

# Environmental Tracer Techniques in Groundwater Investigations

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## INTRODUCTION

Groundwater is an important source of water supply for the various uses and its increasing demands in agricultural, industrial and domestic sectors necessitates proper water resources assessment and management strategies. Improper management of groundwater resources can lead to various troubles such as higher pumping cost, reduction in yield, failure of wells, sea water intrusion to fresh water aquifers in coastal regions, sub marine groundwater discharge (SGD) and land subsidence. For proper assessment of groundwater resources and groundwater budgeting we need to investigate hydro-geological parameters and aquifer characteristics more precisely.

The groundwater investigation has been an important issue during last two decades due to unsustainable abstraction, deteriorating water quality and emerging pollution threats to potable resources. This has been reported in the numerous studies carried out globally (Rodell et al., 2009; Tiwari et al., 2009; Wada et al., 2012) as well as in Indian subcontinent (Chopra and Krishan, 2014a,b; Krishan et al., 2014a-c; 2015a-c; MacDonald et al., 2013, 2014, 2015; Rao et al., 2014). The satellite based observations by Rodell et al. (2009); Tiwari et al (2009) and Wada et al (2012) have shown that there is a significant net loss in terrestrial water storage (TWS). Therefore, to develop effective water management plans for characterizing and understanding the reasons requires higher resolution field-based observations.

In this article, modern techniques based on environmental isotopic tracer measurements are discussed to understand the response of groundwater resources for sustained abstraction. Environmental tracers have become a common tool to understand groundwater flow processes, water budget, origins, chemical reaction processes, recharge sources and zones of deep aquifers and retention time (young and old waters) including validation or calibration of flow and transport models using groundwater age (Lapworth et al., 2014a,b; 2015). These techniques are based on measurement of environmental tracers like: radon, chlorofluorocarbons (CFCs), sulfur hexafluoride (SF<sub>6</sub>), noble gases, stable isotopes and environmental tritium which are discussed below.

## RADON

Radon is a naturally occurring radioactive element colourless, odourless, chemically inert gas (forms stable molecules with highly electronegative ions), no taste, fairly

soluble in water and organic solvents. It is an intermediate product in the uranium decay chain as:

uranium-238 (half life: 4.5 billion years) ⇒ radium-226 (half life: 1600 years) ⇒ radon-222 gas has time to leak into the air (half life: 3.8 days) ⇒ lead-210 (half life: 22 years) ⇒ lead-206 (stable).

Natural radon is an excellent tracer for identifying areas of significant groundwater discharge (Krishan et al., 2015d) because of its conservative nature, short half-life, high abundance in groundwater compared to surface water and easiness in measurement. <sup>222</sup>Rn activities in groundwater are often 2-4 orders of magnitude higher than those of seawater (Moore, 1996; Sekulic and Vertacnik, 1996); hence, even after large dilutions in the coastal waters, they can be detected at very low concentrations (Burnett and Dulainova, 2003). <sup>222</sup>Rn is particularly useful in locating submarine freshwater springs as radium may not enrich under such conditions. One of the limitations of <sup>222</sup>Rn is that, being an inert gas, it evades into the atmosphere. From the continuous monitoring of <sup>222</sup>Rn in coastal waters, it is possible to quantify submarine groundwater discharge (SGD).

SGD can be detected on the basis of four different conditions depending upon the relationship between EC and radon in water.

**Table 1 :** The comparison of EC and radon levels in different conditions (Krishan et al., 2015d)

Sl. No.	Condition	Process
1	Increase of Radon and decrease of EC	Fresh water SGD
2	Increase of Radon and increase of EC	Saline SGD
3	Decrease of Radon and decrease of EC	Fresh Surface water
4	Decrease of Radon and increase of EC	Sea water

In general, submarine groundwater discharge studies help to plan for the optimum groundwater exploitation of coastal aquifers keeping the seawater interface well within the coastal zones. Also, ideal sites for the construction of subsurface barriers to arrest the groundwater discharge could be explored.

## Sample Collection and Analysis

The water samples are collected from the hand pumps and the water level of these hand pumps is measured. The wells are purged through pumping for 15 min to ensure sample quality. All the water samples are collected in special glass bottles (250 mL capacity) designed for radon in-water activity measurement ensuring minimum radon loss by degassing (Krishan et al., 2014e, 2015f) and without any air contact.

