

Isotope Applications for Coastal Groundwater

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INTRODUCTION

Isotopes are the atoms of an element having same atomic number (Z) but different atomic weight (A). In other words, the atoms of an element having different number of neutrons (N) but same number of protons or electrons are called isotopes. For example, hydrogen has three isotopes having the same atomic number of 1 but different atomic masses or weights of 1, 2 and 3 respectively i.e.,

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

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

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

Similarly oxygen has eleven isotopes, ${}^{12}O$, ${}^{13}O$, ${}^{14}O$.. ., ${}^{22}O$, but except ${}^{16}O$, ${}^{17}O$, and ${}^{18}O$ all other isotopes are radioactive and their existence in nature is very small (half life vary from 150 seconds to few femto seconds - of the order 10-15 seconds) therefore, we normally talk about only three isotopes of oxygen i.e., ${}^{16}O$, ${}^{17}O$, and ${}^{18}O$. The carbon also has three isotopes ${}^{12}C$, ${}^{13}C$ and ${}^{14}C$. Isotopologues are molecules that differ only in their isotopic composition eg., $H_2{}^{18}O$ and $H_2{}^{16}O$ are oxygen related isotopologues of water. Naturally occurring elements in waters contain about 1700 stable and unstable (radioactive) isotopes, commonly referred to as environmental isotopes.

APPLICATIONS IN HYDROLOGY AND WATER RESOURCES

Isotopes have wide applications in hydrological investigations and provide vital informations for the better management of water resources. Isotopes also helps in understanding various hydrological processes. Isotope techniques using "environmental isotopes" are commonly used in the developed countries by meteorologists, hydrologists, and hydrogeologists in the study of water. The use of these techniques is also increasing in our country, but still it has not gained momentum due to inadequate laboratory facility and analytical know how. Study of the isotopes of oxygen and hydrogen in water, or of elements contained in dissolved salts which have the same behaviour as water, enable exact recording of phenomena affecting the occurrence and movement of water in all its forms.

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

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

SURFACE WATER

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

GROUND WATER

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

METEOROLOGICAL

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

FORMAT OF PRESENTING THE STABLE ISOTOPE DATA

Measurements of stable isotopes are done in terms of abundance ratios i.e. atomic mass of heavy atom to the atomic mass of light atom of isotopologues. However, instead of the absolute abundance ratio only the relative difference with respect to a reference is determined. The difference is designated by a Greek letter δ , expressed in per mill (‰) and is defined as follows:

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

Where R's are the ratios of the 18O/ 16O (for δ18O) and D/H isotopes (for δD) in case of water.

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

The reference standards normally considered are SMOW (Standard Mean Ocean Water)/ VSMOW (Vienna Standard Mean Ocean Water), SLAP (Standard Light Antarctic Precipitation) and GISP (Greenland Ice Sheet Precipitation). Over the period of use, the old standards have been consumed. Therefore, other reference standards have been developed in due course of time. These are and now VSMOW-2, SLAP-2 and GISP-2 (supplied by International Atomic Energy Agency, Vienna, Austria), NBS-1 and NBS-1A (supplied National Bureau of Standard, now National Institute of Standards and Technology, USA).

The values of measured abundance ratios (2H/1H and 18O/16O) in SMOW and VSMOW are given in Table 1.

Table 1. Measured abundance ratios in international standard reference material

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

δ¹⁸O SLAP = -55.50‰ VSMOW; δDSLAP = -428.0‰ VSMOW

δ¹⁸O GISP = -24.76‰ VSMOW; δDGISP = -189.5‰ VSMOW

To understand how δ values are calculated from ratios, one can do the following simple exercise. If the 18O/16O and 2H/1H ratios in a sample are given to be 0.0020104 and 0.00015735 respectively, its oxygen and hydrogen isotopic compositions (δ18O = 2.59‰ and δD = 10.27‰) with respect to VSMOW can be easily calculated using Equation (1) and the isotopic ratios for VSMOW, as given in Table 1

ISOTOPE FRACTIONATION

In general, as a result of mass difference, as compared to heavier isotopologues (eg., H218O or and HD16O), lighter isotopologues (H216O) evaporate faster (during evaporation of water), condense slower (during condensation of vapour to water), reacts faster in a chemical reaction and show higher diffusivity in molecular kinetics. Due to this differential characteristic

of isotopologues, during any phase change process (evaporation of surface water or condensation of vapour (eg., rainout process)) the heavier isotopologues (e.g. H₂¹⁸O or and HD¹⁶O) gets enriched in the condensate phase (such as the liquid water for the case of phase transition from liquid water to its vapour) compared to and lighter (H₂¹⁶O) isotopologues.

For, example, during rainout, the precipitating water gets enriched in heavier isotopes (while the remaining vapor gets progressively depleted with heavier isotopes). This differential partitioning of isotopes between the two phases is known as the isotope fractionation.

The fractionation continues till the process of phase change continues and accordingly, the enrichment of denser phase by heavier isotopologues. On reaching the thermodynamic equilibrium fractionation process ceases and the system is said to be at equilibrium fractionation. Non-equilibrium fraction is also termed as kinetic fractionation.

As a result of fractionation both $\delta^{18}\text{O}$ (for H¹⁸O and H¹⁶O) and δD (for HDO and HHO) changes proportionately (approximately) in a given thermodynamic condition. Therefore, a plot between $\delta^{18}\text{O}$ and δD usually leads to a linear graph.

GLOBAL METEORIC WATER LINE (GMWL)

Craig (1961a) for the first time showed that $\delta^{18}\text{O}$ and δD in fresh surface waters (representing precipitation on global scale) correlate linearly by equation;

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

The regression line between $\delta^{18}\text{O}$ and δD is referred to as Global Meteoric Water Line (GMWL).

Rozanski et al.(1993) compiled the isotope data of precipitation from 219 stations of the IAEA/WMO operated Global Network for Isotopes in Precipitation (GNIP). This refined relationship between ¹⁸O and D in global precipitation (Figure 1) is given by:

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

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

Dansgaard defined a parameter (*d*-excess), defined as;

$$d\text{-excess} = \delta\text{D} - 8 \times \delta^{18}\text{O} (\text{‰}) \quad (4)$$

Dansgaard (1964) reviewed the global distribution pattern of stable isotope content in precipitation and related the spatial distribution of heavy isotope content to environmental parameters, such as altitude, latitude, amount of precipitation, air temperature and degree of continentality. All of these factors reflect the degree of washout from the air mass, and to some extent, the water vapor history from the source to the site of precipitation.

