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Submitted in partial fulfilment of the requirements for the
award of the degree of

# Master of Science

# In

# Geology

By

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**Under the supervision of**

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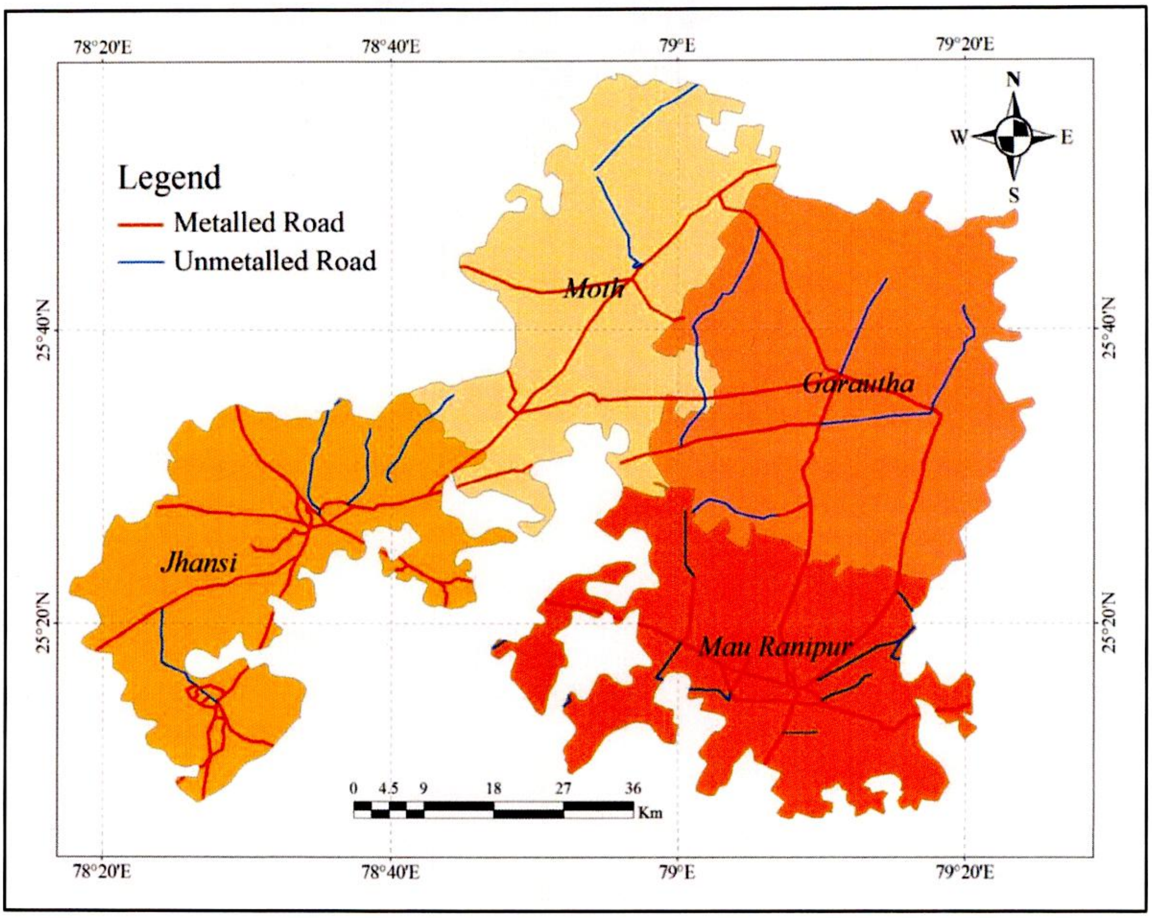
**Roorkee – 247667**
**(Year 2015-16)**

# "ISOTOPIC INVESTIGATIONS OF GROUNDWATER OF MOTH BLOCK OF JHANSI DISTRICT, BUNDELKHAND REGION"



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Date: 15 April 2016

SKINDAR KHAN

# ABSTRACT

Isotopes in hydrology give a direct insight into the movement and distribution processes within the hydrological system. Water in its natural state contains environmental isotopes and conclusions may be drawn from their abundance variations. The isotopes commonly employed in hydrological investigations are the heavy stable isotopes of the water molecule, deuterium and oxygen-18 and the radioactive isotopes, tritium and carbon-14. The stable isotopes are excellent indicators of the circulation of water, while the radioactive isotopes are of special value in detecting the residence time, assuming no contamination of the water has occurred. The application of these techniques in connection with surface and groundwater in India are discussed briefly with four case studies. It can be concluded that these techniques complement the more traditional hydrological and hydrogeological methods employed in water resource investigations and that their use should be encouraged. In recent years, the increasing threat to ground water quality due to human activities has become a matter of great concern. Jhansi area sprawling and incoming of new industries around it have increased concern about the fate of groundwater quality. The report presents an assessment on isotopes composition of groundwater quality index of Moth block of district Jhansi. Twenty groundwater samples from different places of study area (Moth block) were collected The stable isotopes of oxygen and hydrogen incorporated in the water molecule ($^{18}O$ and $^{2}H$) have become an important tool not only in Isotope Hydrology, routinely applied to study the origin and dynamics of surface and ground waters, but also in studies related to atmospheric circulation and palaeoclimatic investigations. A proper understanding of the behaviour of these tracers in the water cycle is required for a meaningful use of these tools in any of these disciplines. Our knowledge of the vertical distribution and the factors controlling the stable isotope ratios of oxygen and hydrogen in atmospheric moisture derives from a limited number of observations and vertical profiles in the atmosphere. An international programme jointly operated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO), and operational since 1961, has resulted in the development of a dedicated database to monitor isotope ratios in precipitation in more than 500 meteorological stations world-wide. The main features of the spatial and temporal variations of stable isotope ratios of oxygen and hydrogen in precipitation and atmospheric moisture at the global scale are presented based on the analysis of limited data on water vapour, data obtained by the Global Network for Isotopes in Precipitation (GNIP) and the few observations at high latitudes.

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# CHAPTER 1

## 1.0 Introduction

The depletion in availability of water quantity and deteriorating water quality has posed a threat to the country, because these problems affect the lives of millions of people. The rapid growth of population coupled to steady increase in water requirements for agricultural and industrial development have imposed severe stress on the available freshwater resources in terms of both the quantity and quality, requiring consistent and careful management of water resources for their sustainable development.

For acquiring better quality of water, we need the continuation and extension of hydrological research. In this respect, the development and practical implementation of isotope methodologies in water resources management has proved to be very important. Isotope studies applied to a wide spectrum of hydrological problems, related to both surface and groundwater resources, as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, often referred to as "Isotope Hydrology".

Isotopes have wide applications in hydrological investigations and provide vital information for the better management of water resources. Isotopes (stable and radioactive) of both environmental as well reactor produced are routinely used as tracers in hydrology for various hydrological investigations (1) e.g., aquifer-aquifer interconnection, surface water-groundwater interrelation, source of groundwater salinity and pollution, origin of geothermal waters, efficacy of artificial recharge, dynamics in lakes, source of recharge & estimation of recharge to the groundwater etc.

A water molecule undergoes various natural phenomena in a hydrological cycle of which the two main physical processes responsible for the formation of precipitation are evaporation and condensation. When water from the ocean evaporates the lighter isotopes of hydrogen and oxygen go into vapour form preferentially while in condensation process the heavier isotopes will condense preferentially. Both these processes impart the variation of isotopic composition in the water molecules by fractionation of isotopes. The extent of such variation depends on various meteorological conditions, i.e. temperature, humidity, state of equilibrium of the process etc. In spite of several contributing factors, actual variation in isotopic composition in meteoric waters even at global scale is very small, which is measured using Isotope Ratio Mass Spectrometer (IRMS).

Groundwater in India is at risk of contamination due to rapid and unplanned urbanization, industrialization and indiscriminate disposal of domestic, industrial, agricultural and mining wastes. Public ignorance of environment and related considerations, lack of provisional basic social services, indiscriminate disposal of increasing anthropogenic wastes, unplanned application of agrochemicals, and discharges of improperly treated sewage/industrial effluents; result in excess accumulation of pollutants on the land surface and contamination of water resources. Subsurface leaching of contaminants from landfills as well as seepage from canals, rivers and drains cause severe degradation of the groundwater quality in urban areas. Adsorption/dispersion processes in the soil zone, degrees of evaporation/ recharge and lateral inter-mixing of groundwater determine the level of contaminations in groundwater. In recent years, scarcity of clean and potable drinking water has emerged as the most serious developmental issue in the major cities of India.

In Uttar Pradesh, due to the rising population and thereby increasing demand of water for various purposes its scarcity is becoming evident and getting prominent day by day. In addition to these there are regional imbalances on account of spatial and temporal distributions. Conspicuous to frequent climatic and hydrological droughts, the Bundelkhand region in Uttar Pradesh (and also in Madhya Pradesh) experiences severe agricultural droughts. With majority of population living below poverty line and their livelihood dependant on agriculture and livestock rearing, severe scarcity of food grains and fodder has hit hard on their lives. Administratively, Uttar Pradesh portion of Bundelkhand region (herein after called as UP Bundelkhand) comprises of 48 blocks under the jurisdiction of 7 districts. The geographical area of the UP-Bundelkhand is 2.94 Mha which is about 12.21% of that of the State. Depending upon the economic considerations and infrastructure development, UP-Bundelkhand is the poorest region in comparison with western, central and eastern regions of the state. Natural and other resources are distinct and abundant in case of western, central and eastern regions; southern region, i.e., U.P. Bundelkhand has only 4.96% of the State's Population, low population density of 280. This region is prone to frequent floods and droughts; only recently, a severe continuous four year cycle drought (2004-08) has been witnessed in the region. Bundelkhand region in central plains in India is situated between longitude $78^0$ 20'N and $81^0$ 40'N and latitude $23^0$ 20'E and $26^0$ 20'E and comprises of 13 districts covering 7.08 Million Hectares (Mha), out of which six districts comprising of 4.12 Mha are in Madhya Pradesh and seven districts comprising of 2.94 Mha are in Uttar Pradesh. The districts in Madhya Pradesh are Sagar, Damoh, Datia, Panna, Chattarpur, and Tikamgarh and in Uttar Pradesh are Jhansi, Lalitpur, Jalaun, Hamirpur, Banda, Mahoba and Chitrakoot. The area is bounded by Vindhyan Plateau in south to river Yamuna in north, river Ken in east and rivers Betwa, Sindh and Pahuj in west. While the geographical area of Bundelkhand region in Madhya Pradesh is

39% more than that in Uttar Pradesh, population in Bundelkhand region of Madhya Pradesh is around 28 % lesser than that in Uttar Pradesh. Despite the fact that normal rainfall in Madhya Pradesh portion is 17 % more than that in Uttar Pradesh and rainfall pattern being more drought prone in Uttar Pradesh as compared to Madhya Pradesh, higher percentage of population in Uttar Pradesh is attributed to age old and higher level of development of irrigation in Uttar Pradesh. About 82% of the population is dependent on agriculture in both the States. While the Yamuna flows from west to east, its first order tributaries viz., Betwa, Ken, Sindh, Pahuj, Gharara, Bagain and Paisuni flow from south to north. Second order tributaries of the Yamuna namely, Dhasan, Jamuni, Birma, Sonar, Patna, Bewas, Kopra etc., also drain the area. The entire drainage forms a part of Ganga basin. The region generally slopes from south to north. The elevations in the area range from 626 m above mean sea level (amsl) in southern part to 93 m amsl near the Yamuna. The area in Madhya Pradesh is conspicuous of undulating rocky ravine topography coupled with level plains, while the area in Uttar Pradesh gradually slopes from mild ravines to level plains near the Yamuna. Almost entire region of Bundelkhand (UP and MP) is prominently of Vindhyan rocks in southern part and Granites of different kinds at different depths with alluvium soils on top mixed with rocky and boulder outcrops here and there. The geology, hydro-geology, hydrology, soils and the climatic distribution are directly responsible for the agricultural growth and consequently to the livelihood of people in Bundelkhand (both UP and MP).

## 1.1 Basic of Isotope Technique

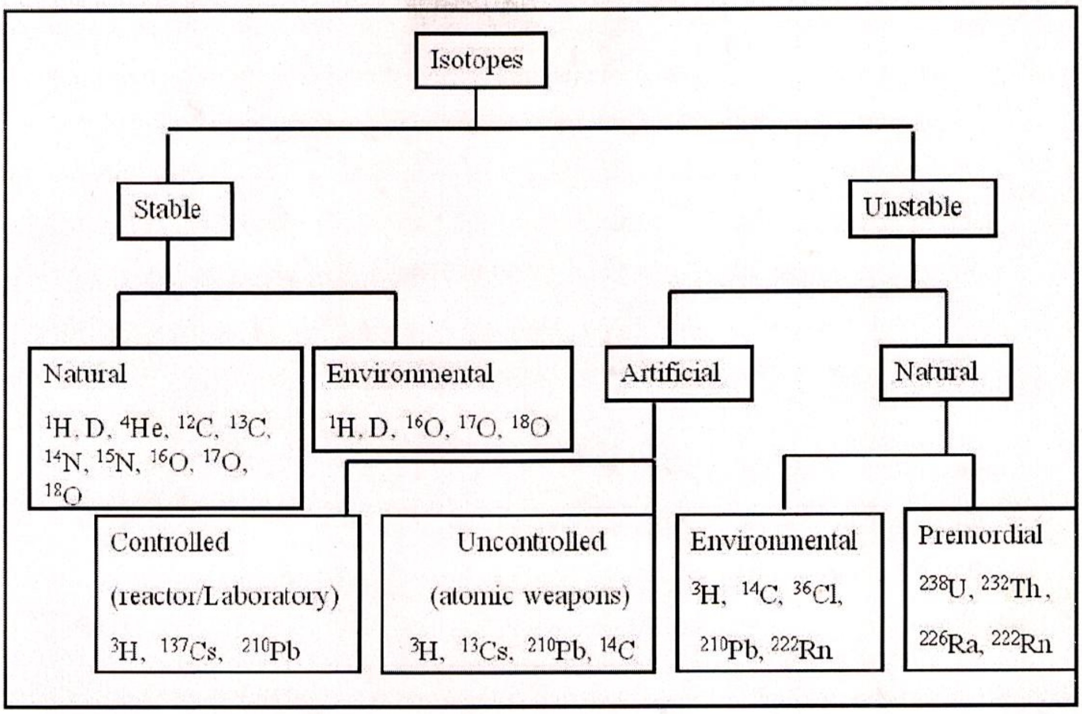
Isotopes are the atoms of an element having same atomic number (Z) but different atomic weight (A). In other words, the atoms of an element having different number of neutrons (N) but same number of protons or electrons are called isotopes. For example, hydrogen has three isotopes having the same atomic number of 1 but different atomic masses or weights of 1, 2 and 3 respectively i.e., ${}^{1}_{1}H_{0}$, ${}^{2}_{1}H_{1}$ and ${}^{3}_{2}H_{2}$.

Similarly oxygen has eleven isotopes, $^{12}$O, $^{13}$O, $^{14}$O, $^{15}$O, $^{16}$O, $^{17}$O, $^{18}$O, $^{19}$O, $^{20}$O, $^{21}$O and $^{22}$O, but except $^{16}$O, $^{17}$O, and $^{18}$O all other isotopes are radioactive and their existance in nature is very small ( half life vary from 150 seconds to few femo 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.

## 1.2 Classification of Isotopes

Isotopes can be classified in two important categories, (i) stable isotopes and (ii) unstable isotopes. Stable isotopes are the atoms of an element, which are satisfied with the present arrangement of proton, neutron and electron. On the other hand, unstable isotopes are the atoms of an element which do not satisfy with the present arrangement of atomic particles and disintegrate by giving out alpha ( $\alpha$ ), beta ( $\beta$ ) particles and/or gamma ($\gamma$) radiation etc. and transform into an another type of atom. This process continued till the stable nuclide (element) is formed. Because of disintegration or the property of giving out radiation, the unstable isotopes are also called radioactive isotopes. For example, $^{1}H$ and $^{2}H$ are stable isotopes while $^{3}H$ is unstable. Similarly $^{12}C$ and $^{13}C$ are stable isotopes while $^{14}C$ is unstable. On the other hand, isotopes of oxygen ($^{16}O$, $^{17}O$ and $^{18}O$) are stable.

Isotopes can also be classified as natural and artificial isotopes, i.e., the isotopes that occur naturally are called natural isotopes while those produced in a reactor or laboratory under controlled conditions are known as artificial isotopes. Normally the artificially produced isotopes are radioactive while stable and radioactive, both types of isotopes occur naturally. Another category of isotopes has been devised that is called environmental isotopes. These isotopes have different types of categories i.e. naturally occurring stable and radioactive isotopes and radioisotopes introduced into the atmosphere due to anthropogenic activities etc. The environmental radioisotopes whether naturally occurring due to cosmic ray interaction with various gaseous molecules or anthropogenically produced and become the part of hydrological cycle are safe in normal conditions and do not pose any threat to human health. The following diagram gives a clear picture about the classification of various isotopes.



## 1.3 Stable Isotopes

As described earlier, the atoms of an element which do not decay with time or take infinite time to decay are called stable isotopes of that element. Over 2000 isotopes of 92 naturally occurring elements have been identified out of which several hundred are stable isotopes. But for hydrological investigations, we talk much about hydrogen and oxygen stable isotopes. As we know water molecule is made up of two hydrogen atoms and one oxygen atom therefore, many combinations ($^{18}O$) are possible out of which $^{1}H^{1}H^{16}O$, $^{1}H^{1}H^{16}O$, $^{1}HD^{16}O$, 'HD$^{18}$O, $^{1}H^{1}H^{17}O$ and $^{1}HD^{17}O$ are important. The natural occurrence of few very important types of water molecules is given below:

$H_2{}^{16}O$ ~ 997640 ppm (99.7640 %)
$H_2{}^{18}O$ ~ 2040 ppm (0.204 %)
$HD^{16}O$ ~ 320 ppm (0.032 %)

There are few other stable isotopes ($^{3}He$, $^{6}Li$, $^{11}B$, $^{13}C$, $^{15}N$, $^{34}S$, $^{37}Cl$, $^{81}Br$ and $^{87}Sr$) which have been found useful in many hydrological studies. These stable isotopes are popularly called environmental stable isotopes as they are available in the environment and introduced in the hydrological cycle naturally. Thus the investigator does not require them to either purchase or inject into the system for carrying out hydrological studies.

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. For example heavy water $^{2}H_2{}^{16}O$ ($D_2{}^{16}O$) has a mass of 20 compared to normal water $^{1}H_2{}^{16}O$ which has a mass of 18. Similarly heavier stable molecule of water $D_2{}^{18}O$ has a mass 22. This is because of the variation in the number of neutrons. However, the absolute abundance ratio of isotopes is not usually measured in natural waters and in other components. Only the relative difference in the ratio of the heavy isotopes to the more abundant light isotope of the sample with respect to a reference is determined. The difference is designated by a Greek letter $\delta$ and is defined as follows:

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

Where R's are the ratios of the $^{18}O/{}^{16}O$ and D/H isotopes in case of water.

The difference between samples and references are usually quite small, $\delta$ values are therefore, expressed in per mille differences (‰) i.e. per thousand, $\delta$ (‰) = $\delta$ x 1000.

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

If the $\delta$ 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 VSMOW (Vienna Standard Mean Ocean Water)

Craig evaluated the isotopic ratios of SMOW as;

$$^{18}O/{}^{16}O = (1993.4 \pm 2.5) \times 10^{-6} \text{ and } D/H = (158 \pm 2) \times 10^{-6}$$

VSMOW has the same $^{18}O$ content as defined in SMOW but its D-content is 0.2 ‰ lower.

