

SR-31



UNDP PROJECT  
DEVELOPING CAPABILITIES FOR HYDROLOGICAL RESEARCH  
IND/90/03



**USE OF ENVIRONMENTAL ISOTOPES  
IN HYDROLOGY**

**Bhishm Kumar**

**NATIONAL INSTITUTE OF HYDROLOGY  
JALVIGYAN BHAWAN  
ROORKEE-247 667 (INDIA)**

## PREFACE

The use of isotopes in hydrology is now not new to the scientific community. But, most of the people understand that only artificially produced radio-isotopes can be used for various hydrological investigations while the environmental isotopes which comprise stable and radioactive isotopes both have numerous applications in the field of hydrology, besides the fact, that the availability of these radioisotopes is free of cost and also they do not pose any threat to the human being from health hazard point of view. The only negative point associated with the use of environmental isotopes is that, costly instrumentation is required for their analysis in comparison to artificial radioisotopes.

The National Institute of Hydrology has recently established a Nuclear Hydrology Division and Nuclear Hydrology Laboratory. There is a provision in the UNDP project to get the scientists of the Institute trained in the developed countries in this field. In this regard the training of a scientist working in this Division, namely Dr Bhishm Kumar has been arranged at Paris University (South), France on the topic "Use of environmental isotopes in hydrology" under the supervision of Prof. J Ch.Fonts. This report has been prepared by Dr Bhishm Kumar as a status report on the above referred topic under the UNDP Project No.IND/90/003 entitled, "Developing Capabilities in Hydrology". The report provides the detailed information about the various activities carried in India and gaps including the various environmental isotopes techniques which can be used in hydrology.

(SATISH CHANDRA)  
DIRECTOR

## ABSTRACT

The use of isotopes in hydrology is now not new to the scientific community. But, most of the people understand that only artificially produced radio-isotopes can be used for various hydrological investigations while the environmental isotopes which comprise stable and radioactive isotopes both have numerous applications in the field of hydrology, besides the fact, that the availability of these radioisotopes is free of cost and also they do not pose any threat to the human being from health hazard point of view. The only negative point associated with the use of environmental isotopes is that, costly instrumentation is required for their analysis in comparison to artificial radioisotopes.

The use of environmental isotopes is also not very popular in India alike in developed countries, but, few of the organisation like BARC, Bombay and NGRI, Hyderabad are using there isotopes in a very limited way.. However, the expertise required for the use of environmental isotopes in hydrology is still to be developed. The present report deals with the basic concepts of environmental isotopes, their variations in nature, applications of environmental stable and radioactive isotopes in the field of hydrology, detection and measurement techniques and gaps, the present status of the use of environmental isotopes in India has also been described in brief.

## CONTENTS

	PAGE NO.
ABSTRACT	i
1.0 INTRODUCTION	1
2.0 ENVIRONMENTAL ISOTOPES	3
2.1 Stable Isotopes	4
2.1.1 Variation in Stable Isotopic contents of Groundwater	8
2.1.2 Variation in Stable Isotopic Contents of Precipitation	8
2.2 Environmental Radioisotopes (Tritium and Carbon)	10
2.2.1 Variation of Tritium and Carbon in Precipitation	13
2.2.2 Variation of Tritium and Carbon in Subterranean Waters	13
3.0 APPLICATION OF ENVIRONMENTAL ISOTOPES	14
3.1 Surface water and Groundwater Interaction	15
3.2 Water Balance of Lakes	17
3.3 Origin of Recharge Sources And Paleowaters	18
3.4 Leakage Between Aquifers	21
3.5 Geothermal Systems	22
3.6. Dating of Groundwaters	27
3.7 Sedimentation in Lakes and Reservoirs	31
3.8 Ice And Snow dating/gauging/melt	38
3.9 Groundwater Pollution (Salinization)	42
4.0 SAMPLING AND MEASUREMENT TECHNIQUES FOR ENVIRONMENTAL ISOTOPES	43
4.1 Sampling Techniques	43
4.2 Measurement Techniques	51
5.0 REVIEW OF THE STUDIES CARRIED OUT IN INDIA	58
5.1 Using Stable Isotopes	58
5.2 Using Environmental Radioisotopes	61
6.0 GAPS AND FUTURE PROSPECTS IN INDIA	63
List of organisations engaged in isotope hydrology work in India	67
REFERENCES	68

## 1.0 INTRODUCTION

The use of isotopes as a tool to obtain various useful hydrological information is well known among the scientific and engineering community. Nuclear methods are being used in the field of hydrology for the last 50 years. In beginning, the use of radioisotopes was much more popular and even in vogue but, in present days, due to various specific problems, the users try to employ as much as possible, the applications of environmental isotopes, mostly stable isotopes which are price less and harmless to human being.

Nuclear/isotope hydrology may be categorized under three headings,

- 1) The use of variations in the environmental isotopic composition of water
- 2) The use of artificial radioactive tracers
- 3) The use of radioisotope instruments

This report however deals with only one category i.e. applications related with the use of environmental isotopes. Basically, the isotope techniques are based on two basic properties of isotopes i.e. the ability to detect in very low concentrations and they subject to variations in their concentration/intensity when subjected by various natural processes or attenuated when interact with various media.

An isotope is the atom of an element having same atomic number but different atomic weight. The weight of an atom is denoted by symbol 'A' while atomic number by 'Z'. For example, the Hydrogen and Oxygen posses 3 isotopes each, i.e.

$^1\text{H}$  - Normal atom of Hydrogen with Atomic Number(Z) = 1 and Atomic Weight(A) = 1

- $^2\text{H}$  - Known as Deuterium - an stable isotope with At. No.(Z) = 1 and At. Wt.(A) = 2
- $^3\text{H}$  - Know as Tritium - a radioactive isotope with At. No. (Z) = 1 , At Wt.(A) = 3 and half life( $T_{1/2}$ ) = 12.5 yrs.
- $^{16}\text{O}$  - Normal atom of oxygen with At. No.(Z) = 8 and At. Wt.(A) = 16
- $^{17}\text{O}$  - A stable isotope of oxygen with At. No.(Z) = 8 and At. Wt.(A) = 17
- $^{18}\text{O}$  - A stable isotope of oxygen with At. No.(Z) = 8 and At. Wt.(A) = 18
- C - Carbon has also three isotopes,
- $^{12}\text{C}$  - Normal carbon atom with (Z) = 6 and (A) = 12
- $^{13}\text{C}$  - A stable isotope of carbon with (Z) = 6 and (A) = 13
- $^{14}\text{C}$  - A radioactive isotope of Carbon with (Z) = 6 and (A) = 14

Radioactive (unstable) isotope emit alfa( $\alpha$ ) particles, beta( $\beta$ ) particles and gamma( $\gamma$ ) radiations during their transformations from unstable to stable. The  $\alpha$  particle is a doubly ionized helium atom and owing to its mass(4) ,it is comparatively heavy. Its penetration power is very less and is of no direct use. The  $\beta$  particle is an election ejected from the nucleus with an energy ranges from few keV to Mev are of great use for various hydrological investigations. The  $\gamma$  radiations have the large penetration power and therefore can be used as an important tool for various important hydrological investigations. The neutrons are also emitted by many atoms when particles from other atom are interacted. Therefore, two elements are used (Ra/Be, Am/Be etc.) to get the neutron particles, which are also used as a tool for the study of soil moisture variations.

Because of radioactive in nature, these radioisotopes pose a threat to the human being for the excess exposer of various radiations which are very harmful to the human being after a certain limit. However, the stable isotope, as they do not radiate

any types of particles/radiations, they are quite safe and can be used without any fear. Nevertheless, the radioactive isotopes are harmful, but, they can be detected with easy and comparatively cheaper instruments while very costly instruments are required for the measurement of stable isotopes. However because of harmless in nature and field work can be done by semiskilled or even unskilled person, the use of stable isotopes in the hydrology is increasing day by day with the increase in the facilities for their measurements at various laboratories in India.

This report deals with the use of environmental stable and unstable isotopes for various studies in the field of hydrology, their measurement techniques, status of their use in India and Gaps for which expertise is required to be developed in India for carrying out the systematic studies .

## 2.0 ENVIRONMENTAL ISOTOPES

Environmental isotopes can be defined as those isotopes, both stable and radioactive (unstable) which occur in atmosphere / environment in varying concentrations with respect to place and time over which the investigator has no direct control. The most commonly used environmental stable isotopes are Deuterium, Oxygen-18, Carbon-13 and radioisotopes Tritium ( $^3\text{H}$ ) and Carbon-14. Silicon-32, Cs-137 and Pb-210 etc. are also used as environmental radioisotopes for few specific studies in Hydrology.  $^{32}\text{Si}$  is potentially attractive because, its half life (100 yrs) is between that of  $^3\text{H}$  and  $^{14}\text{C}$ . A number of measurements have been made in India<sup>(1)</sup> but, it has not been used widely. Argon-39<sup>(2)</sup> has also been investigated and research is still in progress, but the disadvantage of using both Si-32 and Ar-39 is that large amount of water (a few tonnes) is required to provide required amount of sample for measurement.

## 2.1 STABLE ISOTOPES

D and  $^{18}\text{O}$  are the most widely used stable isotopes while  $^{17}\text{O}$ , being of similar nature of  $^{18}\text{O}$  except less atomic weight is not used.  $^{13}\text{C}$ , although is a stable isotope is used for the interpretation of the  $^{14}\text{C}$  concentration, a radio isotope for dating of waters.

It was not until 1929 that  $^{18}\text{O}$  and  $^{17}\text{O}$  were discovered in natural material; this was achieved with in a few months by Giauque and Johnston(1929)<sup>(3)</sup> while interpreting the adsorption bands in the spectrum of atmospheric oxygen. The authors were not able to predict the reliable value for the abundance of these isotopes, but estimated them to be about one part in 1250 for oxygen-18 and about one part in 10,000 for  $^{17}\text{O}$ . Mecke and Childs (1931)<sup>(4)</sup> determined the ratio  $^{16}\text{O}:^{18}\text{O}:^{17}\text{O} = 630:1:0.2$  using the adsorption band spectra of the  $\text{O}_2$  molecule in air. The currently accepted value for the relative abundance of isotopes in air oxygen is 99.759: 0.037: 0.2039<sup>(5)</sup> which is equivalent to an  $^{18}\text{O}/^{16}\text{O}$  ratio of 1:489. Later work, particularly in the years followed by World War II, showed that variations of up to 10 % occur in natural abundance of  $^{18}\text{O}$  derived from different natural sources. With the further increase in precision, it is meaningless to speak of the abundance of oxygen until the source of the sample analysed was carefully specified.