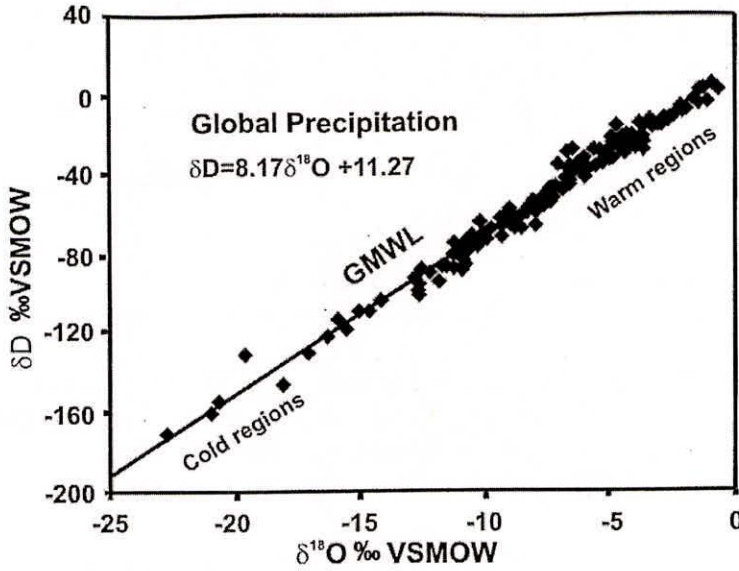


Fig. 1 The linear regression line between $\delta^{18}\text{O}$ & δD of global precipitation sample monitored at 219 stations of IAEA/WMO global network (after Rozanski et al. 1993).

Latitudinal Effect: Water vapours or precipitation depletes in heavier isotopes with the increase in latitude. This is interpreted Yurtsver and Gat (1981) as due to decrease in temperature with increase in latitude from equator to pole. The tropical and subtropical oceans constitute the major source of water vapour. With the poleward transport, isotopic composition of water vapour depletes as a consequence of rainout process and decreasing water vapour content in the atmosphere and lower temperatures of condensation.

This is supported by the observed relation between annual average and monthly average temperatures as given below:

$$\delta^{18}\text{O} = 0.695 T_{\text{annual}} - 13.6 \text{ (VSMOW)} \quad (5)$$

$$\delta\text{D} = 5.6 T_{\text{annual}} - 100 \text{ (VSMOW)} \quad (6)$$

$$\delta^{18}\text{O} = (0.338 \pm 0.028) T_{\text{monthly}} - 11.99 \text{ (VSMOW)} \quad (7)$$

The variations in $\delta^{18}\text{O}$ are on the order of -0.6% per degree of latitude for continental stations of the North America, Europe and about -2% per degree latitude for the colder Antarctica stations. One may expect very low gradients in the low latitudes where over 60% of atmospheric water vapours originate.

Amount effect: The amount "effect" is clearly observed in areas where temperature does not show a clear seasonality during the year. On tropical islands, where the observed seasonal variation of temperature cannot account for isotopic variations, the observed variability is controlled by the amount of precipitation, indicating the degree of rain-out from the original air mass.

The continentality effects: Represent a progressive removal of moisture from the original air mass moving from the ocean towards the continent. The preferential removal of heavy isotopes

during the first stages of precipitation leads to a progressive depletion of precipitation moving inland. Therefore, coastal precipitations are isotopically enriched while the colder inner continental regions receive isotopically depleted precipitation with strong seasonal differences. On average, there is about -2‰ depletion in $\delta^{18}\text{O}$ per 1000km from seacoast.

Altitude effects: Precipitation progressively depletes in δ -values with increase in altitude, mainly, due to two reasons:

1. Decrease in temperature with increase in altitude
2. Rainout process increases with increase in altitude due to orographic effect.

In general, $\delta^{18}\text{O}$ varies between -0.15 to 0.5 ‰ per 100m rise in altitude and δD depletes between -1 to -4 ‰ per 100m increase in altitude. This effect is used in the identification of location/altitude and source of springs. Source of precipitation can also be identified by knowing the altitude and continental effects.

Seasonal Effects: The seasonal effect is seen in temperate and high-latitude stations (depleted values in winter and enriched in summer). This reflects the variations in temperature of condensation, to some extent differences in air mass trajectories and sources of vapour (local and regional water vapour), and change in amount of precipitation. Increase in temperature increases the effect of evaporation in the falling raindrops and enriches the precipitation in D and ^{18}O . This effect is least when precipitation occurs in large amount or with high intensity.

