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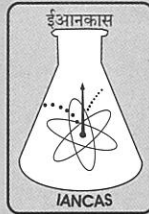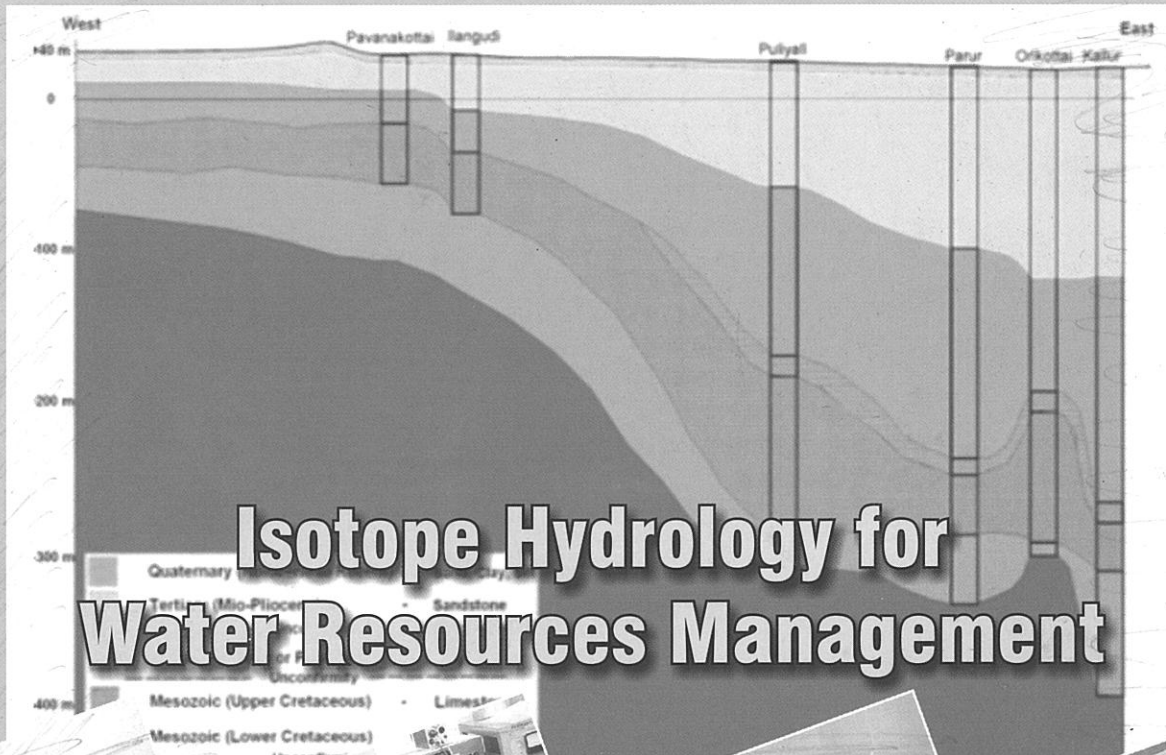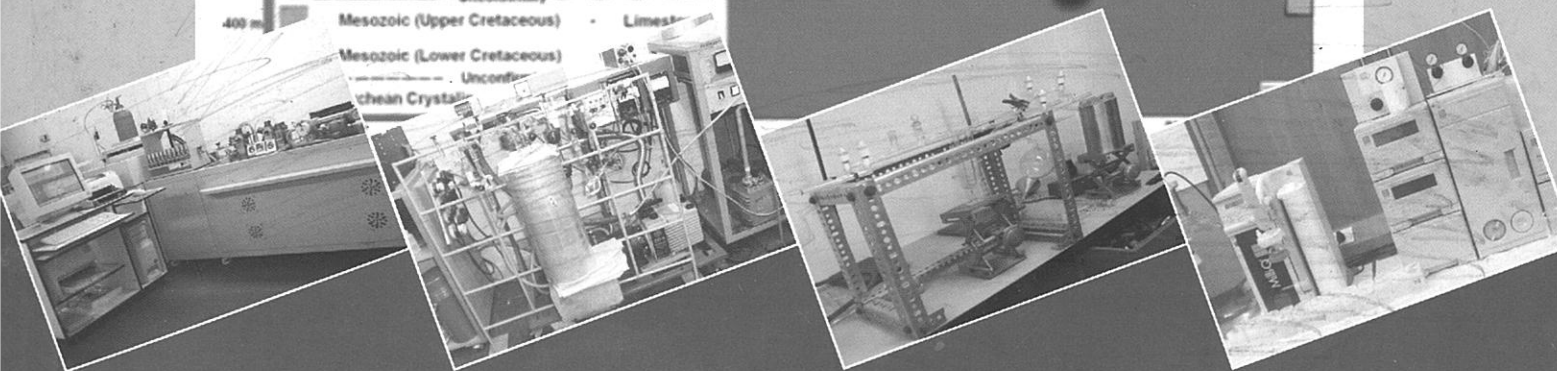## Bulletin

**INDIAN ASSOCIATION OF NUCLEAR CHEMISTS
AND ALLIED SCIENTISTS**

Isotope Hydrology for
Water Resources Management

CONTENTS

Editorial

Water is the most important natural resource for all living things on the earth. Groundwater is used for drinking, agriculture, industries etc. and the demand for fresh water is continuously increasing. Rapid growth of population coupled with ever-increasing demand for water has imposed severe stress on available fresh water resources, both in quantity and quality. Disposal of untreated domestic and industrial wastes lead to serious contamination problems. Hence adequate methodologies are needed for sustainable and reliable development of water resources. Proper remedial measures are required for aquifer clean-up.

Isotope-based methodologies are quite promising for this purpose. Artificial isotope techniques are used to quantify the natural recharge, stream flow measurements, groundwater velocity and flow-direction, leakage and seepage in dams, reservoirs and canals, oil field investigation, sediment transport studies in port areas etc.

The current bulletin highlights the recent advances about the various applications of isotope techniques in hydrology. It covers applications of both artificial and environmental isotope techniques for sustainable water resources development and management. I am thankful to Dr. Shivanna for his excellent support as the Guest Editor.

Basics of Stable Isotope Hydrology

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Abstract

"Isotope Hydrology", an interdisciplinary field, is a comparatively young scientific discipline, which evolved around 1950s, when it was first realised that the methods of nuclear physics and chemistry for the detection of isotopes could have valuable applications in hydrology as well. The conventional tools of isotope hydrology are the isotopes of the constituent elements of the water molecule (H_2O) itself, i.e., the isotopes of hydrogen and oxygen. Next addendum were the solutes and isotopes of elements of solutes and their chemistry, which included radiocarbon (^{14}C), that enabled water dating via the decay of ^{14}C in the carbon dissolved in the waters. Later on, many more methods were added in isotope hydrology including, purposely injected radioactive tracers and some non-isotope (environmental tracers) methods i.e. dissolved noble gases etc. Therefore, from a modern point of view, isotope hydrology may be defined as the application of "environmental isotopes and tracers" to study (parts of) the hydrological cycle. The present article looks into basis of application of stable environmental isotopes in hydrology and their existing measurement techniques.

The oceans are the ultimate source of all fresh waters on the earth. Evaporation at ocean surface forms clouds and then it moves to continent side, owing to pressure difference created by unequal heating of atmosphere, and condensation at higher altitudes again forms liquid water. This traversing path of water molecules in the hydrological cycle is accompanied with variation in isotopic composition at every stage. The various natural phenomena leave their signature on the water molecules. In isotope hydrological investigations this signature is decoded by measuring the isotopic composition of water samples and the type of processes the molecules have undergone is deciphered. The extent of such variation depends on meteorological conditions such as temperature, humidity, state of equilibrium of the process, amount and intensity of rainfall and geographic locations such as northern or southern hemisphere, latitude, altitude etc. In spite of all such contributing factors in isotopic variation, actual variation in meteoric waters even at global level is very small (a few ppm only). This small isotopic ratio variation is routinely measured with Gas Source Isotope Ratio Mass Spectrometer (GSIRMS). Since measuring absolute isotopic ratios are tedious, requiring sophisticated mass spectrometer system and is an unnecessary exercise for hydrological investigations, difference of isotopic ratio w.r.t. to an internationally accepted standard is generated and applied for all isotope hydrological studies.

Introduction

Isotopes (stable and radio) of both environmental as well reactor produced are routinely used as tracers in hydrology for various hydrological investigations e.g. aquifer-aquifer interconnection, surface water-groundwater interconnection, source of groundwater salinity and pollution, origin of geothermal waters, efficacy of artificial recharge, dynamics in lakes, source of recharge & estimation of recharge to the groundwater etc.

The selection of a tracer, whether radio or stable isotope or both, depend on the problem under investigation. Generally, if the area under investigation is large, stable isotopes are the choice. The stable isotopic composition of water is modified by meteoric physico-chemical processes leading to characteristic isotopic signature of precipitation and recharge waters in a particular environment at a specific site. This signature then serves as a natural tracer for the origin of groundwater at that site.

The fundamental concepts of tracer methodology indicate that a tracer should have the same physical and chemical behavior as the traced material. Water would be the ideal tracer for tracing water in the hydrological cycle. But the pertinent question is how to distinguish and detect the water tracer in the hydro system. The isotopes come to our help here. Chemically water molecule (H_2O) is made up of two atoms of hydrogen and one atom of oxygen. Hydrogen and oxygen have three naturally occurring isotopes namely

Protium	^1H	Oxygen -16	^{16}O
Deuterium	^2H or D	Oxygen -17	^{17}O
Tritium	^3H or T	Oxygen -18	^{18}O

"Isotopic" water molecules

Species	Mass (amu)
$HH^{16}O$	18
$HH^{17}O$	19
$HH^{18}O$	20
$HD^{16}O$	19
$HD^{17}O$	20
$HD^{18}O$	21
$DD^{16}O$	20
$DHD^{17}O$	21
$DD^{18}O$	22

Though a number of isotopic species of the water molecule are possible, the following are more relevant to the isotope hydrology because of their higher abundance.

Species	Normal abundance (ppm)
$H_2^{16}O$	997,680
$HD^{16}O$	320
$H_2^{18}O$	2,040

$H_2^{17}O$ has a very low (370 ppm) abundance in nature and is not of much significance in hydrology as we get same information as from $H_2^{18}O$ (2040 ppm). In meteoric waters even at global scale, isotopic variation of a few ppms only is observed. Routinely measuring such a small differences in absolute abundances is not easy and requires sophisticated mass spectrometric equipment. Further, the data sets so generated from different laboratories will suffer from tremendous problems in comparing. The good thing about these data is the information of variation of the stable isotope compositions with respect to a standard is good enough for isotope hydrologists rather than determining their absolute values. Generally, the stable isotopes are measured as the ratio of the two most abundant isotopes of a given element.

The universally accepted standard for reporting stable isotope compositions of natural waters for hydrogen and oxygen isotopes is the Standard Mean Ocean Water (SMOW). It is a logical and natural choice for the standard since all fresh water on the planet is derived from the oceans, which represents 97.2 % of the water in the hydrosphere and they being a very large water body, there is no appreciable change in their isotopic composition with time. For other isotopes, standards are listed below.

Isotopic concentrations are expressed as the difference between the measured ratios of the sample and the reference, over the measured ratio of the reference. Mathematically, the error between the apparent and true ratios is cancelled. The universally accepted way to report the isotopic compositions of natural water is in per mil (parts per thousand) deviations (δ) from the SMOW as shown below:

$$\delta = \left(\frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 1000$$

$$\text{e.g. } \delta^{18}O = \left[\frac{\left(^{18}O/^{16}O \right)_{sam} - \left(^{18}O/^{16}O \right)_{SMOW}}{\left(^{18}O/^{16}O \right)_{SMOW}} \right] \times 10^3$$

The present day Isotope Ratio Mass Spectrometer can measure the δ value with a sensitivity of about 1‰ for deuterium and 0.1‰ for oxygen-18. Considering that the normal range of variations of D and ^{18}O in nature are approximately -500 to $+100$‰ and -60 to $+10$‰ respectively, and that the relative variation of D is about 8 times that of ^{18}O, the sensitivities obtainable in mass spectrometers are more than adequate for most purposes.

The traversing path of water molecules in the hydrological cycle is accompanied with variation in isotopic composition at every stage. The various natural phenomena leave their signature on the water molecules. If this signature

Isotope	Ratio	% natural abundance	Reference (ppm) (Abundance ratio)	Commonly measured phases	Application in hydrology
^2H	$^2H/^1H$	0.015	VSMOW (155)	H_2O, CH_4	Origin of water
^{13}C	$^{13}C/^{12}C$	1.11	VPDB	CO_2, Carbonates	Source of carbonates, Groundwater dating
ht^{15}N	$^{15}N/^{14}N$	0.366	Air N_2 (3677)	N_2, NH_4NO_3, N-organics	Pollution marker
^{18}O	$^{18}O/^{16}O$	0.204	VSMOW (2005)	H_2O, CO_2, SO_4^{2-}, NO_3^-	Origin of water
^{34}S	$^{34}S/^{32}S$	4.21	CDT	SO_4^{2-}, Sulphides, H_2S, S-organics	Origin of salinity, Redox condition of aquifer
^{37}Cl	$^{37}Cl/^{35}Cl$	24.23	SMOC (0.324)	Saline waters	Source of pollution
^{87}Sr	$^{87}Sr/^{86}Sr$	07.00	USGS Tridacna, Sea Water	Solution	Provenance of water
^{11}B	$^{11}B/^{10}B$	80.1	NISTRM 951 - (A Sodium borate)	Solution	Source of pollution

is decoded by measuring the isotopic composition then the type of processes the molecules have undergone, can be deciphered. The two main physical processes responsible for the formation of precipitation in a hydrological cycle are evaporation and condensation. Both of the processes contribute in the variation of isotopic composition of the water molecules. The extent of such variation depends on meteorological conditions such as temperature, humidity and state of equilibrium of the process etc.

Isotope Fractionation

Isotope fractionation is the partial separation of isotopes of an element between two or more chemical species or phases. This causes change in isotopic composition of the element in two reservoirs.

Mechanism of Isotope Fractionation

Two classes of basic mechanisms and two strange ones exist for fractionating isotopes:

- The two basic mechanisms are:
  - equilibrium isotope fractionation, which is due to differences in bond energies of isotopes in compounds
  - kinetic isotope fractionation, which is due to differences in average velocity or reaction rates of different isotopes

  Both depend only on the mass of the isotope and are called mass dependent fractionation; both will fractionate, say $^{18}O/^{16}O$ about twice as much as $^{17}O/^{16}O$.

- The strange mechanisms are mass-independent fractionation;
  - dependent on quantum mechanical symmetry terms that occur for molecules like O_3 and SO_2 and reflects only the identity (not mass) of atoms, so fractionates ^{17}O and ^{18}O equally.
  - dependent on isotope-specific wavelengths of photo-dissociation reactions and is thought perhaps to have been relevant in the solar nebula.

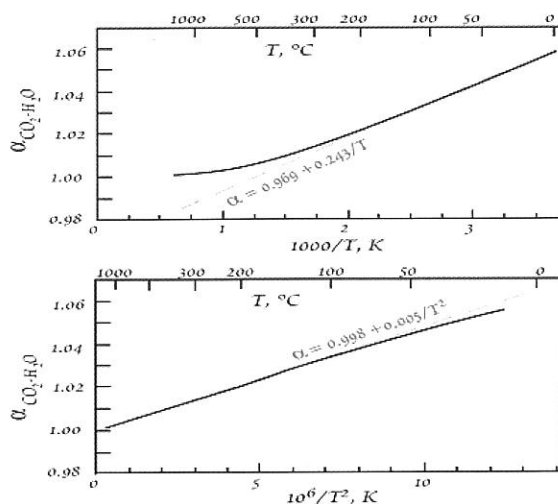### Equilibrium Isotope Fractionation

It controls the distribution of isotopes in the case that a system approaches thermodynamic equilibrium.

- Tends to be most relevant for high temperature problems Igneous and (to a certain extent) metamorphic rocks

  - Some meteoritic processes
  - Hydrothermal interactions
- Tends to be less important in processes involving gas phases, biological reactions, or transport

  Isotopes distribute themselves among compounds in a way that minimizes the energy of the system. The sensitivity to mass comes in through the vibrational modes of interatomic bonds.

Temperature Dependence of Equilibrium Isotope Effects

The equilibrium fractionation factor decreases with increase of temperature.

Calculated value of $\alpha^{18}O$ for CO_2–H_2O, shown vs. $1/T$ and $1/T^2$. Dashed lines show that up to ~200° C, $\alpha = 0.969 + 0.0243/T$. At higher temperatures, $\alpha = 0.9983 + 0.0049/T^2$.

Kinetic Isotope Fractionation Effects

Kinetic isotope effects occur in fast, incomplete, or unidirectional processes like evaporation, diffusion, and biological reactions. Consider an ideal gas. Every molecule has, on average, the same kinetic energy $E = 1/2\ mv^2$. The average velocities of two molecules with different masses due to isotopic substitution therefore follow the relationship

$$\frac{\langle v_1 \rangle}{\langle v_2 \rangle} = \sqrt{\frac{m_2}{m_1}}$$
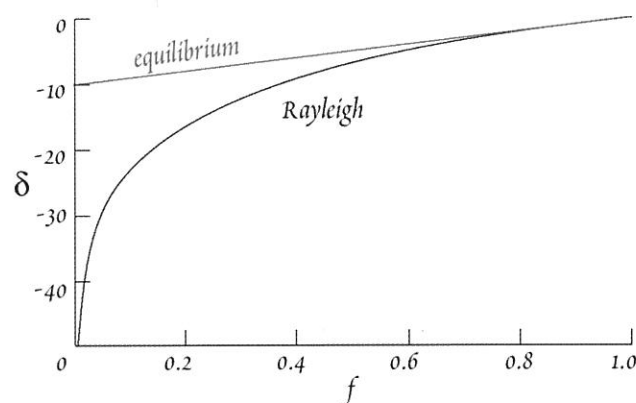
Fractionation of isotope ratio during equilibrium and Rayleigh condensation. d is ‰ difference between the isotopic compositions of the initial vapor and when fraction f of the vapor remains.

Hence the light isotopic species will diffuse faster in the gas phase. Kinetic fractionation effects can be much larger than equilibrium fractionations. This is the result of two factors:

- Equilibrium fractionation factors depend on the imbalance between forward rate constants and reverse rate constants for different isotopes; kinetic factors depend only on the forward rates. Both rates are likely to

be faster for light isotopes, so reverse reaction diminishes the fractionation.

- The open-system effect (Rayleigh type), whereby both the distillate and the residue can become highly fractionated.

Of all the various reasons for isotopic fractionations, the most important, from the point of view of hydrology is the higher volatility of the lighter $H_2{}^{16}O$ compared to the heavier species. The fractionation factors for all processes, where the process proceeds so slowly that equilibrium conditions are practically established at the interface of the two phases, the fractionation factor α

Of all the various reasons for isotopic fractionations, the most important, from the point of view of hydrology is the higher volatility of the lighter $H_2{}^{16}O$ compared to the heavier species. The fractionation factors for all processes, where the process proceeds so slowly that equilibrium conditions are practically established at the interface of the two phases, the fractionation factor α is simply the ratio between the vapor pressure of lighter component (p) and the heavier component (p^1) (P^1<P). It is also defined as the ratio between the isotopic compositions in the liquid phase and the vapor phase. At t =25°C, α are as follows:

$$\alpha_D = \frac{P(H_2{}^{16}O)}{P^1(HDO)} = \frac{(D/H)_{Water}}{(D/H)_{Vapour}} = 1.079$$

$$\alpha_{{}^{18}O} = \frac{P(H_2{}^{16}O)}{P^1(H_2{}^{18}O)} = \frac{({}^{18}O/{}^{16}O)_{Water}}{({}^{18}O/{}^{16}O)_{Vapour}} = 1.0094$$

The above equations indicate that the vapor is depleted by ~8% in deuterium and ~0.9% in oxygen–18 relative to liquid water. Fractionation factors are temperature dependent and decreases with increase in temperature and have a range of 1.106 to 1.029 for deuterium and 1.0111 to 1.0033 for oxygen respectively from 0°C to 100°C. This leads to the important conclusion that in the normal range of temperatures in hydrological investigations, the enrichment or depletion is unidirectional. The vapor is always depleted in heavy isotopes relative to the liquid and the condensate is always enriched in heavier isotopes relative to the vapor. Condensation is an equilibrium process and occurs at 100% relative humidity where as evaporation normally occurs under non-equilibrium conditions and is controlled by kinetic isotope effect. The exact fractionation value depends on factors such as relative humidity and turbulence at the air-sea interface. The kinetic evaporation effect is bigger than the subsequent equilibrium condensation effect. Isotope values of atmospheric moisture originate from both equilibrium and kinetic effects.

Isotopic Characteristics of Meteoric Water

Most meteoric waters have negative $\delta^{18}O$ and δD values. The 'meteoric water' with the lowest $\delta^{18}O$ and δD values is Antarctic ice with a $\delta^{18}O$ = -50‰. The weighted mean value of $\delta^{18}O$ in meteoric water is -4.0‰ if the average groundwater is -7‰ and the average glacial ice is -30‰. It is

just about balances for the earth as a closed system. During the last glacial maximum, when the ^{16}O-enriched continental ice sheets were at their greatest a real extent, the $\delta^{18}O$ of seawater was +1‰ based on mass balance considerations. If the present day continental ice sheets of Antarctica and Greenland were to melt, the $\delta^{18}O$ of seawater would decrease to about -0.6‰, and maybe down to -1.5‰VSMOW.

Isotopic Characteristics of the Oceans

In the early days of stable isotope studies, oxygen and hydrogen isotopes were reported relative to the oxygen and hydrogen isotope value of seawater. The H and O isotope values of seawater are not perfectly uniform in the world's oceans. The $\delta^{18}O$ value ranges from −1.5‰ in Antarctic Bottom Water (ABW) to +0.5‰ in North Atlantic Deep Water (NADW). In marginal marine environments like the Baltic Sea, $\delta^{18}O$ may be as low as −5 to −7‰, whereas in hot arid regions like the Red Sea, values as high as 1.8‰ are found. In practice nobody had ever used seawater as a genuine laboratory standard. Instead, NBS -1 (Potomac River water) was used, and Harmon Craig defined SMOW relative to NBS-1. This prompted the International Atomic Energy Association to prepare a large aliquot synthetic water standard with an isotope value close to seawater. The new standard was called Vienna SMOW, and all modern O and H isotope measurements are made relative to this standard.

## The Global Meteoric Water Line (GMWL)

In 1961, Harmon Craig published his GMWL that defines the relationship between $\delta^{18}O$ and δD of global precipitation. He proposed the relation

$$\delta D = 8\delta^{18}O + 10 \text{ SMOW}$$

This is now updated to

$$\delta D (H_2O) = 8.17 (\pm 0.07) \, \delta^{18}O (H_2O) + 11.27 (\pm 0.65) ‰ \text{ VSMOW (Rozanski et al. 1993)}$$

This GMWL is actually made up of many local MWL and is only an approximation for what is going on. It was quickly recognized that cold regions have low $\delta^{18}O$ values and warm regions have high $\delta^{18}O$ values. This fact has led to a substantial increase in our understanding of the hydrological cycle.
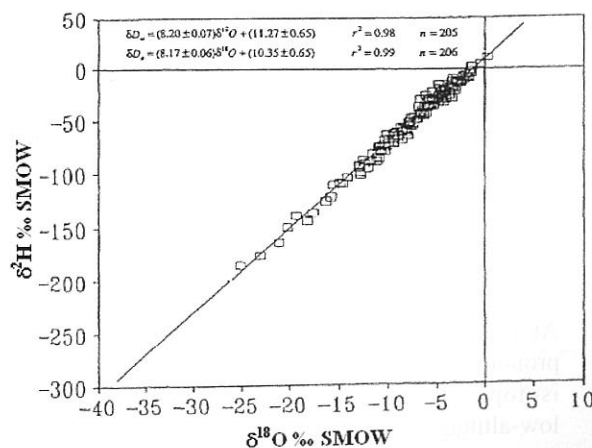
Rayleigh Condensation

It is expressed as $R = R_o f^{(\alpha - 1)}$, where R_o is the vapor's initial isotope ratio value and R is the value after a rainout event. The fraction f is the residual vapor reservoir in the cloud. The fractionation factor α is for equilibrium water-vapor exchange at the prevailing in-cloud temperature. Equilibrium condensation is generally the case in clouds, where humidity = 100%. In a Rayleigh function, α is expressed as product-reactant (i.e. α_{l-v}). In the case of ^{18}O, this would be $\alpha^{18}O_{l-v} = 1.0094$ at 25°C, but will increase as the temperature drops.

Rainout

The only way to produce precipitation is by cooling an air mass. This occurs by adiabatic expansion (no loss of enthalpy) as warm air rises to lower pressures, or by radiative heat loss. When the dew point is passed, water vapor condenses to maintain thermodynamic equilibrium, and it will rain or snow. As an air mass leaves its source (usually in the subtropics) it cools as it rises above the continents or as it moves to higher latitudes. This cooling induces precipitation that distills the heavy isotopes from the water vapor in the air mass. The remaining vapor becomes progressively depleted in ^{18}O and ^{2}H according to a Rayleigh-type condensation. Precipitation with relatively high isotope values (compared to the air mass vapor) falls from the clouds. As precipitation continues however, the water vapor remaining attains lower and lower values resulting in precipitation attaining lower and lower values. This results in the so-called continentality effects and orographic effect that produces precipitation with very low values at high latitudes and altitudes. The relationship between isotope values and temperature allow us to estimate seasonal variability, altitude, latitude and paleoclimatic effects.

For condensation to occur, cooling must take place. Cooling can take place by

1. Lifting over a mountain range.
2. Warm moist air rising.
3. Warm moist air ramped over cold dry air.
4. Air mass warms over lake or ocean and is then lifted and cooled over land (lake effect).
5. Air mass moves to center of the continent during the winter (cooling it).

Controls on the isotope value of precipitation are

1. Isotope value of source
2. Rate of evaporation of source
3. Isotopic evolution of air mass
4. Relative humidity during precipitation (raindrops may evaporate or gain mass as they fall).
5. At high latitudes the amount effect becomes less pronounced as evaporation is lessened. Near the poles, isotope values are near those predicted by the low-altitude temperature. This is because precipitation

often forms at low altitudes and consists of ice particles that are not as subject to exchange with environmental vapor.

