

**BASICS OF ISOTOPES AND APPLICATIONS IN HYDROLOGY
AND WATER RESOURCES**

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BASICS OF ISOTOPES AND APPLICATIONS IN HYDROLOGY AND WATER RESOURCES

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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, continuous and ample water supply. The assessment of quality, supply, and renewal of resources is a well known problem, but it is becoming critical with the growth of population and rapid industrialization.

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

Isotopes can play a vital role in studying the soil moisture variation, its movement and recharge through unsaturated zone. Origin, age, distribution of waters in a region including occurrence and recharge mechanism, interconnections between groundwater bodies and identification of recharge sources and areas can be easily studied using environmental isotopes. Isotopes can also be applied to study the dynamics of lakes and reservoirs, leakage/seepage from dams/canals, river discharge in mountainous regions, sedimentation rates in lakes and reservoirs, surface water and groundwater interaction and sources and tracing of pollutants including sea water intrusion and salinization mechanism. Snow and glacier melt runoff and snow gauging can also be done effectively using isotope techniques.

The use of isotopes in hydrology was introduced in early 1950^s when the radiocarbon dating technique was employed for determining the age of groundwaters. After that a number of applications of isotopes were successfully tried and used to find the effective solutions of various hydrological problems in the developed countries. Later on the International Atomic Energy Agency (IAEA), Vienna, Austria, an independent intergovernmental organisation with in the United Nations System, took a leading role in the development and use of isotope techniques in hydrology. Now a days, isotope techniques are used frequently in the developed countries while their use in the developing countries is increasing slowly.

The applications of environmental isotopes had been initiated in India in early 1960^s by the Tata Institute of Fundamental Research, Bombay to determine the age of groundwaters and recharge to groundwater bodies in Gujarat and Rajasthan. Later on Bhabha Atomic Research

Centre (BARC), Bombay took lead to spread the use of isotope techniques in hydrology in India. Now a days, Physical Research Laboratory, Ahmedabad; National Geophysical Research Laboratory, Hyderabad; National Institute of Hydrology, Roorkee; Defence Research Laboratory, Jodhpur; Nuclear Research Laboratory, Indian Council for Agricultural Research (ICAR), Delhi; Centre for Water resources Development & Management (CWRDM), Kozhikode; UP Irrigation Research Institute, Roorkee; UP Ground Water Department, Lucknow and few more central and state government organisations are actively involved in the isotope hydrology work in India.

ISOTOPES - BASICS

Atom consists of a positively charged nucleus surrounded by a cloud of negatively charged particles called electron which revolve around it. The diameters of atoms are of the order of 10^{-8} cm while nuclei of atoms are about 10^{-12} cm (1000 times less). In nucleus, most of the atom's mass is concentrated. The nucleus contains different types of particles that interact with each other but proton and neutron are considered to be the main constituents. The proton is a positively charged particle while neutron is a neutral particle. The combination and distribution of positive and negative charge of an atom makes it neutral in normal conditions. The details of prominent atomic particles are given below:

Proton - positively charged; mass - 1.672648×10^{-27} Kg ; **Electron** - negatively charged; mass - 9.10986×10^{-31} Kg or 1/1836 times of mass of proton; **Neutron** - neutral (no charge); mass - $1.6749543 \times 10^{-27}$ Kg

Isotopes

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 and one electron revolving around the nucleus in an orbit.

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

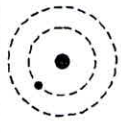
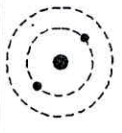




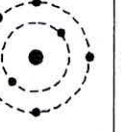
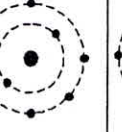
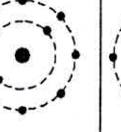
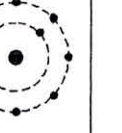
3_1H_2 - one more neutron added to the nucleus of 2_1H_1 .

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 ${}^{14}C$.

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.