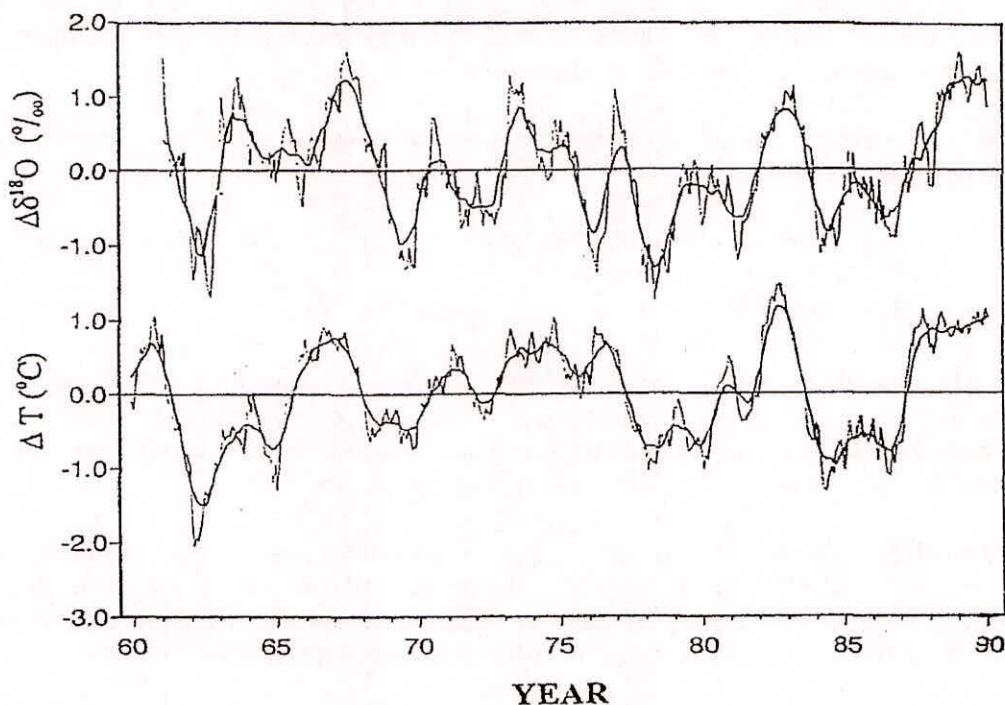


Fig. 2 Smoothed temporal variation of $\delta^{18}\text{O}$ data of monthly precipitation and temperature at the station Vienna, Austria.

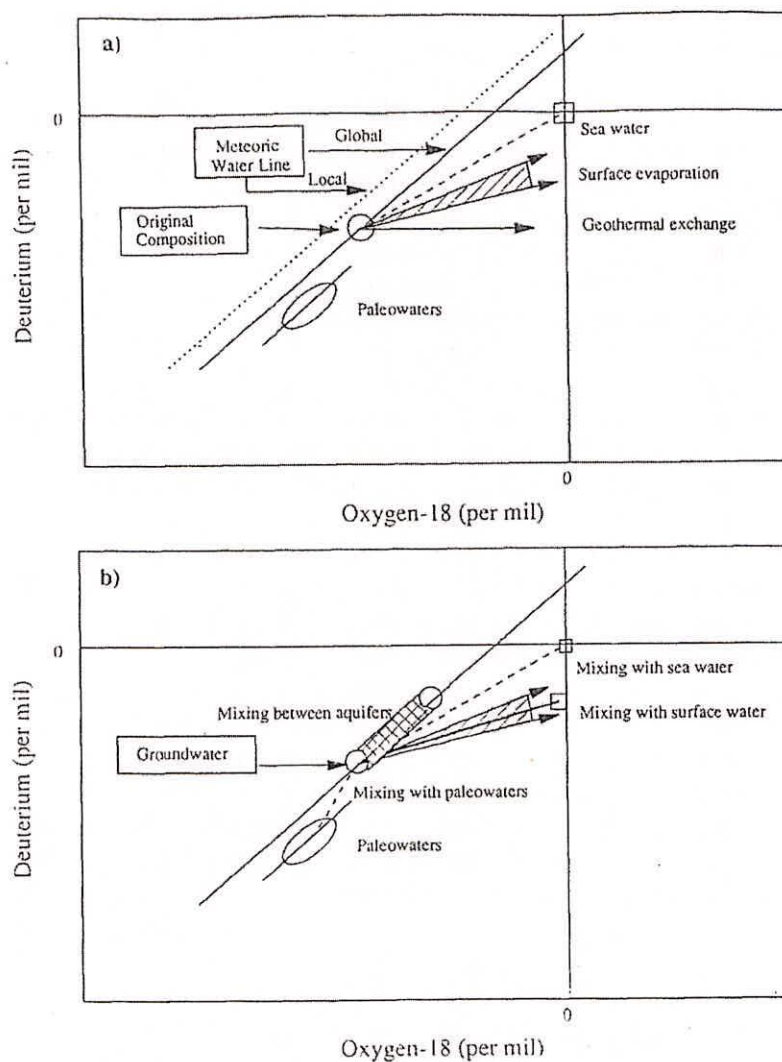


Fig. 3 Characteristic $\delta^{18}\text{O} - \delta\text{D}$ relations for different processes a) Related to processes b) Related to hydrological applications

In general, isotopic composition of rainfall results from superimposition of all the above effects. The observed temporal variations of $\delta^{18}\text{O}$ values of precipitation and corresponding surface air temperatures for the station in Vienna, Austria, is shown in Fig. 2 as an example. The possible $\delta^{18}\text{O} - \delta\text{D}$ linear relations expected for various processes of practical interest in hydrology are shown in Fig. 3.

APPLICATIONS

Due to their conservative nature stable isotopes are used in tracing hydrological system. In groundwater system these are used to finger-print history of the processes involved in formation and circulation of .Stable isotopes are commonly employed in studying hydraulic

relations between groundwater and surface waters, for estimating mixing proportions of different sources, evaporation loss, component flows (component-tracing); and or between different aquifer units within a given groundwater system.

Recharge zones: The variations induced in stable isotopic composition of precipitation due to altitude effect provide label for the recharge to the groundwaters at different elevations, thus enabling assessment to be made of the replenishment areas.

Base flow study: The isotopic composition of river waters draining higher altitude precipitation often have significantly different isotopic content than the adjacent aquifer, providing the basis for study of hydraulic relations between river-aquifer system, or assessing the recharge to the adjacent aquifer through such line-sources.

Lake water Groundwater Interaction: The enrichment of the ^{18}O and 2H isotopic contents of surface water bodies in lakes or reservoirs due to direct surface evaporation provides a natural label for them, so that hydraulic inter-relations between such water bodies with groundwater can be investigated.

Rainfall-runoff processes: The component flows involved in the runoff process such as baseflow and overland flow within a given basin can effectively be quantified through simple mass balance considerations of the stable isotopic composition of the river water prior to and during the individual rainfall events. The results of hydrograph separation based on such observations in different sizes of surface catchment basins indicate that the contribution of the groundwater to the total hydrograph of the basin can be substantially higher than that envisaged through classical concepts so far applied (Hino & Hasebe, 1986; Hooper & Shoemaker, 1986). These studies are also important contributions to delineation of the fluxes and their pathways in the basin, which is most relevant to understanding of the processes involved in stream acidification and pollution due to diffused sources.

