Concepts of Isotope Hydrology

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1. 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 day, isotope techniques are used frequently in the developed countries while their use in the developing counties 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 groundwater 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.

2. 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

2.1 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., ${}^{1}_{1}H_{0}$ only one proton in nucleus and one electron revolving around the nucleus in an orbit, ${}^{2}_{1}H_{1}$ - one neutron added to the nucleus of ${}^{1}_{1}H_{0}$ atom, ${}^{3}_{2}H_{2}$ one more neutron added to the nucleus of ${}^{2}_{1}H_{0}$ (Fig 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) (Fig. 1). For example, $^{3}_{1}H$ and $^{3}_{2}He$ 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, $^{2}_{1}H_{1}$ and $^{3}_{2}He_{1}$ are the isotones.

2.2 Classification of Isotopes

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

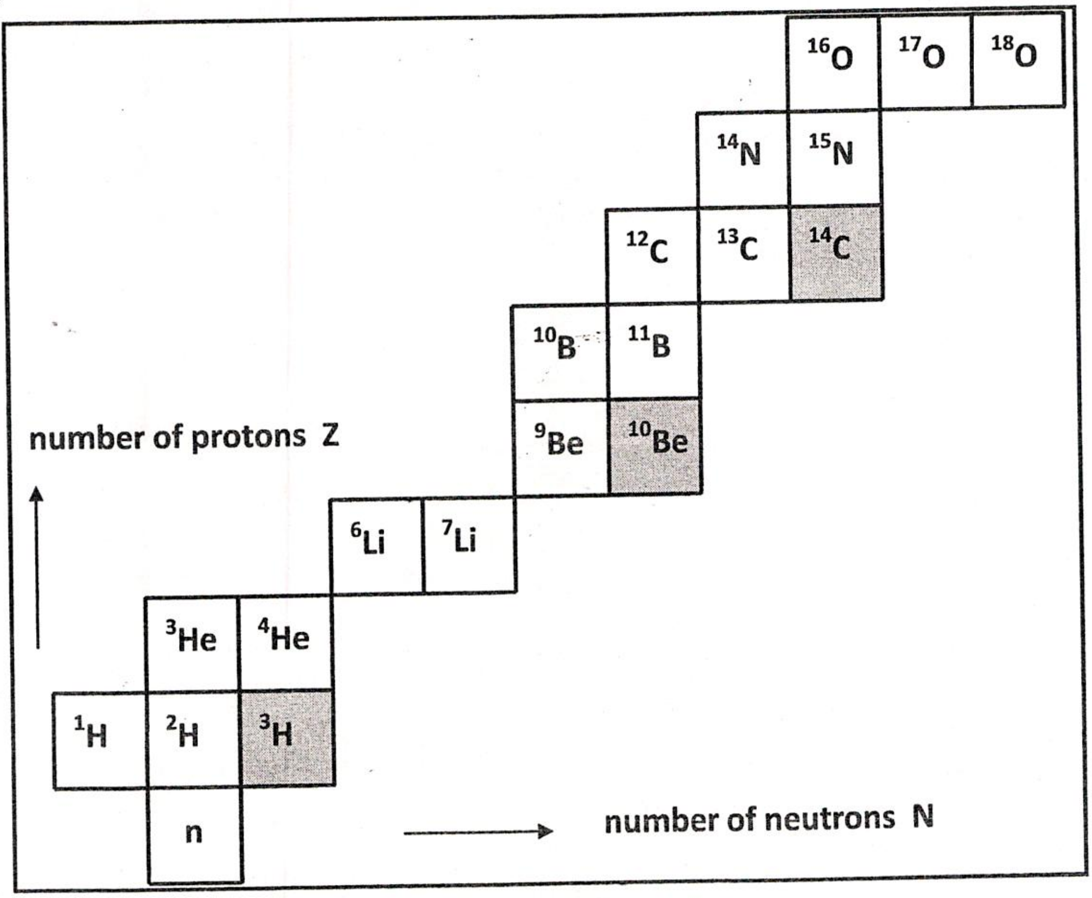
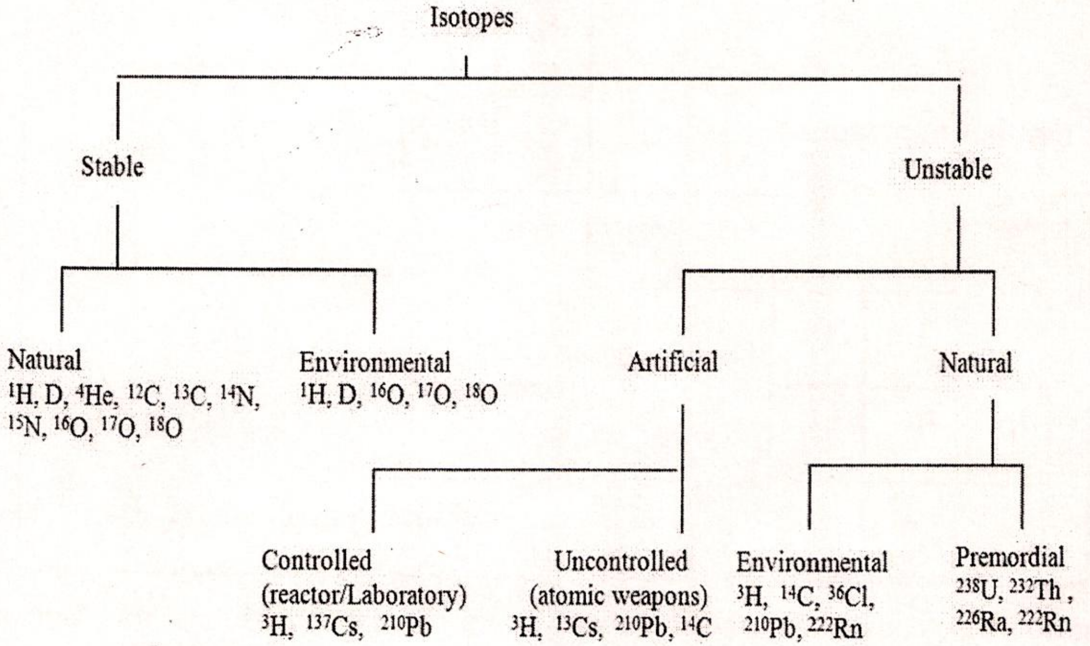


Figure - 1 Isotopes of an element (equal Z) are found in a horizontal row, isobars (equal A) along diagonal lines, isotones (equal N) in vertical columns. The natural radioactive isotopes of H, Be, and C are marked grey

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

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.