$^{222}\text{Rn}$  measurement of ground water samples is to be carried out using a radon-in-air monitor RAD-7 (Durridge Co. Ltd) using RAD H<sub>2</sub>O technique with closed loop aeration concept (Lee and Kim, 2006). RAD H<sub>2</sub>O technique employs closed loop concept, consisting of three components, (a) the RAD7 or radon monitor, (b) the water vial with aerator and (c) the tube of desiccant, supported by the retort stand. On the RAD7 Wat-250 protocol is selected for the vial of 250 mL capacity as same was used for water sampling (Krishan et al, 2014e, 2015f). The extraction efficiency should be 95%.  $^{222}\text{Rn}$  activities are expressed in kBq m<sup>-3</sup> (disintegration per hour per m<sup>3</sup>) with 2 r-uncertainties. At the end of the run (30 min after the start), the RAD7 prints out a summary, showing the average radon reading from the four cycles counted, a bar chart of the four readings, and a cumulative spectrum. The radon level is calculated automatically by the RAD7.

## CHLOROFLUOROCARBONS (CFCs) AND SULFUR HEXAFLUORIDE (SF<sub>6</sub>)

Chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF<sub>6</sub>) are important trace gases for finding the groundwater residence time (Darling et al., 2012). The build-up in the atmosphere of these gases since 1930s from anthropogenic organic compounds ranging from aerosol propellants to refrigerants offers a suitable way of dating waters up to ~60 yrs old. However as a result of various environmental regulations limiting the use of CFCs, current production estimates are less than half of the peak values of the late 1980s.

CFC-11 (CFC13), CFC-12 (CF<sub>2</sub>Cl<sub>2</sub>) and CFC-13 (C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub>) have relatively long residence times in the atmosphere (44, 180 and 85 years, respectively), where they undergo equilibration with surface waters as a function of temperature.

## Sample Collection and Analysis

Groundwater is to be sampled using existing hand pumps and tube wells and the sample locations are recorded using Garmin global positioning system. Prior to sampling boreholes are purged (minimum 3 borehole volumes) to ensure a fresh sample is collected. Groundwater chemistry was monitored carefully for a range of field parameters including electrical conductivity (EC), pH, oxidation-reduction potential (ORP) temperature measurement using a flow-through cell (Fig. 1). Only after stable field readings are obtained, samples are to be collected.



Fig. 1 : Sample collection for CFCs and SF<sub>6</sub>

CFC and SF<sub>6</sub> samples are to be collected unfiltered and without atmospheric contact in sealed containers by the displacement method of Oster (1994). This method ensures that the sample is protected from possible atmospheric contamination by a protective jacket of the same water.

CFCs and SF<sub>6</sub> are measured by gas chromatography using an electron capture detector (GC- ECD) following cryogenic pre-concentration (IAEA, 2006). The detection limit for CFC concentrations in water is 0.01 pmol/L, while for SF<sub>6</sub> it is 0.1 fmol/L. Both CFC and SF<sub>6</sub> analysis should ideally be calibrated to a bulk air standard collected at an atmospheric monitoring station, preferably one of the AGAGE network (<http://agage.eas.gatech.edu/>).

The gases are well-mixed in the atmosphere (Fig. 2) so their input functions are not area-specific as is the case with tritium. While any one of these trace gases can in principle provide a groundwater age, when two or more are measured on water samples the potential exists to distinguish between different modes of flow including piston flow, exponential flow and simple end-member mixing (Darling et al., 2012).

CFCs are detectable in lower concentrations than tritium, and are, therefore, more sensitive indicators of modern water where modern and old water mix. In addition to acting as tracers of modern water, CFCs can yield actual recharge ages when mixing and environmental contamination are significant. The sensitivity of the CFC dating method depends on the rate of change of the atmospheric CFC concentration with time, and thus the ability to date very young water will diminish with time.

### Characteristics of CFCs and SF<sub>6</sub> (Darling et al., 2012)

- Each tracer may have limitations in their application for estimating groundwater residence times, in particular, the CFCs may be affected by pollution, and/or degradation under anaerobic conditions, and excess SF<sub>6</sub> is problematic in some settings due to terrigenic production.
- Interpreting trace gas indicators relies on consideration of mean recharge temperature, altitude and incorporation of excess air.
- The phenomenon of 'excess air' incorporated during recharge has an insignificant effect on the CFCs, but a larger effect on SF<sub>6</sub>.

