Chapter 4
Environmental Isotopes in Groundwater Applications

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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 largely. Wherever people live, they must get a clean and continuous water supply as a primary requirement. The assessment of quality, supply and renewal of resources of water is a well known problem, but it is becoming critical with the growth of population and rapid industrialization.

Water resources management, to sustainably meet the current and future water demands, needs to have a comprehensive assessment of the quality and quantity of the resources. The assessment of both quality and quantity of water, though well recognised, is hampered due to non-availability of detailed hydrological information and understanding. Generally in our country, the available hydrological data/information is either incomplete or has wide gaps in it. These gaps are particularly acute with respect to groundwater resources.

It is estimated that more than 97% of the Earth's available water is saline and out of the rest 3% fresh water, 97% is located underground. Though groundwater is a vital resource, yet it is often poorly understood and poorly managed.

Stable and radioactive isotope techniques are cost effective tools in hydrological investigations and assessments, and are critical in supporting effective water management. Isotopes help 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 has greatly increased 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

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have the same behaviour as water, enable exact recording of phenomena affecting the occurrence and movement of water in all its forms. 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 nuclear methods have been evolved. It is, therefore, now very easy to solve many hydrological problems related to planning of water resources, agriculture, industry and habitation using isotope techniques, which were very difficult, sometimes impossible to tackle in the past.

The use of isotopes in hydrology was introduced in early 1950's with the application of radiocarbon dating technique for determining the age of groundwater. After that, the application of isotopes is being successfully used to find the effective solutions of various hydrological problems in the developed countries. Later on the International Atomic Energy Agency (IAEA), Vienna, an independent intergovernmental organisation within the United Nations system, took a leading role in the development and use of isotope techniques in hydrology. Presently, isotope techniques are used frequently in the developed countries while their use in the developing counties is increasing slowly.

In groundwater, isotopes are commonly employed to investigate:

- Sources and mechanisms of groundwater recharge;
- Groundwater age and dynamics;
- Interconnections between aquifers;
- Interaction between surface water and groundwater;
- Effectiveness of artificial recharge measures;
- Groundwater salinization; and
- Groundwater pollution.

2 Isotopes

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., ${}_{1}^{1}H_{0}$, ${}_{1}^{2}H_{1}$, and ${}_{1}^{3}H_{2}$ (Fig. 4.1). 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, and carbon has three isotopes ^{12}C, ^{13}C and ^{14}C.

There are two more terms i.e., isobars and isotones that are used to differentiate and distinguish the atoms of different elements showing similarities in physical and chemical properties. Isobars have same atomic weight ($Z + N$), i.e., ${}^{76}Ce_{32}$ and ^{76} Se_{34}; or ${}^{58}Fe_{26}$ and ${}^{58}Ni_{27}$, but different atomic number. Isotones have same number of neutrons but different atomic number, i.e., ${}^{37}Cl_{17}$ and ${}^{39}K_{19}$ (both have 20 neutrons in the nuclei). Electronic configurations of atom of some light elements are shown in Fig. 4.2.

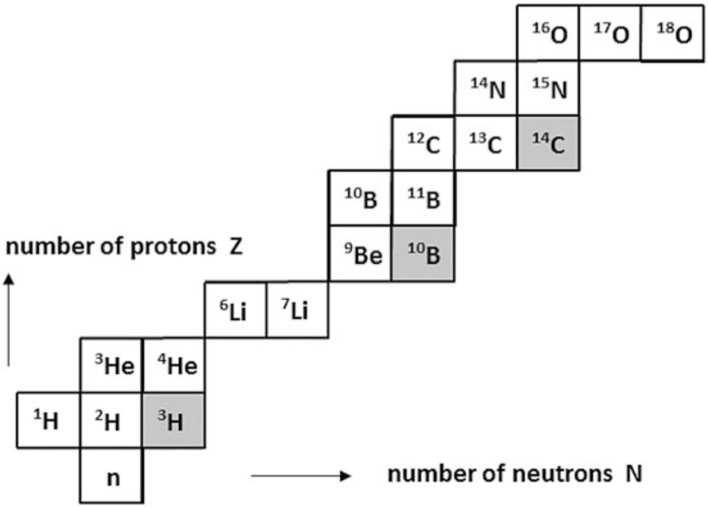


Fig. 4.1 The isotopes of an element (equal *Z*) are found in a horizontal row, isobars (equal *A*) along diagonal lines, isotones (equal *N*) in vertical columns. The natural radioactive isotopes of H, Be, and C are marked grey

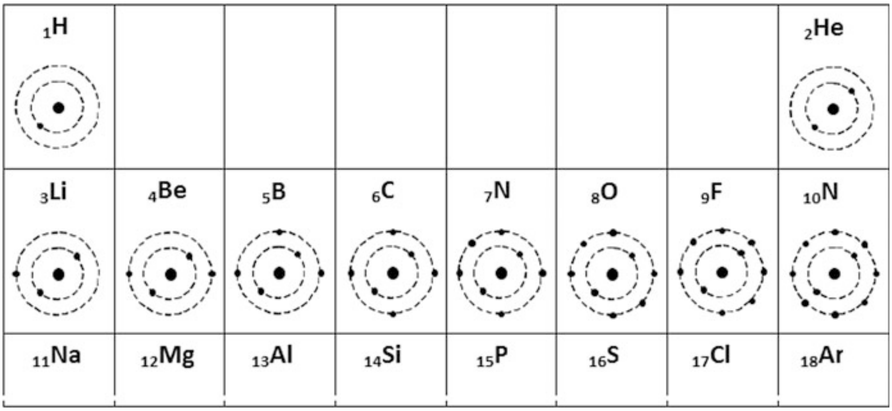


Fig. 4.2 Electronic configurations of atoms of various light elements

2.1 Classification of Isotopes

Isotopes are classified in two important categories: (i) stable isotopes and (ii) unstable isotopes.

Isotopes are also 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. Both, stable

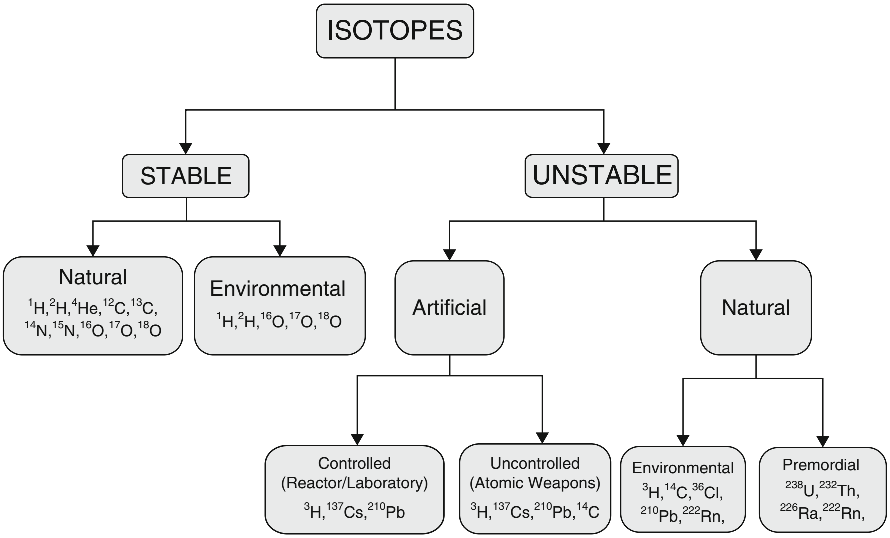


Fig. 4.3 Classification of isotopes

and radioactive isotopes occur naturally and some of the radioactive isotopes are produced artificially.

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 becoming the part of hydrological cycle are safe in normal conditions and do not pose any threat to human health.

Classification scheme of various isotopes is shown in Fig. 4.3.

2.2 *Stable Isotopes*

Stable isotopes of an element are the atoms, which do not decay with time or take infinite time to decay. The atoms are satisfied with the present arrangement of proton, neutron and electron. 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 ^{2}H, ^{18}O and ^{13}C.

As water molecule is made up of two hydrogen atoms and one oxygen atom, therefore, isotopically 18 types of water are possible, out of which $^{1}H^{1}H^{16}O$, $^{1}H^{1}H^{18}$

Table 4.1 Stable isotopes with their natural abundance and reference standards used for ratio measurements

Isotope	Ratio	% natural abundance	Reference (abundance ratio)	Commonly measured phases
^2H	$^2H/^1H$	0.015	VSMOW (1.5575×10^{-4})	H_2O, CH_2O, CH_4, H_2, OH^- minerals
^3He	$^3He/^4He$	0.000138	Atmospheric He (1.3×10^{-6})	He in water or gas, crustal fluids, basalt
^6Li	$^6Li/^7Li$	7.5	L-SVEC (8.32×10^{-2})	Saline waters, rocks
^{11}B	$^{11}B/^{10}B$	80.1	NBS 951 (4.04362)	Saline waters, clays, borate, rocks
^{13}C	$^{13}C/^{12}C$	1.11	VPDB (1.1237×10^{-2})	CO_2, carbonate, DIC, CH_4, organics
^{15}N	$^{15}N/^{14}N$	0.366	AIR N_2 (3.677×10^{-3})	N^2, NH_4^+, NO_3^-, N- organics
^{18}O	$^{18}O/^{16}O$	0.204	VSMOW (2.0052×10^{-3}) VPDB (2.0672×10^{-3})	H_2O, CH_2O, CO_2, sulphates; NO_3^-, carbonates, silicates OH^- minerals
^{34}S	$^{34}S/^{32}S$	4.21	CDT (4.5005×10^{-3})	Sulphates, sulphides, H_2S, S-organics
^{37}Cl	$^{37}Cl/^{35}Cl$	24.23	SMOC (0.324)	Saline waters, rocks, evaporites, solvents
^{81}Br	$^{81}Br/^{79}Br$	49.31	SMOB	Developmental for saline waters
^{87}Sr	$^{87}Sr/^{86}Sr$	$^{87}Sr = 7.0$ $^{86}Sr = 9.86$	Absolute ratio measured	Water, carbonates, sulphates, feldspar

O, $^1HD^{16}O$, $^1HD^{18}O$, $^1H^1H^{17}O$ and $^1HD^{17}O$ are most abundant. The natural occurrence of very abundant types of water molecules is given below:

$$^1H_2{}^{16}O^{\sim}9,99,680\ \text{ppm}\ (99.9680\%)$$
$$^1HD^{16}O^{\sim}320\ \text{ppm}\ (0.032\%)$$
$$^1H_2{}^{18}O^{\sim}2,040\ \text{ppm}\ (0.204\%)$$

Natural abundance and reference standards of some important isotopes used in hydrological studies are shown in Table 4.1.

2.2.1 Isotopic Notations and Measurements

Stable isotopes are measured in terms of abundance ratios i.e. atomic mass of heavy atom to the atomic mass of light atom. For example, heavy water ($^2H_2{}^{16}O$) has a mass of 20 compared to normal water $^1H_2{}^{16}O$ which has a mass of 18. Similarly, heavier stable molecule of water $^2H_2{}^{18}O$ has a mass 22. This is because of the variation in the number of neutrons. The absolute abundance of isotopes is not

Table 4.2 Oxygen and hydrogen δ-values of the major water reference material

Name	Material	Status	Distribution	$\delta^{18}O$[‰]	$\delta^{2}H$[‰]
VSMOW	Water	CM	IAEA, NIST	0	0
SLAP	Water	CM	IAEA, NIST	−55.5	−428
GISP	Water	RM	IAEA, NIST	−24.78 ± 0.08 Gonfiantini et al. (1995)	−189.73 ± 0.87

usually measured in natural waters and also in other materials. 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:

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

where R's are the ratios of the $^{18}O/^{16}O$ 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, $\delta\,(‰) = \delta \times 1000$.

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

If the δ value is positive, it refers to the enrichment of the sample in the heavy-isotope species with respect to the reference and negative value corresponds to the sample depleted in the heavy-isotope species.

The reference standards normally considered are SMOW (Standard Mean Oceanic Water) and VSMOW (Vienna Standard Mean Ocean Water). VSMOW has the same ^{18}O content as defined in SMOW but its D-content is 0.2‰ lower. Other standards for calibration of oxygen and hydrogen isotopes are SLAP (Standard Light Antarctic Precipitation), and GISP (Greenland Ice Sheet Precipitation). The isotopic values of the standards are given in Table 4.2.

2.3 Radioisotopes

The 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 continues 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.

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

Table 4.3 Various radioisotopes with their half-life, decay mode and principal sources

Isotope	Half-life (years)	Decay model	Principal sources
^{3}H	12.43	β^-	Cosmogenic, weapons testing
^{14}C	5730	β^-	Cosmogenic, weapons testing
^{36}Cl	301,000	β^-	Cosmogenic and subsurface
^{39}Ar	269	β^-	Cosmogenic and subsurface
^{85}Kr	10.72	β^-	Nuclear fuel processing
^{81}Kr	2,10,000	ec	Cosmogenic and subsurface
^{129}I	1.6×10^7	β^-	Cosmogenic, subsurface, nuclear reactors
^{222}Rn	3.8 days	α	Daughter of ^{226}Rn in ^{238}U decay series
^{226}Ra	1600	α	Daughter of ^{230}Th in ^{238}U decay series
^{230}Th	75,400	α	Daughter of ^{234}U in ^{238}U decay series
^{234}U	2,46,000	α	Daughter of ^{234}Pa in ^{238}U decay series
^{238}U	4.47×10^9	α	Primordial

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

hydrogen (tritium) in the form of water molecule ($^{3}H_2O$) 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 are part of hydrological cycle, are used. This has reduced the use of artificial radioisotopes tremendously, as the radioisotopes are considered to be a health hazard both by the user as well as by the public.

The details of various radioisotopes with their half-lives, decay mode, principal sources etc. are given in Table 4.3.

2.4 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 (^{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 year) is between that of ^{3}H and ^{14}C. 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.

Environmental tritium is used to date the groundwater upto 50 years, while carbon-14 is used upto the age of 40,000 years.

3 Fractionation of Stable Isotopes

Among the different properties of isotopic substances, one that is of particular importance for hydrologists is their slightly different physico-chemical behaviours that lead to isotopic fractionation effects. Isotopic fractionation is the basis for its utilization in stable isotope geochemistry, isotope geology, biogeochemistry, paleo-oceanography and others. For instance, the analysis of the ratio of stable oxygen isotopes in calcium carbonate, secreted by organisms like belemnites, mollusks and foraminifera and buried in deep-sea sediments, has permitted the reconstruction of paleo-temperatures for the last 150 million years or so (McCrea 1950; Epstein et al. 1953; Emiliani 1966).

3.1 Isotope Fractionation

According to classical chemistry, the chemical characteristics of isotopes, or rather of molecules that contain different isotopes of the same element (such as $^{13}CO_2$ and $^{12}CO_2$) are same. Largely this is true; however, if sufficiently accurate measurement are made using modern mass spectrometers, tiny differences in chemical as well as physical behaviour of so-called *isotopic molecules* or *isotopic compounds* can be observed. Differences in chemical and physical properties arising from variations in atomic mass of an element are called "*isotope effects*". This phenomenon can be observed as a result of change in isotopic composition by transition of a compound from one state to another (liquid water to water vapour), or by conversion of one compound into another compound (carbon dioxide into plant organic carbon), or due to difference in isotopic composition between two compounds in chemical equilibrium (dissolved bicarbonate and carbon dioxide).

It is well known that the electronic structure of an atom of an element essentially determines its chemical behaviour, whereas the nucleus is more or less responsible for its physical properties. Because all isotopes of a given element contain the same number and arrangement of electrons, a far-reaching similarity in chemical behaviour is the logical consequence. However, this similarity is not unlimited; certain differences exist in physicochemical properties due to mass differences. The replacement of any atom in a molecule by one of its isotopes produces a very small change in chemical behaviour. The addition of one neutron can, for instance, depress the rate

Table 4.4 Characteristic of physical properties of $^{1}H_2{}^{16}O$, $^{2}H_2{}^{16}O$ and $^{1}H_2{}^{18}O$

S. No.	Property	$^{1}H_2{}^{16}O$	$^{2}H_2{}^{16}O$	$^{1}H_2{}^{18}O$
1	Density (20 °C in g cm^{-3})	0.997	1.1051	1.1106
2	Temperature of greatest density (°C)	3.980	11.240	4.300
3	Melting point (760 Torr, in °C)	0.00	3.810	0.280
4	Boiling point (760 Torr, in °C)	100.00	101.420	100.140
5	Vapour pressure (at 100 °C, in Torr)	760.00	721.600	
6	Viscosity (at 20 °C, in centipoise)	1.002	1.247	1.056

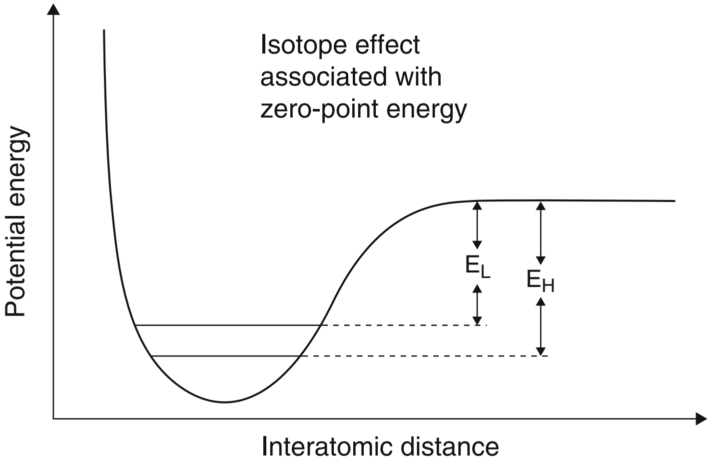


Fig. 4.4 Schematic potential energy curve for the interaction of two atoms in a stable molecule or between two molecules in a liquid or solid. (After Bigeleisen 1965)

of chemical reaction considerably. Furthermore, it may lead, for example, to a shift of the lines in the Raman and IR spectra. Such mass differences are most pronounced among the lightest elements. For example, some differences in physio-chemical properties of $^{1}H_2{}^{16}O$, $D_2{}^{16}O$, $^{1}H_2{}^{18}O$ are listed in Table 4.4. To summarize, the properties of molecules differing only in isotopic substitution are qualitatively the same, but quantitatively different.

Differences in the chemical properties of the isotopes of H, C, N, O, S and other elements are determined experimentally. These differences in the chemical properties can lead to considerable separation of the isotopes during chemical reactions.

The theory of isotope effects and a related isotope fractionation mechanism is discussed here briefly. Differences in the physicochemical properties of isotopes arise as a result of quantum mechanical effects. Figure 4.4 shows schematically the energy of a diatomic molecule as a function of the distance between the two atoms. In the figure, the upper horizontal line (E_L) represents the dissociation energy of the light molecule and the lower line (E_H) that of the heavy one is actually not a line, but an energy interval between the zero-point energy level and the "continuous" level.

This means that the bonds formed by the light isotope are weaker than bonds involving the heavy isotope. Thus, during a chemical reaction, molecules bearing the light isotope will, in general, react slightly more readily than those with the heavy isotope.

Isotopic composition of an element in a certain compound changes by the transition of the compound from one physical state or chemical composition to another.

