerned organizations and individuals. However, the effectiveness of these programs has not been assessed at the desired scale as it is difficult using conventional techniques. Isotope techniques have the potential to assess the effectiveness of these programs using environmental isotopes.

The effectiveness of artificial recharge measures can be studied with the use of environmental isotopes (either δD or $\delta^{18}O$ and 3H , if required) provided the artificially recharged water has different isotopic composition than the natural recharge. However, if the same water is used for artificial recharge through prolonged infiltration by constructing earthen bunds, the isotopic composition of ponded water is changed due to evaporative enrichment. The isotopic indices (δD or $\delta^{18}O$) of precipitation, groundwater (without artificial recharge component), surface water being used for artificial recharge are determined and then the isotopic composition of the groundwater (from the study area) are determined at different time intervals (minimum monthly frequency). The use of two component model can reveal the percentage of mixing of artificially recharged water at different time. If the groundwater samples are collected from different locations around the site/s of artificial recharge, then the effect and extent of recharge (%) can be determined in different directions. 3H values of groundwater can confirm the recent recharge due to artificial measures.

An example of Ozar Watershed study in District Nasik, Maharashtra

The results of $\delta^{18}\text{O}$ analysis for groundwater, precipitation and canal water samples are given in Table-1. The distribution of $\delta^{18}\text{O}$ in groundwater and the groundwater flow pattern in the Ozar watershed is shown in the Figure 2a. The groundwater samples collected for environmental tritium analysis were carried out by liquid scintillation counting and were found in the range of 14-16 TU. These values are comparable to the Hatnur Canal (~12.6 TU), the water of which is used for artificial recharge through earthen channels, and much different from the rainfall in the area which show a typical value within the range of 5 to 6 TU. The Hantur Canal originates from the Tapi River which drained a large area. Therefore, it can have different T.U. values (high and low) depending upon the sources of water and time period. We have observed high T.U. values in canal water. The groundwater, being mostly recharged through the canal water, also has T.U. values comparable to canal water. However, the T.U. values of canal water might be higher during certain other period during which samples could not be collected, but the higher values of groundwater reflect it. The T.U. in rainwater could not be observed more than 5T.U. in Ozar watershed. Therefore, it is inferred that the groundwater is dominated by recharge from canal water through earthen channels and rainfall recharge component is comparatively very less. Moreover, the data reflect that the groundwater is young with negligible aquifer storage.

It is seen from Table-11 that the most depleted and enriched $\delta^{18}\text{O}$ values of the groundwater in Ozar watershed are -2.2‰ and 0.0‰ respectively. If we compare the monthly average values of $\delta^{18}\text{O}$ (neglecting spatial variations) of groundwater with the surface impoundment i.e., the earthen channels that carry canal water, it is seen that in the month of June, the groundwater is more depleted than the surface water (Figure 15(b)). This indicates the effect of evaporation on surface water that results in the enrichment of isotopic composition. In the month of July, the isotopic values of both systems get closer probably due to mixing of water from earthen channels that infiltrated during the month of June as enrichment in isotopic composition of groundwater is clearly seen (Fig. 15(b)).