Urey<sup>(6)</sup> discovered deuterium in 1931 by identifying its atomic spectrum. The natural concentration of deuterium was estimated to be  $\text{D}/\text{H} = 1/4000$  by Urey et al.(1932)<sup>(7)</sup>. Morita and Titani (1938)determined the deuterium content of Osaka tap water to be  $\text{D}/\text{H}=1:62000$  in the year 1938. Almost pure  $\text{D}_2\text{O}$  as well as  $\text{H}_2\text{O}$  depleted in deuterium were prepared in 1934 by electrolytic decomposition of water and thus the study of the physical properties of heavy water became possible.



The early studies carried out using isotopic water molecules and geological materials were reviewed by Rankama (1954)<sup>(8)</sup>. The large differences between  $D_2O$  and normal water in properties such as vapour pressures, density, equilibrium constants and reaction rates added momentum to the study of the so called "isotope effect" on phase equilibria, reaction rates and transport processes which involved the isotopic water species. A major break through in the measurement of natural isotope abundances came with the mass spectrometer developed by Nier/Mekinney with the help of which direct measurement of the ratio became possible.

The stable isotopes of water molecule i.e.  $^1H$ ,  $^2H$ ,  $^{16}O$ ,  $^{17}O$  and  $^{18}O$  do not decay with time, but it is significant that various species are formed like  $^1H_2^{16}O$ ,  $^1H^2H^{16}O$ ,  $^1H_2^{18}O$ ,  $^2H_2^{18}O$  ( $D_2^{16}O$ ),  $H_2^{17}O$ ,  $D_2^{17}O$ ,  $HD^{17}O$ ,  $HD^{18}O$  and  $D_2^{18}O$ . All of these occur in natural waters but only  $H_2^{16}O$ ,  $H_2^{18}O$ ,  $HD^{16}O$  and  $H_2^{17}O$  molecules are of importance for various hydrological studies. However, in terrestrial materials, the  $^{17}O$  geochemistry echoes that of the 5.5 times more abundant  $^{18}O$ , and this is also usually not considered separately. Therefore, in most of the cases, the abundance ratios of the isotopic pairs  $^{18}O/^{16}O$  and  $D/H$  are considered. For an stable isotope to be useful for hydrological studies, the characteristics are desirable.

1. The relative mass difference of common to rare isotopes of the element should be large. The isotopes of heavy elements may not show significant separation in nature because of the difference of their weight.
2. The abundance of the rare isotopes must be substantial and in contrast with the dominant isotope.
3. The occurrence of some natural process modifies the relative abundance of an element's isotope in a system. Therefore, the

variations must be measured with precision. The absolute measurement of isotope ratios is analytically difficult, therefore relative isotopic ratios are measured. The variations of D/H ratio are 5 to 8 times bigger in natural waters than those of  $^{18}\text{O}/^{16}\text{O}$ , however, variations of  $^{18}\text{O}/^{16}\text{O}$  can be measured with a precision 10 times higher in natural waters than those of D/H.

Deuterium and oxygen-18 occur in the oceans in concentrations of about 310 PPM and 1990 ppm for the molecular species  $\text{HDO}$  and  $\text{H}_2^{18}\text{O}$  respectively. The ratios in concentrations of these isotopes in natural waters is measured in an isotope ratio mass spectrometer and are expressed in the delta ( $\delta$ ) notations.

$$\delta = (R_s - R_{\text{std}}) / R_{\text{std}} \quad (2.1.1)$$

Where,

$R_s$  - is the isotope ratio (D/H or  $^{18}\text{O}/^{16}\text{O}$ ) of sample

$R_{\text{std}}$  - is the isotope ratio (D/H or  $^{18}\text{O}/^{16}\text{O}$ ) of the standard

Delta ( $\delta$ ) values are expressed in part per mil (thousand) deviation from a standard and denoted by '%.' symbol.

For example,  $\delta^{18}\text{O} = -11$ , means that the sample contains 11 parts per thousand less  $^{18}\text{O}$  than the standard.  $\delta$  for  $^{13}\text{C}$ ,  $^{34}\text{S}$ , and  $^{15}\text{N}$  can be defined in a similar manner.

The universally adopted standard for deuterium and oxygen-18 is SMOW (Standard Mean Ocean Water). This refers to a hypothetical water whose hydrogen and oxygen isotope ratios are close to the mean isotope ratio of ocean water<sup>(9)</sup>. Subsequently, a standard water sample prepared by IAEA, known as VIENNA-SMOW(V-SMOW) whose oxygen content is the same as that of SMOW but deuterium content

is lower by 0.2 %. is also used for the measurement of  $\delta$  values. But for all practical purpose, V-SMOW and SMOW are considered identical since the accuracy of measurements is usually 1 % and 0.1 % for deuterium and oxygen-18 respectively.

When water changes state through condensation or vaporisation, an isotopic fractionation occurs because of the difference in vapour pressures and diffusion velocities in air of the different isotopic species of water. Water vapour in equilibrium with liquid water is depleted in the heavy isotopic species with respect to the liquid phase. The degree of isotopic fractionation is inversely related to temperature.

There is a seasonal change in the stable isotopic composition of precipitation at a given location, with more depleted values occurring in the colder months. Also, more depleted values are obtained at higher latitudes. Precipitation falling at higher elevations is more depleted than that falling at lower elevations; this latter property is of particular utility in hydrological applications. Precipitation at continental locations is more depleted than that which falls nearer the coast.

In contrast to the condensation process, evaporation does not take place under equilibrium conditions. The effective fractionation factors are greater than the equilibrium values. When water undergoes evaporation the lighter isotopic species preferentially leave the surface, so the remaining water becomes enriched by stages in the heavy isotopic species. The degree of enrichment depends on the temperature, the relative humidity of the atmosphere, and the hydrological balance of the surface water body. The enrichment of oxygen-18 is about one order of magnitude less than deuterium. An important process which controls the enrichment of the surface water is molecular exchange, which occurs between the surface water and the atmospheric water vapour.

The deuterium and oxygen-18 values of natural waters obey the following general correlation:

$$\delta D = a \delta^{18}O + d \quad (2.1.2)$$

For waters which have not been subjected to evaporation the value of  $a$  is 8 and the average global value of  $d$  for precipitation is 10. The stable isotopic composition of natural waters is often plotted on a  $D/^{18}O$  diagram.

### 2.1.1 Variation in stable isotopic content of groundwater

The stable isotope content of groundwater is normally equal or near to the average content of precipitation in the recharge area. The differences of  $D$  and  $^{18}O$  are more or less contemporary in groundwaters to those of precipitation in recharge zones. If, for example, the recharge zones of two aquifers are at different altitudes, the isotopic composition of water from the two aquifers will also differ. When the age of ground water is more than a few thousand years, their heavy isotopic content may be noticeable different from that of the actual recharge waters, this is due to intervening climatic variations, and especially changes in temperature and humidity. If the ground waters are recharged by surface waters, their isotopic composition can be affected by the partial evaporation to which the waters may have been subjected before infiltration. In this case, the waters will be enriched in heavy isotopes (less volatile) and their values of  $\delta D$  and  $\delta^{18}O$  will no longer have a linear relation and isotopic composition of groundwater will provide information on its origin.

### 2.1.2 Variation in stable isotopic content of precipitation

Water vapour which evaporates from the ocean is depleted in deuterium and oxygen-18 contents with respect to oceanic water as  $HDO$  and  $H^{18}O$  which are less volatile than  $H_2O$ . When the

atmospheric vapour is subjected, following cooling, to successive condensation producing snow and precipitation, the heavy isotopes condense first and the remaining vapour is more and more depleted for D and  $^{18}\text{O}$ . Therefore, successive precipitations are also more depleted of heavy isotopes. Since the degree of condensation depends on the temperature, one should expect that the values of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  are correlated with the temperature of formation of precipitation. Correlation with temperature gives rise to isotopic variations according to season, winter rain is depleted by heavy isotopes in comparison with summer rain. The heavy isotope content of rain decreases with altitude and also get affected due to variations in latitude. Thus rainfall at colder temperatures, higher altitudes and latitudes and greater distance from the ocean will be characterized by isotopically lighter  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values.

Both the absolute and relative amounts of these isotopes change when water is removed by phase changes. For example, during condensation water molecules containing the lighter isotope have a higher vapour pressure and hence enrich the gas phase, while the heavier isotope forms precipitation more readily. Equilibrium phase changes affect deuterium and  $^{18}\text{O}$  in a constant ratio and their values are linearly related in rainwater according to a general world wide acceptable equation;

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10 \quad \text{McCraig(1961)}^{(10)} \quad (2.1.2.1)$$

Condensation is an equilibrium reaction, where as kinetic effects became more important during evaporation which results in additional fractionation. Fractionation is a process that separates the isotopes of an element. The depletion or enrichment of a heavier isotope relative to lighter one is reflected by different  $\delta$  values. Fractionation process are the result of physical and chemical reactions. Owing to different thermodynamic properties, molecules with different masses have different rates

of diffusion, evaporation, condensation, freezing and melting.

Thus phase changes such as condensation of rain separate the isotopes in physical fractionation. Chemical fractionation occurs due to the different bond energies of different isotopic molecules. Heavier isotopes prefer a higher bond strength than lighter isotopes, so the isotopes may be separated in chemical reactions. There are two types of chemical fractionation, kinetic and equilibrium. Kinetic fractionation is due to relative velocity and vibrational frequency of the molecules and is irreversible. In equilibrium chemical reactions, the isotopes are continuously exchanged rather than separated by unidirectional movement. The heavy isotopes are enriched in the compound that will hold the isotope most strongly. The solid phase is enriched in the heavier isotopes according to equilibrium fractionation. Physical and chemical fractionation thus affect the isotopic ratios of a system. Fast reactions tend to accentuate kinetic effects and slow reactions accentuate equilibrium effects. Lakes and open systems have  $\delta D$  and  $\delta^{18}O$  values that deviate from the world wide rainfall line because they are subjected to evaporation. Repeated evaporation and condensation leads to progressively lighter isotopic values in the vapour phase.

## 2.2 ENVIRONMENTAL RADIOISOTOPES( Tritium and Carbon )

Tritium ( $^3H$ ) and Carbon-14( $^{14}C$ ) are the most widely used environmental radioisotopes. However, there are few other environmental radioisotopes like S1-32, S-34, Ar-39, Cs-137, and Pb-210 which are used for few specific studies in hydrology. But, here, we will restrict our discussion only up to tritium and C-14 while the other environmental radioisotopes will be discussed under the section of applications of environmental isotopes.

## TRITIUM:

As already described, tritium is the radioisotope of hydrogen that have half life 12.5 yr.(12.43 yr) and emits low energy beta radiation( $E_{max} = 18 \text{ KeV}$ ). Environmental concentrations of tritium in natural waters are measured in terms of TU(tritium unit) which is an isotope ratio. Therefore, it is not a unit, but, simply a ratio and is also referred in terms of TR(tritium ratio). One TU or TR has an isotopic ratio of  $^3\text{H}/\text{H} = 10^{-18}$ . One litre of water with a concentration of 1 TU produces 7.2 dpm (0.12 Bq).

