

Societal Benefits of Isotope Techniques in Water Resources

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Abstract

Water is a precious national resource requiring efficient management and conservation. The task is a challenging one in Indian context, due to the diverse climatic and hydrologic ecosystems. Isotope hydrology activities of Radiochemistry and Isotope Group of BARC have contributed significantly to the management and conservation of water resources in water scarce regions by implementing isotope technologies. In isotope hydrology, ratios of isotopes of elements like Oxygen and Hydrogen of water molecule as well as Nitrogen, Carbon and Sulphur of dissolved salts are measured to establish the source of water, contaminants and assess the sustainability of water resources. This information is used to devise strategies for better water conservation and also to identify and isolate the contaminant sources. Only in very specific and localized studies, radioactive tracers produced in a nuclear reactor are used. Using isotope technology, recharge zones of several drying springs in mountainous regions of India have been identified. Construction of suitable artificial structures at the identified zones (altitudes) helped in enhancing the discharge rate and extending the duration of spring flows. Precise information on groundwater recharge condition, interconnections among aquifers and groundwater contamination has also been obtained through isotope technology. This information is critical to strategize plans for improving the groundwater resources in drought prone as well as contaminated

regions of India. This chapter showcases the BARC's endeavours towards successfully developing and implementing isotope technology in various parts of India, that provide solutions to key challenges in water sector.

Keywords: *Isotope tracers; water resources; radioisotopes; water contamination, groundwater sustainability; aquifer interconnections*

1. Introduction

Water is present in our solar system from the beginning and was formed by the thermonuclear fusion process that produced various elements and their compounds. Total amount of water on the earth constitutes about 0.4% by volume, which is equivalent to $8.2 \times 10^9 \text{ km}^3$ [1]. However, most of this water is not available in free form since it is bound in rocks and minerals constituting the upper crust and mantle. The available water (hydrosphere) is about $1.4 \times 10^9 \text{ km}^3$, which is 17% of the total water present on the earth. Of this reserve, 97.5% is stored in the oceans as saline water while only 2.5% is freshwater that is fit for human consumption. 79% of freshwater reserves is trapped in icecaps and glaciers, which are difficult to access. Rest amount is distributed as groundwater (20%) and surface water (1%). Fig. 1 shows the total water distribution in the form of pie charts [1]. Oceans are the ultimate source of all fresh waters on the earth. Evaporation at ocean surface forms clouds, which then move to continent side owing to pressure difference created by unequal heating of the atmosphere. The clouds condense at higher altitudes to form liquid water / snow. This traversing path of water molecules in the hydrological cycle is accompanied with variation in isotopic composition at every stage, which is mainly controlled by the meteorological conditions, like relative humidity, temperature, rainfall characteristics and geographic locations such as northern or southern hemisphere, latitude, altitude, etc. The ideal tracer for tracing water in the hydrological cycle would be water itself. This, however, is challenging as it involves differentiation of different water molecules [2-4] but can be achieved through isotopes. Chemically, the water molecule (H_2O) consists of two atoms of hydrogen and one atom of oxygen [4-6]. Both, hydrogen and oxygen have three naturally occurring isotopes, viz., ^1H , ^2H (D) and ^3H (T) and, ^{16}O , ^{17}O and ^{18}O , respectively. Though several isotopic species of water molecule are possible, H_2^{16}O (99.76%), HD^{16}O (320 ppm) and H_2^{18}O (2040 ppm) are more relevant for isotope hydrology because of their higher abundance [6, 7].

Isotope hydrology is the science that uses relative distribution of H and O isotopes in water molecules to infer processes that are otherwise difficult to unravel by conventional techniques [2, 5]. As a scientific discipline, isotope hydrology started around 1950s when it was first realized that methods of nuclear physics and chemistry for the detection of isotopes could have valuable applications in hydrology. In the beginning, isotopes of hydrogen and oxygen atoms were widely used tools of isotope hydrology. Later on, many more isotopes (of dissolved salts) were added to isotope hydrology applications, including injected radioactive tracers as well as non-isotope tracers (dissolved noble gases). Isotope hydrology is now defined as “*the application of environmental isotopes and tracers to study the source, origin, distribution and dynamics of water in various components of hydrosphere*”.

In the last few decades, application of isotopic methods and isotopic data in hydrological studies has received a rapid utility and wide publicity. The commonly used isotopes are both stable (^2H , ^3He , ^{11}B , ^{13}C , ^{15}N , ^{18}O , ^{34}S , ^{37}Cl , ^{87}Sr) and radioactive (^3H , ^{14}C , ^{36}Cl , ^{32}Si , ^{39}Ar , ^{85}Kr , ^{226}Ra ,

^{222}Ra , ^{238}U , ^{235}U , and ^{232}Th). Stable isotopes are primarily used to determine the origin of specific solutes in groundwater, geochemical evolution of groundwater, processes controlling the solute mobilization and transport. Radioisotopes on the other hand are mainly useful in estimating the absolute or apparent age of water. This provides the estimate of residence time of groundwater (saturated zone). Typical hydrological investigations include aquifer-aquifer interconnection (aquifer: water containing geological formation), groundwater - surface water interconnections, causes for groundwater salinity and contamination, effectiveness of artificial structures on groundwater recharge, lake dynamics and sedimentation rate, sustainability of aquifers, paleochannels, geothermal and climate investigations, etc. In some specific cases, mainly in local scales, injected tracers are used to determine the groundwater velocity and flow direction [8-10].

Isotopic techniques are well-established and field-verified and are being applied in many water resource assessment, development, and management programs since these techniques are easy to apply and also economically beneficial [2, 5, 10]. In some occasions a single isotope analysis can provide considerable information about hydrological process as compared to costlier classical investigations. This article provides a gist of principles of isotope hydrology, measurement techniques and some success stories demonstrating the potential of isotope techniques for societal applications.