Mass-dependent isotope fractionation takes place due to three processes, namely *thermodynamic* (in physical or chemical equilibrium systems), *kinetic* (in one-way (bio)chemical reactions) and *transport fractionation* during diffusive processes.

Within the hydrologic cycle, the variability in the isotope composition results primarily from mass-dependent isotope fractionation accompanying the phase transitions and transport processes in the cycle.

The differences in physical and chemical properties of isotopic compounds (i.e. chemical compounds consisting of molecules containing different isotopes of the same element) are brought about by mass differences of the atomic nuclei. The consequences of these mass differences are two-fold:

1. The heavier isotopic molecules have a lower mobility. The kinetic energy of a molecule is solely determined by temperature: $kT = ½\, mv^2$ (k = Boltzmann constant, T = absolute temperature, m = molecular mass, v = average molecular velocity). Therefore, molecules have the same $½\, mv^2$, regardless of their isotope content. This means that the molecules with larger m necessarily have a smaller v. Some practical consequences are: (a) heavier molecules have a lower diffusion velocity; and (b) the collision frequency with other molecules – the primary condition for chemical reaction – is smaller for heavier molecules; this is one of the reasons why, as a rule, lighter molecules react faster.
2. The heavier molecules generally have higher binding energies.

Examples of this phenomenon are:

- $^{1}H_2{}^{18}O$ and $^{1}H^{2}H^{16}O$ have lower vapour pressures than $^{1}H_2{}^{16}O$; they also evaporate less easily, and
- in most chemical reactions the light isotopic species reacts faster than the heavy. For example, $Ca^{12}CO_3$ dissolves faster in an acid solution than does $Ca^{13}CO_3$.

In isotope equilibrium between two chemical compounds, the heavy isotope is generally concentrated in the compound, which has the largest molecular weight.

3.2 Equilibrium and Kinetic Fractionation

The isotope fractionation can occur due to physicochemical reactions under: (i) equilibrium condition; and (ii) non-equilibrium condition and also due to molecular diffusion. In the first case, reactant and product interact for sufficiently long duration so that isotopic equilibrium is established, whereas in the second case, sudden change in temperature or addition or removal of product or reactant prevents the isotopic equilibrium in a given physicochemical reaction. In the molecular diffusion, product under isotopic equilibrium slowly diffuses out of the product reservoir but the product reservoir may remain in isotopic equilibrium with large reservoir of reactant. Although these three types of fractionating processes are known to occur, for all practical purposes, fractionations are conveniently grouped into two major classes namely, equilibrium and kinetic. Isotopic fractionation can occur during: (i) equilibrium isotopic exchange reactions, and (ii) non-equilibrium (kinetic) processes.

3.2.1 Equilibrium Fractionation

Equilibrium exchange reactions involve thermodynamic equilibrium between the two phases during a phase change process during which redistribution of the isotopes between the two phases (products and reactants) takes place. When forward and backward rates of phase change reaction are equal, the thermodynamic equilibrium is said to have been attained. The equilibrium fractionation is primarily governed by the binding energy of the isotopologues in two phases (isotopologues are molecules of a substance that differ in their isotopic composition). Since the binding energies depend on temperature, the equilibrium fractionation depends on temperature. The heavier isotopologues get concentrated in the phase in which they have greater binding energy. As a 'rule of thumb', among different phases (vapour, liquid, solid) in which H_2O can exist, the denser the phase, the more it tends to be enriched in the heavier isotopes (D and ^{18}O).

The natural example of an equilibrium fractionation is vapour to liquid phase change in cloud, where liquid phase remains in contact with surrounding vapour and is believed to have attained the isotopic equilibrium with vapour phase, before it rains out from the cloud.

3.2.2 Non-equilibrium or Kinetic Fractionation

In systems out of equilibrium, forward and backward reaction rates are not identical, and isotope reactions become unidirectional and irreversible. This can happen due to sudden change in temperature or sudden addition or removal of product or reactant. Under these circumstances, relative amount of the reactant or product suddenly changes and hence the two cannot attain thermodynamic equilibrium with each other. Isotope fractionation due to such reactions is called non-equilibrium or kinetic fractionation. Although this is a non-equilibrium fractionation, it still strongly depends on temperature, like equilibrium fractionation.

Natural example of this type of fractionation is sudden uplift of warm vapour loaded air mass and resultant cloud burst; immediate removal of vapour emanating from water bodies (lakes, flowing rivers, surface water spread for irrigation etc.) due to strong winds etc.

3.2.3 Diffusive Fractionation

Fractionation due to differences in diffusive velocities is a variant of the non-equilibrium or kinetic fractionation. In this case, different isotopic molecules diffuse out of the bulk reservoir, with different diffusive velocities. Unlike the kinetic fractionation caused by sudden temperature change or sudden addition/ removal of mass, which has strong temperature dependence, the diffusive fractionation is strongly governed by diffusive velocities and has only slight temperature dependence, which for all practical purposes can be ignored in actual calculations of fractionation factors. The diffusive fractionation is also referred to as transport fractionation in some literature.

Natural scenarios where diffusive fractionation occurs are evaporation from open water body and diffusion of vapour from surface of water to air above. In isotope hydrology, the most accepted model for non-equilibrium evaporation from a water body involves diffusion of water vapour across a hypothetical microns thin boundary layer over the liquid water interface. The boundary layer has virtually 100% water saturation. This layer is in isotopic equilibrium with the underlying water column. Between the boundary layer and the mixed atmosphere above is a transition zone through which water vapour is transported in both directions by molecular diffusion. It is within the transition zone that non-equilibrium fractionation arises due to the fact that diffusive velocity of ${}^{1}H_2{}^{16}O$ in air is greater than that of ${}^{2}H^{1}H^{16}O$ or ${}^{1}H_2{}^{18}O$.

The vapour over ocean is isotopically depleted with respect to ocean water and the total fractionation is the sum of: (1) the equilibrium fractionation between ocean water and thin boundary layer; and (2) the diffusive fractionation between boundary layer and mixed atmospheric air above.

3.3 Rayleigh Distillation

The rain (or snow) is produced when an air mass containing vapour cools. The cooling occurs by (i) adiabatic (without loss of heat) expansion as the warm air rises to lower pressure; or (ii) radiative loss of heat. When the temperature of the air parcel drops below the dew point (temperature at which relative humidity is 100%) vapour condenses into liquid (rain) or snow (solid), in order to maintain the thermodynamic equilibrium at that temperature. The vapour and condensate remain in an intimate contact at a given temperature in the cloud. If the temperature drops further, condensation of vapour proceeds further and if temperature increases, the evaporation of liquid or snow occurs. The first condensates are tiny particles which float and remain in close contact with vapour under equilibrium. When tiny particles coalesce and sufficiently massive particle is formed, it begins to fall under gravity. This is how we receive rain on ground.

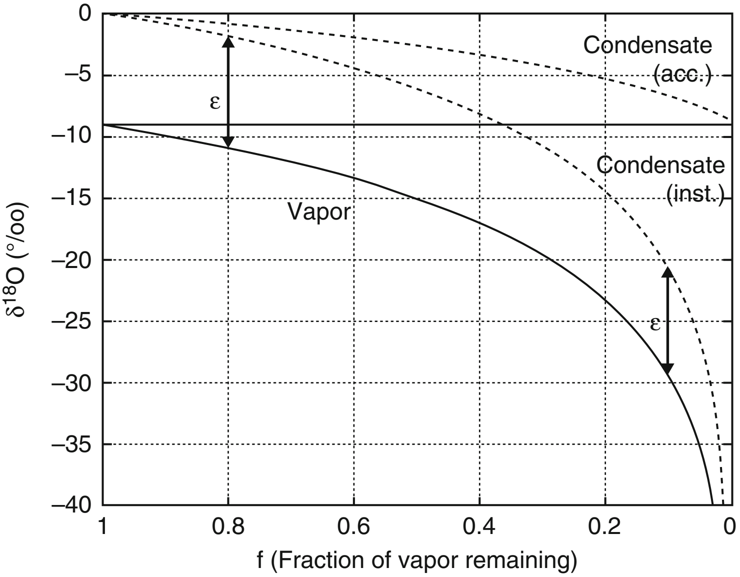


Fig. 4.5 Rayleigh fractionation process of water condensing from vapour. The oxygen isotope fractionation between reservoir (vapour) and the instantaneous product (condensate, inst.) is constant. When no vapour remains ($f = 0$), the accumulated product (condensate, acc.) has the same isotopic composition as the initial vapour since the vapour has completely condensed (horizontal line)

During equilibrium condensation at prevalent in-cloud temperature, isotopic molecular species differentially partition between vapour and liquid (or solid) phase such that more condensed phase is always enriched in heavier isotopes and vapour is depleted in heavier isotopes. Thus, with progressive rainout along the wind trajectory from marine vapour source region into continental interiors, the remaining vapour becomes progressively more and more depleted in heavier isotopes (Fig. 4.5). At every stage of rainout, the condensate is always enriched in heavier isotopes compared to vapour. Since vapour is progressively depleted at successive stage of rainout, the resultant rain at succesive stage is also isotopically depleted.

The effect of the admixture of evapotranspiration flux on the isotopic composition of the downwind atmospheric vapour and subsequent precipitation depends on the details of the evapotranspiration process. Transpiration returns precipitated water essentially un-fractionated back to the atmosphere, despite the complex fractionation in leaf water (Forstel 1982). Transpiration restores both the vapour mass and the heavy isotope depletion caused by the rainout in such a way that the next rainout event is not as depleted as it would have been without the transpiration flux. Under such circumstances, the change in the isotopic composition along the air mass trajectory is only due to the net loss of water from the air mass, rather than being a measure of the integrated total rainout. This causes apparent reduction in the downwind isotopic gradient. The evaporated water, on the other hand, usually gets depleted in heavy species relative to that of transpired vapour, thus restoring the vapour mass to the downwind cloud but reducing its isotopic composition. This may cause apparent increase in the downwind isotopic gradient.

3.4 Global Meteoric Water Line

Due to kinetic and equilibrium processes during evaporation from the ocean and subsequent condensation, δD and $\delta^{18}O$ in the air moisture and precipitation vary with temperature during condensation and with relative humidity during evaporation (Clark and Fritz 1997). The stable isotope ratios of air moisture reflect both the origin of the air-mass and the conditions under which condensation occurs.

Craig (1961) observed that the δD and $\delta^{18}O$ in the precipitation are linearly related, if it has not been evaporated. The relation between δD and $\delta^{18}O$ in precipitation is expressed by the equation:

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

This equation, known as the "*Global Meteoric Water Line*" (GMWL), is based on precipitation data from locations around the globe, and has an $r^2 > 0.95$ (Fig. 4.6). This high correlation coefficient reflects the fact that the oxygen and hydrogen stable isotopes in water molecules are intimately associated.

Subsequent global monitoring of the stable isotopic composition of precipitation (IAEA Global Network for Isotopes in Precipitation – GNIP) has refined this relationship (Rozanski et al. 1993), as:

$$\delta D = 8.13\,\delta^{18}O + 10.8‰(VSMOW)$$

Craig's line is only global in application, and is actually an average of many local or regional meteoric water lines, which differ from the global line due to varying climatic and geographic parameters (Clark and Fritz 1997). Local lines may differ from the global line in both slope and deuterium intercept. Nonetheless, GMWL provides a reference for interpreting the provenance of groundwater.

The slope and intercept of the "Local Meteoric Water Line" (LMWL), which is the line derived from precipitation collected from a single site or set of "local" sites, can be significantly different from the GMWL. In general, most of these local lines have slopes of 8 ± 0.5, but slopes in the range of 5 and 9 are not uncommon.

Several processes cause waters to scatter away from the GMWL. Water that has evaporated or has mixed with evaporated water typically plots below the meteoric water line along lines that intersect the GMWL (or LMWL) at the location of the original un-evaporated composition of the water. In such waters, slopes in the range of 2 to 5 are common. Geothermal exchange also increases the ^{18}O content of waters

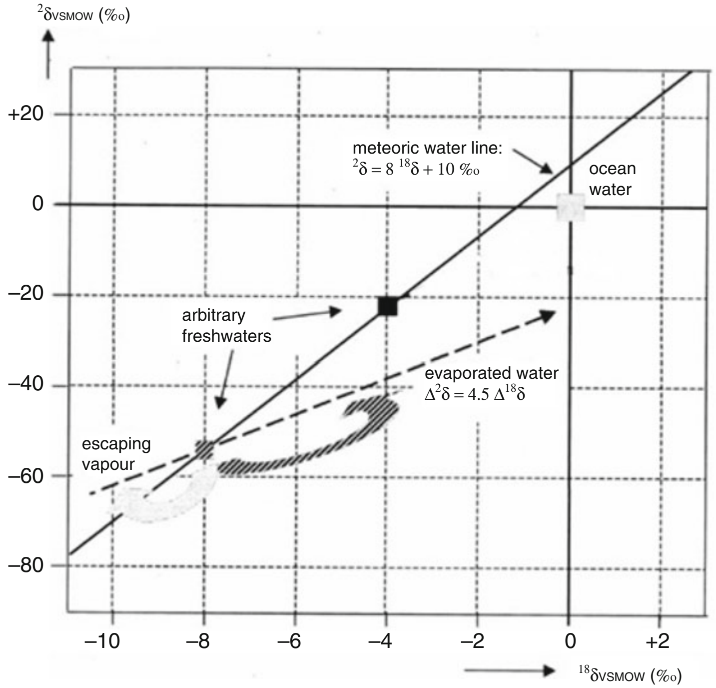


Fig. 4.6 Relation between $\delta^{18}O$ and δD for estuarine mixing and for evaporating surface water. Because the evaporation is a non-equilibrium process, isotope fractionations involved are not necessarily related by a factor of 8, as is the equilibrium condensation process

and decreases the ^{18}O content of rocks as the waters and rocks attempt to reach a new state of isotopic equilibrium at the elevated temperature. This causes a shift in the $\delta^{18}O$ values, but not the δD values of geothermal waters. Low temperature diagenetic reactions involving silicate hydrolysis can sometimes cause increases in the $\delta^{18}O$ and δD values of waters.

3.5 *Isotope Effects*

In principle, variations in $\delta^{18}O$ and δD are coupled under conditions of isotopic equilibrium with slope of 8, but under non-equilibrium (due to complicated kinetic process), the slope of GMWL deviates. The variation of isotopic composition in water/vapour is governed by various factors like latitude/annual temperature, altitude, season, distance from sea, amount of rain, etc. These are called as *isotope effects* and are described below, in brief.

3.5.1 Latitude/Annual Temperature Effect

As discussed earlier, the stable isotopic composition of precipitation on a global scale depends on two processes: (i) formation of atmospheric vapour by evaporation in regions with the highest surface ocean temperatures, and (ii) progressive condensation of the vapour during transport to higher latitudes with lower temperatures.

The progressive rainout process based on the Rayleigh fractionation/condensation model, results in a relation between the observed annually averaged δ^{18}O and δD values of the precipitation and the mean surface temperatures in reasonable agreement with the observed values from the GNIP data network.

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

$$\delta^{18}\mathrm{O} = 0.695\,T_{\mathrm{annual}} - 13.6‰\mathrm{SMOW}\ \mathrm{and},\ \delta D = 5.6\,T_{\mathrm{annual}} - 100‰\mathrm{SMOW}$$

If monthly temperatures are used, then

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

On an average, 1‰ decrease in average δ^{18}O corresponds to 1.1 to 1.7 °C decrease in the average annual temperature. As latitude increases, the temperature decreases, therefore isotopic composition depletes in precipitation. Polar Regions are located at the highest latitudes and 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. The variation of δ^{18}O is of 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.

3.5.2 Continental Effect

Precipitation depletes in heavier isotopes of water molecules as clouds move away from the coastal parts. On average, δ^{18}O depletes about −2‰ per 1000 km from seacoast. Global T-δ^{18}O relationship ($\delta^{18}\mathrm{O} = 0.695\ T_{\mathrm{annual}} - 13.6‰$ SMOW) changes significantly due to continental effect.

3.5.3 Altitude or Elevation Effect

Precipitation progressively depletes in δ-values with increase in altitude. This is mainly due to two reasons: (i) decrease in temperature with increase in altitude, and (ii) rainout process increases with increase in altitude due to orographic effect.

In general, $\delta^{18}O$ and δD depletes in the range of -0.15 to -0.5‰ and -1 to -4‰ respectively per 100 m 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.

3.5.4 Seasonal Effects

Variation of δD and $\delta^{18}O$ due to change in season is called seasonal effects. Mainly two factors are responsible for the seasonal effects, i.e., (i) variation in temperature with respect to seasons, and (ii) change in amount of precipitation.

Evaporation and evapo-transpiration increases with increase in temperature. Local or regional water vapours mix with the water vapours originated from the sea and enrich the precipitation in $\delta^{18}O$ and δD. Increase in temperature increases the effect of evaporation in the falling raindrops and enriches the precipitation in δD and $\delta^{18}O$. This effect is least when precipitation occurs in large amount or with high intensity.

3.5.5 Amount Effect

Isotopic composition of the precipitation also depends on the amount of rain: heavier rain events, or greater monthly precipitation amounts, result in more negative δD and $\delta^{18}O$ values. Dansgaard (1964) proposed two major explanations for this amount effect, i.e., (i) lower ambient temperatures cause the formation of clouds with lighter isotopic composition (temperature effect) and also causes heavy precipitation; and (ii) falling raindrops undergo evaporation, enriching the falling rain in the heavy isotopes. This effect is less severe when ambient temperatures are low or when the amount of rain is large.

The amount of monthly rain varies during the year, causing a seasonal variation in the isotopic composition.

3.6 Distribution of Stable Isotopes

3.6.1 Natural Abundance of Stable Oxygen Isotopes

As mentioned earlier, oxygen has three stable isotopes, ^{16}O, ^{17}O and ^{18}O, with abundances of 99.76, 0.035 and 0.2%, respectively (Nier 1950). Variation in ^{18}O values in natural materials has a range of almost 100‰ (Fig. 4.7). ^{18}O is often enriched in (saline) lakes subjected to a high degree of evaporation, while high-altitude and cold-climate precipitation, especially in the Antarctic, is low in ^{18}O. Generally, in the hydrological cycle in temperate climates, values of ^{18}O do not exceed 30‰.