There are two sources of environmental tritium. The first results from the interaction of cosmic ray produced neutrons in the upper atmosphere with nitrogen atoms i.e.  $1 \text{ }^{14}\text{N} + n = ^3\text{H} + ^{12}\text{C}$ .

The second source is the thermonuclear explosions which derived since 1952. The atmospheric testing injected periodic pulses of tritium into the atmosphere so that the concentrations in precipitation increased by three orders of magnitude in the northern hemisphere in 1963 above that arising from the cosmic ray source (5-20 TU). Its concentration was also increased in the southern hemisphere but only by two orders of magnitude because of lower ratio of land to ocean and also most of the thermonuclear tests were carried out in the northern hemisphere.

The IAEA/WMO monitor the concentrations of tritium over the world with the help of more than 100 stations installed at different places. It has been observed that the concentration of tritium in the environment now has been reached near to the values, so called, pre bomb levels. However, it has also been reported that in some areas, the concentration of environment tritium is still increased, due to the release from nearby nuclear facilities. Thus care must be taken in the interpretation of tritium data in such areas.

## CARBON:

Carbon-14 is the radioactive isotope of carbon which emits beta radiation ( $E_{\max} = 156 \text{ keV}$ ). Its half life is 5730 yr. The concentrations of carbon-14 are presented in percent modern carbon (PMC). The modern carbon-14 value is referred to 1950 and is equal to 95% of the radiocarbon concentration of the National Bureau of Standards (NBS) oxalic acid standard.

The carbon-14 is produced in the environment indirectly by the interaction of cosmic radiations i.e. the cosmic ray produced neutrons react with nitrogen atoms ( $^{14}\text{N} + n = ^{14}\text{C} + \text{H}$ ). The radioactive carbon-14 produced in the environment is oxidized to carbon dioxide and become the part of the atmospheric carbon dioxide reservoir. Normally, the production of C-14 in the environmental natural process is a continuous process and its concentration remains more or less constant at a given place. However, the variation in the C-14 concentration varies with respect to place and time due to various factors. Recently, the C-14 contents in the atmospheric  $\text{CO}_2$  has slightly decreased due to the production of  $\text{CO}_2$  by industrial combustion but C-14 content has increased in the recent past due to thermonuclear explosions.

Carbon-14 although is not a isotopic tracer of the water molecule, but it occurs in water as various species of dissolved inorganic carbon. The non conservative nature of C-14 as a tracer for water demands the use of a complete chemical analysis of water including the measurement of  $\delta^{13}\text{C}$  inputs. The amount of C-13 is expressed in  $\delta^{13}\text{C} \text{ }^0\text{/}\text{oo}$  and is compared to the PDB standard which has a ratio  $^{13}\text{C} / ^{12}\text{C}$  more or less equal to the average ratio of marine lime stone (which gives  $\delta^{13}\text{C} = 0$ ). Environmental carbon has an average of  $\delta^{13}\text{C} \text{ } 7 \text{ }^0\text{/}\text{oo}$  and that of biogenic origin



has 25 ‰ due to the isotopic fractionation in chlorophyllic synthesis, however significant variations in the ratio  $^{13}\text{C}/^{12}\text{C}$  is observed in different plants.

The age of groundwater can be determined by measuring the decay rate and dilution factors of C-14 concentrations. Water as old as 49,000 - 50,000 yr can be dated with C-14 techniques. Fractionation of C-13, a stable isotope provides information on carbonate solution that causes the dilution of Carbon-14. Photosynthesis, bacterial activity and other chemical reactions also, are the causes of fractionation of carbon isotopes which help in identifying the source of carbon.

### 2.2.1 Variation of tritium and Carbon-14 in Precipitation

The tritium and carbon concentrations in the precipitation has been monitored in an IAEA/WMO project at more than 100 stations spread over world wide. The data of concentration of isotopes in precipitation are published periodically<sup>(11-16)</sup>.

Since 1952, when the thermonuclear explosions started, an enormous quantity of tritium and carbon injected into the environment. The concentration of tritium increased from 5TU to 5000 - 10,000 TU in 1963-64 and thereafter started decreasing following the restrictions of explosions.

A knowledge of the tritium and carbon (dissolved CO<sub>2</sub>) concentrations in the precipitation is a prerequisite for estimating the input functions of these radioisotopes in a given area for interpreting their concentrations in groundwaters.

### 2.2.2 Variation of Tritium in Sub-terrain Waters

It is now a fact that the tritium concentration was very less in the environment (5TU) before 1952. But as, it can be detected in very minute quantity, even the quantity of 5TU or low values,

the studies related to the dating of waters have been carried out by many workers. In general, the following predictions rules were used for the analysis of the tritium data in waters till 80'S.

- i. If the amount of tritium is less than 3-5 TU, the age of water can be predicted prior to the starting of thermonuclear explosion era (prior to 1952).
- ii . If the amount is more than 15-20 TU, the recent component of water is available i.e.age of water is not very high i.e. after 1952.
- iii. If the amount is made up between 5 and 20 TU, the recent water is present and mixed with old water.

The study of the time variation of the amount of tritium may give very important information on water circulation time and about the characteristics of the reservoir.

### 3.0 APPLICATION OF ENVIRONMENTAL ISOTOPES

The environmental isotopes, both, stable and radioactive are being used extensively as a reliable tool in hydrological investigations. Environmental isotopes have wide applications both in surface water and groundwater hydrology. The details of the following applications of environmental isotopes have been described in brief in the coming sections.

- i. Surface water and Groundwater interaction
- ii. Water balance of lakes
- iii Origin of recharge sources and Paleowaters
- iv. Leakage between aquifers
- v. Geothermal systems
- vi. Dating of Groundwaters
- vii. Sedimentation in lakes and reservoirs
- viii. Ice and Snow dating/gauging/melt
- ix. Groundwater Pollution(Salinization)

There are numerous applications of environmental isotopes, however few of them could not be even listed here.

### 3.1 Surface Water and Groundwater Interaction

The value of this approach is that it provides a mean for identifying the actual mass transport of water. It is based on the fact that the surface water system normally has a different stable isotopic composition than that of recharge by infiltration of local precipitation. In case of a river system, the river will be transporting water which has originated as precipitation falling at higher elevations than the area where the surface-groundwater relation is under investigation. It is due to the altitude effect.

When saturated air moves upward it cools, which causes condensation. Consequently heat is released which counteracts cooling. The resulting change in temperature with altitude is called adiabatic lapse rate. The wet adiabatic lapse rate varies with altitude, but a value of  $0.6^{\circ}\text{C} / 100\text{ m}$  is reasonable. For  $^{18}\text{O}$ , the temperature dependence during wet adiabatic cooling is about  $0.5\% / ^{\circ}\text{C}$ . Hence, it is possible that the change in isotopic composition in precipitation with altitude will be between  $-0.2$  and  $-0.3\%$  per  $100\text{ m}$  for  $^{18}\text{O}$ .

As a result of the altitude effect, the stable isotopic composition of the river water will be more depleted than that of groundwater derived from infiltration of local precipitation. This distinct difference helps in identifying the contribution of one to the other.

In case of river contributing to the groundwater regime there are two possible sources of recharge to groundwater, viz. infiltration of local precipitation and infiltration of river water. In such conditions the accuracy of the estimate of the

proportion of infiltrated river water depends upon the accuracy of the estimates of stable isotopic indices of these two potential sources of recharge and the difference between these indices. An estimate of the river index may be made on the basis of samples from the river. This should be done at different times and especially at high river stage to ascertain whether there are any significant variations in stable isotopic composition. If variations are evident then the mean value weighted for discharge should be used. The preferable approach is to sample groundwater close to the river where piezometry indicates river water as the source of recharge. The estimation of the index for recharge by infiltration by local precipitation may be based on measurements of groundwater away from the influence of the river or, if sufficient data are available, on the peak value of the skewed frequency distribution. If the errors in estimates of the indices of the two potential sources of recharge are not greater than the analytical error, then the accuracy in the estimate of the proportion is better than 10%. In practice the limitations of the method are not in the method itself, but in the availability of meaningful samples.

In most of the cases, the stable isotope  $^{18}\text{O}$  are utilized for determining the contribution of groundwater to the river flow. If  $R_1$  and  $R_2$  are the isotopic composition of the groundwater and the river, respectively and  $m_1$  and  $m_2$  are the fractions of groundwater and river, respectively in the admixture, while  $R_{AM}$  is the isotopic composition of the admixture, then the isotopic balance and mass balance equations are

$$m_1 \cdot R_1 + m_2 \cdot R_2 = R_{AM} \quad (3.1.1)$$

and

$$m_1 + m_2 = 1 \quad (3.1.2)$$

From the above two equations we have

$$m_1 = (R_2 - R_{AM}) / (R_2 - R_1) \quad (3.1.3)$$

### 3.2 Water Balance of Lakes and Reservoirs

Gat et al(1968)<sup>(17)</sup> outlined that a number of terms in the water balance equation of a lake (given below) are unknown and additional relationships are necessary for calculating the values of those unknown terms or verifying their estimates. In fact, the parameters related with evaporation, inflow outflow, and leakage are difficult to be measured with help of conventional methods. Nuclear methods specially stable isotopes have potential to be used to determine these parameters, provided the lake is isotopically well mixed.

$$\Delta V_l / \Delta t = \sum_i F_{in,i} - F_{out} - E + P \quad (3.2.1)$$

Where  $V_l$  is the lake volume,  $F_{out}$  is the flux (in flowing or out flowing) streams,  $P$  the direct precipitation up to the lake (which is often merged into the inflow term,  $\sum_i F_{in,i}$ ) and  $E$  the evaporation.  $\Delta$  - values have to be averaged over the period of observation ( $\Delta t$ ) and over the lake's entire area. A great number of lake studies have been carried out in the past few decades abroad<sup>(18-23)</sup>.

In case of salt lakes, the salts which do not partake to a large degree in the water to atmosphere transition, are very useful traces for establishing additional balance equations specially,  $Cl^-$ , magnesium<sup>(24-25)</sup> and lithium content, were found reasonably conservative under a variety of situations. However, this method fails when the leakage/seepage of the salt water takes place and contribute the unknown quantity of salt<sup>(26)</sup>.

The water balance of lakes have the following major components as already described above i.e.

Inflow from surface runoff and precipitation

Outflow by river

Sub surface inflow and outflow of groundwater

Outflow by evaporation

Stable isotopes are most useful in the lake water balance studies in the determination of outflow by evaporation and inflow and outflow of groundwater. The other two parameters can be directly measured using the conventional methods. However, to asses the factors involved in the evolution of the isotopic composition of a lake, it is better to consider first some simple systems to gain the experience and to know the effect of different processes involve individually with high accuracy, i.e. one should take up the lake studies in the following order if at all it is possible; i) water bodies drying up without inflow ii) Lake without outflow - so called terminal lake iii) Lakes at constant volume(water level controlled by overflow over a dam).