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

${}^1_1\text{H}$ 							${}^2_2\text{He}$ 
${}^3_3\text{Li}$ 	${}^4_4\text{Be}$ 	${}^5_5\text{B}$ 	${}^6_6\text{C}$ 	${}^7_7\text{N}$ 	${}^8_8\text{O}$ 	${}^9_9\text{F}$ 	${}^{10}_{10}\text{Ne}$ 
${}^{11}_{11}\text{Na}$ a	${}^{12}_{12}\text{Mg}$	${}^{13}_{13}\text{Al}$	${}^{14}_{14}\text{Si}$	${}^{15}_{15}\text{P}$	${}^{16}_{16}\text{S}$	${}^{17}_{17}\text{Cl}$	${}^{18}_{18}\text{Ar}$

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, ${}^1_1\text{H}$ and ${}^2_1\text{H}$ are stable isotopes while ${}^3_1\text{H}$ is unstable. Similarly ${}^{12}_6\text{C}$ and ${}^{13}_6\text{C}$ are stable isotopes while ${}^{14}_6\text{C}$ is unstable. On the other hand, isotopes of oxygen (${}^{16}_8\text{O}$, ${}^{17}_8\text{O}$ and ${}^{18}_8\text{O}$) are stable.

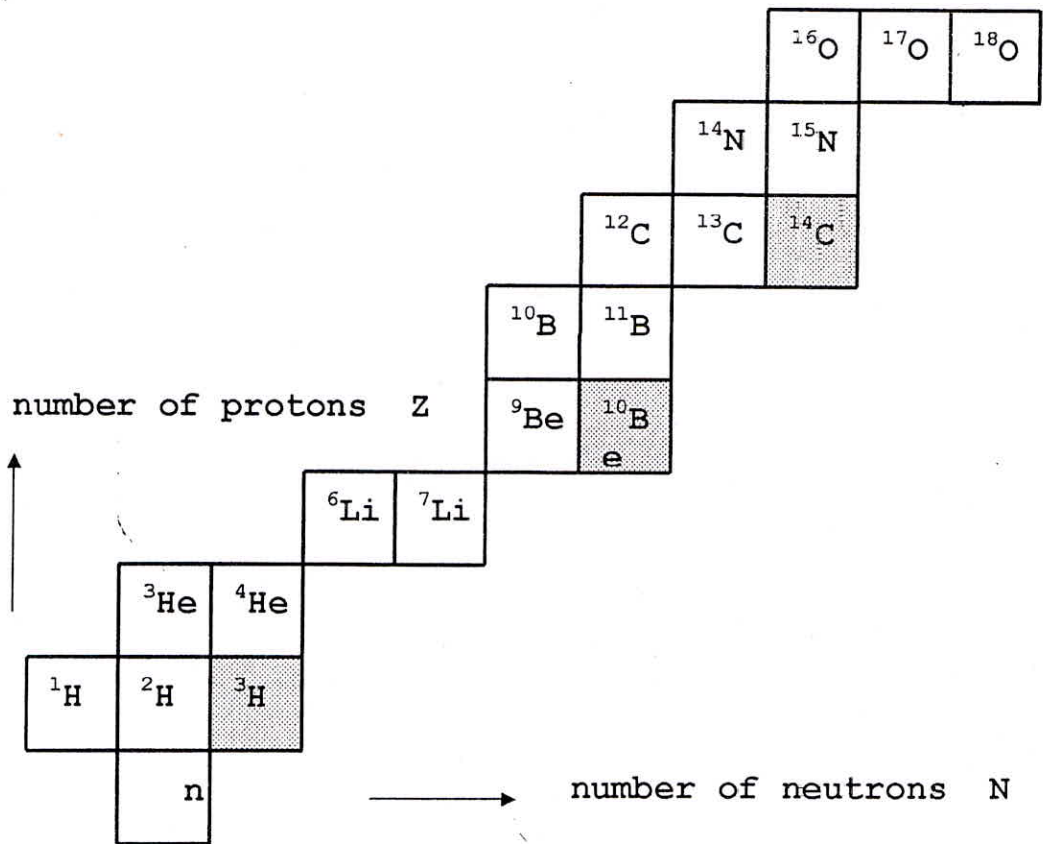
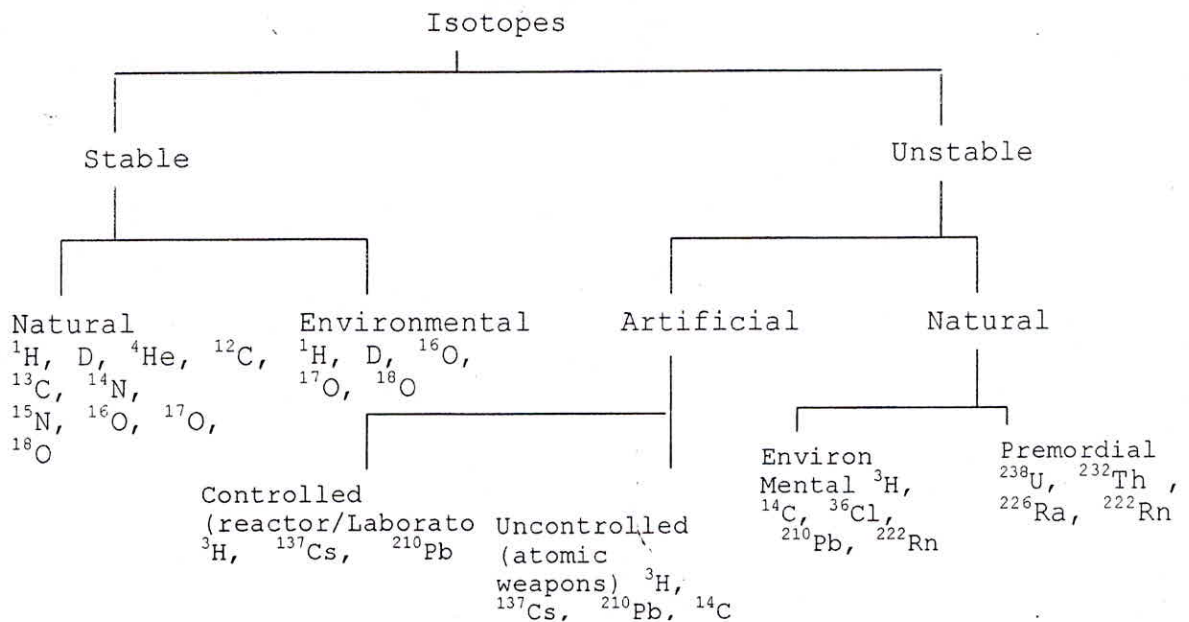