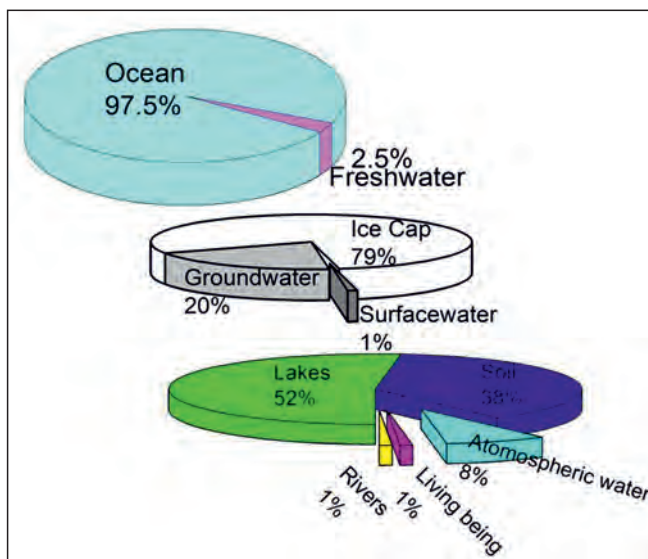


Figure 1: Global water distribution; data source Ref. [1]

2. Principles of isotope hydrology

Application of isotopes in hydrology is achieved through tracing the path of water molecules from their origin as rain / snow falls, through their recharge to subsurface reservoirs, and finally ending at their appearance in an aquifer system [9, 10]. Evaporation and condensation are the main processes in hydrological cycle that contribute variations in isotopic composition of water molecules. It happens because of isotope fractionation, which is defined as the partial separation of isotopes of an element between two or more chemical species or phases, leading to changes in the isotopic composition of element in two reservoirs. The two basic fractionation mechanisms

are equilibrium isotope fractionation and kinetic isotope fractionation. The former is due to the difference in bond energies of isotopes in compounds while the later is due to differences in average velocity or reaction rates of different isotopes. Both the mechanisms depend only on isotope mass and hence termed as mass-dependent fractionation.

Equilibrium isotope fractionation: It controls the distribution of isotopes in systems that approach thermodynamic equilibrium. Isotopes distribute themselves among compounds to minimize the energy of the system. The sensitivity to mass comes in through the vibrational modes of inter-atomic bonds. Isotope fractionation is valid only in systems that do not proceed to completion. Isotope fractionation factor (α), which is used to quantify the extent of an isotope effect, is given by the ratio of the heavy to light isotope in the product divided by that of the corresponding reactant ratio [1-3]. Condensation is an equilibrium process and occurs at 100% relative humidity whereas evaporation normally occurs under non-equilibrium conditions and is controlled by kinetic isotope effects. The exact fractionation value depends on factors such as relative humidity and turbulence at the air-sea interface.

Kinetic isotope fractionation: This occurs in fast, incomplete or unidirectional processes like evaporation, diffusion and biological reactions. For example, molecules with light isotopic species will diffuse faster in the gas-phase leading to fractionation. Kinetic effects are much larger than equilibrium effects and depend only on the forward reaction rates. Of all the various reasons for isotopic fractionations, the most important one is the higher volatility of the lighter H_2^{16}O compared to the heavier species. This makes vapor lower in deuterium by $\sim 8\%$ and ^{18}O by $\sim 0.9\%$ relative to liquid water. Therefore, 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 [3, 4, 7]. A schematic diagram of the isotope fractionation is depicted in Fig. 2.

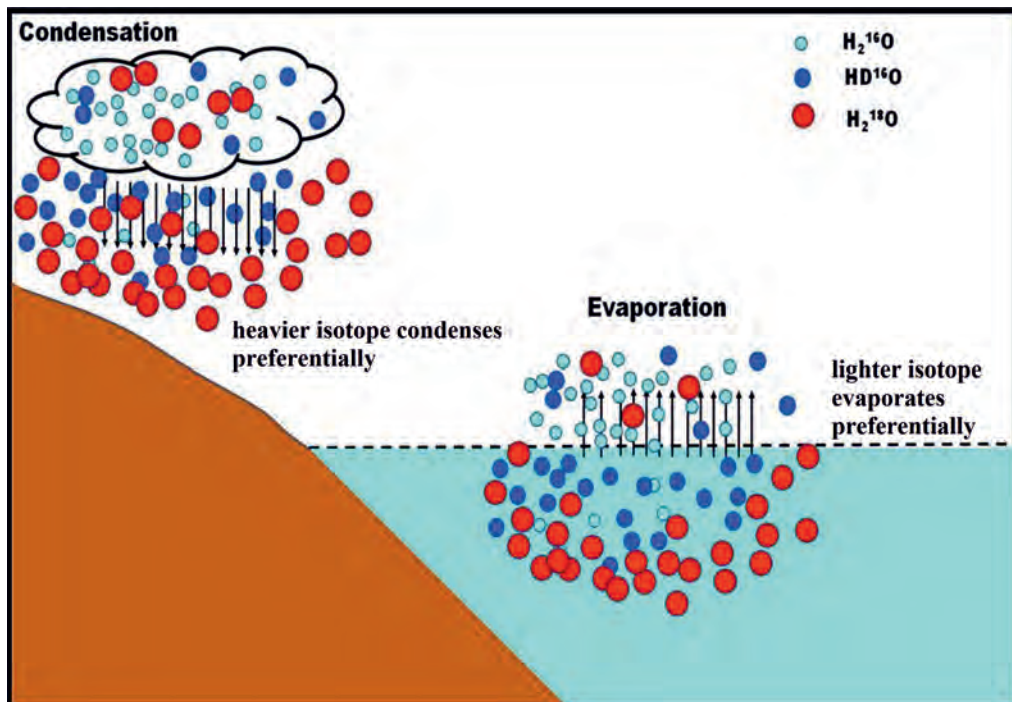


Figure 2: Schematic of isotope fractionation

Fractionation also occurs during chemical changes due to difference in vibrational frequencies of chemical bonds. The lighter isotope is more reactive, hence the final products are enriched in lighter isotopes while the reactants are enriched in the heavier isotopes. For example, during acid hydrolysis of calcium carbonate, calcium hydroxide, which is the product, contains more of ^{16}O (depleted in heavy isotope) and CO_2 contains more of ^{18}O (enriched in heavy isotope). This happens due to less bond energy of $\text{C}-^{16}\text{O}$ than $\text{C}-^{18}\text{O}$ and hence greater ease with which the $\text{C}-^{16}\text{O}$ in the reactant carbonate can be broken [9].

δ Definition: The abundance of ^{18}O in the terrestrial materials ranges from 1900 to 2100 ppm (average value 2000 ppm). Similarly, ^2H abundance in sea water is 350 ppm. It is difficult to accurately measure the absolute isotopic abundance in every compound on a routine basis. Moreover, in hydrological studies, it is sufficient to determine the relative isotopic abundance with respect to a given standard. Therefore, the isotope data is normally expressed in relative terms and is determined easily and accurately by an isotope ratio mass spectrometer. The relative deviation denoted by δ (delta) value and is defined as follows [6];

$$\delta = \left(\frac{R - R_{std.}}{R_{std.}} \right) \times 10^3$$

where ' R ' and ' $R_{std.}$ ' are sample isotope ratio ($^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, etc.) and standard isotope ratio, respectively. Since δ value is normally quite small, it is multiplied by thousand and expressed in parts per thousand (per mil or ‰). A sample with $\delta^{18}\text{O}$ value of +10‰ indicates that it is more enriched in ^{18}O by 10 ‰ (or 1%) relative to the standard. Similarly, a value of -5‰ represents that the sample is depleted in ^{18}O by 5‰ (0.5%) compared to the standard. Water samples of meteoric origin, such as precipitation, atmospheric moisture, surface water and groundwater are commonly depleted in heavier isotopes as compared to water from oceans. Hence, δ values are negative.