### 3.3 ORIGIN OF GROUNDWATERS/RECHARGE SOURCES AND PALEOWATERS

The groundwater originates as precipitation, therefore, the amount of recharge to groundwater system is related with the storage capacity of a system and thus determines the maximum available resources for exploitation. However, in many cases, the recharge and water flow are rather complex and more information of the actual process is desirable. The environmental isotopic methods provide a valuable approach to understand these complex phenomena as well as to test the validity of the alternative hypothesis.

The use of environmental isotopes is based on the temporal and spatial variability of the isotope content of water. These effects are summarised below in brief.

a) Altitude effect

Groundwater originating from precipitation at high altitude either directly or by rivers draining high altitude catchment basins can be distinguished from recharge originating from low altitude precipitation. This effect is most useful in regimes having orographic precipitation, where there is a regular relationship between land-surface altitude and condensation temperature of precipitation.

The observed range of variation of  $^{18}\text{O}$   $\delta$  per 100 m is between -0.16 and -0.7 with an average value of -0.25.

b) Latitude effect:

The environmental stable isotope content of precipitation shows a marked dependence on latitude, thus groundwater replenished by rivers spanning significant latitude zones can be distinguished from local recharge.

c) Deuterium Excess

The change in the evaporation rate due to the geographic effect result in the excess contents of stable isotopes thus the different relationship of D -  $^{18}\text{O}$  is obtained i.e.,

$$D = 8 \text{ }^{18}\text{O} + 22 \quad (3.3.1)$$

which is quite different from the general relationship observed in northern hemisphere i.e. ,

$$D = 8 \text{ }^{18}\text{O} + 10 \quad (3.3.2)$$

This difference can be used in the border areas of climatic zones where precipitation on the coastal mountains can be mediterranean or oceanic origin.

d) Fractionation effect

The open water evaporation creates a fractionation in the contents of D and  $^{18}\text{O}$  which effectively labels surface reservoirs. The application of this effect can be best understood by taking the studies related with surface water and ground water interactions.

e) Seasonal Recharge:

The isotopic content of groundwater may indicate the seasonal dependency of recharge due to occurrence of precipitation on seasonal basis and variations of temperature accordingly. A number of studies have been carried out by various scientists for mediterranean karstic systems <sup>(27-29)</sup>.

f) Modern Recharge:

In order to identify the period of recharge (modern), the tritium content can be analyzed as its half life is short (12.43 yr) and because of its high levels in the atmosphere since the beginning of atmospheric testing of thermonuclear devices in 1952. The availability of tritium in water samples indicate the presence of some component of modern recharge. However, now a days, due to ban on the testing of nuclear devices and long period (about 40 yrs.) passed, the tritium contents analysis of water samples may not be that much effective in prediction of modern recharge.

The modern recharge may also be defined as the meteoric waters i.e. the groundwater which derived directly from precipitation or from fresh surface waters, usually by recharge through an



unsaturated soil zone. The isotopic composition of the meteoric ground waters generally matches that of local precipitation, at least in the humid climate zones.

#### PALEOWATERS:

Paleowaters are meteoric waters which originated in the more distant past, especially in periods during which different climatic conditions prevailed. The distinction between these two groups of water is somewhat arbitrary. Owing to cooler and more humid conditions during the pleistocene glaciations, reservoirs replenished during pluvial episodes are characterized by a low deuterium excess, accompanied by relatively depleted  $^{18}\text{O}$  and D contents as compared to modern recharge. It has been observed that a D-excess of 10 is produced with 70 % of relative atmospheric humidity while a D-excess of 5 % is produced with about 85 % of relative atmospheric humidity. The prior case is related with the modern precipitation while the later is with the old groundwaters. However, precautions should be taken while using stable isotopic data and C-14 data in identifying paleowaters. A general discussion on paleowaters is given in IAEA monograph on stable isotope hydrology<sup>(30)</sup>.

#### 3.4 Leakage between Aquifers

Leakage between different aquifers separated by layers of low permeability is of considerable importance in the development and use of groundwater. Aquifers which are underlain or overlain by semi permeable strata are referred to as leaky aquifers. Generally, the leakage of groundwater is deduced from piezometric gradients and the solution of the unsteady flow situation is given by pumping test data with the help of some empirical equations. However, radioactive tracers are used in order to study the leakage between aquifers, but, if the two aquifers are isotopically (stable) different, stable isotopes can also be used

for this purpose. As the stable isotopes do not undergo any change therefore, simultaneous use of deuterium and oxygen - 18 is the best method to study the leakage between two aquifers.

If no difference in deuterium and oxygen-18 content are found, the tritium, carbon-13, carbon-14 and sulphur-34 measurements and hydrochemical data can be used for the study of leakage.

### 3.5 GEOTHERMAL WATERS

The interior part of the earth is an almost infinite reservoir of thermal energy and its proper utilization may be a boon to the human being. However, due to limitations of available technology, it is inaccessible in most of the cases and we are not in a position to utilize the natural resource of energy in a desired manner.

If the following conditions prevailed, the electricity production can be undertaken with the help of thermal water system:

- i) High temperature (  $150^{\circ}\text{C}$  ) and high enthalpy (150cal/g) of the fluid.
- ii) Depth of geothermal reservoir not greater than about 3 km.
- iii) Adequate volume of the reservoir (  $5 \text{ Km}^3$  )
- iv) Sufficient reservoir permeability to ensure adequate fluid production by each well.
- v) Impermeable cover of the reservoir to avoid diffuse losses of fluid at the surface.
- vi) Sufficient rate of renewal of the fluid in the reservoir in order to ensure a continuous transfer of energy to the surface and to the power plant.

Although, it is not possible to fulfill all these conditions by a thermal system, but, some of these conditions can be fulfilled only if water is the major fluid component of the thermal reservoir.

#### ORIGIN OF GEOTHERMAL WATERS AND PROCESSES

In past when the use of isotopic methods was not explored, no geochemical tools were available to identify the origin of water in high temperature hydrothermal systems. For a long time, it was assumed that they are of magmatic and/or juvenile origin. It was after 1950 that systematic survey/measurements of the hydrogen and oxygen isotopic composition of water and steam from well known geothermal fields proved the origin of geothermal waters from the meteoric origin. In most of the cases the D/H ratio has been found identical to that of the local groundwater proving their common origin from meteoric water infiltration.

The D and  $^{18}\text{O}$  have successfully used in the identification of the origin of geothermal waters, but the exchange of hydrogen and oxygen with the minerals found in the rocks which is very slow at low temperature is greatly accelerated at high temperature which lead to the complications as the  $^{18}\text{O}$  content of water increases while that of rock decreases.

Further, the mixing of water of meteoric origin with Juvenile water or with magmatic water complicate the processes of geothermal waters. When geothermal water of meteoric origin mixed with Juvenile water, the plot of  $^{18}\text{O}$ , D would tend to converge at a single point representing the isotopic composition of juvenile water and in case of magmatic water, the D/H ratio would not remain constant in all cases but, would move towards that of the magmatic water present in the geothermal system.

### (A) Variation of Isotopic Composition during rise of Thermal Waters to the Surface

There are two main processes which affect the composition of isotopes during their rise to the surface,

- a) Steam separation due to adiabatic expansion of thermal fluids with decreasing pressure.
- b) Dilution and mixing with waters derived from shallow sources.

In first case, the mode of phase separation i.e. single step or continuously, is the key deciding factors of change of isotopic composition. However, maximum effects have been found from single step separation. The second case need not to be elaborated as it depends upon the situation (hydrogeology of the area) and is self explanatory.

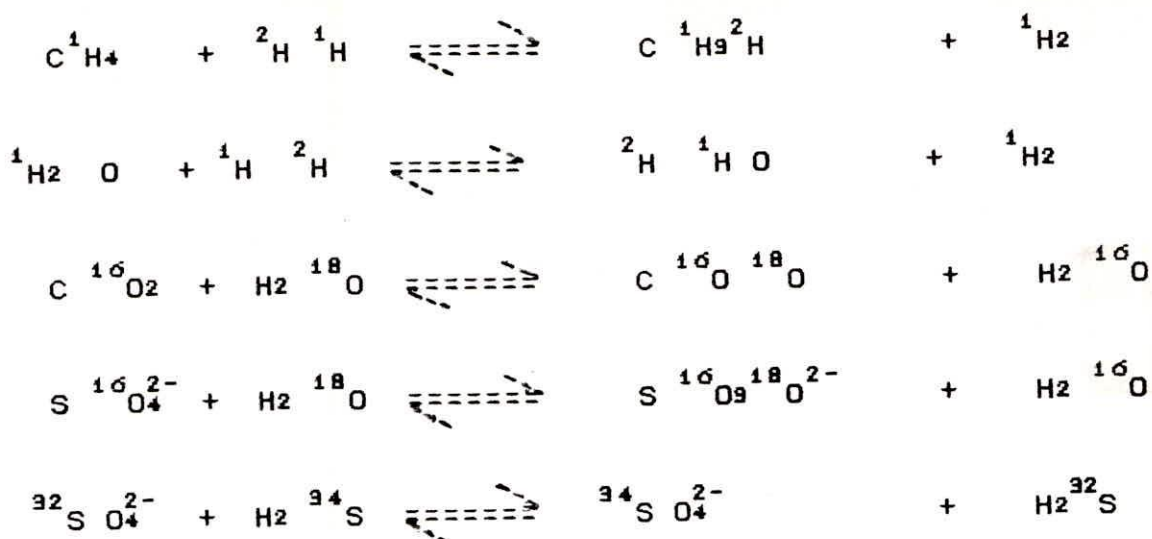
### (B) Variation in Isotopic Composition of T.W. at the Surface

Rapid evaporation of thermal water is the major factor which affect the isotopic composition of thermal waters at the surface. The increase in  $^{18}\text{O}$  by more than 10% or more has been commonly observed for close to stagnant steam heated pools.

### ISOTOPE GEOTHERMOMETERS

The relative distribution of isotopes in geothermal water at different depth is a temperature dependent phenomenon; therefore, in principle be used to evaluate deeper temp. The concept of using isotope thermometers is based on the exchange reactions which take place during the various process and are directly related with the temperature.





The empirical or thermodynamic constants for the above reaction are expressed in terms of  $\alpha^{(31)}$  i. e.,  $\alpha_{A,B} = R_A / R_B$  where,  $R_A$  and  $R_B$  are the ratio of heavier to lighter isotope in component A or B.