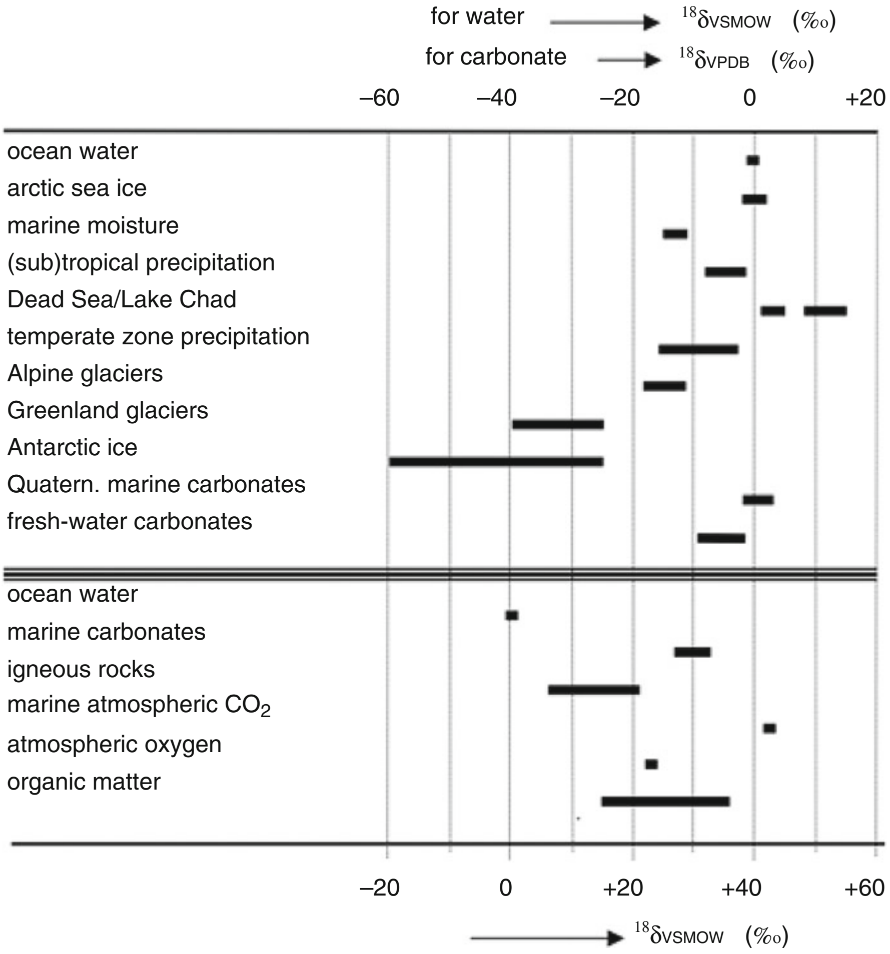


Fig. 4.7 Variation of ^{18}O in natural compounds

3.6.2 Natural Abundance of Stable Hydrogen Isotopes

The chemical element hydrogen consists of two stable isotopes, ^{1}H and ^{2}H (D or Deuterium), with an abundance of about 99.985 and 0.015% and an isotope ratio ^{2}H/^{1}H 0.00015 (Urey et al. 1932). This isotope ratio has a natural variation of about 250‰, higher than the ^{18}O variations, because of the relatively larger mass differences between the isotopes (Fig. 4.8). As with ^{18}O, high ^{2}H concentrations are observed in strongly evaporated surface waters, while low ^{2}H contents are found in polar ice. Variations of about 250‰ are present in the part of the hydrological cycle.

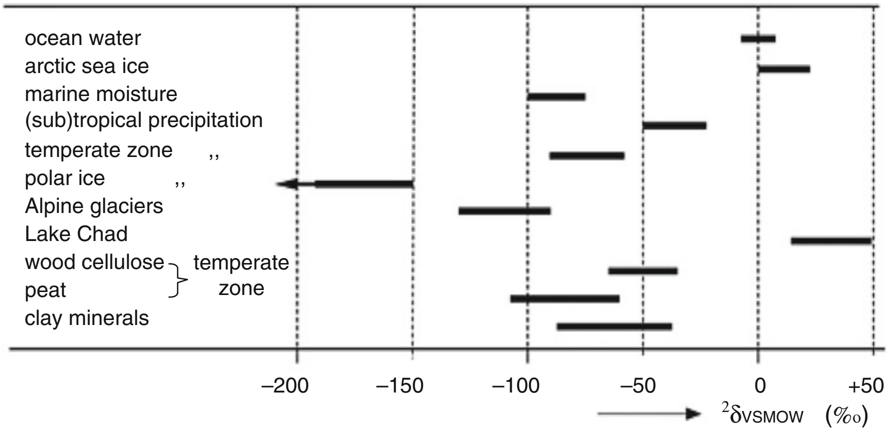


Fig. 4.8 Variation of δ^2H in natural compounds

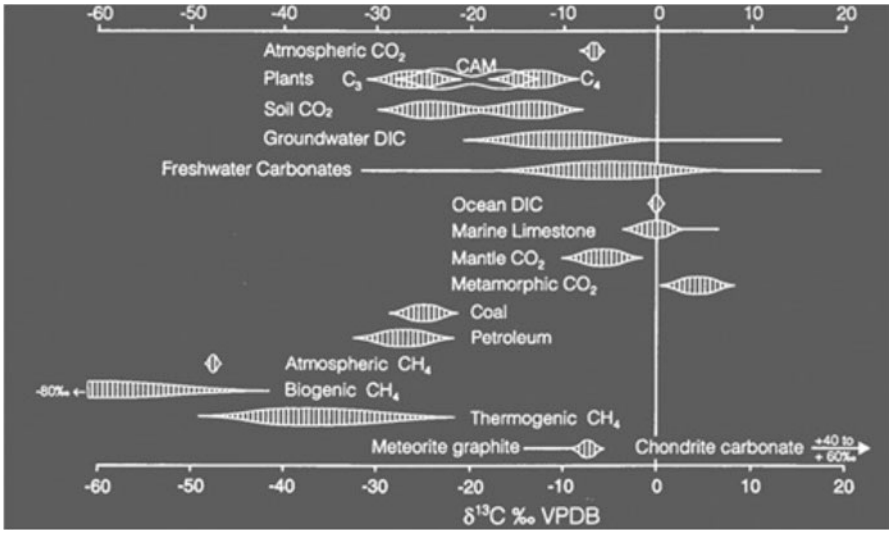


Fig. 4.9 Variation of ^{13}C in natural compounds

3.6.3 Natural Abundance of Stable Carbon Isotopes

There are two naturally occurring stable isotopes of carbon: 12 and 13, which occur in a natural proportion of approximately 99:1. Stable carbon isotopes are utilized differentially by plants during photosynthesis. Most plants in temperate climates follow C3 photosynthetic pathway that yield δ^{13}C values averaging about −26.5‰. Grasses in hot arid climates follow a C4 photosynthetic pathway that produces δ^{13}C values averaging about −12.5‰. The range of variation of 13C in natural materials is shown in Fig. 4.9.

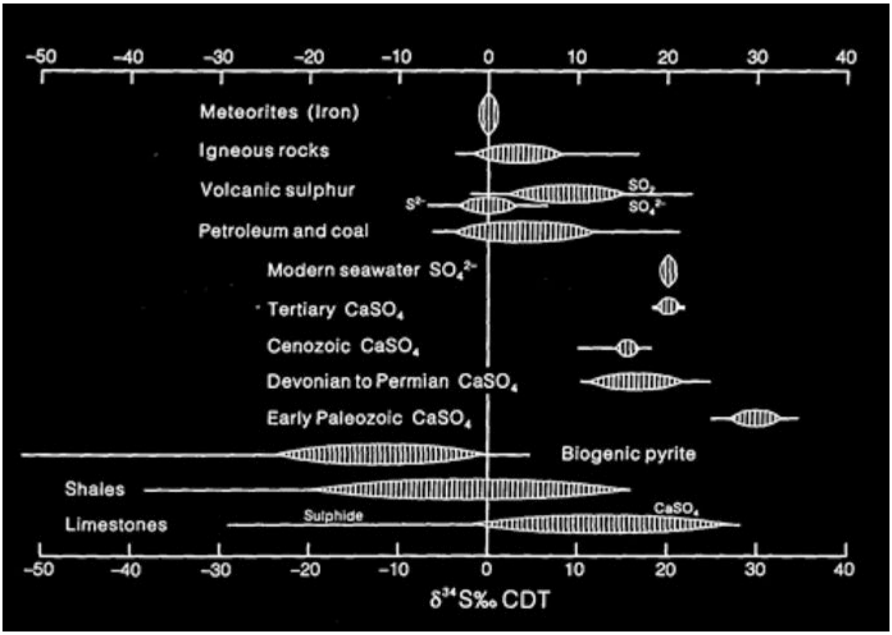


Fig. 4.10 Variation of ^{34}S in natural compounds

3.6.4 Natural Abundance of Stable Sulphur Isotopes

Sulphur (^{34}S) is a major element of sea water and marine sediments and is an essential nutrient for vegetation. A summary of the ranges for ^{34}S in natural materials is shown in Fig. 4.10. Meteorites and magmatic ^{34}sulphur are close to standard Canon Diablo Troilite (CDT), Values exceeding +20 are found associated with evaporates and limestone. Negative $\delta^{34}S$ values are typical of diagenetic environments where reduced sulphur compounds, such as pyrites in shales, are formed (Krouse 1980).

3.6.5 Natural Abundance of Stable Nitrogen Isotopes

Nitrogen (^{15}N), the stable isotope of nitrogen is being used for hydrological studies, particularly for tracing the source and pathways of NO_3 contamination in groundwaters. The combination of ^{15}N and ^{18}O in NO_3 provides a tool to distinguish between nitrates of different origins. The range for ^{15}N in natural materials is shown in Fig. 4.11.

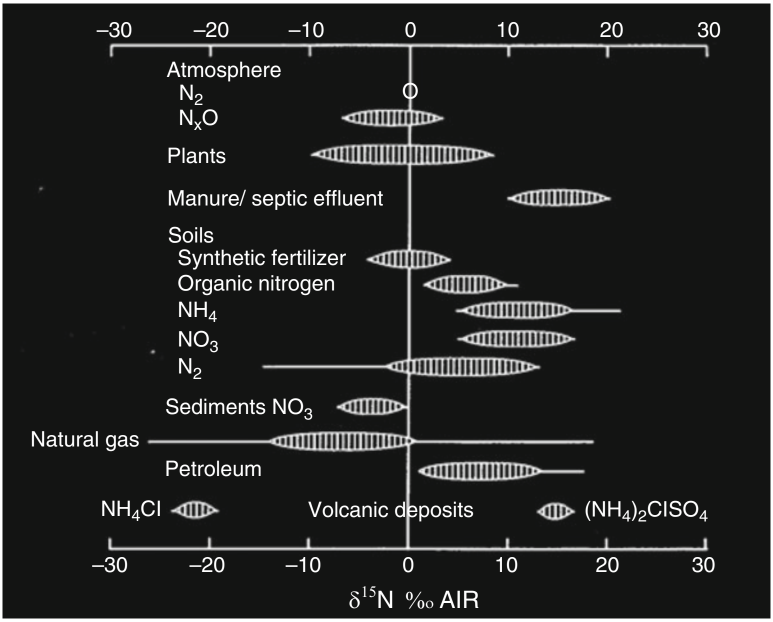


Fig. 4.11 Variation of ^{15}N in natural materials (Amberger and Schmidt 1987; Böttcher et al. 1990; Létolle 1980)

4 Groundwater Age Dating

Groundwater age is defined as the amount of time that has elapsed since a particular water molecule of interest was recharged into the subsurface environment system until this molecule reaches a specific location in the system where it is either sampled physically or studied theoretically for age-dating. On the other hand, groundwater *residence time* is the time taken by the water molecules to travel from the recharge area to the discharge area of the aquifer (Modica et al. 1998). It is the time interval between infiltration and exfiltration of water molecule in the subsurface media. This definition indicates that groundwater age is the groundwater residence time, but only at the discharge area.

Groundwater age is an intrinsic property of the groundwater molecule, like other parameters such as electrical conductivity, and temperature (Goode 1996; Etcheverry and Perrochet 2000; Bethke and Johnson 2002). Thus, age and groundwater are not two separable components, as the water starts aging from the instance it enters into the subsurface. Therefore, as soon as a water molecule enters the subsurface, it becomes groundwater and it has an age.

Dating method is the key criterion in differentiating and classifying groundwater age into three major groups: young, old and very old. Young groundwaters can be dated using techniques whose dating range extends from less than a year to about 50 or 60 years – post thermonuclear bombs or CFC-free groundwaters. Old groundwaters can be dated with methods whose range is between 60 and 50,000 years. Finally, very old groundwaters can be dated using techniques whose coverage ranges from 50,000 to 100,000 years to more than a few tens of millions of years.

The total volume of groundwater resources on the earth is about 23×10^6 km^3 (Gleick 1993). About 4–8 $\times$ 10^6 km^3 of this circulates continuously within the hydrologic cycle (Freeze and Cherry 1979; Gleick 1993) and is called as **active water**. The rest is sometimes referred to as **dead water**. Dead groundwater includes connate water (water entrapped in the sediments during deposition), magmatic water (water contained within magmas deep in the earth), metamorphic water (water produced as a result of recrystallization during metamorphism of minerals), and marine water (seawater intruded into coaster aquifer). Dead water also refers to stagnant waters in isolated envelopes in deep regional aquifers that are not in full hydraulic connection with the surrounding water (Mazor and Nativ 1992). With regard to groundwater dating, **active waters** are of greater interests because they are the main source of water used for various purposes.

A groundwater sample may contain waters that have originated from various recharge areas and input points. The result of such a situation is a sample that consists of many fractions with different ages. This phenomenon is referred to as **mixing** and represents a major challenge to age-dating practice. Similarly, age is subjected to the various processes governing mass transport in aquifers, such as advection, dispersion and mixing. When these processes are active, the age of a groundwater sample cannot be a single number, because the sampled mixture may consist of numerous fractions with different ages. Dispersion and transport of groundwater age fulfil the same function as mixing, but at a micro-scale level. The dispersion of groundwater ages (or residence times) is primarily due to heterogeneous groundwater velocities and hydrodynamic dispersion.

A groundwater sample contains billions of water molecules. In a well-mixed groundwater system, anyone of these molecules may have its own distinct particular age. **Mean age** or the age measured by isotopic and chemical methods, is practically the average of ages of all molecules in the sample. Statistically speaking, mean age is the first moment (i.e., the average) of the age distribution. Understanding the type of statistical age distribution of various ages in a groundwater sample is a must if one has to describe the age of a given sample. This can only be done through application of mathematical models. In situations where groundwater flow can be modelled accurately, the first moments (e.g., mean, variance, and skewness) of the age or residence time distributions can be simulated with temporal moments equations of the advective-dispersive type (e.g., Harvey and Gorelick 1995; Varni and Carrera 1998). Other recent mathematical approaches combining advective-dispersive equations and the reservoir theory (Etcheverry and Perrochet 2000; Cornaton and Perrochet 2005) yield the full age distributions at any point of an aquifer and the residence time distributions at its outlets.

4.1 Tools for Dating Groundwater

There are basically two different ways of estimating groundwater age at a given point in the aquifer: (i) by environmental tracers, and (ii) by groundwater flow modelling. A number of isotope methods can be used to assess mean residence times. The more routinely applied techniques are based on the decay of radionuclides. Those with a long half-life (^{14}C, ^{36}Cl, ^{39}Ar and ^{81}Kr) can be used to date paleo-groundwaters. Short-lived radioisotopes (^{3}H, ^{32}Si, ^{37}Ar, ^{85}Kr and ^{222}Rn) and those produced by man's nuclear activities over the past five decades (^{3}H, ^{36}Cl and ^{85} Kr) indicate modern recharge.

The "sub-modern" period in the dating range between modern waters and paleo-groundwaters is problematic. While this >45 to ~1000 years range can potentially be filled by ^{39}Ar dating ($t_{1/2} = 256$ yr), this method requires rather ideal aquifers, very large samples, complicated sample preparation techniques and special counting facilities. Very few laboratories can afford this and, therefore, ^{37}Ar dating has not developed into a routine tool.

4.2 Dating Young Groundwaters

To date young groundwaters (0–60 years old), ^{3}H, $^{3}H/^{3}He$, ^{4}He, ^{85}Kr, CFCs, SF_6 and ^{36}Cl techniques are used. Dating methods for young groundwaters are typically applicable to unconfined shallow aquifers only, while those methods for dating very old groundwaters are often for deep, confined aquifers. It is, therefore, safe to argue that only dating methods for old groundwaters can be used for both confined and unconfined aquifers.

4.2.1 Tritium Method

Hydrogen has three isotopes: ^{1}H (common hydrogen or protium, H); ^{2}H (deuterium, D); and ^{3}H (tritium, T). Protium has one proton, deuterium has one proton and one neutron, and tritium has one proton and two neutrons. Deuterium (also referred to as heavy stable isotope of hydrogen) and protium are stable, but tritium is radioactive with a half-life of 12.32 years. Tritium is produced in the atmosphere due to the interaction of the cosmic rays produced neutrons in the upper atmosphere with nitrogen atoms:

$$^{14}N+^{1}n=^{3}H+^{12}C$$

Apart from the natural production, lot of tritium was added to the atmosphere due to testing of thermonuclear devices during 6th and 7th decades of the twentieth Century.

Tritium dating is used to trace water sources and to determine age of recent materials (maximum upto age of 50 ± 1 year). Tritium dating provides means to estimate the time since recharge to groundwater system occurred and susceptibility of the groundwater system to contamination. Sources directly fed by rainwater contain the same tritium levels as rainwater. Tritium values are reported in tritium units (TU).

$$1\,\mathrm{TU} = \frac{1(^{3}\mathrm{H})}{10^{18}(^{1}\mathrm{H})} = 7.1\,\mathrm{dpm}/l = 0.12\,\mathrm{Bq}$$

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

$$^{2}_{1}\mathrm{H} \rightarrow ^{3}_{2}\mathrm{He} + \beta$$

Therefore, with the passage of time, the concentration of tritium in the groundwater decreases according to the decay law.

$$C = C_0 \ln e^{-\lambda t} \mathrm{or}\, ^{3}\mathrm{H} = ^{3}\mathrm{H}_0 \ln e^{-\lambda t}$$

where C or ^{3}H is the concentration of tritium in the water sample, C_0 or $^{3}\mathrm{H}_0$ is the concentration of tritium in the recharge water, or the initial value. λ is the decay constant of tritium, 0.056 yr.$^{-1}$. Tritium is of special value in detecting recent recharge because of its short half-life of 12.32 years and because of high levels of tritium in the atmosphere since the beginning of atmospheric testing of thermonuclear devices in 1952. Direct age estimation using tritium is difficult due to variable input of tritium, since 1952.

Tritium concentrations in environment are routinely measured (monthly averages) at various gauging stations fixed by IAEA/WMO since 1961. Tritium contents in the environment has reached to its normal value i.e., normally the natural level of tritium vary between 5 and 15 TU according to the geographical location of the area. The existence of tritium in a water sample is a definite proof of the presence of some components of modern recharge. Therefore, if tritium content is observed to be 10 TU, the groundwater may be of recent origin and if it is 5 TU, then the groundwater may be 12.32 years old (uncorrected).

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

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

Major *advantages* of using this method are: (i) it is a well-established and a well-known method with plenty of references, (ii) laboratory facilities are worldwide and the cost of analysis is relatively small, (iii) it is the only tracer that is part of the water molecule, and (iv) tritium is still regarded as a supplementary dating method.

The *disadvantages* of this method are: (i) the method is approaching its expiry date, and (ii) due to the strong latitudinal variation, it is difficult to precisely determine the initial value.

4.2.2 Tritium Helium (^{3}H/He) Method

The fading of the tritium dating method has led to revive an old technique, namely ^{3}H/^{3}He, to replace it. By measuring ^{3}H together with its daughter ^{3}He, true ages can be determined through calculations that do not rely on complicated tritium input function. In ideal circumstances, the method is remarkably accurate for groundwater upto 40 years old.

There are four sources for ^{3}He in the groundwater, i.e., atmospheric, in-situ, tritium decay and from mantle.