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 SLAP (Standard light Antarctica precipitation), and GISP (Greenland ice sheet precipitation).

**Table 1: Stable isotopes with their natural abundance and reference standards used for ratio measurements**

| Isotope | Ratio | % natural Abundance | Reference (abundance ratio) | Commonly measured phases |
|---|---|---|---|---|
| $^{2}H$ | $^{2}H/^{1}H$ | 0.015 | VSMOW ($1.5575 . 10^{-4}$) | H2O, CH2O, CH4, H2, $OH^-$ |
| $^{3}He$ | $^{3}He/^{4}He$ | 0.000138 | Atmospheric He ($1.3. 10^{-6}$) | He in water or gas, crustal fluids, basalt |
| $^{6}Li$ | $^{6}Li/^{7}Li$ | 7.5 | L-SVEC ($8.32 . 10^{-2}$) | Saline waters, rocks |
| $^{11}B$ | $^{11}B/^{10}B$ | 80.1 | NBS 951 (4.04362) | Saline waters, clays, Borate, |
| $^{13}C$ | $^{13}C/^{12}C$ | 1.11 | VPDB ($1.1237. 10^{-2}$) | CO2, carbonate, DIC, CH4, |
| $^{15}N$ | $^{15}N/^{14}N$ | 0.366 | AIR N2 ($3.677.10^{-3}$) | $N^2$, NH4 , NO3 , N-<br>+ - |
| $^{18}O$ | $^{18}O/^{16}O$ | 0.204 | VSMOW ($2.0052 . 10^{-3}$)<br>VPDB ($2.0672 . 10^{-3}$) | H2O,CH2O,CO2, sulphates $NO^-$, carbonates,silicates |
| $^{34}S$ | $^{34}S/^{32}S$ | 4.21 | CDT ($4.5005. 10^{-3}$) | Sulphates, sulphides, H2S, S-organics |
| $^{37}Cl$ | $^{37}Cl/^{35}Cl$ | 24.23 | SMOC (0.324) | Saline waters, rocks, |
| $^{81}Br$ | $^{81}Br/^{79}Br$ | 49.31 | SMOB | Developmental for saline waters |
| $^{87}Sr$ | $^{87}Sr/^{86}Sr$ | $^{87}Sr$=7.0<br>$^{86}Sr$=9.86 | Absolute ratio measured | Water, carbonate |

### 1.4 Radioactive Isotopes

The phenomenon of disintegration of unstable atoms to the stable form is called radioactivity. The unit of radioactivity is denoted by Curie (Ci) and one Curie is equal to $3.7 * 10^{-10}$ disintegrations per second. In case of very low activity, it is also denoted by Becquerel (Bq) and one Becquerel is equal to one disintegration per second (1 dps). The activity per unit gram is known as specific activity and it is denoted by Curies/mille Curies/micro Curies per gram. The energy of disintegration or radiation is denoted by KeV or MeV.

### Half Life

The time in which the radioactive element decays to one half (1/2) of its initial strength is known as half life. Different radioisotopes have different half lives and the decay rate is a characteristic property of an atom.

### Radioactive Isotope of carbon

Carbon-14 is produced in the atmosphere primarily due to interaction of cosmic rays with nitrogen gas molecule. It is also produced due to various anthropogenic activities like burning of fossil fuel etc.

$^{14}N + n \rightarrow {}^{14}C + p$

Thermal neutrons required are produced by reactions between very high-energy primary cosmic ray protons and molecules of the atmosphere. $^{14}C$ thus formed very soon oxidises to $^{14}CO$, and ultimately to $^{14}CO2$ which mixes with the inactive atmospheric CO2 and becomes part of the atmospheric CO2 reservoir. Like tritium, carbon-14 has also been added to the atmosphere since 1952 as a result of testing thermonuclear devices. The $^{14}C$ concentration before the thermonuclear tests was about 100% modern carbons (pmc). This corresponds to 13.56 dpm/g of carbon. The thermonuclear tests increased the atmospheric $^{14}C$ concentrations in the northern hemisphere from 100 pmc to nearly twice that value. The atmospheric $^{14}C$ peaked in 1963 and decreased subsequently due to moratorium of tests. $^{14}C$ decays according to: $^{14}C \rightarrow {}^{14}N + \beta^-$ with maximum $\beta^-$ energy of 156 keV and a half-life of 5730 ± 40 years (Godwin, 1962).

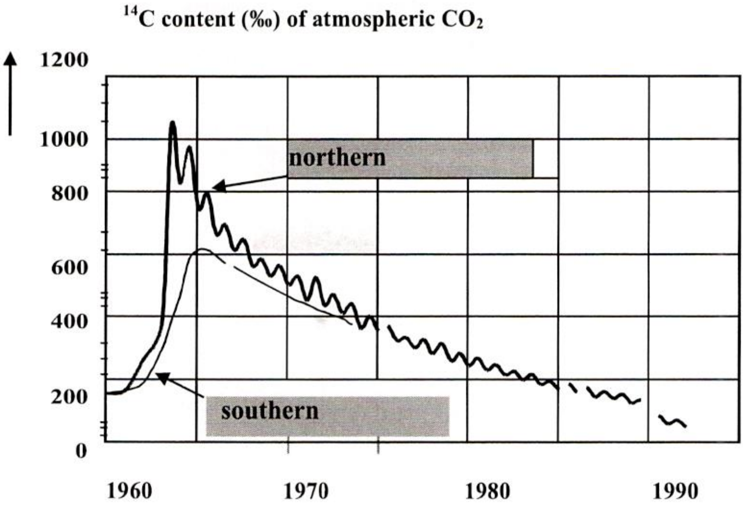


**Figure 1: Curve representing the natural $^{14}$C northern hemisphere content of atmospheric CO2 (data for Nordkapp, Norway, representative for the northern hemisphere).**

Originally the half-life was thought to be 5568 years, right half-life, because of the natural variations in the $^{14}$C content of atmospheric CO2 during geologic times and deviating from the present. These errors were even larger. Nowadays the *$^{14}$C calibration*, based on the known $^{14}$C content of tree rings with exactly known age, removes both errors at once.

Carbon-14 is not an isotopic tracer of water molecule and like $^{13}$C occurs in water as various species of DIC. The non conservative nature of Carbon-14 as a tracer for water molecule demands the use of complete water chemistry as well as measurement of $\delta^{13}$C of DIC for proper interpretation of $^{14}$C data. Atmospheric CO2 exchanges with oceanic dissolved carbon (primarily bicarbonate) and most $^{14}$CO2 molecules enter the oceans and living marine organisms. Some are also assimilated by land plants, so that all living organisms, vegetable as well as animal, contain $^{14}$C in concentrations about equal to that of atmospheric CO2. The principal input of $^{14}$C to the groundwater occurs in the unsaturated zone where the partial pressure of CO2, as a result of root respiration and decay of organic matter, is normally higher than CO2 dissolved in precipitation. Commonly the CO2 pressure in soil reaches or exceeds $10^{-2}$ atmosphere. Production of carbon 14 in atmosphere and its assimilation with water is shown in ***Figure*** .2

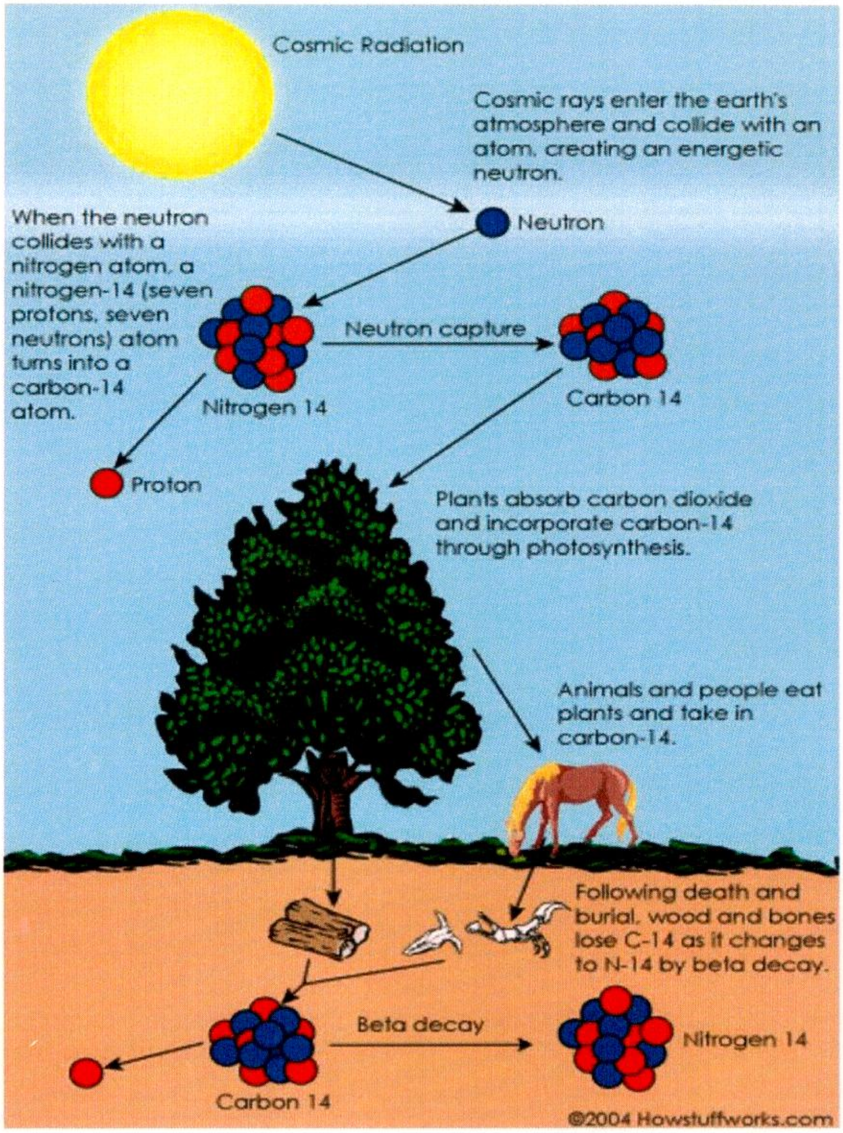


**Figure 2: Origin and distribution of $^{14}C$ in nature**

These processes produces large amount of $HCO3^{-}$ (or $CO3^{-2}$ depending on the pH). In the above reaction the dissolved carbon comes from both biogenic as well as solid carbonate. Hence the carbon-14 activity of biogenic CO2 will be diluted by carbon coming from leaching of carbonate which could be very old and hence carbon-14 free. This leads to dilution of the initial carbon-14 content.

The use of $^{14}C$ as a dating tool is based on the following decay equation $A = A0\ e^{--\lambda t}$ and hence

$t = 8270 \ln A_o/A_t$

Where, $A_o$ and $A_t$ are the initial and final $^{14}C$ activities respectively.

In routine $^{14}C$ dating initial $^{14}C$ content is known by analysis of tree rings. However in hydrology the situation is much more complicated, the origin of C in water is less certain than that it is for plant and animal carbon.

Many different models have been suggested in the literature for predicting the initial $^{14}C$ activity. The carbon-14 method can be used for dating groundwater in the range 3000 to 40,000 years

***Radioactive Isotope of Hydrogen***

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

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

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

$$^{3}H \rightarrow {}^{3}He + \beta^{-}$$

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

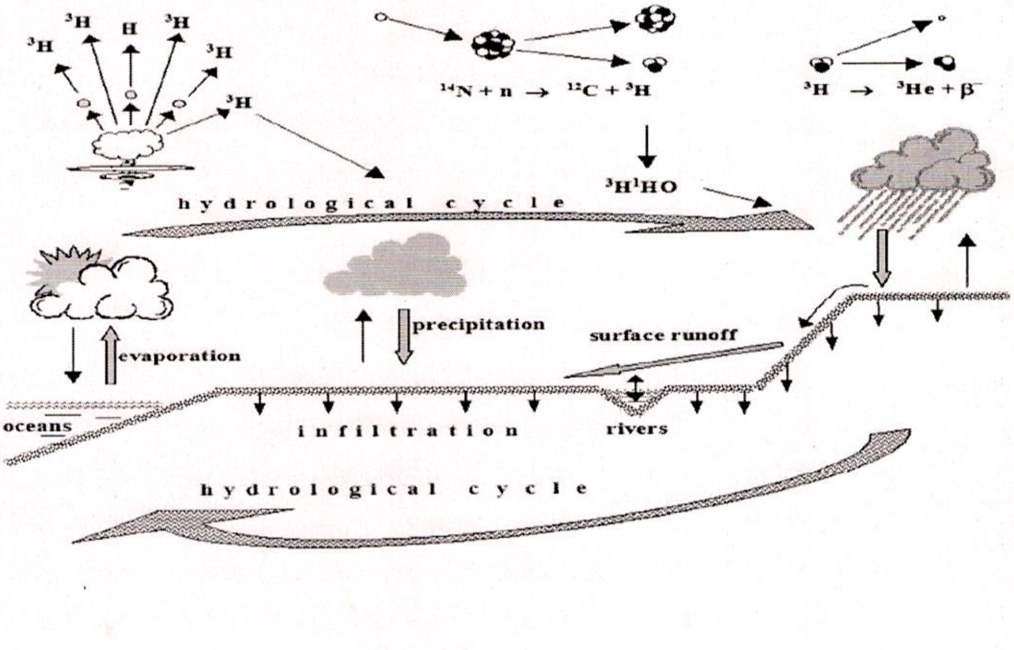


**Figure 3: Origin and distribution of 3H in nature. Contrary to 14C, the turnover of 3H is very fast, except where it is fixed in glacier ice or groundwater**

According to a recent re-evaluation, a more preferable value is 4500 ± 8 days (equivalent to

12.32 year).

Under undisturbed natural conditions the 3H concentration in precipitation was probably about 5 TU, which is equivalent to a specific activity of about 0.6 Bq/L (Roether, 1967).

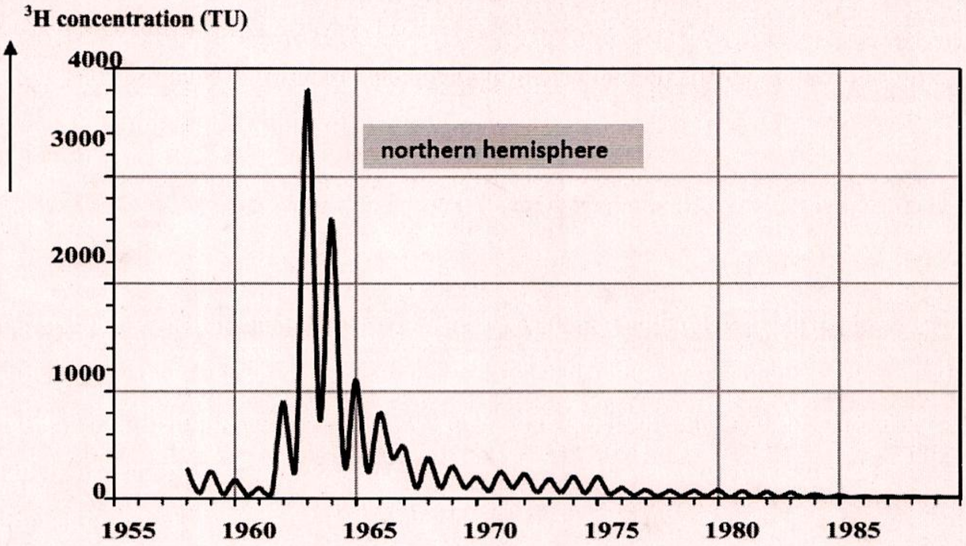


**Figure 4: Smoothed curve representing the average 3H content of precipitation over the continental surface of the Northern hemisphere.**

However, tritium is also produced in the atmosphere due to testing of atomic devices similar to cosmogenic tritium. The level of tritium in atmosphere increased due to the testing of nuclear devices during 1960-70.

Tritium is also produced artificially under controlled conditions in laboratory/ reactor.

### 1.5 Environmental Isotopes

Environmental isotopes, both stable and radioactive (unstable), occur in the Earth's environment in varying concentrations with respect to location and time over which the investigator has no direct control. Environmental isotopes are neither required to be purchased nor to be injected as these are freely available and automatically injected in the hydrological cycle. Earlier only artificially produced radioactive isotopes were used but with the better instrumentation facilities, now a day environmental isotopes are used more and more except in few cases where artificial radioisotopes can only be useful.

The most commonly used environmental stable isotopes are Deuterium (D), Oxygen-18 ($^{18}$O), Carbon-13 ($^{13}$C) and radioisotopes Tritium ($^{3}$H) and Carbon-14 ($^{14}$C), Nitrogen-15 ($^{15}$N), Chlorine-36 etc. Silicon-32 ($^{32}$Si), Caesium-137 ($^{137}$Cs) and Lead-210 ($^{210}$Pb) etc. are also used as environmental radioisotopes for few specific studies in Hydrology.

Silicon-32 ($^{32}$Si) is potentially attractive because, its half life (100 yr) is between that of $^{3}$H and $^{14}$C. A number of measurements have been made in India but, it has not been used widely. Argon-39 ($^{39}$Ar) has also been investigated and research is still in progress, but the disadvantage of using both $^{32}$Si and $^{39}$Ar is that large amount of water (a few tons) is required to provide required amount of sample for measurement.

**Table 2: Environmental Stable Isotopes:**

| **Isotope** | **Ratio** | **%natural abundance** | **Reference (ppm)** | **Commonly measured phases** | **Application in hydrology** |
|---|---|---|---|---|---|
| $^{2}$H | $^{2}$H/$^{1}$H | 0.015 | VSMOW (155) | H | Origin of water |
| $^{13}$C | $^{13}$C/$^{12}$C | 1.11 | VPDB | CO , Carbonates 2 | Carbonates source |
| $^{15}$N | $^{15}$N/$^{14}$N | 0.366 | Air N2 (3677) | N , NH NO | Source of pollution |
| $^{18}$O | $^{18}$O/$^{16}$O | 0.204 | VSMOW (2005) | H O.CO . SO $^{-2}$. | Origin of water |
| $^{34}$S | $^{34}$S/ $^{32}$S | 4.21 | CDT | SO $^{-2}$,Sulphides, H S | Origin of salinity, Redox condition of |
| $^{37}$Cl | $^{37}$Cl/ | 24.23 | SMOC (0.324) | Saline waters | Source of pollution |
| $^{87}$Sr | $^{87}$Sr/ | 07.00 | USGS Tridacna, | Solution | Provenance of water |
| $^{11}$B | $^{11}$B/$^{10}$B | 80.1 | NISTRM 951 – (Sodium borate) | Solution | Source of pollution |

**Table 3: Environmental Radioisotopes**

| **Isotope** | **Half life (years)** | **Type** | **Energy( MeV)** | **Applications in hydrology** |
|---|---|---|---|---|
| Tritium ($^{3}$H) | 12.3 | β | 0.019 | Young groundwater dating |
| Carbon ($^{14}$C) | 5730 | β | 0.156 | Old groundwater dating |
| Chlorine-36 ($^{36}$Cl) | $3.1 \times 10^{5}$ | β | 0.714 | Very old groundwater dating |
| *Cesium-137 ($^{137}$Cs) | 30 | γ | 0.661 | Sediment dating |

## 1.6 Artificial Isotopes

Artificial isotopes are used primarily to provide the necessary information to solve relatively local hydrological problems like leakage from dams / reservoirs or to define ground water protection zones. They are also used to identify water flow patterns in highly soluble and fractured rocks like karst where the flow of the ground water is relatively fast, measurement of discharge of streams in mountainous regions and estimation of recharge to groundwater due to rainfall and irrigation.