3. Stable isotopes

In 1961, Harmon Craig found that the changes of ^{18}O and ^2H contents in meteoric waters are fairly well correlated, and the equation to best fit line of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data of global precipitation is found to be; $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 10$. This line is referred as Global Meteoric Water Line (GMWL), which is a culmination of many Local Meteoric Water Lines (LMWL), later it is updated using more number of samples covering the globe as $\delta^2\text{H} = 8.17 * \delta^{18}\text{O} + 11.27$ [4,11]. The plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ is used to understand the impact of various physical, chemical and biological processes on the stable isotopic composition of water in an area (Fig. 3). The isotopic variations are controlled by geographical parameters such as altitude, latitude and distance from the coast. The isotope systematics in precipitation indicate, i) a gradual depletion in the heavy isotopic content when moving from lower to higher latitude (latitude effect), ii) a decrease in $\delta^2\text{H}$ and $\delta^{18}\text{O}$, when traversing from coast to continental areas (continental effect), iii) a seasonal variation of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is related to variation in temperature during different seasons (seasonal effect), iv) a decrease in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ contents with increasing altitude (altitude effect) with typical gradients in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ being 1.5 to 4‰ and 0.2 to 0.5‰ per 100 m, respectively, v) a negative correlation between isotopic content and the amount of rainfall (amount effect) with a typical depletion of ~1.5‰ in $\delta^{18}\text{O}$ per 100 mm of rainfall [2, 5, 9].

The $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ relationship for precipitation in any given region, however, often differs from the GMWL. In order to relate the isotopic composition of any water sample to GMWL,

deuterium excess parameter ($d = \delta^2\text{H} - 8 * \delta^{18}\text{O}$) is used [6,7]. Deuterium excess is a measure of the relative proportions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of a given water sample. This parameter can be used to infer physical parameters such as humidity, air and surface temperatures of the source area responsible for the transport of vapor to the site of precipitation.

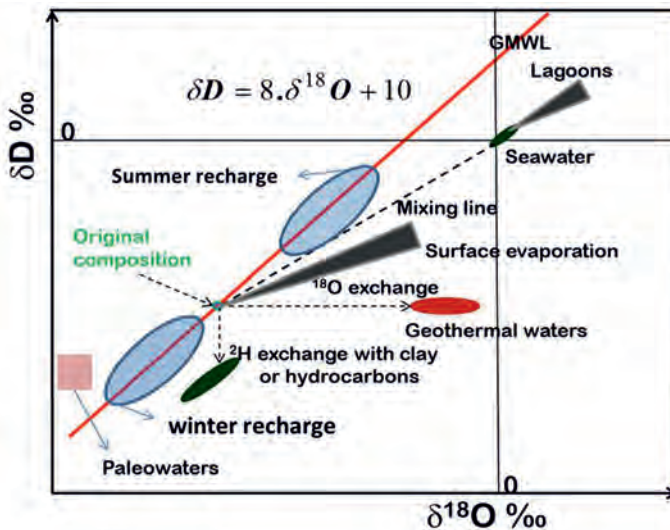


Figure 3: Variations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (δD) values from the original composition on reference GMWL due to various physicochemical processes

The variations in isotopic content of the meteoric waters are typically in few ppm. Hence a sophisticated mass spectrometric equipment is used to routinely measure such small differences with respect to a standard. The universally accepted standard for reporting stable isotope compositions of natural waters for hydrogen and oxygen isotopes is the Standard Mean Ocean Water (SMOW). Currently, Vienna supplied standard (VSMOW) is being used by many laboratories for reporting isotope data. Ocean water is a logical and natural choice for the standard since all fresh water on the planet is derived from the oceans, and being a very large water body there would be no appreciable change in the isotopic composition with time. The natural isotopic abundances and standards used for some of the common isotopes in hydrology along with their applications are given in Table 1 [2, 10].

Table 1: List of isotopes of hydrological significance, references and their applications

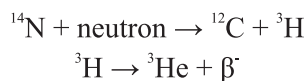
Isotope	Ratio	% Abundance	Reference	Measured phases	Applications
^2H	$^2\text{H}/^1\text{H}$	0.015	VSMOW	$\text{H}_2\text{O}, \text{CH}_4$	Origin of water
^{13}C	$^{13}\text{C}/^{12}\text{C}$	1.11	VPDB	$\text{CO}_2, \text{Carbonates}$	Pollution and dating
^{15}N	$^{15}\text{N}/^{14}\text{N}$	0.366	Air N_2	$\text{N}_2, \text{NH}_4\text{NO}_3$	Pollution marker
^{18}O	$^{18}\text{O}/^{16}\text{O}$	0.204	VSMOW	$\text{H}_2\text{O}, \text{CO}_2, \text{SO}_4^{2-}, \text{NO}_3^-$	Origin of water
^{34}S	$^{34}\text{S}/^{32}\text{S}$	4.21	CDT	$\text{SO}_4^{2-}, \text{H}_2\text{S}$	Salinity & aquifer redox condition
^{37}Cl	$^{37}\text{Cl}/^{35}\text{Cl}$	24.23	SMOC	Saline waters	Source of pollution
^{87}Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	07.00	USGS <i>Tridacna</i>	Solution	Provenance of water
^{11}B	$^{11}\text{B}/^{10}\text{B}$	80.1	NISTRM 951	Solution	Source of pollution

Sampling for oxygen-18 and deuterium does not require any filtration or preservation. A 50 mL, double capped, glass or polyethylene bottle is filled directly from the source (at site) in such a way that there is no air bubble trapped inside and tightly capped. During sampling, storage and transportation to the laboratory; special care should be taken to avoid any evaporation [10].

Commonly used equipment for the stable isotope measurements is Isotope Ratio Mass Spectrometer (IRMS). The mass spectrometer is attached to a multi-flow unit, which is an automated sample injection system for the measurement of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in aqueous samples. For $\delta^{18}\text{O}$ analysis, 200 μL of water is equilibrated with a mix gas (5% CO_2 in Helium) at 2 bar pressure under 30°C for 6 hours. After the equilibration, the headspace gas is injected into the mass analyser for isotopic ratio determination. For $\delta^2\text{H}$ measurement, approximately 0.2 mL water sample is equilibrated with mix gas (10% H_2 in He) at 2 bar pressure along with a Hokko bead platinum catalyst. Temperature is maintained at 30°C for 90 minutes and the equilibrated gas is then injected into the mass analyser. The obtained values are normalized on SLAP / VSMOW scale. The 2σ precision of measurement for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is $\pm 0.1 \text{ ‰}$ and $\pm 0.5 \text{ ‰}$, respectively [12].