The tritium-helium method measures the relative abundance of tritium and ^{3}He in a groundwater sample. The amount of ^{3}He from the decay of tritium is measured along with the amount of tritium remaining in the water. That sum is equal to the amount of tritium that was present at the time of recharge, or the initial value. Mathematically we write:

$${}^{3}\mathrm{H}_0={}^{3}\mathrm{H}+{}^{3}\mathrm{He}_{\mathrm{tri}}\mathrm{and}{}^{3}\mathrm{H}={}^{3}\mathrm{H}_0\ \ln e^{-\lambda t}$$

Combining these two equations

$$\begin{aligned}{}^{3}\mathrm{H} &= ({}^{3}\mathrm{H}+{}^{3}\mathrm{He}_{\mathrm{tri}})\ln e^{-\lambda t} \rightarrow \ln e^{-\lambda t}={}^{3}\mathrm{H}/({}^{3}\mathrm{H}+{}^{3}\mathrm{He}_{\mathrm{tri}}) \rightarrow t\\ &= 1/\lambda \ln\left({}^{3}\mathrm{He}_{\mathrm{tri}}/{}^{3}\mathrm{H}+1\right)\end{aligned}$$

It is clear from the equation that in order to measure the age of a groundwater sample, we simply need to measure its tritium and $^{3}\mathrm{He}_{\mathrm{tri}}$ simultaneously.

Main advantages of the method are (i) the resolution of this method is high in average situations (moderately thick unsaturated zone, limited sources of helium, etc.), (ii) data collected can be used for both ^{3}H/^{3}He and tritium methods, (iii) this method will be applicable for a long time, i.e., its effectiveness is not reduced in the future as is the case with methods like CFCs, tritium, etc., and (iv) this method does not need the initial value, a parameter that is fundamental and problematic for many of the dating methods.

Disadvantages of ^{3}H/^{3}He method are (i) sampling and analysis are expensive and laboratory facilities are not available worldwide, and (ii) it is difficult to separate tritiogenic helium from the other type of helium.

4.2.3 Krypton-85 (^{85}Kr) Method

Krypton (Kr) is a colourless and inert gas (so-called noble gas) belonging to the 8th group of the Mendeleyev's periodic table. Krypton is highly soluble in water, together with Xenon. Typically atmospheric Kr ranges from 7.61 to 12.57 × 10^{-8} cm^3 STP/g and from 2.26 to 3.80 × 10^{-8} cm^3 STP/g in groundwater and seawater respectively (Ozima and Podosek 2001).

Natural production of ^{85}Kr takes place in small amounts in the atmosphere by spallation and neutron activation of stable ^{84}Kr.

$$^{84}\mathrm{Kr}_{36} + n \rightarrow {}^{85}\mathrm{Kr}_{36} + \gamma$$

Manmade ^{85}Kr is produced by the fission of plutonium and uranium. The main anthropogenic sources of ^{85}Kr to the atmosphere are, therefore, nuclear weapon testing and nuclear reactors used for both commercial energy production and plutonium weapons production.

^{85}Kr disintegrates by beta decay to stable ^{85}Rb. In this respect, it can be used as a "clock" or a radioactive tracer.

$$^{84}\mathrm{Kr}_{36} \rightarrow {}^{85}\mathrm{Rb}_{37} + \beta^{-}$$

However, its use in age-dating is more based on its nearly linear increasing concentration in the atmosphere. Atmospheric ^{85}Kr is dissolved in rainwater and is carried out to the unsaturated and then saturated zones. The higher is the concentration of ^{85}Kr, the younger the groundwater age. Also, due to the short half-life (10.76 years) and minimal natural production in the Earth, the absence of ^{85}Kr verifies that groundwater is older than 1950. If ^{85}Kr is combined with an additional radioactive isotope with a similar half-life (such as ^{3}H), additional confidence in the results can be gained. ^{85}Kr is commonly used with tritium because the two tracers have similar half-lives but completely different input functions. Its short half-life and increasing concentrations in the atmosphere make ^{85}Kr a potential replacement for ^{3}H as tritium levels continue to decline.

Main advantages of the method are: (i) this method is much less sensitive to degassing than the other dating methods for young groundwaters, as this method is based on isotopic ratio (^{85}Kr/Kr), (ii) in anoxic environments and in CFCs and SF_6-contaminated areas, ^{85}Kr may prove to be superior because of low contamination possibility, (iii) the method may continue to be used in future also, because atmospheric concentration of ^{85}Kr is still on the rise, and (iv) geochemically ^{85}Kr is inert.

Disadvantages of ^{85}Kr method are: (i) large sample-size required, (ii) high costs due to the specialized measurement methods, (iii) in uranium-rich aquifers, some proportion of ^{85}Kr gets mixed and masks the atmospheric component of ^{85}Kr or make it difficult to be distinguished, and (iv) in aquifers with thick unsaturated zones, there is a significant time lag for transport of ^{85}Kr to the saturated zone (Cook and Solomon 1995), which may lead to overestimation of groundwater ages.

4.2.4 Chloroflourocarbons (CFCs)

Like tritium, CFCs, otherwise unwanted contaminants, resistant to degradation are now being utilized as a useful marker for modern groundwater. Atmospheric CFC concentrations have been increasing since 1940s, providing a characteristic input function. CFCs have been extensively used to trace oceanic circulation patterns over the past decade but some recent studies (Thompson and Hayes 1979) have documented their usefulness for dating young groundwaters.

Atmospheric CFCs, dissolved in percolating precipitation water, reach the groundwater system after passing through the unsaturated zone. Groundwater CFCs ages are obtained by converting measured CFCs concentrations in the groundwater sample to equivalent air concentrations using known solubility relationships developed for CFC-11 and CFC-12 (Warner and Weiss 1985), for CFC-13 (Bu and Warner 1995) and the recharge temperature (Cook and Herczeg 1998). The life time of CFC-11, CFC-12 and CFC-13 is 45, 100 and 85 years respectively.

Equivalent atmospheric concentration (or sometimes called "apparent atmospheric concentration") of CFCs can be computed by the equation given by Cook and Herczeg (1998), i.e.

$$\mathrm{EAC} = \mathrm{CFCs}_{\mathrm{gw}}/S \times MW$$

where EAC is the equivalent atmospheric concentration, $\mathrm{CFCs}_{\mathrm{gw}}$ is the concentration of CFCs in the groundwater, S is the solubility in $\mathrm{molkg}^{-1}\ \mathrm{atm}^{-1}$, and MW is the molecular weight of CFCs with unit of g/mol.

Main advantages of using the CFC method are: (i) presence of CFCs is a good indicator of post-1945 recharged groundwater. CFC-113 indicates post-1965 recharged groundwater, (ii) input function is relatively well known because spatial variations in atmospheric CFCs concentration are relatively moderate, (iii) it is possible to date the groundwater sample by EAC of one species and also by ratio of various species, (iv) concordant ages from various species may help to understand the geochemical processes in the aquifer, and (v) cost of analysis is cheap compared to all other methods.

Disadvantages of CFCs method are: (i) the method is losing its applicability (post-1990s), (ii) many parameters such as excess air, recharge temperature, degradation of CFCs, etc., can influence the accuracy of the ages, and (iii) great care is needed for sampling, and large errors may be introduced if proper guidelines are not followed.

4.2.5 Sulphur Hexafluoride (SF_6) Method

Sulphur (or sulfur) hexafluoride, SF_6, is a colourless and odourless gas used in the electric power industry, in the semiconductor industry, in the production of magnesium and aluminium for degassing melts of reactive metals, in blood products, in running shoes, and as intraocular gas tamponades for a wide range of complicated vitreoretinal diseases etc. SF_6 is primarily of anthropogenic origin but also occurs naturally in minerals, rocks, and volcanic and igneous fluids. It is the most potent greenhouse gas with an estimated atmospheric lifetime of 1935–3200 years. SF_6 is a conservative tracer for groundwater studies and behaves identically to bromide (Wilson and Mackay 1993). In addition to its use in dating young groundwaters, SF_6 is applied: (i) to estimate longitudinal dispersion coefficients in rivers, (ii) in the study of groundwater nitrate pollution, (iii) to estimate gas exchange rate in streams, and (iv) as a natural atmospheric tracer.

Atmospheric SF_6 is dissolved in rain and snow. Like other atmospheric-derived gas tracers, the amount of the dissolution is a function of the concentration of SF_6 in the air and the air temperature. Higher the atmospheric concentration, higher is the amount of the dissolution. Infiltrating rain- and snow water carry dissolved SF_6 into the unsaturated zone and finally to the saturated zone. Therefore, we can date a groundwater sample based on presence and concentration of its SF_6. The dating range of this method is X-1970, where X is the date the groundwater is sampled for dating; e.g., in year 2010, the dating range of the method would be 0–40 years.

Main advantages of the method are: (i) the concentration of SF_6 in the atmosphere continues to rise and the method is, therefore, going to hold effective until this trend is stopped or reversed, (ii) the atmospheric input is relatively well known, and the subsurface addition of SF_6 is thought to be insignificant, and (iii) the narrowness of the dating range is a plus in those situations where precise time scales are of interest.

Disadvantages of CFCs method are (i) groundwater ages obtained by the SF_6 method do not include the travel time of groundwater in the unsaturated zone. If this time is long, the ages obtained are substantially different from what is defined as groundwater age, (ii) the age range of this method is narrow, (iii) the knowledge about subsurface or natural production of SF_6, microbiological degradation, and other unfriendly causes is limited, and (iv) the main anthropogenic source of SF_6 is in the middle latitude of the Northern Hemisphere; hence the applicability of the methods in the other parts of the world is doubtful.

4.3 Dating Old and Very Old Groundwaters

Constraining the age of groundwaters that are clearly sub-modern or older can be important in establishing the long-term potential for aquifer recharge. For groundwater development and management policy, the question of renewability is most important. The methods to age-date old groundwaters (60–50,000 years old) include mostly ^{14}C, but less used and indirect methods such as ^{32}Si, ^{39}Ar, ^{18}O, ^{2}H, and conservative and reactive tracers are also being utilized.

4.3.1 Carbon Dating

Radiocarbon dating, or *carbon dating*, is a radiometric dating method that uses the naturally occurring radioisotope carbon-14 (^{14}C) with half-life 5730 ± 40 years to determine the age of carbonaceous materials up to about 50,000 years. Carbon-14 dating of groundwater is done by measuring ^{14}C activity in its dissolved inorganic carbon. ^{14}C is the leading tool in estimating the age of palaeo and fossil groundwaters. The method is based upon the incorporation of atmospherically derived ^{14}C from the decay of photosynthetically-fixed carbon in soil. Radiocarbon in the soil is taken into solution as dissolved inorganic carbon ($DIC = CO_{2(aq)} + HCO_3^- + CO_3^{2-}$) or as dissolved organic carbon (DOC).

Atmospheric ^{14}C is dissolved in the percolating rainwater and reaches the water table. In groundwater, ^{14}C starts decaying to nitrogen:

$$^{14}C_6 \rightarrow {}^{14}N_7 + \beta^-$$

If no further ^{14}C exchange occurs, measurement of the remaining ^{14}C atoms can be used to date groundwater following the first-order kinetic rate law for decay:

$$C = C_0\,e^{-\lambda t}$$

where C_0 is the activity assuming no decay occurs (initial activity or activity at $t = 0$), and C is the observed or measured activity of the sample. The groundwater dating by ^{14}C ranges in age from 870 to 19,000 years if 10% and 90%, respectively of the original atoms are assumed to have decayed. However, ages up to 40,000 years or longer have been reported by this method.

Main advantages of the method are: (i) it is an old and well-established method that has been proved and developed by considerable research during the last half-century, (ii) sampling and analysis for this method are now routine and cheaper than the majority of the dating methods, (iii) it is the only popular method available to date old groundwaters and to fill the dating range between young and very old groundwaters, and (iv) the deficiencies, the principles, and the positive points of the methods are all well known.

Disadvantages of ^{14}C method are: (i) it is an extremely difficult task to determine the correct initial value due to the various processes that modify ^{14}C signature of the percolating rainwater, (ii) a large number of geochemical reactions modify the concentration of ^{14}C in the groundwater, and (iii) having pointed out the above two major obstacles, it is safe to argue that the ^{14}C method is often a semi-quantitative technique.

4.3.2 Chlorine-36 (^{36}Cl) Method

The long half-life of ^{36}Cl (301,000 years) and generally simple chemistry of Cl^- makes this radioisotope an interesting tool for dating very old groundwater. Interest in application of ^{36}Cl is now increasing in recharge studies, groundwater infiltration rates and rates of erosion. Groundwater dating is based on two fundamental methods: (1) decay of cosmogenic and epigenic ^{36}Cl over long periods of time in the subsurface, or (2) in growth of hypogenic^{36}Cl produced radiogenically in the subsurface.

Groundwater in recharge areas derives cosmogenic^{36}Cl from two sources: atmospheric production and epigenic or surface production. Atmospheric ^{36}Cl is produced in the upper stratosphere through the bombardment of argon gas by cosmic radiation, according to:

$$^{40}\mathrm{Ar} + \mathrm{p} \rightarrow {}^{36}\mathrm{Cl} + \mathrm{n} + \alpha(67\%)$$
$$^{36}\mathrm{Ar} + \mathrm{n} \rightarrow {}^{36}\mathrm{Cl} + \mathrm{p}(33\%)$$

where n = neutron, α = alpha particle and p = proton.

Atmospheric residence time is minimal and ^{36}Cl, together with stable Cl^-, is washed to the surface by precipitation or arrives as dry fallout. Common ^{35}Cl in the atmosphere can also be irradiated by cosmic flux to produce ^{36}Cl and gamma radiation.

$$^{35}\mathrm{Cl} + \mathrm{n} \rightarrow {}^{36}\mathrm{Cl} + \gamma$$

The principle of this method is simple. It is based on the radioactive decay of ^{36}Cl in the subsurface groundwater system. Above the Earth's surface, ^{36}Cl (atmospheric ^{36}Cl) with an initial value, $^{36}\mathrm{Cl}_0$, enters groundwater by rainwater infiltration. After time t, it decays to ^{36}S and ^{36}Ar

$$^{36}\mathrm{Cl}_{17} \rightarrow {}^{36}\mathrm{Ar}_{18} + \beta^- + v$$
$$^{36}\mathrm{Cl}_{17} \rightarrow {}^{36}\mathrm{S}_{18} + \beta^- + v$$

and reaches a new concentration, ^{36}Cl, according to the decay equation

$$C = C_0\,\mathrm{e}^{-\lambda t}$$

If the initial concentration (C_0) and the present concentration (C) are known, then the length of time that the ^{36}Cl has resided in the subsurface groundwater system can be calculated. Chlorine-36 dating method is capable of dating groundwaters with an age range of 46,000 to 1,000,000 years if we assume that 10% and 90%, respectively, of the original ^{36}Cl atoms are disintegrated.

Main advantages of the method are: (i) the long half-life of ^{36}Cl makes this method suitable for dating very old groundwaters, and (ii) measured ^{36}Cl values may be used for other hydrologic applications, in addition to their use in dating.

Disadvantages of ^{36}Cl method are: (i) too many sources for ^{36}Cl and initial value problem, (ii) underground sources and sinks of ^{36}Cl, limiting to suggest limiting the dating range of ^{36}Cl to 500,000 to 1,000,000 years only (Phillips 2000), (iii) applicable only to limited regions, because this method is suited only for deep regional aquifers, (iv) not applicable to saline aquifers with chloride concentration of more than 150 mg/L, and (v) high cost of analysis and sample preparation, and inadequate availability of laboratories worldwide.

4.4 Applications of Groundwater Age Data

Groundwater age data can be used to evaluate the renewability of groundwater reservoirs, to constrain the parameters of groundwater flow and transport models, to study groundwater flow paths and vertical and horizontal flow velocities, to identify paleo-climate conditions (in combination with isotopes), to estimate groundwater recharge, to determine fracture and matrix properties and water velocities in fractured rock environments, to help study the trend of groundwater pollution, to identify past seawater level fluctuation, to manage groundwater-driven dryland salinity, to map susceptibility of groundwater systems to contamination, and to be used in many more hydrological applications such as mixing, groundwater–surface water interaction, and seawater intrusion.

4.4.1 Replenishment of Groundwater Reservoirs

The most important and the unique application of groundwater age concept is renewability or replenishment of the groundwater resources. Groundwater age is, as yet, the only sound and concrete piece of scientific evidence to show that groundwater resources are recharged by modern precipitation, or else, the extracted groundwaters were accumulated in the aquifers by slow infiltration processes that happened a very long time ago. This application is more highlighted in the arid zones where due to the scarcity and periodicity of the rainfall, the question of recharge (if any) often remains open (Payne 1988). An important fraction of young water within an extracted water sample is an indication of an actively renewable reservoir; the opposite, i.e., a considerable amount of old water in the sample, depicts a poorly recharging reservoir and/or significant internal mixing processes.

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

4.4.2 Prevention of Over-Exploitation and Contamination of Aquifers

Increase in the population density often leads to an exponential increase in the demand on the aquifer. Once residences or industries are established, it is very difficult to limit their water supply. Over-development can eventually lead to limited supply, with the greatest effects being to those districts farthest from the aquifers recharge zone (supply source). By measuring the age of the water at certain time intervals within a district's well field (say once every five years), it would be possible to identify over-exploitation before it happens.

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

4.4.3 Estimation of Rate of Groundwater Recharge

This particular usage of groundwater age data is perhaps the most widely applied of all. Figure 4.12 illustrates in a simple way the approach to calculate the recharge rate to a groundwater system by age data. The procedure is to have either:

1. A minimum of two ages along the vertical line at the point of interest, i.e., age data must be obtained from a piezometer nest, which comprises at least two piezometers opened to the aquifer at different depths, or

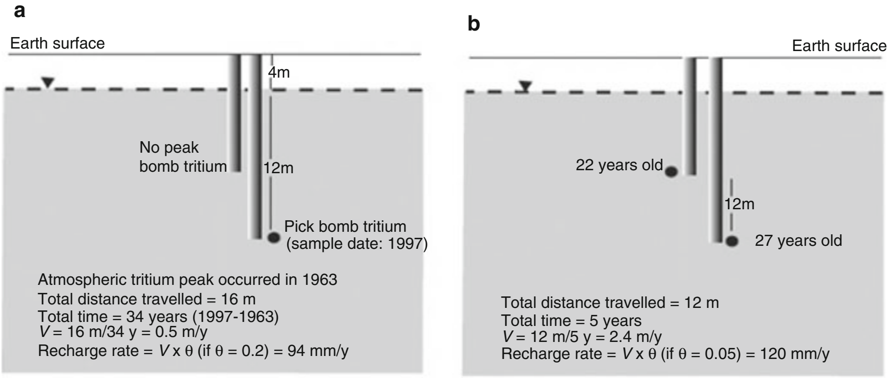


Fig. 4.12 Determination of groundwater recharge rate: (**a**) by locating bomb peak tritium; (**b**) by measuring groundwater ages at two points along a vertical profile such as at a piezometer nest

2. The vertical position of the bomb peak tritium in the aquifer. It should be noted that the groundwater flow should consist of only one vertical component with negligible horizontal movement.

The second approach may not be particularly accurate because of the difference between the flow rates in the saturated and unsaturated zones.

4.4.4 Estimation of Groundwater Velocity

The velocity of groundwater flow can be calculated if we measure the age of groundwater at two separate points along a particular horizontal flow line. The ages should be measured at nearly the same depth and on the same flow line in order to avoid the effect of three-dimensional flows (Fig. 4.13).