Isotopic Equilibrium in Water-Vapor Exchange

The difference in vapor pressure between $H_2{}^{18}O$ and DHO leads to their differential evaporation rates. During equilibrium fractionation this leads to ~8 times the decrease in Deuterium compared to $\delta^{18}O$ in the vapor at 25°C and this ratio increases with decrease in temperature as the equilibrium fractionation factor for D/H fractionation is more sensitive to temperature in compare with $^{18}O/^{16}O$ fractionation which is expected looking at the % mass difference between the pairs.

$$(\delta D_{vapor} / \delta^{18}O_{vapor})$$

At 25°C

$\delta^{18}O_{vapor} = -9.3‰$ 8.17
$\delta D_{vapor} = -76‰$

At 10°C

$\delta^{18}O_{vapor} = -10.6‰$ 8.77
$\delta D_{vapor} = -93‰$

At 0°C

$\delta^{18}O_{vapor} = -11.6‰$ 9.13
$\delta D_{vapor} = -106‰$

Humidity and Kinetic (Non Equilibrium) Evaporation

The rate of evaporation determines how close to equilibrium a water-vapor pair can be. The faster the evaporation, lesser opportunity is available for exchange between the two phases. Increasing evaporation, therefore results in an increased kinetic or non equilibrium isotope effect. Kinetic effects are related to

Humidity,
Surface temperature,
Wind speed (actually shear at the water surface),
Salinity

At low humidity, water-vapor exchange is minimal; therefore evaporation is a non equilibrium process. Lots of people have looked at isotope effects during non equilibrium evaporation of surface water. Basically, they find that the $\delta^{18}O$ and δD values of surface water become progressively higher as evaporation proceeds.

Deuterium Excess "d-excess" in Meteoric Waters

Under conditions of 100% humidity, the vapor is in isotopic equilibrium with seawater and in theory the first rain should plot on a MWL through seawater on the δD v $\delta^{18}O$ plot. It doesn't, however, because of the diffusion related to the kinetic isotope effect, which is a function of relative humidity difference between the bulk atmosphere and the boundary layer. When humidity is low (h = 50%) the vapor is strongly depleted of the heavier isotopic molecules and precipitation plots above seawater, and even above the

GMWL. When humidity is about 85%, precipitation plots are very close to the global meteoric water line. Accordingly, global atmospheric water vapor forms with an average humidity of about 85%, and produces precipitation on a line that is displaced from seawater by +10‰ for δD. Craig's meteoric water line for global precipitation, therefore, has a deuterium excess of 10‰. The d-excess stems from differences in the kinetic isotope fractionation effect between isotopic molecules containing D, and those containing ^{18}O. Dansgaard proposed in 1964 the use of the value, d, to characterize the deuterium excess in global precipitation. The value d is defined for a slope of 8, and is calculated for any precipitation sample as: $d = \delta D - 8\delta^{18}O$

The correlation between temperature and $\delta^{18}O - \delta D$ controls the position of precipitation on the meteoric water line. From this correlation we can derive isotope effects due to seasons, altitude, latitude, continentality and paleoclimates.

Slope of the Meteoric Water Line

Calculated to be 8.2, the slope can be affected by the evaporation of rain as it falls. In arid environments, the slope of the meteoric water line is much less than 8 and typically in the range of 3-5 which is a characteristic of evaporating water. However, the evaporation of falling rain increases the humidity in the air column. This increase in humidity also increases the slope.

Geographical Parameters Affecting Isotopic Values of Precipitation

Due to the above effects isotopic composition of rainwater are related with the geographical parameters such as latitude effect, altitude effect, continental effect, seasonal variations, amount effect and paleoclimates. Considering the complexity of hydrological cycle, it may be surprising that ^{18}O and ^{2}H behave at all predictably.

Latitude Effect

Approximately 65% of the world's water vapor originates between 30°N and 30°S latitudes. Pole ward transport of vapor is associated with rainout and a resultant decrease in available moisture. The spread in the data in fig. is related to several factors.

1. Isotope values of precipitation collected at mid-latitude continental stations are in general lower than coastal or marine stations located at the same latitude. This is especially clear in the Northern Hemisphere.

2. There is a strong vertical gradient in isotope values of atmospheric vapor that results in a tendency to observe lower values at higher altitudes. The best example is the Izobamba station in the Andes near the equator at 3058 m a.s.l., which has an isotope value similar to those found at mid latitudes.

3. Some tropical stations show a pronounced amount effect.
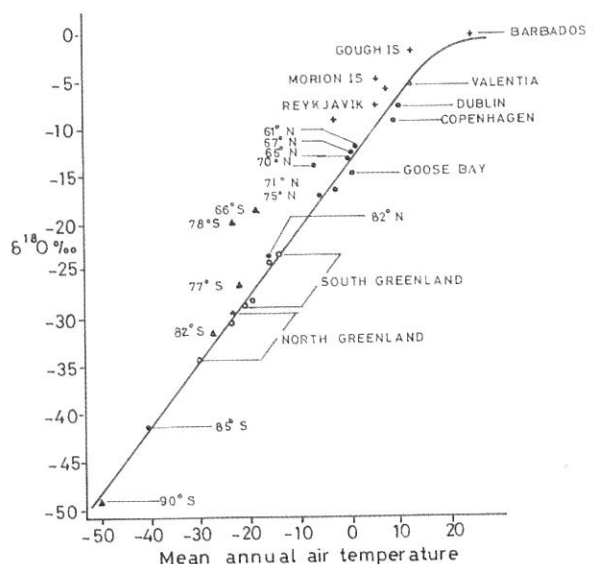
4. Regional temperature anomalies may result in the average isotopic composition of precipitation falling off of the latitudinal trend. For example, Reykjavik, Lista, Isfjord, and Valentia) have higher values than other same latitude sites because of the Gulf Stream temperature effects. A substantial contribution of local vapor for some stations may also contribute to this effect.

Altitude Effect

In general, the distribution of δ values mimics the topography, with mountain chains showing up clearly low values of heavier isotopes at higher altitudes. This is called the altitude or orographic effect. Any time a vapor mass gets pushed up a hill, the air will cool adiabatically (through expansion) resulting in precipitation. The lower temperatures at higher altitudes result in low δ-values. This decrease in δ-value is about −0.15 to −0.5‰ per 100m rise in altitude for $\delta^{18}O$ and about −1 to −4‰ for δD. This effect has been used to determine areas of recharge in hydrological studies.

Altitude effect-δD and $\delta^{18}O$ values in precipitation decrease with increasing altitude (the orographic influence over rainout).
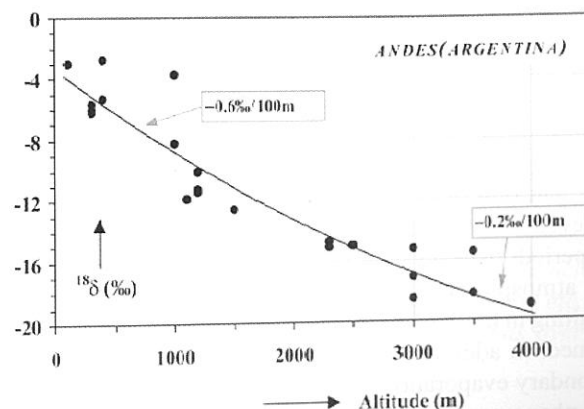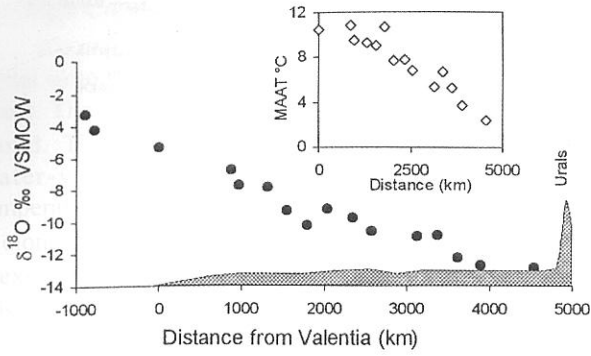
Continental Effect

There is a tendency to observe lower values of heavier isotopes in rain waters as it moves away from the coastline. This is called the continental effect. The same mechanism is responsible for both effects (altitude & continental): gradual removal of moisture from air masses that move inland, or are orographically lifted, coupled with preferential removal of heavy isotopes during condensation. This implies that the ocean is a major source of water vapor over the continents. Such an assumption might however, not always be correct. Large inland water bodies such as lakes or empirics seas could impart a significantly different isotope value upon the vapor derived from the ocean.

Seasonal Variation

Seasonal effects are generally coupled with continental effects such that high latitude mid continental sites has highly variable $\delta^{18}O$ and δD values seasonally. This variation provides a convenient way to estimate seasonal timing of recharge, circulation of groundwater, and the general effect of a precipitation event on a watershed. The regular variation from low δ-values in the winter to high in the summer at mid to high latitudes is due to several factors.

1. Seasonal temperature variation- influences the amount of moisture in the atmosphere and the Rayleigh distillation of that moisture.

2. Seasonal variation in evapotranspiration induces seasonal changes in the atmospheric water balance.

The figures below show that seasonal effects are more pronounced at northern hemisphere observation stations compared to that of southern hemisphere because of higher continentality (lower coastal influence)

Amount Effect

The observation of considerably depleted water during the event of heavy rains is known as amount effect. During the periods of heavy rains more of the water is squeezed from the atmospheric vapor (clouds) by rapid condensation resulting in less isotopic separation between vapor and water formed. In addition, owing to high humidity the degree of secondary evaporation also reduces .The net result of these two phenomena is depleted rainwaters.
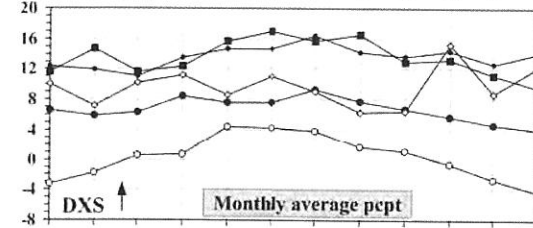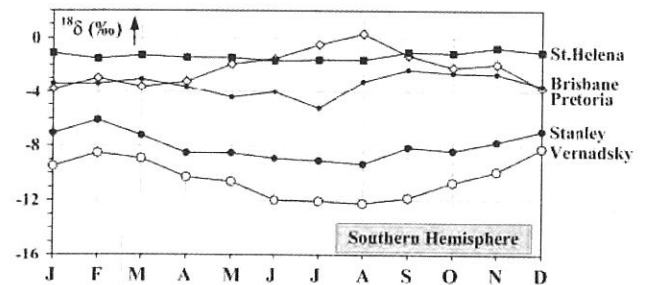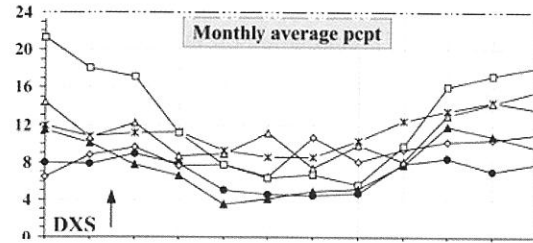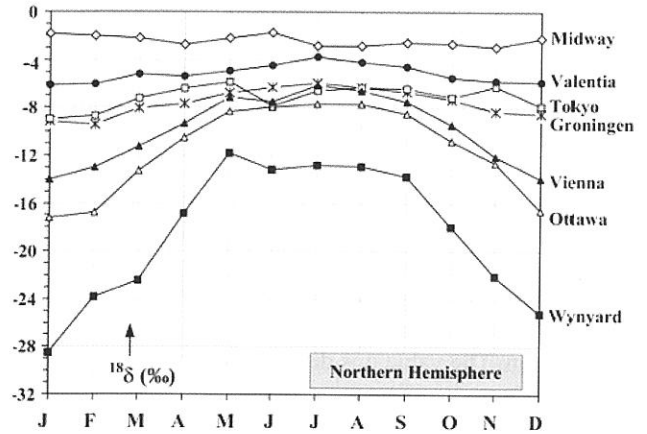

Amount effect- δD and $\delta^{18}O$ values decrease with increasing intensity and duration of rainfall

Paleoclimatic Effect

Paleoclimatic meteoric waters can have entirely different isotopic signatures. It may not fall along modern GMWL. The rainwaters of wet period would be highly depleted compared to that of arid period which could be enriched. Even the evaporated paleoclimatic waters can be distinguished from modern day waters as the starting isotopic composition of the paleo-waters would be different.

Importance of δD - $\delta^{18}O$ Relationships in Hydrological Studies

The observation that isotopically depleted waters are associated with cold regions and enriched waters from that of warm regions was recognized as a tool for characterizing groundwater recharge environments, and is now the basis of
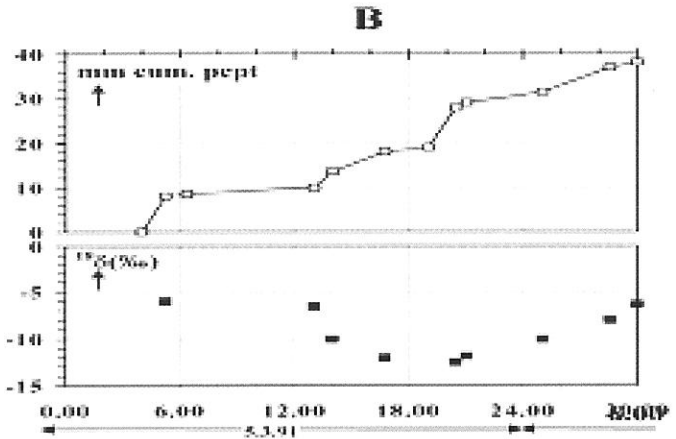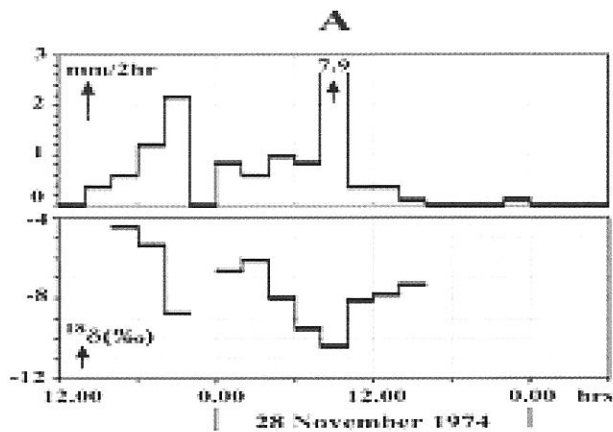
Time sequence of the isotopic composition of precipitation during showers; examples are shown for two cases of convective storms: A) rain intensity in mm/2 hours (Mook et al., 1974); B) cumulative rain over variable periods.

δD - δ¹⁸O Relation for different processes
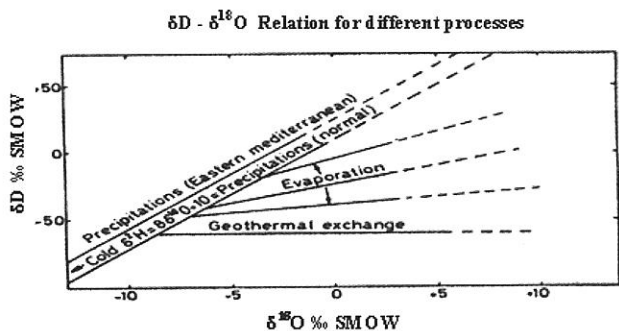
groundwater provenance studies. The δD - $\delta^{18}O$ relationships of water samples from a study area are of great importance to isotope hydrology. The method provides a clue as to whether a given groundwater body is receiving or from an evaporating body such as a lake or a reservoir. The conditions under which the δD - $\delta^{18}O$ line deviates from slope 8 are as indicated in the above figure.

During evaporation also the linear correlation between δD - $\delta^{18}O$ in the remaining liquid fraction is conserved and evaporating waters show lower slopes of the order of 3 to 5. In geothermal exchange, only ^{18}O content is modified, as at high temperature water gets enriched in ^{18}O with the oxygen in the hot rocks, which have usually a higher ^{18}O compared to

water. The intersection of the geothermal δD - $\delta^{18}O$ line with meteoric line represents their source of recharge.

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Groundwater Recharge (Natural, Artificial) Studies Using Isotope Hydrology Techniques

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Introduction

Groundwater is an important source of water supply for drinking and irrigation. It caters to more than 45% of the total irrigation in India. The contribution of groundwater to irrigation to achieve self-sufficiency in food grains in the past 3 decades is phenomenal. The increasing demands for the development of groundwater resources for agricultural, industrial and domestic sectors necessitates proper water resources assessment and management strategies. Improper management of groundwater resources can lead to various problems such as higher pumping cost, reduction in yield, failure of wells, sea water intrusion to fresh water aquifers in coastal regions and land subsidence. For proper assessment of groundwater resources and groundwater budgeting, one of the key hydro-geological parameters is natural recharge or annual groundwater replenishment rate.

The watershed or basin is a natural hydrogeomorphological drainage unit having distinct surface water divides as boundaries. It comprises the total catchment area of a particular river or stream that contributes runoff water to the flow cycle. Groundwater recharge evaluation, when carried out in a representative watershed or river basin is useful for estimating safe yield and for better water resources management strategies.

Groundwater (Natural) Recharge

The two principal types of natural recharge to groundwater are direct/primary and indirect/secondary. The direct recharge results from vertical percolation of precipitation through soil and unsaturated zone. The indirect recharge results from percolation through beds of surface water bodies such as tanks, ponds, lakes, streams, canals and return flows from surface water applied irrigation etc.

The principal replenishment to groundwater resources on a regional scale is by direct recharge. The factors affecting natural recharge rates are amount and intensity of rainfall, gap between rainfall events, infiltration capacity of surface soil, evapotranspiration, surface topography, compaction and structure of soil, hydrologic conditions etc. These conditions impose a limit on the minimum amount of rainfall required to affect groundwater recharge. The rate at which water table recharge occurs also depends upon the thickness of the unsaturated zone. Where the unsaturated zone is thin, recharging waters can reach the water table fast, resulting in a localized groundwater mound. Soil moisture percolating through the unsaturated zone beneath upland areas takes longer time to reach the water table. Recharge varies across catchments, because the controlling factors vary both in their nature and size. The various recharge processes (direct,
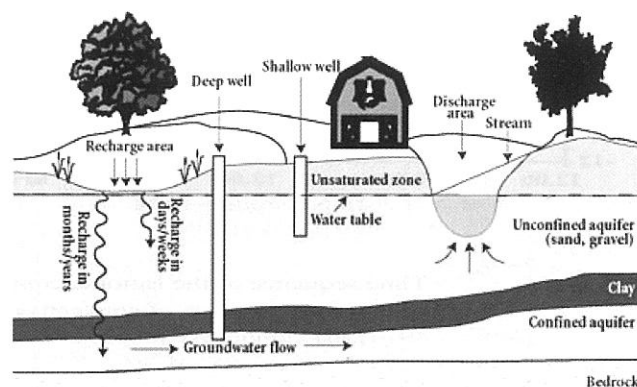

Fig. 1 *Various routes of groundwater natural recharge in a fictitious hydro-geological setup (Source [2])*

indirect) that can occur in a fictitious hydro-geological set-up is depicted in Fig. 1.

Groundwater (Artifical) Recharge

The increasing demand for water has increased awareness towards the use of artificial recharge to augment ground water supplies. Stated simply, artificial recharge is a process by which excess surface water is directed into the ground – either by spreading on the surface, by using recharge wells, or by altering natural conditions to increase infiltration – to replenish an aquifer. It refers to the movement of water through man-made systems from the surface of the earth to underground water-bearing strata where it may be stored for future use. Artificial recharge (sometimes called planned recharge) is a way to store water underground in times of water surplus to meet demands in times of shortage [1,2].

Augmentation of groundwater resources becomes necessary, when, in a given area or basin the annual development of groundwater exceeds the annual replenishment (or the natural recharge). Or when the natural recharge is slow and not upto the expected/required level, we have to go in for artificial recharge of groundwater. Artificial recharge of groundwater is done by direct and indirect means. Various methods of (direct) artificial recharge can be broadly classified in to two, viz. surface techniques and sub-surface techniques. The surface techniques include; (i) Contour bunds, (ii) Percolation tanks, (iii) Recharge pits, (iv) Irrigation tanks (with and without recharge pits), (v) Channel modification by finger dykes, (vi) Individual well recharge. The sub-surface techniques include; (i) Sub-surface dykes, (ii) Recharge tube wells, (iii) Recharging trenches and (iv) Injection wells (Fig. 2). The suitability of a method is
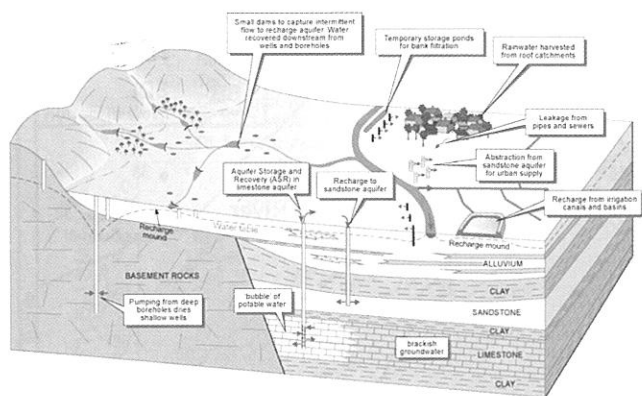
Fig. 2   Various methods of groundwater artificial recharge (Source [2])

governed by the availability of water for artificial recharge, geological/hydro-geological conditions, climatic conditions and time and money. The indirect means of artificial recharge include; enhanced streambed infiltration (induced infiltration) and conjuctive wells.

Isotope (Tracer) Methods

Various aspects of estimation of the groundwater recharge have been dealt with and reported elsewhere [3,4]. Of the two broad techniques used for natural recharge estimation, tracer and hydrological, the former is site specific, whereas the latter method usually provides information on a regional scale. The hydrological method includes water balance studies, lysimetric measurements, hydro geological method, net flow analysis etc.

The tracers (isotopic, chemical) used in recharge can be grouped into environmental tracers (i.e., those that are already present in the atmosphere) and applied tracers (i.e., introduced in planned experiments). The tracer methods [5-12] for the estimation of natural recharge are; i) environmental tritium method, ii) environmental chloride method, iii) stable isotope method and iv) applied tracers method. Quantification of recharge using applied tracers is relatively new. Applied tracers are used in planned experiments aimed at collecting some hydrological information or in specific hydro-geological investigations. Radioisotopes are preferably used as tracers, since they can be detected at low levels and can be introduced in small quantities without large disturbances to soil or its moisture content.

Sometimes due to the likely annual/seasonal changes in the previously mentioned governing parameters of ground water recharge (natural, incidental or artificial), the application of conventional (water-balance based) methods to evaluate/understand groundwater recharge becomes very difficult, particularly in arid/semi-arid regions. In addition, in groundwater systems, with no or sparse records available on rainfall, pumping rates, water level fluctuations and information on changes in land-use pattern, the use of water balance methods becomes very difficult or impossible to apply. Alternate method could be based on "tracer concept".

Tracing of water movement in ground water regime by making use of environmental isotopic species of water (HDO, $H_2^{18}O$, HTO) and its solute (^{14}C, ^{13}C, ^{34}S) is one such promising method.

The basic principle of application of isotope method for understanding/evaluating groundwater recharge is similar to any other hydrological investigations and that is essentially, as mentioned above, based on the concept of "tracing", in which either intentionally introduced isotopes or naturally occurring (environmental) isotopes are employed. The tracing method in hydrology is effected by the physical processes, such as evaporation and condensation, during which the associated waters, depending on their geographical locations, get labeled naturally with a distinct isotopic signatures. By tracing the naturally labeled isotopic signatures spatially and temporally it is possible to obtain several information related to groundwater recharge and associated hydrological processes.

Occasionally, reactor produced artificial isotopes such as ^3H, ^{82}Br, ^{131}I etc are being used to obtain groundwater recharge related information. Apart from radiological hazard considerations, the other main criteria for selection of the artificial radiotracers is based on the time-scales involved in groundwater recharge processes. Environmental isotopes (radioactive/stable) have the distinct advantage over injected (artificial) tracers in that they facilitate the study of various hydrological processes on a much larger temporal and spatial scale through their natural distribution in a system. Thus, environmental isotope methodologies are unique in regional studies of water resources to obtain time and space integrated characteristics of hydrological systems. The use of artificial tracers generally is effective for site-specific, local applications.

Under some favourable hydro-geological conditions and wherein single type of artificial recharge measure is being followed, say percolation tank method, quantitative estimate on the percentage contribution of the recharge method to the groundwater system is possible using tracer balance equations, called as two-component mixing model, as shown below:

$$m_s = [R_{pg} - R_{g,t}] / [R_{pg} - R_{s,t}] \qquad (1)$$

where, m_s : The fraction of artificial recharge water in the admixture (groundwater having some component of artificial recharge water) at any distance from the recharge structure, R_{pg} : The isotopic composition of pure groundwater, $R_{g,t}$: The isotopic composition of the admixture at any distance at time, t, $R_{s,t}$: The isotopic composition of the artificial recharge water at time, t

In case of more than one method of artificial recharge being adopted in a groundwater regime, additional (independent) tracer balance equations are required, based on chemical constituents (major, minor) in the associated waters. From the percentage contribution of the artificial recharge methods, delineation of the command area (also
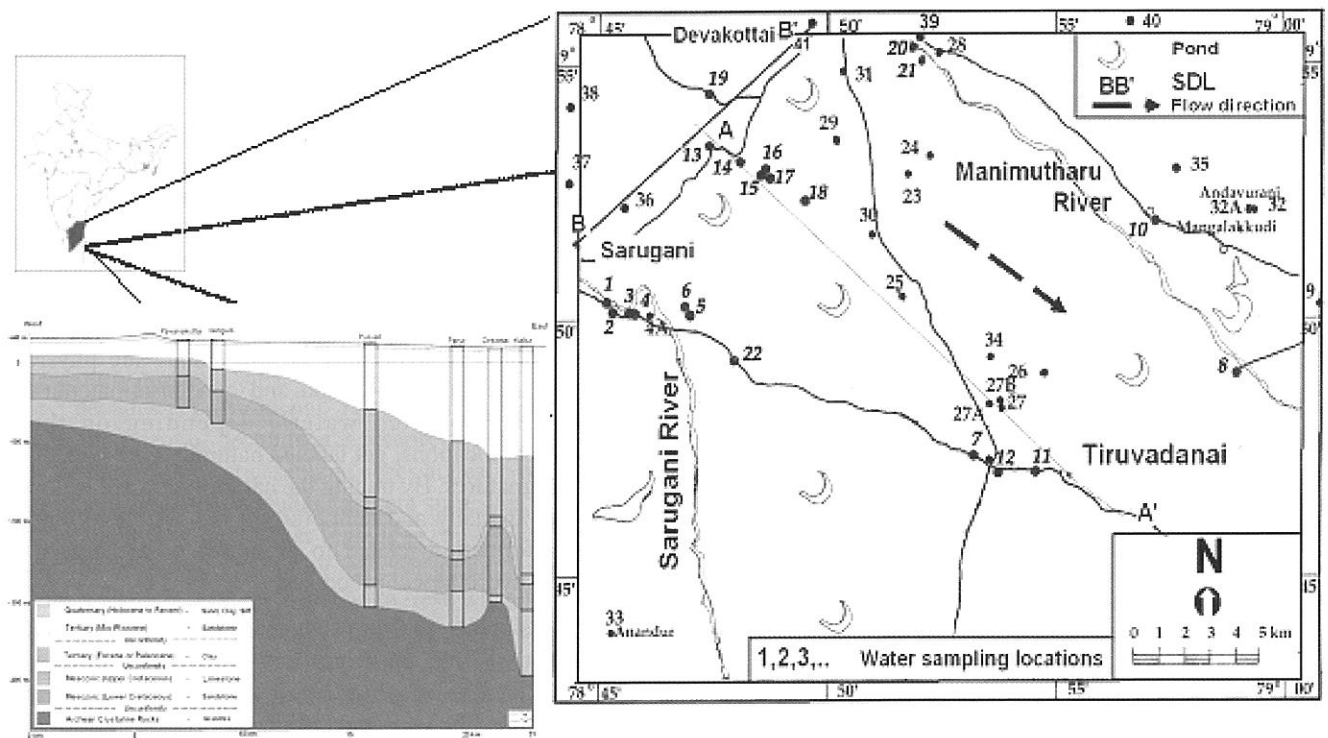
Fig. 3 Location map of Tiruvadanai Aquifer and its hydro-geological section and sampling locations

called as influence area) of the artificial recharge methods is possible.