2.3 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. But for hydrological investigations, we talk much about hydrogen and oxygen stable isotopes. The basic fact-sheet of the isotopes of oxygen and hydrogen is given in *Table* - 1. The oxygen has three natural stable isotopes (^{16}O, ^{17}O, ^{18}O). The most abundant oxygen isotope (^{16}O) is a principal isotope i.e. formed during stellar evolution, directly by stars that were made exclusively of hydrogen. Most ^{16}O is thus, synthesized at the end of the helium fusion process in stars. Other isotopes of oxygen are secondary isotopes, meaning that their nucleosynthesis requires seed nuclei. The oxygen has fourteen radioactive isotopes but all of them decay in less than 123 seconds with ^{15}O having the longest half-life of 122.24 s; and ^{12}O having the shortest half-life 580×10^{-24} s. The hydrogen has two natural stable isotopes (^{1}H - Protium and ^{2}H - Deuterium) and one natural radioactive isotope (^{3}H - Tritium). There are synthetic radioactive isotopes of hydrogen ^{4}H to ^{7}H with half-lives in the range of 10^{-22} s.

Since oxygen and hydrogen together form a water molecule, isotopes of oxygen and hydrogen are collectively referred to as water isotopes in literature.

Table - 1

Fact sheet of isotopes of oxygen and hydrogen
(Compiled from (CRC, 1980) and other literature)

Name (Symbol)	**Oxygen (O)**	**Hydrogen (H)**
Atomic number	8	1
Standard Atomic Mass	15.9994(3) g/mol	1.00794(7) g/mol
Chemical Series	Non-metals, chalcogens	non-metals
Group, period, block	16, 2, p	1, 1, s
Electronic configuration	$1s^2\ 2s^2\ 2p^4$	$1s^1$
Stable isotopes and their Natural abundance	^{16}O: 99.762% ^{17}O: 0.038% ^{18}O: 0.200%	^{1}H: 99.985% ^{2}H (or D): 0.015%
Isotopic mass	^{16}O: 15.9949146 u ^{17}O 16.9991315 u ^{18}O 17.999160 u	^{1}H (Protium): 1.00782503 u ^{2}H (Deuterium): 2.01410177 u
Abundance ratio	$^{18}O/^{16}O = 0.002004171$ $= 2004.17\times 10^{-6}$	$^{2}H/^{1}H = 0.0001500225$ $= 150\times 10^{-6}$
Radioactive isotopes	Oxygen has fourteen radioactive isotopes from ^{12}O to ^{15}O and from ^{19}O to ^{28}O All radioactive isotopes have half-life less than 3 minutes	Hydrogen has one radioactive isotope ^{3}H (tritium) With half-life of 12.32(2) years, which [redacted] decays to ^{3}He.

2.3.1 Isotopic Molecular Species of Water (Isotopologues)

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 9 possible combinations of these 2 isotopes of hydrogen and 3 isotopes of oxygen are possible, which gives rise to following 9 isotopic molecular species, also referred to as water isotopologues. These 9 possible isotopic molecules of water are: (1) $^{1}H_2{}^{16}O$; (2) $^{1}H_2{}^{17}O$; (3) $^{1}H_2{}^{18}O$; (4) $^{1}HD^{16}O$; (5) $HD^{17}O$; (6) $HD^{18}O$; (7) $DD^{16}O$; (8) $DD^{17}O$; (9) $DD^{18}O$. The four most abundant isotopic molecules of water are given in Table - 2 along with their relative abundance and molecular masses.

Any water or vapour reservoir is basically composed of the above nine isotopologues, with minor variation in relative abundance of these isotopologues, caused by their differential partitioning in two phases during phase change processes within hydrological cycle. Consequently, different hydrological resources (vapour, rain, groundwater, river water, snow, and glacier) have only slightly different isotope abundance ratios ($^{18}O/^{16}O$, $^{17}O/^{16}O$ or D/H). For example, surface water of Arabian Sea may have $^{18}O/^{16}O$ ratio of 0.002006 and that of Himalayan snow may have this ratio of 0.001960. The differences in abundance ratios in various reservoirs are so small that expressing the isotopic composition of various reservoirs in terms of abundance ratios is not practical. Therefore, instead of expressing the isotopic compositions in terms of absolute abundance ratios, it is expressed in terms deviation of abundance ratio from an international standard reference material. The conventional way of expressing isotopic composition is discussed in the following.

Table - 2

The four most abundant isotopologues of water and their molecular masses

Isotopologue	$H_2{}^{16}O$	$H_2{}^{18}O$	$H_2{}^{17}O$	$HD^{16}O$	$D_2{}^{16}O$
Relative natural abundance	99.78%	0.20%	0.03%	0.0149%	0.022 ppm
Molecular mass	18	20	19	19	20

There are few other stable isotopes (^{3}He, ^{6}Li, ^{11}B, ^{13}C, ^{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 details of these isotopes with other useful information are given in Table - 3.

Table – 3

Stable isotopes with their natural abundance and reference standards used for ratio measurements

Isotope	Ratio	% natural	Reference	Commonly measured phases
^{2}H	$^{2}H/^{1}H$	0.015	VSMOW (1.5575x10^{-4})	H_2O, CH_20, CH_4, H_2, OH^- minerals
^{3}He	$^{3}He/^{4}He$	0.000138	Atmospheric He (1.3x 10^{-6})	He in water or gas, crustily fluids, basalt
^{6}Li	$^{6}Li/^{7}Li$	7.5	L-SVEC (8.32 x 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 x 10^{-2})	CO_2, carbonate, DIC, CH_4, organics
^{15}N	$^{15}N/^{14}N$	0.366	AIR N_2 (3.677x10^{-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 x 10^{-3})	H_2O,CH_20,CO_2,sulphates NO_3^-, carbonates, silicates OH^- minerals
^{34}S	$^{34}S/^{32}S$	4.21	CDT (4.5005 x 10^{-3})	Sulphates, sulphides, H_2S, S-organics
^{37}Cl	$^{37}Cl/^{35}Cl$	24.23	SMOC (0.324)	Saline waters, rocks, Saline waters, rocks,
^{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 compositions are normally expressed in δ–notation, as deviations of heavy to light isotopic ratios relative to an international standard of known composition, in units of parts per thousand or per mil (denoted as ‰). The isotopic composition in terms of δ values can be calculated using following equation.

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

In the above equation, R_{sample} and $R_{standard}$ denote the ratio of heavy to light isotope (e.g. $^{18}O/^{16}O$ or D/H) in the sample and standard respectively. The oxygen and hydrogen isotopic compositions are normally referred to as δD and $\delta^{18}O$. Both, δD and $\delta^{18}O$ values, are usually reported relative to an international standard reference material such as SMOW (Standard Mean Ocean Water; (Craig, 1961b) or the equivalent VSMOW (Vienna-SMOW; (Gonfiantini, 1978)).