4. Radioisotopes

Tritium (T or ^3H): The radioactive isotope tritium (^3H) is used for dating very young groundwater (< 50 years). Natural tritium is produced in the upper atmosphere by the bombardment of nitrogen with fast neutrons. ^3H atoms then combine with oxygen to form tritiated water (^3HHO) and enters the hydrological cycle. Tritium decays through beta (β^-) emission and forms ^3He . Reaction schemes for tritium production and its decay are shown below.



Tritium concentrations are reported in tritium units (TU), where one tritium unit having an activity of 0.118 Bq / kg (3.19 pCi / kg), is equivalent to one atom of ^3H per 10^{18} atoms of ^1H . Measurement of tritium is carried out by a liquid scintillation counter after low temperature electrolytic enrichment. The enriched sample is mixed with a scintillation mixture of solvent,

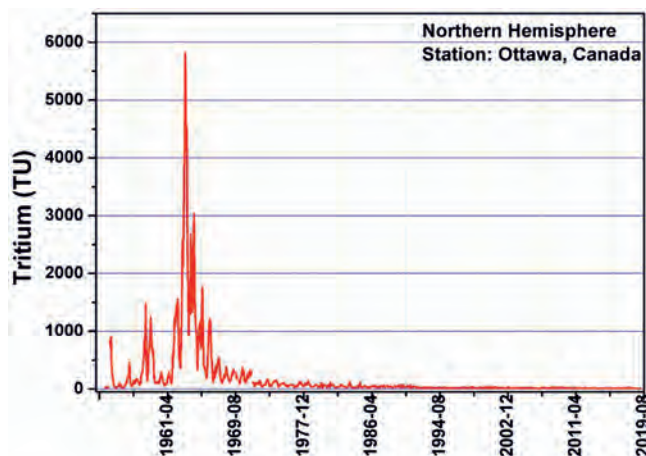


Figure 4: Temporal variation of ^3H content in precipitation over the Northern Hemisphere (data source: <https://inis.iaea.org>)

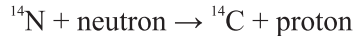
emulsifier and solute. Electrons obtained from tritium decay excite the solvent, which then transfers its energy to the solute and results in scintillation (emission of light photons) as a consequence. These light pulses are detected and counted.

Even though natural tritium production in the atmosphere is negligible, tritium activity in the atmosphere increased mainly during 1960s from the atmospheric testing of thermonuclear bombs (Fig. 4). Since the last major tests, thermonuclear bomb tritium in the last four decades has been greatly enervated by oceans and the amount of tritium is now approaching natural levels. As a consequence, quantitative elucidation of mean residence time of groundwater from tritium data has become difficult and involves complex calculations. However, the tritium data is commonly used for qualitative interpretations. Depending upon the tritium levels in measured water sample, apparent ages can be inferred from Table 2 shown below [2,10].

Table 2: Inferred water ages from tritium activity

Tritium activity (TU)	Inferred age
< 1	Sub-modern – recharged prior to 1952
1 – 5	Mixture between sub-modern and recent recharge
5 – 15	Modern (<5 to 10 years)
> 30	Considerable component of recharge from 1960s or 1970s
> 50	Dominantly the 1960s recharge

Carbon-14: Radiocarbon (^{14}C) is a cosmogenic isotope of carbon with a half-life of 5730 years. It is useful for age dating as well as tracing hydrological processes. ^{14}C is formed in the atmosphere when neutrons interact with ^{14}N (nitrogen) as shown below.



Subsequently, ^{14}C reacts with atmospheric oxygen to produce $^{14}\text{CO}_2$ and enters the hydrological cycle as bicarbonate (HCO_3^-); either by reacting with moisture or through root respiration. Much of the ^{14}C has been added to the atmosphere due to the nuclear bomb tests during the 1960s. Based on the time passed by groundwater in aquifers the ^{14}C activity reduces, and this decrease in activity is used to deduce the residence of groundwater, typically over several thousand years [2, 10].

For ^{14}C sampling in natural water, the dissolved inorganic carbon (DIC) is collected from about 100 L of water by precipitating BaCO_3 . A carbonate-free, saturated BaCl_2 solution is used for this purpose to avoid cross contamination of ^{14}C from reagents. The DIC precipitation is facilitated by converting all DIC into carbonate form by raising the pH of water sample to above 10, by adding NaOH . To speed up the settling of BaCO_3 precipitate, Ferrous ammonium salt (coagulant) and poly acrylamide (settler) are added. Supernatant solution is decanted to collect BaCO_3 precipitate, which is treated with phosphoric acid to generate CO_2 . This CO_2 is trapped using a cryostat (liquid nitrogen). Trapped CO_2 is stored over 30 days for radon decay and then passed through carbon absorber and scintillator mixture followed by counting in a liquid scintillator counter. The ^{14}C activity is reported as percent Modern Carbon (pMC). The minimum detection limit for ^{14}C is 1 pMC. The typical ages measured by this technique are up to ~ 40,000 years. Very low levels of radiocarbon are measured using Accelerator Mass Spectrometer (AMS), which can allow estimation of groundwater ages up to 80,000 years [13].

Direct estimation of groundwater age from measured ^{14}C data can yield an overestimated or underestimated value. This is due to the fact that the initial ^{14}C activity can be changed by many

geochemical processes mainly from the dissolution of the fossil carbon present in the aquifer or re-dissolution of vadose zone carbonates. Therefore, the groundwater ages need to be corrected according to aquifer conditions to arrive at most reliable values. In addition to ^3H and ^{14}C , there are several other naturally occurring radioisotopes that are used for both age dating as well as other hydrological applications. The list of the commonly used radioisotopes in hydrology is given in Table 3.