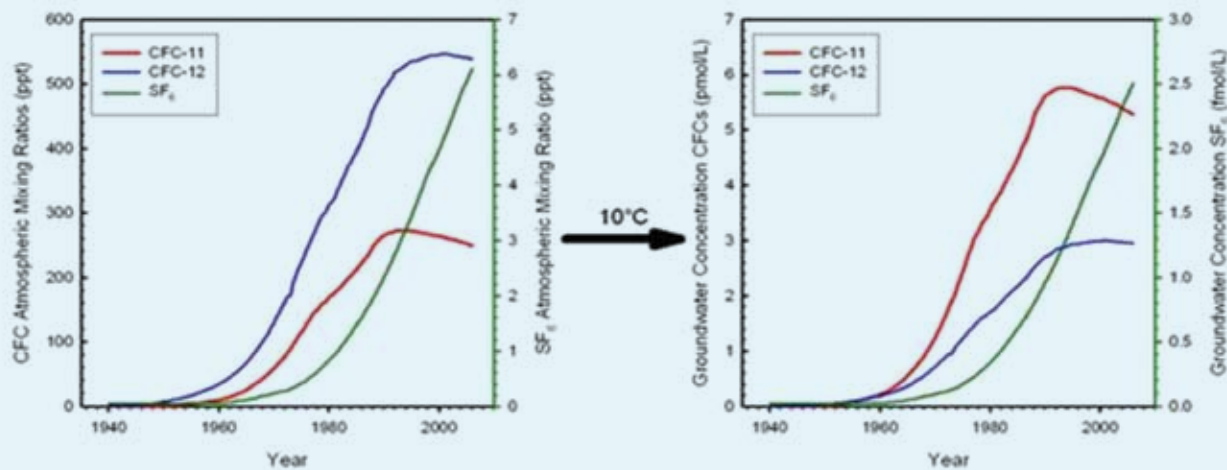


Fig. 2 : Concentrations of CFCs, SF<sub>6</sub> in atmosphere and groundwater

- Various models used are: Lumped parameter models (LPM) typically used to describe some of the variation seen in groundwater mixtures include the piston flow model (PFM), exponential mixing model (EMM), partial exponential model (PEM), dispersion model (DM) and binary mixing models (BMM).
- In some instances it is possible to use two tracers with different input functions to assess which mixing model to use for estimating mean residence times (MRT), e.g. SF<sub>6</sub> and CFC-12.
- If SF<sub>6</sub> data are found to be significantly contaminated with terrigenous sources and not suitable for groundwater dating. In light of this, two plausible mixing models; PEM and DM (with a dispersion parameter of 0.5) can be used for comparison to estimate mean residence times.
- These models used are based on realistic conceptual models which include considerations of groundwater flow, well-field configuration, lithological controls and well screening. Groundwaters from boreholes that are partially screened (screens sections may be up to 20 m) are likely to be a mixture of groundwater ages with different flowpaths.
- A limitation of using modern tracers is that they are not able to trace mixing of groundwaters older than 60 years and are therefore estimated calculated mean ages are susceptible to non-linear mixing of groundwaters of different ages.
- In the future, with the main CFCs are already declining in the atmosphere, new anthropogenic trace gases are likely to take their place.

### NOBLE GASES

The noble gases make a group of chemical elements with similar properties. Under standard conditions, they are all odorless, colorless, monatomic gases with very low chemical reactivity. The six noble gases that occur naturally are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and the radioactive radon (Rn). Noble gases have

been measured in seawater, groundwater, ice cores, and rocks in order to address a variety of important problems in environmental science such as air-sea gas exchange, marine biological production, groundwater temperatures, firm temperature and thickness, surface exposure ages, etc.

### SAMPLE COLLECTION AND ANALYSIS

Tube wells/hand pumps are purged prior to sampling (minimum 3 borehole volumes) to ensure a fresh sample is collected and samples are to be collected after the constant values of electrical conductivity (EC), pH, oxidation-reduction potential (ORP) temperature measurement using a flow-through cell as shown in (Fig. 1). The samples are collected in a copper tube (Fig. 3).

Noble gases can be used to investigate the hydrogeology of the alluvial aquifer system. The noble gases Ne, Ar, Kr and Xe can be used to estimate groundwater recharge temperatures. Their dissolved concentrations are considered to be controlled by the average temperature at the water table during recharge, based on assumptions regarding their solubility equilibrium with water (Fig. 4). They also enable the quantification of ‘excess air’, i.e., the forcible solution of air bubbles resulting from movements of the water table. Using Ne, Ar and Kr input data, recharge temperatures and excess air were estimated using a range of interpretive physical models in Noble90, a least squares inverse modelling programme. Closed equilibrium (CE) and the partial re-equilibrium model (PR) can be used to interpret the noble gas temperature data.