**Table 4: Artificial Radioisotopes**

| Isotope | Half life | Chemical form | Applications in hydrology |
|---|---|---|---|
| Tritium ($^{3}H$) | 12.43 y | HTO | Groundwater recharge rate and flow |
| Cobalt-60($^{60}Co$) | 5.3 y | K [Co(CN) | Groundwater recharge rate |
| Bromine-82($^{82}Br$) | 36 h | NH Br | Groundwater velocity, effluent dispersion |
| Gold-198($^{198}Au$) | 2.7 d | HAuCl | Seepage entry and exit points in dams |

## 1.7 Isotope fractionation

Stable isotope variations result from isotope fractionation which occurs during physical and chemical processes. Examples of physical processes which could lead to isotopic fractionation are evaporation of water or condensation of vapour.

During evaporation, the residual liquid is enriched in the heavier isotope molecule because the lighter molecules move rapidly and hence has a greater tendency to escape from the liquid phase–there is a difference in the volatility between the two molecular species.

Chemical fractionation occurs because a chemical bond involving a heavy isotope is stronger than that with light isotope.

Fractionation may occur during both equilibrium and non-equilibrium conditions. Condensation is predominantly an equilibrium process whereas evaporation occurs under non-equilibrium conditions.

## 1.8 Isotopic Notations and Measurements

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. For example heavy water $^{2}H2^{16}O$ ($D2^{16}O$) has a mass of 20 compared to normal water $^{1}H2^{16}O$ which has a mass of 18. Similarly heavier stable molecule of water $D_2^{18}O$ has a mass 22. This is because of the variation in the number of neutrons. However, the absolute abundance ratio of isotopes is not usually measured in natural waters and in other components. Only the relative difference in the ratio of the heavy isotopes to the more abundant light isotope of the sample with respect to a reference is determined. The difference is designated by a Greek letter$\delta$ and is defined as follows:

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

Where R's are the ratios of the $^{18}O/ {}^{16}O$ and D/H isotopes in case of water.

The difference between samples and references are usually quite small, $\delta$values are therefore, expressed in per mille differences (‰) i.e. per thousand, $\delta$ (‰) = $\delta$ x 1000.

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

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

The reference standards normally considered are SMOW (Standard Mean Oceanic Water) and VSMOW (Vienna Standard Mean Ocean Water)

$(^{18}O/^{16}O)$SMOW = 1.008 $(^{18}O/ ^{16}O)$ NBS-1

(D/H) SMOW = 1.050 (D/H) NBS-1

Craig evaluated the isotopic ratios of SMOW as;

$^{18}O/ ^{16}O = (1993.4 \pm 2.5) \times 10^{-6}$ and $D/H = (158 \pm 2) \times 10^{-6}$

VSMOW has the same $^{18}O$ content as defined in SMOW but its D-content is 0.2 ‰ lower. 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 SLAP (Standard light Antarctic precipitation), NBS-1 and NBS-1A (National Bureau of Standard) and GISP (Greenland ice sheet precipitation).

## 1.9 Global Meteoric Water Line

The relation between $\delta D$ and $\delta^{18}O$ can be written in a standard form (equation for straight line) i.e.;

$\delta D$‰ $= A\, \delta^{18}O + d$. (***Figure 5***).

Where A is the slope and d is the intercept of $\delta D$ - $\delta^{18}O$ line of fresh global meteoric waters.

One can develop regional and local meteoric water lines on the pattern of standard relationship between $\delta D$ and $\delta^{18}O$ valid on regional or local levels.

For northern hemisphere: $\delta D= 8\delta^{18}O + 10$ For southern hemisphere: $\delta D= 8\, \delta^{18}O +22$

New relationship, Rozonski (1993): $\delta D= 8.13\, \delta^{18}O+10.8$

$\delta D$ and $\delta^{18}O$ in water vapours at low altitudes in the atmosphere differs considerably than the isotopic composition in clouds or precipitation.

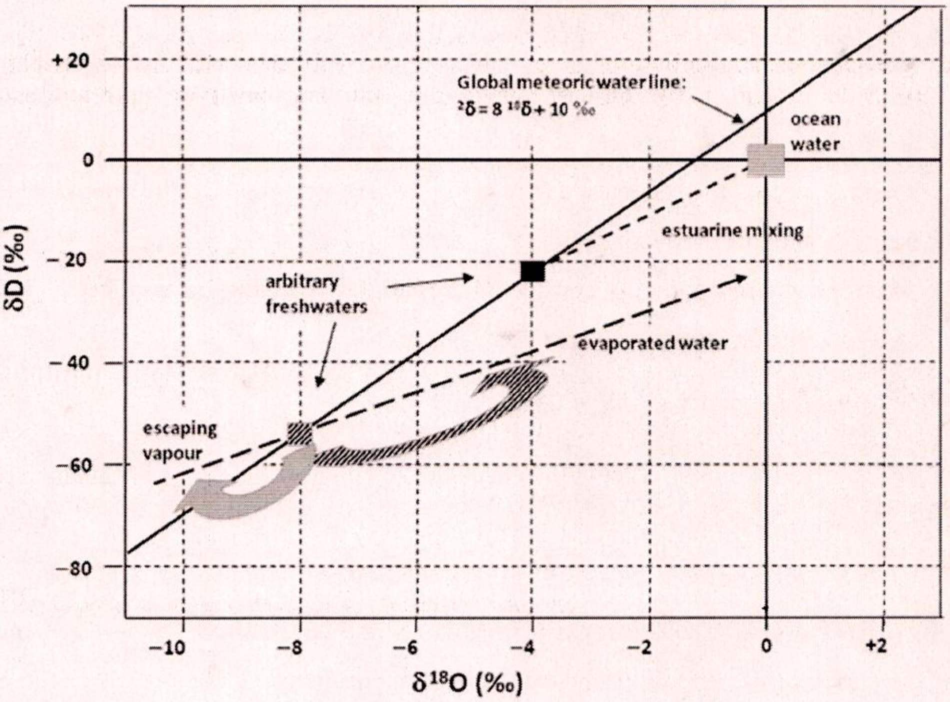


**Figure 5: Relation between $\delta^{18}$and $\delta^{2}$for estuarine mixing and for evaporating surface water. Because the evaporation is a non-equilibrium process, isotope fractionations involved are not necessarily related by a factor of 8, as is the equilibrium condensation process.**

**Isotope Effects**

Variation of isotopic composition in atmosphere is also governed by various factors like, latitude, altitude, distance from sea, amount of rain, etc. These are called as isotope effects and described below.

**Latitude Effect**

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

$\delta^{18}O$ = 0.695 Tannual - 13.6™SMOW; δ D = 5.6 Tannual -100™ SMOW

$\delta^{18}O$ = (0.338± 0.028) Tmonthly - 11.99™VSMOW

On average there is a 1™ decrease in average $\delta^{18}O$ corresponding to the average annual temperature. As latitude increases, the temperature decreases, therefore isotopic composition depleted in precipitation. Polar Regions are located at the highest latitudes and also at the end of Rayleigh rainout process, thus precipitation has maximum depleted values in heavier isotopic composition.

Thus, water vapours or precipitation depletes in heavier isotopes with the increase in latitude. In low latitudes, water vapours depletes very less in heavier isotope species of water molecule. $\delta^{18}O$ varies 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.

### Continental Effect

Precipitation depletes in heavier isotopes of water molecules as clouds move away from the coastal parts.

On average, $\delta\ ^{18}O$ depletes about -2 ‰ per 1000km from seacoast.

Global T-$\delta^{18}O$ relationship - $\delta^{18}O = 0.695T_{annual} -13.6$ ‰ SMOW changes significantly due to continental effect.

### Altitude or Elevation effect

Precipitation progressively depletes in δ-values with increase in altitude.

Mainly due to two reasons:

Decrease in temperature with increase in altitude

Rainout process increases with increase in altitude due to orographic effect.

In general, $\delta^{18}O$ varies between -0.15 to 0.5 ‰ per 100m rise in altitude. δD depleted 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 Effect

Variation of δD and $\delta^{18}O$ due to change in season is called seasonal effects. Mainly two factors are responsible for the seasonal effects

Variation in temperature with respect to seasons and

Change in amount of precipitation.

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

# CHAPTER 2

## 2.0 DESCRIPTION OF THE STUDY AREA

This study is based on the isotopes composition for develop the ground water quality index for drinking and other various purposes. Study area covers the Moth block, Jhansi is located in the Bundelkhand region of central India.

### 2.1 About Jhansi district

Jhansi district in the southwestern part of the Uttar Pradesh lies between $25^0$ 07’ and $25^0$ 57’ north latitude and $78^0$ 10” and $79^0$ 25” east longitudes. Administratively, Jhansi is divided into four Tehsils namely Jhansi, Moth, Gauratha and Mauranipur and eight blocks namely Babina, Badagaon, Bamaur, Bangra, Chirgaon, Gursrai, Mauranipur and Moth. Total geographical area of the district is 5024 sq. km. The total district's population was 1998603 out of which 1057436 were males and 941167 females as per 2011 census. Physiographically, the area can be divided into two zones i.e. Southern Bundelkhand pediplane zone and Northern highly eroding composite Plain zone.

Rainfall is the ultimate source of surface, ground, green and blue water resources for raising biomass and other utilities. The average annual rainfall of Bundelkhand in Uttar Pradesh is 876.1 mm with a range of 786.6 to 945.5 mm. About 90% of the rainfall is received in the monsoon season of July to September in about 30-35 events or spells. Rainfall variation within the season is important for crop production and rain in September is crucial for the maturity of Kharif crops and sowing of Rabi crops. Delayed on set of rains, early withdrawal or long dry spells in between also lead to drought like situation.

Main source of irrigation in the district is through ground water and canal. Total length of canal is 1236 km by which 75235 hectare area is irrigated. There are 89 no. of government tubewells through which 3806 hectare area is irrigated. Irrigation by private tubewell is 8678 hectare. Hence 54% area is irrigated by ground water. Net sown area is 326767 hectare and net irrigated area is 196078 ha. The ratio of net irrigated area to net sown area is 60%. For drinking water supply pipe line schemes and India Mark II hand pump exist in the district. There are 739 India Mark II hand pumps for providing water to 863342 persons. The area is chiefly drained by the river Betwa and minor rivers like Dhasan and Pahuj. The Betwa and Pahuj rivers are tributaries of Yamuna and Dhasan is tributary of Betwa. The major tributaries of Dhasan are the Lakheri, Sukhnai, Kurera etc which are mainly ephemeral. All three main rivers are perennial.

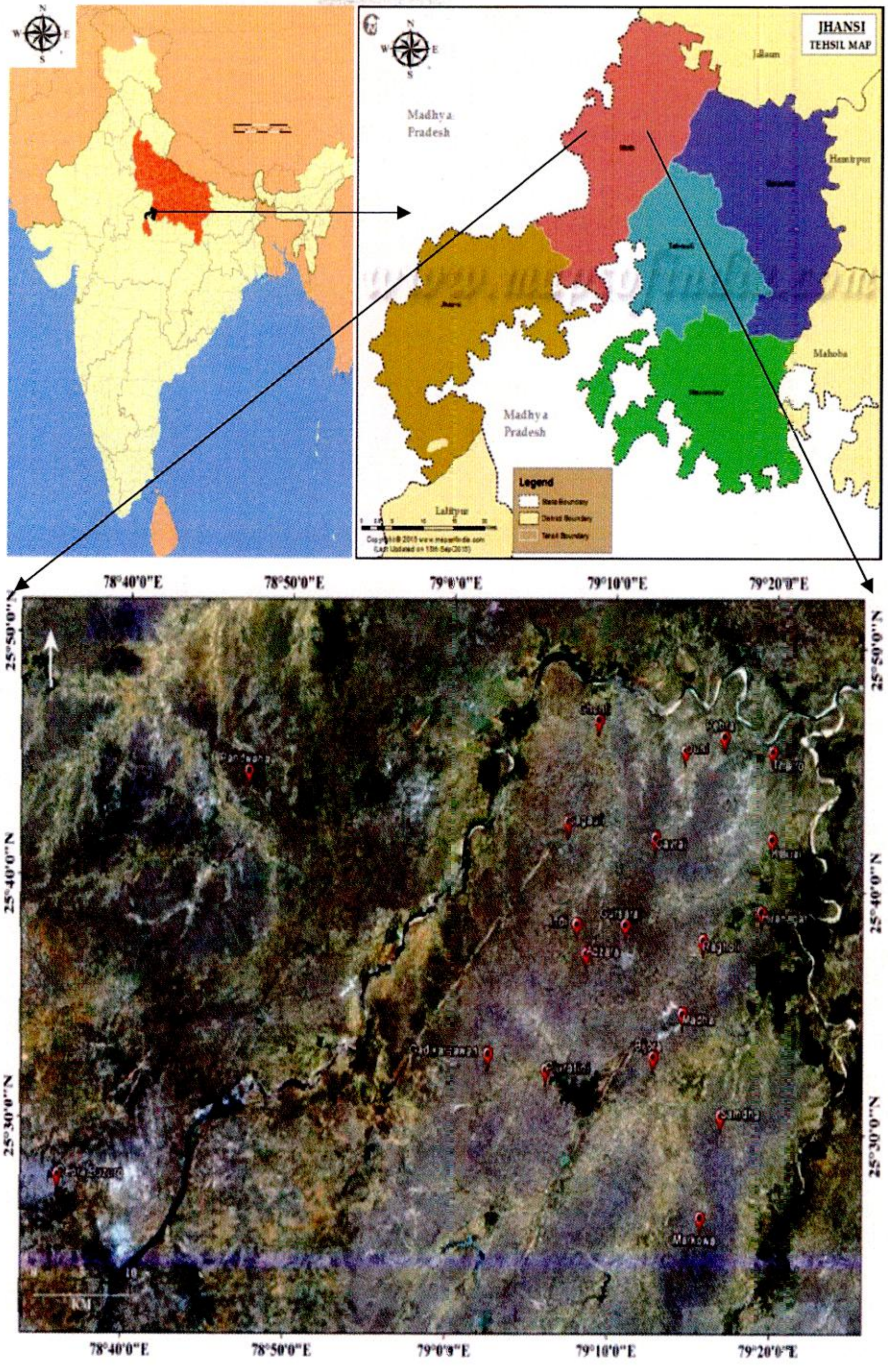


Figure 6: Location map of Moth block, Jhansi district

## 2.2 Geography and extent

The Bundelkhand region of India was selected as the study area for this research project. This region comprises of 13 districts; 7 districts from southern parts of Uttar Pradesh namely (Jhansi, Jalaun, Lalitpur, Hamirpur, Mahoba, Banda and Chitrakoot) and 8 districts from northern parts of Madhya Pradesh namely (Datia, Tikamgarh, Chattarpur, Damoh, Sagar and Panna). The total geographical area of the study area is approximately 29418 km2 which extends from 23°10'N to 26°27'N in Latitude and 78°40'E to 81°34'E in Longitude .The range of altitude in the study area varies from 600 m above the mean sea level in the southern parts to 150 m near above the mean sea level in the northern parts near the Yamuna River.

## 2.3 Geology Bundelkhand

Central Indian shield is considered to be one of the regions on planet earth which preserved a record of the evolution and the history of the early crust having Archean-palaeoprotozoic rocks. There are four continental nuclei (Dharwar, Singhbhum, Aravalli and Bastar) with a protocontinental nucleus called the Bundelkhand craton in central India. The Bundelkhand Craton is bounded by Vindhyan Supergroup of rocks to the east, west and south. South-western fringe is marked by a relatively small outcrop of the Deccan trap basalt and the northern part is hidden under the Indo-Gangetic alluvium [1]. Geology of Bundelkhand complex has been described by number of workers [(2), (3), (4), (5), (6), (7)] who reported various rock types in the area. Meddlicott (8) reported the occurrence of green stone dyke and quartz reef for the first time and suggested a prior origin for quartz reef. According to Pati et al. (1) more than 1500 mapable quartz veins/ reefs are presently exposed in the Bundelkhand Craton which is the most spectacular feature .

Geologically, Bundelkhand presents a mixture from different eras, from the earliest days of the formation of the earth, when its upper crust cooled and solidified, till recent times.

From the earliest period, older than 2500 million years, are granite-like formations called gneiss and so-called Bundelkhand Granite.

Much of the area of Datia, Jhansi, Lalitpur, Tikamgarh Chhatarpur, Panna and Sagar districts, and southern portions of Chitrakoot and Mahoba districts is granite country, marked by outcrops of great diversity in mineral composition and size, ranging from small patches to large hillocks.

A striking feature of the granite country, which has impacted settlement patterns and agriculture, is the presence of long and narrow rocky ridges, known as quarts reefs and dolerite dykes. Often, these wall-like natural features intercept the course of streams, leading to formation of water bodies and enabling the creation of large artificial lakes.

From later geological eras (570 to 900 million years ago) , we get diamond fields in Panna, extensive limestone deposits in Damoh, Chhatarpur and Datia, basaltic rocks in southern Lalitpur and sandstone deposits in Panna and Sagar.

Massive sandstone and limestone cliffs are seen in the Vindhyan hills which girdle the granite country.

The most recent geological deposits are alluvium, in the form of sand, silt or clay, brought down by north-flowing rivers.

The entire Bundelkhand region is divided into four important geological systems along the Uttar Pradesh and Madhya Pradesh. They are Archaean, Vindhyan, Transitional and Recent systems. In Archaean system, the geological systems are made up of metamorphic and igneous rocks. There as having these systems are crystalline and impermeable which make up a poor aquifer (1-5lps) and high runoff potential regions. The Vindhyan system holds relatively more ground water (5-25 lps) because they are developed from massive sandstone and limestone escarpments. The Transitional systems are comprised of sedimentary layers of sandstone and limestone of preVindhyan and post Aravali period. These systems have a nature of being a reasonable aquifer (5-25 lps).The Recent system is contained with high ground water yield potential (20-40 lps) due to large scale alluvial deposits (NRAA, 2008).

## 2.4 Soils and mineralogy

Soil is one of the most significant natural resource, which is essential for the life support on earth. Soil plays an important role in the production of crops in agriculture. The Bundelkhand region is endowed with a classified range of soil type, texture and hydrological group.As far as soil type is concerned, in southern parts of Bundelkhand, deep and medium black soil is found, mixed red & black, red & yellow soil is found in central parts, and alluvial in the northern parts. These soils are regionally known as Rakar and Parwa in red soil group and Kabar and Mar in black soil group. Soils of heavy black and light red types are widely distributed in the region. The classification of soil texture and hydrological soil group in Bundelkhand region done by the Food and Agriculture Organization (FAO) states that, it is covered with mostly sandy clay loam textured soil with D type Hydrological Soil Group (HSG) in Uttar Pradesh and Clay textured soil with D type HSG in Madhya Pradesh. The two major minerals distributed over the Bundelkhand region are Kaolinite and Montmorillonite. The Central Bundelkhand regions have Kaolinite whereas Montmorillonite is found is parts of Northern and Southern Bundelkhand as per National Bureau of Soil Survey and Land Use Planning (NBSS&LUP).