The equilibrium constants  $\alpha_{A,B}$  can be related with the fractionation constants  $\delta_A$  and  $\delta_B$  within  $\pm 20\%$  variation by the relation,

$$\Delta_{A,B} = \delta_A - \delta_B \approx 10^3 \ln \alpha_{A,B} - 1000(\alpha_{A,B}^{-1})$$

The temperature dependent of equilibrium constants  $\alpha$  is generally expressed in terms of

$$10^3 \ln \alpha = A + BT^{-1} + CT^{-2}$$

with T on the Kelvin scale.

Presently a number of isotopic thermometers are in vogue depending upon the suitability of their use like,

i) Carbon Dioxide - Methane isotopic Geothermometer, suitable to measure temperature ranging from 100 - 400 °C using the relation,

$$1000 \ln \alpha = -238.28 + 288.9 \times 10^3 T^{-1} + 31.86 \times 10^6 T^{-2}$$

ii) Methane - Hydrogen Isotopic Geothermometer, suitable to measure temperature up to 200 °C using the relation,

$$1000 \ln \alpha = -238.28 + 288.9 \times 10^3 T^{-1} + 31.86 \times 10^6 T^{-2}$$

iii) Water-Hydrogen Isotopic Geothermometer, suitable to measure temperature ranging from 100-400 °C using the relation,

$$1000 \ln \alpha = -217.3 + 396.8 \times 10^3 T^{-1} + 11.76 \times 10^6 T^{-2}$$

iv) Carbon Dioxide - water vapour Isotopic Geothermometer suitable to measure temperature ranging from 100 - 400 °C using the relation,

$$1000 \ln \alpha = 8.87 + 7.849 \times 10^3 T^{-1} + 2.941 \times 10^6 T^{-2}$$

v) SO<sub>4</sub><sup>2-</sup> - H<sub>2</sub>O isotopic geothermometer, suitable to measure temperature ranging from 0 - 200 °C and 0 - 300 °C Using the relations,

$$1000 \ln \alpha = 3.251 \times 10^6 T^{-2} - 5.6 \quad \text{and}$$

$$1000 \ln \alpha = 2.88 \times 10^6 T^{-2} - 4.1 \quad \text{respectively}$$

vi) SO<sub>4</sub><sup>2-</sup> - H<sub>2</sub>S isotopic Geothermometer suitable to measure temperature up to 260 °C using the equation,

$$1000 \ln \alpha = 6.04 \times 10^6 T^{-2} + 2.6$$

This relation can be used successfully for the system sulfate - hydrogen sulfide, but, the lack of equilibrium at deeper depth and sampling problems are some of the limitations associated with this geothermometer.

### 3.6 DATING OF GROUNDWATERS

Many radioisotopes are produced in the environment by interaction of neutrons from cosmic rays with nitrogen. The nature of decay of these environmental radioisotopes can be used to detect the age of groundwater or other materials also. Radioisotopes mixed with water vapors in environment and entered into ground water bodies with precipitation water.

Presently, three groundwater dating techniques are available;

- i) Tritium dating
- ii) Radiocarbon dating
- iii) Silicon-32 dating

The first two dating techniques are popularly known but the third one is still in the developing stage.

#### TRITIUM DATING:

##### TRITIUM:

- Tritium is a radioisotope (an atom of hydrogen)
- Half life 12.43 years
- Emits low energy beta radiations ( $E_{max}$  18 KeV)
- Environmental tritium occurs in the precipitation from two sources

(1) From the interaction of the cosmic ray produced neutrons in the upper atmosphere with nitrogen atoms;



(2) Man-made, principally from the detonation of thermonuclear devices

- Environmental concentrations of tritium in natural waters are denoted as an isotope ratio in terms of tritium unit (TU)
- One TU has an isotopic ratio of  $^3\text{H} / ^1\text{H} = 10^{-8}$
- One litre of water with a concentration of 1 TU produces 7.2 dpm (0.12 Bq)

### GEOUNDRWATER DATING WITH $^3\text{H}$

- Direct age estimation using tritium is difficult due to variable input of tritium, since 1952.
- Tritium concentration in environment are routinely measured (monthly averages) at various gauging stations fixed by IAEA/WMO since 1961.
- Qualitative approach can be used to distinguish between old water (pre bomb) and waters containing at least a contribution of recent precipitation

#### (1) FOR AGE MORE THAN 30 YEARS

If the tritium contents  $\leq 47.0$  are observed in the high continental latitudes and 1.T.U are observed in low and mid maritime latitudes, the age of the groundwater may be above 30 years, but as the more time has been passed and the tritium contents in the environment has reached to its normal value; the use of environmental tritium for the determination of age of groundwater (pre bomb or post bomb) is now not feasible.

#### 2) FOR AGE MORE THAN 30 YEARS

Varied contents of tritium can be analyzed in accordance with the data available for tritium concentrations in environment.

Local  $^3\text{H}$  contents should be taken into care at the time of interpretation tritium concentration.



## SAMPLE COLLECTION, DETECTION AND MEASUREMENT

Ground water samples can be collected, in a routine way, in a double screwed cap water bottle (may be plastic type). Fresh ground water should be taken for correct estimation of age. Environmental tritium can be detected with the help of LSC with or without enrichment or by using Gas counting system. The detection level is 10 TU in Low level LSC, 1 TU with enrichment and 0.2 TU in gas counting after electrolytic enrichment Å 15 to 30 fold. Mass spectrometric measurements are also possible with comparable sensitivities.

Generally 8-10 ml water sample is required for the tritium measurements. For small sample volume, gas counting is preferred. For gas counting, the sample water is converted into hydrogen gas. However some more details are also discussed in section 4.0.

### RADIOCARBON DATING:

#### CARBON-14:

- Carbon-14 is a radioactive isotope of carbon.
- Its half life is 5730 years.
- It emits beta radiations  $E_{\text{max}} = 156 \text{ Kev}$
- Environmental concentrations are expressed as a percentage of modern Carbon-14 (PMC)
- Mean natural sp. activity of C-14 is considered to be equal to 13.56 dPm per gm. of Carbon which is referred to as 100PMC
- Environmental C-14 produced in the upper atmosphere as discussed in section 2.2 .
- C-14 is oxidized to  $\text{CO}_2$  and becomes part of the atmospheric  $\text{CO}_2$  reservoir.
- C-14 has also been added to atmosphere since 1952 (Thermonuclear devices)

- C-14 is not an isotopic tracer of water molecule, but it occurs in water as various species of dissolved inorganic carbon.
  - For practical purposes, the activity of MC is 0.95 of the sp. activity of the carbon of oxalic acid (NBS)
- CO<sub>2</sub> enters into the water cycle by two main processes (neglecting direct dissolution)
- (1) By pure chemical process of dissolution buffered by solid carbonate
  - (ii) By biochemical production of CO<sub>2</sub> and bicarbonated

#### GROUNDWATER DATING WITH <sup>14</sup>C

By knowing the percent modern of carbon, one can calculate the age of the water sample. Age calculation using C-14 dating is neither simple nor very accurate as several corrections are to be done before arriving at any conclusion.

While dating groundwaters using C-14 dating techniques, the factors like chemical (dilution) and isotopic(exchange), dissolved carbon of pure biogenic origin and dissolved carbon of mixed origin should be taken into account.

#### SAMPLE COLLECTION, DETECTION AND MEASUREMENT:

1 to 5 gm of carbon-14 is needed for the measurements. 50 -200 lits. of fresh ground water is collected in a sealed container depending upon inorganic carbonate & bicarbonate contents.

CO<sub>2</sub> is extracted from the water sample by :

- (1) Gas evolution method
- (ii) As BaCO<sub>3</sub> by precipitation method

After purification,  $\text{CO}_2$  can be counted directly or after conversion to  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_6$  or  $\text{CH}_4$ , in a proportional (gas) counter.  $\text{CO}_2$  can also be counted by LSC i. e. ,

- (i) Absorbed in a absorber - scintillator
- (ii) Converted to benzene

#### Detection limits

$\pm 0.2$  to  $\pm 0.1$  modern carbon with LSS

$\pm 0.05$  pmc with gas counting

However, some more details are described in section 4.0 .

### 3.7 SEDIMENTATION OF LAKES AND RESERVOIRS

Reservoirs, Dams and lakes are important in the conservation of a very basic national resource-waters. The difference between the calculated design life and real (due to postulated rates sedimentation) has caused serious problems particularly in the developing countries. The loss of storage capacity due to unwanted sedimentation can have a profound effect on the functioning and objectives of the water system. Recent examples of some of these effects can be found in Burma, India, Indonesia, Kenya, Nigeria, Pakistan and Sudan <sup>(32-33)</sup> .

In broad terms, solution of the problems requires a full study of the catchment with the following aspects:

- i) To measure erosion effects within it and identify the sediment sources, including those related to particular land usage;
- ii) To identify areas of sediment storage;
- iii) To measure temporal changes in sediment storage;
- iv) To measure transport of eroded materials or sediment,
  - a) overland (including aeolian processes), and
  - b) by fluvial processes

- v) To determine sedimentation rates in reservoirs and lakes;
- vi) To measure changes in sediment distributions in reservoirs and lakes;
- vii) To acquire data from which to generate soil loss prediction equations.

Environmental isotopes like Cs-137 and Pb-210 can be used for the study of sedimentation rate in the reservoirs, dams and lakes.

A) Determination of sedimentation rates in Lakes and Reservoirs using environmental Cs-137 as a radioactive tracer

Cesium-137 is produced in the atmosphere due to the test of nuclear weapons. Since 1954, it has been globally detectable. It emits gamma radiations with the energy peak of 0.662 MeV and has half life of 30.1 years. Cs-137 is strongly adsorbed on fine particles like clay minerals, silts and humic materials<sup>(34-37)</sup>. In fact, the variation in the intensity of Cs-137 content of surface soils per unit area is linked with the intensity of fallout, percentage of clay and silt and cation exchange capacity. It follows that all surface soils with an adsorptive capacity will have a Cs-137 content and therefore be able to act as a self tracer. In a catchment, accumulation of a sediment layer by a reservoir is a measure of its trap efficiency. A comparison of Cs-137 content of catchment soils with that of the associated reservoir sediments shows a pronounced build-up of the latter.

Since the nuclear weapons were mainly tested in the northern hemisphere, the fallout of Cs-137 is approximately 4 times greater at comparable northern versus southern latitudes. The amount of Cs-137 deposited on the earth has been measured at precipitation stations, many locations installed by IAEA and WMO and the data may be used to determine the cumulative input of Cs-137. Examples of such input have been shown in the reports of measurement from global network of US and UK monitoring stations.

The sedimentation rates can be calculated from the depths of the 2 principal time horizons i.e. 1955 and 1964, in the Cs-137 concentration profile.