Table 3: Environmental radioisotopes used in hydrology

Isotope	Ratio	% Abundance	Half life	Applications in hydrology
Tritium (^3H)	$^3\text{H}/^1\text{H}$	10^{-16}	12.3 years	Young groundwater dating
Carbon (^{14}C)	$^{14}\text{C}/^{12}\text{C}$	10^{-10}	5730 years	Old groundwater dating
Chlorine-36 (^{36}Cl)	$^{37}\text{Cl}/^{35}\text{Cl}$	10^{-13}	3.1×10^5 years	Very old groundwater dating
Radium-226 (^{226}Ra)	Daughter product of ^{238}U series		1600 years	Submarine groundwater discharge (SGD) and geothermal investigation
Radon-222 (^{222}Rn)	Daughter product of ^{238}U series		3.8 days	Groundwater dating, surface water infiltration, SGD

5. Stable isotopes of dissolved species

Besides ^2H and ^{18}O , other stable isotopes are also used in hydrological studies. These include, ^{13}C , ^{15}N and ^{34}S , which occur as dissolved compounds in the form of carbonates, nitrates and sulfates, respectively [9]. These isotopes are measured using mass spectrometers in respective gaseous forms and their isotopic variations are useful not only in source identification but also in

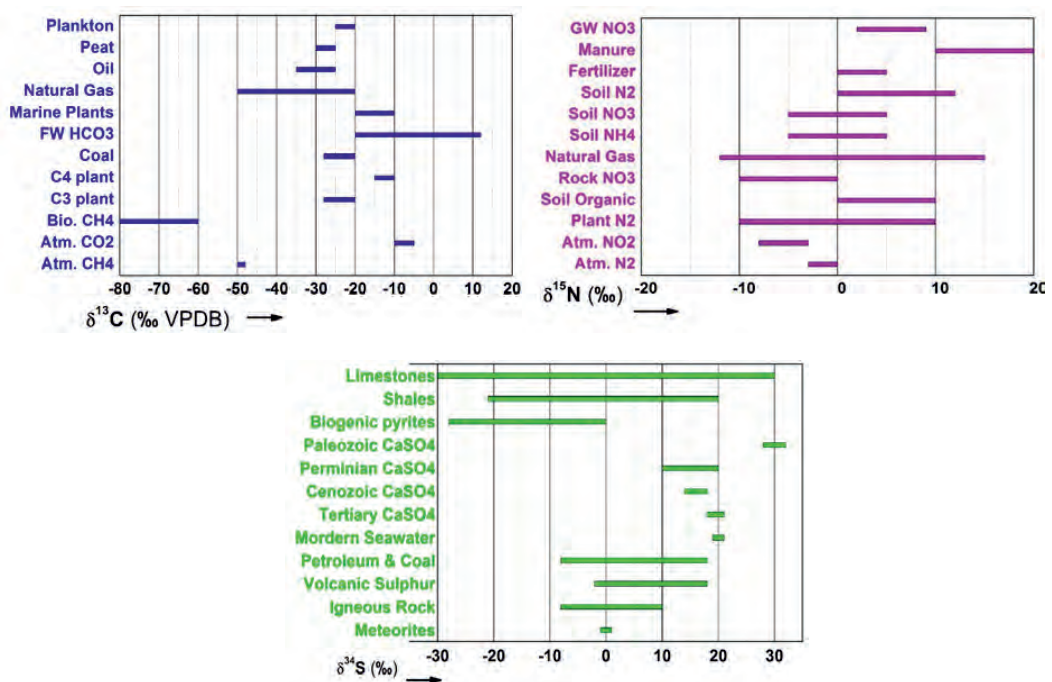


Figure 5: a) $\delta^{13}\text{C}$, b) $\delta^{15}\text{N}$ and c) $\delta^{34}\text{S}$ distribution in selected natural compounds

understanding the geochemical processes. Typical ranges of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ in different sources are shown in Fig. 5 (a-c).

6. Applications

The isotopes, both naturally occurring or man made (radioactive or stable) are used as tracers of water molecules and understand the processes occurring during their natural circulation in a given hydrological system. Isotope applications are highly diverse in nature and are used for implementing policies on water, mapping of the aquifers, restoring water sources, identifying the exact sources of pollution and improving water conservation practices. Many studies are being carried out in the domain of eco-hydrology as well, to study the human impacts on all dimensions of hydrological cycle and ecosystem. A few important applications are briefed in this article taking selected case studies.

Groundwater recharge: The importance of groundwater recharge studies has grown manifold in the past few decades due to rapidly raising apprehensions over the impacts of changing climate and human interferences on the availability and consumption of groundwater resources. This is especially true for drought-prone regions like north Gujarat. A clear understanding and knowledge is important for better management of available groundwater resources.

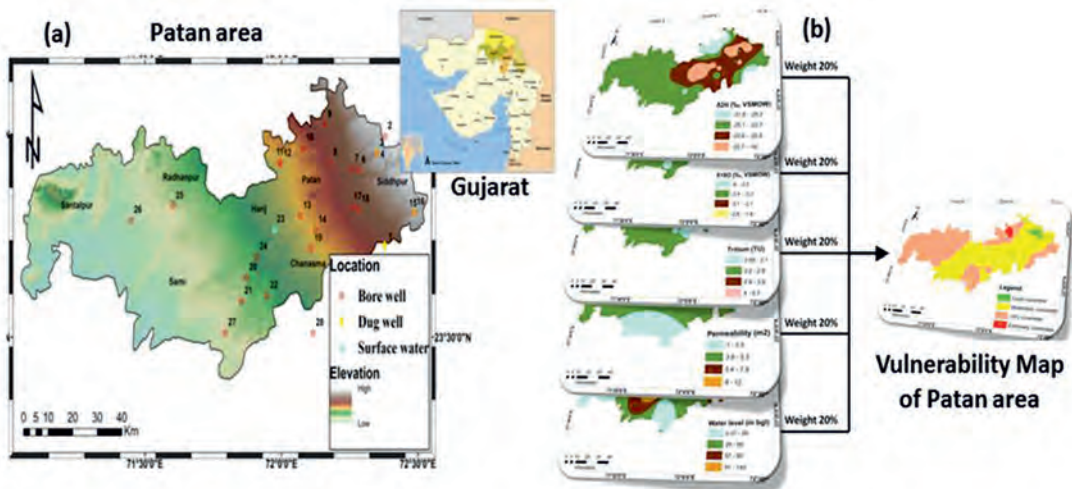


Figure 6: a) Study area of Patan district, Gujarat and b) vulnerability map

However, understanding spatial influence on groundwater recharge in inherently complex multi-aquifer systems is a challenging task and isotope tools are proven to be useful in these challenging cases [15]. The isotope signature of groundwater reflects the source of recharge and temperature of precipitation during recharge. Mean elevation of precipitation from where the groundwater recharge mainly occurs can be assessed by studying the vertical isotopic gradient of precipitation in the study region. This information can be obtained from the weighted mean isotopic data and elevation data of precipitation.

An isotope investigation was taken up in over-exploited regions of Gujarat with an objective to identify the most potential zones of recharge to groundwater and interactions among multiple water-bearing zones (Fig. 6a). The results showed that groundwater exists in mainly three zones

and all are dominantly recharged by meteoric source. The top shallow zone (up to 150 m depth) is mostly brackish to saline with very little recharge from rainwater (3-12%) whereas the confined intermediate and deep zones receive recharge from foot hills of Aravali. Age dating of groundwater samples indicated younger age (about 1500 years) to deep groundwater samples in the north-eastern part which increases to > 6500 years towards south-western parts of the investigated area, indicating north-eastern part is the potential zone for recharge to groundwater. The isotope results when integrated with chemical and lithological information provided insights into the vulnerability of groundwater towards contamination (Fig. 6b). Groundwater recharge studies have also been carried out in semi-arid and arid zones of India such as Jaisalmer (Rajasthan), Chitradurga (Karnataka), Buldhana (Maharashtra), Srikakulam (Andhra Pradesh), Nalgonda (Telangana), etc. [14-17].