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

4.4.5 Identification of Groundwater Flow Paths

Groundwater flow paths in both vertical and horizontal directions can be determined by having ages that increases along the inferred flow lines. Accurate information

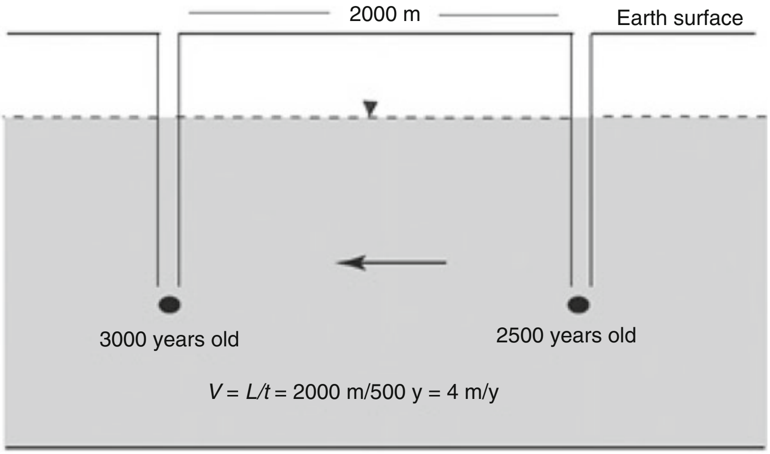


Fig. 4.13 Measurement of groundwater flow rate using groundwater age determination in two different boreholes

about the groundwater flow path is needed in many water resources projects such as in construction of dams (determining different routes that water stored in the dam lake/reservoir may escape), movement of plumes, mixing between different quality groundwaters, and study of surface water–groundwater interaction. Establishing flow directions in various parts of a deep, long regional aquifer is another example for use of groundwater age data.

4.4.6 Confirming the Parameters of Groundwater Flow and Transport Models

Groundwater flow models are increasingly employed as a powerful tool to help manage the groundwater resources. These models usually require an extensive volume of data and parameters, the quality of which is the key to the success of the modelling exercise. Estimation of some of these parameters such as hydraulic conductivity values, specific yields, and aquifer geometrics is always prone to some degree of error. Groundwater age data are the more precise data that can be incorporated into the models to complement the existing data, to eliminate some uncertainties, to serve as model independent calibration data for groundwater transport models (Dörr et al. 1992), and to verify flow models especially those that predict the travel time of source water to wells.

4.4.7 Identification of Mixing between Various End Members

The ages of those groundwaters that are mixtures of various components are helpful to calculate the mixing ratios and to identify the origin of each end member. For this purpose, it is necessary to apply a minimum of two dating methods from different ranges; for instance, an old dating method and a young dating method (it is also possible to identify mixing by having the ratios of the three CFC-11, CFC-12 and CFC-13, which are all for dating young groundwaters). The ages obtained from different dating methods are cross-plotted. On the plots, the best-case scenario would be to have a mixing line joining the oldest sample to the youngest sample.

In such a situation, a simple two end-member equation can be applied.

$$As = Ay(x) + A_0(1 - x)$$

where As is the age of sample in question, Ay is the age of youngest sample, A_0 is the age of oldest sample, x is the percentage of young fraction in the sample, and $(1 - x)$ is the percentage of old fraction in the sample.

Such mixing calculations allow hydrogeologists to study surface water–groundwater interaction and to investigate diffuse flow and conduit flow in fractured rocks aquifer.

4.4.8 Study of the Pre-Holocene Climate

Evidence from groundwater systems may be used to help interpret the timing and nature of climatic changes during the Pleistocene era (Metcalfe et al. 1998). Groundwaters that are old or very old can be studied to identify the type of climate during which they entered the subsurface environment. To achieve this objective, first we have to know the age of groundwater. Then we have to study those parameters of groundwater that are climate indicators such as oxygen-18 isotope values. Combination of these two pieces of evidence will lead to an understanding of the pre-Holocene climate.

4.4.9 Evaluating the Pollution of Groundwater

The isotopic tools for groundwater dating are important because shallow, young groundwaters provide drinking water supply in many parts of the world and also are the most vulnerable to contamination from anthropogenic activities.

Most contaminants, especially human-induced ones, have entered aquifers recently, perhaps not earlier than 100 years ago. Further, groundwaters that were polluted 100 years ago or earlier have so far had enough time to be purified through natural processes because of their long contact with the subsurface environment. Based on these assumptions, the following conclusions can be drawn:

(i) If a water sample is older than 100 years, it should be pollution free.
(ii) For old groundwaters, the contamination risk is low.
(iii) For young groundwaters, the contamination risk is high.
(iv) Along the age line, the concentration of the contaminants should decrease, i.e., older groundwater should show less contamination (concentration of the contaminants should be less).
(v) For a set of groundwater samples, if a contaminated groundwater sample is dated as young, we can be sure that the dating exercise was most probably undertaken correctly and the age data obtained can be used for other purposes.
(vi) If there is a meaningful negative correlation between the age of groundwater and the concentration of the contaminants (the older the age, the lower the concentration of the contaminants), it would then be possible to predict the extent and timing of contamination plume, i.e., concentration reaches to what level and at what time.
(vii) If there is a positive correlation between the age of groundwater and the concentration of contaminants (the older the age, the higher the concentration of the contaminants), it would then be logical to conclude that contaminants are gradually degraded over time.

4.4.10 Estimating the Travel Time of Groundwater Plume to the Points of Interest

By having the age of groundwater, we can:

(i) Predict the time required for a present-day polluting source (a leaking fuel station, for instance) to inflict damage on the water quality at the location of interest.
(ii) Predict the timing of the effect of land-use changes.
(iii) Determine the likely sources of contaminants whose initial applications occurred during a specific time period. The age of the groundwater will help to determine if the sources of contamination can be traced to recent events, or if other unknown sources of contamination exist that would warrant further investigation.
(iv) Estimate the time span required for self-purification of a polluted aquifer after removal of the pollutant.
(v) Determine whether there is enough time for natural purification of surface waters recharging aquifers (e.g., river water) whose quality should improve during the course of travel underground to make them suitable for domestic usages.

4.4.11 Mapping of Vulnerable Shallow Aquifers

Construction of vulnerability map for the aquifers is a relatively modern exercise. These maps can be used by resource protection agencies to focus prevention programmes on areas of the greatest concern and to help prevent contamination of groundwater resources by identifying areas that are at greater risk of pollution. One of the earliest methods to evaluate vulnerability of the aquifers is DRASTIC, which considers seven factors: *d*epth to water, net *r*echarge, *a*quifer media, *s*oil media, *t*opography, *i*mpact of vadose zone media, and hydraulic *c*onductivity of the aquifer (Aller et al. 1985). Generally, groundwaters with a high percentage of young water should be rated as highly susceptible, while those with a high fraction of old water should be regarded as insusceptible or less susceptible.

4.4.12 Assessment of Radioactive Waste Disposal Facilities

Among all of the investigations concerning the safety and feasibility of storing radioactive wastes underground, a high degree of certainty is needed to assure that the contaminants will not leach from the wastes. The likely maximum rates of future groundwater movements can be obtained from knowledge of the past history of flow events in the area under consideration. Aquifer pumping tests, applied tracer tests, and water-level measurement studies all lack the capability to measure aquifer hydraulic properties, *and associated likely changes*, over very large temporal and spatial scales. For this reason, groundwater age data are of prime importance and can provide invaluable information on the hydraulic properties of the waste disposal facilities.

4.4.13 Site Specific Applications

Some of the applications of groundwater age data have been undertaken on a site-specific basis. These include the evaluation of atmospheric acid deposition (Robertson et al. 1989; Busenberg and Plummer 1996), estimating rates of geochemical and geo-microbial processes in the unsaturated zone (Plummer et al. 1990; Chapelle et al. 1987), estimating longitudinal dispersivitiy coefficient (Solomon et al. 1993), determining hydraulic conductivity and transmissivity of the aquifers (Phillips et al. 1989; Hanshaw and Back 1974), finding the origin of methane in gas hydrate deposits (Fehn et al. 2003), identifying groundwater inflow into artificial lakes (Weise et al. 2001), evaluating ecosystem health (Chesnaux et al. 2005), quantitatively describing groundwater flow and hydrogeology (Boronina et al. 2005), and estimating volume of aquifer storage and location of recharge and extracting information on the rates of geochemical and microbiological processes in aquifers.

5 Application of Isotopes in Groundwater Management

Groundwater assessment and management has great significance for a country like India. It is becoming more critical with the growth of population and rapid industrialization. The issue of groundwater management involves reliable assessment of available water, scope for augmentation, distribution, reuse/recycle, pollution, and its protection from depletion and degradation.

Isotopes are being used extensively for studying the soil moisture variation and its movement; recharge through unsaturated zone; origin, age, occurrence and distribution of groundwater in a region recharge mechanism, determination of groundwater flow direction and velocity; interconnections and interaction between aquifers; and identification of recharge areas and sources. Isotopes can also be applied to study surface water and groundwater interaction; tracing sources of pollutants including sea water intrusion and salinization mechanism.

Isotopic methods are normally used in conjunction with conventional hydrological, hydrogeological and geochemical or water-chemical techniques, to provide additional and valuable information for solving hydrological problems. In recent years, a number of complex groundwater problems have been resolved successfully using isotopic methods.

5.1 Groundwater Recharge

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

5.1.1 Artificial Radioactive Isotope Tracers (Tritium Tagging) for Estimating Groundwater Recharge

Artificial radioactive isotopes (produced in laboratory or reactor) can be used as water tracers. The artificial tracers have the advantage over environmental tracers that they are injected in a controlled way and that the concentrations are high enough to be easily detected. The disadvantage is that it is non-natural, which means it may be environmental hazardous and that experiments can only be made at specific points and at specific times.

The most commonly used artificial tracer isotope for groundwater studies is tritium (^{3}H) as HTO, which is applied below the root zone or in the groundwater depending on the purpose of the study.

Artificial radioactive isotope tracer method, also known as, *Tritium tagging technique* was developed by Zimmermann et al. (1967a, b), Blume et al. (1967) and Munnich (1968a, b) with the assumption that the movement of soil moisture in an unsaturated zone is similar to piston type flow. Any water applied to the ground surface, either from precipitation or from irrigation, will infiltrate and percolate by pushing equal amount of water beneath it further down. The amount of moisture content of the last layer in the unsaturated zone is added to the groundwater as recharge. Blume et al. (1967) suggested that the tracer should be introduced/injected below the ground surface (preferably below the root zone), otherwise it may be lost by evaporation or evapotranspiration.

Soil water moves along a range of different pathways. Local field heterogeneity should bring about a considerable dispersion of pollutants or of a tracer. However, field experiments of Zimmermann et al. (1967a and 1967b) and Blume et al. (1967), showed "piston flow" type behaviour of soil moisture in nearly homogeneous soils; infiltrating water simply pushes the old water downward. This means that the soil moisture profile may change shape, but no newly percolated water bypasses water that has previously percolated below the root zone. In the above-mentioned

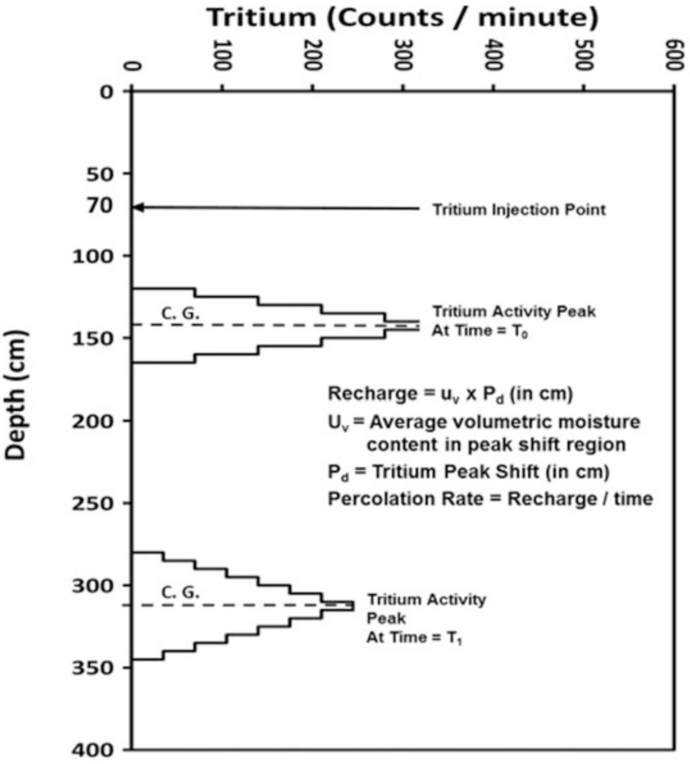


Fig. 4.14 Shifting of injected tritium with respect to the movement of infiltrated water

experiments, the broadening of the peak of the injected tracer was of the same magnitude as expected by molecular diffusion only. In addition, experiments conducted in the alluvial tracers of north India by Bahadur et al. (1977) showed broadening of the tracer peak comparable to the spread by molecular diffusion. It seems that if the flow is slow, the lateral mixing, mostly from molecular diffusion, in rather homogeneous soils between moisture packets having different flow velocities is quite effective, thus indirectly counteracting vertical dispersion.

In the course of water infiltration, an injected or environmental tracer is carried along with the soil water. The position of the peak tracer concentration can be monitored in the soil profile. From the temporal displacement of the tracer, percolation rate or moisture flux, and the groundwater recharge can be estimated, provided the measurements are taken below the root zone so that all water movements are directed downwards. Zimmermann et al. (1967a) used deuterium and tritium as tracers and called the method of tracing the peak as “tracer tagging” technique. The principle of how percolation rates are determined from tracer monitoring is illustrated in Fig. 4.14.

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

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

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

If the experiment is for a full season or full year, the moisture flux corresponds to the recharge over a season or year, although the particular soil water particles do not reach the groundwater during the particular year when the observations are made.

Case Study: Recharge to Groundwater in Bundelkhand Region of U.P., India Using Tritium Tagging Technique

Bundelkhand region in India faces acute water deficiency due to higher losses of rain and surface waters. Keeping in view the prevailing conditions in Bundelkhand region, it was necessary to estimate the correct value of recharge to groundwater due to monsoon rains, which is the main source (Kumar and Nachiappan 1995).

Tritium was injected at 25 sites before the start of monsoon rains. Soil samples were collected from the injected sites in the month of November and recharge percentages were determined. Since sampling was carried out in November, the water input for the irrigation was also taken into account while determining the percentage of recharge. Estimated recharge to groundwater ranged from 6 to 34 cm. This variation may be due to different types of soil, topography, hydrogeology, groundwater level conditions, cropping pattern, rainfall pattern, evapo-transpiration and several other local factors which are very difficult to account for.

Based on the estimated data and rainfall for the 25 sites, an empirical relation was developed (Fig. 4.15) between rainfall-recharge process that fairly satisfy the variation of recharge values. The equations developed distribute the data in two groups A and B given by the equations:

$$\text{Group A} \qquad \mathrm{Rg} = 29.316 \ln(P) - 111.259 \qquad (r = 0.83) \qquad (4.1)$$

$$\text{Group B} \qquad \mathrm{Rg} = 12.861 \ln(P) - 48.757 \qquad (r = 0.85) \qquad (4.2)$$

where Rg is recharge to groundwater in cm and P is rainfall/precipitation in cm.

5.1.2 Environmental Tritium Technique

The radioactive isotope of hydrogen, i.e. tritium (^{3}H), released from thermonuclear explosions in the atmosphere made possible a way of estimating groundwater recharge. The cosmogenically produced tritium, which is produced and assimilated

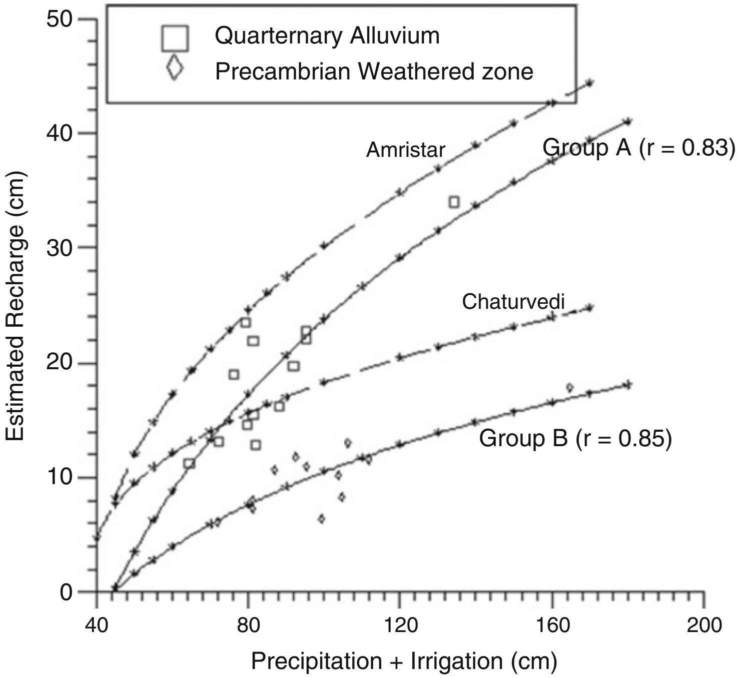


Fig. 4.15 Correlation of estimated recharge (cm) with precipitation

in the atmospheric water vapour, is brought down to earth's surface by precipitation. Before 1952, the tritium concentration in precipitation was low, but after thermonuclear testing began in the atmosphere in 1952, tritium concentrations in precipitation suddenly increased and reached a record-high concentration in 1963–64 in the northern hemisphere. In India, the peak concentration of bomb derived tritium in 1963 was more than 1000 TU. The fact that water originating from precipitation, which has fallen before 1952, has lower tritium concentration than water contributed by later precipitation has been used for tracing groundwater.

Assuming that more recent infiltrating water pushes previously infiltrated water, the bomb tritium of the infiltrated precipitation of a particular year can be found in a soil profile. The tritium concentrations in the soil profile may be moderated due to dispersion and molecular diffusion. Among others, Munnich et al. (1967), Sukhija and Shah (1976) in India, and Andersen and Sevel (1974) in Europe have used bomb-released tritium for the evaluation of groundwater recharge in Europe and India, respectively. An example of tritium concentration in soil profile is given in Fig. 4.16.