Fig. 2.2.1 The isotopes of an element (equal Z) are found in a horizontal row, isobars (equal A) along diagonal lines, isotones (equal N) in vertical columns. The natural radioactive isotopes of H, Be, and C are marked grey.

Isotopes can also be classified as natural and artificial isotopes, i.e., the isotopes that occurs 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.



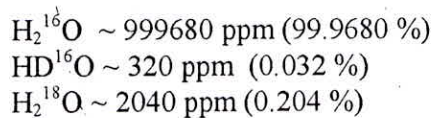
Stable Isotopes

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 $^1\text{H}^1\text{H}^{16}\text{O}$, $^1\text{H}^1\text{H}^{18}\text{O}$, $^1\text{H}^2\text{H}^{16}\text{O}$, $^1\text{H}^2\text{H}^{18}\text{O}$, $^1\text{H}^1\text{H}^{17}\text{O}$ 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:



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 Peedee formation of South Carolina in USA.

The chemistry of groundwater is strongly dependent on Carbonate geochemistry. The $\delta^{13}\text{C}$ of

soil CO₂ 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 CO₂ which has a δ¹³C of -7. Water which passes through unsaturated zone towards the water table will become saturated with this CO₂ and the δ¹³C of dissolved inorganic carbon will reflect the composition of recharging waters.

Modification of ¹³C 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 δ¹³C values close to 0. Similarly the δ¹³C of metamorphic carbonate sequences are close to 0, unless magmatic CO₂ played a role in its formation. In such cases ¹³C values between -5 to -2 could be expected. These values are considerably enriched compared to soil CO₂. As a result carbonate dissolution will bring about an enrichment in ¹³C in the dissolved aqueous carbon.