Groundwater contamination: Clean water in India is mostly derived from groundwater, which is being impacted by many natural and anthropogenic activities. Arsenic and fluoride contamination of groundwater is mainly geogenic in nature, while nitrate contamination and salinity can be attributed to anthropogenic activities. Uranium contamination has also been reported in some parts of India especially from northwestern parts and it is mostly attributed to geogenic sources [18-20]. Iron is another contaminant of geogenic source, but is a lesser health hazard. Localized pockets of high iron content are observed in Bihar, Uttar Pradesh, Kerala and North Eastern States. An isotope investigation was carried out in Ilkal area of Bagalkot District, Karnataka where growing incidences of dental and skeletal fluorosis in residents were reported (Fig. 7a) [21]. The possible source of fluoride in this region is fluoride bearing minerals present in granitic rocks, which could have contributed either through weathering of rocks in the subsurface or through rock polishing industrial wastes (Fig. 7b). Fluoride levels ranged between

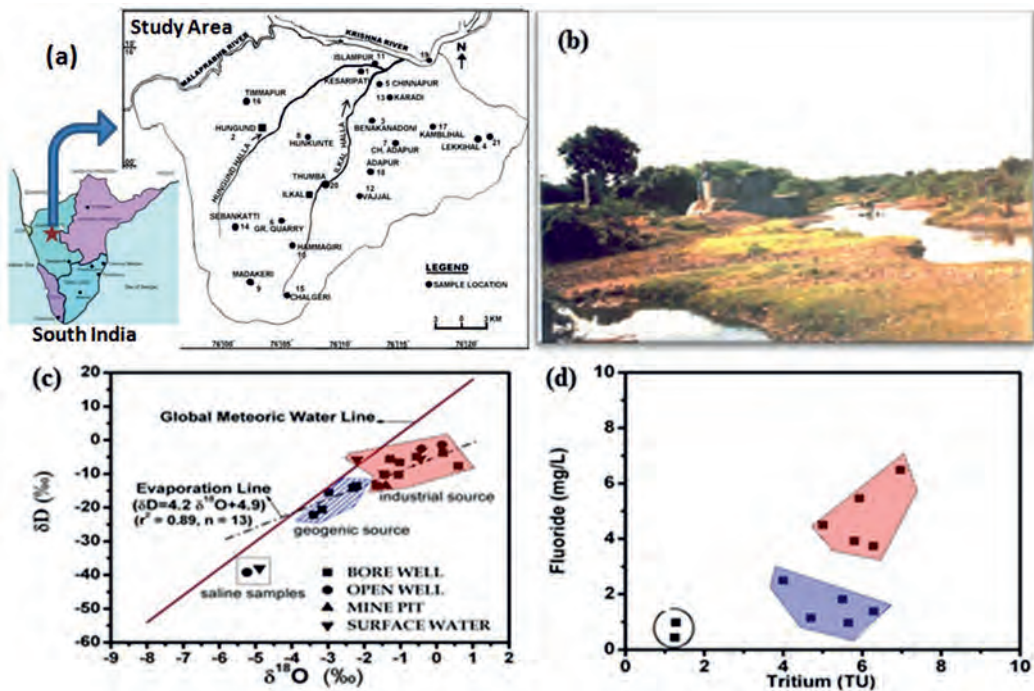


Figure 7: a) Fluoride affected Ilkal area, b) rock power dump site, c) $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ plot and d) fluoride (F) vs. tritium plot

0.1 and 6.5 mg/L with over 75% of the samples contaminated. Isotope results indicated that affected groundwaters are evaporated in nature, and more so near the surface water bodies (Fig. 7c). Environmental tritium data (Fig. 7d) further helped in delineating groundwater zones where fluoride contamination is derived from anthropogenic inputs (rock polishing industries) and natural input (rock weathering). Fluoride contamination studies were also carried out in Talcher (Odisha), Nalgonda (Telangana), Jaipur (Rajasthan), Bathinda (Punjab), etc. [21-23].

Uranium contamination: Dissolved uranium concentrations are highly sensitive to geochemical conditions as well as host rock composition. High redox potential and elevated levels of uranium concentration in rocks are correlated with the uranium contamination in groundwater. Recently studies were extended to understanding the geochemical processes and any other anthropogenic influence that is acting as driving force for such high uranium levels, mostly in the southwestern part of Punjab, where uranium contaminated groundwater is reported. In addition, this region is also facing depletion in water levels, high salinity, fluoride and nitrate pollution issues. A thorough investigation was carried out using isotope tools, to assess the uranium contamination in groundwater of southwest Punjab.