In this method, it is assumed that the amount of water from the soil surface to the soil depth, where the 1963–64 tritium peak is located, is the measure of recharge from that time until the time of investigation. In the other method, the tritium concentration of the water lost as evaporation of surface runoff as well as of the

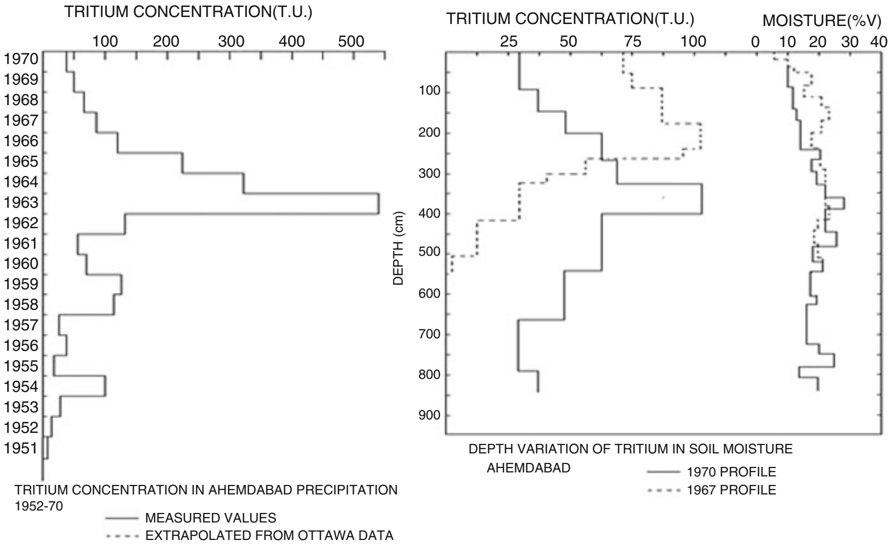


Fig. 4.16 Tritium concentration (without decay correction) in precipitation at Ahmedabad (1952–1970). (*Source:* Sukhija and Shah 1976)

water percolating below the root zone is, at any time, assumed to equal the concentration of the precipitation. The accumulated percolation, *R*, which will contribute to groundwater recharge, is simply given by,

$$R = P\left(M_s/M_p\right)$$

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

5.1.3 Environmental Stable Isotopes Technique

The stable isotopes ^{18}O and D (^{2}H) in precipitation are being used for a long time as potential tracers for natural waters yet they have been little exploited for measuring percolation. The flux of HDO and $H_2{}^{18}O$ from an open water body to the atmosphere is relatively low as compared to the flux of the lighter $H_2{}^{16}O$ because of the lower vapour pressure of the former species, which causes fractionation in evaporation and condensation processes. In cold climate, seasonal stable isotopic composition of precipitation is rather well reflected in soil moisture, whereas in semi-arid climate, the isotope picture of soils is rather complex due to strong fractionation caused by high evaporation rates from the soil.

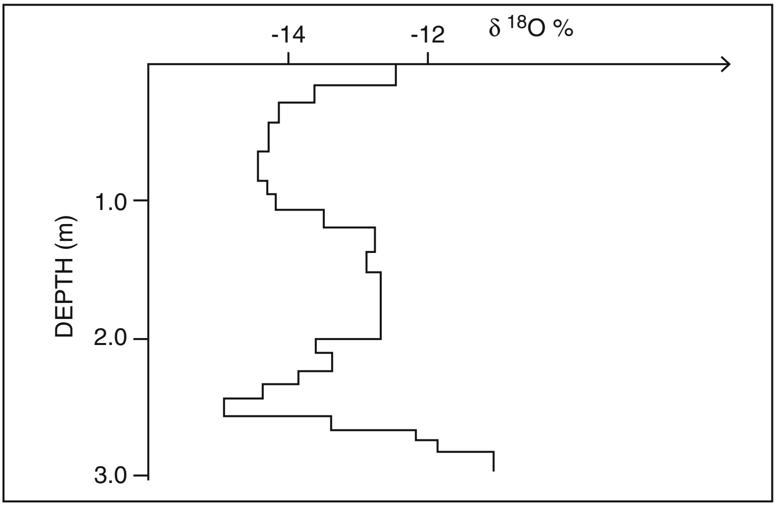


Fig. 4.17 Oxygen-18 profiles in soil moisture patterns indicating infiltrated water in different years

Soil water infiltrated during two periods with a time span of a year can be identified within a soil profile on the basis of stable isotopic composition of either deuterium (^{2}H or D) or oxygen-18 (Fig. 4.17). Therefore, the total amount of percolated water during the year can be estimated simply by totalling the amount of soil water between the two depths where the soil water from the two periods is found. Reduction should be made for eventual residual water.

Mathematically expressed, the annual percolation, R, which will later contribute to groundwater recharge, is

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

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

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

Application of both the environmental isotope methods (radioactive as well as stable isotope method) is restricted to sites where the percolating water of peak tritium concentration has not yet reached the groundwater table. In fact, the environmental tritium method was relatively more useful only until mid-1970s. Most of bomb tritium has by now mixed with the groundwater and the soil profiles have more or less a constant concentration of tritium.

5.2 Groundwater Flow Velocity and Direction

Single well and multi-well dilution techniques are employed using artificial radioactive isotopes to determine the groundwater velocity and direction of flow. In fact, single well dilution method, also called point dilution method can be used to determine both, the velocity and direction of flow using some special probe but multi-well method can be used to determine filtration velocity, transit velocity and direction of flow without using any special probe.

5.2.1 Single Borehole Dilution Technique

Single borehole dilution technique can be employed to obtain direct measurement of filtration velocity in a water bearing formation under natural or induced hydraulic gradient. The filtration velocity interpreted in conjunction with other parameters can provide valuable information about an aquifer.

The dilution rate of the solution, which is homogeneously dispersed in a volume V in the borehole, is related to the horizontal water flow velocity V_f by the equation:

$$V_{\mathrm{f}} = (\pi d/4\varphi)\ \ln\ (Co/C)$$

where '*d*' is the diameter of bore hole, Co is the initial concentration of the tracer at time $T = 0$ and C is tracer concentration at time $T = t$ and φ is the distortion factor which compensate the effect deformation caused by the presence of the bore hole (distortion of flow lines takes place).

The value of φ depends on borehole geometry and permeability in the area of borehole (aquifer, filter tube and filter gravel used) and can be determined theoretically or through model experiments. However, for small borehole, having diameter of 2", its value can be taken as 1, while for large diameter borehole, its value may be taken as 2 or even more. Other factors which affect the dilution rate of the tracer are vertical currents, artificial mixing of the tracer, molecular diffusion etc.

Actual filtration velocity in a borehole can be determined by using the empirical relation,

$$V_{\mathrm{f}} = Vo\{1 - \exp\ (-hD/L)\}$$

where Vo is the actual filtration velocity averaged over the filtration velocities of different currents, h is the height of water column in bore hole and D is the distance of the borehole from the central line of canal or river. L is length of one side curved surface of the canal or river. This relation is not valid in the case of natural groundwater flow velocity measurements. The diffusion velocity in case of tritium has been observed very low, i.e., of the order of 0.5 cm per day by many investigators.

5.2.2 Multi-well Dilution Technique

In this technique, the radioisotope is injected in one borehole, called the main borehole, and either a probe is placed or water samples are collected in/from another borehole constructed at some distance. In fact, if the natural groundwater velocity is to be observed, boreholes are made in a circle keeping the main borehole at the centre. By knowing the travel time of radioisotope from main borehole to the borehole under observation, and distance of borehole, the velocity of transit is determined. The multiplication of specific yield of the aquifer with transit velocity provides the estimate of filtration velocity or groundwater flow velocity. Similarly, if the flow velocity is observed in all the bore holes made around the main borehole, the direction of flow is the direction of borehole in which the maximum velocity is observed.

5.3 Origin of Groundwater

All groundwater of economic interest originates as precipitation. Thus the amount of recharge to a groundwater system, along with the storage capacity of the aquifer, determines the maximum available resources for exploitation. Under favourable conditions (that is, aquifers where the barrier boundaries and the inputs and outputs are well defined) it is possible to construct a simple conceptual model of the system to obtain a water balance. Nevertheless, in many cases, where recharge and water flow are rather complex, more information of the actual process is desirable. Knowledge of the recharge process is also important for preventing deterioration of water quality by salinization and pollution. The environmental isotopic methods provide a valuable approach to understand these complex phenomena as well as to test the validity of the alternative hypothesis.

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

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

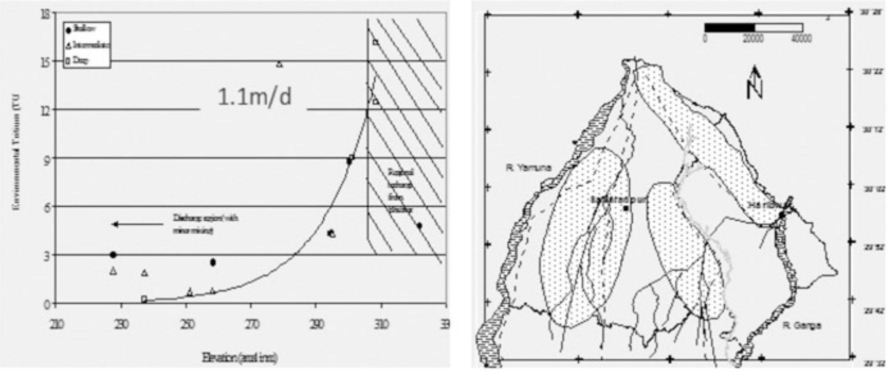
Latitude Effect The stable isotope content of precipitation shows a marked dependence on latitude (depletes with increasing latitude); thus, groundwater replenished by rivers spanning significant latitude zones can be distinguished from local recharge.

Deuterium Excess Another geographic effect on the stable isotope content that can be applied effectively is the shift in the d-excess (defined as δD-δ^{18}O), relating to the source of atmospheric moisture. It is noticed that in the eastern Mediterranean and similar marine belts of rapid evaporation, the resulting precipitation has a d-excess of 22; quite different from the general northern hemisphere precipitation d-excess of 10. This difference can be used in the border areas of climatic zones, where precipitation on the coastal mountains can be of Mediterranean or oceanic origin.

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

Case Study: Identification of Recharge Zones and Recharge Sources in Districts Haridwar and Saharanpur

National Institute of Hydrology carried out a study to identify recharge zones and recharge sources in the Saharanpur district of Uttar Pradesh in the year 1998 (NIH 1999; NIH 2000). For the study, about 130 groundwater samples were collected, from all the geohydrological regions viz., Bhabhar, Tarai and plains, from shallow (upto 50 m), intermediate (50–100 m), and deeper aquifers (>100 m) during the pre-monsoon season of 1998. A few samples for rainfall were also collected. The samples were analyzed for stable isotope and tritium dating. The stable isotopic index for rainfall at various sites in the study area was estimated using IAEA data for rainfall available at New Delhi and using the altitude effect of 0.31‰ per 100 m increase in altitude. The shallow aquifer samples were found to be depleted with respect to rainfall composition while deeper aquifers were found depleted. Using tritium and stable isotopic data, the recharge zones were mapped and the flow velocity for groundwater flow in the deeper aquifer in the eastern Saharanpur district (now Haridwar District) were computed (Fig. 4.18). It was found that the recharge zone of the deeper aquifers is located in the Siwalik (TU~16). Tritium content in



(A) (B)

Fig. 4.18 (**a**) Estimation of groundwater velocity from variation in environmental tritium content in Solani-Ganga Interfluve, and (**b**) Recharge zones identified on the basis of tritium content in Districts Haridwar and Saharanpur

groundwater at a site at Laksar town (in the groundwater flow direction) was measured to be ~1 TU, indicating groundwater velocity to be 1.1 m/d for deeper aquifer.

Major conclusions drawn from the isotopic investigations are: (i) the major recharge zones are located in Bhabhar-Siwalik area and extend over an altitude range of 500–1000 m above the mean sea level, (ii) a local recharge zone exists in the south of Roorkee towards Purkazi town, (ii) shallow aquifers in the Solani-Yamuna interfluve are recharged locally and those in Solani-Ganga interfluve are recharged mainly from Bhabhar-Siwalik region, (iii) the Upper Ganga Canal and Eastern Yamuna Canal are effective in recharging the shallow aquifer over a width of few kilometres, (iv) the deeper aquifers are semi-confined to confined type and are not recharged vertically, and (v) mean groundwater velocity in the Solani-Ganga interfluve is about 1.1 m/d.

The recharge zones identified on the basis of isotopic analysis are given in Tables 4.5 and 4.6.

5.4 Recharge Zones and Sources to Aquifers/Springs

5.4.1 Recharge Zones of Deeper Aquifers

Until the end of twentieth century, groundwater was mostly abstracted from the shallow aquifers and was believed to be safe, free from pathogenic bacteria and from suspended matter. However, with the increase in population and urbanization, and due to technological advancement, the stress on deeper aquifer has increased, mostly because the shallow aquifers have either drying-up or been contaminated. In fact, the deeper aquifers are not only catering the present need of fresh water but also these

Table 4.5 Isotope characterization of shallow aquifers

Area type	Site name & altitude (msl)	$\delta^{18}O$ (‰)		TU	Interfluve type	Possible recharge sources
		Local rainfall	Groundwater			
Tarai-Plains away from rivers and canal network	Chhutmalpur (295 m)	−6.8	−5.8	Intermediate aquifer TU = 17.8)	Solani-Yamuna	100% local precipitation recharge Enrichment due to evaporation
Plains, close to canal	Roorkee (265 m)	−6.7	−7.6	–		Rainfall - 73% and canal seepage 27%
Plain region away from rivers and canal system	Gagalhedi (280 m)	−6.7	−5.3	7.2		100% local precipitation recharge
	Nakud (263 m)	−6.7	−5.5	11.7		100% local precipitation recharge
Plains, near river Yamuna	Toda (247 m)	−6.6	−6.7	–		Rainfall - 96% and Canal seepage 4%
Plains, close to River Ganga	Chandpuri Kalan (228 m)	−6.5	−7.8	3.0	Solani-Ganga	87% from middle Siwalik (~700 m) and 13% from local precipitation

Table 4.6 Isotope characterization of deeper aquifers in Solani-Yamuna interfluve

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

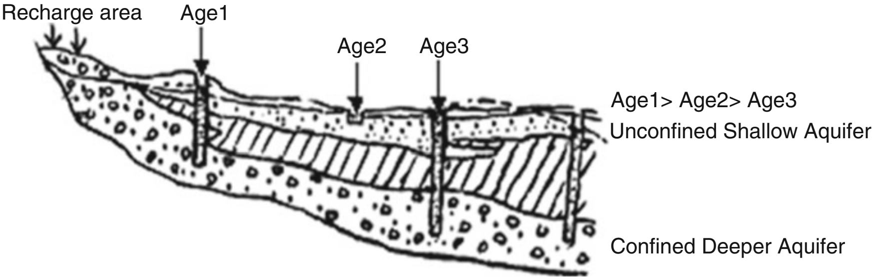


Fig. 4.19 Representation of recharge and discharge zones in confined aquifers

will be the only potential source of fresh water in future. The deeper aquifers for which recharge zones may be located at far-flung areas (Fig. 4.19), may suffer adversely by the various anthropological activities that may either reduce the recharge area or contaminate the recharge source. Once the recharge zones are identified, these can be protected from the anthropogenic activities.

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

Case Study: Groundwater Recharge in Bist Doab, Northwest India

Comparing the groundwater and precipitation isotope signatures, Lapworth et al. (2015) established the dominance of local modern meteoric sources in both shallow and deep regional groundwater recharge in Bist Doab of Northwest India (Fig. 4.20). In few shallow groundwater samples and one canal sample, the isotopic signatures were found to deviate from the regional meteoric water line, indicating significant evaporative enrichment prior to recharge.

The study further indicates that even at a depth of 160 m, groundwater isotope signatures are consistent with local modern rainfall sources (Fig 4.20a and c) and together with the Noble Gas Recharge Temperature (NGT) and $\delta^{18}O$ results from this study suggest that palaeo-water (e.g., Wieser et al. 2011), if present in this region, is deeper than 160 m below ground level (bgl).

Further, the analysis of modern tracers (CFC-12 and CFC-11) has indicated that majority of deep boreholes have a significant component of modern recharge reaching depths of at least 150 m. The presence of significant quantities of tracer in deep boreholes has been considered to be due to the vertical migration of groundwater in the subsurface. This is supported by sedimentary logs from this region which show that while low K horizons are prevalent within the sedimentary sequence (0–150 mbgl), they have limited lateral continuity (Bowen 1985; Singh

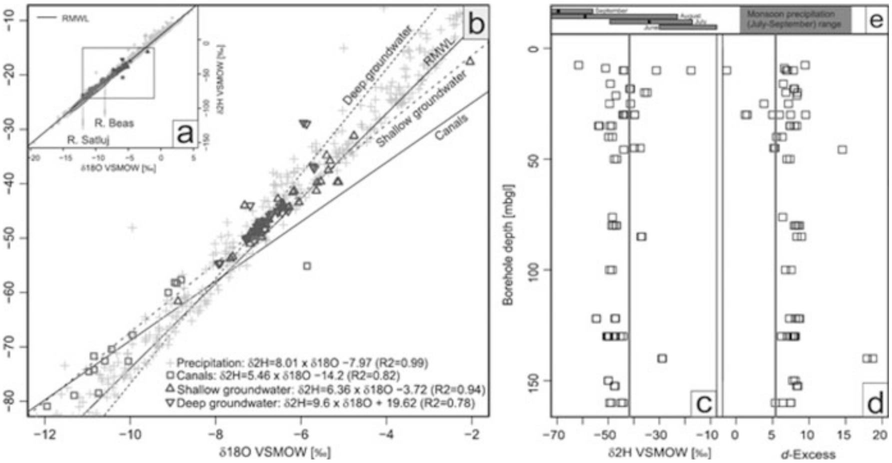


Fig. 4.20 (**a**) Cross plot of $\delta^{18}O$ versus δ^2H for groundwater, canals and precipitation within the study area. (**b**) Cross plot of $\delta^{18}O$ versus δ^2H for data extent for groundwater and canal points. (**c**) Depth variation in δ^2H for groundwater and solid line shows amount-weighted δ^2H for precipitation. (**d**) Depth variation in groundwater d-Excess and solid line shows amount-weighted δ^2H and d-Excess for precipitation. (**e**) median and interquartile ranges for local precipitation data, and monsoon (June–September) precipitation ranges for d-Excess. Note *x* axis on same scale as for Fig. 4.20c and d

et al. 2015), and analogous sedimentary settings in India (Kumar et al. 2007; Samadder et al. 2011; Sinha et al. 2013).

5.4.2 Recharge Zones of Springs

In order to identify the recharge zones of springs, the water samples of springs are collected along with precipitation samples from different altitude. The δD and $\delta^{18}O$ of samples are analysed along with environmental tritium of spring water. The altitude effect in the study area is established. The δD vs $\delta^{18}O$ plot is used to determine the isotopic value of spring water. If the sample data fall on the evaporation line, the line is extended back to get the real isotopic value of spring water if it would have not been subjected to evaporation. After determining the isotopic value of spring water (either δD or $\delta^{18}O$), the altitude of the recharge area is determined using the altitude effect equation.

Case Study: Identification of Recharge Zones of Springs at Gaucher, Uttarakhand

A study was conducted jointly by Isotope Applications Division, Bhabha Atomic Research Centre, Mumbai and Himalayan Environmental Studies and Conservation Organization, Dehradun to identify the recharge areas at Gauchar area of Chamoli, Uttarakhand (Shivanna et al. 2008).

Stable isotope data of precipitation collected from three different heights of the valleys, viz. 1180, 990 and 800 m above mean sea level (amsl) during September 2004 show that $\delta^{18}O$ varied from −10.0 to −8.2‰ and δ D varied from −69.2 to −56.3‰. The isotopic composition of spring water varied from −7.7 to −7.0‰ for $\delta^{18}O$ and from −57.9 to −50.3‰ for δD.