#### SAMPLE COLLECTION

The undisturbed sediment samples are collected from the bed of the lake, reservoir or dam from the desired location with a core cutter up to the depth of 20 to 100 cm. But, some practical difficulties are associated in the collection of undisturbed bed sediment samples, i.e.,

- i) The soft sediments in upper 20 cm.(may be more) depths may be disturbed during collection (penetration) and it may vary with different degree of compaction with increasing depth.
- ii) The sediment sample may be disturbed during removal with the help of core cutter(tube) due to suction effect.

The core tube ranges up to 1 metre in length and 5 cm in diameter can be used for the collection of sediment samples from the bed using a hand cover, or a piston or box corer. However, gravity core sampling is convenient. Mackereth corer - a remotely operated pneumatic core can be used for this purpose.

The sediment samples (cores) are cut into 1 cm section and placed in a polythene bag. The Cs-137 core sections are analyzed by gamma ray spectrometry using Ge(Li) or intrinsic Germanium detectors.

#### Sediment Redistribution Measurements in Reservoir and Lakes

The transport and spatial distribution of sediments entering into an impoundment are functions of the balance between the flow velocities, gravitational forces and the secondary forces of flow turbulence. In the case of reservoirs, draw-down procedures can be

a very powerful initiator of sediment flows and redistribution. Three generalized zones of sedimentation are given for reservoir <sup>Wiebe and Drennan, 1973</sup>; for sedimentary process in lakes, see <sup>Sly, 1978</sup><sup>(38-39)</sup>.

- i) The upper zone in which complex deltas form as a result of flows entering the reservoir retaining their identity for some distance into the reservoir pool. The deltas grow outward by the formation of foreset (longitudinal flow) beds and upward through topset beds.
- ii) The intermediate zone in which the residual river velocity, waves and wave-induced currents transport and deposit most of the river's wash load, and some of the fine sediments eroded from the banks of the reservoir, to form bottom set beds of fine clays, silts and colloids.
- iii) The lower zone containing sediments eroded from the reservoir banks and transported by waves and wave-induced currents.

The relevance of these sediment classifications can be seen in the work of Simpson et al. (1976)<sup>(40)</sup> in the Hudson River estuary, New York. They were able to classify three main types of distribution of <sup>137</sup>Cs in estuary sediment cores:

- (a) Relatively low activities (  $19 \text{ mBq g}^{-1}$  ) generally confined to the upper 5-10 cm of sediment and associated with subtidal banks.
- (b) Higher activities than in (a) of about  $90 \text{ mBq g}^{-1}$  in the top 10 cm decreasing rapidly to about  $7 \text{ mBq g}^{-1}$  in the 10-15 cm layer and sometimes distributed down to 40 cm with an activity of about  $1 \text{ mBq g}^{-1}$ . This type of profile was interpreted as being indicative of a high sedimentation rate in a shallow protected environment.

(c) Profiles with variable but high activities of about 70 mBq g<sup>-1</sup> down to 40 cm and, in one case, down to 250 cm. Cesium-137 activity below 40 cm was stated by /simpson et al. (1976) to be a clear indicator of rapid sediment accumulation. It is speculated that temporal changes in <sup>137</sup>Cs profiles along a transect at each of the three zones could be interpreted as changes due to redistribution or accretion in exactly the same way that McHenry and Bubenzer (1982)<sup>(41)</sup> interpreted changes in field distribution <sup>137</sup>Cs .

#### SOIL LOSS ESTIMATION FROM Cs-137 Data

The loss of Cs-137 from the catchment and its relationship with trap efficiency provides useful information about the impact of land use on soil erosion and reservoir life time. However, previous studies related with the environmental mobility of some fallout, radio-isotopes showed that for some species (Sr-90, Cs-137), which are firmly adsorbed by soil colloids and minerals, there is a relationship between radionuclide loss and soil loss. For Cs-137, an empirical relationship of the form  $Y = A (x / b)^n$ , where Y is <sup>137</sup>Cs loss, x is the soil loss and b, A and n are respectively constant, coefficient and exponent gave a good fit to the data. Specifically, Wischmeier and Smith<sup>(42-43)</sup>, have obtained an empirical relationship between soil loss and loss of Cs-137, i.e.

$$Y = 1.6 x^{0.68}$$

Where y is radionuclide loss as a percentage of radionuclide input, and x is the soil erosion in tonns per hectare.

## Depth Distribution of Cs-137 in Soils

The movement of  $^{137}\text{Cs}$  through a soil profile depends on a number of factors inherent to the particular soil type and its chemical and physical properties. The results of a number of investigators (Beck, 1966; McHenry et al., 1973; Ritchie et al., 1972; Baltakmens and Gregory, 1977; Garland, 1979; Campbell et al., 1982<sup>(44-49)</sup>) showed that in undisturbed soils,  $^{137}\text{Cs}$  is usually distributed exponentially as a function of depth within the top 10 cm of soil. On some soils, the profile may extend to 15-30 cm (Brown et al., 1981a; Baltakmens and Gregory, 1977<sup>(50,47)</sup>). The type and quality of protection afforded to soil by different plant and vegetation covers affect the retention and distribution of  $^{137}\text{Cs}$ .

On the basis of an extensive comparison of  $^{137}\text{Cs}$  levels in various broadly based geomorphic units in a catchment, Campbell et al. (1982) described a model for the  $^{137}\text{Cs}$  distribution. Qualitatively the main features are as follows:

- i) Sites suffering little or no erosion have high concentrations of  $^{137}\text{Cs}$  in the upper surface layers. These are the sites most likely to represent the 'total' input of  $^{137}\text{Cs}$  in to the basin, less the loss due to radioactive decay. The trap efficiency for  $^{137}\text{Cs}$  is greatest in forested or wooded sites; the concentrations are therefore used in quantitative calculations to indicate the base level of  $^{137}\text{Cs}$  input to the drainage basin (see also Ritchie et al., 1974; McCallan et al., 1980; Brown et al., 1981a<sup>(51,52,50)</sup>).
- ii) Sites on uncultivated hilltops and slopes that have undergone some erosion exhibit a truncated  $^{137}\text{Cs}$  profile with depth. When the upper surface layers are removed by a succession of erosion events, a new soils profile develops owing to a



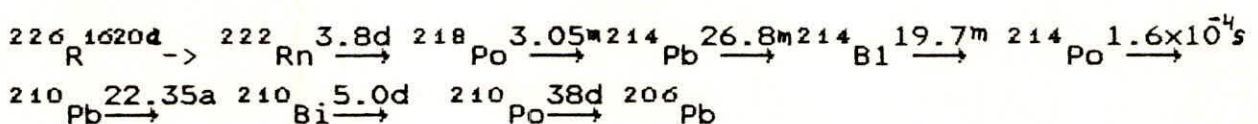
superposition of the prevailing fallout on the residual soil  $^{137}\text{C}$  concentrations. These profile changes have opened up the possibility of identifying sediment sources due to either sheet or gully erosion. Sediments derived from gully erosion will have a lower  $^{137}\text{Cs}$  concentration than those from sheet erosion (Ritchie et al., 1972a)<sup>(53)</sup>.

iii) Sites under cultivation have a relatively even distribution of  $^{137}\text{Cs}$  within the cultivated layer. The total amount of  $^{137}\text{Cs}$  is generally lower than that in uncultivated soils (Loughran et al., 1982; McHenry et al., 1973; McHenry et al., 1978; Ritchie and McHenry, 1973)<sup>(54-57)</sup>. Differences in total  $^{137}\text{Cs}$  in the cultivated soil profile indicate losses of soil materials containing  $^{137}\text{Cs}$  (silt + clay) and may be further correlated with an index of soil erodibility.

iv) In sites undergoing active sedimentation,  $^{137}\text{Cs}$  levels may vary markedly (Ritchie et al., 1975)<sup>(55)</sup>.

#### $^{210}\text{Pb}$ METHOD

$\text{Pb}-210$  is a naturally occurring radionuclide in the  $^{238}\text{U}$  decay series. It emits gamma radiation and its half life is 22.35 years. It is present in the atmosphere as a result of following series of events.  $^{226}\text{Ra}$  present in the earth's crust decays to rare gas  $^{222}\text{Rn}$  which diffuses into the atmosphere at an average rate of 42 atoms/sec and decays to  $\text{Pb}-210$  via a series of short lived daughters. The decay series is as given below:



Half life

The direct input of unsupported  $^{210}\text{Pb}$  (the amount not in equilibrium with its parent  $^{222}\text{Rn}$ ) to lakes and reservoirs is result of dry and wet fallout.

### 3.8 ICE AND SNOW DATING/GAUGING/MELT

The isotopic content of the snow cover gives valuable information about the isotopic variation of the snow, which falls down to the mountains and contributes to the snow cover accretion. primarily, the isotopic contents of the fresh snow are Deuterium Tritium and Oxygen-18; out of these three contents, two content -Deuterium and Oxygen-18, are stable isotopes.

#### EFFECT OF VARIOUS CHANGES ON THE ISOTOPIC CONTENTS OF A SNOW COVER

Measurements of isotopic contents in temperate snow covers does not change during the melting periods even if rainwater and meltwater percolates. In case a considerable amount of water percolates with a  $\delta$ -value, which does not correspond to the equilibrated  $\delta$ -value of the snow; the mean value of deuterium and Oxygen-18 values of the snow cover is changed. After a long time the isotopic content of water makes a homogeneous mixture with the isotopic contents of the snow and, thus, there is an increase in the value of the entire snow cover. After a strong rainfall, significant changes have been noticed in the isotopic content (Stichler et al. (1976), Krouse et al. (1972), Herrmann et al. (1981) (59-61)). Therefore, the study of the isotopic content can also be used for distinguishing melt water and rain, allowing a detailed observation of the water movement

The transition in snow and glacier ice also brings about changes in the isotopic content. It is observed that the original isotopic distribution on account of the seasonal and climatic variations in the isotopic contents of precipitation will be changed within the glacier either between polar (cold) as well as

ice fields and temperate glaciers (with percolating melt water during the ablation period) also between the firn zone and the compact glacier ice. It is observed that the course from different polar regions, the damping of Oxygen-18 seasonal variations as a function of the resident time of the respective layer in the field. Dansgaard et al. (1973) (62). It has been observed that the station differing in the accumulation rates show that the diffusion will be more effective with decreasing accumulation rate. The value of Oxygen-18 becomes more in the firning process up to the ice formation, than the annual accumulation rate of the isotopic contents. In certain conditions either percolating melt water, formation of ice lenses or slow molecular diffusion processes govern the changes in the homogeneity of the isotopic contents. In temperate glacier ice, diffusion processes do not play significant role, because, they relatively stay for less than a few thousand years. At such places, isotopic contents of ice and melt water get intermixed within the body of the glacier. These isotopic contents are affected by any or the combination of the following

- i) The change in the isotopic concentration in snow is also observed. This has been documented by measurements of deuterium and oxygen-18 contents in the snow samples collected from different parts of the world. It has been observed that the  $\delta^{18}\text{O}$  -values differ not only in their absolute values, but, also in the slopes of the mostly linear relation between the  $\delta^{18}\text{O}$  -value and the altitude due to the local climatic conditions. It is observed that the fractionation factor for deuterium to Hydrogen and that of oxygen-18 to Oxygen-16 ratios between ice and liquid water at  $0^{\circ}\text{C}$  are 1.020 and 1.003 respectively. This means that  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of glaciers are higher by 20%. and 30%. respectively, than those of the glacier melt water.