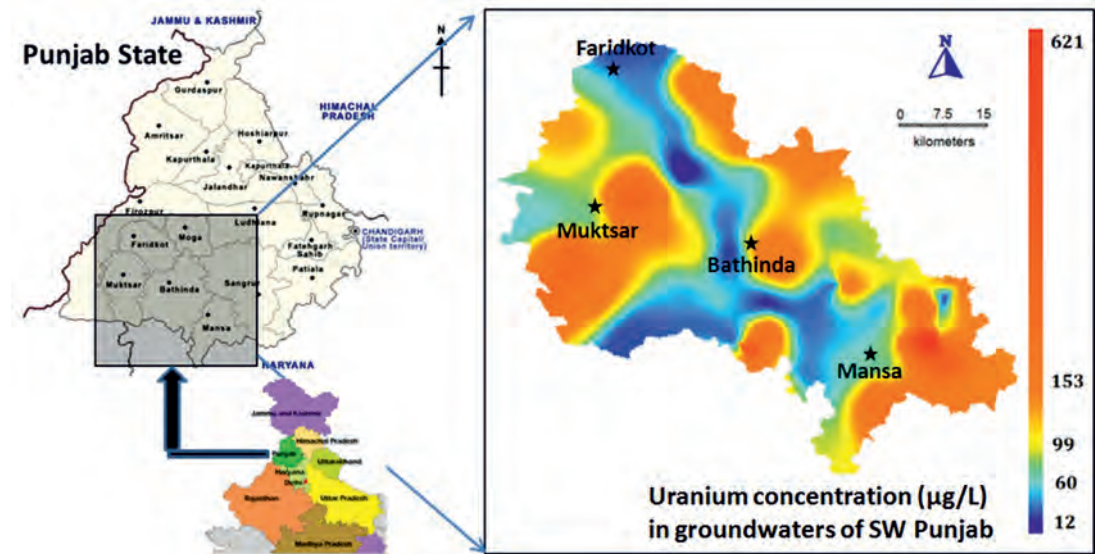


Figure 8: Location map of southwest Punjab with contour of dissolved uranium

From isotope and geochemical investigation, it was concluded that the high uranium concentration is spread over several parts in four districts of southwest Punjab. Typical uranium concentration in groundwater ranged from 12.2 to 620 µg/L (Fig. 8). The highest uranium contamination was reported in Mansa district with 620 µg/L. Spatial distribution of dissolved uranium indicated higher concentration in the east, north, west and in few patches in the south zones. Relatively lower values were found in the central part of the study area. From the vertical profile, it can be seen that the shallow zone up to 50 m bgl (below ground level) is contaminated with uranium as compared to the deeper zones. This suggested that widespread contamination is not occurring in the deep zone. The irrigation return flow contains high bicarbonate content due to root zone respiration from crops. This allows formation of stable uranium-carbonate species and allows migration to distant places from its source. The ^{13}C isotope data confirmed the contribution of irrigation return flows towards high bicarbonate in shallow groundwater. The

isotope results also helped in establishing the uranium-radon linkages in groundwater (Fig. 9). The isotope study has provided the nature of groundwater recharge and possible mechanism of contamination, which is necessary for implementing proper management strategies [18-20,25]. Uranium contamination studies are being carried out in Kadapa (Andhra Pradesh) and Dausa (Rajasthan).

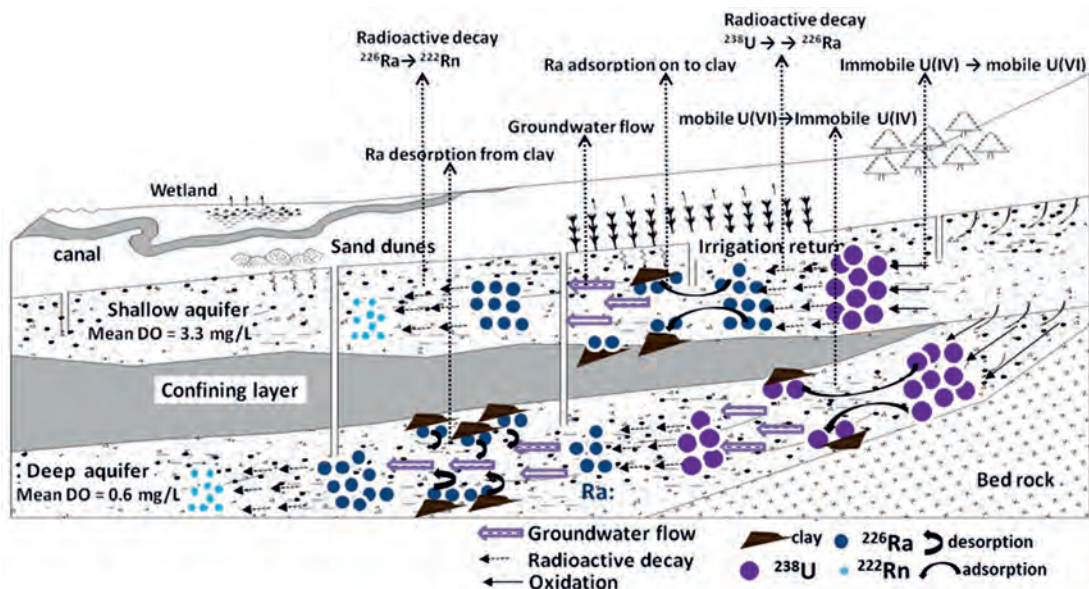


Figure 9: Schematic diagram of U-Rn correlations in shallow and deep zones, southwest Punjab [18]

Seawater intrusion: The possible causes for groundwater salinity are dissolution and flushing of dry salts by rainwater, evaporative enrichment, mixing of saline water and connate sea water or fossil sea water. These processes are clearly differentiated using isotope signatures of affected waters. In order to establish the type and extent of groundwater salinization in coastal Tamil Nadu, an isotope study was carried out in alluvial and hard rock zones of coastal Tiruvanmiyur aquifer. The overall hydrochemistry of most of the groundwaters is generally fresh with electrical conductivity (EC) $< 1500 \mu\text{S}/\text{cm}$. However, a few samples from semi-confined aquifer are found to be brackish to saline with EC ranging up to $30,000 \mu\text{S}/\text{cm}$. Isotopic analysis of the most of the fresh water samples indicated meteoric source in unconfined and semi-confined zones. The recharge seems to occur without significant evaporation prior to infiltration (sample data fall on meteoric water line). In some places the isotope data showed a slightly enriched stable isotopic signature and the data fall away from the local meteoric water line. The contribution of evaporated surface water such as backwater to groundwater could be the cause for the observed isotopic enrichment and brackish quality of water. A positive correlation was observed between the salinity of the waters and their isotopic values, which can be attributed to mixing between meteoric water and marine sources such as sea water or saline brines. These marine sources seem to have evolved through seawater modification or seawater intrusion. Chloride and $\delta^{18}\text{O}$ correlations indicated that salinity is mostly attributed to dissolution of aquifer sediments. The brackish and saline waters are found to be about 11000 and 7000 years old, respectively. Based on the isotope, geochemical and lithological information, a conceptual map was prepared depicting the groundwater flow in Tiruvanmiyur aquifer, which is catering the

fresh water needs of Chennai City (Fig. 10). Many coastal regions were studied for groundwater salinization problem including, Kudankulam, Nagapattinam and Minjur (Tamin Nadu), Midnapore (West Bengal), Vishakapattinam (Andhra Pradesh), Palgarh (Maharashtra) and Delang-Puri (Odisha) [26-28]. Similarly, inland salinity is also studied using isotope techniques in Purna basin (Maharashtra), Haryana and Punjab [29].