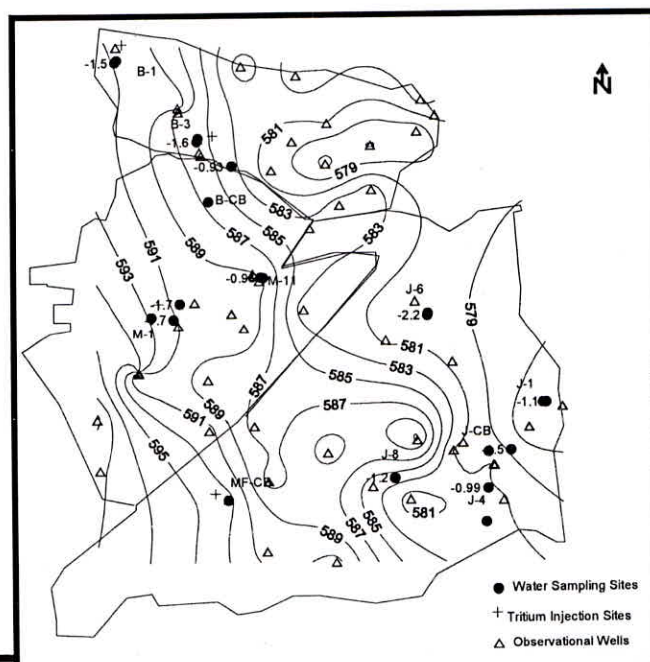


Figure 15(a): Groundwater level contours in the post monsoon season of 1997, stable isotope ($\delta^{18}\text{O}$) composition (‰) of groundwater in the Ozar watershed, Nashik

The evaporation effect further enriched isotopic contents of small quantity of water stored in channels due to no supply from canal in the month of August, while the groundwater also show a little enriching trend due to delayed contribution from precipitation and channel water.

Table 11: Results of $\delta^{18}\text{O}$ for groundwater, precipitation and canal water samples collected from Ozar watershed

S. No.	Society	Well No.	$\delta^{18}\text{O}$ ‰				
			Jun-2000	Jul-2000	Aug-2000	Sep-2000	Oct-2000
1	Mahatma Phule	M-1	-1.7	-0.8	-1.3	-0.5	0.1
2	Mahatma Phule	M-11	-0.9	0.0	-0.9	-0.4	-0.5
3	Banganga	B-1	-1.5	-0.5	0.3	-1.1	1.8
4	Banganga	B-3	-1.6	-0.8	0.0	-0.4	-0.2
5	Jay Yogeshwar	J-1	-1.1		-1.1	-1.3	-1.3
6	Jay Yogeshwar	J-4	-1.0	-0.7	-1.2	-1.2	-0.6
7	Jay Yogeshwar	J-6	-2.2	-0.3	-1.2		-1.6
8	Jay Yogeshwar	J-8	-1.2	-1.3	-0.4	-1.2	-1.1
	Average of well samples		-1.4	-0.6	-0.7	-0.9	-0.4
9	Rain		-4.7	-2.7	-4.4	-3.3	-
10	Earthen Channel	Near M1	-0.4	-0.7	0.5	0.3	0.6
11	Earthen Channel	Near B3	-0.3	-1.4	0.6	-0.4	-0.9
12	Earthen Channel	Near J-1	-1.2	-1.0	0.65	0.0	-0.8
	Average of channel samples		-0.6	-1.0	0.6	0.0	-0.4

In the month of September, the input from canal is provided to the earthen channels therefore, the isotopic contents of channel water comparatively deplete and so in the Ozar watershed. However, the $\delta^{18}\text{O}$ of groundwater in the month of October is found identical to that of the earthen channel in the Ozar Watershed. This fact clearly indicates that major recharge to the groundwater is from the impoundments across the channels locally called as Bandharas. The contribution from rainfall or canal (channel) to groundwater is determined using the following relation based on $\delta^{18}\text{O}$ values of end members.