CASE STUDIES

Groundwater mixing

Unlike most geochemical tracers, 2H and ^{18}O are inert and conservative in mixing relationships. Therefore, stable isotopes can serve to quantify groundwater mixing at the local to watershed scale where mixing between groundwaters of different recharge origins, from different aquifers, and flow systems, can take place. Mixing between two distinct groundwaters (end-members) is quantified by simple linear algebra using δD or $\delta^{18}\text{O}$. Figure 4, for example, shows the fraction (X) of groundwater A in a mixture of two groundwaters A (δA) and B (δB). in a mixture of A and B. The proportion of mixing for a given sample in a two-component mixing system will then relate directly to its position on the mixing line, according to:

$$\delta_{\text{sample}} = X \cdot \delta\text{A} + (1-X) \cdot \delta\text{B} \quad (8)$$

An example of two-component groundwater mixing is given in Fig. 5. Two mineral springs, the Hamei Zohar and Hamei Yesha springs, are seen to lie on a fresh water-Dead Sea mixing line, indicating these springs are formed by intermixing of Dead Sea water (brine)

brought to the surface with the emerging local fresh water recharged at the Judean Mountains (Gat et al., 1969).

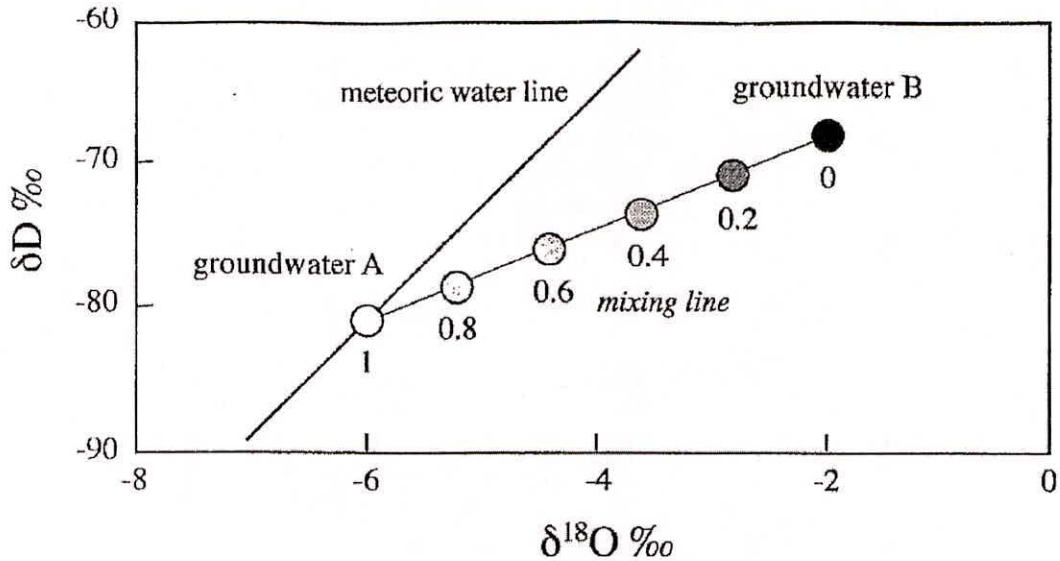


Fig. 4 Fractional mixing of two groundwaters quantified on the basis of their isotopic composition, and it is shown as the fraction of groundwater A

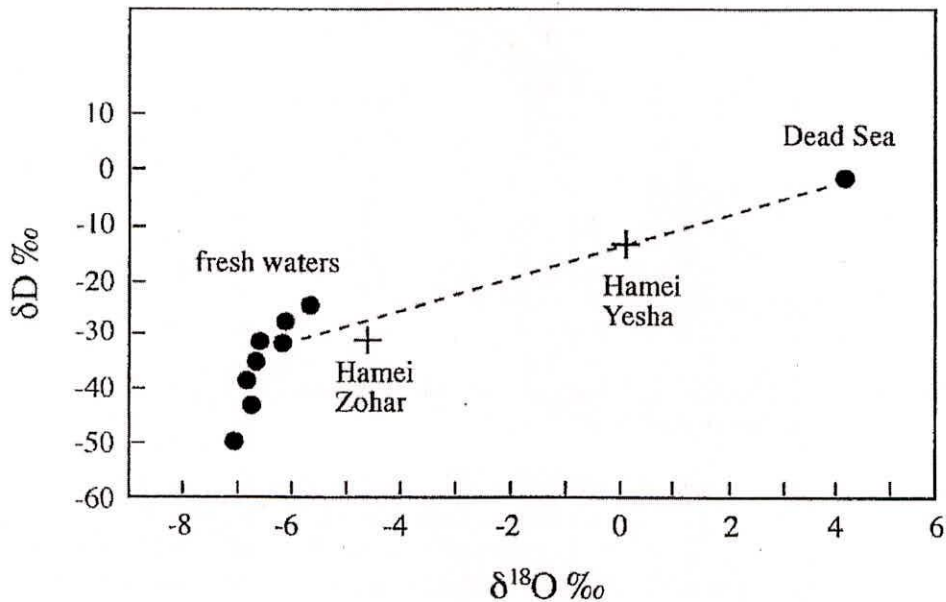


Fig. 5 Isotopic composition of two mineral springs on the Dead Sea shores, indicating these springs are formed by intermixing of Dead Sea brine with local fresh water (Gat et al., 1969)

In Fig. 6, three end-members of recharge to the groundwater system are isotopically distinct: (1) lake water; (2) rain water; and (3) sea water. The isotopic composition of samples from the lake and also from many rivers, hot springs, wells, and springs, are seen to lie on a straight line distinctly different from the local meteoric water line. A regression carried out on

these samples results in a line with a slope of about 5.0, which is characteristic of open water bodies subjected to evaporation. A point for the rain water, which is a potential source of recharge to the groundwater system, is marked in Fig. 6 on the extension of the line at the intersection with the local meteoric water line. The values of -36‰ δD and -6.0‰ $\delta^{18}\text{O}$ are considered to be representative of the local rain water. The alignment of data points on this lake water-rain water mixing line (LRL) is explained by simple mixing, in varying proportions, of the isotopically depleted local rain water and enriched lake water which leaks from Lake Ikeda. On the other hand, data points for some rivers, wells, and hot springs do not align on the LRL (Fig. 6). They exhibit a positive δD shift of 2-3 ‰ and scatter between the LRL and the sea water-rain water mixing line (SRL). This is indicative of contribution of sea water to these waters.