A few groundwater recharge (natural, artificial) studies using environmental isotopes are given below in brief:

Coastal Sedimentary (Cretaceous) Aquifers of Tiruvadanai, Tamilnadu, India

The aquifer forms part of the Tamilnadu Coastal Plain, with an elevation of 9 to 20 m amsl [13]. Two ephemeral rivers, namely Sarugani and Manimutharu, respectively, drain in the south and north of the aquifer and carry floodwater during monsoon into the Bay of Bengal. The area receives rainfall from both SW- and NE monsoons. More than 60% of the total rainfall is due to the NE monsoon (October-December). The spatial distribution of rainfall in the Tiruvadanai taluk is quite non-uniform with the average annual rainfall for 85 years being 830 mm.

Alluvial deposits (clay, silt, sand) of Recent to Sub-Recent age, cover most part of the taluk. A small batch of crystalline rock is exposed in the western corner of the district. Tertiary sediments are exposed on a narrow band in the western part adjoining the crystalline rocks. Due to an unconformity in the geological succession, the older sedimentary (Cretaceous period) formations are not exposed in this taluk, they are encountered in deep tube wells.

In the Tertiary formations (friable sandstones, compact clay), the ground water occurs under phreatic conditions. In central part of the taluk, where the Tertiary and Cretaceous formations are overlain by moderately thick alluvium, confined and semi-confined conditions exist. The exploratory tube wells in the area indicated that a siliceous aquifer, which lies just above the granitic basement, has a good potential of fresh ground water. The aquifer system that overlies the fresh water aquifer is mostly saline, and a thick sticky clay bed separates these two systems of aquifers (Fig.3). This deeper freshwater bearing potential aquifer (depth: 100 m to a few hundreds of meter), along with a few freshwater zones in the Tertiary formation, has been successfully tapped for drinking water supply for the last several years. The recharge area for the productive deeper aquifer and the Tertiary aquifer is identified in the ridge-area running parallel to Sarugani-Devakottai Line.

The continuous exploitation of the aquifer over 15 years, for serving over 600 villages in one of the drought prone district of Tamilnadu namely Ramanathapuram, has resulted in the drop of piezometric head in the range 5-20 m, with the maximum being at the center of the basin. Hence, in order to protect the aquifer, the life-line of the district, from possible water quality changes due to vertical and lateral leakages and other ill effects of over-exploitation, a few pilot scale artificial recharge measures (Channel modification by Finger dykes, Recharge pits, Recharge tube wells, Irrigation tanks with recharge pits etc) are being undertaken at the recharge area of aquifer by the Tamilnadu Water Supply and Drainage (TWAD) Board.

At the request of TWAD Board, environmental isotopes (^2H, ^{18}O, ^3H, ^{13}C, ^{14}C) were used in conjunction with hydro-geology, hydro-chemistry and in-situ physio-chemical parameters (EC, Temp., etc) to understand the recharge processes of the coastal and sedimentary aquifers of Tiruvadanai and then to evaluate the
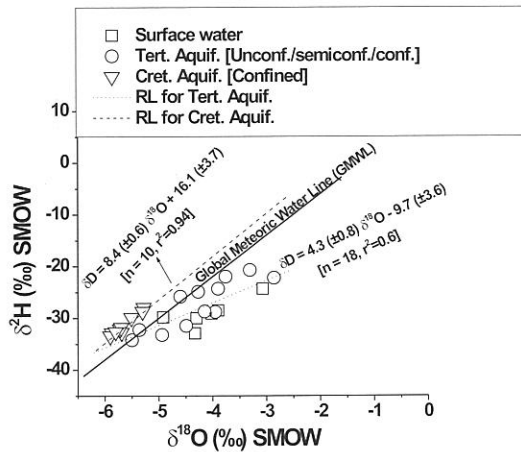
Fig. 4 δ^2H-$\delta^{18}O$ plot (NE Monsoon sampling)

Fig. 5   Variation in $\delta^{18}O$ down-gradient

effectiveness of pilot-scale artificial recharge measures in augmentation of the groundwater system.

The results of isotopes and chemical analyses of various water samples from the study area (rivers, rainwater, ground waters and water samples from the artificial recharge structures) collected in different seasons during 2003-2005 (Figs. 4-7) indicated the following:

- Water samples from tube wells located near the two ephemeral rivers and tapping the unconfined and semi-confined zones of the Tertiary aquifers showed enriched stable isotopes, indicating possible surface water contribution to the aquifers. They also measured very low tritium content (2-3.5 Tritium Units, TU) compared to that of the surface water and present day precipitation value (~6 TU), indicating that the aquifer waters could be a mixture of old and recent components of recharge waters. [A comparatively higher tritium content of the water samples from the tube wells located near to the north-bounded river (~ 3.5 TU) than that from the tube wells located near to the south-bounded river (~ 2 TU), probably indicates the difference in the transmissivity of the soils of the two regions and the related recharge processes.]
- Water samples from tube wells located at the recharge areas (lying parallel to Sarugani-Devakottai Line) and lying far-way from the two (bounded) ephemeral rivers and tapping the unconfined zones of the Tertiary aquifers measured tritium contents less than 1.5 TU, indicating negligible modern component of groundwater recharge with the source being surface water bodies.
- Except for a few samples, the seasonal variations in isotopic contents of the above two types of water were not significant, indicating the slow movement of water in the unsaturated zone whereby the possible seasonal variations are reduced.
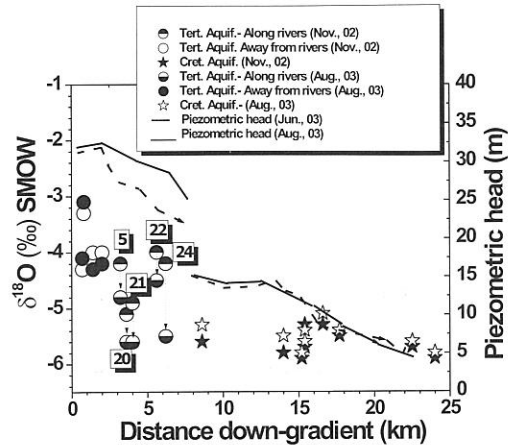- The ^{14}C of the dissolved inorganic carbon (DIC) in the waters of the above two types of water samples measured

a value of ~70 percent modern carbon (pmc) which again corroborates the tritium findings.

- The ^{14}C of the dissolved inorganic carbon in the waters of the Cretaceous aquifer measured very low values (<1 pmc) and also the stable isotopes (^2H, ^{18}O) fall on a different regression line on ^2H-^{18}O plot, indicating that the waters are very old and probably recharged during a different climate. [Env. ^3H content of Cretaceous aquifer was <1 TU].
- The distribution of various hydro-chemical species along the general groundwater flow direction of the aquifer showed a decreasing trend for some species along the general groundwater flow direction

Thus, from the investigation, it was concluded that the modern day natural recharge to the Tertiary aquifers is a slow process with a given years rainfall reaching water table after several years. Also, the recharge through artificial means to both Tertiary and Cretaceous aquifers appears, to be very low. The waters in the fresh water bearing Cretaceous aquifer appear to have recharged during a different period and climate. Indirectly, since the possible recharge for the cretaceous aquifer is through the exposed Tertiary formations in the western area of the aquifer system, the observed increase in yield of the artesian flowing wells located at the discharge area of the cretaceous aquifer is mostly due to the hydraulic pressure acting on the aquifer system during the (very low) percolation process at the recharge area of the Tertiary formation and aided by the steep gradient of the aquifer and not due to a fast mass transfer in the Cretaceous aquifer. Suitable river for planning large-scale artificial recharge measures for the aquifer system could be north bounded ephemeral river (Manimutharu) rather than the south bounded ephemeral river (Sarugani). These findings would benefit the groundwater authorities for planning large-scale artificial recharge measures and for careful exploitation and prevention of the aquifer from the ill-effects of over-exploitation.
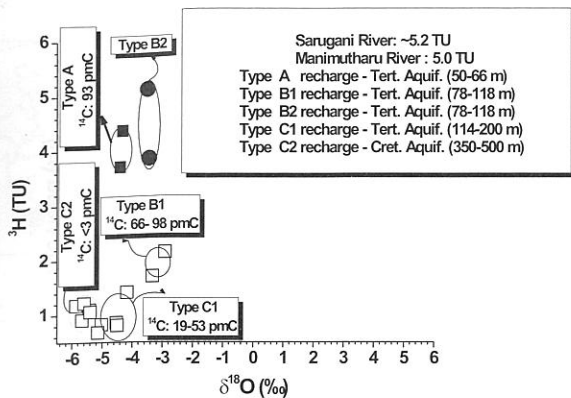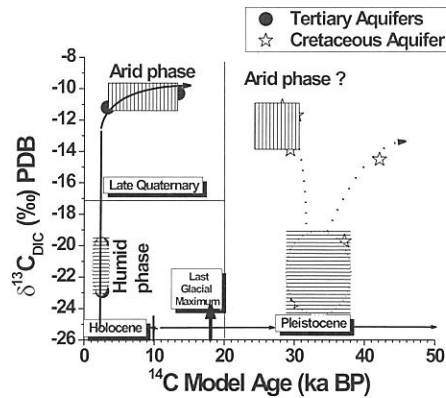
Fig. 6 ^3H vs $\delta^{18}O$ [August 2003]

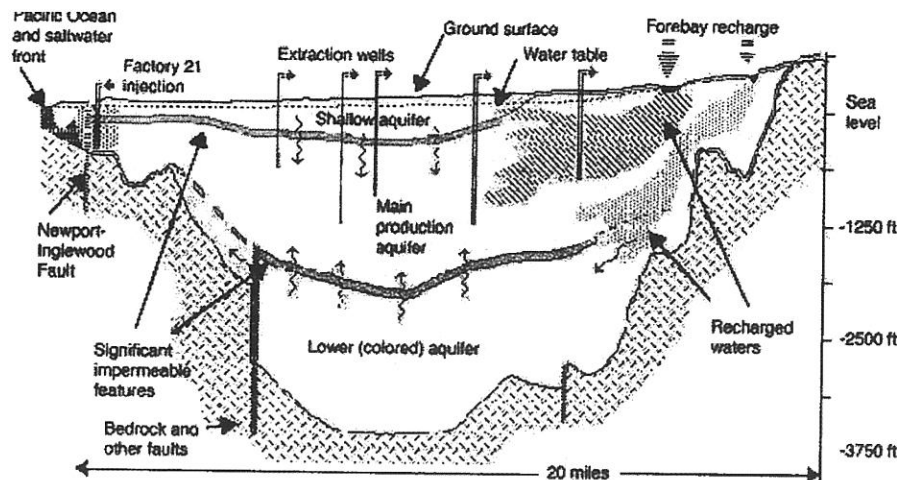Fig. 7 $\delta^{13}C$ vs ^{14}C model ages

Fig. 8 Vertical cross-section of the Orange County basin (Source [14])

Orange County, California

The Orange County Water District (OCWD), California manages a groundwater basin that provides 70% of the domestic water supply in the northern part of the County [14]. The remaining 30% is purchased and imported from outside the district. On an average annual basis, roughly 270,000 acre feet of water are extracted from several hundred production wells located within the middle production aquifers of the basin. These units can be over 1000 ft thick, and generally extend the entire width of the basin, from the "Forebay" area (under mostly phreatic conditions) toward the confined "Pressure Zone" that abuts the Pacific Ocean and New-port-Inglewood Faults (Fig. 8). The principal aquifer materials include permeable sands, sandstone, gravels and conglomerates of the surficial alluvium and the La Habra and San Pedro formations and semi-permeable interbedded silts, siltstones and clays. At the bottom lies a relatively impermeable Tertiary basement.

To sustain this rate of withdrawal, OCWD maintains an active artificial recharge operations by which about 20,000 acre feet of water, on an annual basis, to the groundwater basin. This is achieved by diverting large portions of the base flow of the Santa Ana River and additional imported water into a series of infiltration basins and abandoned gravel pits in the Forebay along or nearby the upper reaches of the river. Water recharged in the Forebay can easily be drawn into the middle aquifers, as well as a shallow aquifer in the Pressure Zone.

An investigation was carried out using a numerical model and complementary series of isotope analyses ($^3H/^3He$, ^{18}O), with an objective being to obtain an improved scientific basis to understand flow paths, migration rates, and residence times of recharged groundwater, as well as to identify the source composition of water produced in wells near the artificial recharge operations being carried out at the Orange County, California.

The $^3H/^3He$ results obtained from the investigation indicated that older waters are found at greater depths. Two of the deeper wells immediately adjacent to Anaheim Lake measured apparent ages of 12 and 18 y, respectively, suggesting that the well water would easily meet a one-year residence time requirement of the artificial recharge operations. In shallower zones, a range of ages was found. Very young (<1 yr old) waters found beneath and to the west of Anaheim Lake suggested the opposite, namely, the

recharge spreads rapidly into downgradient locations in the aquifer. This is consistent with an abundance of gravely materials in the alluvium and hydraulic conductivities in the range of 200 to 1000 ft/day.

Imported water from the Colorado River water is used throughout Southern California and is frequently used to recharge Anaheim Lake. Compared with local precipitation, the Colorado River water is markedly depleted in the ^{18}O isotope and has a distinct oxygen isotope ratio (^{18}O) that was easily identified in local groundwater regime. Thereby analyses of the ^{18}O ratio was used to assess the fate and dilution of water released in Anaheim Lake by distinguishing the presence and concentration of Colorado River water in downstream wells.

Thus from the study (numerical model, isotopes) it was concluded that while numerical model calibration was greatly aided by isotopic source and residence time analyses, the model also provides unique insights on the interpretation of isotope data themselves. Isotopic estimates of groundwater age help to discriminate the source and concentration of various waters used for artificially recharging the aquifer system. However, the results also suggest that groundwater reaching a well spans a wide ranging distribution of age, demonstrating the importance of geologic heterogeneity in affecting flow paths, mixing and residence times in the vicinity of recharge basins and wells.

Arid and Semi-arid Regions of Jordon

Jordan is one of the arid and semi-arid regions of the world with 90% of the country receiving less than 200 mm of annual rainfall. In the recent years, artificial recharge and surface water harvesting has been given an utmost priority and importance in the county. An environmental isotopes (D, ^{18}O, ^3H) investigation was carried out in Jordan to evaluate

Fig. 9   Isotope study of waste water recharge in Tunisia (tritium isolines)

the efficiency of artificial recharge to the groundwater due to four reservoirs (two each at the highland and main escarpment of the Jordan Valley graben) [15]. The aquifer, which is outcropping at upper dams, is formed from chert and limestone at Siwaqa reservoir; overlain by basalt at Khlidiya reservoir (upland areas) and at the valley (i.e., at Kafrain and Shueib reservoirs) the aquifer is basically sandstone.

During 1995-2001 several monthly sampling campaigns were carried out at the four reservoir sites and from the surrounding wells to collect water for the isotopes and chemical analysis. From the results of isotope analysis a few qualitative information on the contribution of each reservoir and their influencing areas were obtained. Thus it was concluded that the percentage contribution of the four reservoirs in artificially recharging the local groundwater is low and that possibly is due to increased siltations at the four reservoirs.

The Nabeul-Hgammamed Alluvial Coastal Aquifer, Tunisia

A project was implemented for studying the artificial recharge of waste water in the Nabeul Hgammamed alluvial coastal aquifer. Due to intensive pumping and salinization, the aquifer is practically exhausted and useless. Hence an artificial tritium investigation was carried out to know the aquifer's capacity to purify itself over a long period of time and to study the mixing processes between older and younger water resources.

About 32,000 m3 of waste water, labeled with a radioactive 3H (~ 1.2 kBq/l), was injected into a well, continuously for 42 days. The movement of the labeled water in the aquifer was observed periodically through a systematic sampling of the aquifer waters and subsequent measurement of their concentration in the laboratory using liquid scintillation counter. From the tracer concentration measurements (Fig. 9), it was found that the labeled water showed a dynamic water movement after 394 days. The information obtained helped the local water authorities in better planning of a large-scale project to artificially recharge waste water with the aim of using it for irrigation purposes [16].

Rialto-Colton Basin, San Bernardino County, California

In a recent study, three different geochemical and isotopic models to assess the impact of a water-banking program in the Rialto-Colton Basin, San Bernardino County, California [17]. A one-dimensional mass-balance model was used to determine the mass transfer of constituents between the dissolved phase and aquifer materials and to determine the environmental carbon-14 (^{14}C) ground-water age at specific wells along four flow paths through the Rialto-Colton Basin. The ^{14}C isotope was used to determine the age of ground water on timescales ranging from recent to more than 20,000 years before present. To determine age at a given location in an aquifer, the ^{14}C activity was measured
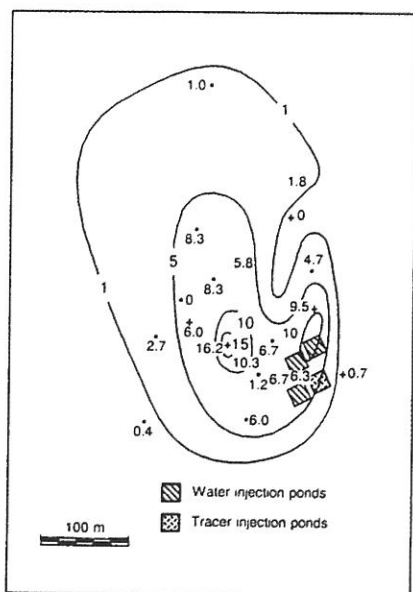
and the age was calculated as the time required to reduce the activity of the influent to that measured by radioactive decay, with corrections for geochemical reactions. The dominant reactions that affect C^{14} activities in the Rialto-Colton Basin are silicate weathering, clay precipitation, cation exchange, calcite precipitation or dissolution and oxidation of organic matter. Ground-water ages ranging from 200 to 16,000 years before present were obtained. A three-dimensional finite-element reactive-transport model (Hydrogeobiochem) was developed to simulate C^{14} activities, which are calibrated with measured data, over the entire aquifer. This model includes the geochemical reactions from the one-dimensional modeling and steps for computing C^{14} activities and age. From the model studies, an assessment on the movement of water through the aquifer and a study on the mixing of different recharge sources, including artificially recharged imported water, was made.

Mugali Chetla Tanda Watershed in Anantapur district of Andhra Pradesh, India

A research study has been carried out to evaluate the economically viable depth of desiltation in old tanks to achieve a substantial increase in percolation and storage [18]. An experimental study was taken up on a pilot basin in two tanks (an old minor irrigation tank and a newly constructed percolation tank) within the Mugali Chetal Tanda Watershed in Anantapur district of Andhra Pradesh. Geology of the watershed is mainly granites and gneisses (Precambrain rocks). The infiltration test using double ring infiltrometer with a constant head was performed on undisturbed tank soil. The test was repeated at a close-by site with removal of silt of different thickness. Tritium (isotope of hydrogen) was used to understand and to follow the downward movement of infiltrated water.

The study indicated that in the case of irrigation tank, a steady state infiltration rate of 67 mm/h has increased to 350 mm/h with the removal of 65 cm silt showing a six-fold increase in infiltration rate. Infiltration rate was found to be reducing by removal of 25 cm and 50 cm silt and the analysis of soil fraction indicated presence of clay at these depths. The study at percolation tank indicated that the infiltration rate of 10-20 mm/h has increased to a maximum of 310 mm/h with removal of 40 cm silt. The tritium tracer migration study supported a faster movement of percolated water at desilted sites by showing a greater dilution of tracer concentration and deeper penetration. The research study strongly supports a necessity of carrying out infiltration studies at different places within the tank bed area with removal of varying thickness of silt to decide the optimal level of desiltation especially in old tanks before commencing the revival of the tank system for improving the water harvesting efficiency and percolation.

Hard-rock Regions of Maharashtra, India

Percolation tank is a small earthen dam constructed across a suitable cross-section of a natural stream. The surface runoff during the monsoon period is collected in the tank and under favourable soil and rock conditions, the water is expected to percolate and recharge groundwater system and thus help in improving the yield of the wells located in its command area, particularly in summer. The command area consisting of 20-30 dug wells, usually covers an area of few square kilometers. Environmental isotopes were used to study the efficacy of percolation tanks in artificially recharging groundwater systems in their command area.

Hinganigada Percolation Tank is located in Dhond taluk, Pune district of Maharashtra. The tank is shallow with an average depth of ~ 4 m and it impounds about 1 Mm^3 of water during the monsoon season [19]. The dug wells (Fig. 10) in the command area penetrate soft rock overburden and the fissured hard rock (Deccan Trap) which is exposed in the tank bed. The seepage medium consists of fissured hard rocks with joint planes and fractures.

Samples were collected from the tank and the wells and analysed for ^{18}O. The locations of samples collected are shown in Fig. 10. As the ^{18}O values of the tank-water collected from shallow and deep levels of the tank at various times are similar, the tank was considered well mixed (i.e., no stratification of the reservoir). The temporal variations of

Fig. 10 Location of samples in the Hinganigada Percolation tank and its command area
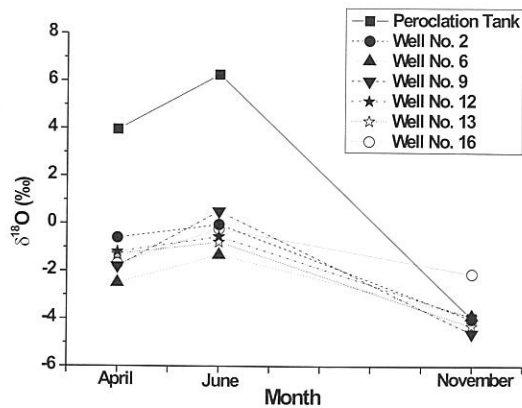
Fig. 11 *Seasonal variations of ^{18}O of d/s wells*

Fig. 12 *%v contribution of the tank to d/s wells*

^{18}O (Fig. 11) of the tank water and few downstream dug well indicated similar ^{18}O response, indicating fast groundwater flow between the tank and well. The tank water contribution to each well was computed using a two-component mixing model, as shown in Eq. (1). The R_{pg} value was taken as – 4.5 per mille, which was the value of a well sample collected from the upstream side of the tank and hence not influenced by the tank water. The tank water contribution to the well has been plotted with respect to its distance from the dam and presented in Fig. 12. From the figure, it can be seen that the percentage contribution decreases with distance, of the well from the tank. The scatter of points in the figure is due to the fact that the flow is mostly through the secondary porosity (fissures of the hard rocks). The wells near the tank received about 50% contribution from the tank. Similar studies were carried out at a few other percolations tanks in Maharashtra.

A few more similar studies were carried out in a few more percolation tank systems in Maharashtra and in the desert regions of Rajasthan.

Cauvery Delta Basin, Tanjavur, Tamilnadu, India

Usually prior to implementing any artificial recharge measures for augmenting groundwater resources of a particular site, feasibility studies are sometimes very essential, particularly in case of a multi-aquifer system with varying water quality. One of the important hydrogeological information looked into during the feasibility studies is the interconnection between the various aquifers. A few such case studies have been carried out as part of feasibility studies for artificial recharge and reported in literatures.

One such study was carried out in the Cauvery delta area of Tanjavur in Tamilnadu. As part of the investigation to study the feasibility of artificial recharge of groundwater aquifers in the Cauvery delta area in Tamilnadu, an isotope and geochemical (D, ^{18}O, Cl) study was carried to verify whether the shallow and deep water bearing zones were interconnected [20]. The study area consists of Quaternary alluvium (sand, silt, clay), extending to a depth of 30 m, deposited by the Cauvery river and its distributaries. The
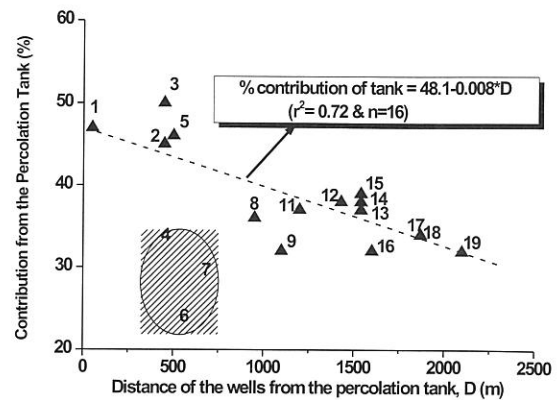
upper Quaternary alluvium is underlain by Pliocene formation. The shallow aquifer in the Quaternary formation is located at a depth of 10 to 20 m while the deep aquifer in the Pliocene formation is present at depths ranging from 40 to 80 m. From the geological cross-section, it was observed that the deposition of the shallow and deep aquifers is very erratic and the thickness of the intervening clay, clayey sand or gravel also varies. The clay and sand content of the aquifer also differ widely. The piezometric data of shallow and deep aquifers at a few places in the area indicated negligible water level difference between the aquifers owing to no clay bands between the aquifers and thereby the aquifer is under un-confined condition at those places. At other places the intervening clay makes the deeper aquifer to be semi-confined.