### 2.5 Climate

The climate of the Bundelkhand region is semi-arid in general. It is one of the hottest regions of India. The minimum temperature varies from 6°C to 12°C and the maximum temperature variation is from 38°C to 48°C. Chattarpur district is recorded to have the lowest temperature while Banda district scores for the highest temperature record in Bundelkhand region. Bundelkhand gets a moderate annual rainfall, fluctuating from 750 mm in the north western parts, to 1250 mm in the south eastern parts. However rain is an inconsistent; an inundation is generally trailed by stretched period of no rain.

### 2.6 Rainfall pattern and agriculture season

The occurrence of rainfall events over this region is twice in a year due to which two major agricultural seasons namely Kharif and Rabi subsist. The major rainfall events show during the month of July to end of the month of September because of South West Monsoon. These events contribute around 90% of total rainfall in the region and support the entire Kharif season for the maturity of Kharif crops as well as the sowing of Rabi crops. The minor rainfall events appear during the month of January and February down to Western disturbances. The occurrence of these trivial events is important for the Rabi season as the agriculture of a large part in the Bundelkhand region depends on it.

### 2.7 Water resources

Most of the agricultural areas of the Bundelkhand in Uttar Pradesh are under irrigated water supply whereas the maximum agriculture in Madhya Pradesh is dependent upon rain-fed practice. Betwa, Ken and Dhasan are three most important rivers adding to the irrigation systems in Bundelkhand. Also the existence of areas of mixed practices for water supply is evenly distributed over both the states. These areas have their water supply from either minor irrigation systems like ground water, tanks, small reservoirs etc. or precipitation water depending on the availability. However, ground water is the largest source of water supply for agriculture in the region after rain-fed practice. The water yield from ground in the region is very low due to hard rock hydro-geological conditions except a belt along the Yamuna River.

### 2.8 Agriculture

A total of 51% and 43% of geographical area of Bundelkhand region is under cultivation in UP and MP respectively. Larger part of the agriculture in Bundelkhand region is rain-fed as compared to irrigated practice. The Rabi sowing (69%) leads over Kharif (31%) in Bundelkhand region conflicting to other agro-ecologies, which is an irony (NRAA, 2008, 2011). In Kharif season, Rice is the major crop which is grown in irrigated and rain-fed areas all over the Bundelkhand. The other Kharif crops are Black Gram/Urd, Green Gram and Red Gram/Arhar, which are raised to a limited proportion of area during the Kharif season. Contrasting to this scene, the major crops to be cultivated during the Rabi season are Wheat and Gram in rain-fed areas while in irrigated parts these crops may or may not be under cultivation. The additional Rabi crops which are cultivated in Bundelkhand are Lentil/Masur, Black Gram and Green Gram. Apart from food grains and pulses, the region also shares a hand on oil seeds, Sugarcane and other crops in the normal rainfall. The region is good with pulses and cereal production but deficient in oil seeds.

### 2.9 Population

The combined population of Bundelkhand region from UP and MP is approximately 50 million out of which 80% population rely on agriculture. The agriculture dependent population includes marginal, small, medium and large farmers whose 96% income is earned by crop and livestock enterprise.

# CHAPTER 3

## 3.0 METHODOLOGY

## 3.1 SAMPLING PROCEDURE FOR ISOTOPES IN WATER

### 3.1.1 General information

**Sample Bottles**

The most secure vessels for storage are glass bottles, allowing storage of at least a decade as long as the seal is not broken. Gases diffuse much more slowly through glass than through plastic. However, handling and transportation of glass bottles require extra care. High-density polyethylene (HDPE) or polypropylene (PP) bottles are recommended to avoid loss of samples during transportation and for storage of a few months (water and carbon dioxide easily diffuse through low-density plastics). Bottles with narrow mouth and double caps or caps with positive seals (plastic inserts, neoprene, etc.) are recommended. Avoid rubber caps as these may contain bacterial colonies.

**Labels**

A proper labelling format for a study may be prepared that can be pasted on the sampling bottles. In the format the following details may be provided:

Time & Location: Day, date & time of sampling, site name, lat-long of site, altitude in meters above msl, sample collector's name.

Type of water: Water type as river, drain, precipitation, air/gas, ice/snow, river, lake, ocean, open well, hand pump, tube well, piezometer, spring, fresh/saline water, etc) sampling depth, total depth (water body/ well/ piezometer etc.),

Field parameters: sample amount, in-situ physico-chemical measurement details (field temperature, sample temperature, alkalinity, conductivity, pH, DO, EC, discharge rate, flow velocity, salinity, filtration and preservation, etc.) if conducted), any preservatives if used; isotopes to be analysed for the collected sample.

Notes for Log-Book: Identification marks for location identification & route map, This include; information like, geological setting, sampling method (depth-water sampler, bailer, submersible suction pump, grab sampler, etc.), condition of sampling site (newly installed piezometer, regularly pumped well, unused open well, artesian well, etc.), environmental conditions (Arid, semi–arid, tropical, humid, etc.), other hydro meteorological and hydro geological data (precipitation, temperature, water level/table, type of soil/lithology, runoff, discharge of river/stream), data source etc as they may be helpful in the interpretation of isotopic data.

Labelling should be short and unique. Always use waterproof markers or suitable pencils.

**Storage**

Preservation is not generally required for the most of the isotopes. In certain cases however, sample preservation may become necessary as chemical reactions and biological activity can alter the isotopic composition of the sample. A small amount (~0.5 mL per litre sample) of sodium azide (NaN2) or mercuric chloride is added to the sample to avoid biological activity. Samples should be stored at 4°C, if they are to be stored for a longer time.

### 3.1.2 Precipitation sampling (for D, $^{18}O$ and $^{3}H$)

Precipitation occurs in different forms i.e., rain, snow, hailstone and fog or mist, depending upon the altitude and geographic location. In case of precipitation sampling for stable isotopes, the most important aspect is to avoid evaporation because during evaporation, the isotopic composition of the water sample is strongly affected. For example, a 10% loss of sample results in an isotope enrichment of about 10‰ in $^{2}H$ and 2‰ in $^{18}O$

Fill the sample bottles completely. If there is chance of freezing during air transports fill the bottles two-thirds full.

#### Rainwater Sampling

Rainwater sampling unit although preferable to install in a meteorological observatory but can be installed at a desired place if the observatory at the nearby site is not available. Depending upon the aim and requirements of an investigation, precipitation could be also collected for every event, weekly, monthly, quarterly, etc.

The rain water is collected in the standard rain gauge which is read and emptied as soon as possible after each rain event, if practicable, or each morning. After reading the gauge the precipitation should be poured into a 5-litre plastic bottle with a good cap to avoid evaporation. Keep this container in a cool, dark place.

It is absolutely essential that the water be transferred after every precipitation or every day and the rain collector be dried again with a clean dry cloth or tissue before returning it to its collecting position.

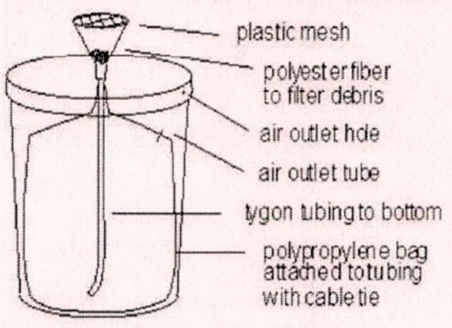
At the end of the month, all the water in the container must then be shaken before filling the bottles to be sent for analysis.

If the amount of water collected in any month exceeds 5 litres, then a second 5-litre bottle should be used to accumulate the excess water. At the end of the month all the water from both containers must then be mixed before filling the bottles with samples for sending it to laboratory for analysis.

The required sample amount for tritium analysis is ~550 ml and for stable isotope (D and $^{18}$O) is 20 ml.

Relevant information like location, date (period), and amount of total rainfall should be clearly marked on the labels of the bottles.

To avoid evaporation during sampling, different types of sample collectors are available as oil type, Ball-type, Bag-tubing type and very large sample volume (> 100 litres). Two such designs are shown in the attached figures. The collector part contains a funnel with wide mesh netting to keep out large leaves and other windblown debris. A ping-pong ball situated above the chamber in the funnel helps the water to seep into the chamber and retaining the debris to go into the chamber. However, debris or insects get caught under the ball can be a problem for water vapour to escape, or removal of ball by animals



Bag-tubing type precipitation collector

**Figure 7**: **Ball-type and Bag-tubing type precipitation collectors**

In a bag with tubing arrangement a tube extends from funnel to bottom of bucket – when bucket fills, only water in the tubing can evaporate from collector. The polypropylene bag inside the container inflates slowly with filling of precipitation. A tiny hole in the bag provides outlet for air for filling of water smoothly. On of the disadvantage of this sampler is development of algae in the bag especially when installed in the forested region.

### 3.1.3 Surface water sampling for $^{2}H$, $^{18}O$ and $^{3}H$

Surface water bodies such as rivers, canals, ponds, lakes, reservoirs, and oceans etc can be sampled for isotopic measurements of $^{2}H$, $^{18}O$ and $^{3}H$ as well as for other isotopes. In general, surface water collection poses few problems. The isotopic composition of water is extremely sensitive to evaporative loss. Therefore, river water samples for isotopic analyses should be collected, stored and transported with utmost care, according to the specific procedures given below. The high level of precision and accuracy in isotopic measurements, achievable by a modern mass spectrometer, is meaningful only when integrity of samples is assured. The following, protocols should be followed for the surface water sampling:

River, stream, canal samples should be collected from the mid-stream sections or flowing portions from about 30cm below the water surface (shallow depth surface water sampling) can be done at multiple depth. Accordingly, the representative water samples are collected from epiliminion, thermo cline and hypoliminion of deepwater bodies. Record temperature, pH, EC at the multiple depth of sampling if possible.

1. Standing/stagnant water should be avoided as the section might have been affected by evaporation or contamination.
2. Sampling at the confluence should be done with great care due to problems of incomplete mixing. Sampling just before the confluence will provide isotope characteristics of joining tributaries.
3. River Water Sample is to be filled in the supplied 1-litre HDPE bottles and tightly sealed with inner stub and pilferage proof cap.
4. The sample bottles should be thoroughly cleaned by the river water from the same source being sampled.
5. After filling the sample bottles up to the brim (living just enough space for the stub), press- fit the inner stub tightly into the mouth of bottle until it is ensured that there is no leakage from the bottle.
6. In case if the bottle is leaking even after fixing the stub, carefully pull out and discard the old stub and use the new one.
7. To inhibit the biological activity sodium azide or mercuric chloride in very minor quantities may be necessary

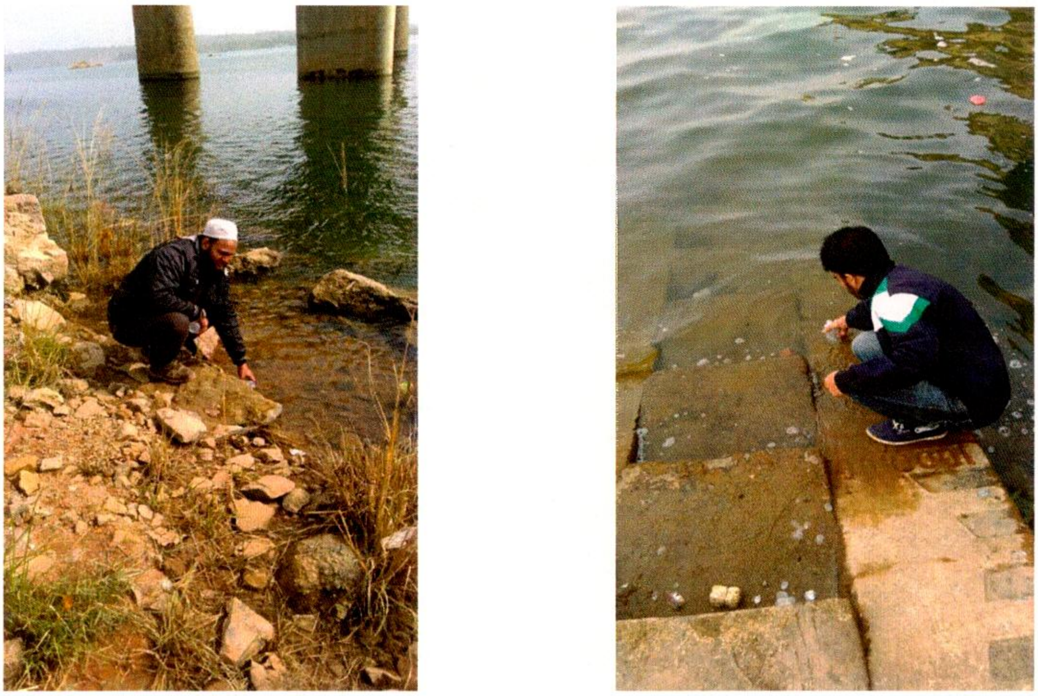


**Figure 8: A view of surface water sampling**

### 3.1.4 Sampling of unsaturated zone water

The isotopic profile of soil moisture can provide information on groundwater recharge. Samples are often taken from the soil as such. The most common methods to extract water from the soil profile in the laboratory are (i) vacuum distillation, (ii) freeze drying, (iii) squeezing, and (iv) centrifugation. In some special cases replacing methods (Ingraham & Shachel 1992) have also been used in applying a wetting liquid that replaces water in the sediment pores. In sediments and soils close to the land's surface, for instance during the vegetation period or in dry lands, the water has to be extracted either by dilution or by heating the core material under vacuum.

Moisture from soil cores can be extracted from one of the four methods – (i) vacuum distillation, (ii) freeze drying, (iii) squeezing using wetting liquids, and (iv) centrifugation. Water samples extracted through squeezing or centrifuge methods could be used for chemistry as well as for isotope analyses of water as well as of solutes whereas water extracted through heating under vacuum could only be used for stable isotopes alone.

Water samples from the unsaturated zone can also be collected by using suction cups. The suction cups mostly are permanently installed in the unsaturated zone. Suction cups with 20μm pore size are well adapted to most sediment in the vadose zone. However, the pore sizes of it are to be adapted to the main pore sizes of the sediment. Suction cups should consist of inert materials like ceramics or sinter materials. The under pressure employed should not differ too much from the prevailing one, to avoid degassing of the water. Since flow and water content in the unsaturated zone are mostly low, sampling of water always takes a longer time span in case of suction cups. Thus the use of more cups at a time at the same depth is advised to reduce the time span.

### 3.1.5 Groundwater sampling for $^{2}H$, $^{18}O$ and $^{3}H$

Groundwater samples can be collected from hand pumps, private and government tube wells, piezometers, springs, artesian wells, open wells/dug wells etc. However, it is necessary to ensure that a sample represents in situ groundwater without any contamination, evaporation, or effect of exchange with the atmosphere. Further, groundwater quality and isotopic composition may vary with depth and location. Therefore, the best way to collect the representative groundwater samples is to first collect the hydrogeological data of the study area. This helps to select sampling points and depth of sampling in different aquifers.

Periodic sampling in wet and dry seasons may be necessary to understand spatial and temporal variations.

In mountainous regions, natural springs can be considered as ideal source for sampling groundwater and the dissolved constituents. The sampling point should be located as close as possible to the discharge point of a spring to minimize the loss of gases and to get unaltered representative water sample.

When the groundwater samples are to be collected from shallow aquifers, hand- pumped wells and shallow tube wells can be used after purging the standing water column for 10 minutes. Dug wells are subjected to evaporation and therefore it is not suitable for sampling. Such samples should be avoided if a nearby shallow hand-pumped well or tube well is available. If Dug Well water is to be used then only use those dug wells which are being heavily used daily and collect water samples during peak hours of withdrawal. Unused Dug Wells should not be sampled. A hand-pump or the Dug Well in the immediate vicinity of any surface water body (lake, stream, canal, etc.) should not be sampled.

Most of the production wells that are developed by various agencies/individuals for irrigation purposes tap groundwater from the deeper aquifers. These sources may be used to sample the deeper groundwater. But in these cases, the groundwater could be a mixture of groundwater from different depth horizons. Wells of different depths with single screens are preferred to wells with multiple screens. Piezometers constructed to monitor groundwater in different aquifers are most suitable for isotopic analyses. Positive pressure systems (submersible pumps) should be used to avoid degassing. Air jet pumps must be avoided, as the atmospheric air will alter the samples. Tube wells should be operated for 10-15 minutes to flush out the standing water column before sampling. One should check the plumbing system prior to sampling to avoid inadvertent sampling of groundwater mixed with water softeners and purifiers, aeration with atmospheric air, etc. as these alter the water chemistry and isotope composition of dissolved constituents in groundwater.

The following details may be recorded in groundwater sample submission details: Locality name, village name, Taluka, district, Lat/Long, Altitude, Survey of India

Toposheet No. Date of sampling

Groundwater source type: Hand pump, tubewell, dug-cum borewell, dugwell Depth drilled (m) Screen depth (m)

Aquifer type: 1st, 2nd, 3rd aquifer etc; confined, semi-confined, un-confined etc Physico-Chemical quality details: Temp, EC, pH, colour, turbidity, major ions, DO Any other observations: Pumping condition, discharge, suitability for regular use etc

**Figure 9: A view of ground water sampling**

**Table5: Summary of sampling for$^{2}$H,$^{18}$O and$^{3}$H in precipitation, surface water, vadose water, and groundwater.**

| Isotope | Method of Analysis | Analytical precision | Sample amount | Preservation and sampling bottle | Storage |
|---|---|---|---|---|---|
| $^{18}$O | IRMS | ± 0.1 ‰ | 10 mL | no preservative, plastic bottle | >1 year |
| $^{2}$H | IRMS | ± 1 ‰ | 10 mL | no preservative, plastic bottle | >1 year |
| $^{3}$H | Enrichment + LSC | ± 0.8 TU | 500 mL | no preservative, plastic bottle | Decay: $T_{1/2}$=12.32 a |
|  | Propane synthesis | ± 0.1 TU | 1000 mL | no preservative, glass bottle |  |
|  | $^{3}$He in-growth + MS | ± 0.1 TU | 50 mL | no preservative, glass bottle |  |

## 3.2 CONCEPTS OF GROUNDWATER AGE DATING AND VARIOUS DATING TOOLS-AN OVERVIEW INCLUDING YOUNG GROUNDWATER AGE DATING

### 3.2.1 Groundwater age

Groundwater may not necessarily have age as good as some wines, but some very good aquifers in the world host groundwater many thousands of years old. The "age" of a groundwater has important implications for water resource management.

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. By this definition, what most researchers' measure is the age of groundwater, not its residence time? One could also suggest that groundwater age is the groundwater residence time, but only at the discharge area (i.e. at the discharge area, groundwater age equals groundwater residence time).

Relatively recent researchers (Goode, 1996; Etcheverry and Perrochet, 2000; Bethke and Johnson, 2002) explained that groundwater age is an intrinsic property of the groundwater molecule, like other parameters such as electrical conductivity, EC, and temperature. This means that age and groundwater are not two separable components. The reason is that water starts aging from the first day it enters the subsurface. This means 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.

### 3.2 .2 Young, Old and Very Old Groundwater

As far as relative age is concerned, groundwater is divided into three major groups: young, old and very old. The range of ages covered by available dating methods is the key criterion in differentiating and classifying among various age groundwater. Young groundwater can be dated using techniques whose dating range extends from less than a year to about 50 or 60 years- post thermonuclear bombs or CFC-free groundwater. Old groundwater can be dated with methods whose range is between 60 to 50,000 years. Finally, very old groundwater can be dated using techniques whose coverage ranges from 50,000- 100,000 years to more than a few tens of millions of years.