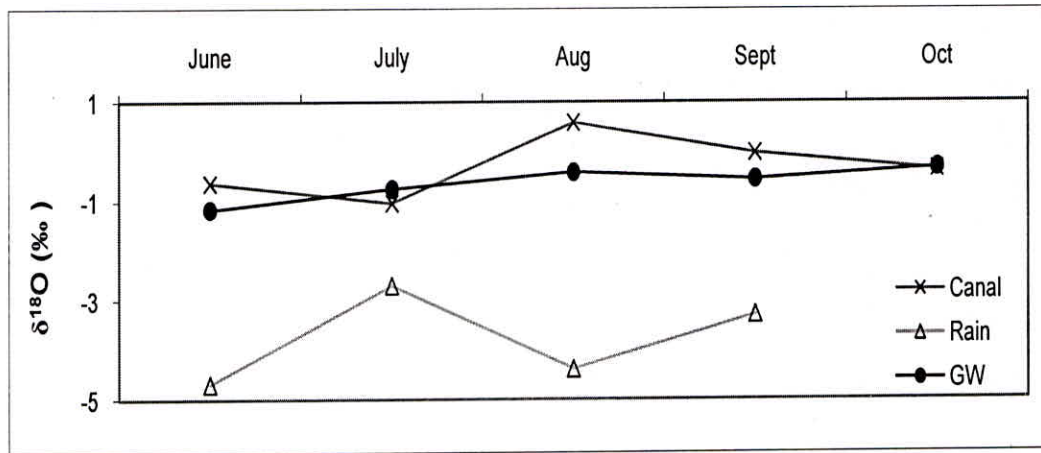


Figure 15(b): Variation of δ¹⁸O of channel water, groundwater and precipitation with time in Ozar watershed, Nashik

$$m_{ch} = (\delta^{18}O_{gw} - \delta^{18}O_p) / (\delta^{18}O_{ch} - \delta^{18}O_p) \quad \text{or} \quad m_p = (\delta^{18}O_{gw} - \delta^{18}O_{ch}) / (\delta^{18}O_p - \delta^{18}O_{ch})$$

Where, m_p and m_{ch} are the contributions of precipitation and channel water to groundwater respectively while $\delta^{18}O_{gw}$, $\delta^{18}O_p$, and $\delta^{18}O_{ch}$ are the corresponding oxygen-18 values of groundwater, precipitation and channel water (Table 12)

Table 12: Recharge percentage due to canal water supplied through channels and rainfall in different months

Recharge in (%) due to	June	August	September	October
Canal or Channel (M_{ch})	80	74	73	100
Rainfall (M_p)	20	26	27	0

Figure 15(c) clearly indicates the percent contribution of rainfall to groundwater in Ozar watershed. The percent of artificial recharge to groundwater through earthen channels can be estimated by subtracting percent of rainfall recharge from 100 as shown in Fig. 15(c). A straight line relation between the amount of rainfall and $\delta^{18}O_p$ values also enables to determine the percent contribution of rainfall to groundwater.

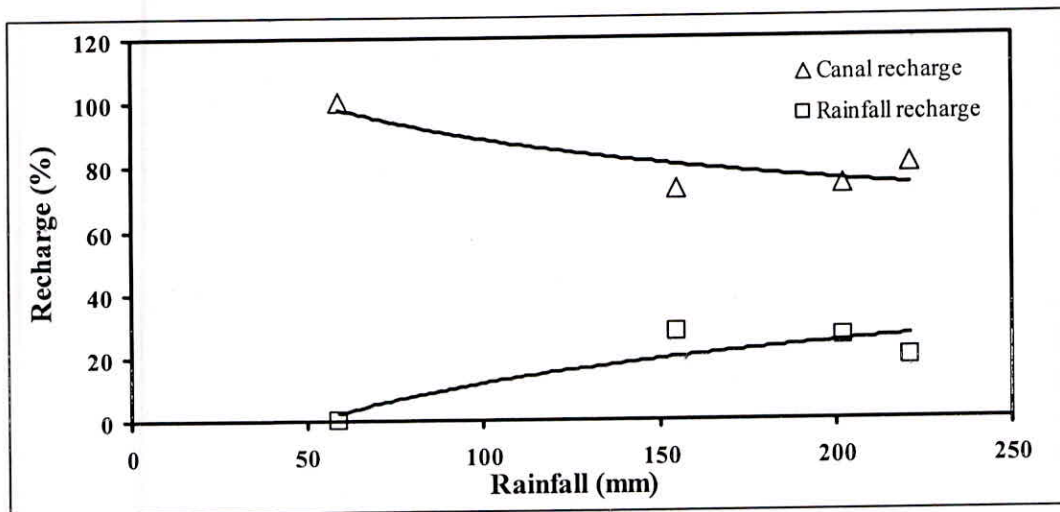


Figure 15(c): Percent recharge to groundwater due to rainfall and canal water in Ozar watershed, Nashik

6. SURFACE WATER AND GROUNDWATER INTERACTION

The river and groundwater interaction may be studied by groundwater modeling, channel water balance, isotope mass balance method and/or by statistical method using the river and groundwater water level fluctuation data. The statistical method based on Darcy's law involves analyses of the river water levels and groundwater levels adjacent to the river. Here, we will discuss only isotope mass balance method.