Fig. 3 : Copper tube for noble gas sampling



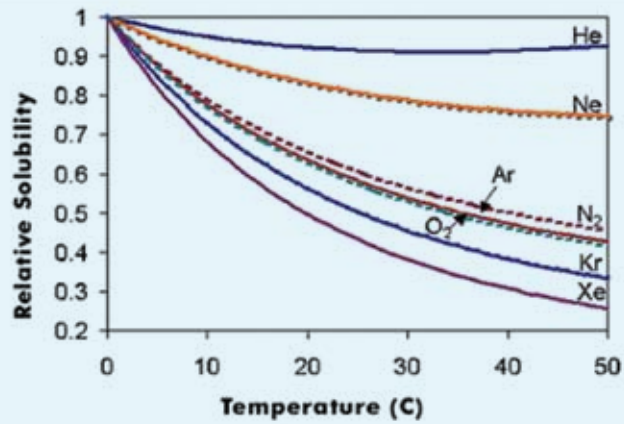


Fig. 4 : Solubility equilibrium of noble gases at different temperatures

The first general model was proposed by Stute et al., (1995). It explains the fractionation of the excess air by diffusion controlled partial re-equilibration (PR model) of the initial amount of excess air. It may be written as:

$$C_i = C_i^*(T, S, P) + A \cdot z_i \cdot e^{-F D_i / D_{Ne}}$$

$$(i = \text{He, Ne, Ar, Kr, Xe}) \quad (1)$$

where  $C_i^*(T, S, P)$  are the moist air solubility equilibrium concentrations in  $\text{cm}^3\text{STP/g}$  as functions of water temperature, salinity, and total atmospheric pressure,  $A$  is the STP-volume of dry “excess air” per g of water,  $z_i$  is the volume fraction of gas  $i$  in dry air,  $F$  is the fractionation parameter describing the degree of diffusive re-equilibration, and  $D_i$  are the molecular diffusion coefficients.

### STABLE ISOTOPES

The atoms of an element which do not decay with time or take infinite time to decay are called stable isotopes. Water stable isotopes ( $\delta_{18}\text{O}$  and  $\delta^2\text{H}$ ) are tracers of physical processes water molecules undergo between evaporation from the ocean and arrival in the aquifer via recharge by rainfall (Clark and Fritz, 1997; Krishan et al, 2012a,b; 2013a,b; 2014d,f; 2015e) and are considered powerful tool to trace the origin and movement of water throughout the hydrological cycle. As  $\text{H}_2\text{O}$  molecules travel through hydrological cycle, various isotopic molecular species, having different isotopic combinations of oxygen ( $^{18}\text{O}$  and  $^{16}\text{O}$ ) and hydrogen ( $^1\text{H}$  and  $^2\text{H}$  or  $\text{D}$ ) in them are differentially partitioned between vapour, liquid and solid phases, imparting distinguishable isotopic signature to all the three phases. Long-term average amount weighted isotope values for precipitation can be used to compare with groundwater isotope values to understand recharge sources and processes (Lapworth et al., 2014b, 2015).

A water molecule is formed by combination of two hydrogen atoms (any two of the two stable isotopes;  $^1\text{H}$  and  $\text{D}$ ) and one oxygen atom (any one of the three stable isotopes  $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ ). Thus, 9 possible combinations of these 2 isotopes of hydrogen and 3 isotopes of oxygen are possible and the four most abundant isotopic molecules of water are given in

Table 1 along with their relative abundance and molecular masses.

Table 1 : The four most abundant isotopologues of water and their molecular masses

Isotopologue	$\text{H}_2^{16}\text{O}$	$\text{H}_2^{18}\text{O}$	$\text{H}_2^{17}\text{O}$	$\text{HD}^{16}\text{O}$	$\text{D}_2^{16}\text{O}$
Relative natural abundance	99.78%	0.20%	0.03%	0.0149%	0.022 ppm
Molecular mass	18	20	19	19	20

There are 4 commonly used international standard reference materials, namely, SMOW (Standard mean ocean water), VSMOW (Vienna standard mean ocean water), SLAP (Standard Light Antarctic Precipitation) and GISP (Greenland Ice Sheet Precipitation). The values of measured abundance ratios ( $^2\text{H}/^1\text{H}$  and  $^{18}\text{O}/^{16}\text{O}$ ) in SMOW and VSMOW are given in Table 2 while SLAP and GISP are given in Table 3.