The SMOW defined by Craig (1961b) never existed physically. It was hypothetical water calibrated relative to the isotopic content of NBS-1, a sample from the Potomac River catalogued by former NBS. The $^{18}O/^{16}O$ ratio in SMOW was 1.008 times that in NBS-1 and the $^{2}H/^{1}H$ ratio in SMOW was 1.050 times that in

NBS-1. Subsequently, the IAEA prepared the standard water from distilled sea water that was modified to have an isotopic composition close to SMOW. This reference was identified as VSMOW (Vienna Standard Mean Oceanic Water). The values of measured abundance ratios ($^2H/^1H$ and $^{18}O/^{16}O$) in SMOW and VSMOW are given in *Table – 4- 4.*

Table – 4

Measured abundance ratios in international standard reference material

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

To understand how δ values are calculated from ratios, one can do the following simple exercise. If the $^{18}O/^{16}O$ and $^2H/^1H$ ratios in a sample are given to be 0.0020104 and 0.00015735 respectively, its oxygen and hydrogen isotopic compositions ($\delta^{18}O$ = 2.59‰ and δD = 10.27‰) with respect to VSMOW can be easily calculated using Equation (1) and the isotopic ratios for VSMOW, as given in Table – 44.

In addition to the commonly used SMOW and VSMOW, there are two more international standard reference materials, namely, SLAP (Standard Light Antarctic Precipitation) and GISP (Greenland Ice Sheet Precipitation). The oxygen and hydrogen isotopic compositions of SLAP and GISP are given in Table - 5- 5.

Table - 5

The oxygen and hydrogen isotopic compositions of SLAP and GISP

Standard Light Antarctic Precipitation (SLAP)	Greenland Ice Sheet Precipitation (GISP)
$\delta^{18}O_{SLAP} = -55.50‰$ VSMOW	$\delta^{18}O_{GISP} = -24.76‰$ VSMOW
$\delta D_{SLAP} = -428.0‰$ VSMOW	$\delta D_{GISP} = -189.5‰$ VSMOW

2.3.3 Global Meteoric Water Line (GMWL)

Craig (1961a) for the first time showed that in spite of the great complexity in different components of the hydrological cycle, $\delta^{18}O$ and δD in fresh surface waters (representing precipitation) correlate on a global scale. The regression line between $\delta^{18}O$ and δD is referred to as meteoric water line. Craig's global meteoric water line (GMWL) defines the relationship between [illegible]O and [illegible]D in global meteoric water (i.e. derived from precipitation) as:

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

It must be noted that Craig's GMWL is based on fresh surface water and not the actual precipitation.

Improving the precision of the Craig's GMWL, Rozanski et al.(1993) compiled the isotope data of precipitation from 219 stations of the IAEA/WMO operated Global Network for Isotopes in Precipitation (GNIP). This refined relationship between ^{18}O and D in global precipitation (*Figure*) is given by:

$$\delta D=8.17(\pm 0.07)\times\delta^{18}O+11.27(\pm 0.65)\ (\text{‰ VSMOW}) \qquad (3)$$

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

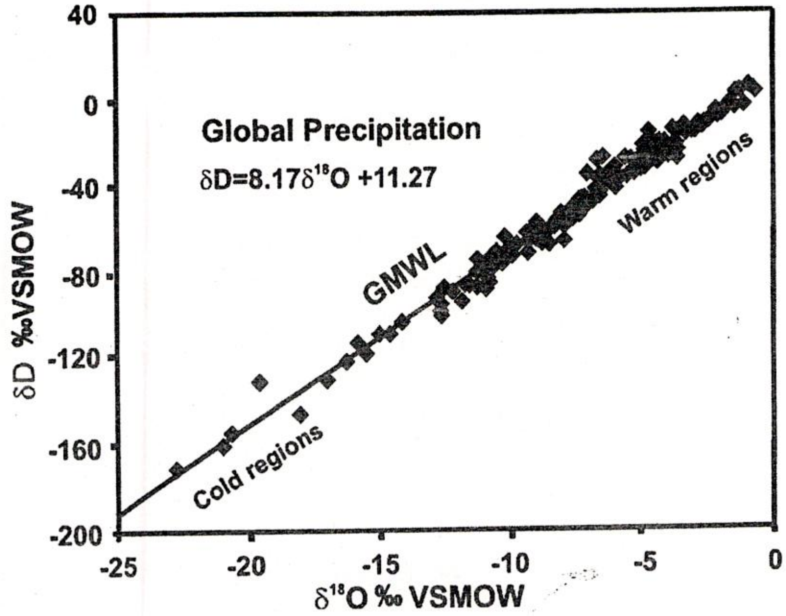


Figure - 2. The linear regression line between ■^{8}O and ■ of global precipitation samples. Data are weighted average annual values for precipitation monitored at 219 stations of IAEA/WMO global network. Redrawn from Rozanski et al (1993).

The GMWL indicates that the isotopic composition of meteoric waters behave in a fairly predictable fashion. The GMWL is average of many local or regional meteoric water lines, which may differ somewhat in slope and intercept from each other due to varying climatic and geographic parameters. A Local Meteoric Water Line (LMWL) can differ from global line in both slope and deuterium intercept. Nonetheless, GMWL provides a reference for interpreting the hydrological processes and provenance of different water masses.

There are specific reasons why the slope of the GMWL is around 8 and deuterium intercept is around 10. Further, the ■^{18}O- ■D regression lines for local precipitation (LMWL) and for any other H_2O reservoir can differ from GMWL in slope and intercept. This deviation of slope and intercept from that of GMWL provides important insights about the hydrometeorological processes operating in a given geographical region or at a given time.

In order to understand why the slope of GMWL is around 8 and what does it signify, the following exercise may be necessary.

Analogous to Equation $\delta = \delta_0 + \varepsilon \ln f$ (Rayleigh Equation), following two equations can be set up for oxygen and hydrogen isotopes.

$$\delta^{18}O = \delta^{18}O_0 + \left({}^{18}\varepsilon \times \ln f\right) \tag{4}$$

$$\delta D = \delta D_0 + \left({}^{2}\varepsilon \times \ln f\right) \tag{5}$$

By eliminating the term in f, following equation can be derived:

$$\delta D = \delta^{18}O \times \left(\frac{{}^{2}\varepsilon}{{}^{18}\varepsilon}\right) + \left[\delta D_0 - \delta^{18}O_0 \times \left(\frac{{}^{2}\varepsilon}{{}^{18}\varepsilon}\right)\right] \tag{6}$$

Equation (6) is a straight line (y = mx+c) in the coordinates of δ^{18}O and δD, which is nothing but the GMWL. It can be noticed by comparing Equations(2) or (3) with (6) that the slope of the regression lines correspond to ratio $\left({}^{2}\varepsilon / {}^{18}\varepsilon\right)$ i.e. the ratio in which ^{18}O and D are partitioned between vapour and liquid phases during condensation. From 6 it is seen that at 25°C temperature the ratio $\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}}\right)$ has a value of 8.1, nearest to the slope of GMWL. This, however, is just a close approximation. In fact, the ratio $\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}}\right)$ varies only narrowly between 8 at 30 °C and 9 at 0°C. Therefore, the slope 8 of GMWL only signifies the ratio of fractionation for hydrogen and oxygen under equilibrium condition which is around 8. It is important to understand that the slope 8 of GMWL does not signify condensation temperature of ~25°C, but it conveys that the condensation is largely under equilibrium.