Principle

The approach is based on the fact that if the rivers originates at higher altitudes and has a different stable isotopic composition than that of groundwater that is recharged by infiltration of local precipitation then stable isotopes can be used to understand river and groundwater interaction. In most of the cases, the stable isotope ^{18}O is utilized for determining the contribution of groundwater to the river flow. If R_g and R_r are the isotopic composition of the groundwater and the river, respectively and m_g and m_r are the fractions of ground water and river, respectively in the admixture, while R_{am} is the isotopic composition of the admixture, then the isotopic balance and mass balance equations can be written as

$$m_g R_g + m_r R_r = R_{am}$$

and

$$m_g + m_r = 1$$

From the above two equations, we have

$$m_r = (R_{am} - R_g) / (R_r - R_g)$$

Therefore, by knowing the value of R_g , R_r , and R_{am} , the fraction of river water mixed with ground water can be evaluated.

In addition, environmental tritium can be used to understand the contribution of the Yamuna River to the groundwater in the study area as the mixing of river water reduces the groundwater ages.

Case Study of the Yamuna River

The present study is being carried out using isotope mass balance method. Isotopic tracers provide a mean for identifying the actual mass transport of water in the hydrologic cycle. The approach is based on the fact that the river Yamuna originates at higher and normally has a different stable isotopic composition than that of groundwater being recharged by infiltration of local precipitation. In case of a mountainous river, the river transports water, which has generally been originated from precipitation falling at higher elevations than the area where the surface-groundwater relation is under investigation. The difference in isotopic composition of these waters is due to altitude effect. The isotopic composition for ^{18}O in precipitation changes between -0.2 and -0.3 ‰ per 100 m with altitude. Thus, the stable isotopic composition of the river water is more depleted than that of groundwater derived from infiltration of local precipitation. This distinct difference helps in identifying the contribution of one to the other. The studies carried out by NIH, Roorkee and few others have revealed that the river Yamuna has stable isotopic signatures ($\delta^{18}\text{O}$) in the range of -8 ‰ to -9 ‰ while the groundwater in Delhi region varies between -6 ‰ to -7 ‰ where recharge due to precipitation dominates. Therefore, stable isotopes of hydrogen and oxygen have been used to determine the contribution of groundwater to river or vice versa at the selected locations in the study area.

In case of river Yamuna contributing to the groundwater regime, there are two possible sources of recharge to groundwater, viz. infiltration of local precipitation and infiltration of river water. In such conditions, the accuracy of the estimate of the proportion of infiltrated river water depends upon the accuracy of the estimates of stable isotopic indices of these two potential sources of recharge and the difference between these indices. An estimate of the river index has been made on the basis of samples from the river during the monsoon season, as this is the time when majority of the recharge in the river banks take place. The estimation of the index for recharge due to infiltration by local precipitation may be based on measurements of groundwater away from the influence of the river or, if sufficient data are available, on the peak value of the skewed frequency distribution. If the errors in estimates of the indices of the two potential sources of recharge are not greater than the analytical error, then the accuracy in the estimate of the proportion is better than 10%. In practice, the limitations of the method are not in the method itself, but in the availability of meaningful samples.