The isotope results of water samples collected from the shallow and deep aquifers and surface waters (river channels, canals, ponds etc) at different seasons indicated that isotopically (D, ^{18}O) the aquifers are different with enriched values at the shallow aquifer, possibly due to the recharge from the surface channels (Fig. 13). There was no clear seasonal variation in the isotopes of the deep aquifer
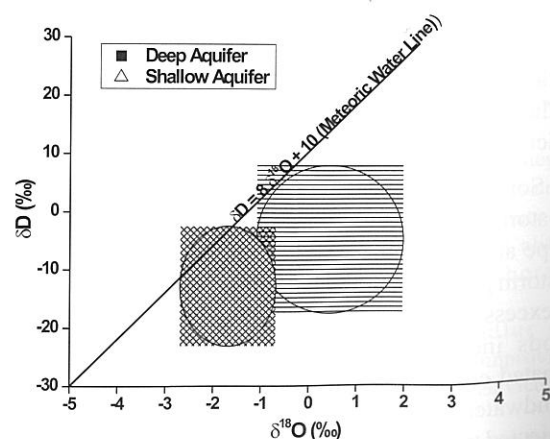

Fig. 13 *δD-$\delta^{18}O$ plot, Cauvery delta basin, Tanjavur*

water but the Cl⁻ content showed some seasonal variation. In the shallow aquifers, certain places showed some seasonal variation in stable isotopes but not in Cl⁻. This shows possible leakage from deep aquifer to the shallow aquifer. Thus, from the investigation it was concluded that the shallow and deep aquifers are generally not interconnected except at a few places which was confirmed from the piezometric data.

Mountainous region of Gaucher area, Chamoli District, Uttarakhand

A model project [21] was taken up in the mountainous region of Gaucher area, Chamoli District, Uttarakhand to identify the recharge areas of a few (seasonal springs for the purpose of implementing rainwater harvesting measures to augment recharge to the spring. The investigation indicated;

- The springs are seepage waters through the shallow zone (weathered and fractured),
- The chemistry of high-altitude springs is similar to that of precipitation, whereas water–rock interactions contributes to increased mineralization in low-altitude springs,
- The stable isotopic variation in precipitation suggests that the altitude effect for Gaucher area is –3.8‰ and –0.55‰ for δ^2H and δ^{18}O, respectively, per 100 m rise in elevation.
- Based on local geology, geomorphology, hydrochemistry and isotope information, the possible recharge areas inferred (Valleys-1: at +1250 m; Valley-2: at +1330 m; Valley-3: at +1020 m).

Water conservation and recharge structures such as subsurface dykes, check bunds and contour trenches were constructed at the identified recharge areas, respectively, for controlling the subsurface flow, rainwater harvesting and for augmentation of groundwater recharge. As a result, during and after the following monsoon, the discharge rates of the springs not only increased significantly, but also did not dry up even during the dry period.

Semi-arid region of Karnataka, India

Environmental isotope and injected tracer techniques were used to estimate the contribution of storms as well as annual precipitation to groundwater recharge and its circulation, in the semi-arid region of Bagepalli, Kolar district, Karnataka [22].

Some of the groundwater samples collected during the post-storm periods were found to be highly depleted in stable isotope and with higher d-excess relative to that of the the pre-storm period groundwater samples. Significant variation in d-excess in the groundwater collected during two different periods indicated different origin of air masses. The estimated component of the storm event of 600 mm to the groundwater was in the range of 117-165 mm. Subsequently an injected tracer (^{3}H as HTO) experiment was carried out to estimate the direct recharge of the groundwater and was

estimated to be ~33 mm of the 550 mm annual rainfall in 1992.

There was no significant variation in the env. ^{3}H content of the post- and pre-storm groundwaters indicating fast circulation of groundwater.

Arid areas of Rajasthan, India

An integrated study on groundwater recharge and behaviour of contaminants in the unsaturated zones in Saraf ki Dani, Sihania and Lakrasar site in Barmer district of western Rajasthan (Fig. 14a,b) have been studied in 1999[23]. Unsaturated zone core samples were collected in the above sites and the soil water was extracted by vacuum distillation and analysed for ^{2}H, ^{18}O while for chemistry elutriation method of extraction was used. Precipitation
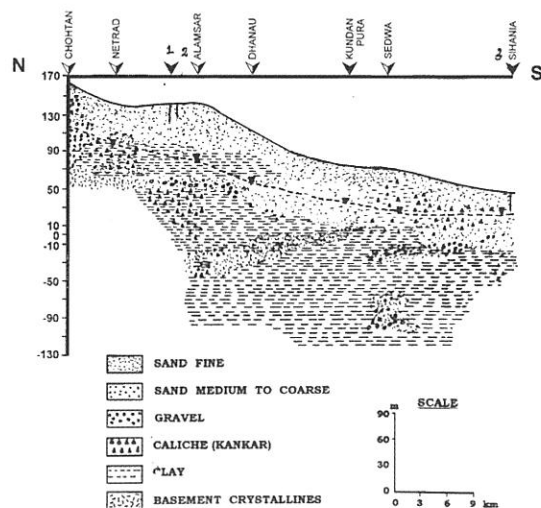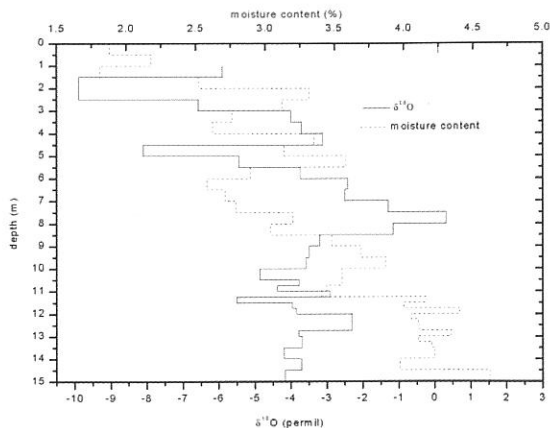

Fig. 14a Location map

Fig. 14b Geological section

Fig. 14c Depth vs.d^{18}O and moisture content [Sihania]

samples were collected from the nearest meteorological station, namely Chohtan for analysis of ^2H, ^{18}O and chemistry.

The chloride profile obtained was used for groundwater recharge estimation. The groundwater recharge in the above sites ranged from ~10 to 18 mm per annum. From the $\delta^{18}O$ profiles at Sihania and Lakrasar, depleted $\delta^{18}O$ values were observed at a depth of ~2 m which could be attributed to heavy rains that occurred in 1998. From δ^2H - $\delta^{18}O$ plot of samples from Sihania site II, two groups of samples were seen: one showing strong evaporation and other showing much less evaporation. Depth-wise distribution of F$^-$, SO$_4^{-2}$ and NO$_3^-$ at Sihania site II confirmed evaporative concentration during dry period and the same was substantiated by the depth-wise $\delta^{18}O$ values of the core samples. Enrichment of NO$_3^-$ in the profile could possibly be due to fixation of nitrogen by leguminous plants.

Finally, under some conditions, a few researchers (e.g., [24]) have used noble gas to distinguish groundwater that has been artificially recharged quickly through basins, as well as infer the temperature of groundwater at the time of its recharge. Also, limited applications of other isotopes such as ^{34}S (SO$_4^{2-}$) for artificial recharge studies elsewhere in the world are reported in a few literatures/documents.

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Isotope Techniques to Investigate Civil Engineering Problems

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Introduction

Seepage or leakage from the dam, reservoirs, lakes, canals and tunnels is one of the serious problems for civil engineers and engineering geologists, especially in the areas, where unconsolidated sedimentary bed and major joints and faults in hard rock occur. Seepage is linked to problems of great economical importance, especially when dealing with earthen dams, the seepage or leakage may represent a serious threat to dam stability. In other cases, the problem is derived from loss of water itself. Seepage or leakage can occur from hydraulic structure, dam foundation, bottom of the reservoir and discharge channels. In many cases drainage occurs through geological formation such as faults, fractures joints, etc. But it may not be visible. It gets dispersed in the surrounding geological formation. The important techniques used to investigate the seepage or leakage from dams reservoirs, canals, tunnels, etc. are mainly two types. They are (a) non-tracer techniques and (b) tracer techniques.

Non Tracer Techniques

In non-tracer techniques, geological and hydrological reconnaissance survey is the starting point for any investigation. Whenever the emerging of seepage water is invisible and the infiltrating water from the reservoir undergoes mixing with groundwater before emerging, there is need to go for water balance studies (Σ input - Σoutput = leakage), relationship between the reservoir and groundwater levels at dam site. Water injection tests and hydrochemistry provide information on transit time of infiltrated water (qualitative) mixing with other groundwater, difference between groundwater and reservoir water levels and hydro-chemical variation in seepage water after crossing the geological formation, temperature of emerging water will give information regarding elevation at which infiltration is taking place and if any stratification in the reservoir. Correlation between reservoir and leakage water temperature provides information to determine the elevation of the infiltration zones as well as hydraulic connections of springs or boils, which are fed by the reservoir. But many times these techniques are not sufficient and the results obtained through these methods are known to have failed.

Tracer Techniques

Let us define a tracer. Tracer is a substance carried by water, which will provide information concerning the hydrodynamics of the system. A tracer can be totally natural or it can be introduced intentionally. The tracer should have a number of properties in order to distinguish itself from bulk material. For most uses, its behavior has to be more or less similar to that of bulk material in the system, but it has to be easily distinguishable from the bulk. It should be relatively inexpensive to use and should be easily detect with widely available and simple technology. Generally an ideal tracer does not exist, because of the complexity of the natural system. The selection and use of tracer is an art as it is a science.

In 1950's radioactive tracers were developed and in 1960's environmental isotopes (stable as well as radioactive isotopes) became an invaluable tracing tools. With the advent of isotopic tracers and the availability of advanced instrumentation for the analyses of stable and radioactive isotopes, the tracer methods for hydrology and hydraulics have received a great impetus. Mainly isotopic tracers are classified into two groups: environmental isotopes and artificial radiotracers.

Environmental Isotopes

Environmental isotopes like stable deuterium (^{2}H), Oxygen – 18 (^{18}O), and radioactive tritium (^{3}H) are naturally present in water as HDO, H_2^{18}O and HTO, respectively. These have exactly the same physico – chemical behavior as the normal water molecule (H_2O) and make an ideal tracer for water. These isotopes are useful for identification of seepage or leakage source. The natural isotopic composition of a given sample of water depends on the origin of water and its history. By comparing the isotopic compositions of the seepage or leakage water and its suspected sources, it is possible to confirm or rule out possibility of interconnections. It is always better to go with combination of other methods.

Artificial Tracers

Artificial tracers are chemical dye tracers, metal complexes and radioactive isotopes. These tracers can be used for flow measurement in the bore hole, measurement of infiltration and localization of preferential infiltration zones at the bottom of the reservoirs as well as interconnections between reservoir and emerging water. Radioisotope tracers like HTO, NH_4 ^{82}Br and K_3 $[^{60/58}$Co $(CN)_6]$ satisfy the physico – chemical behavioral requirements of good water tracer. Though HTO is an ideal water tracer, whenever natural tritium is hydrological interest in the area of investigation it is prudent not to inject large doses of artificial tritium. As an β^- emitter, tritium is not detectable in situ. On the other hand anionic ^{82}Br and the $K_3[^{60/58}$Co$(CN)_6]$ complex are γ^- emitters, which can be detected in situ.

^{82}Br is probably the most commonly used artificial isotopic tracer in view of its short half life (36 hours) and high energy γ^-emission. These tracers can be used to investigate many problems related to hydrology and hydraulics. It may also sometimes be necessary to select a tracer, which is removed from the water and adsorbed on to
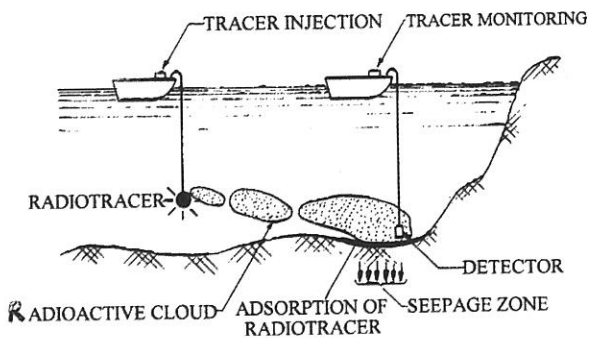
Fig. 1   Tracer Study in Dams & Reservoirs

Fig. 2   Borehole Tracer Logs in Aliyar Dam Study, South India

Fig. 3&4 Lakya Dam Site & Tracer response at seepage

the soil matrix as the water enters the soil during seepage (Fig.1). Such tracers like ^{198}Au and ^{140}La, as chlorides are practically useful to locate areas of high seepage on reservoir beds. In seepage studies the combined approach of non-tracer techniques as well as tracer techniques are always necessary to achieve better results.

Seepage and leakage investigations in dams, reservoirs, tunnels and canals

A few dams, reservoirs, tunnel and canal seepage and leakage investigations carried out in India are as follows:

1.   Aliyar Dam, Tamil Nadu

2.   Lakya Dam, Karnataka

3.   Poip Dam, Maharashtra

4.   Borda reservoir, Maharashtra

5.   Chaskaman Dam, Maharashtra

6.   Salal Tail Race Tunnel, Jammu, etc.

7.   Chilla Hydel Channel in Uttar Pradesh

Seepage investigation in Aliyar Dam, Tamil Nadu

A radiotracer study was carried out at the Aliyar dam in Tamil Nadu. This Tracer study was intended to locate the seepage paths in the masonry spillway portion of the Aliyar dam. About 52GBq of ^{82}Br diluted in 6000L of water were injected into a cavity in the reservoir that was suspected of being the main entry point of seepage.

Water was injected into the cavity before and after the tracer injection in order to establish steady flow conditions. Gamma logs were made of series of gauge holes available in the body of the dam. Interconnected fissures were located by tracer detection and the radiation intensity was assumed to indicate the relative amount of seepage (Fig.2). The hole was successfully grouted on the basis of the tracer information, and the seepage was arrested. Similarly, experiments were carried out at Bhadra Dam in Karnataka State, India, where ^{82}Br was released into the reservoir so that its movement could be followed with a scintillation probe lowered from a boat, and then the borehole drilled along suspected seepage
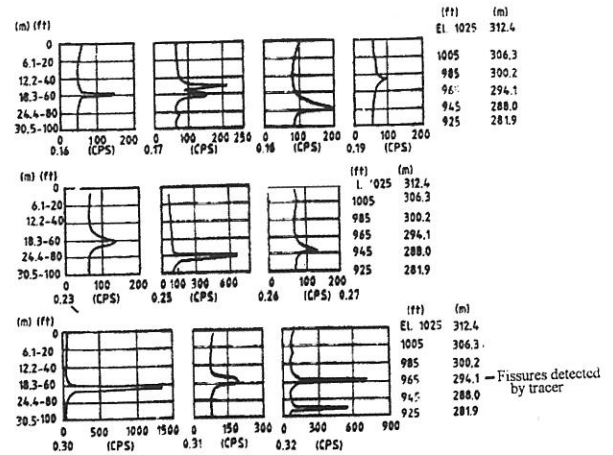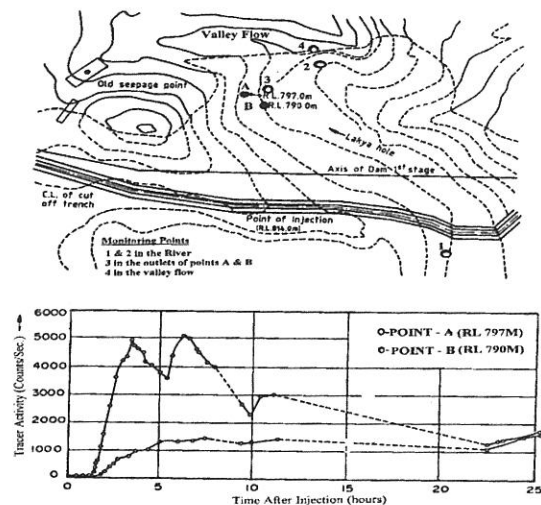
paths were logged. The actual path of leakage was delineated by these radiotracer tests.

Lakya Dam, Karnataka.

The Nature of a large fissure noticed at the Lakya Dam site of the Kudremukh Iron Ore Project, Karnataka, was investigated using radioactive bromide tracer (3). The aim of the study was to investigate the possibility of the any hydraulic connection between the future reservoir (now it has completed and operating) and downstream of the river or to any other point in the valley (Fig. 3) through the fissure. As a part of the experiment, water was injected into the fissure at a rate of 2m/min since the fissure was dry. The injection caused two seepage points to appear downstream. After achieving equilibrium hydraulic connections, ^{82}Br was instantaneously injected into the fissure.

The seepage points and the river water continuously monitored. Interpretation of the tracer responses (Fig.4) at the seepage points and river water monitoring helped in concluding that;

(a) The river was not connected to the fissure,

(b) The flow from the injection to the seepage points was not a pipeline or conduit flow,

(c) The fissure was localized and was not part of any extended geo-fault.

Poip Dam, Maharashtra

Poip minor irrigation dam was constructed across Malvan Valley in Konkan region of Maharashtra (Fig. 5). Every year the reservoir level goes down below sill level within 3 to 4 months after the monsoon, though as per design,

it is expected to hold water till completion of the rabbi season. But it is found that some land 2km downstream of the dam is benefited as wells in this area are getting abundant water even in summer season, which was not the case before the construction of the tank. Hence, radiotracer studies were carried out at Poip dam site to investigate the seepage direction and velocity of groundwater in the vicinity of the dam (5). The radio tracer experiments attempted were two fold (Fig. 5, 6, 7 and 8); to (a).determine the seepage velocity using single well dilution technique (b).seepage flow

Fig. 5   Location of Poip Dam Site

Fig. 6   Single-well dilution probe for groundwater velocity measurement
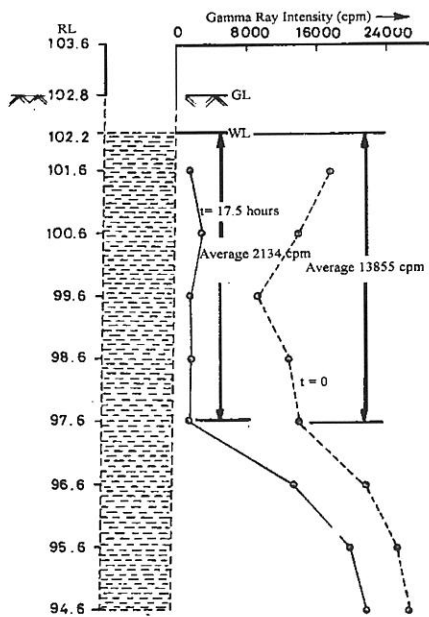
Fig. 7   Radiotracer logging in bore hole
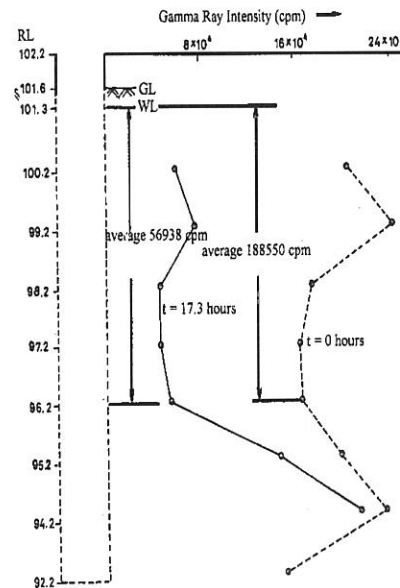
Fig. 8   Multiwell Radiotracer Experiment at Poip Dam Site

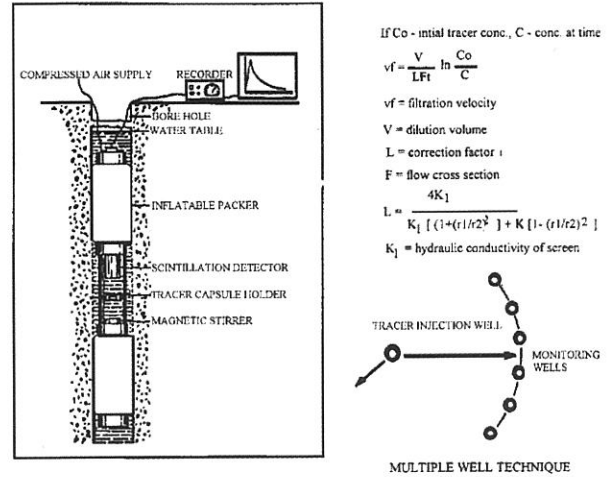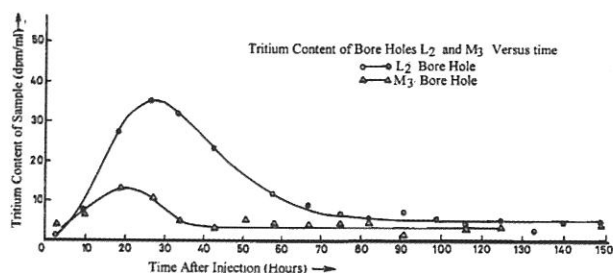Fig. 9   Radiotracer distribution on the Reservoir bed

direction using multiple well technique. Horizontal and vertical groundwater velocities in a few boreholes were measured using ^{82}Br as tracer. It was observed that most of the seepage occurred under the dam through the lateritic soil. Direction of the seepage was studied using tritium as tracer. The direction of flow of seepage was towards the natural stream in the study area.

Borda Reservoir, Maharashtra

Under the minor irrigation scheme of government of Maharashtra, a minor irrigation dam was constructed in limestone terrain at Borda in Yavatmal District. On completion of dam in 1988, it was found that the reservoir was unable to retain the water for a longer period. A radiotracer study was carried out to locate the seepage zones in the reservoir. Four tracer injections each of 25mCi of ^{198}Au in the form of HauCl$_4$ were made in the reservoir for 10min at the flow rate of 300ml/min at a depth of 1.5m using peristaltic pump. Radiotracer ^{198}Au was selected because it moves along the flow induced by seepage and gets absorbed onto soil at the seepage ones on the reservoir bed. Its position was then located using scintillation detector which was towed from a boat. Figure -9, show the distribution of radiotracer on the reservoir bed. The study indicated general seepage through reservoir bed. It was also possible to demarcate the high seepage zone which was located along the two streams feeing.

Chaskaman Dam, Maharashtra

Irrigation department, Government of Maharashtra, have constructed an earthen dam with masonry spillway, to store about 24million 3m of water in the Chaskaman reservoir situated in Khed Taluk, Pune district (Fig.10). Due to environmental and rehabilitation problem, construction work progressed in a phased manner. When the first phase was completed to a height of 26m, the catchment area experienced heavy rains, which led to impoundment of the reservoir and heavy seepage were observed at about 300m downstream of the dam. The seepage was of the order of 3-4 Cusec. To establish the connection of seepage and reservoir water and to demarcate the zone of seepage, injected radiotracer experiments were carried out. Totally five
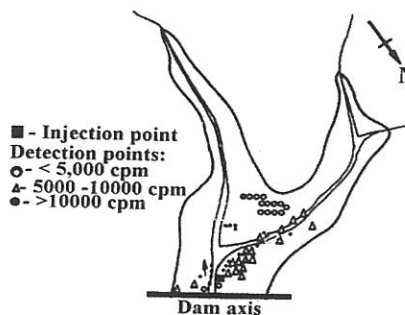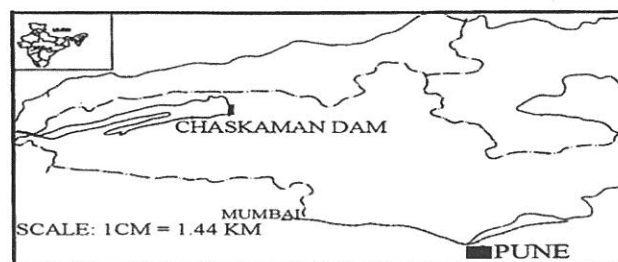

Fig. 10 Location Map of Chaskaman Dam

experiments were conducted. Three experiments to establish the interconnection between the reservoir water and the seepage in the downstream of the dam and the remaining two experiments to measure groundwater velocity in the bore holes located on the dam axis. In all these experiments radiotracer ^{82}Br was used. Tracer was injected into reservoir /boreholes and the concentration of the tracer was monitored using scintillation detector. From these experiments, interconnection between reservoir water and boils were established(transit time of seepage was ~41m/2hours) and the filtration velocities were in the range of 0.i to 4.0m/d. Region of high velocity represents the seepage zone that was ~60m depth in the boreholes(6).

Salal Tail Race Tunnel, Jammu, North India

During the construction of a tail race tunnel through dolomitic lime stone hill (height~100m) for the Salal Hydroelectric Project in Jammu, several seepages were encountered. The tunnel 2.4km long, 11m in diameter, was intended to carry the tail water from the power house and put them back into the river Chenab. Tunneling was mainly through highly fractured, and jointed, often crumbly and sheared dolomitic rock. High seepages were noticed, whenever a shear zones were pierced. Maximum seepage (>100L/s) occurred at about 800m from the outlet, where many shear zones intersect. The River Chenab hugs the hill through which the tunnel passes. The source of the seepages was investigated [7] by analyzing the seepage water and other water samples in the area for environmental isotopes δD, $\delta^{18}O$ (stable) ^3H,) and electrical conductivity. A single set of sample was collected in July1984.
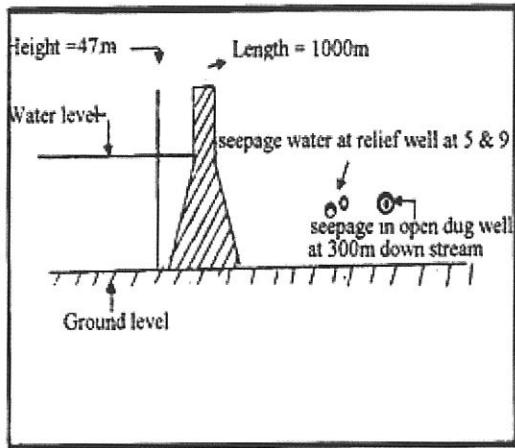
Fig. 11 Schematic Diagram of Chaskaman Dam

Fig. 12 Salal Hydroelectric Project – Isotope & Conductivity Profile

The δD, δ¹⁸O relationship of the samples collected is presented in Fig.11, from the figure it can be seen that the isotopic composition of seepage from the tunnel is distinctly different from those of the River Chenab and other surface waters in the area. Hence the local surface water was not contributing to the springs. River Chenab had depleted in isotopic composition as it originates from higher altitudes in the Himalayas.