There are few other stable isotopes (³He, ⁶Li, ¹¹B, ¹⁵N, ³⁴S, ³⁷Cl, ⁸¹Br and ⁸⁷Sr) 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 occur 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
^2H	$^2\text{H}/^1\text{H}$	0.015	VSMOW ($1.5575 \cdot 10^{-4}$)	H_2O , CH_2O , CH_4 , H_2 , OH^- minerals
^3He	$^3\text{He}/^4\text{He}$	0.000138	Atmospheric He ($1.3 \cdot 10^{-6}$)	He in water or gas, crustal fluids, basalt
^6Li	$^6\text{Li}/^7\text{Li}$	7.5	L-SVEC ($8.32 \cdot 10^{-2}$)	Saline waters, rocks
^{11}B	$^{11}\text{B}/^{10}\text{B}$	80.1	NBS 951 (4.04362)	Saline waters, clays, borate, rocks
^{13}C	$^{13}\text{C}/^{12}\text{C}$	1.11	VPDB ($1.1237 \cdot 10^{-2}$)	CO_2 , carbonate, DIC, CH_4 , organics
^{15}N	$^{15}\text{N}/^{14}\text{N}$	0.366	AIR N_2 ($3.677 \cdot 10^{-3}$)	N_2 , NH_4^+ , NO_3^- , N-organics
^{18}O	$^{18}\text{O}/^{16}\text{O}$	0.204	VSMOW ($2.0052 \cdot 10^{-3}$) VPDB ($2.0672 \cdot 10^{-3}$)	H_2O , CH_2O , CO_2 , sulphates NO_3^- , carbonates, silicates OH^- minerals
^{34}S	$^{34}\text{S}/^{32}\text{S}$	4.21	CDT ($4.5005 \cdot 10^{-3}$)	Sulphates, sulphides, H_2S , S-organics
^{37}Cl	$^{37}\text{Cl}/^{35}\text{Cl}$	24.23	SMOC (0.324)	Saline waters, rocks, evaporites, solvents
^{81}Br	$^{81}\text{Br}/^{79}\text{Br}$	49.31	SMOB	Developmental for saline waters
^{87}Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}=7.0$ $^{86}\text{Sr}=9.86$	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 (‰) = $\delta \times 1000$.

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

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 $\delta\text{D} - \delta^{18}\text{O}$ line of fresh global meteoric waters.

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

$$\text{For northern hemisphere: } \delta\text{D} = 8\delta^{18}\text{O} + 10$$

$$\text{For southern hemisphere: } \delta\text{D} = 8\delta^{18}\text{O} + 22$$

$$\text{New relationship (1993) for northern hemisphere: } \delta\text{D} = 8.17 \delta^{18}\text{O} + 11.27$$