Establishment of sampling Stations

In the first phase, existing shallow groundwater abstraction points such as hand-pumps and shallow tube wells were identified along the riverbed along one section on

both the sides of the river. As the sufficient observation wells were not available and also measurement of water levels was not possible, ten piezometers were installed along one section during April 2007 to June 2007. Five of the piezometers were installed on the Delhi side and other five on the UP side to monitor the effect of pumping on groundwater conditions. (Fig 16)

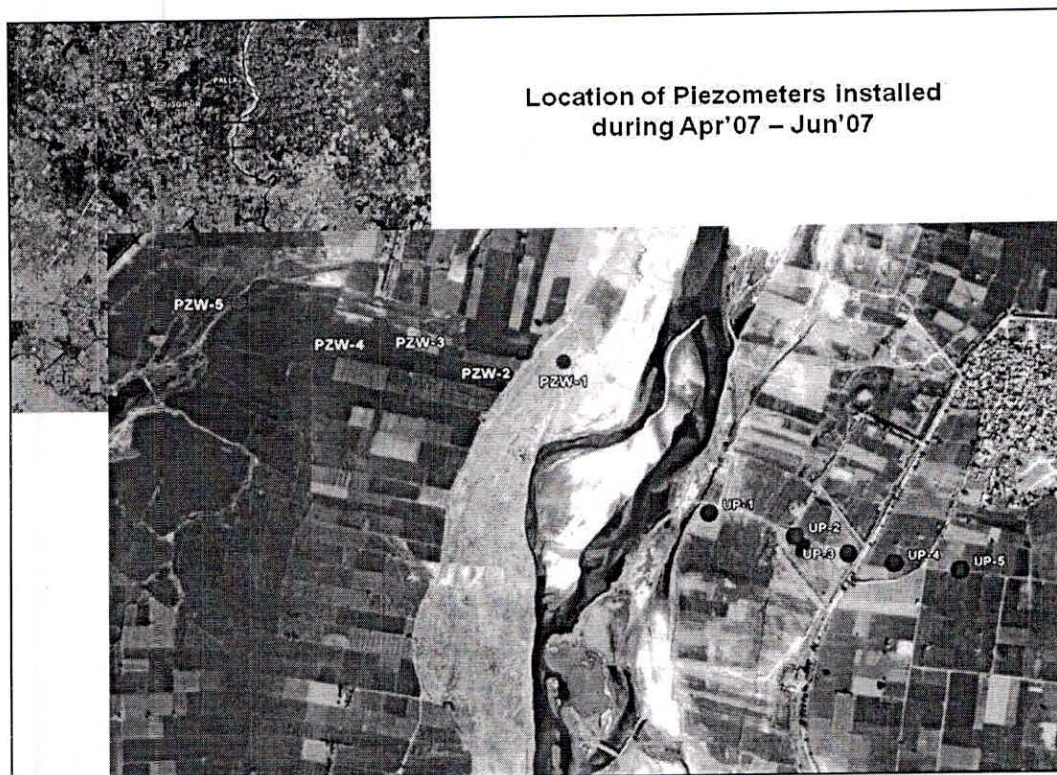


Fig. 16: Location of piezometers installed on both the sides of the river to study the effect of pumping

Water Sampling and Water Level Monitoring

Oxygen and hydrogen isotopes are invaluable to hydrological studies as these are part of the water molecule itself. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values may be used to assess evaporation during recharge, stream – aquifer interconnectivity, and mixing between different bodies of water within the basin. Similarity of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values between stream and aquifer may indicate interconnectivity, whereas isolated aquifers may contain waters with different $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values. Stable isotope systematics of waters around surface water bodies may be used to trace movement of seepage into / from nearby groundwater systems.

Groundwater samples are being collected at an interval of 7 days (every Sunday) from piezometers on Delhi side and at an interval of 14 days (every alternate Sunday) from piezometers on UP side. While collecting the samples water levels are also monitored in the piezometers (Fig. 17).

A few more water samples are being collected on both the sides. Also samples from one ranney well and one tube well are also collected to check the component of river water in the water being pumped from the area.