The variation of δD, δ¹⁸O, ³H and electrical conductivity along the length of the tunnel are presented in the Fig. 12. The δ¹⁸O was nearly constant along the tunnel and had an average value of -7.7‰. The tritium values of the seepage waters varied from 19 TU near the outlet of the tunnel to a maximum of 81TU at a distance of 850m from the outlet of the tunnel. The River Chenab had a tritium content of 23 TU and represented recent precipitation. Higher tritium content and EC of the seepage water indicated that they were local precipitation water percolating through the fractures in the dolomites. The Ec and the tritium profiles were nearly similar showing that the Ec and tritium values could be correlated. They could be correlated to the thickness of the rocks above the tunnel and hence to the length of the percolation paths of the precipitation waters.

The residence time of the seepage water was computed by comparing their tritium values with those of New Delhi and Kabul precipitation. A piston flow was assumed and tritium output values for New Delhi and Kabul were used to determine the residence time of seepage water in the Salal Dolomite. The results showed that the seepage were 10 to 15 years old precipitation water stored or percolating in the fractured dolomite.

Seepage Study of Chilla Hydel Channel, Uttar Pradesh

Chilla Hydel Channel is part of Garhwal Rishikesh Hydel Scheme in Uttar Pradesh. The channel, which has a bed width of 12.5 m and depth of over 9m, starts at the Virabhadra barrage near Rishikesh and reaches the Chilla Power House, about 14 km downstream Fig. 13. The channel runs along the left edge of the Ganga valley & its discharge
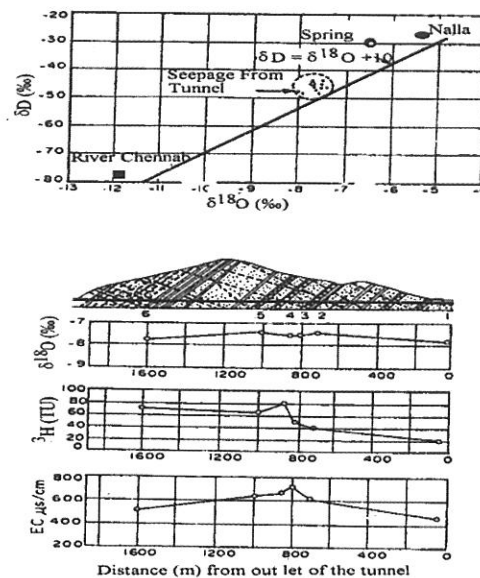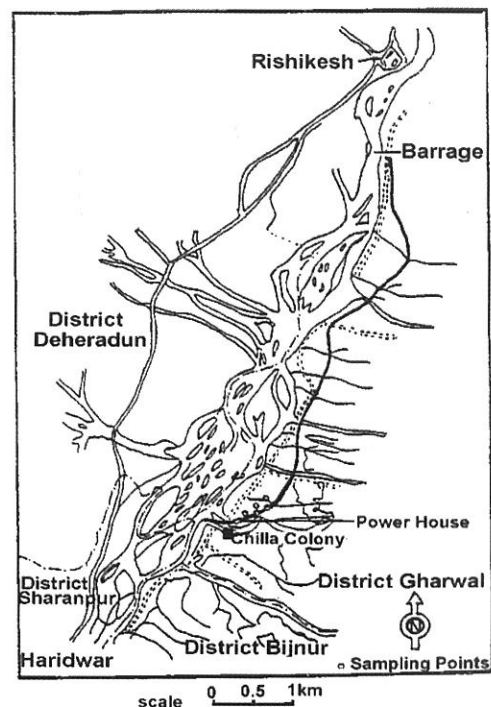
Fig. 13 Chilla Hydel Channel

was about 600 m³/s. After commissioning of the channel in 1980, several springs were started in the right bank of the channel and seepage was suspected from channel. To identify the source of seepage, water samples were collected from channel, springs and groundwater for the measurement of stable isotope δ²H and electrical conductivity. The results are given in the Table 1.

TABLE 1. ^{2}H&EC values of samples collected near Chilla Hydel Channel

1.	Channel water	-72 ‰	EC 110µS/cm
2.	Spring water	-55 ‰	EC 450 µS/cm
3.	Groundwater	-54 ‰	

The results showed that, isotopically channel water was depleted, where as groundwater and spring waters were enriched. The origin of springs was due to the reduction of ground level due to the earth work coupled with the hydrostatic pressure exerted by the channel itself.

Conclusion

Solving the problems of leakage and seepage from reservoirs and dams with a reasonable success requires a detailed knowledge of the geology, hydrogeology, hydrochemistry and hydraulic behavior of the affected geological formations. Such information cannot be obtained from a single method and isotope hydrology cannot be practiced in isolation. Best results are obtained when isotope data are interpreted along with the other above mentioned methods.

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Dating of Groundwater using Environmental Tritium and Carbon-14

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Introduction

Tritium and Carbon-14 exist in the environment due to continuous production in the atmosphere by cosmic ray induced reactions and as a consequence of thermonuclear explosions, operations of nuclear plants and other industrial outputs. The hydrosphere is labeled on a local and global scale with these nuclides. Therefore, measurements of concentration changes in time and space of these isotopes can provide information on the source and dynamics of water bodies and thus, in conjunction with other data, are employed successfully in hydrological investigations in the last few decades.

The "age" of groundwater has important implications for water resources management. Using groundwaters that are not actively recharged is mining. On the other hand, groundwater that is part of the modern recharge hydrological cycle is continuously renewed. Its exploitation is potentially sustainable. Deep groundwaters can be a mixtures of old and modern inputs. However, the presence of even a minor component of modern recharge is important because it indicates a hydraulic connection with an active flow system.

A number of isotope methods can be used for groundwater dating (Table 1). Those with a long half-life (^{14}C, ^{36}Cl, ^{39}Ar, and ^{81}Kr) can be used to date paleo groundwater. Short-lived radioisotopes (^3H, ^{32}Si, ^{37}Ar, ^{85}Kr and ^{222}Rn) indicate modern recharge.

TABLE 1. Radioisotopes of potential use in groundwater dating

Isotope	Mode of decay	Half-life	Time scale
^{222}Rn	α	3.8 days a	Days to week
^{85}Kr	β^-	10.7 a	Months to decades
^3H	β^-	12.43 a	Year to decades
^{39}Ar	β^-	270 a	10^2 years
^{32}Si	β^-	170 a	50 to 1000 years
^{14}C	β^-	5,730 a	10^3 to 10^4 years
^{81}Kr	EC	210,000 a	About a million year
^{36}Cl	β^-	301,000 a	About a million year (Decades for bomb ^{36}Cl)

Tritium

Tritium (^3H or T) is probably the most commonly employed radioisotope used to identify the presence of modern recharge. It is an isotope of hydrogen, emits low energy (18 keV) beta radiation with a half life of 12.32 years. Tritium is produced in the upper atmosphere (stratosphere) from the bombardment of nitrogen by the flux of neutrons in the cosmic radiation.

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

The ^3H thus formed enters the hydrologic cycle after oxidation as HTO. It finally decays as follows;

$$^3H \rightarrow {}^3He + \beta^-$$
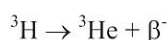
[$E_{\beta max}$ = 18 keV and a half-life of 12.32 years (Lucas and Unterweger, 2000)].

Owing to the low probability of the nuclear reaction and short residence time (Rozanski et.al, 1991) of ^3H in the atmosphere, the natural ^3H concentration in the air is very low. The mean production rate of tritium is 0.28 atoms $cm^{-2}s^{-1}$. Low level tritium concentrations are expressed in Tritium Unit (TU). One TU or TR (Tritium Ratio) corresponds to one tritium atom per 10^{18} atoms of hydrogen. A concentration of 1 TU is equivalent to a specific activity of 0.12 Becquerel (Bq) per litre of water.

Since 1952, the natural tritium levels of a few TU have been swamped by large-scale inputs of tritium into the stratosphere as a consequence of thermonuclear tests. The contribution of this artificial tritium in precipitation reached its maximum level around 1963, which was 10^2 to 10^3 fold increase above natural levels (Fig. 1). The 1963 bomb tritium peak became the marker and used in many hydrological cycles. A large part of the ^3H as well as ^{14}C produced by the nuclear explosions has been injected into the stratosphere and returns to the troposphere each year during spring and early summer. This causes the seasonal variation in both ^3H and ^{14}C, more pronounced in the former, because of the residence time of H_2O to which ^3H is coupled in the atmosphere is very small (in the order of weeks). Owing to the nature of input and circulation pattern wide variations are observed in tritium concentration in precipitation.

Tritium concentration in precipitation increases towards mid and high latitudes and it is a few times higher in the northern hemisphere compared to that in the Southern Hemisphere (Fig. 2). Also, continental precipitation has in general higher tritium levels than marine precipitation. In recent years tritium concentration of precipitation at most marine stations have returned to the presumed natural levels. Both qualitative and quantitative approaches to dating groundwater with tritium are possible.
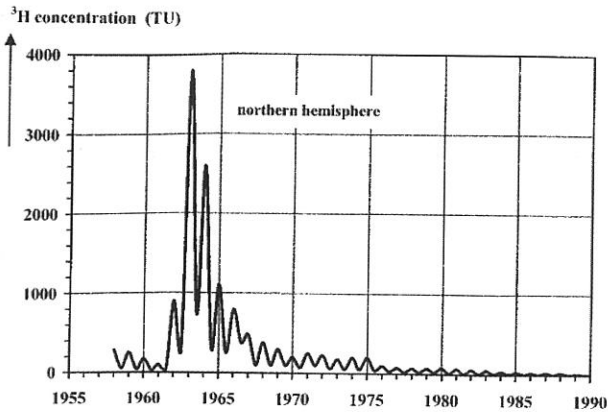
Fig. 1 ^3H content of precipitation over the continental surface of the Northern hemisphere
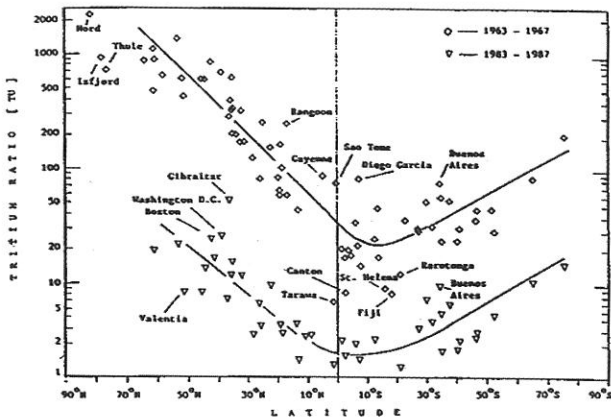

Fig. 2 Latitudinal distribution of tritium concentration of monthly precipitation for oceanic (coastal and island) stations of the IAEA/WMO global network

Radioactive decay (Piston flow model)

$A_t = A_0 e^{-\lambda t}$

A_0 = Initial tritium activity (TU)

A_t = Residual activity remaining after time t

$\lambda = \ln2/t_{1/2}$, $t_{1/2}$, = 12.32 years

For piston flow model, a recharge date can be estimated from decay lines (Fig. 3). Back extrapolation along a decay line from a measured tritium value for a given sample would intersect the precipitation curve at the years when the infiltration took place. The problem with this approach is its simplicity which assumes that only one year precipitation has contributed to the water sample. More commonly, the tritium input is a multi year average. We need to calculate more realistic input function with a model that accounts for mixing and decay in the recharge environment.

Input Function for ^3H in Groundwater (Mixing Model)

In most cases groundwater is a composite of several years precipitation which have contributed to this water through mixing within the unsaturated zone, and by flow
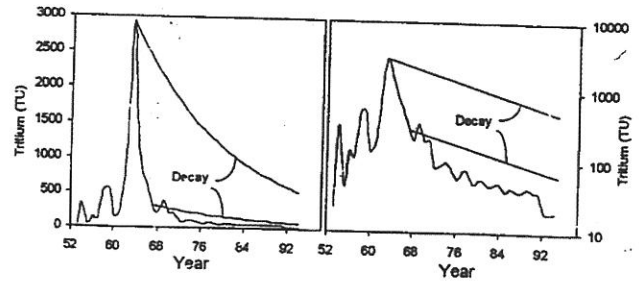

Fig. 3 Decay of tritium from a given inputs from precipitation

through the recharge area where additions to the water table continually contribute to the groundwater. Once this groundwater has moved into a confined zone or to depths where it no longer receives additions from the surface, its ^3H content will decrease by decay. The ^3H concentration in this groundwater parcel will be a function of its residence time in the recharge environment.

The multi year ^3H input function can be determined from the weighted contribution of ^3H from each year, with a correction for decay of each year's precipitation contribution during storage in the recharge area. The input function for tritium in precipitation can be approximated by this approach, using a decay model of recharge. The model assumes that each groundwater component along the flow system has received the same weighting of multi year contributions from precipitation in the recharge environment. Figure 4 shows recharge models for annually averaged tritium curve for Ottawa. Extrapolation from a measured value for groundwater sampled at a given date to the most appropriate recharge input curve provides an estimate of groundwater residence time beyond the recharge environment.

Qualitative Interpretation of Tritium Data

In the last several decades since the last major tests, thermonuclear bomb tritium has been greatly attenuated by oceans and the levels are now approaching that of natural atmospheric production. As a consequence the quantitative interpretation of groundwater mean residence time may be extremely difficult but, qualitative interpretation can be made easily.

For continental regions

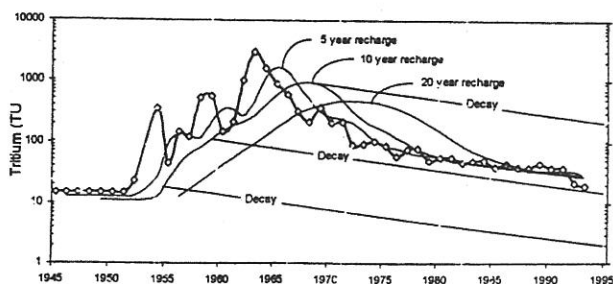|	
<1 TU	Submodern – recharged prior to 1952
1 t0 ~4 TU	Mixture between submodern and recent recharge
5 to 15 TU	Modern (<5 to 10 yr)
>30 TU	Considerable component of recharge from 1960s or 1970s
>50 TU	Dominantly the 1960s recharge.

For coastal and low latitude regions

Fig. 4 Tritium fallout (weighted annual average) in precipitation collected at Ottawa with decay models for initial tritium in groundwater

|	
<1 TU	Submodern – recharged prior to 1952
1 t0 ~2 TU	Mixture between submodern and recent recharge
2 to 8 TU	Modern (<5 to 10 yr)
10 to 20 TU	Residual bomb tritium present
>50 TU	Considerable component of recharge from 1960s or 1970s

Groundwater Dating with ^3H-^3He

^{3}He is produced by radioactive decay of tritium ^{3}H. As long as water parcel is in contact with the atmosphere, ^{3}He produced by tritium decay (^{3}He$_{tri}$) is rapidly removed from the water to the atmosphere by gas exchange. Thus, the concentration of dissolved ^{3}He in the water parcel remains near the atmospheric equilibrium concentration. As soon as water parcel is isolated from the atmosphere the concentration of ^{3}He in water increases because the produced ^{3}He can no longer escape by gas exchange. The ratio between ^{3}He$_{tri}$ and ^{3}H is a measure for the apparent water age which is the time elapsed since the water was last in contact with the atmosphere. ^{3}H-^{3}He apparent water age is given by

$$\tau = 1/\lambda \ln (1 + {}^3He_{tri}/{}^3H)$$

where $\lambda = 0.05599$ yr^{-1} (decay constant of ^{3}H).

Carbon-14

The natural occurrence of the radioactive carbon isotope, ^{14}C or radiocarbon, was first recognized by W.F. Libby (1946). It is naturally formed in the transitional region between the stratosphere and troposphere about 12 km above the earth's surface through the nuclear reaction:

$$^{14}N + n \rightarrow {}^{14}C + p$$
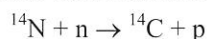
The thermal neutrons required are produced by reactions between very high-energy primary cosmic ray protons.

^{14}C decays according to: $^{14}C \rightarrow {}^{14}N + \beta^-$ with a maximum β^- energy of 156 keV and a half-life of 5730 ± 40 years (Godwin, 1962). Originally the half-life was thought to be 5568 years, so that during the first decade or two ^{14}C age determinations were based on the "wrong" half-life. Later, when the more accurate half-life become known, so many ^{14}C ages were already published that, in order to avoid confusion, it was decided that the original half-life should continue to be used for reporting ^{14}C ages. It was meanwhile known that ages would still be in error, even using the right half-life, because of the natural variations in the ^{14}C content of atmospheric CO_2 during geologic times and deviating from the present. These errors were even larger. Nowadays the ^{14}C calibration, based on the known ^{14}C content of tree rings with exactly known age, removes both errors at once.

Molecules of the atmospheric ^{14}C thus formed very soon oxidize to ^{14}CO, and ultimately to $^{14}CO_2$, which mixes with the inactive atmospheric CO_2. $^{14}CO_2$ molecules enter the oceans and living marine organisms. Some are also assimilated by land plants, so that all living organisms, vegetable as well as animal, contain ^{14}C in concentrations about equal to that of atmospheric CO_2. The production and distribution of ^{14}C in nature occurs through series of chemical and biological processes, which has become stationary throughout much of geologic time. As a consequence, the concentration of ^{14}C in the atmosphere, oceans and biosphere reached a steady-state value, which has been almost constant during a geologic period, which is long compared to the life span of a ^{14}C nucleus. This natural concentration, ^{14}C /^{12}C, is of the order of 10^{-12}, which is equivalent to a specific activity of about 0.226 Bq/gC (13.56 disintegrations per minute per gram of carbon).

Due to its gaseous form of CO_2 and long residence time in troposphere ^{14}C is much more efficiently mixed in troposphere than tritium. Recent data on ^{14}C activities from atmospheric CO_2 show a rather good homogenization of the ^{14}C content of atmospheric carbon on global scale. In the case of tritium, radiocarbon produced by thermonuclear tests led to an increase (temporary doubling) in the atmospheric ^{14}C content of the northern hemisphere (Fig. 5). The mean natural atmospheric ^{14}C content is fairly uniform and for all practical purposes is assumed to be constant in the past.

Three modes of reporting ^{14}C activities are in use, in part analogous to the conventions internationally agreed (IAEA) for stable isotopes (Stuiver and Polach, 1977; Stuiver and Van der Plicht, 1998). The absolute (specific) ^{14}C activity that is the ^{14}C radioactivity is expressed in Bq/gC or dpm/gC.

It is extremely difficult to make an absolute measurement of a ^{14}C activity. Moreover, the absolute ^{14}C content of a sample is generally not relevant. Therefore, the sample activities are compared with the activity of a standard. In reality, the number of ^{14}C counts is related to the number of counts from the standard under equal conditions.

This results in a ^{14}C activity ratio or ^{14}C concentration ratio:

$$^{14}a = \frac{{}^{14}A_{sample}}{{}^{14}A_{reference}} = \frac{{}^{14}A}{{}^{14}A_R} = \frac{{}^{14}C_{decay\ rate\ in\ the\ sample}}{{}^{14}C_{decay\ rate\ in\ the\ reference}}$$

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$$= \frac{^{14}C_{\text{concentration in the sample}}}{^{14}C_{\text{concentration in the reference}}}$$

The symbol ^{14}A may be used for the ^{14}C content (radioactivity or concentration) of a sample, whether the analytical technique applied is radiometric or mass spectrometric (AMS). Under natural circumstances the values of ^{14}A are between 0 and 1. In order to avoid the use of decimals, it is general practice to report these values in %, which is equivalent to the factor 10^{-2}. Thus, ^{14}C activity can be calculated in percent Modern Carbon (pMC), where as 100 pMC = 13.56 dpm/g of carbon. In several cases the differences in ^{14}C content between the project samples are small. Therefore, the use has been taken over from the stable-isotope field to define relative abundances. The relative ^{14}C content (activity or concentration), $\delta^{14}C$, defined as the difference between sample and reference ^{14}C content as a fraction of the reference value:

$$\delta^{14}C = \frac{^{14}A - ^{14}A_R}{^{14}A_R} \times 10^3 \text{‰}$$

The values of δ are small numbers and therefore generally given in per mil (‰), which is equivalent to the factor 10^{-3}.

It has been seen that during any process in nature isotope fractionation occurs, not only for the stable isotopes but also similarly for the radioactive isotope such as ^{14}C. Neglecting this effect would introduce an error in an age determination, because the original ^{14}C content of the material would be different from what we assume. The degree of fractionation is nicely indicated by the $\delta^{13}C$ value of the material. An example is the apparent difference in age between C_3 plants such as trees ($\delta^{13}C \approx -25$‰) and a C_4 plant such as sugar cane ($\delta^{13}C \approx -10$‰), each assimilating the same atmospheric CO_2. Therefore, in defining the standard activity, but also in the treatment of all ^{14}C data, ^{14}C results are normalised to the same $\delta^{13}C$ value. It is generally assumed from theoretical consideration that the isotopic enrichment is generally two times larger for ^{14}C than ^{13}C. By international agreement all ^{14}C results are normalised for a deviation of the $\delta^{13}C$ value from !25‰, with the exception of Ox_1, which has been normalised to -19‰. Therefore, normalised ^{14}C activity of the sample can be written as

$$^{14}A_{SN} = ^{14}A_{SC}\left[1 - \frac{2(\delta^{13}C_S + 25)}{1000}\right]$$

Where,

$^{14}A_{SC}$ = corrected net activity of sample
$^{14}A_{SN}$ = normalised and corrected net activity of sample
$\delta^{13}C$ = carbon-13 content of the sample

The ^{14}C standard activity or concentration was chosen to represent as closely as possible the ^{14}C content of carbon in naturally growing plants. The ^{14}C standard activity does not need to be (in fact it is not) equal to the ^{14}C activity of the standard. The primary modern reference for radiocarbon
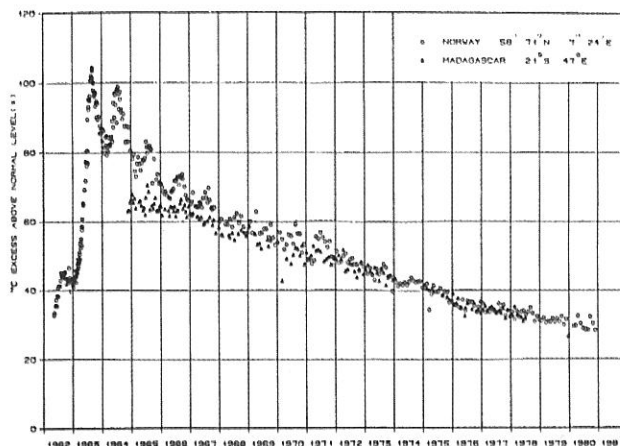
Fig. 5 ^{14}C concentration in atmospheric CO_2, representative fornorthern (Norway) and Southern (Madagascar). The graph is taken from Nydal (1983)

dating is defined as 95% of the count rate in 1950 of a batch of oxalic acid from U.S. National Bureau of Standard. The activity of primary standard corresponds to Arizona wood grown in 1890 (therefore uncontaminated by fossil fuels CO_2) whose activity was corrected for ^{14}C decay to correspond to AD 1950 (Karlen et al., 1966). By international agreement, $\delta^{13}C$ of oxalic acid (Ox1) has been taken as -19‰ with respect to PDB. Therefore, normalised ^{14}C activity of the standard can be written as

$$^{14}A_{ON} = 0.95Ox1 = 0.95 {}^{14}A_{Ox1}\left[1 - \frac{2(\delta^{13}C_{Ox1} + 19)}{1000}\right]$$

This $^{14}A_{ON}$ corresponds to 100 pMC and is equal to specific activity of 13.56 dpm/gC or 0.226 Bq/gC. Because the original supply of oxalic acid has been exhausted, a new batch of oxalic acid (Ox2) is available for distribution by the NIST (formerly US-National Bureau of Standards). Through careful measurement by a number of laboratories (Mann, 1983), the ^{14}C activity has become related to that of the original Ox1 by:

$$^{14}A_{Ox2} = (1.2736 \pm 0.0004) \times {}^{14}A_{Ox1}$$

Both activities refer to AD1950. Consequently the standard activity is:

$$^{14}A_{ON} = 0.7459Ox2 = 0.7459 {}^{14}A_{Ox2}\left[1 - \frac{2(\delta^{13}C_{Ox2} + 25)}{1000}\right]$$

Where, the $^{14}A_{ON}$ values for Ox1 and Ox2 refer to the activity of the material in 1950, irrespective of the time of measurement.

From the atmospheric reservoir, CO_2 enters into the water cycle by two main processes – chemical processes and biochemical production

Chemical Process

The following chain reactions take place in the free waters

$$CO_2(gas) \leftrightarrow CO_2(aqueous)$$
$$CO_2(aqueous) \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{--} + H^+$$
$$CO_3^{--} + Me^{++} \leftrightarrow MeCO_3$$
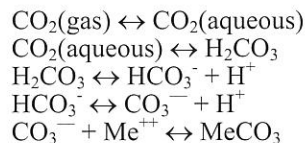
Where Me^{++} is generally Ca^{++} but can include Mg^{++}, Fe^{++} and sometimes $2Na^+$ in highly saline continental brines. This $MeCO_3$ then gives total dissolved inorganic carbon (TDIC)

Biochemical Production

The assimilation of atmospheric CO_2 by plants is accompanied by release of CO_2 in the soil zone. This occurs by fermentation and decay of organic material (fulvic and humic acid) but mainly by respiration in the root zone. This biogenic CO_2 then gives total dissolved inorganic carbon (TDIC) according to several processes depending upon local geological conditions. All these processes which produces large amount of HCO_3^- or CO_3^-, if pH tends to increase can be divided into (1) those in which all dissolved carbon is of organic origin and (2) those in which the dissolved carbon comes from both biogenic CO_2 and solid carbonate. For the former, the ^{14}C activity of TDIC will exclusively reflect that of the CO_2 sources, for the latter the ^{14}C activity of biogenic CO_2 will be diluted by the carbon coming from the leaching of the solid carbonate since it is generally very old and inactive. The chemical dilution of ^{14}C may be observed even in non-carbonate situation due to secondary formation of calcite by geochemical reactions. Consequence is that the age estimation of TDIC can not simply be done by using modern activity (100 pMC) as initial activity. TDIC in any form of carbon can undergo isotopic exchange with gaseous CO_2 when present i.e. unsaturated zone.