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

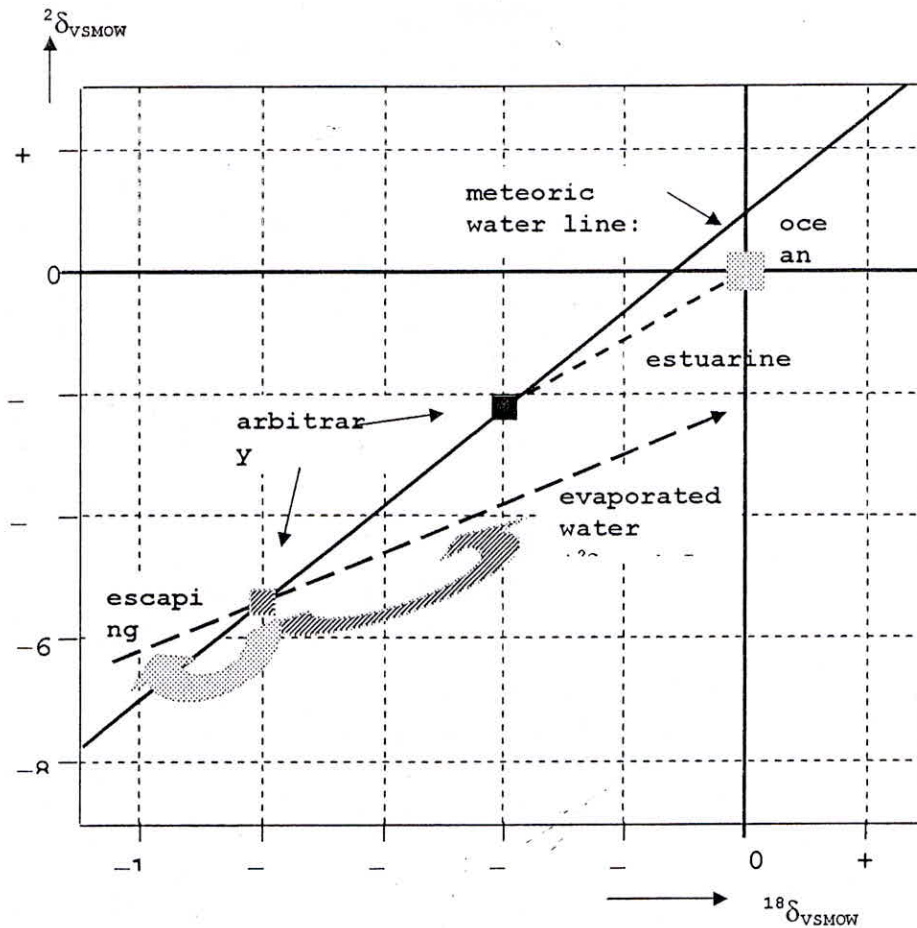


Fig. 2.3. Relation between ${}^{18}\delta$ and ${}^2\delta$ for estuarine mixing and for evaporating surface water. Because the evaporation is a non-equilibrium process, isotope fractionations involved are not necessarily related by a factor of 8, as is the equilibrium condensation process.

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

The relations established by Dansgard in 1964 and later by Yurtsver and Gat (1981) using annual average and monthly average temperatures are given below:

$$\delta^{18}\text{O} = 0.695 T_{\text{annual}} - 13.6 \text{ (VSMOW)}$$

$$\delta\text{D} = 5.6 T_{\text{annual}} - 100 \text{ (VSMOW)}$$

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

It is clear from the above equation that on average there is a 1‰ decrease in average $\delta^{18}\text{O}$ corresponding to the average annual temperature.

We know that as latitude increases, the temperature decreases. We also know that the Polar Regions are located at the highest latitudes and also at the end of Rayleigh rainout process: Therefore, the water vapours or precipitation depletes in heavier isotopes with the increase in latitude. The variations in $\delta^{18}\text{O}$ are on the order of -0.6‰ per degree of latitude for continental stations of the North America, Europe and about -2‰ per degree latitude for the colder Antarctica stations. One may expect very low gradients in the low latitudes where over 60% of atmospheric water vapours originate. Thus due to increase in temperature gradients also increases and the latitudes, the isotopic fractionation also increases and the water vapours depleted in heavier isotope species of water molecule.

Continental Effect

The continental effect is observed in the precipitation i.e. the precipitation is depleted in heavier isotopic species of water molecules as we move away from the coastal parts. As we know oceans are that the main source of water vapours, that causes major precipitation on the globe and as vapour mass moves from its source region across a continent, the rain out process depletes the precipitation in $\delta^{18}\text{O}$ and D with respect to the distance from the coast. Therefore, coastal precipitations are isotopically enriched while the colder inner continental regions receive isotopically depleted precipitation with strong seasonal differences. On average, there is about -2‰ depletion $\delta^{18}\text{O}$ per 1000km from seacoast.

The global T- $\delta^{18}\text{O}$ relationship ($\delta^{18}\text{O}=0.695T_{\text{annual}}-13.6\text{‰SMOW}$) significantly changes due to continental effect. It also produces distortions in the latitude effect clearly visible in fig. (3.2 pp 67 C&F). It is interesting to note that no continental gradient is observed over the amazon basin although the dominant weather regimes move from the Atlantic towards the high mountains of the Andes. This might be due to dominating evapotranspiration in the tropical forests that is responsible for the very flat gradients (Salati et.al. 1979).

The T- $\delta^{18}\text{O}$ relationships established for local precipitation in northern Switzerland and the German Black Forest are,

$$\delta^{18}\text{O}_{\text{monthly}} = 0.38 T_{\text{monthly}} - 12.6$$

$$\delta_{\text{Dmonthly}} = 3.7 T_{\text{monthly}} - 85.7$$

The T- $\delta^{18}\text{O}$ relationship for central Switzerland (Pearson et.al. 1991) is somewhat steeper i.e.,

$$\delta^{18}\text{O}_{\text{monthly}} = 0.56 T_{\text{monthly}} - 14.6$$

$$\delta_{\text{Dmonthly}} = 3.72 T_{\text{monthly}} - 182.7$$

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 $\delta^{18}\text{O}$ 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 ($^3\text{H}_2\text{O}$) 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 , $^{226}\text{Ra}/^{241}\text{Am}$ 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.

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_3CO_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.