The intercept of GMWL on the other hand signifies the non-equilibrium fractionation during formation of vapour. If only equilibrium fractionation was prevalent in nature, the intercept of the δ^{18}O- δD regression should have a value of 0. This is because, under equilibrium condition (such as during condensation of vapour in cloud), $\delta D_0 = \delta^{18}O_0 \times \left(\frac{{}^{2}\varepsilon}{{}^{18}\varepsilon}\right)$ and therefore, GMWL should have intercept value of 0 and should have passed through origin $\left[\delta D_0 - \delta^{18}O_0 \times \left(\frac{{}^{2}\varepsilon}{{}^{18}\varepsilon}\right) = 0\right]$.

However, the GMWL has an intercept of ~10, which signifies that original vapour parcel is formed under the condition in which $\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}}\right)$ is considerably different from 8, which means that kinetic fractionation is effective during evaporation from the oceans. The evolution of $\delta^{18}O$ and δD values of meteoric waters begins with evaporation from the oceans, where the rate of evaporation controls the water - vapour exchange and hence the degree of isotopic equilibrium. Increased rates of evaporation impart a kinetic or non-equilibrium isotope effect to the vapour. Kinetic effects are influenced by surface temperature, wind speed (shear at water surface), salinity and, most importantly humidity. At lower values of humidity, evaporation becomes an increasingly non-equilibrium process.

Table – 6

Values of $10^3\ln\alpha$, fractionation factor α, and enrichment ε calculated using Experimental Equations.

Temp. °C	10^3ln ■	■	■	10^3ln ■	■	■	$\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}}\right)$
0	11.75	1.0118	11.82	105.96	1.1118	111.78	9.0
5	11.19	1.0113	11.25	99.00	1.1041	104.06	8.8
10	10.67	1.0107	10.73	92.54	1.0970	96.96	8.7
15	10.18	1.0102	10.24	86.55	1.0904	90.40	8.5
20	9.73	1.0098	9.78	80.97	1.0843	84.34	8.3
25	9.30	1.0093	9.35	75.79	1.0787	78.74	8.1
30	8.90	1.0089	8.94	70.96	1.0735	73.54	8.0
40	8.17	1.0082	8.20	62.24	1.0642	64.21	7.6
50	7.51	1.0075	7.54	54.61	1.0561	56.13	7.3
60	6.93	1.0069	6.95	47.90	1.0491	49.07	6.9
70	6.40	1.0064	6.42	41.98	1.0429	42.88	6.6
80	5.92	1.0059	5.93	36.74	1.0374	37.42	6.2
90	5.48	1.0055	5.49	32.07	1.0326	32.59	5.9
100	5.08	1.0051	5.09	27.90	1.0283	28.29	5.5

2.3.3.1The Deuterium Excess (D-Excess)

The observed intercept of the GMWL was advantageously used by Dansgaard, (1964) to define a parameter (*d*-excess), which can be calculated for individual pair of ■O and ■D using following equation.

$$d\text{-excess} = \delta D - 8 \times \delta^{18}O(‰) \qquad (7)$$

The basic premise behind defining such a parameter is that whenever kinetic fractionation is involved, the net ratio of fractionation for deuterium to oxygen is different from 8. This is because, unlike equilibrium fractionation, the magnitude of kinetic fractionation for oxygen is more than that for hydrogen $\left[\frac{\Delta\varepsilon^{2}\mathrm{H}_{(\mathrm{bl\text{-}v})}}{\Delta\varepsilon^{18}\mathrm{O}_{(\mathrm{bl\text{-}v})}} \approx 0.88\right]$. Since ^{18}O is more fractionated compared to ^{2}H due to kinetic fractionation during evaporation, the liquid phase is relatively more enriched in ^{18}O compared to ^{2}H. Consequently, the resultant vapour is relatively more enriched in ^{2}H compared to ^{18}O, due to kinetic effects. These isotope imprints of kinetic evaporation can be easily detected in the *d*-excess. The average *d*-excess of meteoric waters is ~10‰. As a thumb rule, the *d*-excess of water decreases if it undergoes kinetic evaporation and consequently the *d*-excess of resultant vapour correspondingly increases.

It is must be understood that deuterium excess (*d*-excess) and the deuterium intercept of ■^{18}O- ■D regression lines are two different parameters and should not be confused while interpreting the data set. While deuterium intercept is the property of a dataset under investigation the *d*-excess can be calculated for individual pair of ■^{18}O- ■D. Therefore, based on *d*-excess, individual sample can be separately interpreted whereas intercept is not useful for individual sample. In fact, a set of samples defining a regression line intercept can have very different *d*-excess values.

The *d*-excess as defined above represents the excess ■ than 8 times ■^{18}O for any water or vapour sample. Since magnitude of equilibrium fractionation for D is about 8 times that for ^{18}O, any value of ■ in vapour, in excess of 8 times ■^{18}O signifies the effect of kinetic fractionation due to evaporation. As mentioned earlier, the intercept (~10‰) of GMWL also signifies the kinetic fractionation during evaporation but the difference between intercept and *d*-excess is that the intercept of a meteoric or any other water line is valid for an entire dataset whereas, the *d*-excess parameter can be calculated for a single water sample whose ■ and ■^{18}O values are known.

As the evaporation proceeds, because of relatively higher enrichment of ^{18}O in the residual water, the *d*-excess of the evaporating water body decreases and that of the resulting vapour increases. Therefore, if the original water was meteoric in origin, the residual water not only gets enriched in heavier isotopes but also shows progressively lower *d*-excess values as the evaporation proceeds i.e. its position on the δ^{18}O – δD plot will be below the Local Meteoric Water Line. The resulting vapour on the other hand shows the opposite effect. Further, since condensation is an equilibrium process (with slope ~8), it does not significantly alter the *d*-excess until significant rainout occurs from the same vapour parcel. Thus, *d*-excess provides an additional handle on identifying vapours of different histories and their mixing. Due to the effect of evaporation, most meteoric and subsurface processes shift the δ^{18}O–δD signatures of water to a position below the LMWL. It is rare to find precipitation or groundwater's that plot above the LMWL, i.e., showing higher *d*-excess. However, in low-humidity regions, re-evaporation of precipitation from local surface waters and/or soil water/ water table creates vapour masses with isotopic content that plots above the LMWL. If such vapours are re-condensed in any significant quantity before mixing with the larger tropospheric reservoir, the resulting rainwater will also plot above LMWL, along a condensation line with slope ~8. It is however, important to recall that recycling of water back to the atmosphere in the form of vapour from soil moisture by plant transpiration is a non-fractionating process that does not affect the *d*-excess.