In order to calculate an age in a given sample one must determine the modifications of ^{14}C content of the TDIC which are due to chemical (dilution) and isotopic (exchange) processes i.e. the estimation of initial activity of TDIC. It is defined as its specific ^{14}C content after all chemical and isotopic processes before any radioactive decay has taken place for that given sample. ^{14}C content of TDIC is generally associated with two kinds of system

Dissolved Carbon of Pure Biogenic Origin i.e. no Mixing with Inorganic Carbon

In Equilibrium with Gaseous Phase

In the presence of large reservoir of CO_2 the pH is generally rather low and TDIC is in the form of bicarbonate and H_2CO_3. If b and a are the respective molar concentrations, then the balance is written as

$$(a + b)\delta_{TDIC} = a[\delta_{CO2}(g)-\varepsilon_{ag}] + b[\delta_{CO2}(g)-\varepsilon_g]$$

where δ is ^{13}C content, ε_{ag} is ^{13}C fractionation factor between H_2CO_3 and CO_2 and ε_g is ^{13}C fractionation factor between CO_2 and HCO_3^-

$$(a + b)A_{(0)TDIC} = a[A_{CO2}(g)-2\varepsilon_{ag}] + b[A_{CO2}(g)-2\varepsilon_g]$$

where A is ^{14}C content.

Complete Transformation of Soil CO_2 into TDIC

Complete transformation of soil CO_2 into TDIC takes place by weathering of silicates. Release of alkaline and alkaline earth ions during silicate weathering acts as a absorption trap for CO_2 which is transformed into HCO_3^- in proportion as it formed in a porous soil. In that case

$$\delta(TDIC) = \delta(CO_2)$$
$$A_0(TDIC) = A(CO_2)$$

Dissolved Carbon of Pure Mixed (Biogenic and Mineral) Origin

Open System Equilibrium

A complete exchange occurs with soil CO_2 $^{14}CO_2$ + $H^{12}CO_3^- \rightarrow {}^{12}CO_2 + H^{14}CO_3^-$ In this case the final result is

$$\delta(TDIC) = \delta CO_2 - \varepsilon_g$$
$$A_0(TDIC) = ACO_2 - 2\varepsilon_g$$

Closed System

Empirical approach (By Vogel)

If the area of recharge is clearly known ^{14}C content of TDIC can be compared to that of organic matter at the water table and the ratio would be equal to A_0 assuming that no further isotopic or chemical processes, which could modify the ^{14}C content of TDIC, occur in the aquifer. This approach is not based upon any conceptual treatment. Therefore, it is strictly of local application and any generalisation of A_0 values without experimental support would be meaningless since each system has its own carbon and isotope chemistry.

The chemical mixing model (Tamer's model)

In a carbon system in which solutions of solid carbonate occurs, the bicarbonate has double origin. Half of it comes from biogenic CO_2 and half from leached carbonates. The excess of aqueous CO_2 and H_2CO_3 comes also from biogenic CO_2. The ratio of the carbon of biogenic origin over the total dissolved carbon gives the chemical dilution i.e. the initial activity of TDIC.

$$A_0 = \frac{mCO_2(aq) + 0.5\, m\, HCO_3^-}{mCO_2(aq) + m\, HCO_3}A_g$$

m are molalities and A_g is the ^{14}C content of soil CO_2. A_g = 100 pMC except for post bomb infiltration process.

If the solid carbonate has a significant ^{14}C activity A_c, the balance must be written as

$$A_0 = \frac{\left[mCO_2(aq) + 0.5\, m\, HCO_3^-\right]A_g + \left[0.5\, m\, HCO_3^-\right]A_c}{mCO_2(aq) + m\, HCO_3}$$

This model does not take into account any isotopic exchange or processes like incongruent dissolution of dolomite. However, despite these limitations, such a model can be of help in regions where the solution of solid

TABLE 2. Application of ^{14}C age correction models - recharge parameters and results for groundwater in Oman

T	pH	P_{CO2}	$\delta^{13}C_{soil}$	A_0 ^{14}C	δ_t	mH_2CO_3	$m\,HCO_3^-$
25	6.5	0.007	-18‰	100 pMC	2‰	0.00024	0.00034

Site	^{14}C pMC	Uncorrected age (BP)	Model results (years BP)		
			Chemical mixing model	Isotope mixing model (Pearson)	Isotope mixing model with complete exchange of CO_2 (IAEA model)
55	3.3	30,107	24, 850	19,093	14,304
56	2.3	34,773	29,630	24,031	22,005
57	4.2	28,717	24,169	17, 296	16,984
58	6.3	27,254	21,828	20,533	20,688
62	3.0	31,665	26,412	15,213	17,443
63	7.3	23,696	17,992	12,191	10,649
64	2.7	31,366	31,366	17,088	21,569

(i)   Tritium bearing groundwaters have 760 year BP which reflect degree of uncertainty in the correction model.

(ii)   Tritium free intermediate groundwaters fall in an age bracket of 1300 to 8000 years BP

(iii) Tritium free very old groundwater have modeled ages in the 19000 to 35000 years BP

carbonate does not occur and the isotopic exchange with gaseous CO_2 is insignificant (semi arid regions).

The isotopic mixing model (Pearson Model)

The principal of this model is similar to that of chemical mixing model, except for end members of the mixing which are ^{13}C contents of the soil CO_2 and solid carbonate. It is written in its complete form as

$$A_0 = \frac{\delta_t - \delta_c}{\delta_g - \delta_c}(A_g - A_c) + A_c$$

where δ and A represents ^{13}C and ^{14}C contents respectively and t, c and g refer to TDIC, solid carbonate and soil CO_2 respectively. Sometimes the model was applied in a very simplified way with $\delta_g = -25‰$, $\delta_c = 0$ and $A_c = 0$ (ancient marine carbonate). Thus, the balance can be written as

$$A_0 = \frac{\delta_t}{-25}A_g$$

This model is very useful to give an estimate of all processes of dilution of ^{14}C within dead carbon in the unsaturated zone and in the aquifer. To a certain extent, the model also takes into account the exchange processes with soil CO_2 and solid carbonate since the result of an isotopic exchange can be considered as that of mixing, as long as the amount of exchange remains low. But since no fractionation factor appears in the model, it can not be used when the exchange is extensive. Thus, it appears that with Tamer's approach, Pearson model applies only to systems in which limited CO_2 is available in the unsaturated zone and can not easily interact with TDIC. Practically both models require that system be closed with respect to end members (gaseous

and solid carbon). If the analysis of ^{13}C content of soil gas and solid carbonate in the recharge area are available, Pearson's approach can be considered suitable.

The isotopic mixing model referred to complete exchange with CO_2.

This is called IAEA model and used in several studies. It is like Pearson's model in which fractionation factor has been incorporated. It implies that mixing occurs between two components on one hand solid carbonate and on the other hand the bicarbonate completely exchanged with soil CO_2 (as if it were an open system with respect to soil gas). Corrected for ^{14}C activity of solid carbonate A_c, it results in

$$A_0 = \frac{\delta_t - \delta_c}{\delta_g - \varepsilon_g - \delta_c}(A_g - A_c) + A_c$$

where ε_g is ^{13}C fractionation factor between soil CO_2 and bicarbonate. This model gives consistent results of confined aquifers. Furthermore, this model considers that all the TDIC is in the form of HCO_3^-, i.e. pH is close to 7. In conclusion this model is of interest when water chemistry data are not available.

Some more complicated models can be applied depending upon geological and mineralogical information as well as hydrochemistry of the system.

Knowing the rate of radioactive decay (λ or $T_{1/2}$), the age (T = time elapsed since death) of a carbonaceous sample, organic or inorganic, can be calculated from the measured activity, $^{14}A_{SN}$, if the ^{14}C activity at the time of death, $^{14}A_{initial}$ ($^{14}A_{ON}$), is known using following equation.

$$t = (t_{1/2} / \ln 2) \times (^{14}A_{ON} / {}^{14}A_{SN})$$

ID No.	Location	Well type	EC	$^3H \pm 1\sigma$ (TU)	$^{14}C \pm 1\sigma$ (pMC)	^{13}C (‰)	^{14}C (model age) 91.9 pMC as A_0
D1	Dharmikua	DW	2330	2.1 ± 0.3	79.5 ± 2.2	-9.6	1198
T1	Kishengarh	TW	3460	0.3 ± 0.1	47.3 ± 1.4	-5.7	5492
D2	Kishengarh	DW	4180	1.1 ± 0.2	91.9 ± 1.7	-10.7	0
D3	Kurriaberi	DW	2100	0.5 ± 0.2	58.8 ± 1.6	-8.3	3692
D4	Nathurakua	DW	3040	0.3 ± 0.2	69.3 ± 1.8	-7.9	2334
T2	Ghantiyali	TW	3660	0.5 ± 0.2	31.2 ± 1.2	-4	8932
D5	Ghantiyali	DW	2820	0.6 ± 0.2	54.9 ± 1.5	-7.1	4260
D7	Gajesingh Ka Tar	DW	4620	2.1 ± 0.3	64.9 ± 1.9	-7.7	2876
T3	Ranau	TW	1890	0.6 ± 0.2	48.8 ± 1.5	-7.4	5233
T4	Sadewala	TW	7600	0.4 ± 0.2	6.6 ± 0.9	-7.7	21775
T5	Loungewala	TW	2740	0.4 ± 0.2	10.4 ± 0.9	-5.6	18015
T7	Ghotaru	TW	2270	0.4 ± 0.2	20.7 ± 1.0	-7.3	12324
D12	Ghotaru	DW	3650	1.1 ± 0.2	62.7 ± 1.6		3161
T8	Asutar	TW	2560	0.4 ± 0.2	36.1 ± 1.3	-7.5	7726
D14	Langtala	HP	3400	0.3 ± 0.1	68.6 ± 2.0	-6.2	2418
D15	Langtala	DW	2380	1 ± 0.2	64.8 ± 1.7	-6.9	2889
D17	Dost Mohammad Ka Kuan	DW	1380	1	49.7 ± 1.5	-1.2	5082
D18	Mituwala	DW	6780	0.6	57.9 ± 1.7	-8.5	3820

For ^{14}C, $t_{1/2}$ is 5730 years and this equation simplifies to

t = 8268 ln A_{ON}/A_{SN}

The radiocarbon measurement is termed as conventional radiocarbon age and is expressed in BP (before present). 1950 is the year 0 BP by convention in radiocarbon dating and is deemed to be the 'present'. 1950 was chosen for no particular reason other than to honour the publication of the first dates calculated in December 1949. The International Radiocarbon Dating Standard is the specific activity of Arizona wood grown in 1890 (unaffected by fossil fuel combustion due to industrial revolution) corrected for radioactive decay to 1950. The activity of this standard is 0.226 Bq (13.6 dpm) per g of carbon which corresponds to 100 pMC.

Results

Case Study of Oman

Groundwaters in southern Oman provide a useful case study to test the calculations and compare the model results (Clark et al., 1987). The result has been given in Table 2

Case Study of the Triassic Sandstone Aquifer, U.K.

Groundwaters of the Triassic age Bunter sandstone in the English East midlands were studied by Bath et al. (1979) and provide a good example to study radiocarbon dating with relatively few geochemical complications. The carbon evolutions of the groundwater in a down gradient direction are characterized by increase in mHCO$_3^-$ and $\delta^{13}C_{DIC}$ due to interaction with minor carbonate in the fluvial sediments. Radiocarbon activities decrease from 40 to 60 pMC in the unconfined aquifer region to less than 2 pMC in the deep groundwaters. The low ^{14}C values in the recharge area are evidence that carbonate system evolves under closed system conditions, and isotope mixing model is appropriate for age calculation. Modeled groundwater age matched with oxygen-18 data and ^{14}C modeling results showed three group of groundwaters

Case Study of Jordan

The study was carried out by Bajjali et al., 1977. Atmospheric ^{14}C was measured and found to be 114 ± 6 pMC. Tritium bearing groundwaters in the recharge area averaged 65 pMC. Using empirical approach A_0 (Initial Carbon-14 activity) was considered 65 pMC with a slight correction for fractionation during transfer to the soil.

Case study of palaeo channel in the arid regions of Jaisalmer (western Rajasthan), India

The study was carried out by Sinha and Navada, 2008. ^{14}C age was calculated using empirical approach and given in table 3. Most of the samples have negligible tritium (< 1TU). The highest carbon-14 content of tritium bearing groundwater (> 1TU) has been found 91.9 pMC at Kishengarh location. However carbon-14 content of groundwater having highest tritium content (2.1TU) is

64.9 pMC at Gajesingh Ka Tar location. Isotope mixing or chemical mixing model could not be used because modeled ages did not match with oxygen-18 and deuterium data. Therefore, empirical approach was used and highest measured value of dug well was used as A_0 value. ^{14}C age of tube well samples, are more than 5000 years BP whereas dug well samples are less than 5000 years BP.

Summary

Tritium and carbon-14 are produced in the atmosphere continuously and ground water is labeled with these isotopes through various mechanisms. Age of the young groundwater determination using piston flow model is very simplistic when there is single recharge source and uniform recharge zone. In general, groundwater consists of multiple recharge sources and inhomogeneous recharge zone. In various hydrological studies all over the world, qualitative approaches have been used extensively. Groundwater dating using carbon-14 is also very complicated. One model suitable for one geological formation may not be suitable for another formation. IAEA model have been extensively used in many hydrological studies because it accounts for chemical mixing as well as isotope fractionation. In various hydrological investigations conceptual model (empirical approach) has been found very useful.

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Role of Isotope Technology in Groundwater Contamination Studies

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Introduction

Water is one of the major elements essential for sustenance of all forms of life. Though three fourths of earth's surface is covered by water, most of it is saline and not fit for drinking purpose. Groundwater, which is only 0.06% of total water present on earth, contributes to 98% of drinking water resources on earth; hence it is a valuable natural resource. Groundwater is part of the earth's water or hydrological cycle. A part of the rain fall infiltrates into the soil and the rest of the water evaporates or flows as runoff water into the rivers. The roots of the plants take up a portion of this moisture and some amount is lost through transpiration to the atmosphere, rest will infiltrate further, eventually accumulating above an impermeable bed, saturating available pore space and forming an underground reservoir. Underground strata that can both store and transmit water are termed as 'aquifers'.

Groundwater is generally less susceptible to contamination when compared to surface water. Contamination of surface water may be remedied by proper prevention and control measures, but it is more serious when contaminants enter groundwater system. Contamination remains in groundwater systems (aquifers) for centuries, even millennia, and it is very difficult to be cleaned or remediated. Unpredictable delays and changes in seasonal rain fall pattern, over exploitation and misuse of surface water sources, the rising demand of water for domestic, agricultural and industrial purposes have all urged mankind to opt for indiscriminate exploitation of this valuable groundwater resource.

In Indian context, groundwater plays an important role in meeting the water requirements of agriculture, industrial and domestic sectors. The increasing dependence on groundwater as a reliable source of water for various uses has resulted in its large-scale and often indiscriminate development in various parts of the country [1]. The unplanned development of groundwater resources has led to an increasing stress on the available resources [2]. This is manifested as various undesirable environmental consequences such as long-term decline of groundwater levels, de-saturation of aquifer zones, and increased energy consumption for lifting water from progressively deeper levels and quality deterioration due to saline water intrusion in coastal areas. At the same time, there are areas in the country where groundwater development is still at low-key in spite of the availability of sufficient resources [3].

Groundwater quality problems in India

Inland Salinity

Inland salinity in groundwater is prevalent mainly in the arid and semi arid regions of such as in states like, Rajasthan, Haryana, Punjab and Gujarat and to a lesser extent in Uttar Pradesh, Delhi, Madhya Pradesh Maharashtra, Karnataka and Tamil Nadu. Inland salinity of groundwater is caused due to the depositional environment of the aquifers and also due to the chemical reactions taking place during the movement of groundwater from recharge to discharge area. It may also be caused due to water-logging in canal command and other shallow water table areas [4].

Saline Water Ingress in Coastal Areas

Areas represent zones where land and sea meet and comprises variety of complex environments including deltas, estuaries, bays, marshes, dunes and beaches. Coastal aquifers have boundaries in contact with sea water and are in a delicate dynamic equilibrium with it. Excessive withdrawal of fresh groundwater from these aquifers may disturb this equilibrium, resulting in intrusion of saline water into coastal aquifers. The Indian subcontinent has a dynamic coast line of about 7500 km length. Problem of salinity ingress has been noticed in coastal parts of Tamil Nadu, Saurashtra, Orissa and Pondicherry regions [5-7].

Fluoride

High concentration of fluoride in groundwater beyond the permissible limit of 1.5 mg/L (IS: 10500:1991) is a major health problem in India. Fluoride in excess of permissible limits has been reported from groundwater in 199 districts in 19 states of India [8], mainly in Andhra Pradesh, Rajasthan, Karnataka, Maharashtra, Orissa, Madhya Pradesh, Punjab, Tamil Nadu, Haryana, Gujarat, Bihar, Delhi, Uttar Pradesh, Jharkhand and West Bengal.

Arsenic

The occurrence of Arsenic in groundwater was first reported in 1980 in West Bengal in India. In West Bengal, 79 blocks in 8 districts have Arsenic beyond the permissible limit of 0.01 mg/L. About 16 million people are in risk zone. The most affected districts are on the eastern side of Bhagirathi river in the districts of Malda, Murshidabad ,Nadia ,North 24 Parganas, South 24 Parganas and western side of the districts of Howrah, Hugli and Burdwan. The occurrence of Arsenic in groundwater is mainly in the intermediate aquifer in the depth range of 20-100m. The deeper aquifers are free from Arsenic contamination [9]. Apart from West Bengal, Arsenic contamination in groundwater has been found in the States of Bihar, Chhattisgarh and Uttar Pradesh. In case of Bihar initially

only 2 districts were reported as Arsenic affected but recently Arsenic in groundwater has been reported in all 12 districts have been reported. It has also been reported in Dhamaji District of Assam. The occurrence of Arsenic in the states of Bihar, West Bengal and Uttar Pradesh is in Alluvium formation but in the state of Chhattisgarh it is in the Volcanics exclusively in ancient rift zone [10-12].

Iron

High concentration of Iron in groundwater has been observed in the country [8]. Groundwater contaminated by iron has been reported from Assam, West Bengal, Orissa, Chhattisgarh, and Karnataka. Localized pockets are observed in state of Bihar, UP, Punjab, Rajasthan, Maharashtra, Madhya Pradesh, Jharkhand, Tamil Nadu, Kerala and North Eastern States.

Nitrate

Nitrate is a very common constituent in the groundwater, especially in shallow aquifers. The source is mainly from manmade activities. In India, high concentration of nitrate has been found in many States, the highest value being 3080 mg/L found in Bikaner, Rajasthan.

In addition to the quality problems mentioned above, contamination of groundwater resources due to industrial effluents contributing to the presence of hazardous chemicals including heavy metals in groundwater and urban sewerage resulting in bacteriological contamination have also become serious concerns in many areas in the country in recent decades.

Role of Isotope Technology

It is important to preserve the quality of groundwater in order to meet increasing demand for clean drinking water. In order to achieve this goal, it is imperative to identify the source & origin of groundwater, source of contamination and its movement in subsurface which would help in controlling further contamination and in adopting proper remedial treatment procedures.

Environmental Isotopes

Tracer approach is best suited for studying the hydrological processes. A tracer may be defined as a substance, a labeled chemical or an atom, used to trace the course of a dynamic system, water in this case. Environmental and artificial injected tracers have been established as potential tools in tracing groundwater and also its contaminants. Environmental isotopes are used as a modern, specific and reliable technique in understanding various hydrological processes. The application of isotope techniques in hydrology is based on the use of either the naturally occurring isotopes (environmental isotopes) or intentionally introduced isotopes (artificial isotopes). Generally environmental stable isotopes (^{2}H, ^{18}O, ^{13}C etc.) are used to determine the origin of water and its constituents [13-15] and environmental radioisotopes (^{3}H & ^{14}C) are used for dating groundwater [16]. Other important environmental

isotopes are ^{15}N, ^{34}S, ^{85}Kr and isotopes of radium, thorium and uranium etc. Some of the very important applications of environmental isotopes in hydrology include; Seepage in dams and reservoirs [17, 18], Source of recharge and estimation of recharge to groundwater [19, 20], Efficacy of artificial recharge to groundwater [21], Origin of groundwater salinity and pollution [5-7, 22, 23], Sustainability of deep aquifers, Lake Dynamics & Sedimentation of lakes [24], Dating of groundwater [25], Origin of geothermal waters.

Since the natural variations of environmental stable isotopes (^{18}O, ^{2}H etc.) are usually very small, the only technique that can routinely approach high precision for these isotopic measurements is mass spectrometry where an Isotope Ratio Mass Spectrometer (IRMS) is employed. Hydrological studies do not warrant absolute ratio measurement of isotopes of interest hence, measuring and reporting isotopic variation w.r.t. a standard (e.g. SMOW) is sufficient for the purpose. The isotopic variation is reported as δ value in permil (‰) deviations [26], where R represents isotopic ratio of heavier to lighter isotope.

$$\delta^2H \text{ or } \delta^{18}O \ (\permil) = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$$

$$\text{where} \qquad R = \frac{^2H}{^1H} \text{ or } \frac{^{18}O}{^{16}O}$$

The standard almost universally accepted for oxygen and hydrogen stable isotope variations in natural waters is SMOW (Standard Mean Ocean Water). It corresponds to a hypothetical water having both oxygen and hydrogen isotopic ratio equal to the mean isotopic ratios of ocean water. For ^{13}C sample preparation, the total dissolved inorganic carbonate is precipitated in the field as $BaCO_3$ and in laboratory the precipitate is treated with phosphoric acid and the evolved CO_2 is analyzed for ^{13}C. The standard for ^{13}C measurement is PDB (Belemnite of Pee Dee formation). Similarly for ^{15}N measurement sample preparation is done by either a) Steam distillation method (Kjeldahl method) or b) Resin based method that includes concentration of nitrate on a resin bed and then production of N_2 by combustion in an evacuated sealed quartz tube. The standard is atmospheric nitrogen. Sulfur – 34 measurement of dissolved sulfate is carried out using SO_2, which is produced in two steps from SO_4^{2-}, firstly reduction of SO_4^{2-} to S^{2-} and then oxidation of S^{2-} to SO_2. The standard for S isotope measurements is Canyon Diablo iron meteorite (CDT). The precision of measurement of δ^2H is ±0.5‰ (2σ criterion) and for $\delta^{18}O$, $\delta^{13}C$, $\delta^{34}S$ and $\delta^{15}N$ it is ±0.1‰ (2σ criterion).

Radio-isotopes such as ^{3}H and ^{14}C are measured using liquid scintillation detector. Tritium in natural waters is very low, hence it is enriched electrolytically and measured whereas for ^{14}C, total dissolved inorganic carbonate is precipitated in the field in the form of $BaCO_3$ and the evolved CO_2 is absorbed in carbsorb scintillation mixture and measured.

Injected Isotope

Injected radioactive tracers viz., [82]Br ^{51}Cr, [58]Co and ^{60}Co, ^{131}I and ^{99}Tc, which can be measured in situ, have been proved to be suitable and handy for most of the hydrological applications [18, 20, 23]. High sensitivity of measurement, high specific activity, ease in mixing with water and negligible density effects to the groundwater system, enable radioactive tracers as preferable to other tracers. Selection of radioactive tracer is based on the purpose and duration of the study while meeting safety requirements. [3]H being a part of water molecule is considered as the most ideal hydrological tracer, although in situ radiation detection is not possible. Many researchers in India and abroad have successfully employed nuclear techniques using injected radioactive tracers to determine groundwater recharge [18,20], groundwater flow direction and velocity [23, 27], seepages from canals and reservoirs and aquifer parameters [17,18]. There are two approaches popularly used in finding the dynamics of groundwater; 1. Single well method [28] and 2. Multiple well method.

Single Well Technique

This is also known as Point Dilution Method. In this technique a radiotracer is injected in the borehole and it is stirred thoroughly to make it uniform. The tracer dilution is based on the principle that freshwater flows into the borehole and equal volume of active water leaves the borehole. To know the tracer dilution with time, loggings were carried out at different intervals of time & depths. Groundwater filtration velocity is computed using

$$V_f = \frac{-V}{\alpha \cdot F \cdot t} \cdot \ln\frac{C_o}{C_t}$$

equation, Where V is dilution volume, F is cross section of the dilution volume perpendicular to the direction of undisturbed groundwater flow, α is constant (taken as 2), C_o is initial tracer concentration, C_t is tracer concentration at time t.

Multiple Well Method

A radiotracer is introduced into an injection well and the activity is monitored in the downstream boreholes. The direction of maximum activity corresponds to the direction of flow. The linear velocity can be calculated using the equation,

$$Vt = \frac{X}{T}$$

Where X = distance between injected & monitoring well, T = average time of tracer flow.

Case Studies

There are ample studies demonstrating the usefulness of isotopes in conjunction with hydrochemistry, geology and hydrology to understand the groundwater contamination lucidly and recommend proper remedial actions. Some case studies carried out by us are given below

Investigation of source, origin of groundwater pollutants and their dynamics at Indian Rare Earths Ltd., Kerala [23]

Indian Rare Earths Ltd. is located in Udyogamandal, Aluwa, Kerala in India and has been carrying out chemical processing of Monazite ore for the last 50 years. At present, processing of earlier stocked thorium hydroxide concentrate retrieved from silos is being carried out to produce thorium oxide, nuclear grade ammonium di uranate and small quantity of nuclear grade thorium oxide. The treated effluents after monitoring are discharged into the Periyar River. This area is a highly industrialized area, comprising many pesticide, insecticide, fertilizer and chemical factories. It was found that groundwater within IRE premises was contaminated with acidity and other pollutants. In order to identify the source of contaminants and their concentrations chemical and environmental isotope analyses was carried out and to find out dynamics of pollutants injected radioactive tracer experiments were conducted. For single well technique [82]Br in the form of NH_4Br solution (450 µCi, $t_{1/2}$ = 36 hrs) was injected in the injection well and [82]Br activity loggings were carried out at different intervals of time using NaI scintillation detector coupled with rate meter. For multiple well technique, tritium in the form of tritiated water (1mCi, $t_{1/2}$ = 12.43 yrs) was injected in the injection well and groundwater samples were collected from the four monitoring wells located in the downstream and measured for tritium activity by liquid scintillation counting method.