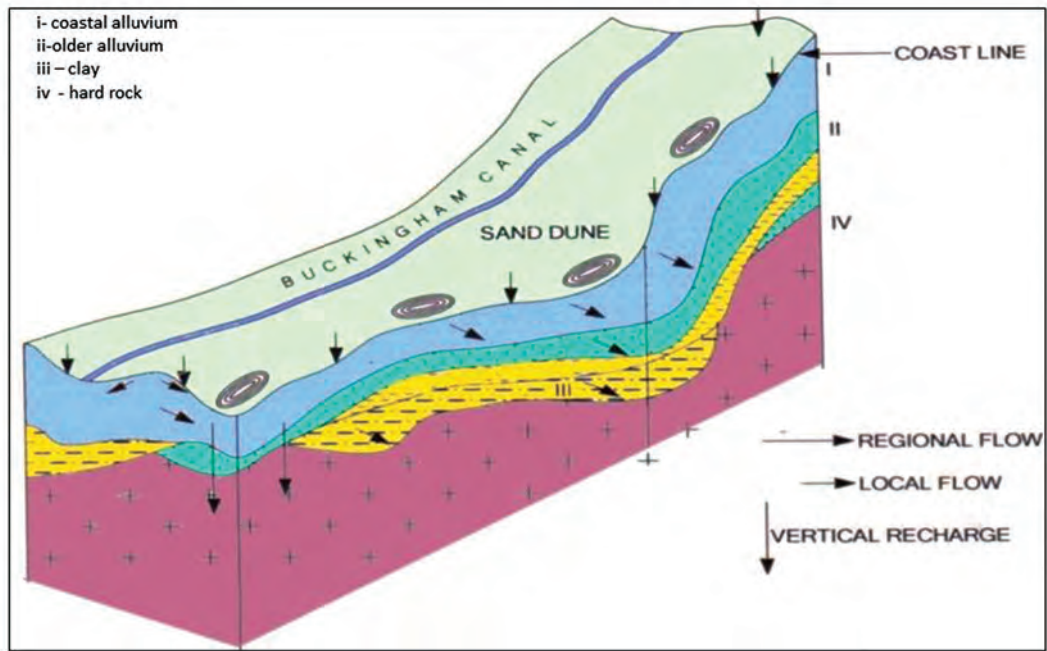


Figure 10: Schematic groundwater flow diagram of Tiruvanmiyur Aquifer (Tamil Nadu)

Recharging drying springs: In Uttarakhand and other Himalayan states, it is reported that about 30% of the natural springs have almost dried up, and an additional 45% of the existing springs are on the verge of drying. This is going to impact the livelihood of approximately 60% of the population in mountainous villages. Most of the villages have been classified as water-scarce and many more are becoming water-scarce. The springs are mainly fed by sub-surface water. It is observed that the spring discharges are reduced due to deforestation in recharge areas, reduction in rainfall infiltration due to artificial structures such as roads and buildings, disturbance in the source of the distribution, poor rainfall, etc. Recharging of springs can be achieved through artificial rainwater harvesting [30]. In order to identify the altitude of most potential recharge zones to the springs, isotope investigation was carried out covering about 50 springs in the state of Uttarakhand. A typical site map is shown in Fig. 11a. The initial observations from spring discharges and stable isotope data indicated that the springs are mainly precipitation recharged and are highly seasonal. The altitude of recharge to springs is estimated using the altitude effect, which was computed by measuring the stable isotope content of rainwater samples collected from different altitudes in the same valley.

A typical plot representing altitude effect ($0.42\% \delta^{18}\text{O}$ per 100 m for Nakuri Gaad area) is shown in Fig. 11b. Based on the identified recharge altitudes, rainwater harvesting structures were recommended and constructed at the sites (Fig. 11c-f). A great improvement in spring

discharges (3 to 5 times) and duration are observed (Fig. 11 g-h). Similar studies were conducted in Himachal Pradesh, Jammu and Kashmir and Sikkim.

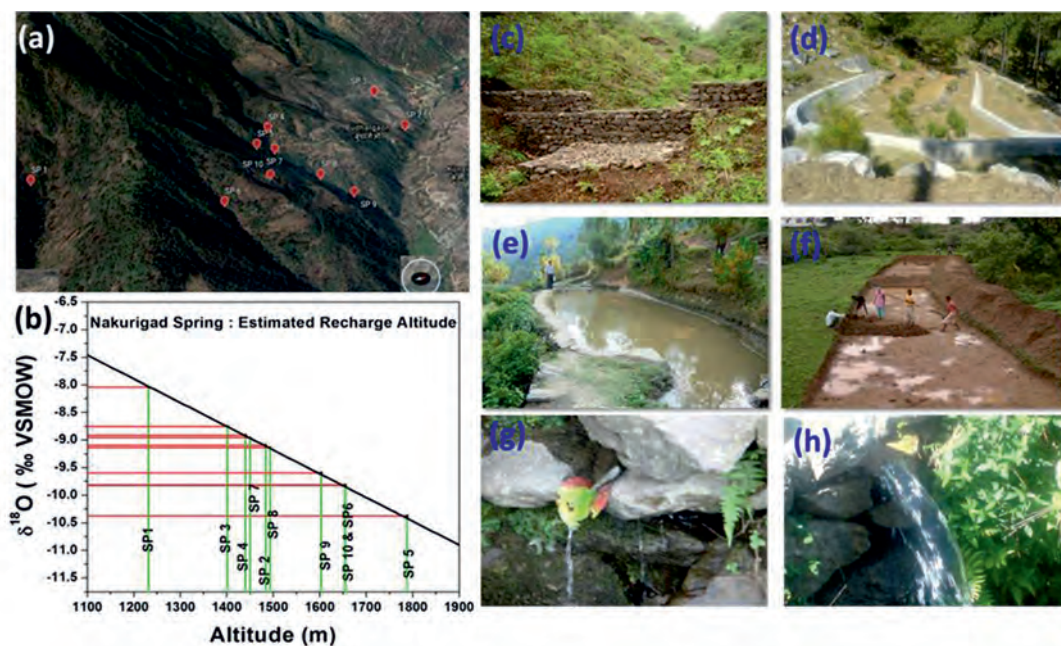


Figure 11: a) Google earth map of spring locations, a typical study site, b) recharge altitude of springs, c) gabion check dam, d) subsurface dykes, e) percolation pond, f) contour trenches and spring discharges g) before and h) after construction

7. Conclusion

Significant advances have been made through application of isotope techniques, which have provided better insights into factors and processes affecting surface water, groundwater and precipitation characteristics. Stable isotopes (^2H , ^{18}O , ^{13}C , ^{15}N , ^{34}S , etc.) find potential applications in understanding the groundwater sources, interconnections and contaminant sources. On the other hand, radioactive isotopes (^3H , ^{14}C , etc.) are being used to date the groundwater and infer the residence time / travel time, which can help not only in deducing the sustainability of water resources but also in evaluating the transport and degradation rates of contaminants. Injected isotopes are very handy for localized studies to determine the groundwater flow and velocity, estimation of recharge and migration of contaminants in saturated and unsaturated zones. Environmental isotopes in conjunction with modelling tools can provide precise and accurate information which can help the water managers and agencies to take up appropriate measures for planning effective water usage and management of water resources. Introduction of laser-based isotope analysers, which can measure both ^2H and ^{18}O simultaneously in a short time and at lower cost as compared to mass spectrometers is going to widen the user base in both research as well as academic institutions and further propagate this technology. Advancement in isotope measurement systems and applications are going to pave a progressive way for a wider and regular use of isotope technology in future.

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