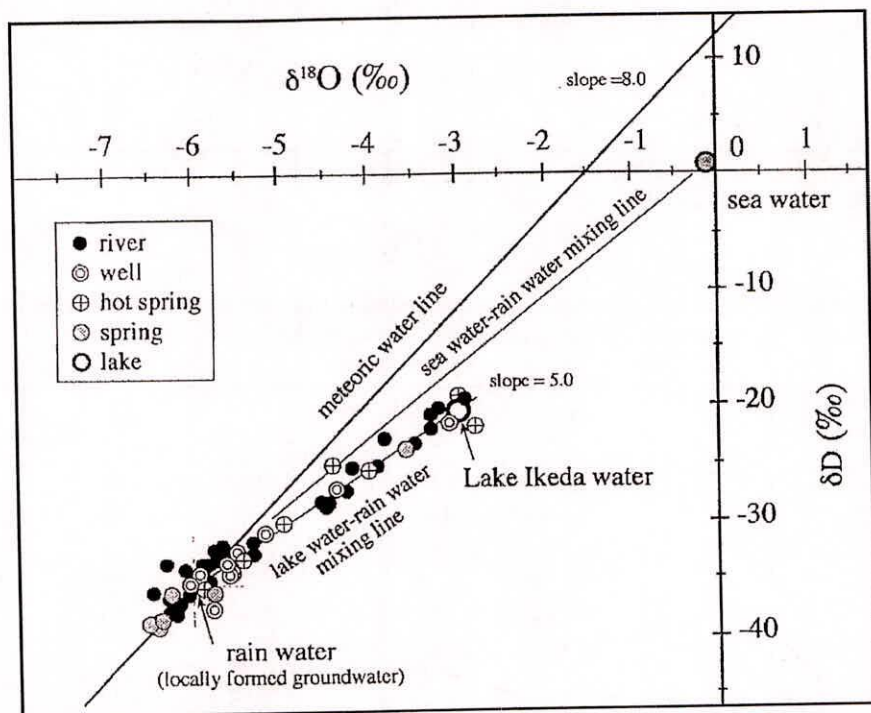


Fig. 6 Plot of $\delta^{18}\text{O}$ and δD for waters around Lake Ikeda, a seepage caldera lake in the southernmost part of Japan (Kawanabe et al., 1999)

A three-component mixing system was identified by Kawanabe et al.(1999) for groundwaters from the seepage caldera lake district in the southernmost part of Japan. The evaporative enrichment in δD and $\delta^{18}\text{O}$ of the Lake Ikeda water, that is the departure of the isotopic composition from the meteoric water line, permits the recognition of the contribution of lake water to the shallow aquifer and to the discharge of springs and rivers located down-gradient the lake. In their study, mixing between lake water, rain water, and sea water was quantified based on the δD vs. $\delta^{18}\text{O}$ diagram (Fig. 6) and $\delta^{18}\text{O}$ vs. Cl^- diagram (Fig. 7).

Fig 7 illustrates the variation of $\delta^{18}\text{O}$ against the Cl^- concentration of samples which plot on the LRL or those of partial sea water origin (Fig. 6). From Fig. 7, it is obvious that the Cl^- concentration is a result of mixing of lake water (Lake Ikeda; -3.0‰ $\delta^{18}\text{O}$; $0.3 \text{ mmol l}^{-1} \text{ Cl}^-$),

rain water (-6.0‰ $\delta^{18}\text{O}$; 0.2 mmol l⁻¹ Cl⁻), and sea water (-0.1‰ $\delta^{18}\text{O}$; 544 mmol l⁻¹ Cl⁻). Based on Fig. 7, mixing proportion of each end-member is calculated by applying a three-component mixing model, which is fundamentally in the same manner as determined for a two-component mixing system.