Chemical data indicate that groundwater is highly acidic (pH: 3 – 7) and has high sulphate (10 to 1100 mg/L), Nitrate (5 to 450 mg/L), Phosphate (0.5 to 10 mg/L) and Fluoride (0.5 to 6 mg/L) concentrations. Groundwater contamination is found in the wells located southeastern side of IRE campus near the Periyar River. Environmental stable isotopic contents varies from $\delta^{18}O$: -3.5 to -1.9 ‰ and δ^2H: -10 to –20 ‰. Samples collected from southeastern side of the IRE campus show slightly enriched stable isotopic composition compared to the samples collected from southwestern side. Environmental isotopic data of the peizometer samples fall on evaporation line indicating that these waters were subjected to evaporation prior to infiltration. From single well method the filtration velocity was computed to be 1.3 cm/day. From tritium activity distribution in the monitoring wells, it is found that maximum tritium activity is found in well no-2 & 3, indicating groundwater flow direction is towards northeast (riverside). Linear velocity of groundwater is calculated and the velocities are found to be 1.33 cm/day. Schematic diagram of point dilution experiment, [82]Br activity loggings and tritium distribution in four monitoring wells is shown in Fig. 1. From these results it is evident that groundwater flows from southern side of IRE premises where FACT is situated. It appears that open drain seen in FACT may be responsible for the groundwater contamination.
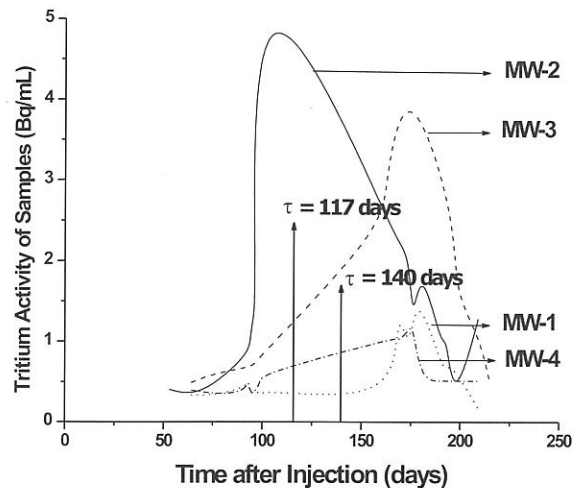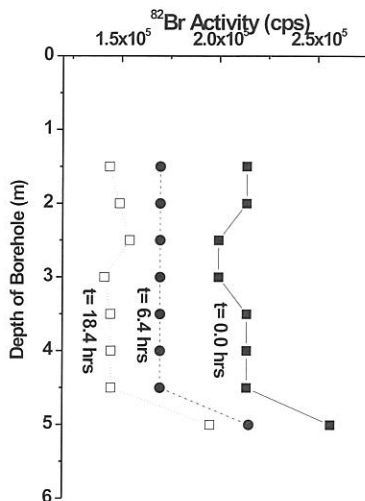
Fig. 1 ^{82}Br activity logging (left), tritium activity distribution (right)

Fluoride contamination in groundwater of Ilkal area, Bagalkot district, Karnataka [22]

In the recent years there has been an increasing concern over the growing health problems of the people living in and around Ilkal area of Bagalkot district. Cases of dental caries, tooth mottling and a few skeletal and dental fluorosis among the residents have been related to the amount of fluoride consumed mainly through drinking water, which is obtained mainly from groundwater. There are several small and large scale rock polishing industries are situated in the study area producing large amounts of liquid and solid wastes for the last two decades. These wastes are dumped into the nearby streams and contaminate surface water bodies. There are two possible sources of fluoride in groundwater, they are, leaching of fluoride-bearing minerals present in the subsurface and contribution from contaminated surface waters. Isotope and hydrochemical tools were employed to identify the source and origin of fluoride and to understand the processes/factors affecting the fluoride release into groundwater.

Chemical data indicates that the groundwater is fresh to saline (85 - 10680 μS/cm) with an increasing trend in electrical conductivity from recharge area to discharge area. Rain, river and lake water samples show fluoride levels < 0.5 mg/L where as samples from mine pit and infiltration gallery show fluoride concentrations from 1.8 - 3.7 mg/L. In the case of dug wells and bore wells fluoride ranges from 0.3 - 4.0 mg/L and 0.4 - 6.5 mg/L respectively. In general fluoride concentration, similar to electrical conductivity, also found to increase from the recharge area to discharge area. Low fluoride zones are seen in northern part near the confluence of streams. Groundwater samples show a positive correlation between fluoride and bicarbonate indicating that higher bicarbonate content promotes fluorite dissolution. From fluoride correlation with sodium and bicarbonate the favorable equilibration reaction can be shown as,
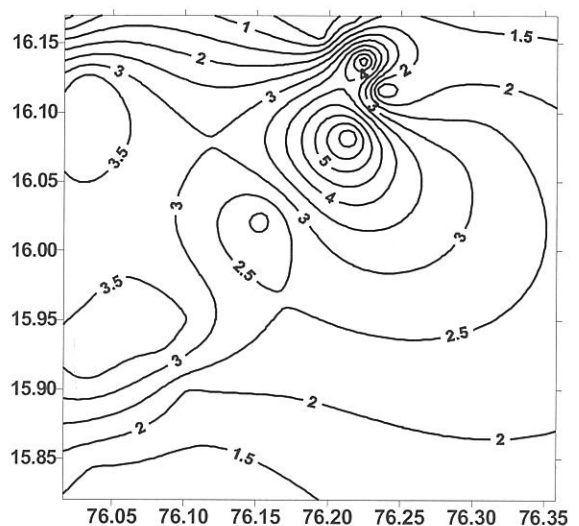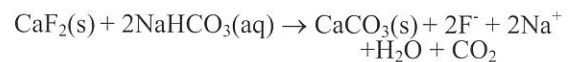

Fig. 2 Contour diagram of fluoride concentration (mg/L) in groundwater of Ilkal

$$CaF_2(s) + 2NaHCO_3(aq) \rightarrow CaCO_3(s) + 2F^- + 2Na^+ + H_2O + CO_2$$

$\delta^{18}O$ variation in groundwater of this area is shown in contour map (Fig. 2). $\delta^{18}O$ enrichment in groundwater is observed from recharge to discharge area and $\delta^{18}O$ variations very closely resemble fluoride variations. Isotope correlations (δ^2H versus $\delta^{18}O$) indicate gradual enrichment along the flow path; this shows the possibility of evaporated surface waters contributing to groundwater (Fig. 3). It is also noted that there is a positive correlation between $\delta^{18}O$ and fluoride concentrations in groundwater. Groundwater contaminated by fluoride is associated with enriched $\delta^{18}O$ composition this further implies contribution from contaminated surface water bodies. Tritium results identify two groups of groundwater, 1) groundwater with high tritium and fluoride < 1.8 mg/L, in which case fluoride is derived from geogenic sources and 2) groundwater with high tritium and high fluoride > 3 mg/L in which case in which
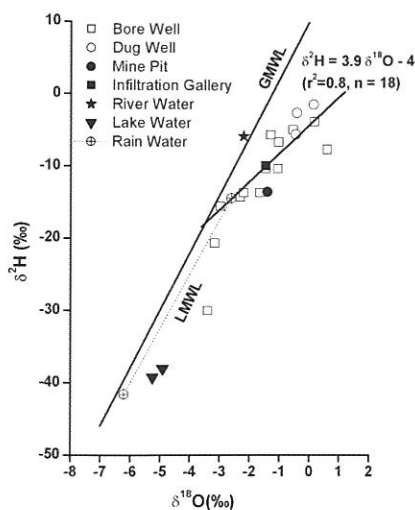
Fig. 3   Plot of $\delta^2 H$ versus $\delta^{18} O$

Fig. 4   Plot of $\delta^2 H$ versus $\delta^{18} O$

case fluoride is mostly from contribution of contaminated surface waters in addition to weathering.

Fluoride contamination of groundwater in Delhi, India [29]

Nearly 50% of the Delhi's total population is almost totally dependent on groundwater for its raw water requirement and groundwater is utilized for nearly 70% of the area under irrigation. The fluoride content in groundwater of this area varies widely from place to place ranging from 0.1-16.5 mg/L. 75% of the samples showed fluoride concentrations exceeding acceptable limit of 1.5 mg/L. A similar observation is noted in ^{18}O content. This wide isotopic variation is due to variation in intensity of rainfall, different contributions from evaporated irrigation water and surface runoff as well as intermixing of groundwater. It is interesting to note that high fluoride groundwater is associated with high ^{18}O content (isotopically enriched) water. This indicates that significant quantities of evaporated irrigation water and surface water from surrounding farmland infiltrate along with the fluoride salts from soils to the groundwater system. Highly skewed distribution of fluoride concentration in groundwater suggests contributions from both point as well as non point sources. Brick industries appear to be a major point source for fluoride in groundwater. The non point sources are irrigation water and surface runoff water dissolving fluoride from surrounding soils. ^{18}O content clearly characterize leaching of fluoride from soil and lateral mixing of groundwater. Hence to protect groundwater from further deterioration, it is desirable to put a control over the use of the deleterious man made inputs and indiscriminate disposal of industrial wastes.
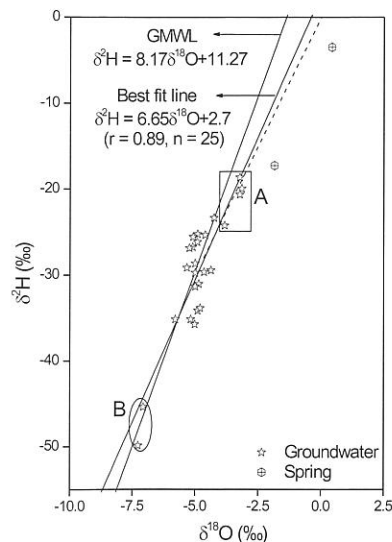
Assessment Brackishness in Groundwater of Kachch Region, Gujarat

Kachchh district, the largest district of India, is one of the most water scarce districts in India. In addition to severe water scarcity, groundwater quality is also found to be brackish in most of the occasions and unfit for drinking purposes. There were reports on the seawater intrusion into the coastal aquifers of Kachchh region and Saurashtra due to over exploitation of groundwater resources. A study employing both the hydrochemistry and isotope techniques was carried out to understand the geochemical processes affecting groundwater quality.

Chemical analysis indicates that groundwater is dominated by sodium and chloride ions and it is not of potable quality in most of the places. The Major and minor ion trends with respect to conservative ion chloride indicate mixing with saline waters and also leaching of salts from the formation. The plot of Na/Cl ratio versus chloride concentrations is used to distinguish between invading and retreating saline water bodies. All the sample data fall above the seawater value of 0.56, indicating flushing of saline water. Depth wise variation of $\delta^{18}O$ in groundwater show very narrow distribution with an average $\delta^{18}O$ value of -4.7 ± 0.7‰. Most of the groundwater samples fall on the global meteoric water line (GMWL) indicating precipitation as the source of recharge (Fig. 4). A few samples show (group A) enriched isotope composition and fall below GMWL indicating contribution from evaporated shallow groundwater or seawater mixing could be the reason for the enrichment in isotopic content. Two spring water collected during the Bhuj earth quake event showed enriched isotope values. Two groundwater samples (group B) show much depleted isotopic composition indicating recharge might
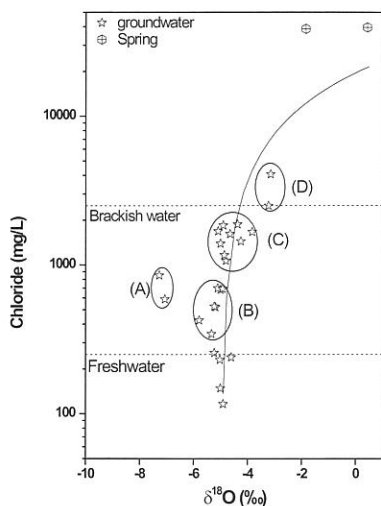
Fig. 5   Plot of Chloride versus $\delta^{18}O$

have taken place during cooler climate or flood events, which needs to be confirmed by groundwater dating.

To identify the sources of brackishness and salinity in groundwater of this region, $\delta^{18}O$ data was plotted against corresponding Cl^- values. A theoretical line indicating conservative mixing of seawater and freshwater (SW-FW) was constructed to assess the deviations. Seawater as saline end member and low EC water as freshwater end member were used for constructing this line. Groundwater samples fall in four different groups as shown in Fig. 5. Group-A samples show depleted isotopic content and slightly brackish in quality. Samples falling in group-B are mostly from upper parts of Cretaceous formation, these samples are brackish in quality. This brackishness in group-A & B can be attributed to acquisition of salts from the formation. Samples belonging to group-C are mostly from deeper Tertiary formations. These samples are brackish to saline in quality and the data fall on mixing line. The salinity in these samples could be due to seawater mixing (intrusion or flushing) or dissolution of marine sediments. It is observed from the δ^2H, $\delta^{18}O$ correlations (Fig. 5) that these samples fall on GMWL, therefore dissolution of marine sediments is the governing mechanism for the observed salinity in these waters. A few samples of this group show enriched isotopic composition and are saline; this is due to mixing between groundwater and evaporated saline water from the shallow zone. Group-D sample are mostly from Quaternary formation and fall below the mixing line. These samples are saline and evaporated. Seawater mixing and evaporation are the processes governing salinity in these waters. Spring water samples fall above the mixing line. The source of salinity in these waters could be possibly due to evaporated seawater which has acquired salts from the formation due to water rock-interaction.

Conclusions

The increasing dependence on groundwater to meet the ever-increasing requirements of a growing population has resulted in the indiscriminate exploitation of this precious resource in many areas of the country, causing several undesirable environmental impacts and is now threatening its long-term sustainability. Problems related to the quality of groundwater, either geogenic or caused by anthropogenic activities also pose constraints in its use for various purposes. Management of groundwater resources is a challenging task due to the considerable variations in its availability and utilization. Isotopes are very promising tools that can be applied in many aspects of groundwater either it is recharge processes or contamination source identification or interconnection between aquifers or dating of groundwater. Many of the environmental isotopes (e.g. ^2H, ^{18}O, ^{13}C, ^{15}N, ^{35}S etc.) are useful in finding out source of groundwater recharge, interconnections between aquifers, surface water groundwater interactions on the other hand radioactive isotopes (e.g., ^{14}C, ^{222}Rn, ^{36}Cl, ^{81}Kr, ^{85}Kr, ^{39}Ar, ^3H, ^3He etc.) can be used to determine groundwater 'ages' or 'travel times', to determine not only sources of contaminants, but also contaminant input histories, transport rates and degradation rates. Injected isotopes are very handy for localized studies to find out the groundwater flow and velocity, recharge contribution and migration of contaminants in saturated and unsaturated zones.

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Isotope Studies on Coastal Aquifer Salinity

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Abstract

Isotopes have been playing an ever increasing role in studies on coastal environment in India. These primarily deal with sea water intrusion, either active or in paleotimes. Environmental isotopes have shown that where there is active sea water intrusion into the coastal aquifer north of the city of Chennai, groundwater salinity in Tiruvanmiyur aquifer, Orissa and West Bengal is largely attributable to Flandrian transgression of the sea during the Holocene (~8000 BP) and also an earlier transgression in the late Pleistocene (~24,000 BP). Isotopes also helped in identifying a potential fresh water aquifer sandwiched between the two saline water bodies. Isotope tracers have been extensively used to investigate many such problems.

Introduction

Isotope Hydrology is a modern tool in hydrological investigations. Isotope techniques are today well established and their utility has been well demonstrated over the last five decades by the efforts of the International Atomic Energy Agency and countries like India. Some Indian examples include studies on Paleo-transgressions of the sea and modern sea water intrusion in the East Coast, Arsenic and Fluoride pollution in groundwaters of West Bengal and Karnataka, river – groundwater interconnection, groundwater recharge processes in Western Rajasthan, studies on some geothermal waters in India, dams and reservoirs leakage, seepage problems and sedimentation studies. Inspite of the well proven achievements in isotope hydrology in India and elsewhere, the methodology needs still to be integrated with other techniques. The reasons are probably that the techniques are more basic science oriented and are equipment – intensive needing elaborate laboratory support.

Isotope techniques in hydrology are largely based on the tracer concept. The general objective is to directly trace the movement of water molecules in any part of the hydrological cycle and derive information on the transport processes and how such processes are affected by other factors. The tracer concept is not entirely new in hydrology. For nearly a century, earth scientists have been using salt tracer like NaCl and later organic dyes for short range tracing of groundwater. Use of environmental stable isotope compositions of natural waters and their variations during condensation, evaporation and exchange processes; use of natural levels of radioactive tritium (^3H) in waters; use of isotopes of carbon (radioactive carbon – 14 and stable carbon – 13), sulphur (sulphur – 34), Boron (^{11}B), Chlorine (^{37}Cl) and nitrogen (^{15}N) in dissolved solids and use of injected radioactive tracers have revolutionised the science of tracer hydrology [1]. A host of other environmental isotopes like radioactive chlorine – 36 in dissolved chlorides and isotopes of dissolved noble gases like argon and krypton are being investigated for their use in hydrological investigations. Today isotope hydrology has come to be recognised as a science in its own right.

In the early sixties, isotope hydrology studies were mainly related to the use of injected radioactive tracers for stream flow measurements, sediment transport studies in ports and harbours and measurement of groundwater velocities. By the seventies, most isotope hydrology investigations were based on the isotopes level naturally present in waters. Currently, well-established applications of isotope hydrology are broadly in the following fields:

- Estimation of rainfall recharge through the unsaturated zone.
- Identification of sources of groundwater recharge and the recharge processes.
- Assessing residence time and residence time distribution in a groundwater system.
- Age dating of groundwater.
- Investigation of groundwater salinisation processes (leaching of salts, evaporative recharge, sea water intrusion).
- Pollutants source, origin and transport in surface water and groundwater.
- Confirming surface water - groundwater and aquifer – aquifer interconnections and quantifying mass transfer.
- Stream flow measurement.
- Seepage in dams and canals.
- Sediment transport studies in port and harbours.
- Sedimentation rates in lakes and reservoirs.

Most of these applications have specific relevance to water scarce areas such as the coastal, arid and semi–arid zones. For best results isotope data are interpreted along with geological, hydrogeological, geophysical, geochemical and paleoclimatological data.

Coastal Aquifer Salinity

Coastal regions are more thickly populated than any other geographical locations for a variety of reasons: land fertility, fishing and maritime trades. The population in the coastal regions is expected to continue to rise. With the advent of sea level rise due to global warming, increasingly greater attention is being paid to coastal environment. Seawater intrusion into coastal aquifer is an area of large interest and this has been extensively studied using natural

isotope tracers at several places including the East Coast of India [2].

Analysis of environmental isotopes present in groundwater and their interpretation along with geochemical and hydrological data gives valuable information such as the existence and location of natural recharge to the aquifer (s), source of salinity, origin of groundwater and residence time or "age" of the water. Coastal aquifer salinity is influenced by the marine environment and the degree of influence is dependent on local geohydrology, level of exploitation, climate changes in the geological and deposition history of coastal sediments.

Case Studies in Coastal Areas

Tiruvanmiyur Aquifer, South of Chennai City

Tiruvanmiyur aquifer is located south of Chennai City along the coast of Bay of Bengal, in Quaternary alluvium underlain by Tertiary and Archaean complex. Owing to the population growth and increased urbanisation and industrialisation, the demand for water supply to Chennai City is ever increasing and this aquifer is indiscriminately exploited by large scale pumping resulting in uncontrolled seawater intrusion. There is a need for detailed investigation on this aquifer for planning of sustainable development and optimal management strategies.

Environmental isotopes ^2H, ^{18}O, ^3H and ^{14}C have been used along with geohydrology and hydrochemistry to assess the hydrodynamics of the aquifer, the quality of groundwater, hydrochemical facies and their evolution, source of groundwater salinity, possibility of sea water intrusion and source of groundwater recharge. Results of our investigation show that:

- Groundwater quality is good in Quaternary and Pliocene aquifers. Groundwater quality is brackish in weathered basement aquifer except at Mettukuppam (saline).
- The source of groundwater salinity at Mettukuppam is due to entrapped seawater & and dissolution of aquifer material. The saline water is about 7000 years old.
- Brackish quality of groundwater in weathered basement zone is due to the leaching of salts from the formation and this water is about 11, 600 years old.
- High fluoride and phosphate in these groundwaters are derived from geogenic sources and the high nitrate content can be attributed to human activities.
- Chances of hydraulic connection between aquifers are remote except at Mettukuppam & Ekkattur.
- Groundwaters of Quaternary and Pliocene aquifers are modern.
- The main source of recharge to this aquifer is precipitation. The principal recharge zone to this aquifer outcrops in the western part of the study area.
- At present there is no indication of modern seawater intrusion into Tiruvanmiyur aquifer [2].

Coastal Midnapore Area, West Bengal

The environmental isotopes ^2H, ^{18}O, ^{34}S, ^3H and ^{14}C have been employed along with hydrogeology, and hydrochemistry to identify the source of salinity, estimate the residence time of saline groundwaters, to investigate the source and origin of fresh groundwater recharge and fresh water – saline water interaction in coastal Midnapore, West Bengal, India

Our results show that:

- The groundwater salinity is primarily due to the Flandrian transgression during the Holocene followed by entrapment of seawater.
- The residence time of these saline waters is about 4000 to 8000 years, which is supported by ^{14}C data.
- The contribution of saline water from coastal estuary and fresh water recharge from north western Midnapore outcrops and their interaction with ancient sea water have produced a complex distribution of saline, brackish, and fresh waters in the shallow (35 – 100m), middle (105 – 155m), and deep (165 – 200m) aquifers [3].

Mahanadi Delta, Orissa

As part of the drinking water supply project, thousands of hand pumps were installed a few years back in the coastal areas of Orissa State. Many of them became quickly unacceptable due to deterioration of water quality. An isotope geochemical investigation was launched which aimed at determining the origin of salinity causing degradation of water quality and at evaluating groundwater recharge conditions.

In this coastal alluvium, multiaquifer system, fresh, brackish and saline groundwaters occur in a rather complicated fashion. The conditions change from phreatic to confined flowing type with increasing depth. ^2H, ^{18}O, ^{34}S, ^3H and ^{14}C as well as major, minor and trace chemical species in surface waters and groundwaters from the area were measured. The findings show that:

- Shallow groundwaters (<50m) are generally fresh and relatively modern. The replenishment occurs through floodplains and outcrops of basement rocks.
- The groundwater salinity in the intermediate zone (50 – 100m) is largely due to Flandrian transgression in the Holocene.
- Fresh modern and deep groundwater (depth >100m) forms a well-developed aquifer, which receives recharge through basement rocks. This could form the main source of groundwater for exploitation.
- The deep saline groundwaters are marine waters entrapped, during Late Pleistocene interglacial stage about 24,000 BP
- Very deep aquifer(depth>300m) occurring in weathered basement and basement rocks may also form a potential aquifer for exploitation. The water here is very good.

- The groundwaters in the aquifers, especially the saline groundwaters are stratified. It appears that the yellow – brown unfossiliferrous sediment horizon sandwiched between dark grey fossiliferrous sediment horizons probably marks the climatic changes, the intertropical aridity during the late Pleistocene [4].

Minjur Aquifer, Chennai

Increasing salinisation of groundwater has been reported in the Minjur aquifer, north of city of Chennai on the East Coast of India. The aquifer is exploited for city water supply. The obvious mechanism of salinisation is intrusion of seawater due to pumping activity. The simple explanation was suspect because of the presence of pockets of hypersaline groundwater close to the coast. The possibility of entrapped marine connate water could not be ruled out.

A large number of water samples were collected from piezometers, tubewells and surface sources and analysed for environmental isotopic (^{2}H, ^{18}O, ^{34}S and ^{3}H) as well as major and minor ionic species. The isotopic composition and hydrochemistry of the hypersaline groundwaters indicate that they are not marine connate waters, but probably owe their salinity to highly saline salt–pan water infiltrating to the deeper zone [5].

Conclusions

Isotope techniques are unique and powerful tools for hydrological investigations and have greater relevance in coastal and water scarce areas such as arid and semi-arid zones in planning for further exploitation of groundwater. The International Atomic Energy Agency and a few other countries including India have an impressive record of achievements in the development and application of isotope methods in many field applications, particularly in the developing countries of Asia, Africa, Middle East and South America. In spite of such achievements, the techniques continue to be practiced more by research physicists and chemists and less by field hydrologists due to inadequate knowledge and training. This situation must be rectified in the larger interests of water resources development and management. There is a need for better dissemination of information among field hydrologists, better access to isotope analysis laboratories and introduction of isotope hydrology in the university curricula.

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Application of Radon in Hydrological Studies

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Introduction

Radon is a colourless, odourless radioactive noble gas (half-life, $T_{1/2}$ = 3.82 days) occurring naturally in the environment. It is produced by the radioactive decay of radium present in the soil and rock. Depending on where the radium sits, a variable fraction of the radon produced can escape to the pore space and thus be available for transport. Even high radium concentrations in the bulk of heavy mineral grains will thus not lead to high radon concentrations in the pore space. On the other hand, low to moderate radium concentrations will lead to high radon concentrations if the radium is present adsorbed on the surface of the grains. The fraction of the radon produced which is available for transport (emanation coefficient) varies between less than 10 % for sandy or gravelly soils to over 70% for some other soils. The transfer of radon from the rock surrounding the groundwater is mostly by diffusion through crystalline lattices and through the cracks and the crystal boundaries. It is expected that radon in groundwater would be correlated with the local uranium/radium abundance in rock and soil. Theoretically, radon can be transported by diffusion at distance of 5-10 m within its life, but in practice, transport distances up to several 100 m are also possible.