Table 2 : Measured abundance ratios in international standard reference material

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

Table 3 : The oxygen and hydrogen isotopic compositions of SLAP and GISP

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

### Sample Collection and Analysis

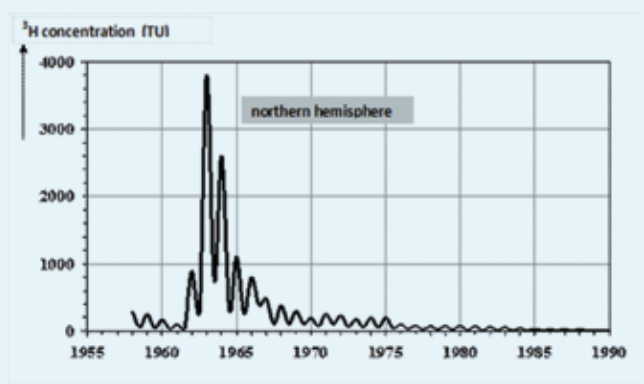
Stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) are analysed on DI-IRMS and CF-IRMS with the minimum error limit within  $\pm 0.1\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 1\text{‰}$  for  $\delta\text{D}$ . The isotopic analyses ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) of collected water samples are done by standard equilibration method in which water samples are equilibrated with  $\text{CO}_2$  and  $\text{H}_2$  (Epstein and Mayeda 1953, Brenninkmeijer and Morrison 1987). The samples are analysed using a Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) to measure oxygen ( $^{18}\text{O}/^{16}\text{O}$ ) and Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS) to measure  $\text{D}/\text{H}$  ratio.  $\delta_{18}\text{O}$  and  $\delta\text{D}$  values are computed using a triple point calibration equation with Vienna standard mean ocean water (V-SMOW), Greenland ice sheet precipitation (GISP) and Standard light Antarctic precipitation (SLAP) standards. The results are expressed by convention as parts per thousand deviations from the V-SMOW the calculation as follows:

$$\delta_{\text{sample}} = [(R_{\text{sample}} - R_{\text{V-SMOW}}) / R_{\text{V-SMOW}}] \times 1000$$

Where, R is the ratio of D/H or  $^{18}\text{O}/^{16}\text{O}$  in sampled water ( $R_{\text{sample}}$ ) or in VSMOW ( $R_{\text{V-SMOW}}$ ).

## ENVIRONMENTAL TRITIUM

Tritium - the radioactive isotope of hydrogen released from thermonuclear explosions in the atmosphere made possible a way for groundwater age dating and recharge estimations. The cosmogenically produced tritium is found entirely in atmospheric vapour and is brought down to earth's surface by precipitation. Before 1952, the tritium concentration in precipitation was low. When thermonuclear tests in the atmosphere began in 1952, tritium concentrations in precipitation suddenly increased and reached a record-high concentration in 1963-64 in the northern hemisphere (Fig. 5).

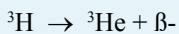


**Fig. 5** : Smoothed curve representing the average  $^3\text{H}$  content of precipitation over the continental surface of the Northern hemisphere.

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



$^3\text{H}$  enters the hydrologic cycle after oxidation to  $^1\text{H}_3\text{HO}$  and finally decays according to:



with  $E_{\beta_{\text{max}}} = 18 \text{ keV}$  and a half-life of 12.430 years (Unterweger et al., 1980).

To clearly understand the residence time of the groundwater in different aquifers the environmental tritium is also a good option where we have to analyse the samples of rain, river and groundwater samples.

## Sample Collection and Analysis

Water samples from precipitation, river water and groundwater from different depths are collected for environmental tritium analysis. To ensure sampling from the concerned aquifer is done the groundwater is flushed adequately or till constant pH and EC is achieved. Then the water samples (600 ml) are collected in air/water tight polypropylene (plastic) bottles after rinsing the bottles by the groundwater that is to be sampled.

Tritium activity is measured in an ultra low level liquid scintillation counter (Quantulus, Perkin Elmer) following electrolytic enrichment. 1 TU is defined as the presence of one tritium in  $10^{18}$  atoms of hydrogen (H) or 0.12 Bq/l water.

## Acknowledgement

Author thanks Director, National Institute of Hydrology, Roorkee; Prof. Alan MacDonald, Dr. Dan Lapworth, Dr. Helen Bonsor, UK for support and encouragement.

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