For estimating the altitude effect, the stable isotopic compositions of the precipitation samples were plotted against their corresponding altitudes. The altitude effect was calculated as the inverse of the slope of the best-fit line. It was found to be −0.55‰ for $\delta^{18}O$ and −3.8‰ for δD per 100 m rise in altitude (Fig. 4.21). Generally, the discharge rates of springs ranged from 0.7 to 120 l/min during the

Fig. 4.21 $\delta^{18}O$ vs altitude of the rainwater samples from Gaucher area. Dotted line indicates the recharge altitudes of the low-altitude springs. (*Source:* Shivanna et al. 2008)

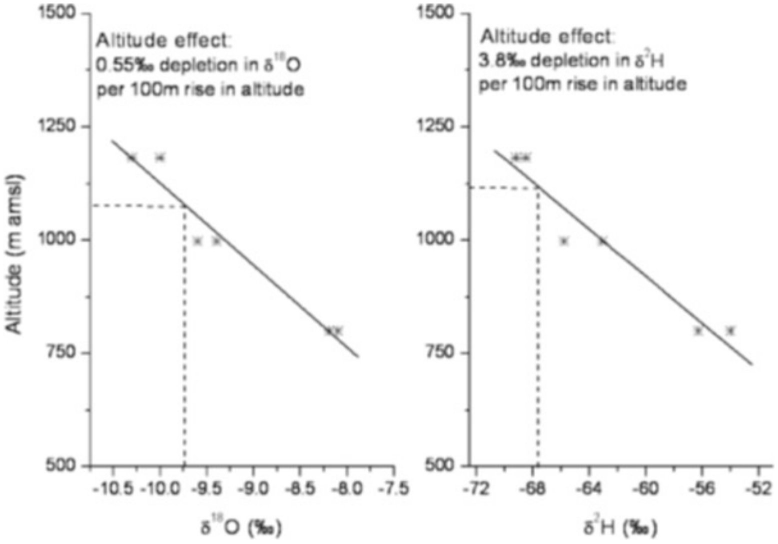


Fig. 4.22 (Right) Subsurface dykes; (Left) New spring that appeared subsequently

monsoon season, which reduced to 0.2–99 l/min within a month after the monsoon. The discharge measurements indicated that all the springs responded instantaneously to the precipitation events.

During summer, most of the high-altitude springs dry up, whereas low-altitude springs continue to discharge with low rates. This shows that low-altitude spring discharges were a mixture of groundwater and precipitation, whereas only precipitation contributed to the high-altitude springs. The tritium content of the low-altitude springs was about 9.5 TU, whereas it was about 11.5 TU for high-altitude springs. This slight variation in tritium content can be attributed to relatively longer residence time of groundwater in low-altitude springs compared to that of high altitude springs. The topography and geology of the area suggests that the presence of thin, weathered, top soil cover underlain by hard and compact quartzite, phyllite and granite with a steep gradient does not allow the rainwater to percolate down, and hence the spring waters were mostly derived from seepage waters. Based on geology, geomorphology, hydrochemistry and isotope information of the study area, the recharge zones to the springs were located at altitudes of 1270, 1330 and 1020 m amsl respectively. At these identified altitudes, water-conservation and artificial recharge structures like subsurface dykes (5 nos.) in valley-1, check bunds (2 nos) in valley-2 and a few trenches in valley-3 were constructed for rainwater harvesting (Fig. 4.22). Monthly spring discharge measurements were carried out during December 2004–April 2005 before the construction of the structures and also during the same period in the following year, after the construction. The cumulative discharge rate of ten springs increased from 375 to 708 l/min during the post-monsoon period. It was found that the discharge rates had not only increased considerably, but also were sustainable even during the dry period. In addition to the existing springs, two new springs also appeared close to the subsurface dykes. The cumulative discharge rate of these new springs was about 67 l/min. The significant increase in the spring discharge rates, their longer duration and formation of new springs can be attributed to proper identification of recharge areas and implementation of artificial recharge structures.

5.4.3 Recharge Sources/Surface Water and Groundwater Interaction

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

One of the important uses of isotopic characterisation of waters is to study the surface water and groundwater interaction. It is based on the fact that the surface water, particularly rivers originating at the higher altitude, normally has different stable isotopic composition than that of groundwater recharged by infiltration of local precipitation where the surface-groundwater relation is under investigation.

In the areas near to bank of the river or lake, there are two possible sources of recharge to groundwater, viz. infiltration of local precipitation and infiltration of river water. In such conditions, the accuracy of the estimate of the proportion of infiltrated river water depends upon the accuracy of the estimates of stable isotopic indices (most common value of the source water) of these two potential sources of recharge and the difference between these indices. An estimate of the isotopic indices of the surface water body is made on the basis of isotopic values measured at different times and especially at different stages/discharge to ascertain whether there is any significant variations in stable isotopic composition with stage discharge. If variations are evident, then the mean value weighted for various stages/discharges is used. The preferable approach is to sample groundwater close to the river where piezometer indicates river water as the source of recharge. The estimation of the index for groundwater generated by infiltration of local precipitation is based on measurements of groundwater away from the influence of the river. If the errors in estimates of the indices of the two potential sources of recharge are not greater than the analytical error, then the accuracy in the estimate of the proportion is better than 10%. In practice the limitations of the method are not in the method itself, but in the availability of meaningful samples.

In most of the cases, the stable isotopes, ^{18}O and D (^{2}H) are utilized for determining the contribution of groundwater to the surface water or vice-versa. If R_1 and R_2 are the isotopic composition of the groundwater and the surface water body, respectively and m_1 and m_2 are the fractions of groundwater and surface water, respectively in the admixture, while R_{am} is the isotopic composition of the admixture, then the isotopic balance and mass balance equations can be written as:

$$m_1R_1 + m_2R_2 = R_{am} \text{ and } m_1 + m_2 = 1$$

From the above two equations, we have

$$m_2 = (R_{am} - R_1)/(R_2 - R_1)$$

Therefore, by knowing the value of R_1, R_2 and R_{am}, the fraction of surface water mixed with groundwater can be evaluated.

Case Study: Surface Water–Groundwater Interaction at Palla, Delhi, Case Study of the Yamuna River at Delhi

To understand the interaction of surface water and groundwater at Palla village in Delhi, National Institute of Hydrology conducted a detailed study during 2007–2010 (Kumar et al. 2012). The study was based on the fact that the River Yamuna originates at higher elevation and normally has a different stable isotopic composition than that of groundwater being recharged by infiltration of local precipitation. In case of a mountainous river, the river transports water, which has generally been originated from precipitation falling at higher elevations than the area where the surface-groundwater relation is under investigation. The difference in isotopic composition of these waters is due to altitude effect. The isotopic composition for ^{18}O in precipitation changes between −0.2 and −0.3‰ per 100 m with altitude. Thus, the stable isotopic composition of the river water is more depleted than that of groundwater derived from infiltration of local precipitation. This distinct difference helps in identifying the contribution of one to the other. The studies carried out by NIH, Roorkee and few others have revealed that the River Yamuna has stable isotopic signatures (δ^{18}O) in the range of −8 to −9‰ while the groundwater in Delhi region varies between 6 and 7‰ where recharge due to precipitation dominates. Therefore, stable isotopes of hydrogen and oxygen have been used to determine the contribution of groundwater to river or vice versa at the selected locations in the study area.

Similarity of δ^{18}O and δ^2H values between stream and aquifer may indicate interconnectivity, whereas isolated aquifers may contain waters with different δ^{18}O and δ^2H values. Stable isotope systematics of waters around surface water bodies may be used to trace movement of seepage into/from nearby groundwater systems.

Groundwater samples were collected at an interval of seven days (every Sunday) from piezometers on Delhi side and at an interval of 14 days (every alternate Sunday) from piezometers on UP side. While collecting the samples water levels were also monitored in the piezometers (Fig. 4.23).

Based on the δ^{18}O variation in groundwater, the river water and the ranney well, the component of river water in the water supply wells was computed (Fig. 4.24). The percentage of water from the floodplain in various months is given in Table 4.7.

The isotopic analysis of the groundwater, river water and pumped wells indicates that percentage of river water in pumped water vary from season to season and from

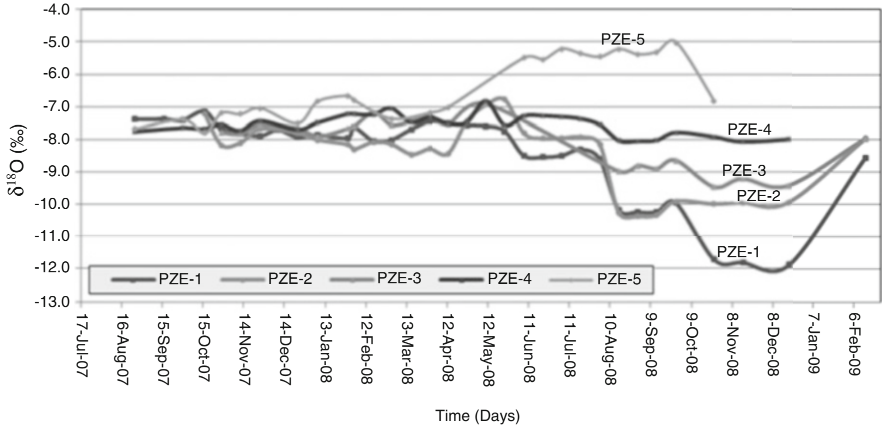


Fig. 4.23 Variation of water levels in piezometers and River Yamuna at Palla in Delhi

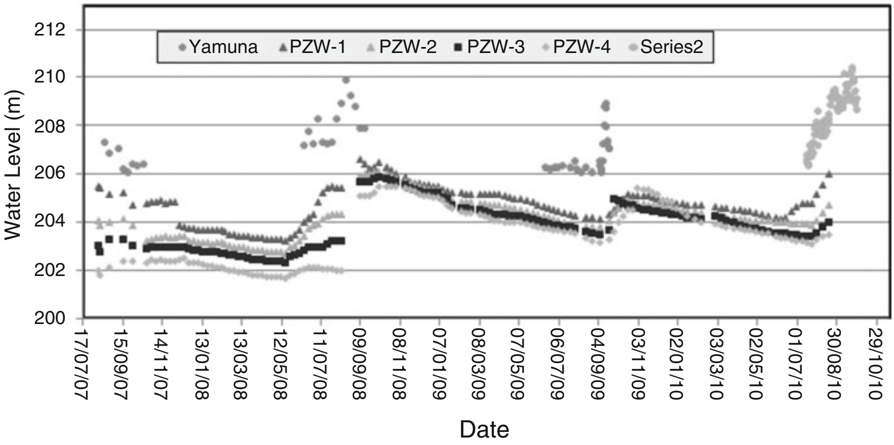


Fig. 4.24 Variation of $\delta^{18}O$ with time in the floodplain of a section across River Yamuna at Delhi

Table 4.7 Component of river water in groundwater pumped from flood plains

Months	$\delta^{18}O$ in ranney well water (‰)	$\delta^{18}O$ in ground water (‰)	Flood plain water in pumped water (%)
Aug-07	−7.9	−6.8	41
Oct-07	−7.9	−6.9	43
Dec-07	−7.8	−7.1	33
Feb-08	−7.1	−6.9	9
Apr-08	−7.4	−6.8	24
Jun-08	−7.6	−6.9	30
Aug-08	−8.0	−7.4	32

year to year. Isotopic analysis of the water samples indicates that River Yamuna recharges groundwater on the Delhi side (Palla sector) more than the UP side during monsoon season (July to October). The recharge on the UP side takes place only during high floods, but on the Delhi side, the recharge occurs even during low floods also. During the years when there is no flood or the floods are of short duration, the contribution of water from the river Yamuna and its floodplain in the pumped water goes upto 50% during monsoon season, which gradually reduces and reaches to the tune of 20% during non-monsoon. During the year of major flooding, the contribution from the River Yamuna and its floodplain to the pumped water becomes 100% during monsoon season, which goes on reducing but continues for longer duration depending upon the availability of recharged water in the floodplain.

5.5 Effectiveness of Artificial Recharge Measures

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

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

For example, the contribution of rainfall (m_p) or channels (m_{ch}) in groundwater can be determined using the following relation based on $\delta^{18}O$ values of end members.

$$\begin{aligned} m_{\mathrm{p}} &= \left(\delta^{18}\mathrm{O}_{\mathrm{gw}} - \delta^{18}\mathrm{O}_{\mathrm{p}}\right)/\left(\delta^{18}\mathrm{O}_{\mathrm{ch}} - \delta^{18}\mathrm{O}_{\mathrm{p}}\right) \\ \text{or}\quad m_{\mathrm{ch}} &= \left(\delta^{18}\mathrm{O}_{\mathrm{gw}} - \delta^{18}\mathrm{O}_{\mathrm{ch}}\right)/\left(\delta^{18}\mathrm{O}_{\mathrm{p}} - \delta^{18}\mathrm{O}_{\mathrm{ch}}\right) \end{aligned}$$

^{3}H values of groundwater can confirm the recent recharge due to artificial measures.

Case Study: Ozar Watershed Study in District Nasik, Maharashtra

Groundwater, precipitation and Hantur Canal water samples from the Ozar watershed were analyzed for δ^{18}O and ^{3}H (Kumar et al. 2009). Tritium in groundwater ranged between 14 and16 TU. These values were comparable to the Hantur canal (~12.6 TU), the water of which is used for artificial recharge through earthen channels, and much different from the rainfall in the area (^{3}H ~5 to 6 TU). Therefore, it is inferred that the groundwater is more dominated by recharge from canal waters through earthen channels and rainfall recharge component is comparatively very less. Moreover, the data reflect that the groundwater is young with negligible aquifer storage.

The contribution of rainfall or channels in groundwater is determined using the following relation based on δ^{18}O values of end members.

$$\begin{aligned} m_{\mathrm{p}} &= \left(\delta^{18}\mathrm{O}_{\mathrm{gw}} - \delta^{18}\mathrm{O}_{\mathrm{p}}\right)/\left(\delta^{18}\mathrm{O}_{\mathrm{ch}} - \delta^{18}\mathrm{O}_{\mathrm{p}}\right) \\ \text{or}\quad m_{\mathrm{ch}} &= \left(\delta^{8}\mathrm{O}_{\mathrm{gw}} - \delta^{18}\mathrm{O}_{\mathrm{ch}}\right)/\left(\delta^{18}\mathrm{O}_{\mathrm{p}} - \delta^{18}\mathrm{O}_{\mathrm{ch}}\right) \end{aligned}$$

where m_{p} and m_{ch} are the contributions of precipitation and channel water to groundwater respectively while $\delta^{18}\mathrm{O}_{\mathrm{gw}}$, $\delta^{18}\mathrm{O}_{\mathrm{p}}$ and $\delta^{18}\mathrm{O}_{\mathrm{ch}}$ are the corresponding oxygen-18 values of groundwater, precipitation and channel water. Figure 4.25 clearly indicates the percent contribution of rainfall in recharging groundwater in Ozar watershed. The percent artificial recharge to groundwater through earthen channels can be estimated by subtracting percent of rainfall recharge from 100. A straight line relation between the amount of rainfall and $\delta^{18}\mathrm{O}_{\mathrm{p}}$ values also enables to determine the percent contribution of rainfall to groundwater.

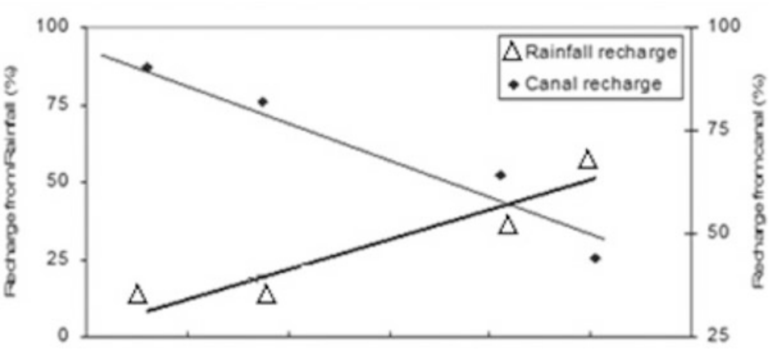


Fig. 4.25 Rainfall recharge to groundwater and the δ^{18}O of precipitation

5.6 Groundwater Salinization

The build-up of salinity in groundwater and soil represents a major wastage of natural resources in arid and semi-arid zones. The salinity of groundwater may occur due to several processes, but, two of them are of major importance, that is (i) salts leached by percolating water; these salts may be evaporative deposits, aeolian transported salts (usually of marine origin) or products of weathering of surface rocks and soils, and (ii) infiltration or mixing of saline surface water, seawater, brines and connate water with groundwater.

Conventionally, ionic ratios, such as, Na^+/Cl, Ca^{+2}/Mg^{+2}, $SO_4{}^2/Cl$ etc. are used to study the source of salinity. However, after transport of the salts by percolating water to the water table and after primary mixing with saline waters, the chemistry of the water may undergo further secondary changes which may make it difficult to identify the mechanism of salinization precisely. The problem of identifying the mechanism of salinization becomes more acute in irrigated areas in arid zones. Leaching is usually local and the soluble salts may not be transported very far from the area of generation/accumulation. Thus, low rainfall and high evaporation rates, which are characteristic of arid zones, tend to concentrate salts in the groundwater. Also, surface drainage is poorly developed in arid regions and has no outlet to permanent stream. These further result in accumulation of salts in these regions.

The use of environmental isotopes, D and ^{18}O, allow distinction of leaching from evaporation. Leaching causes no isotopic change, whereas evaporation leads to isotopic enrichment. Further, the S-34 ($\delta^{34}S/\delta^{32}S$) isotope provides very clear picture about the salinity of marine origin. The isotopic approach is particularly useful in coastal areas where all salinity ultimately originates from marine environment so that little chemical distinction exists amongst salinity originating for example, from sea spray or from direct sea water encroachment from surface lagoons or connate sea water. The stable isotopes along with dating techniques of groundwater in the study of salinization mechanism have been extensively used abroad but comparatively less in India.

In studies dealing with seawater intrusion, the significant difference between sea water and freshwater, particularly for stable isotopes of hydrogen and oxygen, provides a direct means of identifying and studying dynamics of sea water intrusion (pathways, mixing ratios). Furthermore, isotopic evolution during different groundwater salinization processes (i.e. mineral dissolution, leaching of salt formations, or mixing with saline formation waters) exhibit different characteristics, to enable process identification through observations to be made on stable isotope concentrations. Particularly, the use of environmental isotopes, D and ^{18}O, allow distinction of leaching from evaporation. As stated earlier, leaching causes no isotopic change, whereas evaporation leads to isotopic enrichment. In addition, the stable isotopes of sulphur -34 ($\delta^{34}S/\delta^{32}S$) isotope provides very clear picture about the salinity of marine origin.

Radioactive isotopes of ^3H (tritium) and ^{14}C (radiocarbon), with their known input concentrations into the hydrological cycle (both natural and anthropogenic origin) also provide a label for different water bodies enabling tracing of sea water intrusion processes. Their natural production in the atmosphere due to interaction of cosmic radiation with the constituents of air is rather steady state. However, large amounts of these isotopes were also released in to the atmosphere by the nuclear weapon tests carried out during the period 1953 to 1963. The unique radioactive decay property of these isotopes, particularly of radiocarbon with a steady-state input concentration, also facilitates time-domain estimation to be made of the physical parameters related to circulation dynamics of groundwater.