### 3.2.3 Dead Water and Active Water

The total volume of groundwater resources is about 23×106 km3 (Gleick, 1993). About 4-8×106 km3 of this is in the form of active groundwater that circulates continuously within the hydrologic cycle (Freeze and Cherry, 1979; Gleick, 1993). The rest is sometimes referred to as dead water. Dead groundwater include connate water (water entrapped in the sediments during deposition), magmatic water (water contained within magmas deep in the earth), metamorphic water (water produced as a result of recrystallization during metamorphism of minerals), and marine water (seawater intruded into coaster aquifer). Dead water also refers to stagnant waters in isolated envelopes in deep regional aquifers that are not in full hydraulic connection with the surrounding water (Mazor and Native, 1992). With regard to groundwater dating, **active waters** are of greater interests because they are the main source of water used for various purposes.

### 3.2.4 Mixing, Dispersion and Transport of Groundwater Age, Mean Age and Distribution of Ages

#### 1. Mixing

A groundwater sample may contain waters that have originated from various recharge areas and input points. The result of such a situation is a simple that consists of many fractions with different ages. This phenomenon is referred to as mixing and represents a major challenge to age-dating practice.

#### 2. Dispersion and Transport of Groundwater Age

The dispersion and transport of groundwater age have a role similar to mixing. Age is a groundwater property associated to the moving fluid particles. Age is submitted to the various processes governing mass transport in aquifers, such as advection, dispersion and mixing. When these processes are active, the age of a groundwater sample cannot be a single number, because the sampled mixture may consist of numerous fractions with different ages. Dispersion and transport of groundwater age fulfill the same function as mixing, but at a microscale level. The dispersion of groundwater ages (or residence times) is primarily due to heterogeneous groundwater velocities and hydrodynamic dispersion.

### 3. Mean Age and Distribution of Ages

In groundwater sample there are billions of water molecules. In a well-mixed groundwater system, anyone of these molecules may have its own distinct particular age. Mean age or the age measured by isotopic and chemical methods, is practically the average of ages of all molecules in the sample. Statistically speaking, mean age is the first moment (i.e., the average) of the age distribution. Understanding the type of statistical age distribution of various ages in a groundwater sample is a must if one has to describe the age of a given sample. This can only be done by simulation through mathematical models. In situations where groundwater flow can be modeled accurately, the first moments (e.g., mean, variance, and skewness) of the age or residence time distributions can be simulated with temporal moments equations of the advective -dispersive type (e.g., Harvey and Gorelick, 1995; Varni and Carrera, 1998). Other recent mathematical approaches combining advective-dispersive equations and the reservoir theory (Etcheverry and Perrochet, 2001; Cornaton and Perrochet, 2005) yield the full age distributions at any point of an aquifer and the residence time distributions at its outlets.

### 3.2.5 Tools for dating groundwater

There are basically two different ways of estimating groundwater age at a given point in the aquifer. (1) by environmental tracers and (2) by groundwater flow modelling; A number of isotope methods can be used to assess mean residence times. The more routinely applied techniques are based on the decay of radionuclides. Those with a long half-life ($^{14}C$, $^{36}Cl$, $^{39}Ar$ and $^{81}Kr$) can be used to date palaeo groundwaters. Short-lived radioisotopes ($^{3}H$, $^{32}Si$, $^{37}Ar$, $^{85}Kr$ and $^{222}Rn$) and those produced by man's nuclear activities over the past four decades ($^{3}H$, $^{36}Cl$ and $^{85}Kr$) indicate modern recharge.

The "submodern" period in the dating range between modern waters and paleogroundwater is problematic. While this >45 to ~1000 years range can potentially be filled by $^{39}Ar$ dating (t1/2 = 256 yr), this method requires rather ideal aquifers, very large samples, complicated sample preparation techniques and special counting facilities. Very few laboratories can afford this and, therefore, $^{37}Ar$ dating has not developed into a routine tool.

### 3.2.6 Dating Young Groundwater

The techniques used to date young groundwater (0–60 years old) including $^3$H, $^3$H/$^3$He, $^4$He, $^{85}$Kr, CFCs, SF6, and $^{36}$Cl. Dating methods for young groundwater are typically applicable to unconfined shallow aquifers only, while those methods for dating very old groundwater are often for deep, confined aquifers. It is, therefore, safe to argue that only dating methods for old groundwater can be used for both confined and unconfined aquifers.

**Tritium**

Hydrogen has three isotopes: $^1$H (common hydrogen or protium, H); $^2$H (deuterium, D); and $^3$H (tritium, T). Protium has one proton, deuterium has one proton and one neutron, and tritium has one proton and 2 neutrons. Deuterium (also referred to as heavy stable isotope of hydrogen) and protium are stable, but tritium is radioactive with a half-life of years. Tritium dating is used to trace water sources and to determine age of recent materials (maximum up to age of 50 ± 1 year). Tritium dating provides means to estimate the time since recharge to groundwater system occurred and susceptibility of the groundwater system to contamination. Sources directly fed by rainwater contain the same tritium levels as rainwater. Tritium values are reported in tritium units (TU).

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

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

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

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

To date a groundwater sample, we have to measure the concentration of tritium in the sample ($C$ or $^3$H), but we also have to find out what was the concentration of tritium in the recharge water, or the initial value ($C_0$ or $^3\mathrm{H}_0$). 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.

***Pre treatment (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 which forms precipitate with $PbCl_2$.

### Advantages and Disadvantages

#### Advantages

1. Tritium is a well-established and a well-known method with plenty of references.
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 vanished.

### $^3H$ / $^3He$

1. The fading of the tritium dating method has led to revive an old technique, namely $^3H/^3He$, to replace it. By measuring $^3H$ together with its daughter $^3He$, true ages can be determined through calculations that do not rely on complicated tritium input function. In ideal circumstances, the method is remarkably accurate for groundwater up to 40 years old.
2. There are four sources for $^3He$ in the groundwater:
3. **Atmospheric**: The solution of atmospheric $^3He$ in percolating rain- and snow water. This is called atmospheric helium and includes the excess air component.
4. **In situ**: Production of helium from the fission of $^6Li$ by neutrons. This is called nucleogenic helium (in fact, $^3H$ is produced but it decays to $^3He$).

$$^{6}_{3}Li + n \rightarrow {}^{3}_{1}H + \alpha \rightarrow {}^{3}_{1}H \rightarrow {}^{3}_{2}He + \beta$$

5. **Tritium decay**: A portion of $^3He$ in the aquifer is generated by the disintegration of tritium. This is called tritiogenic helium. The increase in the concentration of helium is directly related to the decay of tritium.

*6.* **Mantle:** Mantle releases some $^3$He, which may end up into the groundwater system. The concentration of $^3$He in the groundwater samples is reported as %δ $^3$He:

$$\%\delta\ ^3He = (Rsample - Rat)/Rat \times 100$$

Where, *R*sample is the $^3$He/$^4$He ratio (units in cm$^3$ STP/g H2O) of the water sample, *R*at is the

$^3$He/$^4$He ratio in the atmosphere, which is $1.384 \times 10^{-6}$. Analytical precision for $^3$He is about±1%.

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

$$^3H_0 = {}^3H + {}^3Hetri \qquad \text{and} \qquad {}^3H = {}^3H_0\,\mathrm{In}\, e^{-\lambda t}$$

Combining these two equations

$$^3H = ({}^3H + {}^3Hetri)\,\mathrm{In}\, e^{-\lambda t} \rightarrow \mathrm{In}\, e^{-\lambda t} = {}^3H/({}^3H + {}^3Hetri) \rightarrow t = 1/\lambda\ \mathrm{In}({}^3Hetri/{}^3H + 1)$$

It is clear from the equation that in order to measure the age of a groundwater sample, we simply need to measure its tritium and $^3$Hetri simultaneously.

## Advantages and Disadvantages

### Advantages

1. In average situations (medium-thickness unsaturated zone, limited sources of helium, etc.), the resolution of this method is high.
2. Data collected can be used for both $^3$H/$^3$He and tritium methods.
3. This method will be applicable for a long time, i.e., its effectiveness is not reduced in the future as is the case with some methods like CFCs, tritium, etc.
4. 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 type of helium.

### Chlorofluorocarbons (CFCs)

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

Atmospheric CFCs, dissolved in percolating rain- and snow water, reach the groundwater system after passing through the unsaturated zone. Groundwater CFCs ages are obtained by converting measured CFCs concentrations in the groundwater sample to equivalent air concentrations using known solubility relationships (Warner and Weiss, 1985, for CFC-11 and CFC-12, and Bu and Warner, 1995, for CFC-13) and the recharge temperature (Cook and Herczeg, 1998). The life time of CFC-11, CFC-12 and CFC-13 is 45, 100 and 85 years respectively. Therefore, the first step is to measure the CFCs concentration of groundwater (usually less than 400 pg/kg, 1pg = $10^{-12}$ g). The second step is to determine the air temperature at which the rainfall recharge occurred. This is usually average summer temperature (for regions with summer-dominated rainfall), average winter temperature (for regions with winter-dominated rainfall), and mean annual air temperature (for regions with year-round rainfall). More accurate recharge temperatures can also be obtained by measuring the dissolved gases for each sample location. The third step is to calculate the solubility of the CFCs at the considered temperature (summer, winter or annual) with the use of the Warner and Weiss (1985) relationship. The final step is to use all three steps and the following formula to obtain the equivalent atmospheric concentration (or sometimes called "apparent atmospheric concentration") of CFCs:

$EAC = CFCs_{gw}/S \times MW$ (adapted from Cook and Herczeg, 1998)

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

**Advantages and Disadvantages**

**Advantages**

1. Presence of CFCs is a good indicator of post-1945 waters. CFC-113 indicates post-1965 water.

2. Input function is relatively well known because spatial variations in atmospheric CFCs concentration are relatively moderate.

3. It is possible to date the sample by EAC of one species and also by ratio of various species.

4. Concordant ages from various species may help to understand the geochemical processes in the aquifer.

5. Cost of analysis is cheap compared to all other methods.

**Disadvantages**

6. The method is losing its applicability (post-1990s).

7. Many parameters such as excess air, recharge temperature, degradation of CFCs, etc., can influence the accuracy of the ages.

8. Great care is needed for sampling, and large errors may be introduced if proper guidelines are not followed.

### 3.2.6 Dating Old Groundwater

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

### Carbon Dating

Radiocarbon dating, or *carbon dating*, is a radiometric dating method that uses the naturally occurring radioisotope carbon-14 ($^{14}C$) with half-life 5,730±40 years to determine the age of carbonaceous materials up to about 50,000 years. Carbon-14 dating of groundwater is done by measuring $^{14}C$ activity in its dissolved inorganic carbon. $^{14}C$ is the leading tool in estimating the age of palaeo and fossil groundwater. The method is based upon the incorporation of atmospherically derived $^{14}C$ from the decay of photosynthetically - fixed carbon in soil. Radiocarbon in the soil is taken into solution as dissolved inorganic carbon (DIC = $CO2_{(aq)} + HCO3^{-} + CO3^{2-}$ ) or as dissolved organic carbon (DOC).

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

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

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

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

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

**Sample Collection**: Ground water sample is collected in the form of $BaCO3$ by precipitating the dissolved inorganic carbon (TDIC).

**Extraction of CO2**: Carbon di-oxide is extracted from the precipitate by acidifying it.

$$3CaCO3/3BaCO3+2H3PO4 \longrightarrow 3CO2+3H2O+Ca3\,(PO4)2/\,Ba3\,(PO4)2$$

**Sample Preparation**: Sample is prepared from the extracted CO2 by absorption technique in which CO2 is directly absorbed in Carbosorb – Scintillator mixture.

**Counting:** The absorbed CO2 – scintillator mixture is then counted in liquid scintillation counter for estimating the concentration of radioactive carbon.

**Estimation of $^{14}C$ age**: Specific activity of sample is determined by comparing with standard having known specific activity and is expressed in terms of *pmc*.

**Advantages and Disadvantages**

**Advantages**

1. It is an old and well-established method that has been proved and developed by considerable research during the last half-century. It is applicable to a variety of materials and processes.
2. Sampling and analysis for this method are now routine and cheaper than the majority of the dating methods.
3. It is, in one sense, the only method available to date old groundwater and to fill the dating range between young and very old groundwater.

4. The deficiencies, the principles, and the positive points of the methods are all well known.

**Disadvantages**

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.

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.

Having pointed out the above two major obstacles, it is safe to argue that the $^{14}C$ method is often a semi quantitative technique.

## 3.3 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.

### 3.3.1 Replenishment of Groundwater Reservoirs

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

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

### 3.3.2 Prevention of Overexploitation and Contamination Of Aquifers

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

### 3.3.3 Estimation of Rate of Groundwater Recharge

This particular usage of groundwater age data is perhaps the most widely applied of all. ***Figure10*** illustrates in a simple way the approach to calculate the recharge rate to a groundwater system by age data. The procedure is to have either

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

2. The vertical position of the bomb peak tritium in the aquifer. It should be noted that the groundwater flow should consist of only one vertical component with negligible horizontal movement. The second approach may not be particularly accurate because of the difference between the flow rates in the saturated and unsaturated zones.

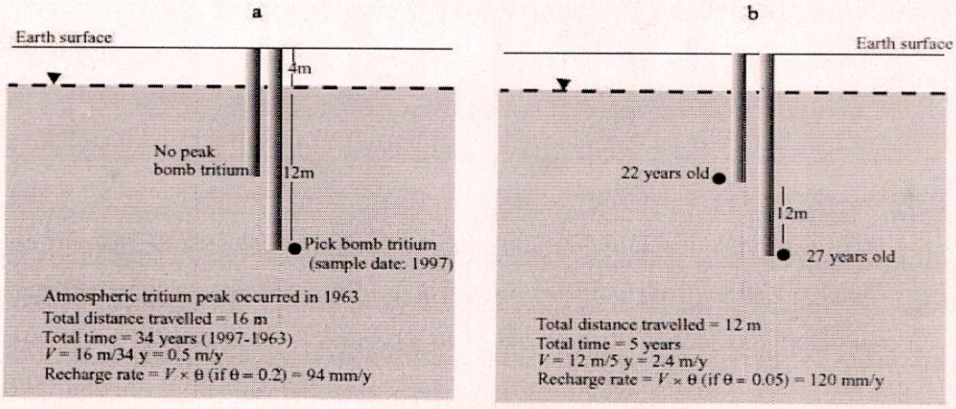


**Figure10. Determination of groundwater recharge rate: (a) by locating bomb peak tritium; (b) by measuring groundwater ages at two points along a vertical profile such as at a piezometer nest.**

### 3.3.4 Estimation of Groundwater Velocity

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

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).

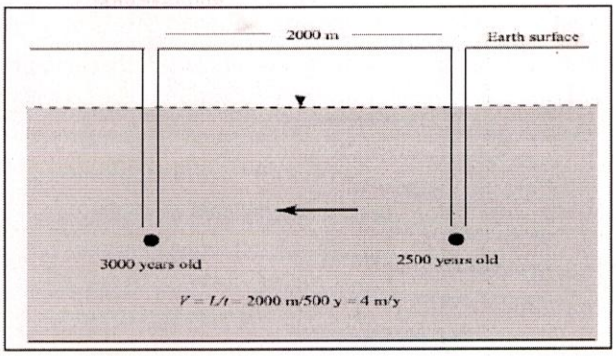


**Figure 11: Calculating groundwater flow rate using ages of groundwater determined in two different boreholes.**

### 3.3.5 Identification of Groundwater Flow Paths

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

### 3.3.6 Study of the Pre-Holocene Climate

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

### 3.3.7 Evaluating the Pollution of Groundwater

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

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

If a water sample is older than 100 years, then it should be pollution free.

For old groundwater, the contamination risk is low.

For young groundwater, the contamination risk is high.

Along the age line, the concentration of the contaminants should decrease, i.e., older groundwater should show less contamination (concentration of the contaminants should be less).

For a set of groundwater samples, if a contaminated groundwater sample is dated as young, then we can be sure that the dating exercise was most probably undertaken correctly and the age data obtained can be used for other purposes.

If there is a meaningful negative correlation between the age of groundwater and the concentration of the contaminants (the older the age, the lower the concentration of the contaminants), it would then be possible to predict the extent and timing of contamination plume, i.e., concentration reaches to what level and at what time.

If there is a positive correlation between the age of groundwater and the concentration of contaminants (the older the age, the higher the concentration of the contaminants), it would then be logical to conclude that contaminants are gradually degraded over time.

## 3.4 ESTIMATION OF RECHARGE TO GROUNDWATER USING TRITIUM

### 3.4.1 Introduction

The process of infiltration governs the recharge to groundwater from surface to the subsequent layers of soil, which is one of the most important parameters to study the movement of water through unsaturated soil. The infiltration may be defined as the process of the water penetrating from ground surface into soil mass.

Estimation of recharge to groundwater is essential for evaluation of groundwater resources. In most of the cases, major source of recharge to groundwater is due to precipitation. However, in the irrigated areas the return seepage also contributes to groundwater recharge significantly.

In addition to the precipitation and irrigation inputs, which contribute to the direct or vertical recharge to groundwater (unconfined aquifers), there is a lateral component of recharge through the sub-surface horizontal flow due to natural hydraulic gradient. The isotope techniques can be employed to estimate the vertical component of recharge.

The vertical component of recharge to groundwater can be estimated using naturally injected environmental isotopes like oxygen-18, deuterium and tritium including artificial tritium, which is required to be injected at the selected sites. In the present study, the artificial tritium has been used to estimate the vertical component of recharge to groundwater.

Tritium is a beta ray emitter having half-life of 12.43 years. It emits beta radiations of 18.6 keV energy. In India, tritium can be obtained from Board of Radiation and Isotope Technology (BRIT), Bhabha Atomic Research Centre (BARC), Trombay, Mumbai.

This method was first applied by Zimmerman et al. (1967 a,b) in West Germany. Munnich (1968 a,b) also studied the moisture movement in the unsaturated zone by Tritium tagging method. The concept of water movement through soils, termed the piston flow model was developed.

### 3.4.2 Tritium tagging method

As it is clear from its name, tritium, a radioactive isotope is used as a tracer to trace the movement of water as it fulfils the requirement of an ideal tracer. An ideal tracer should have the following characteristics:

1. The tracer should behave same as normal water and should not be lost or reiterated due to adsorption or ion exchange. Generally anions and neutral molecules are better in this regard to cations.
2. The tracer should have a high detection sensitivity.
3. The health and handling hazards should be minimum.
4. The duration of the study is generally about 1 to 2 years and hence the radio-tracer should have considerable half life (about 1 year) from the study point of view but less half life from health hazard point of view. Therefore, radio-isotopes are selected keeping in view the both aspects.

### 3.4.3 Tritium as Tracer

1. It behaves similar to normal water as it is a molecule of water.
2. It is a pure beta emitter of low energy (18.6 keV) and belongs to the lowest radio-toxicity class.

3 It can be measured with a high detection sensitivity.

4. It has comparatively long half-life (12.23 years) and hence useful for soil moisture movement studies. The long half-life makes it possible to store the tracer in the laboratory and no particular shielding is required.

### 3.4.4 Principle of the Technique

The principle of the tritium tagging technique is mainly based on the following assumptions [Zimmermann et al. (1967) and Munnich, K.D. (1968)].

The vertically downward movement of soil moisture is very slow due to which the lateral mixing between soil moisture portions of different flow velocities even with the stationary also takes place and the moisture flows in discrete layers in such a way that if any fresh water will be added to the top surface of the soil, the infiltrated layer of the water pushes the older layer downward in the soil system and so on till the last layer of moisture reaches the saturated zone. This concept of water flow in unsaturated zone has been treated as the concept of piston type flow.