A small fraction of rain percolates down through the soil layer eventually to become groundwater. For many ground waters, their isotopic composition has been shown to equal the mean weighted annual composition of precipitation (Bhattacharya et al., 1985; Douglas, 1997; Hamid et al., 1989; Krishnamurthy and Bhattacharya, 1991) (Rank et al., 1992). However, significant deviations from precipitation are also found in several cases. Such deviations from local precipitation are more pronounced in arid zones due to extensive evaporation from the unsaturated zone or even evaporative losses from water table (Allison et al., 1984; Dincer et al., 1974). Considering that only a small percentage of precipitation actually reaches the water table in most situations, the meteoric signal in ground water can get significantly modified. Isotope variations in precipitations get attenuated and seasonal biases in recharge are imparted to the newly formed ground water. This bifurcation of the hydrological cycle between precipitation and surface water on one hand and groundwater on the other hand, ends where groundwater discharges and rejoins surface runoff in streams and rivers. Thus, oxygen and hydrogen isotopes can play a significant role in quantifying relative contribution of groundwater to stream flow and in understanding hydraulic processes in a catchment area.

2.3.3.2 *Interpretative Significance of Slope, Intercept and d-excess*

In order to understand the interpretative significance of various isotopic parameters it is necessary to visualize how various theoretical concepts and equations discussed in the forgoing can be practically used and how it would manifest in the data under a given hypothetical condition.

For example, let us begin with tropical ocean surface water with isotopic composition of ■O = 0‰ and ■ = 0‰. This is indeed a very close approximation to real situation. Suppose evaporation is taking place at 25 °C temperature and under the relative humidity of 85%. Using Equations **Error! Reference source not found.** and **Error! Reference source not found.** one can calculate ^{18}■and ^{2}■values (9.37‰ and 79.3‰ respectively) for 25 °C. Using Equations **Error! Reference source not found.** and **Error! Reference source not found.** one can also calculate ■^{18} ■and ■^{2} ■values (2.13‰ and 1.88‰ respectively) for relative humidity of 85%. The effective total fractionation (■ + can be calculated as the sum of the two types of fractionations, as given in the RHS of Equation **Error! Reference source not found.** . Thus the approximate isotopic composition of ocean vapour can be estimated as ■O = -11.5‰ and ■D = -81.21‰. Using the Rayleigh distillation equation in ■ notations, as given in Equation **Error! Reference source not found.**, one can compute the evolution of the isotopic composition of vapour as it rains out progressively. Correspondingly, one can also estimate the instantaneous isotopic composition of rain in equilibrium with vapour at each stage. The evolution of isotopic composition of vapour and rain, as a function of fraction of original vapour remaining at successive stage of rainout, is shown in *Figure* 3. Important point to be noticed here is that with successive rainout, both the vapour and the rain diminishes in its heavier isotope content as reflected in progressively decreasing ■^{18}O and ■D values. It is also seen that the *d*-excess also decreases with progressive rainout.

This example is just for visualization of isotopic variations. In reality, situations are more complex than simple addition of equilibrium and kinetic fractionation. Formation of atmospheric vapour is a more complex process involving mixing between evaporated water vapour and residual atmospheric water vapour following condensation and rain over sea (Craig and Gordon, 1965). According to the Craig and Gordon (1965) model mass is conserved such that net evaporation equals net precipitation and the mean isotopic composition of outgoing oceanic vapour equals the global mean for precipitation.

As an example, the effect of relative humidity on isotopic evolution of water during evaporation is shown in *Figure* – 44. The isotopic evolution of a hypothetical water sample (■^{8}O = –4‰ and ■D = –22‰; *which is also the mean global precipitation value according to Craig and Gordon (1965) Model*) on the GMWL, as it evaporates under two different Rh regimes (100% and 10%), but at the same temperature (30°C), can be computed. As shown in Figure 4, the water evolves along a line with very low slope and intercept values in case of 10% Rh. However, in case of 100% Rh, water evolves along a line which has slope value slightly greater than GMWL. This simple exercise conveys why lower slope value of any data set is usually ascribed to evaporation.

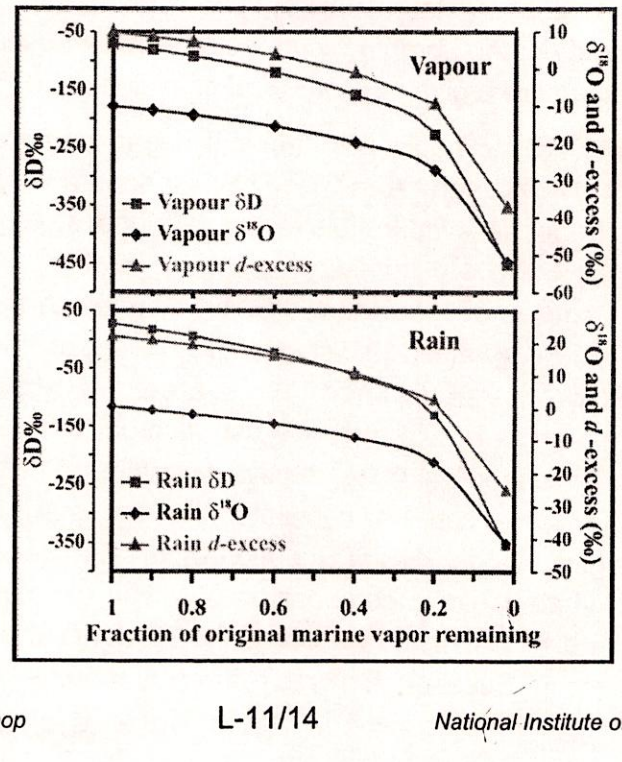


Figure – 3: Isotopic evolution of vapour and rain as a function of fraction of original marine vapour remaining at successive stages of rainout.