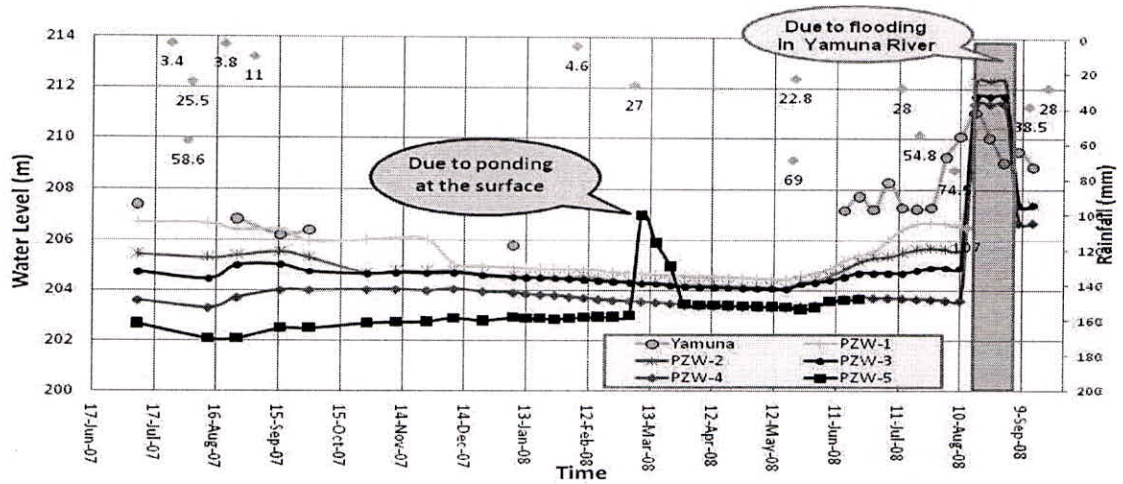


Fig. 17: Variation of water levels on the Delhi side

Most of the piezometers show declining water levels from November onwards, except piezometer PZ-5, which shows some erratic behaviour. In Aug 2008 all the piezometers were submerged due to heavy flood in the Yamuna River.

Groundwater Table in the Palla Area of Yamuna Floodplain (Jul'07 - Sep'08)