On the basis of these assumptions, if a radio-isotope (tritium) is tagged below the active root zone and also not affected by sun heating (say below 75cm to 1m), the tagged radio-isotope will be mixed with the soil moisture available at the depth and act as an impermeable sheet. Therefore, if any water will be added to the top of the soil surface, it will be infiltrated into the ground by pushing down the older water, thus the shift in the tritium peak can be observed after some time (say after laps of one season). But, the tritium peak will be broadened due to molecular diffusion, stream line dispersion, asymmetrical flow and other heterogeneties of the soil media.

The soil samples from the injection point are collected at the interval of 10 or 15 cm depth after pinpointing it very accurately. The soil core so removed are collected and kept in an air-tight plastic container or polythene pack. The soil moisture is obtained from soil samples by vacuum distillation and also the dry density and moisture content determined by gravimetric method using either oven or infra-red moisture balance, the later is preferred due to superiority over the normal gravimetric method. The tritium contents are determined in the soil moisture, obtained by the distillation of the soil samples, with the help of Liquid Scintillation Spectrometer using suitable liquid scintillator. The counting rates so obtained, say counts per minute or per 100 seconds or per 2 minutes depending upon the number of counts obtained per second in order to increase the total number of counts to reduce the statistical error, are plotted with respect to depth and the center of gravity of the tritium peak so obtained is calculated. By subtracting the depth of injection from the C.G. of the tritium peak, the shift of the tritium peak can be obtained. Now as per the principle laid down by the founder investigators (1967), the multiplication of the tritium peak shift and effective average volumetric moisture content in the tritium peak shift region will provide the information of recharge to ground water during the time interval of tritium injection and sampling. The effective average volumetric moisture content in the peak shift region can be obtained by subtracting the field capacity of the peak shift region from the average volumetric moisture content in the peak shift region at the time of sampling. Mathematically the equation for the estimation of percentage of recharge to ground water can be written as:

$$R = \delta_v \, d \, (100/p) \qquad \text{.......................................................................... (1)}$$

where,

R is the percentage of recharge to ground water

$\delta v$ is the effective average volumetric moisture content in the tritium peak shift region

d is the shift of tritium peak in cm

p is precipitation and/or irrigation in cm

## 3.5 MASS SPECTROMETRY

Mass spectrometry is a powerful analytical technique used to quantify known materials, to identify unknown compounds within a sample, and to elucidate the structure and chemical properties of different molecules. The complete process involves the conversion of the sample into gaseous ions, with or without fragmentation, which are then characterized by their mass to charge ratios (m/z) and relative abundances.

This technique basically studies the effect of ionizing energy on molecules. It depends upon chemical reactions in the gas phase in which sample molecules are consumed during the formation of ionic and neutral species.

### 3.5.1 Basic Principle

A mass spectrometer generates multiple ions from the sample under investigation, it then separates them according to their specific mass-to-charge ratio (m/z), and then records the relative abundance of each ion type.

The first step in the mass spectrometric analysis of compounds is the production of gas phase ions of the compound, basically by electron ionization. This molecular ion undergoes fragmentation. Each primary product ion derived from the molecular ion, in turn, undergoes fragmentation, and so on. The ions are separated in the mass spectrometer according to their mass-to-charge ratio, and are detected in proportion to their abundance. A mass spectrum of the molecule is thus produced. It displays the result in the form of a plot of ion abundance versus mass-to-charge ratio. Ions provide information concerning the nature and the structure of their precursor molecule. In the spectrum of a pure compound, the molecular ion, if present, appears at the highest value of m/z (followed by ions containing heavier isotopes) and gives the molecular mass of the compound.

#### Stage 1: Ionisation

The atom or molecule is ionised by knocking one or more electrons off to give a positive ion. This is true even for things which you would normally expect to form negative ions (chlorine, for example) or never form ions at all (argon, for example). Most mass spectrometers work with positive ions.

#### The need for a vacuum

It's important that the ions produced in the ionisation chamber have a free run through the machine without hitting air molecules.

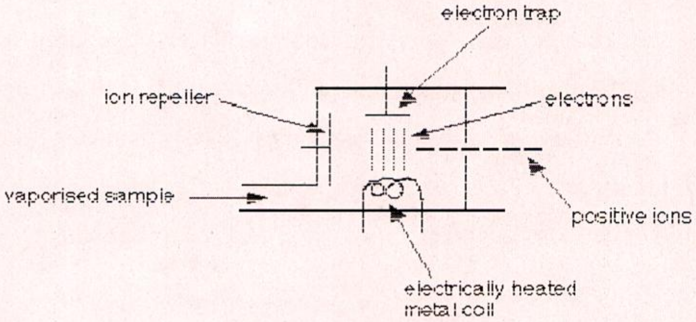


**Figure 12:** ***Ionisation***

The vaporised sample passes into the ionisation chamber. The electrically heated metal coil gives off electrons which are attracted to the electron trap which is a positively charged plate.

The particles in the sample (atoms or molecules) are therefore bombarded with a stream of electrons, and some of the collisions are energetic enough to knock one or more electrons out of the sample particles to make positive ions.

Most of the positive ions formed will carry a charge of +1 because it is much more difficult to remove further electrons from an already positive ion.

These positive ions are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge.

### Stage 2: Acceleration

The ions are accelerated so that they all have the same kinetic energy.

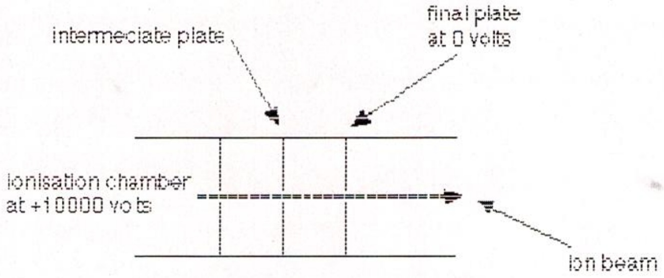


**Figure 13**: ***Acceleration***

The positive ions are repelled away from the very positive ionisation chamber and pass through three slits, the final one of which is at 0 volts. The middle slit carries some intermediate voltage. All the ions are accelerated into a finely focused beam.

### Stage 3: Deflection

The ions are then deflected by a magnetic field according to their masses. The lighter they are, the more they are deflected.

The amount of deflection also depends on the number of positive charges on the ion - in other words, on how many electrons were knocked off in the first stage. The more the ion is charged, the more it gets deflected.

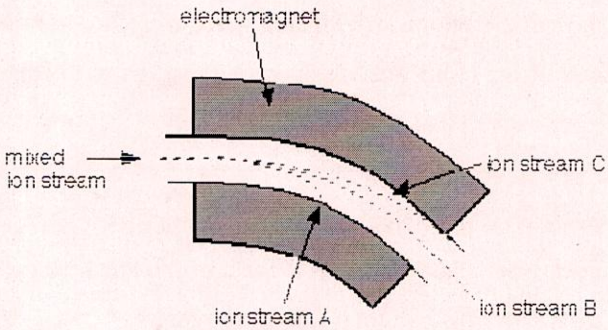


**Figure 14:** ***Deflection***

Different ions are deflected by the magnetic field by different amounts. The amount of deflection depends on:

1. The mass of the ion. Lighter ions are deflected more than heavier ones.
2. The charge on the ion. Ions with 2 (or more) positive charges are deflected more than ones with only 1 positive charge.

These two factors are combined into the ***mass/charge ratio.*** Mass/charge ratio is given the symbol m/z (or sometimes m/e).

For example, if an ion had a mass of 28 and a charge of 1+, its mass/charge ratio would be 28. An ion with a mass of 56 and a charge of 2+ would also have a mass/charge ratio of 28.

In the last diagram, ion stream A is most deflected - it will contain ions with the smallest mass/charge ratio. Ion stream C is the least deflected - it contains ions with the greatest mass/charge ratio.

It makes it simpler to talk about this if we assume that the charge on all the ions is 1+. Most of the ions passing through the mass spectrometer will have a charge of 1+, so that the mass/charge ratio will be the same as the mass of the ion.

Assuming 1+ ions, stream A has the lightest ions, stream B the next lightest and stream C the heaviest. Lighter ions are going to be more deflected than heavy ones.

**Stage 4: Detection**

The beam of ions passing through the machine is detected electrically.

Only ion stream B makes it right through the machine to the ion detector. The other ions collide with the walls where they will pick up electrons and be neutralised. Eventually, they get removed from the mass spectrometer by the vacuum pump.

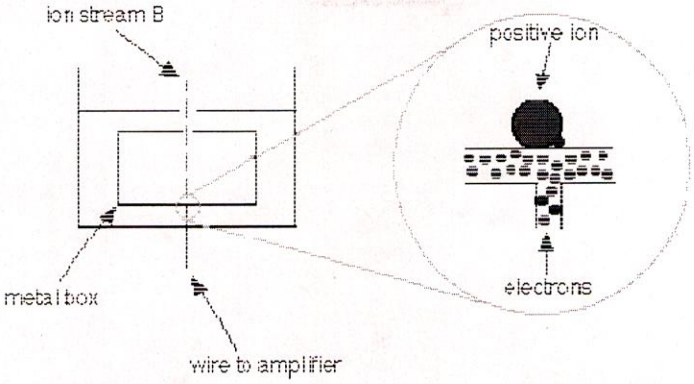


**Figure 15***: Detection*

When an ion hits the metal box, its charge is neutralised by an electron jumping from the metal on to the ion .That leaves a space amongst the electrons in the metal, and the electrons in the wire shuffle along to fill it.

A flow of electrons in the wire is detected as an electric current which can be amplified and recorded. The more ions arriving, the greater the current.

**Detecting the other ions**

How might the other ions be detected - those in streams A and C which have been lost in the machine?

Remember that stream A was most deflected - it has the smallest value of m/z (the lightest ions if the charge is 1+). To bring them on to the detector, you would need to deflect them less - by using a smaller magnetic field (a smaller sideways force).

To bring those with a larger m/z value (the heavier ions if the charge is +1) on to the detector you would have to deflect them more by using a larger magnetic field.

If you vary the magnetic field, you can bring each ion stream in turn on to the detector to produce a current which is proportional to the number of ions arriving. The mass of each ion being detected is related to the size of the magnetic field used to bring it on to the detector. The machine can be calibrated to record current (which is a measure of the number of ions) against m/z directly. The mass is measured on the $^{12}C$ scale.

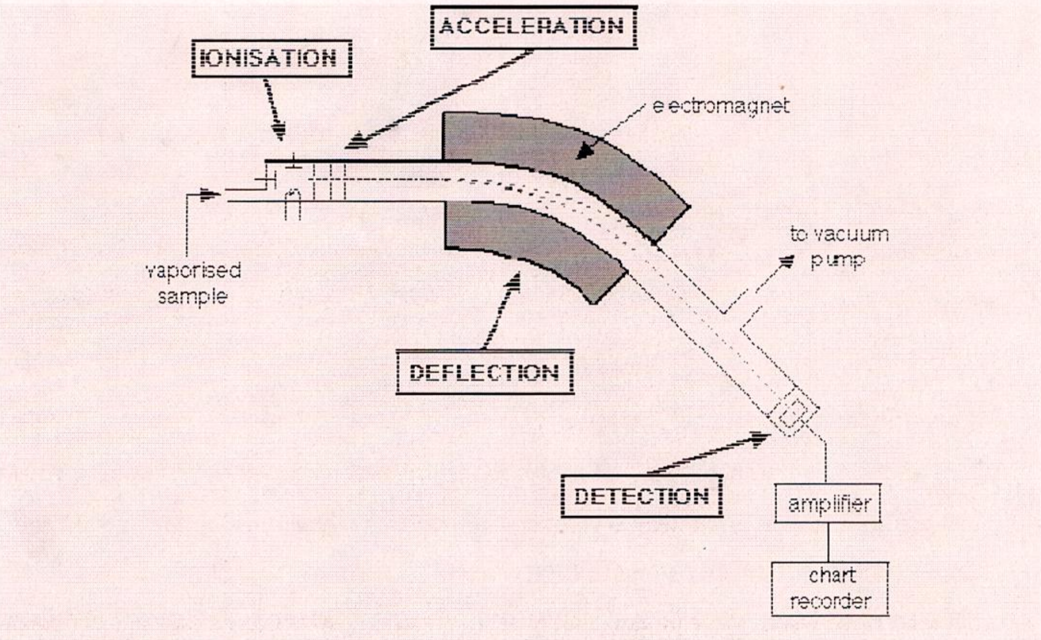
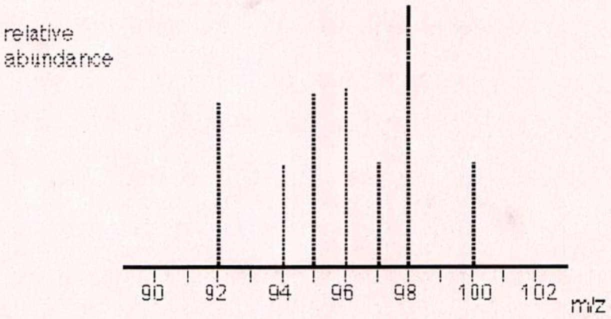


**Figure 16: A full diagram of a mass spectrometer**

**What the mass spectrometer output looks like**

The output from the chart recorder is usually simplified into a "stick diagram". This shows the relative current produced by ions of varying mass/charge ratio.

The stick diagram for molybdenum looks lilke this:



You may find diagrams in which the vertical axis is labelled as either "relative abundance" or "relative intensity". Whichever is used, it means the same thing. The vertical scale is related to the current received by the chart recorder - and so to the number of ions arriving at the detector: the greater the current, the more abundant the ion.

As you will see from the diagram, the commonest ion has a mass/charge ratio of 98. Other ions have mass/charge ratios of 92, 94, 95, 96, 97 and 100.

That means that molybdenum consists of 7 different isotopes. Assuming that the ions all have a charge of 1+,that means that the masses of the 7 isotopes on the carbon-12 scale are 92, 94, 95, 96, 97, 98 and 100.

### 3.5.2 Dual Inlet Isotope Ratio Mass Spectrometer

The basic principle of dual inlet IRMS is a comparison between sample and reference gases. Dual inlet consists of two identical halves: one for the sample gas and one for the reference. An automated dual inlet equalizes sample and reference gas pressures, and hence their major ion beam currents, by adjusting the volumes of two storage reservoirs. The outlet from each half of the inlet is connected to a changeover valve assembly through "balanced" capillaries. This ensures that sample and reference gases both flow from their respective reservoirs at the same rate. As the changeover valve switches, sample and reference gases alternately flow either into the ion source or into a "waste" vacuum line.

The capillaries ensure viscous rather than molecular flow. Although many mass spectrometry applications use molecular flow, it is unsuitable for isotopic measurements because it causes isotopic fractionation. Viscous flow requires the mean free path of the gas molecules to be small compared to the leak orifice. In practice, a pair of stainless steel capillaries, typically 1m long and o.15 mm ID, are used. These are squeezed down at a point near the changeover valve using an adjustable "crimp." This both sets a suitable pressure drop across the crimp to ensure viscous flow through the capillaries and balances the flow from sample and reference reservoirs.

The dual inlet approach is very inefficient in terms of sample usage. Only nano moles are required in the ion source. However, micromole-sized samples must be used simply to maintain a steady flow of gas from the inlet without a significant pressure drop. Also, during analysis, the sample flows to waste 50 % of the time.

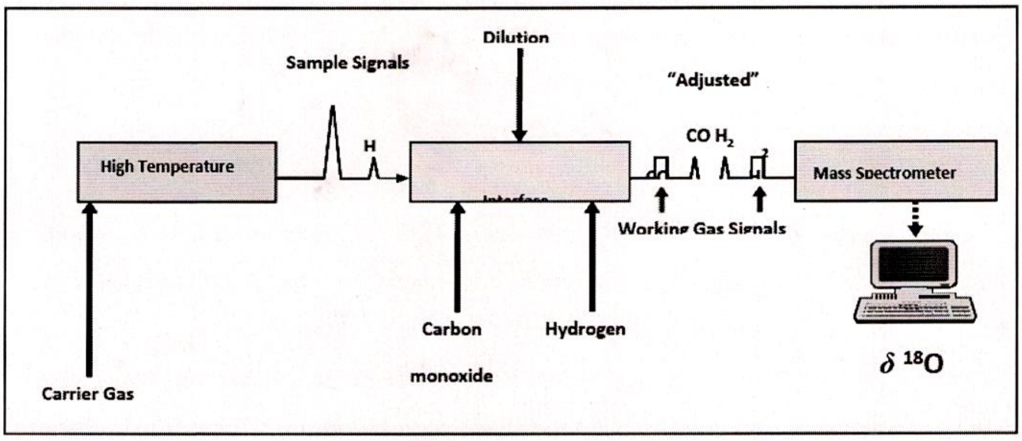


**Figure17.** ***Simple schematic diagram of a TC/EA-IRMS for the determination of*** **δ** $^{2}H$ ***and*** **δ** $^{18}O$

**Multisample manifold:** Sample flasks containing gas samples prepared off-line are attached using vacuum couplings to banks of automatic valves. These valves are then opened sequentially by software to let each gas into the inlet for unattended measurement of a batch of samples. A manifold adds volume to the dual inlet system, however, which means the sample pressure is lower than when admitted directly to the inlet. This requires larger samples (~50 % more) or more frequent use of the cold finger to reach the required precision. Commercial manifolds are built in banks of 10 or 12, with each bank separated from the others by extra valves. This minimizes the increase in total system volume.

"Tube cracker" accessories are used to allow batches of sealed pyrex or quartz tubes (~2 ml) to be cracked, one at a time, under vacuum. This is used for samples from "sealed- tube combustions" where batches of tubes containing sample mixed with reagents are heated overnight in an oven. The tube holder is connected to the manifold by a bellows, then a solenoid pushes it with a rod, snapping the glass inside and releasing the gas.

**Automated acid-dosing system:** This was designed to measure $^{13}C$ and $^{18}O$ from carbonate samples. Carbonate samples fall into a bath of 100 % H3PO4, thermo stated at a temperature for which the fractionation factor for the reaction is known. Ortho phosphoric acid is preferred because it gives very low and reproducible fractionation and exchange compared to other acids, and any residuals are of low vapor pressure. In the reaction

3CaCO3 + 2H3PO4 ↔ 3CO2 + 3H2O + Ca3(PO4)2

only two-thirds of the oxygen present in the carbonate is liberated as CO2. This is accounted for when calculating values relative to PDB or V-SMOW. The CO2 evolved is purified using automated cryo traps and passed to the dual inlet. Samples greater than 250µg can be measured.

### 3.5.3 Continuous Flow Isotope Ratio Mass Spectromete

The two approaches used in continuous flow IRMS are summarized. One is automated nitrogen carbon analysis-mass spectrometry and one is gas chromatography- isotope ratio mass spectrometry.

In the continuous flow technique, solids, liquids, and gases are converted into clean and pure gas prior to introduction into the ion source in a stream of helium. The online sample preparation is done by interfacing with one or more of the sample preparation module; *elemental analyzer* (EA-IRMS), gas chromatograph (GC-IRMS), liquid chromatography (LC-IRMS), a chemical bench (with *Gilson auto-sampler*), gas bench attachment etc. EA-IRMS provides *bulk sample isotope analysis (BSIA)* which is represents data for the average isotopic signal of the entire sample. In elemental analyzers, samples are combusted to CO2, NOx, SO2, and H2O. Depending on the isotopes of the interest, the combustion products are reduced to remove interferences. For example, NOx is converted into N2 and O2. The major issues in combining LC to IRMS are: 1) inefficient interface in solvent removal and 2) conversion of analytic into gases such as CO2 gas without any isotopic effect.