Radioactivity

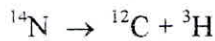
The phenomenon of disintegration of unstable atoms to the stable form is called radioactivity. The unit of radioactivity is denoted by Curie (Ci) and one Curie is equal to 3.7×10^{10} disintegrations per second. In case of very low activity, it is also denoted by Becquerel (Bq) and one Becquerel is equal 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.

Half Life

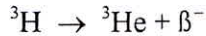
The time in which the radioactive element decays to one half (1/2) of its initial strength is known as half life. Different radioisotopes have different half lives and the decay rate is a characteristic property of an atom.

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 $E_{\beta\text{max}} = 18 \text{ keV}$ 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).

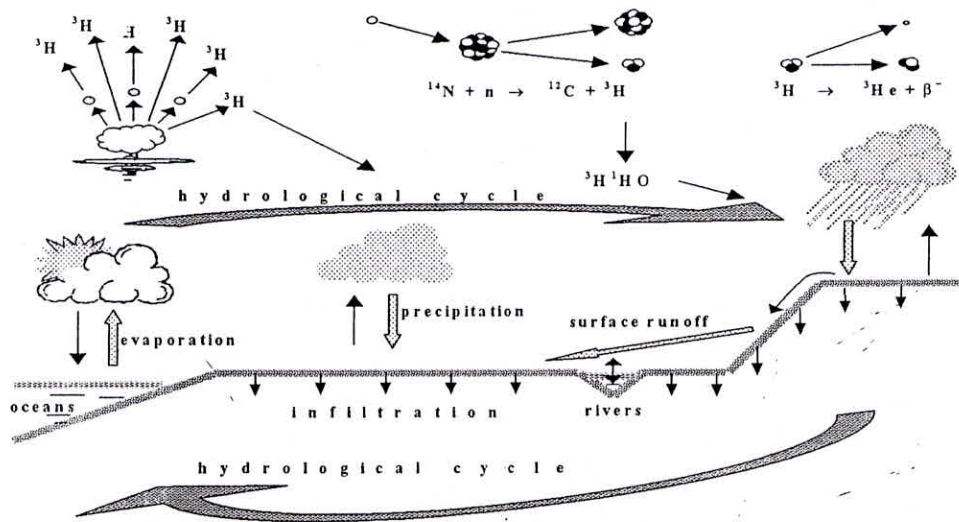
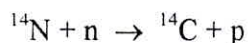


Fig.2.4. Origin and distribution of ^3H in nature. Contrary to ^{14}C , the turnover of ^3H is very fast, except where it is fixed in glacier ice or groundwater.

However, tritium is also produced in the atmosphere due to testing of atomic devices similar to cosmogenic tritium. It is also produced artificially under controlled conditions in laboratory/ reactor.

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..



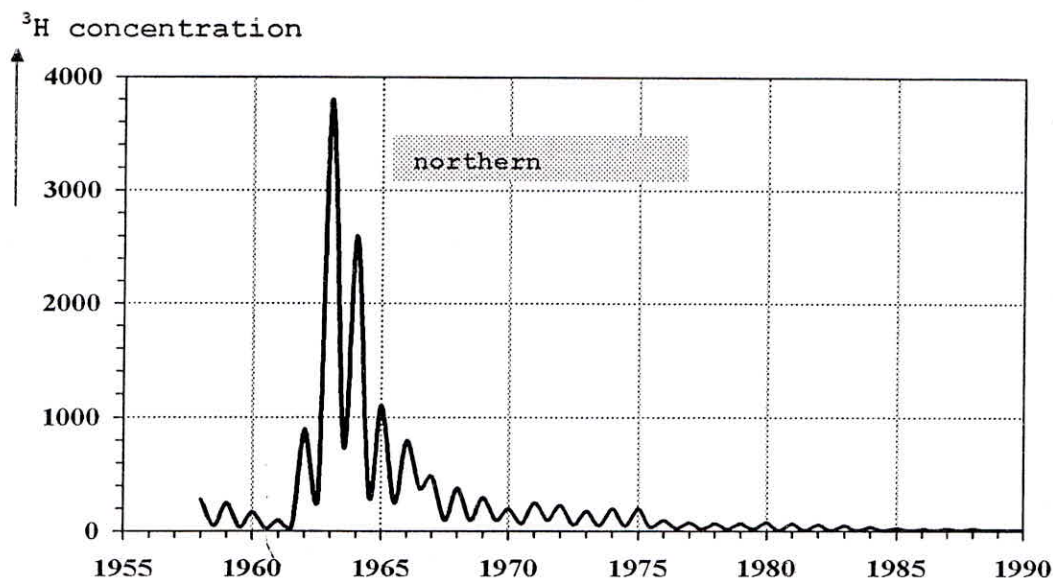


Fig. 2.5. Smoothed curve representing the average ³H content of precipitation over the continental surface of the Northern hemisphere.