Measurement of Radon in Water

Groundwater (Bubbling Method)

Radon can be measured by bubbling air in a closed circuit through the sample (40 to 250 ml) and then determining the radon concentration in the gas phase (Fig. 1). This method is used for the discrete measurement of radon in groundwater. The air volume should pass at least 4 times through the bubbler to get equilibrium between water and air. Temperature dependence of the solubility has to be taken into account, but with the closed circuit method it's influence is considerably reduced. There are different detectors commercially available for the measurement of radon in air. The cheapest ones are passive sensors like track-etch films or electret disks. They have the disadvantage that the result is not immediately available. Among the electronic detectors a system with a Lucas cell coupled to a photomultiplier is still the most sensitive, at a low price. It takes 3 hours until all alpha emitting radon daughter products are built up, but the instrument response function is well known so the measurement can be immediately started after bubbling. However it also takes some time for the radon daughters to decay after purging with fresh air. Both, buildup and decay of the total alpha activity can be approximated by a single exponential with a $T_{1/2}$ of 40 min. There are other electronic monitors based either on a semiconductor detector or an ionization chamber. Those with a semiconductor detector need a large sample volume and an accumulation of
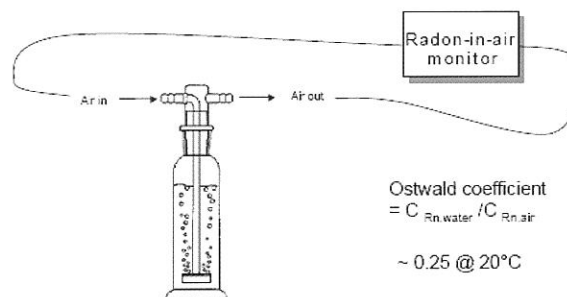

Fig. 1   Bubbling method

the daughter products on the detector by a high voltage to get reasonable sensitivities. They have the advantage that the detector not only counts but has a sufficiently good energy resolution to allow for discrimination between different radon daughters. Counting only pulses in the ^{218}Po ($T_{1/2}$ = 3.1 min.) energy window avoids the problem of the slow response due to the buildup and decay of the radon daughters farther down in the decay chain. Typically out gassing 40 ml samples allow for a detection limit of about 1 Bq/l, 250 ml for around 0.5 Bq/l.

For large series in the lab the best measurement method is liquid scintillation counting (LSC), For LSC only 10 ml water samples are needed. One can either use a scintillator miscible with water or an extractive scintillator, an organic solvent containing the scintillator that does not mix with water. The advantage of a scintillator miscible with water is that one does not have to wait for the buildup of the radon daughters if the sample has been taken at least 3 hours ago, but detection limit is not better than 1 Bq/l (1 h counting time). Well below that, around 0.2 Bq/l, if really needed, it can be achieved by using extractive scintillators and alpha/beta separation and 2 h counting time.

Surface Water (Spraying Method)

Since the ^{222}Rn concentrations in surface waters are very low and due to its short half life, large volumes of water are required for the measurement of ^{222}Rn and hence in-situ monitoring is highly essential. A radon monitoring system developed by Burnett et al., (2001) using a radon-in-air monitor is shown in Fig. 2.

For the in-situ measurement of ^{222}Rn, surface water is continuously pumped from 1 m above the sea bed using a peristaltic pump and sprayed as a jet into an air-water exchanger. The radon thus stripped out from the water is circulated through a closed air-loop via a desiccant tube into a ^{222}Rn counting system. The equilibrium of ^{222}Rn between the liquid and gaseous phase is established within 30 min.
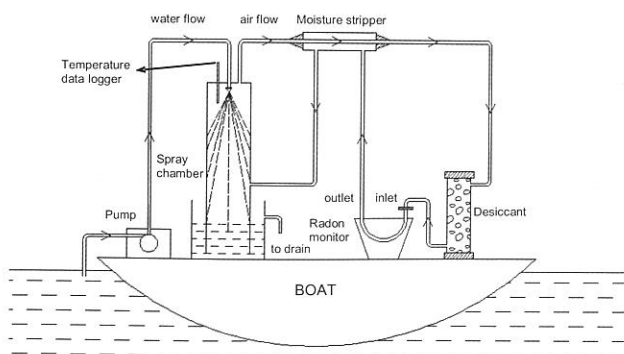
Fig. 2 Schematic sketch of surface water ^{222}Rn monitoring system

Applications of Radon in Hydrological Studies

Estimation of Submarine Groundwater Discharge in Coastal Regions

Coastal areas are natural sites for groundwater discharge from aquifers as they are lying in the down gradient of the continental regions. Submarine groundwater discharge (SGD) can occur whenever hydraulic head is above sea level and an aquifer extends beyond the shoreline to crop out at the sea floor, or is hydraulically coupled with marine waters through permeable bottom sediments. SGD is defined as the flow of freshwater into the ocean from a coastal aquifer, or recirculated seawater through the underlying sediments in the seabed, or a combination of both. The mechanisms and the driving forces for the above two components are quite different: the terrestrial component depends on the hydraulic gradient of the groundwater, the extent and hydraulic conductivity of the aquifer, recharge rates and many other factors, while the marine component is controlled by the local oceanographic conditions such as wave set up, tidally-driven oscillations, current induced pressure gradients and convective circulation of water (thermal or density driven) from the bottom sediments (Taniguchi et al., 2002).

Groundwater discharge, either in the form of concentrated or diffused discharge, could be as large as half the total annual river flow (Moore, 1996). In areas where seepage occurs through permeable sediments, seepage may be very low and undetectable, yet a small upward leakage over a wide area could make an important contribution to the coastal ocean. Alternatively, in karstic aquifers where the flow is intensely channelized and focused, SGD occurs in the form of springs in the beaches and submerged springs in the coastal waters. The detection of SGD may provide as a new source of potable water for various purposes. SGD is also responsible for limiting salt-water intrusion into the coastal aquifer.

SGD also acts as pathways of large concentrations of nutrients, metals, organic compounds and inorganic carbon from the continents to the ocean. Even the SGD from the pristine aquifers can be a source of nitrates and other nutrients to the oceans, as their concentrations are much higher than seawater. Another use of better estimates of SGD would be in the calculation of nonpoint sources of nutrients or chemical contaminants in the coastal waters receiving SGD.

Natural radon is an excellent tracer for identifying areas of significant groundwater discharge because of its conservative nature, short half-life, high abundance in groundwater compared to surface water and easiness in measurement. ^{222}Rn activities in groundwater are often 2-4 orders of magnitude higher than those of seawater, hence, even after large dilutions in the coastal waters; they can be detected at very low concentrations. ^{222}Rn is particularly useful in locating submarine freshwater springs. One of the limitations of ^{222}Rn is that, being an inert gas, it evades into the atmosphere. From the continuous monitoring of ^{222}Rn in coastal waters, it is possible to quantify SGD (Burnett and Dulaiova, 2003).

Since ^{222}Rn is highly enriched in groundwater, SGD can be calculated using ^{222}Rn mass balance in the coastal water. The general steady state ^{222}Rn mass balance equation for the coastal water can be written as:

$$\Psi_{SGD} \times C_{GW}^{^{222}Rn} \times A_{Bott} + F_{Diff}^{^{222}Rn} = I_{CW}^{^{222}Rn} \times \lambda_{^{222}Rn} + C_{Ex}^{^{222}Rn} \times V_B \times \lambda_{Mix} + F_{Atm}^{^{222}Rn} \quad (1)$$

where Ψ_{SGD} is the seepage rate of submarine groundwater (m/d); $C_{GW}^{^{222}Rn}$ is the average ^{222}Rn activity in groundwater (Bq/m^3); A_{Bott} is the bottom area of the bay (m^2); $F_{Diff}^{^{222}Rn}$ is the diffusive flux of ^{222}Rn from the bottom sediments (Bq/day); $I_{CW}^{^{222}Rn}$ is the ^{222}Rn inventory in the coastal water (Bq); $\lambda_{^{222}Rn}$ is the radioactive decay constant of ^{222}Rn (day^{-1}); $C_{EX}^{^{222}Rn}$ is difference in ^{222}Rn activity between coastal water and the open sea (Bq/m^3); V_B is the volume of the coastal water (m^3); λ_{Mix} is the exchange rate between coastal water and open sea (d^{-1}); $F_{Atm}^{^{222}Rn}$ is the atmospheric ^{222}Rn evasion flux across air-sea interface.

^{222}Rn inventory in the coastal water is given by:

$$I_{CW}^{^{222}Rn} = C_{EX}^{^{222}Rn} \times A_{Bott} \times y \quad (2)$$

$C_{EX}^{^{222}Rn}$ is the unsupported or excess ^{222}Rn calculated as the difference between the measured ^{222}Rn activity in the coastal water and the ^{222}Rn derived from the in-situ decay of ^{226}Ra.

Burnett and Dulaiova (2003) continuously measured ^{222}Rn in the sea over a period of time and any change in the calculated time dependent ^{222}Rn inventories were converted into fluxes.

Therefore, for the transient condition, equation (1) can be modified as:

$$\Psi_{SGD} \times C_{GW}^{^{222}Rn} \times A_{Bott} = \frac{\Delta I_{CW}^{^{222}Rn}}{\Delta t} \pm F \quad (3)$$
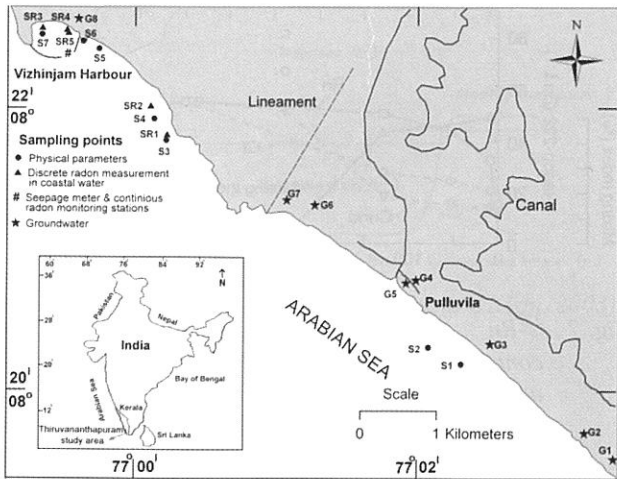
Fig. 3   Location map of SGD study site

where ΔI_{CW}^{222Rn} is the change in ^{222}Rn inventories between two consecutive measurements, Δt is the time interval (generally 2 hour) and F is the correction for diffusion, atmospheric evasion and open ocean exchange fluxes.

Using equation (3), SGD rates can be calculated.

A Case Study

SGD is suspected from a hydrogeological and groundwater modeling study conducted in the shallow aquifers of Vizhinjam, Kerala, India (Fig. 3) (Suresh Babu et al., 2009). Two field monitoring surveys were carried out; the first survey was designed to understand the spatial variability of SGD (Noble et al., 2009), while the objective of second survey was to study the temporal variability of SGD and the effect of tidal conditions (Noble et al., 2010). Groundwater discharge fluxes were also measured in the seabed using a Lee type seepage meter.

Temporal variation of ^{222}Rn activities in the Vizhinjam coast during the 7 days of continuous monitoring is shown in Fig. 4. Comparatively higher ^{222}Rn activities varying from 15 ± 7 Bq/m^3 during high tides to 50 ± 8 Bq/m^3 during low tides are observed in this area indicating significant groundwater inputs. With some exceptions, most of the peaks in radon activity occur at the lowest tides. The observed cyclicity in the ^{222}Rn activities may be because of the lower hydrostatic pressure at low tides causing increased
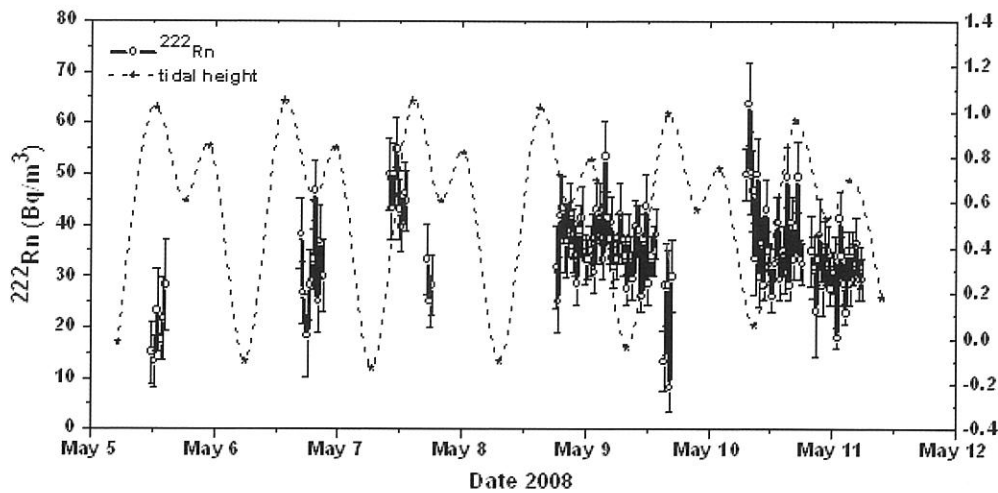

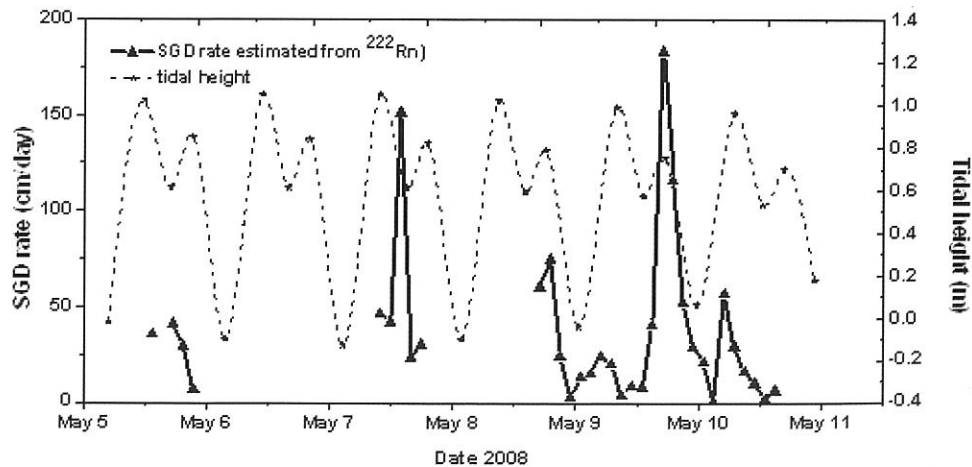Fig. 4   Temporal variation of ^{222}Rn activities in the Vizhinjam coastal waters, (measurement interval – 30 minutes)

Fig. 5   Temporal variation of SGD rates estimated from the ^{222}Rn mass balance model.
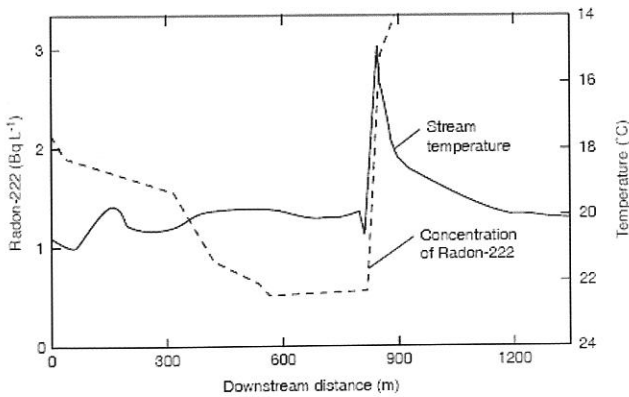
Fig. 6 Stream temperatures and ^{222}Rn concentrations in a 1.2 km reach of a creek in Tennessee, USA (Lee and Hollyday, 1991).

seepage and movement of recirculated seawater through the shallow aquifer and sediments in response to tidal pumping.

The average ^{222}Rn activity in the coastal water is about 33.6.1± 8.7 Bq/m^3 where as in groundwater it is about 4150±3270 Bq/m^3. The temporal variation in SGD rates were estimated using equation (3) and shown in Fig. 5. It is seen that SGD rates are highly variable and is ranging from 3 to 75 cm/day from high tide to low tide, respectively. The estimated average SGD rate is found to be about 37 cm/day. The SGD rates estimated from the ^{222}Rn activities were further confirmed by the same dynamic seepage pattern observed by the seepage meter.

Estimation of Groundwater Contribution to Streams

Radon can be used as a tracer to determine the location and magnitude of groundwater discharge to streams due to the fact that groundwater is having higher radon concentration compared to surface flows. This technique is highly convenient especially in the karst aquifer system, fractured bedrock mountain regions and discharge basin, were traditional methods are not much applicable.

A two component mixing model using ^{222}Rn concentration can be used to quantify the contribution of groundwater to the stream. It is given by:

$$Q_s \times A_s + Q_{gw} \times A_{gw} = Q_m \times A_m \qquad (4)$$
$$Q_s + Q_{gw} = Q_m \qquad (5)$$

Where, Q_s is the rate of stream-flow, A_s is the concentration of ^{222}Rn in the stream at an upstream point, Q_{gw} is the rate of groundwater discharge, A_{gw} is the concentration of ^{222}Rn in groundwater, Q_m is the rate of mixed stream-flow and groundwater flow downstream and A_m is the concentration of ^{222}Rn in mixed water downstream.

A Case Study

Lee and Hollyday (1991) measured ^{222}Rn activities in a stretch of 1.2 km of a creek in Tennessee, USA and found that ^{222}Rn activities had increased from 0.52 to 3.3 Bq/l (Fig. 6). Groundwater from a nearby spring had a concentration of 8.1 Bq/l. Using the increase in ^{222}Rn
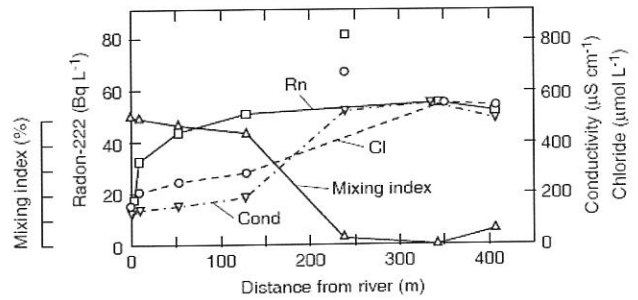

Fig. 7 ^{222}Rn concentration, conductivity, chloride concentration, and the contribution of river to the aquifer as a function of distance from the river (Bertin and Bourg, 1994)
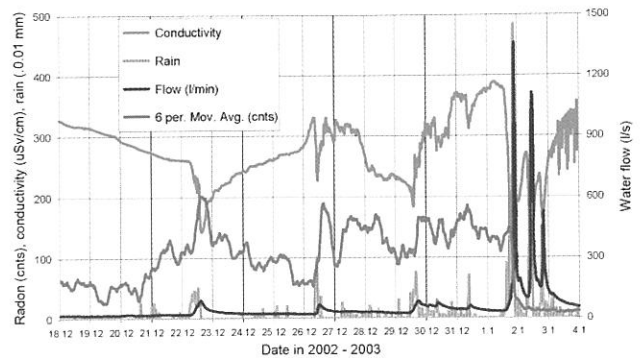

Fig. 8 River water radon and conductivity versus time measured at the outflow of the micro basin area, Luxembourg (Kies et al., 2005)

concentration down-gradient in the sampled reach of the stream (at 880 m downstream), it was determined that 36 per cent of the creek water at that point was contributed by the groundwater through a pool.

Estimation of River Water Infiltration into an Aquifer

Since ^{222}Rn activities in surface water bodies such as rivers etc. are lower than that of groundwater, they can be used as a natural tracer for river water infiltration into an aquifer.

A Case Study

Bertin and Bourg (1994) studied the infiltration of Lot River to an aquifer, in the southwest of France. In the aquifer investigated, the infiltrating river water mixes with groundwater from the neighboring hills. Radon is used to trace the infiltration of river water into the aquifer (Fig. 7). At distances greater than 150 m from the river, ^{222}Rn has a constant value of 55 Bq/l. Mixing ratios were calculated using a ^{222}Rn mass balance model and is shown in Fig. 7.

Hydrograph Separation

Natural isotopic tracers such as ^{18}O, ^{2}H and particularly ^{222}Rn help to distinguish the components dominating the discharge of a river, particularly of 'pre-event waters', 'event waters' and 'post-event waters'. Even with moderate
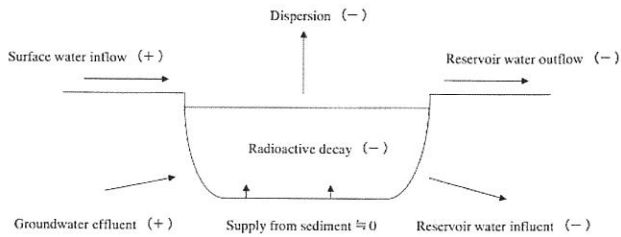
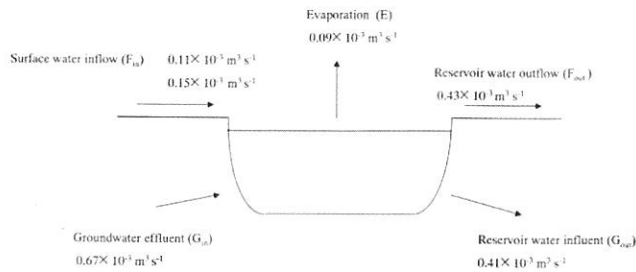Fig. 9 ^{222}Rn balance in a pond (Hamada and Kishi, 2003)

Fig. 10 Summary of water balance in the F pond, Japan ((Hamada and Kishi, 2003)

concentrations in groundwater, radon can be a very sensitive indicator of groundwater input into rivers. Differences in radon content of subsurface waters arise from differences in radon emanation by porous media (bedrock or soil) and from the differences in the degree of subsurface degassing. Hence, simple three-end-member mixing models can be used as a useful framework for river flow separation, the three different waters being superficial water (vadose zone water), soil ground water and bedrock water.

Kies et al., (2005) measured radon together with temperature and electrical conductivity of a stream in a micro basin of Attert River in Luxembourg and separated the contribution of superficial water and groundwater to the river flow. Radon concentrations in the springs (groundwater) range between 10 and 25 Bq/l, which is about a factor 10 higher than river radon concentrations. Superficial water has markedly different radon content from groundwater, the latter differing in radon concentrations if originating from saturated soils or from fractures in the bedrock (Fig. 8). For the period under investigation, every major rain event induced a rapid decrease of the electric conductivity and an increase in radon concentrations because water normally retained in underground fracture zones close to the main flow channels is pushed into the flow channels. ^{222}Rn data is used in a simple mass-balance equation in conjunction with the river discharge data to quantify groundwater inputs to the river.

Water Balance of Lakes

Measurement of ^{222}Rn in a lake and its inflow/outflow components can be used to understand the hydrodynamics and to evaluate its water balance.

By solving radon and water balance equations of a small scale pond, Hamada and Kishi (2003) estimated the
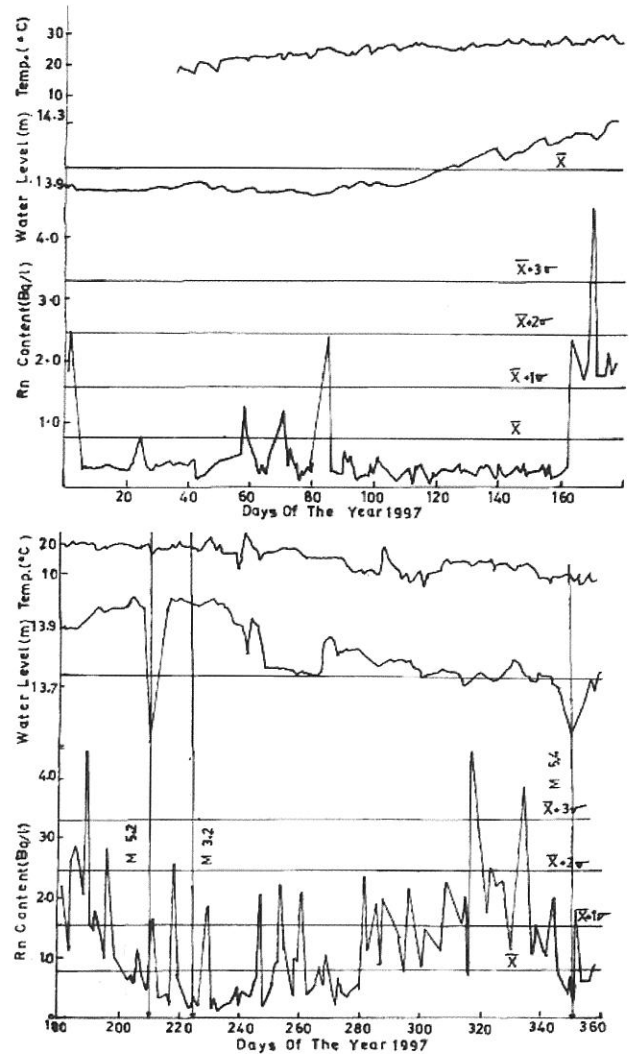

Fig. 11 Daily variation in groundwater radon, water level and water temperature (Singh et al., 1999)

groundwater inflows and subsurface reservoir water outflows (Figs. 9 & 10).

Wetland Studies

Radon can be used to identify groundwater inflow points and mixing processes of a wetland. Radon differs from other environmental tracers in that it allows the groundwater inflow rate to be determined without the need to accurately quantify other components of the water budget.

Cook et al., (2008) measured the radon activity within a shallow wetland (Area= 5000 m^2) in southern Australia and the mean groundwater inflow rate has been estimated from the mean radon activity using a mass balance approach. The estimated groundwater inflow rates varied between 12 and 18 m^3/day.

Delineation of Fractures/Lineaments

Granitic terrains are generally having low primary porosity. The top weathered zones are capable of storing significant quantities of water while the deeper fractures are

not. However, deeper fractures act as good conduits for drawing water from distant weathered zones to which they may be connected. Measurement of ^{222}Rn in soil gas or in groundwater helps to delineate fracture zones for deep groundwater exploration.

For fault plane delineation, ^{222}Rn measurements are generally carried out along traverse lines perpendicular to the direction of the faults. Radon levels at the fault are higher than those away from the faults. Hence faults can be demarcated. Reddy et al (2006) used this technique to demarcate groundwater potential zones (fractures) in a granitic terrain near Hyderabad, Andhra Pradesh.

Earthquake Studies

Continuous measurements of ^{222}Rn in the soil-gas or groundwater can be used as a precursory for earthquakes. Earthquakes are often proceeded by small earth movements and changes in stress that can release trapped gases like radon, helium etc. An increase in monitored radon may presage an earthquake.

Singh et al. (1999) monitored the daily variations of groundwater level, temperature and radon in wells during 1997 and noticed that correlation exist between the significant increases in radon concentration and water level with the seismic events which occurred in Northern India during this period.

Conclusions

It is found that the measurement of dissolved ^{222}Rn in water can be a powerful tool for understanding the various hydrological processes and quantifying the surface water groundwater interactions. Some of the application of ^{222}Rn tracing includes (a) estimation of submarine groundwater discharges in coastal regions (b) estimation of groundwater contributions to streams (c) estimation of river infiltration to aquifers (d) hydrograph separation of rivers (e) computation of water balance components of lakes (f) identifying groundwater inflow points and mixing processes of wetlands (g) delineation of fractures/lineaments for groundwater exploration (h) prediction of earth quakes etc.

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