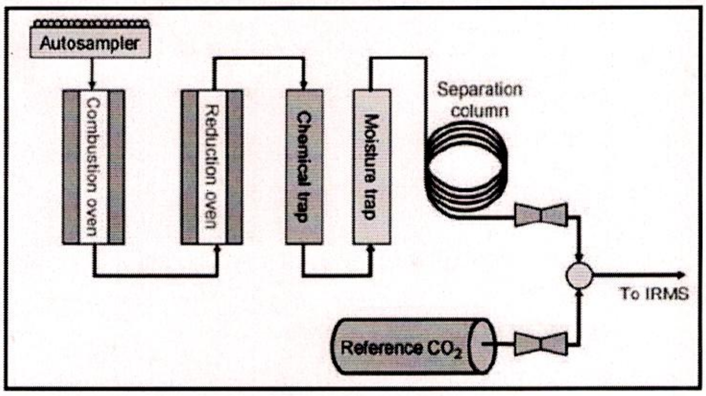


**Figure 18: Sample introduction to IRMS using an auto-sampler, Elemental Analyzer (EA) and GC separator**

The analytic is carried through a chemical trap to remove water that was produced from combustion, and then passed through GC column to separate these compounds (eg, CO2 and N2 peak will get separated). The time separated gases are flown into ion source of IRMS. The continuous flow of sample gases through the system is made in the stream of helium carrier gas. The flow of reference gas is regulated using a dedicated sample introduction interface which toggles quickly between reference gas and the sample using pneumatic actuators.

For operating CF-IRS for N-C isotope analysis, solid or liquid samples are sealed into tin capsules and loaded into an auto sampler. The samples are purged of air by a flow of He in the auto sampler. They are dropped into the vertical combustion tube as a pulse of O2 temporarily replaces the He carrier gas. The combustion tube is packed with an oxidation catalyst of Cr2O3 granules, chopped CuO wire to oxidize hydrocarbons, and Ag wool to trap S and halogens. Flash combustion of the tin raises the local temperature from ~1000 $^{0}$C to ~1700 $^{0}$C, ensuring complete oxidation. Combustion products (CO2, N2, NOx and H2O) are swept into the reduction tube (Cu wires, 600 $^{0}$C) where oxides of N are reduced to N2, and excess O2 are removed. A desiccant trap, such as $Mg(ClO4)_2$, removes water. If only $^{15}N$ and total N is being analyzed, then a suitable alkaline trap (e.g., Carbosorb, BDH, Poole, UK) is used to remove CO2. A packed-column gas chromatography separates N2 fro trace impurities. If measurement of $^{15}N$ and $^{13}C$ from the same sample is required, then care must be exercised in selecting a suitable packing material and operation treatment for the gas chromatography column in order to ensure base line resolution between the N2 and CO2 peaks. A small fraction (~0.1 %) of the effluent from the sample preparation system enters the mass spectrometer through a three way valve and capillary tubing with a crimp to adjust the source pressure of the IRMS. The gas entering the source is analyzed for total N and $^{15}N$ and/or total C and $^{13}C$.

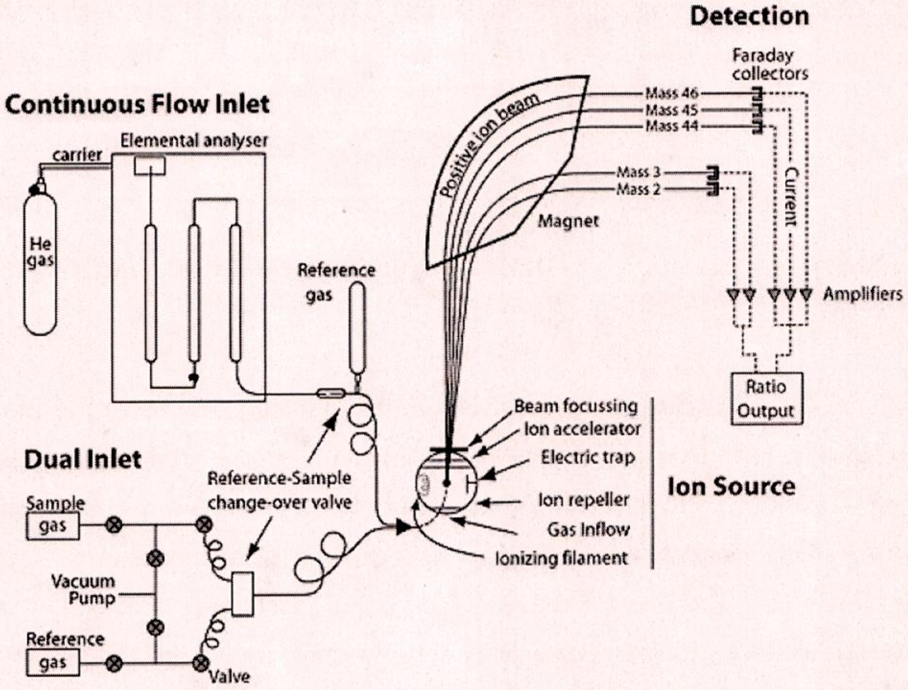


**Figure 19: Components of a Mass Spectrometer**

**Table 6:** ***Comparison between dual-inlet and continuous flow techniques***

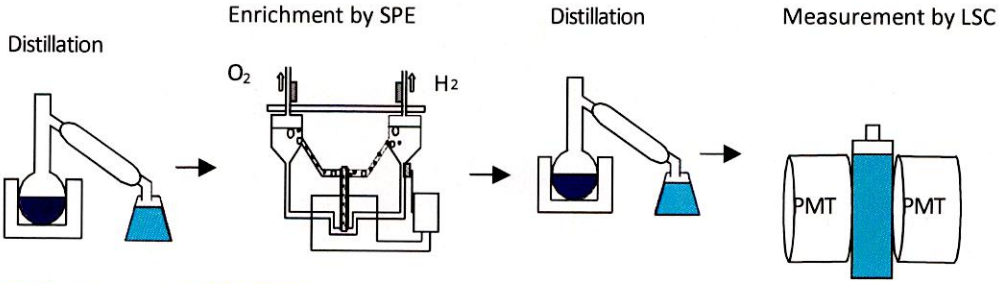
| | **Dual-Inlet** | **Continuous flow** |
|---|---|---|
| Type of gas entering the mass spectrometer | A pure gas (such as CO2) is introduced into the ion source. | A pure gas is entrained as a chromatographic peak within a flow of helium during introduction to the ion source. Thus a mixed gas enters the ion source (e.g |
| How the sample gas and working gas are introduced into the | The gases are repeatedly and alternately introduced into the ion source. | The chromatographic peak of sample is preceded and/or followed by introduction of |
| Signal intensity of sample gas | Sample gas and working gas are carefully balanced by adjustments of bellows to produce nearly identical signals, | Sample gas varies in intensity across the chromatographic peak. |
| Amount of sample required | 10s of µmol, or ~0.5 µmol using a cold finger volume. The sample size is controlled by the need for viscous flow conditions in the capillaries. | 100s of nmol, smaller if systems are optimized (10s of nmol by GC-IRMS). Because viscous flow is provided by the helium stream, there is the possibility of further reduction in sample size by advancements in blank reduction, |

## 3.6 ULTRA LOW LEVEL LIQUID SCINTILLATION COUNTER

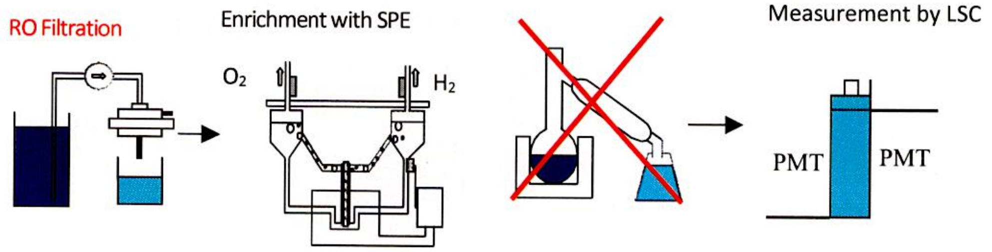
Liquid scintillation counting is the most popular method to measure the tritium concentration in the aqueous solution Low level liquid scintillation counting took much time with a lot of doing to distil off the impurities in the sample water before mixing the sample with the liquid scintillation cocktail. In the light of it, we investigated the possibility of an alternative filtration method for sample purification. In Japan, the tritium concentration in the environmental water has become very low, and the samples have to be treated by electrolysis enrichment with a liquid scintillation analyzer. Using the solid polymer electrolyte enriching device, there is no need to add neither any electrolyte nor the neutralization after the concentration. If we could replace the distillation process with the filtration, the procedure would be simplified very much. We investigated the procedure and we were able to prove that the reverse osmosis (RO) filtration was available. Moreover, in order to rationalize all through the measurement method, we examined the followings: (1) Improvement of the enriching apparatus. (2) Easier measurement of heavy water concentration using a density meter, instead of a mass spectrometer. The concentration of water samples was measured to determine the enrichment rate of tritium during the electrolysis enrichment. . Now, liquid scintillation counting is the most popular method to measure the tritium concentration in the low tritium level water samples such as river water or prsipitation samples. It takes, however, much time with a lot of doing to distil off the impurities in the sample water before mixing the sample with the liquid scintillation cocktail. In the light of it, we investigated the possibility of an alternative method with membrane filters for purification. As published before, the filtration method was proved to be available to be alternatively used for tritium measurement [1][2]. The tritium concentration in the environmental water has become lower than 1.0Bq/kg-H2O which is within the detective limit by the low background liquid scintillation counter. As for the samples close to or lower than the detective limit, the samples have to be treated by electrolysis enrichment with liquid scintillation analyzer. Recently an electrolysis tritium enriching method using a solid polymer electrolyte (SPE) has been developed [3][4]. Using of the apparatus, there is no need to add any electrolyte, nor is the neutralization after concentration. If we could replace the distillation process with the filtration, the procedure would be simplified very much. We investigated the procedure and we were able to prove that the reverse osmosis (RO) filtration was available. Moreover, in order to rationalize all through the measurement method, we are examining the followings: (1) Improvement of the enriching apparatus. (2) Easier measurement of heavy water concentration using a density meter, instead of a mass spectrometer [5]. The concentration of water samples was measured to determine the enrichment rate of tritium during the electrolysis enrichment.

| Apparatuses | Model | Maker |
|---|---|---|
| **Rivers Osmosis Filter** | **S300K3** | **SEIREN Co.,Ltd** |
| **Electrolysis Enriching Apparatus** | **TRIPURE XZ001** | **Permelec Electrode** |
| **Liquid Scintillation Analyzer** | **LSC-LB5** | **LTD. ALOKA CO.,** |
| **Density Meter** | **DMS5000** | **LTD** |

**Previous Procedure**



**Improved Procedure**



### 3.6.1 EXPERIMENT & DISCUSSION

Using the conventional apparatuses in possession, we carried out some experiments and tried to improve the measurement procedure. The using apparatuses are shown in Table 1.

In Fig above the previous and the improved procedures are illustrated. In the second procedure, four processes were changed. (1) The distillation process before the enrichment was replaced by the RO filtration. (2) The cathode of the enrichment apparatus was replaced from SUS to carbon, because the carbon electrode has a bigger separation factor than the SUS's one. (3) The distillation after the enrichment was skipped. (4) The heavy water concentration measurement before and after the enrichment was changed from a mass-spectrometry to a density measurement. These changes could reduce the time necessary for four processes as follows, (1) ~1 day to ~1 hour, (2) ~2 days to ~1 day, (3) ~1 day to 0, (4) ~1 day to ~1 minute (the numbers are corresponding to the numbers written before). Totally, we could reduce much time, keeping accurate tritium concentration measurement.

The same data, which were used in order to improve and simplify the procedure, are shown in table 2. In the last column, the data of another liquid scintillation analyzer are shown for the future reference, because the analyzer is advantageous as the sample volume is smaller.

**Ultra low level liquid scintillation counter**

## 3.7 TRITIUM ENRICHMENT UNIT

### 3.7.1 Introduction

- Just after Voltaic cell was invented at the beginning of eighteenth century, the cell was applied to electrolysis in water and it was found that water is composed of hydrogen and oxygen. Since this discovery stimulated the scientific understanding on the behavior of ions in solution with atomic level, the electrolytic technology spreaded to the various fields such as refining of metals, metal plating, generation of alkaline substances and removal of trace toxic materials in water and soil. And this technology nowadays becomes an important field in electrochemistry.
- Since tritium is generated at the stratosphere by the nuclear reaction of nitrogen and neutron and decays with radioactive half-life of 12.3 years releasing beta-ray, it always exists in a constant amount in nature. On the other hand, large amounts of tritium were produced by the nuclear bomb tests in the atmosphere until the early 1960s and it fell out all over the world, although the concentration of the fallout tritium is lowered to the background level because it passed for several decay times of half-life. Tritium is also generated from atomic power plants and atomic fuel reprocessing plants currently and tritium contaminated waste vapor is released to the air and the wasted water into seawater now in the world. Then the flow of the released waste has to be monitored to know the diffusion process in the environment and to keep the safety in mankind and ecosystem.
- Liquid scintillation counting system is used to count the released electrons by the beta-decay. Lower limit of tritium concentration in a low background liquid scintillation counting system is around 0.4 Bq/L for counting time of 1000 minutes using 100 mL vial (Hagiwara et al., 2012). As tritium concentration in environment is 1 Bq/l or lower and especially lower than 0.5 Bq/L in seawater in Japan (Yamashita &Muranaka, 2011), it is difficult to measure the concentration even using such a low background liquid scintillation counting system. To solve the problem tritium concentration in sample water is enriched by water electrolysis before counting. Since the tritium concentration in the enriched water exceeds the lower limit of the counting system, the concentration can be measured with the sufficient accuracy even for seawater.
- Various methods are proposed to obtain the enrichment factor in the tritium electrolysis in sample water. Among the suggested methods a method using apparatus constant presented by Kakiuchi, M. et al. (Kakiuychi et al., 1991) is noteworthy because the constant is not so fluctuated comparing with a separation factor (Inoue & Miyamoto, 1987). Details are described in the next paragraph.

- Tritium enrichment apparatus by electrolysis is roughly classified into two categories. One is the method using alkaline electrolyte and another is that using solid polymer electrolytic film (SPE film). Electrolysis using SPE film was established firstly by Saito, M. et al. (Saito et al., 1996) and a large current apparatus was developed commercially (Saito, 1996). SPE film is used as a medium to carry hydrogen ions from anode electrode to cathode one in electrolytic cell instead of $OH^-$ in alkaline electrolysis. Since this method has merits that alkalizing and neutralizing process of electrolytic solution is not necessary and there is no limit for electrolytic enrichment factor, this method is used in many groups recently.

### 3.7.2 Electrolytic enrichment of tritium in water

#### Principle of Electrolytic Enrichment

The basic formulas for electrolysis are shown in equation (1)～ (3). (1) is the reaction in anode electrode, (2) is that in cathode one and (3) shows the whole reaction for electrolysis. Tritium, deuterium and light hydrogen exist in water as THO, DHO and $H_2O$, respectively. It is confirmed experimentally that $H_2O$ is easily electrolyzed than THO and DHO. Tritium and deuterium in water thus are enriched after the continued electrolysis. Schematic diagram of electrolytic enrichment using SPE film is depicted in Fig.20 In anode electrode sample water is decomposed into oxygen and hydrogen ion and the generated $H^+$ ion passes through the SPE film. This $H^+$ ion is combined to the electron arrived at cathode electrode through the external electric circuit and is released as hydrogen gas.

$$H2O \rightarrow O2/2+2H{+}{+}2e- \qquad (1)$$

$$2H{+}{+}2e\ \text{-}\rightarrow H_2{}^2H{+}{+}2e-\rightarrow H_2 \qquad (2)$$

$$H_2O \rightarrow O_2/2+ H_2H_2O \rightarrow O_2/2+ H_2 \qquad (3)$$

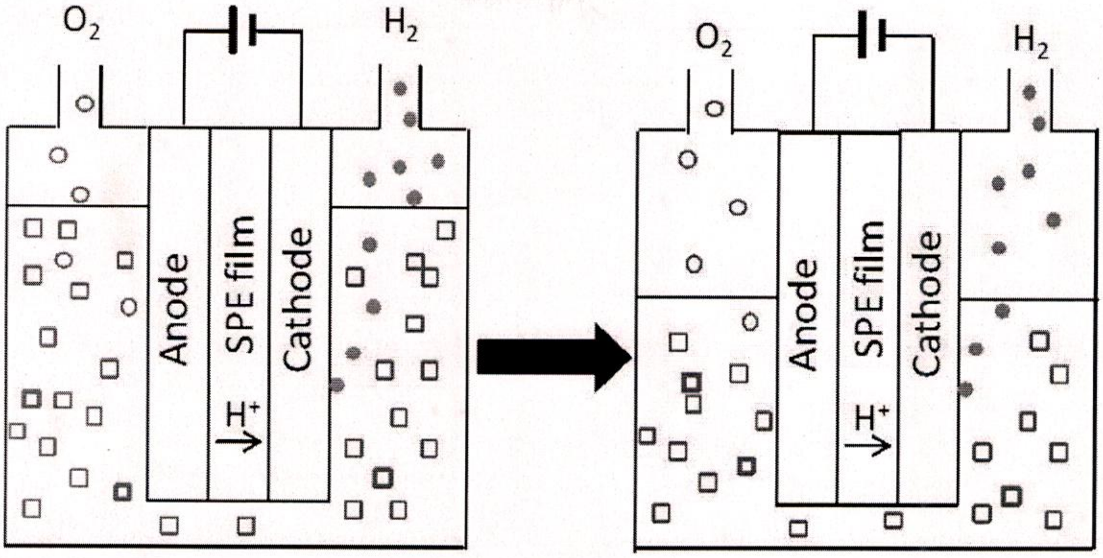


**Figure 20: Electrolytic enrichment of tritium in water.**

Opened squares in the electrolytic cell represent $H_2O$ and those with comparatively thick border show THO or DHO. Opened and filled circles mean oxygen gas and hydrogen gas, respectively. Electrolysis proceeds from left hand figure to right hand one, that is, the number of THO or DHO molecules are not so reduced although those of $H_2O$ molecules are gradually decreased in the process of electrolysis.

### 3.7.3 Method and Apparatus for Electrolytic Enrichment

#### An Electrolytic Enrichment of Tritium Using Alkaline Electrolyte

In the conventional method for electrolytic enrichment of tritium a pair of metal electrode is set in an electrolytic cell and sodium peroxide ($Na_2O_2$) is added to the sample water in the cell to give it the electric conductivity. As the structure of this type of electrolytic cell is so simple that two or more cells can be connected in series and electrolytic enrichment in multiple cells is possible to be electrolyzed at the same time. Schematic diagram of two electrolytic cells in series is shown in Fig.21

On the other hand this method has a disadvantage of a tedious process after the electrolysis that electrolytic material must be neutralized and the precipitation material has also to be removed from the solution. Another demerit of this method is that electrolytic enrichment factor is limited by the solubility of the electrolyte.