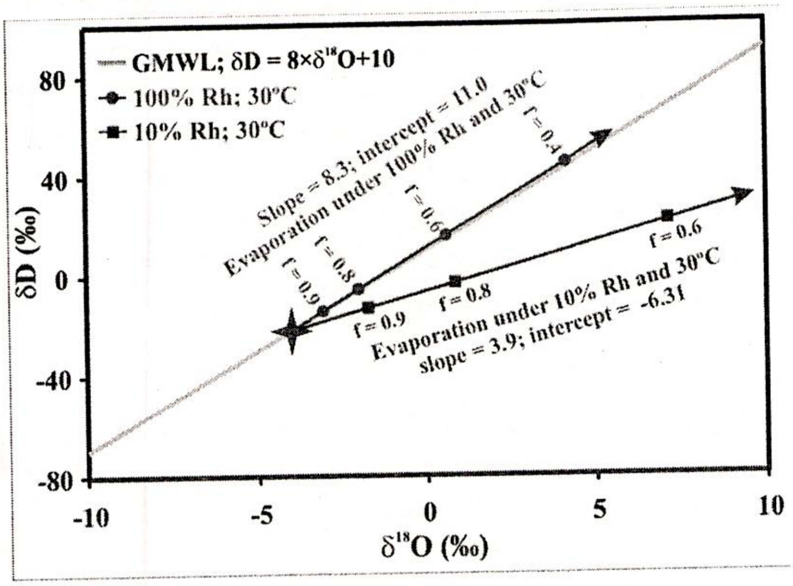


Figure – 4: Isotopic evolution of water (δ^{18}O = –4‰ and δD = –22‰ under different relative humidity conditions but at the same temperature.

These simple fractionation processes are at the core of some of the interpretative aspects.

The slope and intercept of δ^{18}O- δD regression lines for a set of samples and *d*-excess of individual water sample can provide some useful hydrological insights. If the slope of δ^{18}O-δD regression line for a set of samples is less than that of GMWL it is an indication that the water under consideration has undergone certain degree of evaporation. Lower the slope greater the evaporation. The intersection point of LMWL and GMWL is indicative of the average isotopic composition of precipitation at that location. Intersection point of LMWL and δ^{18}O- δD regression line for groundwater is indicative of the average isotopic composition of the surface water from which the groundwater is recharged.

The intercept of the δ^{18}O-δD regression line can provide useful hydrological insights, only if the slope of the regression line is ~8. If the slope is much different from ~8 the intercept can not be assigned any interpretative significance. If the slope of LMWL is ~8 and intercept is >10‰ it is an indication that precipitation is derived from vapour which is produced by kinetic evaporation under considerably lower relative humidity. For example, the Eastern Mediterranean Water Line (EMWL) defined by Gat and Carmi (1970) has slope = 8, but intercept = 22.

The *d*-excess is the most useful parameters in deriving hydrological insights from water isotope data. Lower than average *d*-excess of a rainwater sample could be due to evaporation from falling raindrops or it could as well signify considerable rainout from original marine vapour parcel. Higher (than average) *d*-excess in a particular rainwater sample signifies either formation of marine vapour parcel under lower (than average) relative humidity (for e.g. from Mediterranean Sea) or contribution of recycled vapour from continental areas for that particular event. It may be possible to rule out one the two possible interpretations in case of both high or low *d*-excess values if the *d*-excess value of a sample is interpreted in combination with $\delta^{18}O$ or δD values. For example, if lower *d*-excess values are associated with significantly higher $\delta^{18}O$ values, it indicates the evaporation from falling rain drops because, as discussed earlier, evaporation causes decrease in *d*-excess and increase in $\delta^{18}O$ or δD values. On the other end, considerable rainout from a given vapour parcel results in progressive decrease in both *d*-excess and $\delta^{18}O$.

2.3.4 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.

(i) Latitude Effect:

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

$\delta^{18}O = 0.695\ T_{annual} - 13.6$™ SMOW ; $\delta D = 5.6\ T_{annual} - 100$™ SMOW (8)

$\delta^{18}O = (0.338 \pm 0.028)\ T_{monthly} - 11.99$™ VSMOW (9)

On average there is a 1™ decrease in average $\delta^{18}O$ 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. $\delta^{18}O$ 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.

(ii) Continental Effect

Precipitation depletes in heavier isotopes of water molecules as clouds move away from the coastal parts. On average, $\delta^{18}O$ deplets about -2 ‰ per 1000km from seacoast.

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

(iii) 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, $\delta^{18}O$ 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.

(iv) Seasonal Effects

Greater seasonal extremes in temperature generate strong seasonal variation in isotopes of precipitation. These variations in $\delta^{18}O$ and $\delta^{2}H$ give us an important tool to determine rates of groundwater circulation, watershed response to precipitation, and the time during the year when most recharge occurs. 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.

(v) Evaporation effect

Evaporated water bodies and waters exposed to vapor loss such as lakes, wetland waters, running waters, reservoirs and oceans tend to enrich in their heavy isotope content with respect to the vapor derived out of them. Residual waters that have undergone evaporation plot along a local evaporation line whose slope vary between 4.6 and 5.6 (fig. 3). Another form of evaporation effect results from evaporation of rainfall while the rain droplets are making their way to the ground. In arid and semi arid environments significant evaporation of rain droplets in dry atmosphere can take place resulting in enrichment of rainwater's and deviation from the global meteoric water line.

(vi) Amount effect

Heavy rainfalls tend to be depleted in heavy isotopes compared to lighter isotopes. This is related to several factors principally the limitation of evaporative fractionation of rain droplets in case of heavy rainfalls.

(vii) Continentality effect

As a vapor mass moves from its source region across a continent, its isotopic composition evolves more rapidly due to topographic effects and the temperature extremes that characterize continental climates. Continental stations are characterized by strong seasonal variations in T, which is a reflection of distance from moderating marine and latitude. Coastal precipitations are isotopicallyenriched, while the colder inner continental regions receive isotopically depleted precipitation with strong seasonal differences.

(viii) Paleo-climatic effect

Given the good correlation between isotopes in precipitation and groundwater, climate change should be recorded in fossil or paleogroundwaters. Temperate climates have experienced significant changes in temperature since late Pleistocene time. Such climate changes are manifested by a shift in the stable isotope content of precipitation, and in deuterium excess. This paleoclimatic effect is one the most important tools in identifying paleogroundwater. Late Pleistocene paleogroundwaters from temperate regions will be isotopically depleted with respect to modern waters and shifted along the GMWL towards negative values. The paleoclimatic effect in arid regions is manifested by depletion in stable isotopes with respect to modern waters. In arid regions like the Eastern Mediterranean and North Africa, the modern MWL is characterized by a deuterium excess value of 15 to 30‰. However, in the past, humid climates groundwaters tend to plot on or even below the GMWL.

(viii) Geothermal $\delta^{18}O$ exchange (negative and positive oxygen shifts)

Silicates rocks are natural reservoirs for heavy isotopes of oxygen compared to atmospheric and hydrologic waters. In geothermal systems interaction of rock and water at higher temperature results in release of heavier isotopes of oxygen from the rock and sink of lighter isotopes until equilibrium is reached. This will lead to enrichment of geothermal waters with respect to their heavy isotopes. On the other hand in CO_2 gas reach geothermal systems exchange of oxygen isotopes of water with relatively depleted oxygen isotope of CO_2 leads to depletion of heavy isotopes in waters. Both exchange processes does not affect the hydrogen isotope ratio. Isotope exchange accompanying rock-water interaction in geothermal waters lead to a process called positive or negative oxygen shift.