- ii) Continental effect also influences the  $\delta$ -values. An altitude effect as measured in Greenland for tritium concentration in Antarctica  $\ddot{A}$ Merlivat et al.(1973) and (1977)<sup>(63-64)</sup> can be explained by a tritium exchange with tritium-rich water vapour in the atmosphere.
- iii) Seasonal variations in polar regions of Deuterium, Oxygen-18 and tritium concentration in snowfall can be safely stored within the snow cover for a considerable time  $\ddot{A}$ Moser et al.(1975)<sup>(65)</sup>. Changes in the large scale weather patterns can be visible in the isotopic profile of a snow cover  $\ddot{A}$ Friedman et al.(1972)<sup>(66)</sup>
- iv) Wind drift can change the original isotopic profile of a snow cover especially in the case of dry snow, in areas with little accumulation and strong wind exposure, as in the case in the Antarctica, and on the steep slopes. This complicates the interpretation of the isotope concentration from the snow profile.
- v) Condensation of the atmospheric moisture at the snow surface (hoar-frost) have not been investigated in details, however, they are important for understanding transport phenomenon of water vapour and snow metamorphosis. It is observed that the increase in the deuterium values at the snow surface during the day time, caused by the evaporation of the snow, is compensated in the night by condensation of the available water in air. The same is affected in the fluctuation of the deuterium excess. The absolute value of the deuterium variations has been changed as new air masses with different

humidity and deuterium concentrations were carried into the area. Judy et al. (1970)<sup>(67)</sup> have found deuterium variations in an annual snowpack.

vi) Moser and Stichler (1970)<sup>(68)</sup> observed the variation in  $\delta$  in the range of -4% to 2% per 100m rise in elevation for rain in Central Europe. Pack snow on the other hand showed an increase in deuterium content with rise in elevation which came to be 5% + 3% per 100m rise in elevation. Similar variations have been observed by other investigators Å Bahadur (1976) Ü<sup>(69)</sup>.

vii) Evaporation and melting also affect the concentrations of radioisotopes in the air. The distribution of isotopes derived by the original precipitation near the surface undergoes substantial changes due to uneven accumulation, may be because of drift, in deuterium and oxygen-18 contents. This can badly affect the studies conducted for altitude effect. There are chances that the whole thing may even reverse and lead to absurd results Å Moser et al. (1975) and Friedman et al. (1972) Ü<sup>(65-66)</sup>.

The seasonal variations of the isotope contents in discharges from the glaciers basins can be used to determine ablation periods, mean shares of melt water from different areas, identification of the mean altitudes of separate drainage basins, and resident times of water under different storage conditions Å Ambach et al. (1976) Ü<sup>(70)</sup>. In this carbon-14, tritium, lead-210, chlorine-36, beryllium-10, argon-39 and silicon-32, are considered for isotopic studies. It is apparent that the snow and glacier melt waters are heavily depleted in heavy isotopic content and can be used to distinguish the origin of these waters from that of rainfall at lower altitude or due to groundwater contributions to the river inflows.

### 3.9 GroundWater Pollution (Salinization):

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

Variation in characteristic ions ratios can provide information on the possible source of salinity. However, after transport of the salts by percolating water to the water table and after primary mixing with saline waters, the chemistry of the water may undergo further secondary changes which may make it difficult to identify precisely the mechanism of salinization. The problem of identifying the mechanism of salinization becomes more acute in irrigated areas in arid zones. Leaching is usually local and the soluble salts may not be transported very far. This is partly due to the low rainfall and also the high evaporation rates which are characteristic of arid zones, tend to concentrate salts in the groundwater. Furthermore, surface drainage systems may be poorly developed, having no outlet to permanent stream.

Salinization arising from simple leaching of salts is not accompanied any change in the stable isotopic composition of the leaching water. Thus the salinity generated by leaching of salt can be identified as it is dependent of the stable isotopic composition. On the other hand, the mixing of a saline water with a fresh-water body gives rise to waters of different salinity and different isotopic composition, since the stable isotope content of the source of salinity is different from that of fresh water

body before salinization. As a result, linear-correlations along mixing lines occur between D and  $^{18}\text{O}$  and between these and the concentration of the more conservative ionic species such as chloride. The extreme values of such mixing lines correspond to or are within the limits defined by the fresh water and saline water components.

If the increase of salinity is due to the concentrations of dissolved salts by evaporation, the relationship between  $^{18}\text{O}$  and  $^{16}\text{O}$  values will be typical of an evaporation process.

The stable isotopes in the study of salinization mechanism have been extensively used by various workers abroad but it has not so far been used in India in considerable amount.

#### 4.0 SAMPLING AND MEASUREMENT TECHNIQUES FOR ENVIRONMENTAL ISOTOPES

There are several measurement techniques for environmental isotopes. However, the principle of measurement of environmental stable isotopes and radio-isotopes differs greatly and accordingly the measurement techniques. In order to measure the environmental isotopes, the first step involves is the sampling of water from the various sources of water and then comes the measurement techniques. The details in brief of both are described below.

##### 4.1. Water sampling for environmental isotope analysis

###### A) For Stable Isotopes

It is of utmost importance to know what the sample actually represents when water is sampled for any analysis. In case of a pumped well it is necessary to know the length and location of screens and what aquifer is being tapped. In case of establishing isotopic compositions of individual aquifers sampling from

multi-aquifer wells should be avoided. In general the precautions to be taken for water sampling for isotope analysis are similar as those for chemical analysis. Further atmospheric contamination can be more important for the samples for isotope analysis

Sample bottles should preferably be filled almost completely and be sealed tightly. While glass bottles are better, polythene bottles with tight stoppers may also be used. However, samples should be contained in polythene bottles for the minimum of time because of problems of diffusion and exchange through the walls of the container (Payne, 1983a). Above all it is important to properly and clearly label the sample containers with all relevant information.

Samples for streams and rivers should be taken in the main flow channel and sufficiently far downstream from major inflow areas to ensure good mixing. A long-term index for the river should be based on samples taken at different river stages and the data weighted for discharge.

In case of shallow open wells there is a high probability of evaporation. Therefore the wells which are in use should be chosen and, if at all possible, the water standing in the well should be pumped out or removed so that inflow to the well can be sampled directly. An important consideration is that open wells represent the top of a phreatic system. If this aquifer has an appreciable thickness there may well be stratification in isotopic composition, particularly in the vicinity of effluent rivers. Stratification of age with depth in aquifer may also cause problems of interpretation if the well is screened over a considerable depth. Sampling of groundwater from open reservoirs exposed to the atmosphere should be avoided.



Sampling of groundwaters from pumped wells should be accompanied by information on the well, particularly the location of screens and aquifer tapped, if available. Data on temperature and salinity may sometimes be useful for identification of particular horizons to be sampled. Sampling during drilling of wells provides an opportunity for getting samples from different horizons. However, if rotary drilling is used it is very difficult to avoid contamination by the drilling fluid. Percussion drilling usually provides favorable conditions for sampling for isotope analysis and indeed also for chemical analysis.

#### B) For Environmental Radioisotopes

Similar procedures and precautions are followed for the water sampling for environmental tritium analysis. However, the quantity of water sample for tritium analysis depends on the concentration of tritium in the sample and on the analytical method used. Normally, a sample of 500 ml is adequate, but the amount required should be checked with the analytical laboratory. However, if in any case, the collected sample is less than the required, it should be utilized for the analysis purposes, as, it is possible to analyse smaller quantities with lower accuracy.

In order to collect the water sample for carbon-14 analysis, the precautions which have been described in the preceding sections for the water sampling for environmental stable isotopes and tritium are also taken into account. However, as the carbon-14 dating is possible only for those waters which once come into contact with environment (precipitation) and then cut-off from the active environment, therefore, the sampling is done only in the case of groundwater and not the surface waters.

In past due to non availability of sophisticated instrumentation, huge amount of water sample was required and also a long and tedious procedure was followed. But, in present time due to the advent of advanced instrumentation, only 2 gram of carbon is required for the  $^{14}\text{C}$  dating for which about 60 liters of water is sufficient. However, if the carbon content is lower than 200 ppm in water, a proportionally larger water volume is required. In order to avoid the shipment of large volume of water, a procedure for precipitating the dissolved carbonate species described below is used. In this case, only the precipitated carbon species is shipped to the laboratory for further analysis.

The volume of water required for carbon age determination depends on the concentration of carbonate and bicarbonate in the water. 1.0 grams of carbon are desired for analysis. This corresponds to approximately 5.25 grams of bicarbonate or carbonate.

The minimum volume of water sample required may be calculated from the following relations:

$$V(\text{litres}) = \frac{10.000}{\text{ppm "A"}}$$

ppm "A" = ppm (carbonate + bicarbonate)

$$\text{meq/l} \quad V(\text{litres}) = \frac{167}{B + C/2}$$

where, B = meq/l bicarbonate

C = meq/l carbonate

The carbonate and bicarbonate are ordinarily determined from the "alkalinity" titration using pH 8.0 for carbonate and pH 4.5 for bicarbonate. Any silicate, borate, hydroxide or other strongly basic anion in the water will also be included in the titration

and will give a high alkalinity value. This results in underestimation of the volume of water sample required. Hence as a general rule it is well to take a sample 25% larger than is indicated by the calculation.

The water sample may be collected in any clean container which can be sealed airtight. The main precaution to be observed in sampling for carbon-14 is minimum exposure to the atmosphere. The atmospheric carbon dioxide is contaminated with carbon-14 from fallout and if incorporated into the sample will result in an age determination which is too recent.

Clean drums, glass or polyethylene carboys and other large containers are suitable. Carboys that have contained acid should be well rinsed before using because traces of acid remaining can evolve carbon dioxide gas leading to possible loss of carbonate from the sample.

#### FIELD PRECIPITATION:

It is possible to collect a sample directly in a precipitation apparatus and carry out the precipitation in the field. In this case only a one litre bottle containing the precipitate need be transported to the laboratory from the field sampling site.