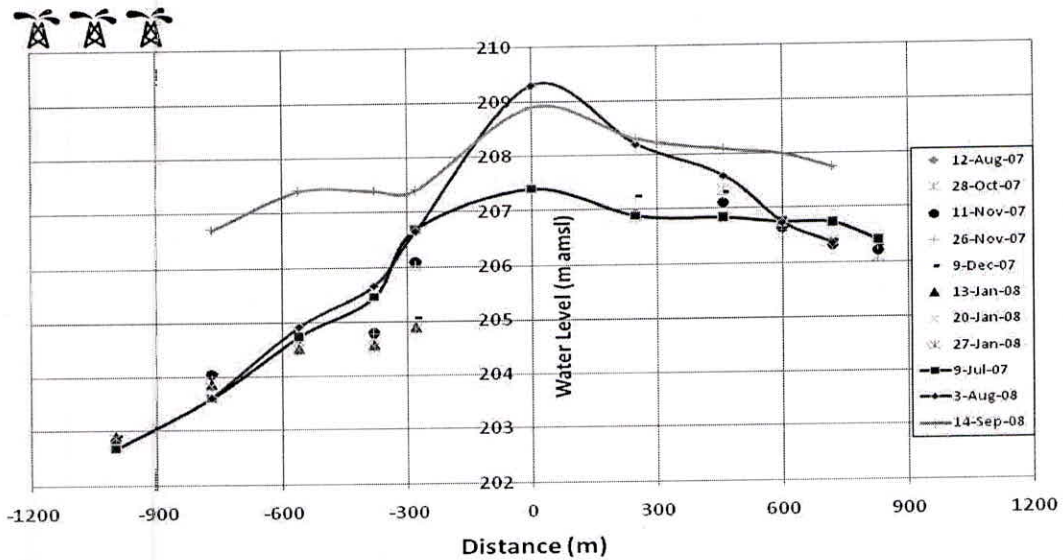


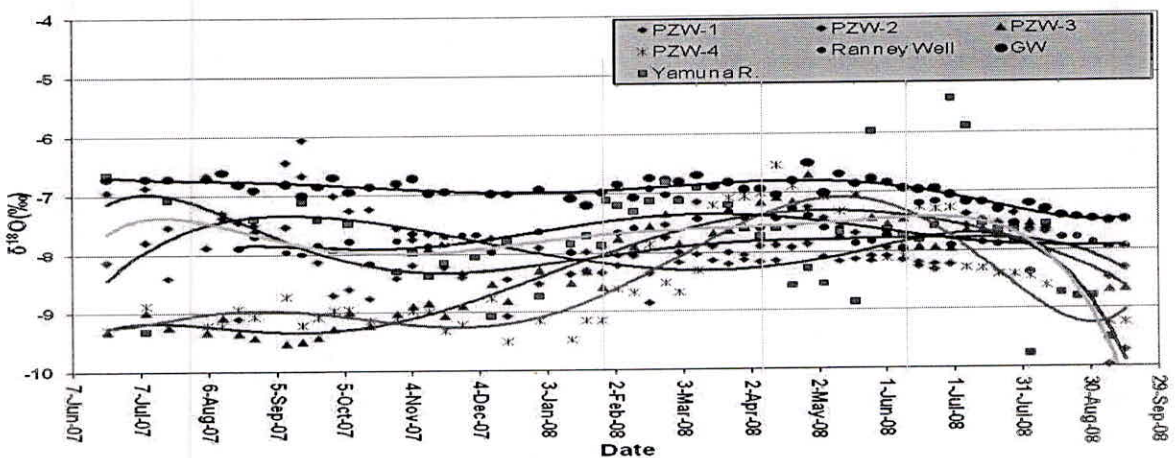
Fig. 18: Position of water table on both sides of the River Yamuna

It has been observed that the decline in water table is more on the Delhi side than on the UP side (Fig. 18).

Isotopic variations in groundwater

As mentioned earlier, samples for isotopic analysis were collected from the piezometers and existing hand pumps and shallow tube wells in the area. The samples were analysed for ¹⁸O and D at Stable Isotope Laboratory of National Institute of Hydrology, Roorkee.

Fig. 19: Variation of δ¹⁸O with time in waters of Palla area



The variation in $\delta^{18}\text{O}$ with time at various piezometers, groundwater and Yamuna River water are shown in Fig. 19. It can be seen from the figure that the composition of groundwater remains almost stable in the range of 6.8 to 7.1‰, whereas, water from other sources show large variation.

Closer look at the data reveals that PZW-1, the piezometer installed closest to the river shows signatures of the river water but more stable than the river (Fig. 20).

Further, the dip in $\delta^{18}\text{O}$ value on 9th July can be seen to move in the groundwater from river towards riverbank (line of pumping), with a velocity of about 2m/day in the river channel and 1m/day in the floodplain (Fig. 21).

Rain water was also collected for analysis of isotopic composition and $\delta^{18}\text{O}$ in the rain varies from -0.41‰ to -7.41‰ .