2.4 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 ^{3}H or T is still widely used for various hydrological studies. There are other varieties 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 - 7 with their half life, decay mode, principal sources and commonly measured phases while other categories of radioisotopes are shown in figure 5 and 6.

Table – 7

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
^{3}H	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.

2.4.1 *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.

2.4.2 *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.

2.4.3 *Radioactive Isotope of Hydrogen*

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

$$^{14}N \rightarrow {}^{12}C + {}^{3}H$$

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

$$^{3}H \rightarrow {}^{3}He + \beta^{-}$$

with $E_{\beta max}$ = 18 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 ^{3}H concentration in precipitation was probably about 5 TU, which is equivalent to a specific activity of about 0.6 Bq/L (Roether, 1967).

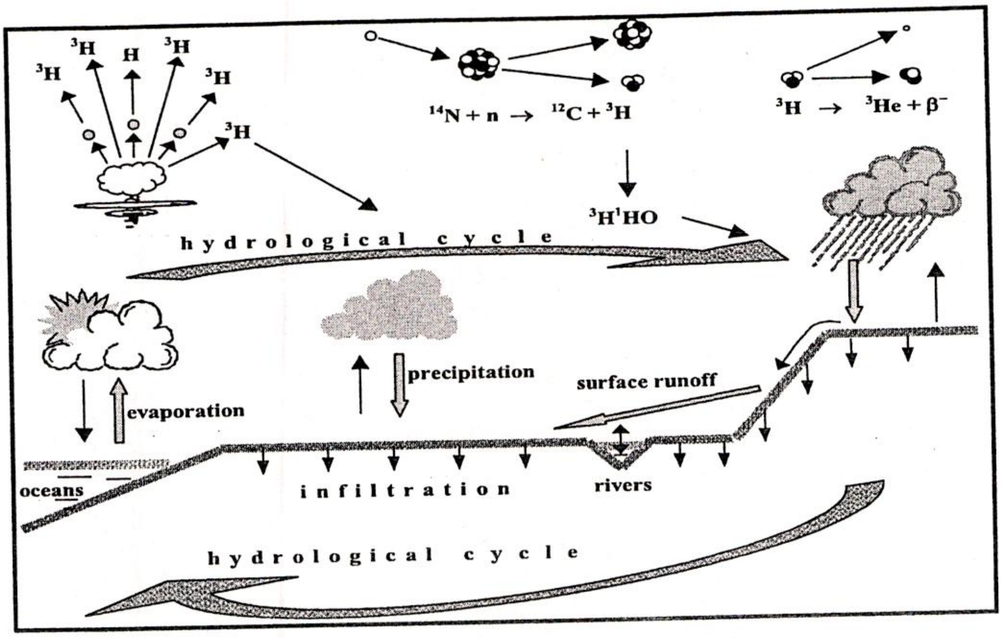


Figure - 5: Origin and distribution of ^{3}H in nature. Contrary to ^{14}C, the turnover of ^{3}H is very fast, except where it is fixed in glacier ice or groundwater.

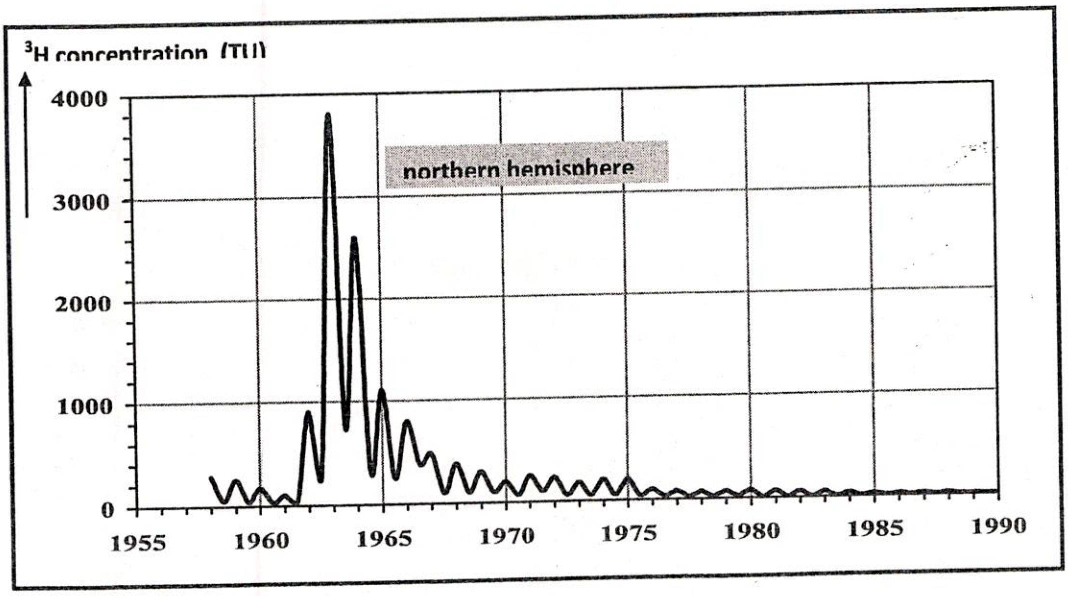


Figure – 6: Smoothed curve representing the average ^{3}H content of precipitation over the continental surface of the Northern hemisphere

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.

2.4.4 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..

$$^{14}N + n \rightarrow {}^{14}C + p$$

Thermal neutrons required are produced by reactions between very high-energy primary cosmic ray protons and molecules of the atmosphere. ^{14}C thus formed very soon oxidises to ^{14}CO, and ultimately to $^{14}CO_2$ which mixes with the inactive atmospheric CO_2 Exchange with oceanic dissolved carbon (primarily bicarbonate), most $^{14}CO_2$ 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. ^{14}C decays according to: $^{14}C \rightarrow {}^{14}N + \beta^-$ with a maximum β^- energy of 156 keV and a half-life of 5730 ± 40 years (Godwin, 1962). The origin and distribution of ^{14}C in nature is shown in figure 5 and 6.

Originally the half-life was thought to be 5568 years, right half-life, because of the natural variations in the ^{14}C content of atmospheric CO_2 during geologic times and deviating from the present. These errors were even larger. Nowadays the ^{14}C *calibration*, based on the known ^{14}C content of tree rings with exactly known age, removes both errors at once.