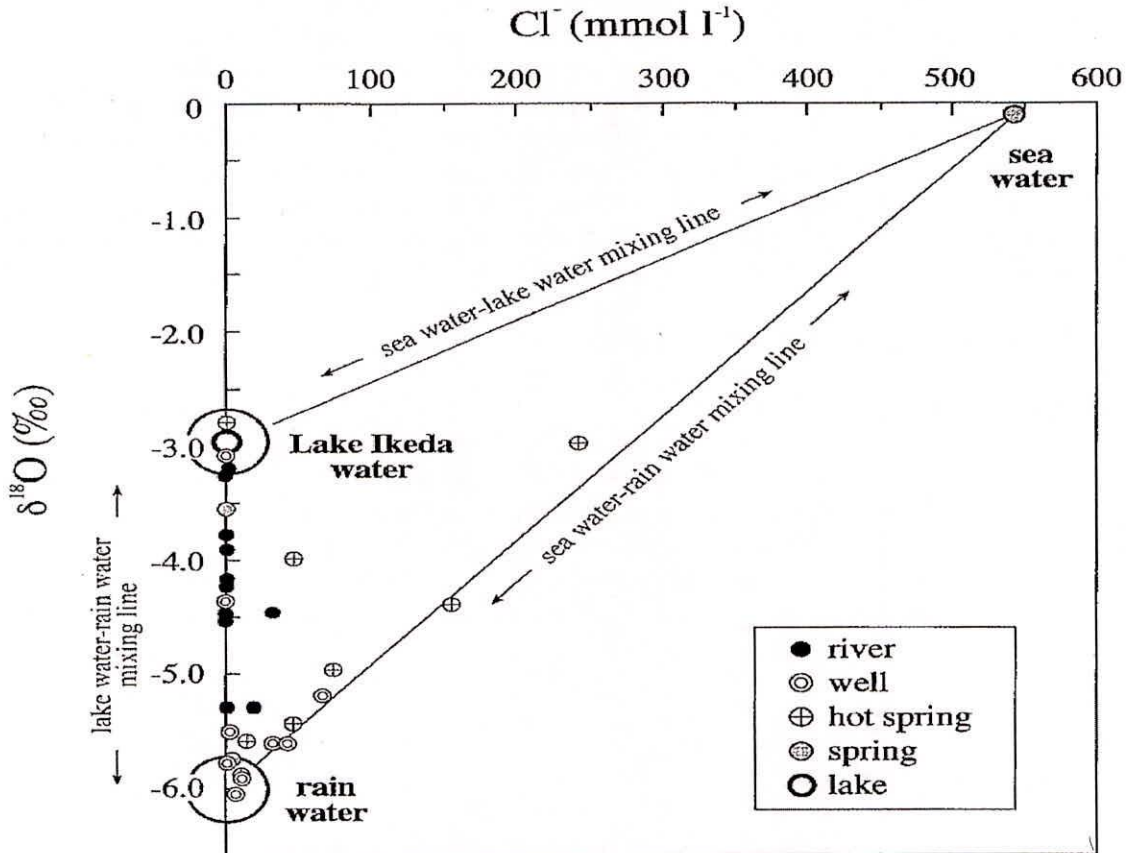


Fig. 7 Plot of $\delta^{18}\text{O}$ and Cl^- concentration for waters in the Lake Ikeda district (Kawanabe et al., 1999)

Paleo-hydrological Studies

Stable isotopes are effectively used for paleo-hydrological studies through delineating the origin of groundwaters replenished mainly during the earlier pluvial periods, which is relevant particularly to the occurrence of groundwater in arid regions. Such paleowaters are often characterized by the relatively low deuterium excess values in addition to their identification through age-dating. A typical example of the use of stable isotopes of ^{18}O and ^2H in studying groundwater genesis is shown in Fig. 8 (Gat, 1983), where groundwaters replenished through recent precipitation and paleowaters in different aquifer systems are identified. The major regional aquifer systems in arid regions of the Middle East and northern Africa, such as Dammam Formation and Umm Er Rhaduma aquifers in the Saudi Arabian peninsula; Nubian Sandstone and Continental Intercalaire aquifer systems in north Africa; have been found to contain paleowaters mainly replenished during earlier pluvial periods.

GROUNDWATER DATING

Groundwater age is defined as the amount of time that has elapsed since a particular water molecule of interest was recharged into the subsurface environment system until this molecule reaches a specific location in the system where it is either sampled physically or studied theoretically for age-dating. On the other hand, groundwater residence time is the time it takes for particles of water to travel from the recharge area to the discharge area of the aquifer (Modica et al., 1998). It is the time interval between infiltrating into, and exfiltrating out of, the subsurface media. It is impossible to find a single molecule of groundwater that has no age. As soon as a water molecule enters the subsurface, it becomes groundwater and it has an age. In groundwater sample there are billions of water molecules. In a well-mixed groundwater system, any one of these molecules may have its own distinct particular age. Mean age or the age measured by isotopic and chemical methods, is practically the average of ages of all molecules in the sample.

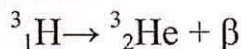
DATING YOUNG GROUNDWATERS

Tritium technique

^3H isotope of hydrogen has one proton and 2 neutrons. It is radioactive with a half-life of 12.32 years. Tritium dating is used to trace water sources and to determine age of recent waters (age of ~50a). Tritium dating provides means to estimate the time since recharge to groundwater system occurred and susceptibility of the groundwater system to contamination. Sources directly fed by rainwater contain the same tritium levels as rainwater. Tritium values are reported in tritium units (TU).

$$1\text{TU} = \frac{1(^3\text{H})}{10^{18}(^1\text{H})} = 7.1\text{dpm/l} \quad \dots \quad (9)$$

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



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

$$C = C_0 \ln e^{-\lambda t} \quad \text{or} \quad ^3\text{H} = ^3\text{H}_0 C_0 \ln e^{-\lambda t} \quad (10)$$

To date a groundwater sample, we have to measure the concentration of tritium in the sample (^3H), we also have to find out what was the concentration of tritium in the recharge water, or the initial value ($^3\text{H}_0$). λ is the decay constant of tritium of 0.056 year⁻¹.

Tritium dating of groundwater samples involves following procedure.

- **Sample Collection:** For tritium analysis the quantity of natural water sample is collected as per the expected level of tritium.

- **Pretreatment** (Primary Distillation): The samples are distilled to remove all dissolved salts that interfere with electrolysis process.
- **Sample enrichment:** After primary distillation, samples are enriched by electrolytic reduction to concentrate the tritium.
- **Distillation of enriched samples** (Secondary Distillation): Secondary distillation is carried out to remove excess Na applied during sample enrichment.
- **Liquid Scintillation Counting**

Advantages and Disadvantages

Advantages

1. Tritium is a well-established method.
2. Laboratory facilities are worldwide and the cost of analysis is relatively small.
3. Tritium can still be regarded as a supplementary dating method.
4. It is the only tracer that is part of the water molecule.

Disadvantages

1. The method is approaching its expiry date.
2. Due to the strong latitudinal variation, it would be difficult to precisely determine the initial value even if the bomb-peak tritium effects on the environment are completely reduced.

³H/ ³He Technique

The technique involves ³H together with its daughter ³He. The concentration of ³He in the groundwater samples is reported as ‰ ³He:

$$\text{‰ } ^3\text{He} = (R_{\text{sample}} - R_{\text{at}}) / R_{\text{at}} \times 100 \quad (11)$$

where R_{sample} is the ³He/⁴He ratio (units in cm³ STP/g H₂O) of the water sample, R_{at} is the ³He/⁴He ratio in the atmosphere, which is 1.384×10^{-6} .

The age equation is given by;

$$^3\text{H} = (^3\text{H} + ^3\text{H}_{\text{etri}}) \ln e^{-\lambda} \quad (12)$$

The term in the bracket is the initial ³He which is equal to un-decayed tritium (³H) plus the decayed tritium (³H_{etri}). It is clear from the equation that in order to measure the age of a groundwater sample, we simply need to measure its tritium and ³H_{etri} simultaneously.

Advantages and Disadvantages

Advantages

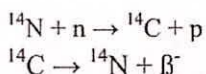
1. Provides high resolution age.
2. This method does not need the initial value, a parameter that is fundamental and problematic for many of the dating methods.

Disadvantages

1. Sampling and analysis are expensive and laboratory facilities are not available worldwide.
2. It is a difficult exercise to separate tritiogenic helium from the other heliums (atmospheric and insitu contaminated ^3He).