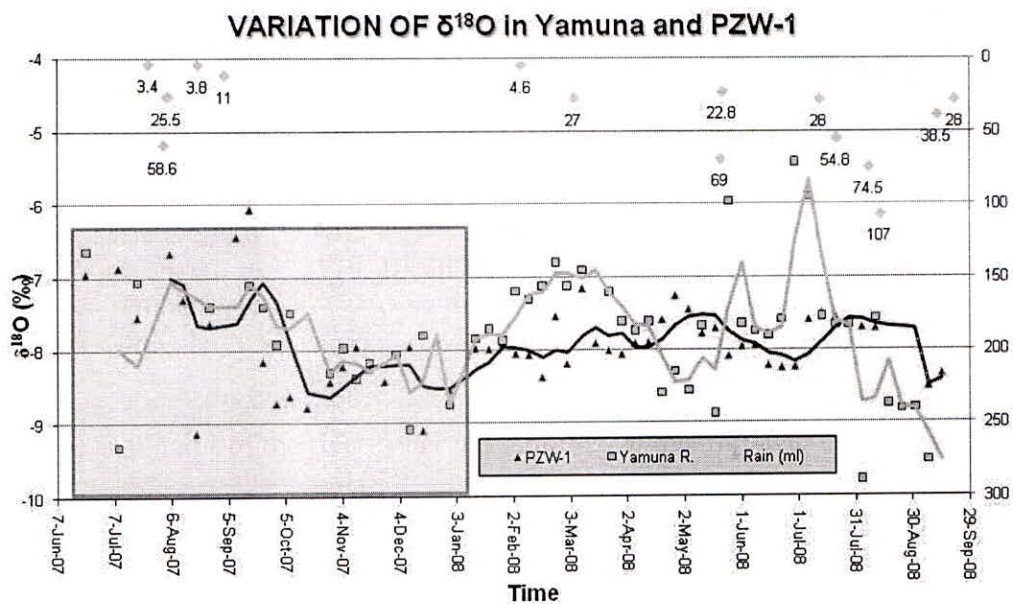


Fig. 20: Isotopic variation in PZW-1 and River Yamuna

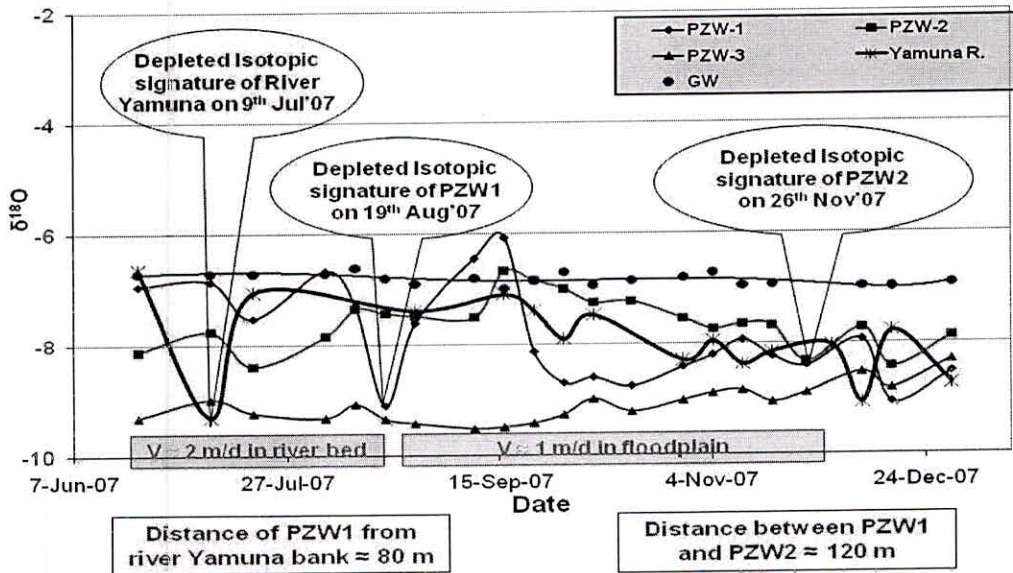


Fig. 21: Movement of depleted peak of $\delta^{18}\text{O}$ from PZW-1 to PZW-2

Based on the $\delta^{18}\text{O}$ variation in groundwater, the river water and the ranney well, the component of river water in the pumped water has been computed. The percentage of water from the floodplain in various months is given in Table 13.

Table 13. ($\delta^{18}\text{O}$ value of the Yamuna River = -9.5‰)

Component of Surface Water in Pumped water in Palla Area

Month	$\delta^{18}\text{O}$ in Ranney Well Water (‰)	$\delta^{18}\text{O}$ in Ground water (‰)	Flood Plain water in pumped water (%)
Aug-07	-7.9	-6.8	41
Oct-07	-7.9	-6.9	43
Dec-07	-7.8	-7.1	33
Feb-08	-7.1	-6.9	9
Apr-08	-7.4	-6.8	24
Jun-08	-7.6	-6.9	30
Aug-08	-8.0	-7.4	32

If the total water pumped by the Ranney wells and the tube wells is considered as 30 mgd, then the component of water from floodplain varies between 12.9 mgd (in Oct'07) to 2.7 mgd (in Feb'08), which is equivalent to 0.565 m³/sec and 0.118 m³/sec respectively.

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