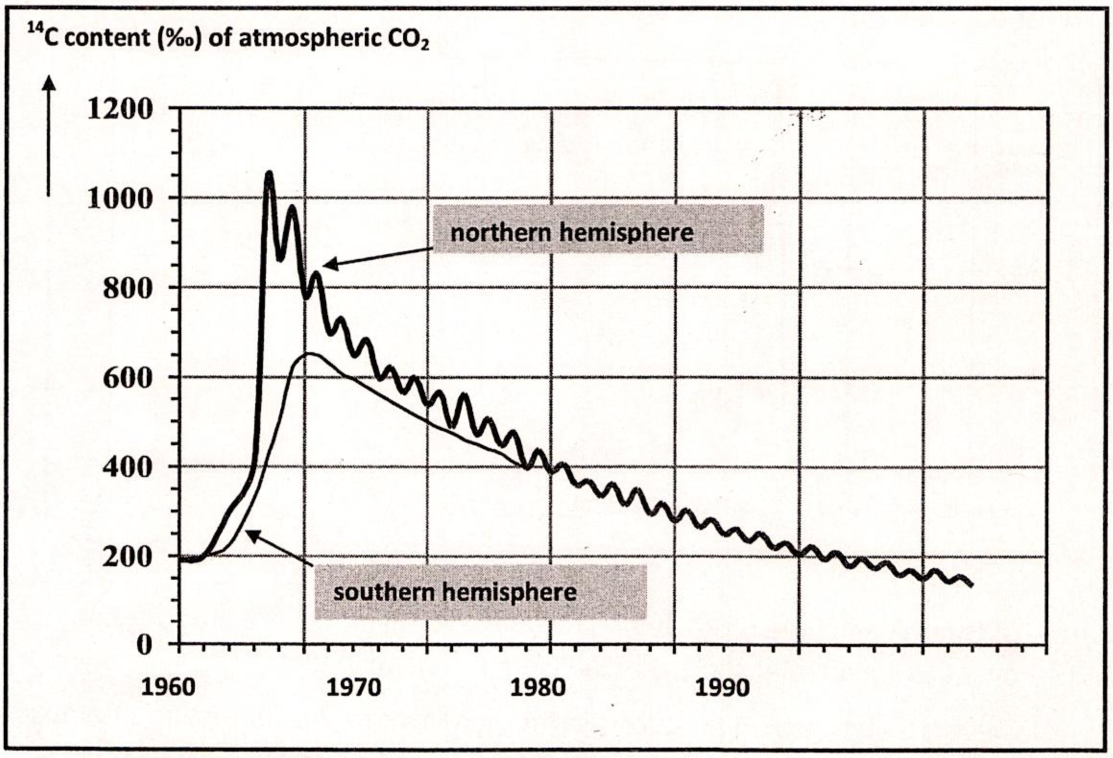


Figure – 7: Origin and distribution of ^{14}C in nature

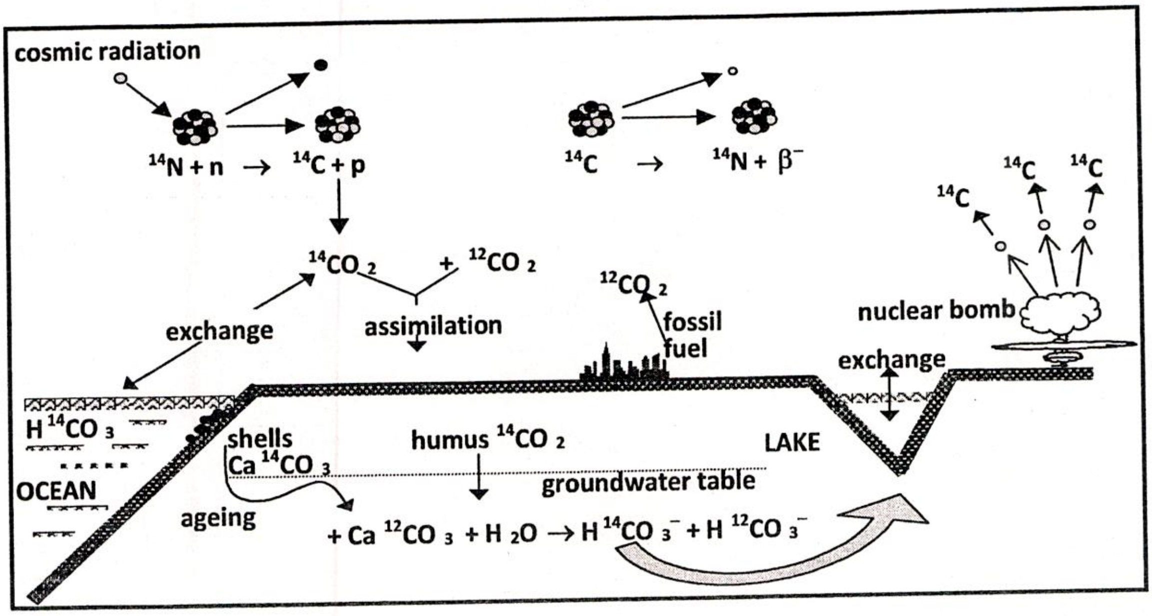


Figure – 8: Curve representing the natural ^{14}C **northern hemisphere** content of atmospheric CO_2 (data for Nordkapp, Norway, representative for the northern hemisphere)

2.5 Environmental Isotopes

Environmental isotopes, both stable and radioactive (unstable), occur in environment in varying concentrations with respect to place and time over which the investigator has no direct control. The most commonly used environmental stable isotopes are Deuterium (D), Oxygen-18 (^{18}O), Carbon-13 (^{13}C) and radioisotopes Tritium (^{3}H) 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 ^{3}H 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. The applications of the isotopes more commonly employed in hydrology are the stable isotopes of the water molecule i.e., deuterium and oxygen-18 and the radioactive isotopes, tritium and carbon-14, given in table Table - 8.

3. Applications of Isotopes in Hydrology

Techniques using "environmental" isotopes are among those that meteorologists, hydrologists, and hydrogeologists use in the study of water. Study of the isotopes of oxygen and hydrogen in water, or of elements contained in dissolved

Table – 8

Application of isotopes in groundwater hydrology

Isotope characteristics and application	**Isotope**			
	Hydrogen		**Oxygen**	**Carbon**
Isotope	^{2}H (Deuterium)	^{3}H (Tritium)	^{18}O (Oxygen-18)	^{14}C (Carbon-14)
Half Life	Stable	12.3 yrs	Stable	5730 yrs
Recent recharge,		x		
Dating, residence time				x
Origin	x		x	
Movement	x		x	
Source of Precipitation	x	x	x	

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 established conventional hydrological ones, so as to provide additional and valuable information for solving many 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.

3.1 Surface Water

- 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

3.2 Ground Water

- Soil moisture variation, movement and recharge
- Origin
- Age
- Distribution
- Occurrence and recharge mechanism
- Interconnections between groundwater bodies
- Identification of recharge sources and areas
- Data on lithology, porosity and permeability of aquifers
- Pollution source and mechanism

3.3 Meteorological

- Variability of environmental conditions
- Movement of clouds and variability in precipitation
- Environmental pollution and mechanism

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 karsts 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 ^{3}H 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.

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