DATING OLD GROUNDWATERS (^{14}C dating)

^{14}C forms in the upper atmosphere and decays to ^{14}N with beta emission as;



The emitted maximum energy of beta is 156 keV and half-life of ^{14}C is 5730 ± 40 years. ^{14}C activity is given in percent Modern Carbon (pMC), where as $100 \text{ pMC} = 13.56 \text{ dpm/g}$ of carbon.

The age equation is given by;

$$a_{14\text{C}} = q a_0 14\text{C} e^{(-\lambda t)} \quad (13)$$

where, $a_{14\text{C}}$ is ^{14}C activity of sample; $a_0 14\text{C}$ is initial activity of sample and q (varies from 0.65 to 1.0) is the dilution in initial activity due to carbon contamination (calcite, dolomite, diffusion of carbon etc.).

Advantages and Disadvantages

Advantages

1. It is well-established method.
2. Sampling and analysis for this method are now routine and cheaper than the majority of the dating methods.
3. The deficiencies, the principles, and the positive points of the methods are all well known.

Disadvantages

1. It is an extremely difficult task to determine the correct initial value due to the various processes that modify ^{14}C signature of the percolating rainwater.
2. A large number of geochemical reactions modify the concentration of ^{14}C in the groundwater. It has been tried to alleviate this problem by taking into account a large number of processes, but an appreciable amount of uncertainty surrounds the validity of this approach and the results obtained.
3. Having pointed out the above two major obstacles, it is safe to argue that the ^{14}C method is often a semi quantitative technique.

APPLICATIONS OF GROUNDWATER AGE DATA

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

Replenishment of groundwater reservoirs

Groundwater age is, as yet, the only sound and concrete piece of scientific evidence to show that groundwater resources are recharged by modern precipitation, or else, the extracted groundwaters were accumulated in the aquifers by slow infiltration processes that happened a very long time ago. This application is more highlighted in the arid zones where due to the scarcity and periodicity of the rainfall, the question of recharge (if any) often remains open. An important fraction of young water within an extracted water sample is an indication of an actively renewable reservoir; the opposite, i.e., a considerable amount of old water in the sample, depicts a poorly recharging reservoir and/or significant internal mixing processes. Information about the age of groundwater is required if one is to confidently define the sustainability of groundwater resources of any particular well field. Estimates of renewable groundwater resources and an understanding of related hydrological processes are critically dependent upon determining the presence and age of modern groundwater.

Prevention of overexploitation and contamination of aquifers

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

Estimation of groundwater velocity

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

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

Identification of groundwater flow paths

Groundwater flow paths in both vertical and horizontal directions can be determined by having ages that increases along the inferred flow lines. Accurate information about the groundwater flow path is needed in many water resources projects such as in construction of dams (determining different routes that water stored in the dam lake / reservoir may escape), movement of plumes, mixing between different quality groundwaters, and study of surface water-groundwater interaction. Establishing flow directions in various parts of a deep, long regional aquifer is another example for use of groundwater age data.

Other applications include

- Confirming the parameters of groundwater flow and transport models
- Determination of mixing between various end members
- Evaluating the pollution of groundwater
- Estimating the travel time of groundwater plume to the points of interest
- Mapping of vulnerable shallow aquifers
- Assessment of radioactive waste disposal facilities
- Identification of recharge areas of few springs

GROUNDWATER SALINIZATION AND SEA-WATER INTRUSION

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

Conventionally, ionic ratios such as Na^+/Cl^- , Ca^{+2} / Mg^{+2} , So_4^{-2} / Cl^- etc. are used to study the source of salinity. However, after transport of the salts by percolating water to the water table and after primary mixing with saline waters, the chemistry of the water may undergo further secondary changes which may make it difficult to identify precisely the mechanism of salinization. The problem of identifying the mechanism of salinization becomes more acute in irrigated areas in arid zones. Leaching is usually local and the soluble salts may not be transported very far. This is partly due to the low rainfall and also the high evaporation rates which are characteristic of arid zones, tend to concentrate salts in the groundwater. Furthermore, surface drainage systems may be poorly developed, having no outlet to permanent stream. The isotopic approach is particularly useful in coastal areas where all salinity ultimately originates from marine environment so that little chemical distinction exists between salinity originating for example, due to slow process of dispersion and diffusion of saline mass or from sea spray or

from direct sea water encroachment from surface lagoons or connate sea water. The stable isotopes along with dating techniques of groundwater in the study of salinization mechanism have been extensively used abroad but comparatively less in India. In studies dealing with sea water intrusion, the significant difference between sea water and freshwater, particularly for stable isotopes of hydrogen and oxygen, provides a direct means of identifying and studying dynamics of sea water intrusion (pathways, mixing ratios). Furthermore, isotopic evolution during different groundwater salinization processes (i.e. mineral dissolution, leaching of salt formations, or mixing with saline formation waters) exhibit different characteristics, to enable process identification through observations to be made on stable isotope concentrations. Particularly, the use of environmental isotopes, D and ^{18}O , allow distinction of leaching from evaporation. Since leaching causes no isotopic change, whereas evaporation leads to isotopic enrichment. In addition, the stable isotopes of sulphur $^{-34}$ ($\delta^{34}\text{S}/ \delta^{32}\text{S}$) isotope provides very clear picture about the salinity of marine origin.