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: $^{14}\text{C} \rightarrow ^{14}\text{N} + \beta^-$ 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, right half-life, because of the natural variations in the ¹⁴C content of atmospheric CO₂ during geologic times and deviating from the present. These errors were even larger. Nowadays the ¹⁴C calibration, based on the known ¹⁴C content of tree rings with exactly known age, removes both errors at once.

Carbon-14 is not an isotopic tracer of water molecule and like ¹³C 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 ¹⁴C data

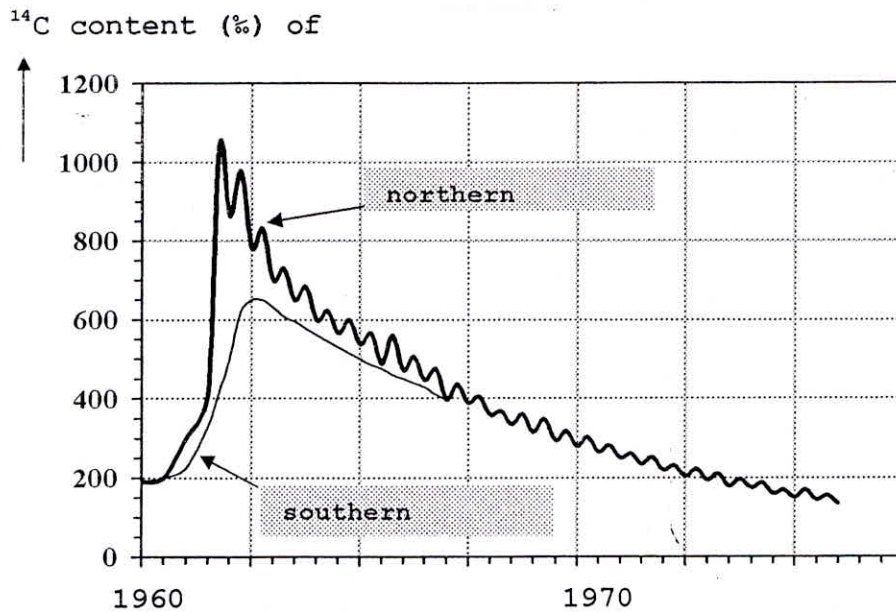
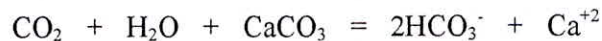


Fig 2.6. Curve representing the natural ^{14}C content of atmospheric CO_2 (data for Nordkapp, Norway, representative for the northern hemisphere).

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



These processes produces 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 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.