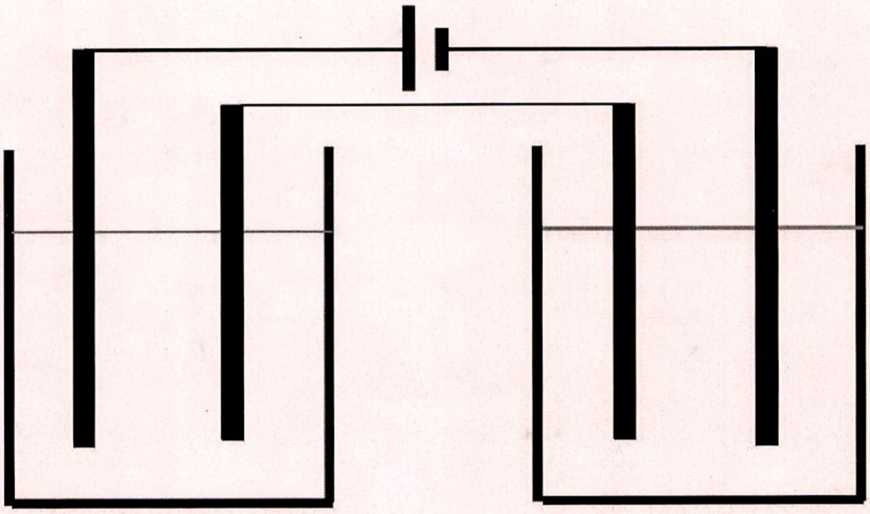


**Figure 21: Electrolytic enrichment of tritium concentration in sample water connecting each cell in series.**

### 3.7.4 An Electrolytic Enrichment of Tritium Using Spe Film

Water electrolysis using SPE film is started by G. E. in USA at 1970s applying fuel cell technology. The used SPE film is a kind of cation exchangeable membrane (NAFION® 117, DuPont).

This membrane is composed of carbon-fluorine backbone chains with many perfluoro side chains containing sulphuric acid groups ($SO_3^-$) and hydrogen plus ion can wade through the groups as depicted in Fig.22.The hydrogen ion reached to the cathode through the membrane film receives an electron from the external electric circuit and pair of hydrogen atoms are connected to be hydrogen gas.

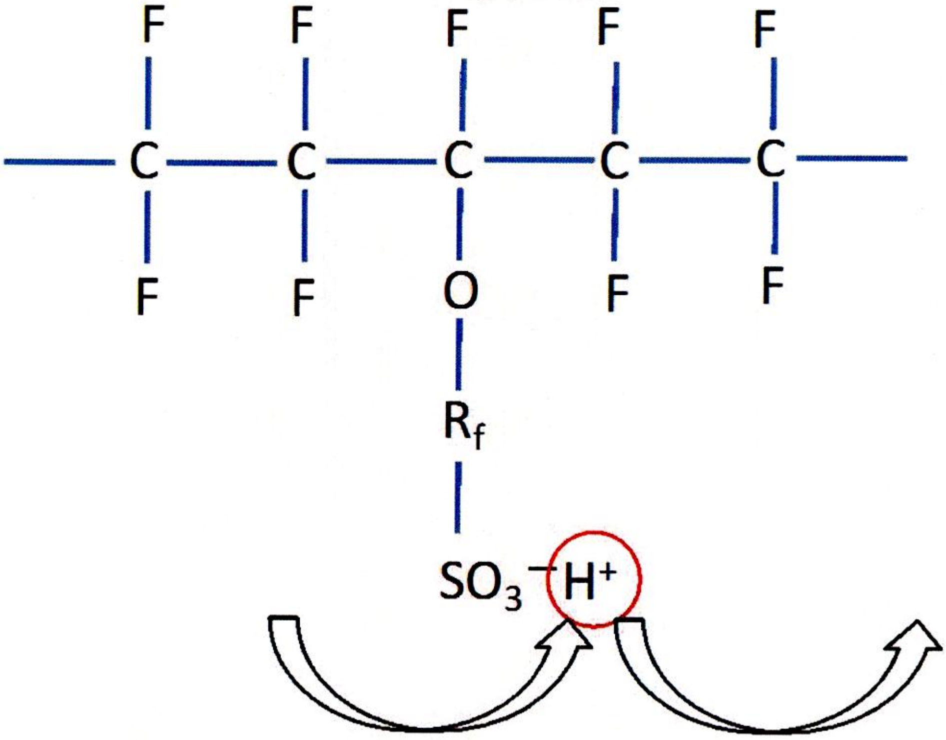


**Figure 22.The structure of SPE film and the transfer of hydrogen ion from a sulfonic acid group to the next one.**

In this method sample water can be enriched by electrolysis without adding any electrolyte to the water and then the tedious process after the electrolysis is not necessary and the enrichment factor is not limited by the solubility of the electrolyte. In addition to these merits electrolytic current can be increased removing generated gases quickly from the surface of both electrodes.

Figure 23: working on enrichment units cells

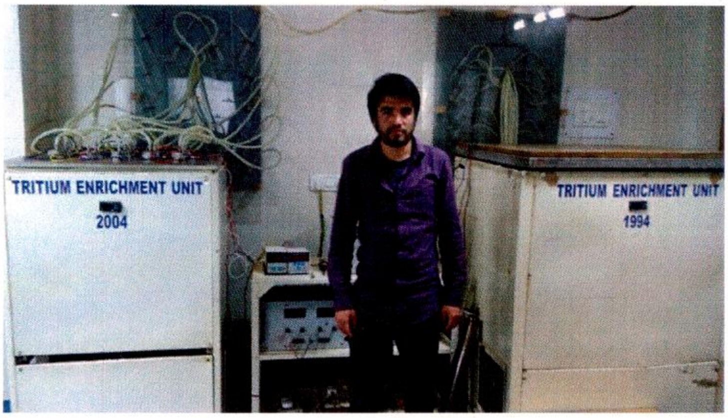


Figure 24: tritium enrichment units

# CHAPTER 4

## 4.0 RESULTS

### 4.1 Isotopic Composition of Rain Water

The isotopic composition of precipitation in study are varies from -5.984‰ to -3.089‰ for $\delta^{18}O$ and -44.015‰ to -27.851‰ for $\delta^{2}H$. The $\delta^{18}O$- $\delta^{2}H$ bi plot of precipitation in the study area (Moth) shows similarity with GMWL (Rozanski *et al.* 1993) (Fig.25) and Indian Meteoric Water Line for the north region (IMWL- North) (Kumar *et al.* 2010). The slightly lower intercept may be due to local climate.

LMWL: $\delta^{2}H = 7.7 \times \delta^{18}O + 5.5;$ $R^{2} = 0.99$ (eq. 1)

IMWL- North: $\delta^{2}H = 8.15 \times \delta^{18}O + 9.55;$ $R^{2} = 0.99$ (eq. 2)

GMWL: $\delta^{2}H = 8.17 \times \delta^{18}O + 11.27;$ $R^{2} = 0.99$ (eq. 3)

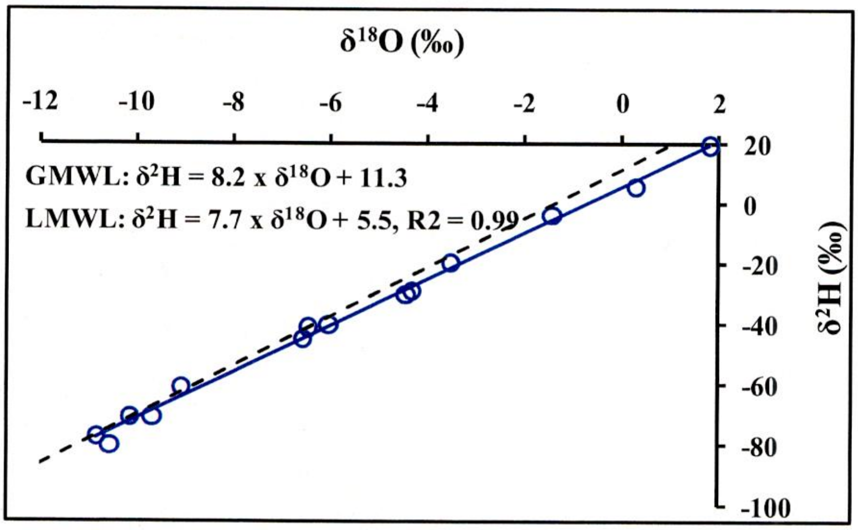


**Figure 25: Isotopic composition of Precipitation of study area**

### 4.2 Isotopic Composition of Groundwater

Groundwater samples collected from the different villages on the basis of grid map. The groundwater samples were collected from existing dug well, hand pump and tube wells. The oxygen isotope ratio ($\delta^{18}O$) of shallow groundwater samples varied from -5.984‰ (minimum) to -3.089‰ (maximum) and hydrogen isotopic ratio ($\delta^{2}H$) from -44.015‰ (minimum) to -27.851‰ (maximum) .(Figure .26)

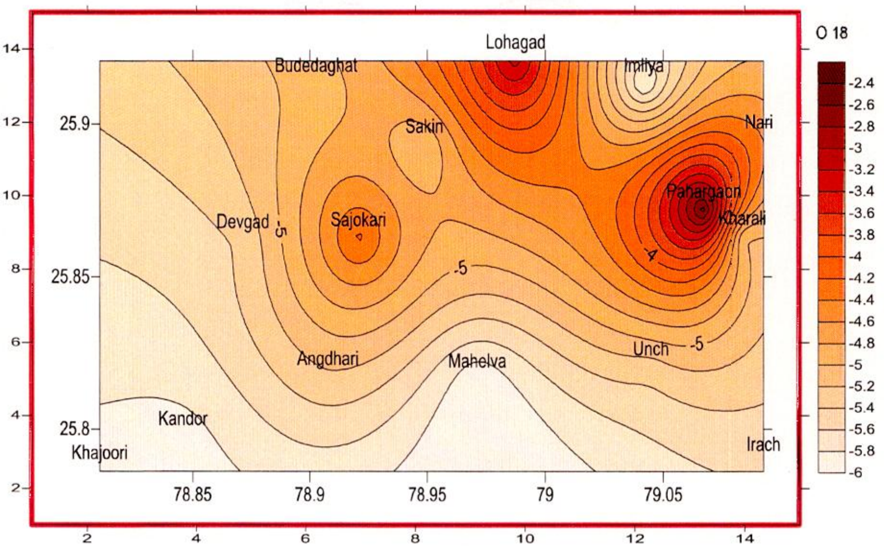


**Figure 26: Isotopic variation ($\delta^{18}O$) of shallow groundwater**

The δ $^{18}$O and $\delta^2$H relationship of shallow groundwater has been developed (Figure27) The regression analysis between $\delta^{18}$O and $\delta^2$H of the data gives the best fit line (BFL) as:

$$\delta^2H = 5.3 * \delta^{18}O - 10.5 \quad (n = 121, r^2 = 0.88) \qquad (4)$$

where as, n is the number of samples, r is the correlation coefficient

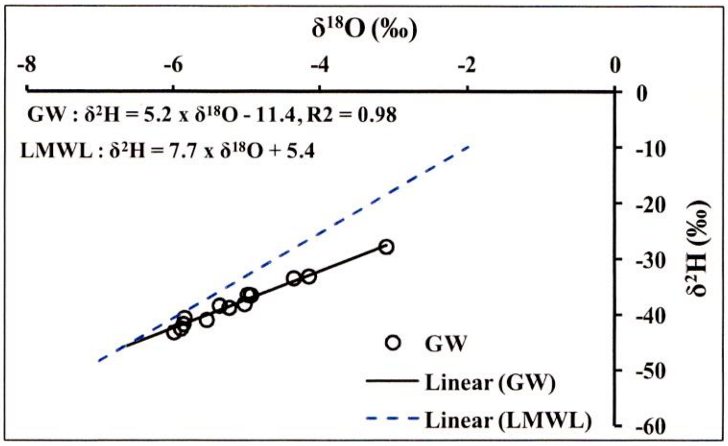


**Figure 27: $\delta^{18}O - \delta^2H$ plot of shallow groundwater of Jhansi district**

### 4.3 d-excess

The isotopic imprints of evaporation are also recorded in the form of a parameter called d-excess. The d-excess or d-index means the surplus deuterium relative to the Craig's Line. The characteristics of the d-index are a) equilibrium processes do not change the d-index for any of the phases, b) non-equilibrium evaporation from a limited amount of water reduces the d-index of the water as long as exchange is not a dominating factor. The extent to which $^{18}$O is more fractionated compared to $^2$H can be defined by Dansgaard (1964) as below:

$$\text{D-excess (d)} = \delta^2H - 8*\delta^{18}O \text{ (‰)}$$

The d-excess (d) as defined above represents the excess $\delta^2H$ than 8 times $\delta^{18}O$ for any water body or vapour. The magnitude of equilibrium fractionation (condensation) for $^2H$ is about 8 times to that for $\delta^{18}O$. Thus due to evaporation (non-equilibrium fractionation) from a water body, the D-excess of the evaporating water decreases while it increases in water vapour.

The d-excess of rain and shallow groundwater ranges 3‰ to 12‰ and 0.086‰ to 5.078‰ respectively. D-excess variation of shallow groundwater shown in Fig

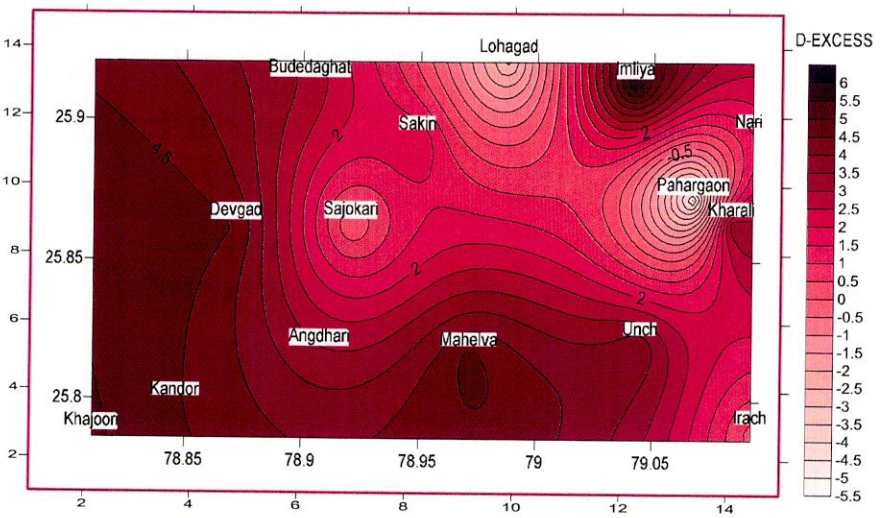


Figure 28: Variation of d-excess of shallow groundwater in Moth area (Jhansi)

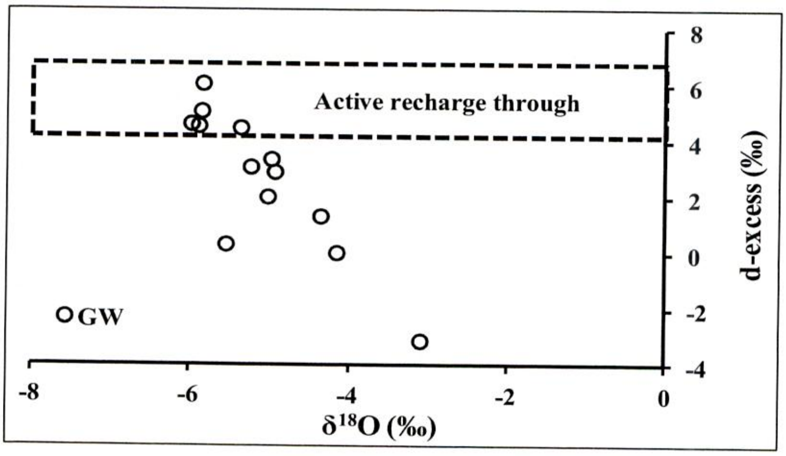


Figure 29: $\delta^{18}O$ - d-excess plot of rain water and groundwater

# CHAPTER 5

## 5.0 CONCLUSIONS

Groundwater is as an important resource for people's day to day life. However the effect of groundwater withdrawals and out-flows are directly measurable through water table conditions in central part of the India. The studies have revealed that isotopes are indicator of recharge sources and zones of groundwater. Further isotope help to know the recharge rate and flow direction and rates of groundwater in any area.

Around 13 groundwater samples were collected from Moth area (Jhansi). The $\delta^{18}O$ values of rain water vary from -5.984‰ to -3.098‰ and $\delta^{2}H$ varies from -44.015‰ to -27.851‰, suggesting SPATIAL VARIATION IN ISOTOPIC COMPOSITION DUE TO VARIATION IN RECHARGE RATE. Groundwater isotopic values fall on the LMWL, indicating local precipitation as the main recharge source, although a few depleted samples falling above the LMWL suggest local canal recharge.

**Table 7: Stable isotopic composition of groundwater in Moth area (Jhansi)**

| S. No. | Grid No. | Village | Longitude | Latitude | δ18O (‰) | δ2H (‰) | d-excess (‰) |
|---|---|---|---|---|---|---|---|
| 1 | 1 | Budedaghat | 78.90 | 25.91 | -4.933 | -36.560 | 2.900 |
| 2 | 2 | Lohagad | 78.99 | 25.92 | -3.089 | -27.851 | -3.141 |
| 3 | 3 | Imliya | 79.04 | 25.91 | -5.840 | -40.656 | 6.065 |
| 4 | 4 | Devgad | 78.87 | 25.86 | -5.364 | -38.429 | 4.484 |
| 5 | 5 | Sajokari | 78.92 | 25.86 | -4.147 | -33.170 | 0.006 |
| 6 | 6 | Sakin | 78.95 | 25.89 | -5.020 | -38.151 | 2.008 |
| 7 | 8 | Nari | 79.09 | 25.89 | -4.351 | -33.495 | 1.314 |
| 8 | 8 | Kharali | 79.08 | 25.86 | -4.978 | -36.468 | 3.359 |
| 9 | 9 | Khajoori | 78.81 | 25.79 | -5.854 | -41.756 | 5.078 |
| 10 | 10 | Kandor | 78.85 | 25.80 | -5.890 | -42.572 | 4.550 |
| 11 | 11 | Angdhari | 78.91 | 25.82 | -5.234 | -38.798 | 3.078 |
| 12 | 12 | Mahelva | 78.97 | 25.82 | -5.984 | -43.246 | 4.627 |
| 13 | 14 | Irach | 79.09 | 25.79 | -5.540 | -44.015 | 0.303 |

## Brief overview of National Institute of Hydrology

INSTITUTE OF HYDROLOGY (NIH) is a premier organization involved in Research and Development under Ministry of Water Resources, Government of India. NIH was established in 1978 with the main objective of undertaking, aiding, promoting and coordinating systematic and scientific work in all aspects of hydrology. It was established as an autonomous society and is fully funded and aided by the Ministry of Water Resources, Government of India. The Institute is located at Roorkee Town in Hardwar District, Uttarakhand, India. Roorkee, the historic town, is a well known educational & research centre with the I. I. T., Roorkee and a number of R & D organizations viz. Central Building Research Institute, Irrigation Research Institute and Army's Bengal Engineering Group. The studies and research activities at the NIH Roorkee are carried out under five Scientific Divisions. Besides in-house research projects, these Divisions undertake various sponsored and consultancy ii projects. As part of the technology transfer program of the Institute, various training courses/workshops are also organized by the Divisions. The five divisions are as follows:

1. Hydrology Division
2. Groundwater Hydrology Division
3. Hydrological Investigations Division
4. Surface Water Hydrology Division
5. Resources Systems Division

## 6.0 REFERENCE MATERIAL

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