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

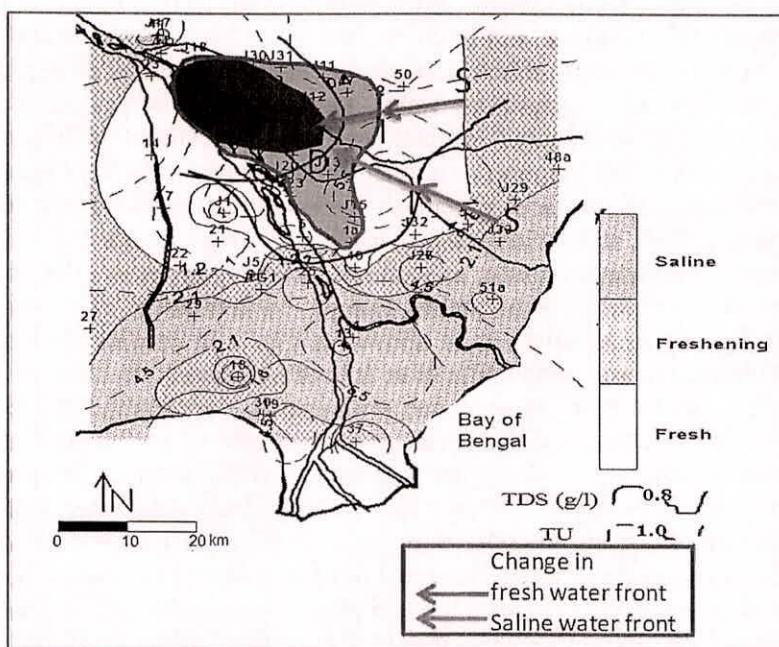
Freshwater derived from precipitation is always isotopically different (contains less species of heavier isotopes) than sea water due to isotopic fractionation processes occurring during evaporation and condensation. In addition, the evolution of stable isotope concentrations during different natural processes, and particularly the resulting relationships between ^{18}O and ^2H concentrations, provide an effective tool for many hydrological applications, such as assessment of the "genesis" (origin) of water, particularly in groundwater systems; for the processes involved in replenishment (process tracing), for estimating mixing proportions of different sources or component flows (component-tracing); and studying hydraulic relationships between groundwater and surface waters or between different aquifer units in a given groundwater system. Thus, stable isotopes provide an effective label for sea water and freshwater to enable tracing of sea water intrusion, as well as identifying processes that may be responsible for water salinization. Evolution of stable isotope concentration of water during different processes related to water salinization is shown in Fig. . In studies dealing with sea water intrusion and salinization process identification, it is often common to consider both isotopic and hydrochemical evolution. Such an approach will enable clear distinction to be made of the salinization process (or processes), for cases where freshwater salinity may be caused by direct sea water intrusion, leaching of salt formations, mineral dissolution, or salt accumulation due to Evaporation (as often encountered in irrigated areas). Typical relationships between salinity and stable isotope content for these processes are shown in Fig. 3. During the processes of leaching salt formations or mineral dissolution, the stable isotope content of the water is not affected while the salinity of water increases. This is a unique feature which will enable identification of such processes based on isotopic and chemical data. The stable isotopes ^{18}O and ^2H are the most conservative tracers during their transport in hydrological systems and their relationship with salinity changes is univocal.

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

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

The groundwater-seawater inter-connection in the Krishna river delta, India was studied by (Nachiappan et al., 2003). Groundwater samples were collected from depths: <30m, 30-60 m and >60 m over a period from 1999 to 2002. River Krishna, its distributaries, sea (Bay of Bengal) water and Prakasam Reservoir samples were also collected. Samples were analyzed for EC, 3H and stable isotopes. A few samples were also analyzed for 14C.

Analysis of these samples showed that the present day salinity in shallow, intermediate and deep aquifers extended over a distance up to 27 km, 32 km and 50 km from the present day seacoast respectively. Groundwater age increases towards the coast. The old groundwater is interpreted to be of paleo-marine origine. The fresh groundwater recharge taking place at Prakasam Barrage, along the canal tract (particularly in the area near Kaza in eastern delta) and along few paleochannels (on which Krishna canals that are laid) is mixing with old groundwater and thereby diluting the pre-existed salinity (Fig. 8). The mixing efficiency appeared decreasing at deeper depths. The results were corroborated with reference to the paleo-coast line, dates on fossil shells, peat/wood and calcrete materials, and chemical.



Allied Application: Submarine Groundwater Discharge (SGD)

Submarine groundwater discharge (SGD), which may be as much as 50% of the total terrestrial freshwater runoff, constitutes a substantial freshwater resource in coastal areas and can be a source of pollution for the marine environment. A combination of radioactive isotopes of radium and radon, and stable isotopes of oxygen, hydrogen and strontium, offer a nearly unique methodology for the assessment and quantification of SGD, which is difficult to achieve with non-isotopic methods. As India has large coast-line isotope research has wide potential for SGD application.

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About NIH and GWRDC



The **National Institute of Hydrology (NIH)** is the premier research Institute in the area of hydrology and water resources in India. The Institute has its headquarters at Roorkee (Uttarakhand), two Centres for Flood Management Studies at Guwahati and Patna, and four Regional Centres at Belgaum, Jammu, Kakinada and Sagar. The Institute was established in 1978 as a research organization at Roorkee. Since inception, the Institute has carried out research studies covering almost all areas of hydrology, and has established contacts with national and international organizations of repute.

The Institute is well equipped to carry out computer, laboratory and field oriented studies with a team of 80 well qualified and trained scientists with excellent academic background. The Institute has state-of-the-art laboratories with latest instruments and facilities. NIH has actively participated in technology transfer activities. With these activities, the Institute has positioned itself as a centre of excellence for research and development in the area of hydrology in the country.



The **Gujarat Water Resources Development Corporation Ltd. (GWRDC)** was created in 1975 with a view to concentrate on groundwater investigation, exploration, management and recharge works in the State of Gujarat. GWRDC is functioning under the Narmada Water Supply & Water Resources Department of Govt. of Gujarat. GWRDC has total 72 offices all over the state of Gujarat with Head Office at Gandhinagar and 4 Circle Offices at Gandhinagar, Ahmedabad and Kherva.

GWRDC has three technical wings, namely (a) Geological Wing (1 Circle), which deals with groundwater investigation and monitoring, (b) Mechanical Wing (1 Circle) which deals with drilling operation and maintenance of rigs vehicles and pumps, and (c) Civil Wing (2 Circles) which deals with maintenance and management of irrigation tubewells, and construction and maintenance of civil works like building, pipeline, construction of recharge works (check dam, deepening of ponds etc.), and lift irrigation schemes. There are four laboratories for chemical and biological analysis of water and soil samples with highly sophisticated instruments. Modern facilities exist for remote sensing data analysis and GIS for groundwater investigations.

Coastal Groundwater Monitoring, Assessment & Management

Training Course under HP-II, Rajkot (March 4-8, 2013)
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Piezometer installed near sea coast in Porbandar (Gujarat) to monitor cyclic water table fluctuations induced by tidal fluctuations.