Freshwater derived from precipitation is always isotopically different (contains less species of heavier isotopes) than sea water due to isotopic fractionation processes occurring during evaporation and condensation. In addition, the evolution of stable isotope concentrations during different natural processes, and particularly the resulting relationships between ^{18}O and ^{2}H concentrations, provide an effective tool for many hydrological applications, such as assessment of the "genesis" (origin) of water, particularly in groundwater systems; for the processes involved in replenishment (process tracing), for estimating mixing proportions of different sources or component flows (component-tracing); and studying hydraulic relationships between groundwater and surface waters or between different aquifer units in a given groundwater system. Thus, stable isotopes provide an effective label for sea water and freshwater to enable tracing of sea water intrusion, as well as identifying processes that may be responsible for water salinization.

During the processes of leaching salt formations or mineral dissolution, the stable isotope content of the water is not affected while the salinity of water increases. This is a unique feature which will enable identification of such processes based on isotopic and chemical data. The stable isotopes ^{18}O and ^{2}H are the most conservative tracers during their transport in hydrological systems and their relationship with salinity changes is univocal.

The identification of sea water intrusion could also be made through the use of tritium and/or radiocarbon concentrations. However, since the concentration of these isotopes also is removed from the system through radioactive decay and changes that may be induced by complex geochemical reactions in the case of radiocarbon, they may present difficulties for this purpose. This is why these radioactive isotopes are more often used for estimating the travel times (transit time) of component flows and to distinguish the present and palaeo-origin of salinity i.e., high salinity with high ages of groundwater indicates either salinity of palaeo-origin or due to very slow process of dispersion and diffusion of marine dissolve salts.

Case Study: Sea Water-Groundwater Interaction in the Coastal Zone of Krishna Delta

The groundwater-sea water inter-connection in the Krishna river delta, India was studied by Nachiappan et al. (2003). To establish the interconnection, groundwater samples (from depths: <30 m, 30–60 m and >60 m) and surface water samples from River Krishna, its distributaries, sea (Bay of Bengal) water and Prakasam Reservoir

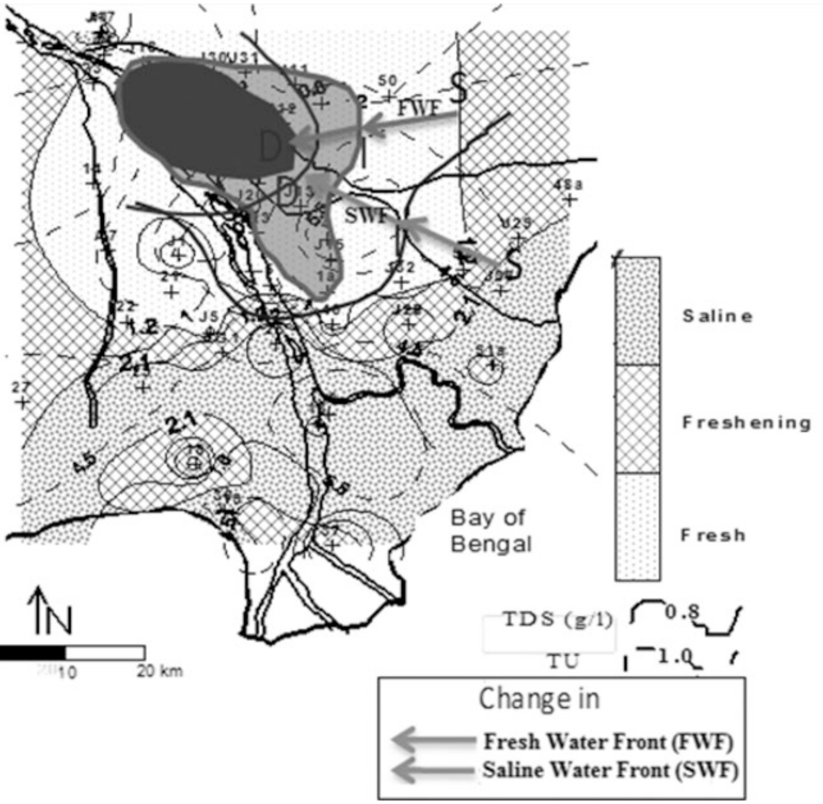


Fig. 4.26 Change in groundwater saline and fresh water interface with depth (S – Shallow, I – Intermediate, D – Deep) in Krishna delta

were collected during 1999–2002. The samples were analyzed for EC, ^{3}H and stable isotopes. A few samples were also analyzed for ^{14}C. Isotopic and chemical data indicated that the present day salinity in shallow, intermediate and deep aquifers extended over a distance up to 27 km, 32 km and 50 km from the present day seacoast respectively. Groundwater age increases towards the coast. The old groundwater in the area is interpreted to be of palaeo-marine origin. The fresh groundwater recharge taking place from Prakasam Barrage, along the canal tract (particularly in the area near Kaza in eastern delta) and along few paleochannels (on which Krishna canals are laid) is mixing with old groundwater and thereby diluting the pre-existed salinity (Fig. 4.26). The mixing was found to decrease at deeper levels. The results were corroborated with reference to the palaeo-coast line, dates on fossil shells, peat/wood and calcrete materials, and chemical data.

5.7 Assessment of Groundwater Potential and Sustainability in Fractured Hard Rocks

In order to address the problem of realistic assessment of groundwater potential and its sustainability in fractured hard rocks, it is vital to study the recharge processes and mechanism of groundwater flow, where heterogeneities and discontinuities play a dominant role. Wide variations in chloride, $\delta^{18}O$ and ^{14}C concentrations of the groundwaters observed in space and time could only reflect the heterogeneous hydrogeological setting in the fractured granites of Hyderabad (India). Isotopic and environmental chloride variations of the groundwater system put forth two broad types of groundwaters involving various recharge processes and flow mechanisms in the granitic hard rock aquifers found in Andhra Pradesh. Relatively high ^{14}C ages (1300 to ~6000 yr. B.P.), $\delta^{18}O$ content (-3.2 to -1.5‰) and chloride concentration (<100 mg/l) are the signatures that identified one broad set of groundwaters resulting from recharge through weathered zone and subsequent movement through extensive sheet joints. The second set of groundwaters possessed an age range Modern to ~1000 yr. B.P., chloride in the range 100 to ~350 mg/L and $\delta^{18}O$ from -3.2 to $+1.7$‰. The $\delta^{18}O$ enrichment and chloride concentration further help in the segregation of the groundwater into different sub-sets characterized by different recharge processes and sources. Based on these processes and mechanisms, a conceptual hydrogeologic model can be evolved to understand the fracture network ant its linkage with recharge sources and their contribution.

5.8 Groundwater Flow in Fractured Rocks

Radon (^{222}Rn) concentrations in unpurged bores can be used as a qualitative indicator of groundwater flow rate. Radon is produced from decay of uranium and thorium minerals in the aquifer and has a half-life of 3.8 days. High concentrations of radon in streams have been used as a quantitative indicator of groundwater discharge. In a similar way, high concentrations of radon in the borehole should indicate active groundwater inflow. If there is zero flow from the aquifer to the borehole, we would expect radon concentrations in the borehole to be zero due to radiogenic decay. However if flow through the well is faster than radon can decay then we would expect significant concentrations of radon in the well. If we assume that the concentrations of ^{222}Rn are uniform in the aquifer over the length of the borehole, then radon concentrations can be related to groundwater flow rate.

A large number of tracer tests have often been used to characterise fractured flow at small scale field sites. However, little effort has been made to use environmental tracers to characterise fracture flow. Environmental tracer techniques have advantages over hydraulic methods, as they can integrate over temporal and spatial scales. Hydraulic methods provide only a ‘snap shot’ of the present day flow regime. However, where possible, both environmental tracers and hydraulic data should be used together to help develop or constrain conceptual and numerical models.

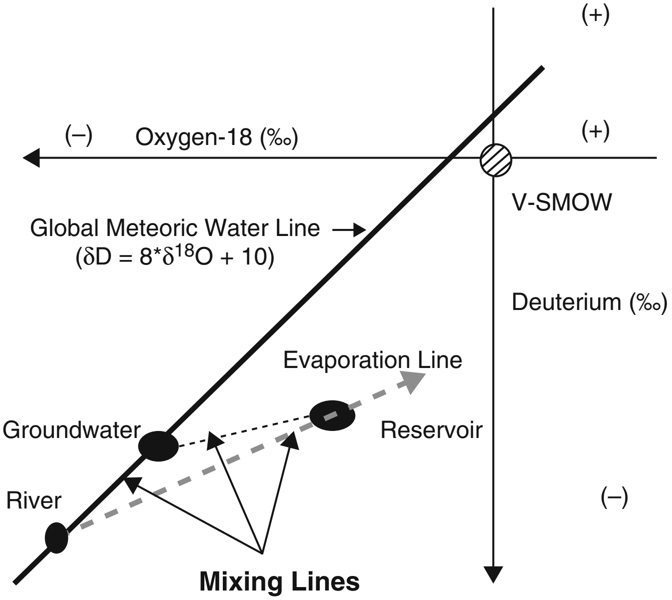


Fig. 4.27 δD and $\delta^{18}O$ relationship of different types of water near a reservoir

5.9 Identifying Leakages from Dams and Reservoirs

Water can escape from reservoirs either as leakage or seepage. It frequently appears below the dam foundation as well as at the abutments through concentrated pathways and emerges downstream forming springs. Concentrated leakage can be a serious problem for these big engineering constructions. In this context the question is asked whether the given leakage (spring) carries water from the reservoir behind the dam or whether it is simply a manifestation of the local hydrological system.

The fact that a surface water body subject to evaporation is changing its isotopic composition in a characteristic way (Fig. 4.27) makes it possible to distinguish between groundwater recharged under typical conditions and waters with an "evaporation history". This distinction becomes obvious when plotting the δD and $\delta^{18}O$ data. The evaporated waters plot on the right-hand side of the global (local) meteoric water line. Significantly, lower or higher ^{3}H values in the leakages, as compared to the characteristic reservoir value, also suggest a different origin of the water. Similarly, $^{13}\delta$ of the dissolved inorganic carbon of reservoir water that is in exchange with atmospheric CO_2 and biological activity is usually significantly higher than that of river inflow and local groundwater. In addition, the chemical composition of the water may provide an additional set of parameters for comparison. Environmental isotopes, both stable and radioactive, can be helpful in identifying the origin of these new occurrences of water near the given reservoir.

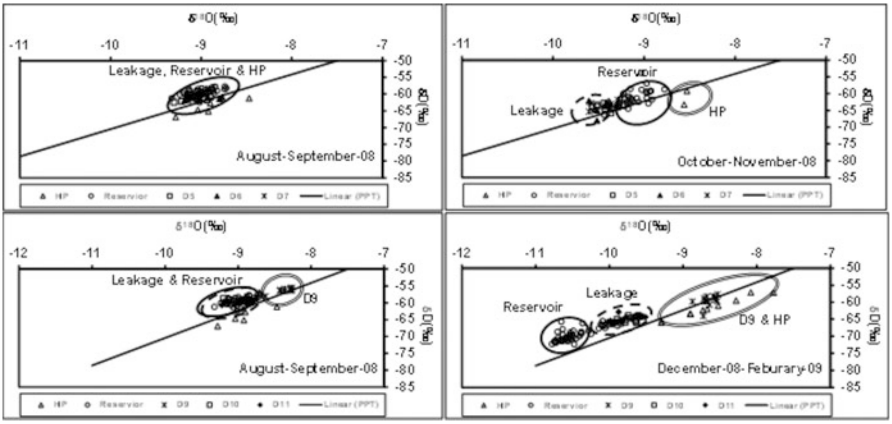


Fig. 4.28 Seasonal variation of δD vs δ^{18}O in groundwater, reservoir surface water and seepage water in inspection galleries Tehri Dam

Case Study: Leakage in Tehri Dam

The isotopic technique was successfully applied to identify the seepage in the inspection galleries of Tehri Dam (Rai et al. 2012). Using the discharge and isotopic composition, two separate fracture zones, responsible for seepage were identified. The reservoir water was the major component in leakage water occurring through seepage galleries.

In order to identify the source of leakage, the δD and δ^{18}O relationship of reservoir and leakage water was studied for the monsoon and post monsoon months (Fig. 4.28).

The seasonal variation in isotopic composition indicated that during monsoon months (August–September), when the reservoir level is above 770 m, isotopic values (δD and δ^{18}O) of reservoir and leakage water fall at the same place. This clearly indicates that the source of seepage water in the drainage galleries was reservoir during monsoon months. However, a different isotopic composition during summer months indicated that when the reservoir level falls below 770 m, the seepage water was groundwater. During the winter months, segregation of isotopic values (δD and δ^{18}O) of the reservoir and the seepage sites indicated that isotopic values (δD and δ^{18}O) of reservoir and leakage water falls under different groups. This was attributed to less contribution from reservoir to leakage/seepage source due to fall of reservoir level after the month of October. During the summer months, isotopic composition became entirely different and discharge was minimal. Thus, the δD and δ^{18}O relationship of reservoir and seepage water confirmed the connectivity of seepage water in drainage galleries D5, D6, D7, D10 and D11 water with the reservoir when the reservoir level is above 770 m. The isotopic values at other locations remained in another group, indicating seepage from groundwater only.

Case Study: Seepage during Tunneling for Salal Hydropower Project

During construction of Tail Race Tunnel for the Salal Hydropower Project in Jammu several seepages were encountered. The tunnelling was through a dolomite

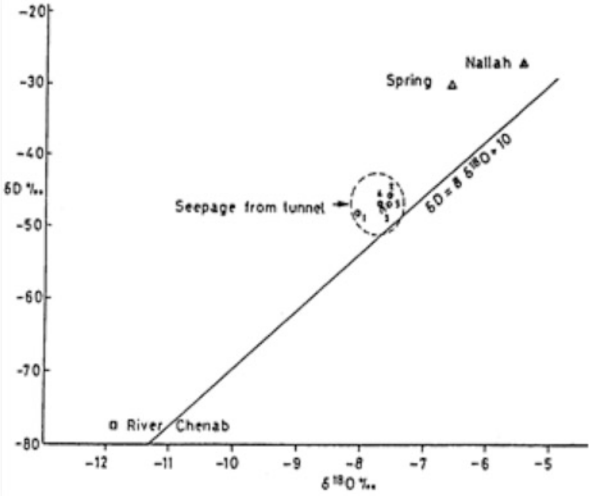


Fig. 4.29 Isotopic composition of sample waters collected in Salal H.P. Project

rock which is highly jointed and often crumbly and sheared. The total length of the tunnel was 2.4 km long and 11 m in diameter. The purpose of the tunnel was to carry the tail waters from the power house and to put them back into the River Chenab. Samples for the analysis were collected from neaby springs, nallahs, River Chenab and the seeping water.

The isotopic results (Fig. 4.29) clearly indicated that the seepage water that has isotopic composition ($\delta^{18}O$ –7.7‰) all along the tunnel is different from isotopic composition of River Chenab (~ −12‰). ^{3}H and EC profile of seepage waters showed a good correlation along the length of the tunnel and was different from the water of River Chenab. Using Piston Flow Model, the age of seepage water was estimated to be 10–15 years. It was concluded that the seepage water is old precipitation water stored or percolating in the fractured dolomite.

In addition to the applications mentioned above, isotope technique has been successfully used to solve problems in arid regions. This includes: isotope studies along the buried river course (considered to belong to the legendary Saraswati) near Jaisalmer; canal (IGNP) groundwater interaction and groundwater salinity canal and return flow in area in Stage I of the command area; groundwater recharge studies in Barmer and Bikaner districts of Rajasthan etc.

5.10 Soil Salinisation

The origin of sulphate—important to differentiate between seawater arid evaporite salt dissolution—can, in some cases, be ascertained with the help of $\delta^{34}S$ and $\delta^{18}O$ values of dissolved sulphate. This is not a common tool, but it is used under special circumstances.

Table 4.8 Role and applications of chemical elements and isotopes in salinity problems

Geochemical/ isotopic tool	Role in evaluating salinity
δ^{18}O, δ^{2}H	Essential indicators with Cl of evaporative enrichment and to quantify evaporation rates, in shallow groundwater environments. Diagnostic indicators of marine and palaeomarine waters.
^{14}C, δ^{13}C	Additional indicator for modern seawater and for dating of saline waters. Half-life 5730 years. Understanding of carbon geochemistry is essential to interpretation.
^{37}Cl/^{35}Cl	Fractionation in some part of the hydrological cycle, mainly in saline/ hypersaline environments may allow fingerprinting.
δ^{87}Sr	Additional indicator of source of groundwater salinity especially in carbonate environments.
δ^{11}B	Additional indicator of salinity source.
δ^{34}S	Indicator of evolution of seawater sulphate undergoing diagenesis. Characterisation of evaporite and other SO_4 sources of saline waters.
^{36}Cl	Half-life 3.01×10^5 years. Thermonuclear production; use as tracer of Cl cycling in shallow groundwater and for recharge estimation. Potential value for dating over long time spans and also for study of long term recharge processes. However, in situ production must be known.
Cl:	Master variable: inert tracer in nearly all geochemical processes; use in recharge estimation and to provide record of recharge history.
Br/Cl	To determine geochemical source of Cl.
Mg/Ca	Diagnostic ratio for (modern) sea water.
Sr, I, etc.	Diagenetic reactions release incompatible trace elements and may provide diagnostic indicators of palaeomarine and other palaeowaters.
Nutrients (NO_3, K, PO_4)	Nitrate accumulation may accompany Cl in aerobic arid environments. Nutrient elements characteristic of irrigation returns.
Organics	Indicator species (e.g. fatty acids) to characterize marine waters of different age. Pesticides etc. diagnostic of irrigation sources of salinity.

A distinct difference in boron isotopes between seawater and terrestrial water is emphasized by ^{11}B values for seawater and groundwater. The isotopic composition of boron in groundwater can be used to quantify seawater intrusion and identify intrusion types, e.g. seawater or brine intrusions with different chemical and isotopic characteristics, by using the relation of δ^{11}B and chloride concentration.

The fundamental relationships between δ^{18}O and δ^{2}H and between δ^{18}O and salinity may be used to identify different salinization pathways. δ^{37}Cl and δ^{11}B can be used to identify the source of salinity in coastal areas. Saline waters are often old waters and advances using long lived radioisotopes (^{39}Ar and ^{81}Kr for example) and gas accumulations (^{4}He) are becoming popular. Advances in the measurement (AMS techniques), use and understanding of ^{14}C, especially using organic carbon, have also provided new impetus to dating approaches. In the real world, therefore, where salinity problems appear to be of a mixed origin, there is now a need to apply a multiple isotope and geochemical approach to understand the salinisation of groundwater systems (Table 4.8).

6 Conclusion

Isotopes have wide applications in groundwater investigations and provide vital information for the better management of water resources. Isotopes also help 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.

These isotopes, both stable and radioactive, occur in the environment in low and varying concentrations with respect to the most abundant isotope of the same element. Environmental isotopes are natural or man-made. In either case, their distribution in the environment is governed by natural processes. Although small, the variations in concentrations of environmental isotopes are measured with high accuracy and provide valuable information on hydrological systems. Processes in the hydrological cycle and interactions between the hydrosphere and atmosphere are responsible for isotopic variations observed in natural waters.

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.

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