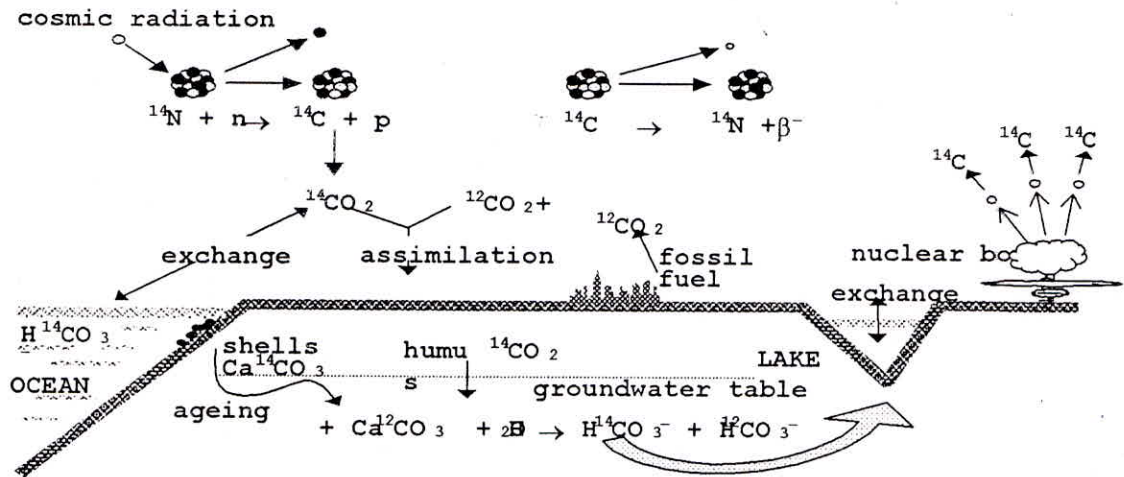


Fig.2.7. Origin and distribution of ^{14}C in nature

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.

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.

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.

APPLICATIONS IN HYDROLOGY AND WATER RESOURCES

Isotopes have wide applications in hydrological investigations and provide vital informations for the better management of water resources. Isotopes also helps in understanding various hydrological processes. Isotope techniques using "environmental isotopes" are commonly used in the developed countries by meteorologists, hydrologists, and hydrogeologists in the study of water. The use of these techniques is also increasing in our country, but still it requires momentum and training of the field persons in this subject. Study of the isotopes of oxygen and hydrogen in water, or of elements contained in dissolved salts which have the same behaviour as water, enable exact recording of phenomena affecting the occurrence and movement of water in all its forms.

Isotopic methods are normally used in conjunction with conventional hydrological, hydrogeological and geochemical or water-chemical techniques, so as to provide additional and valuable information for solving hydrological problems. In recent years, in hundreds of difficult cases, isotopic methods have provided definite, satisfactory results.

The isotopic techniques can be employed in order to study the following aspects related with various branches of hydrology.

Surface Water:

- . Hydrographs separation
- . River discharge measurements
- . Dynamics of lakes and reservoirs
- . Water balance
- . Interconnections of water bodies
- . Leakage through dams,
- . Seepage to subways
- . Suspended and bed load sediment transport
- . Sedimentation rate
- . Evaporation/Evapotranspiration
- . Surface water and groundwater interaction
- . Sources and tracing of pollutants
- . Snow and glacial melt runoff

Ground Water:

- . 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

Meteorological:

Variability of environmental conditions
Movement of clouds and variability in precipitation
Environmental pollution and mechanism
Prediction of Arrival and retreat of Monsoon

Artificial isotopes are used primarily to provide the necessary information to solve relatively local hydrological problems like leakage from dams / reservoirs or to define ground water protection zones. They are also used to identify water flow patterns in highly soluble and fractured rocks like karst where the flow of the ground water is relatively fast, measurement of discharge of streams in mountainous regions and estimation of recharge to groundwater due to rainfall and irrigation.

In recent times, more environmental isotopes are being used such as ^{18}O , D and ^3H which are all constituents of the water molecule. They are ideal tracers and since they are environmental isotopes, there is no difficulty in public acceptance. Similarly, other environmental isotopes like ^{13}C , ^{14}C , ^{15}N , ^{36}Cl , ^{137}Cs and ^{210}Pb etc. are also used to get useful hydrological information.

REFERENCES:

- Clark, I.D., and Fritz, P. (1997).** Environmental Isotopes in Hydrogeology, CRS Press; Boca Raton, 328 pp.
- Fritz, P. and Fontes, J. Ch. (eds).(1980).** Handbook of Environmental Isotope Geochemistry, vol.1, Elsevier, New York, 545 p.
- Gat J R and Gouffier R (eds). (1981).** "Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle." IAEA Technical Reports Science No. 210, 337pp.
- Hoefs J. (1997).** Stable Isotope Geochemistry. 4th Edition, Springer-Verlag, Berlin. 214pp.
- IAEA, Vienna, Austria. (1983).** Guide Book on Nuclear Techniques in Hydrology, TEC_DOC 91/2.
- Kendall, C. and McDonnell, J.J. (eds). (1998).** Isotope Tracers in Catchment Hydrology, Elsevier Science, Amsterdam, 839 p.
- Peer de Groot,** 'Handbook for Stable Isotope Analytical Techniques' two volumes.
<http://www.geocities.com/padegroot/index.html>