The procedure for obtaining the sample for carbon-14 analysis consists of precipitating the carbonates from a water sample in a large funnel-like apparatus of about 60 litres capacity. The procedure is very simple but requires attention to detail, particularly minimizing exposure to air. The precipitate is formed by adding barium chloride to the water after adjusting the pH to convert all bicarbonates to carbonates. A mixed precipitate of barium sulphate and barium carbonate forms. Normally, such a

precipitate is fine grained and requires several hours to settle completely. An iron salt and Praestol, a flocculating agent, are added to promote the formation of coarse agglomerates and shorten settling time. Some waters give very flocculant agglomerates which must be transferred to several sample bottles by siphoning.

The step wise procedure, using a conical precipitation unit is as given below:

1. Set up the precipitation tank in the stand of suitable shape and size m. Be sure the stand has firm, level footing.
2. Rinse the tank with water from the source being sampled.
3. Tightly screw a one litre wide-neck polyethylene bottle into the thread at the bottom of the cone.
4. Fill the tank almost to the neck, ensuring that no extraneous material from hoses, pails etc. get in.
5. Add 5 gram portion of ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). This is provided in individual vials one for each precipitation. Stir to dissolve and distribute uniformly.
6. Add 50 ml of carbonate-free NaOH solution. Stir well and test the bulk solution alkalinity with pH or litmus paper. Add more NaOH as required to achieve  $\text{pH} > 8$ . Do not expose the NaOH solution to the atmosphere any more than necessary.
7. Add 0.5 litre of saturated  $\text{BaCl}_2$  solution. Close the container top and stir well for 5 minutes. A heavy precipitate should form.
8. Add 40 ml Praestol solution. Replace the container top and stir slowly every 3 minutes for about 1 minute during a half hour. If the precipitate is granular, it will settle into the

sample bottle quickly. Use the stirrer to encourage the precipitate to slide down the falls of the funnel into the bottle.

9. Check for complete precipitation by adding a small amount(25-30 ml) of  $BaCl_2$  solution to the top of the tank without stirring. If any cloudiness appears indicating further precipitation, more  $BaCl_2$  and possibly  $NaOH$  solutions must be stirred into the main bulk to ensure complete precipitation.
10. If the precipitate will not all settle into the sample bottle within an hour because of its flocculant nature, insert the plastic tubing through the tank into the sample bottle and slowly siphon precipitate out into another bottle. This will promote drawing in of more precipitate from the funnel. Tapping of the walls of the funnel with the hands will help settling of the precipitate. Continue siphoning into other bottles until all precipitate is out of the funnel. This flocculent precipitate will settle in the bottles overnight. If the extra bottles are required for other sampling, the various portions of precipitate of a single sampling can be combined by pouring off the clear supernatant liquid, slurring the precipitates and pouring them into one bottle.
11. When all precipitate is out of the funnel, close the bottom of the funnel by inserting the rubber stopper fitted on the end of a long rod into the neck of the funnel. Remove the bottle containing the precipitate, cap tightly and label with date, sample number, well number, details of location and any special circumstances.
12. Empty the tank by loosening the rubber stopper by means of its rod. Rinse well and let drain.

13. For additional laboratory analysis of water fill completely a one litre plastic bottle and cap tightly.
14. Check proper labelling of all sample bottles before shipment.

#### REAGENTS

1. Ferrous sulphate ( $\text{Fe SO}_4 \cdot 7\text{H}_2 \text{O}$ ). Provided in individual vials containing 5 grams for each precipitation.
2. Carbonate-free NaOH solution. A saturated solution of NaOH in distilled water is allowed to stand several weeks for  $\text{Na}_2\text{CO}_3$ , which is insoluble in such solution, to settle out. The clear supernatant solution is carefully decanted and subsequently kept protected from the atmosphere to avoid the pick-up of carbon dioxide.
3. Saturated  $\text{BaCl}_2$  Solution. 500 g  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  dissolved in 1000 ml hot distilled water. Any precipitate is allowed to settle and is discarded.
4. Praestol Solution. 5 g Praestol 2900 (polyacrylamide, supplier:Farbenchemie Ges.m.b.h., Vienna, Austria or any other make of Indian firm of good quality) dissolved in 1000 ml boiled (to remove  $\text{CO}_2$ ) distilled water.

The foregoing procedure was developed to permit carbon-14 sampling under the most primitive and remote conditions. For most proper interpretation of radiocarbon measurement in terms of water age, the field measurement of pH and free  $\text{CO}_2$  in water is recommended along with bicarbonate and carbonate titration. Also glass bottles instead of plastic bottles for two litre water samples for further laboratory analysis would be recommended in cases where the transportation conditions assure safe, unbreakable shipment.

## 4.2 MEASUREMENT TECHNIQUES

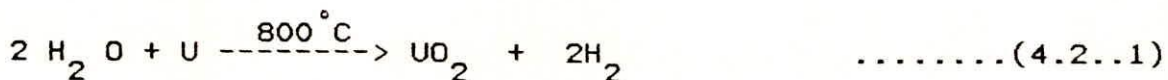
### A) Measurement of environmental isotopes ( $^2\text{H}$ and $^{18}\text{O}$ )

In the following sections, brief description on the methods available for sample preparation for isotope analysis has been presented.

#### i) Measurement of ' $^2\text{H}$ ' content in water samples

Two methods are available for conversion of water to hydrogen gas for mass spectrometer analysis, they are Uranium method and Zinc method.

a) Uranium method: The method was used by Friedman(1953)<sup>(71)</sup>, who first reported accurate hydrogen isotope analysis of natural waters. In this method 5  $\mu\text{l}$  water sample is reduced to  $\text{H}_2$  gas. The reducing agent is uranium turnings and reduction takes place at  $800^\circ\text{C}$ .



The hydrogen produced is collected in a uranium finger at  $80^\circ\text{C}$ . The hydrogen reacts with uranium to produce  $\text{UH}_3$ . When the reaction is completed, the uranium is heated to about  $650^\circ\text{C}$  and the uranium hydride is quantitatively decomposed to release hydrogen.

b) Zinc method: The procedure was introduced by Coleman et al.(1982)<sup>(72)</sup>. About 5  $\mu\text{l}$  of water is reduced with zinc metal in a closed evacuated tube at  $450^\circ\text{C}$  to prepare hydrogen gas.



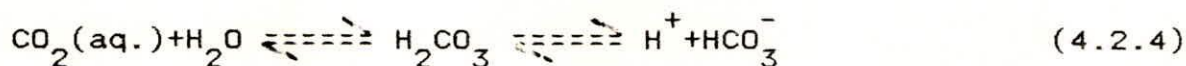
The reduction is carried out in a dryblock furnace and after about an hour the reaction is usually complete. The  $H_2$  gas produced could be directly analysed. The procedure is simple and avoids the memory effect inherent in the uranium method.

ii) Measurement of  $^{18}O$  content in water samples

The most common method for determining the oxygen isotope composition of water is by equilibration with  $CO_2$  and measurement of the isotope ratio of  $CO_2$  mass spectrometrically. Other methods are in general more difficult and are applied only for special purposes or for very small samples of water (Neil and Epstein, (1966); Dugan, (1985) (73-74) .

a) Equilibration method: The method was first described by Epstein and Mayeda (1953) (75) . In this method, isotopic exchange at a fixed temperature between water samples and  $CO_2$  of known  $^{18}O$  content is carried out. The  $^{18}O / ^{16}O$  ratio of the equilibrated  $CO_2$  can be measured which in turn could be related to the isotope ratio of the water sample.

If  $pH < 8$ , the following reactions determine the rate of attainment of chemical and isotopic equilibrium



The reaction  $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$  is instantaneous in comparison with the hydration reaction and hence  $k_h$  is the rate determining in equation (4.2.4).

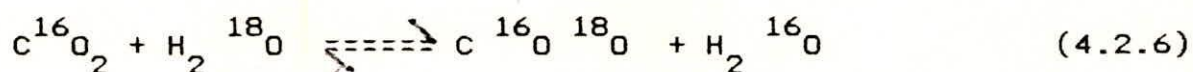


When  $\text{pH} > 8$ , a biomolecular reaction,

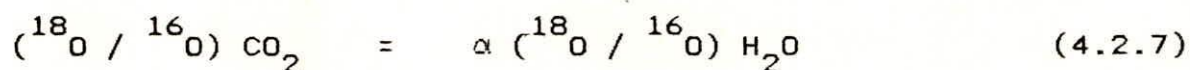


predominates over the hydration reaction and the equilibration is slowed down considerably. Generally waters with  $\text{pH} < 8$  are measured and hence equations (4.2.3) and (4.2.4) will apply. The rate of the gas exchange reaction may be accelerated by stirring or shaking the reaction vessel. This helps in mixing the  $\text{CO}_2$  (gas) thoroughly within the liquid and increases the area of contact between the two phases. By shaking, the gas exchange reaction may be accelerated to such an extent that the hydration reaction alone is rate determining.

The concentrations of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  are very small and the total oxygen is divided essentially between  $\text{CO}_2$  (gas),  $\text{CO}_2$  (aq.) and  $\text{H}_2\text{O}$ . The isotopic exchange reaction hence may be written as



Since the method uses a great molar excess of water to  $\text{CO}_2$ , the  $^{18}\text{O} / ^{16}\text{O}$  ratio of water does not change appreciably during the equilibration. The equilibrated gas has a  $^{18}\text{O} / ^{16}\text{O}$  ratio which is related to that of water through a fractionation factor ( $\alpha$ ).



At  $25^\circ\text{C}$   $\alpha$  has value of  $1.0412 + 0.0001$  according to the measurements made by O'Neil et al. (1975). At  $25^\circ\text{C}$  the variation of  $\alpha$  with temperature is  $-0.00018$  per degree celsius (O'Neil and Adami, 1969)<sup>(76)</sup>.

The 602 E Mass Spectrometer from VG ISOGAS, U.K. dedicated for deuterium measurements is popular but other similar mass spectrometers available for this purpose can also be used for measurement of  $\delta D$  and  $\delta^{18}O$  from the samples prepared by the methods described above. A detail account of sample preparation, analysis and necessary corrections applicable for environmental deuterium and oxygen-18 has been presented by Navada and Kulkarni(1989)<sup>(77)</sup>.

### (B) MEASUREMENT OF LOW ACTIVITY OF $^3H$ IN WATERS

The low concentration of tritium present in natural waters can be measured with higher accuracy by its enrichment using a special device known as tritium enrichment unit before it is finally measured. This consists of a set of 16 cells placed in a cooling unit, a d.c. power supply and a control unit. The 500 gm capacity cell may be used according to IAEA design with minor modifications. The concentric cell has an outer stainless steel anode and a mild steel cathode with teflon insulators.

The air cooled cooling unit mainly helps in keeping the low evaporation losses from the cells during operation. The cells are connected in series and a constant current power supply (75V - 15A) provides the required current. The control unit cuts off the current supply to the cells in case the freezer temperature goes above a pre-adjusted value and also at the end of the enrichment run.

The cells are weighed for their contents, before and after electrolysis, on a top loading electronic balance having 0.01 g readability.

In an enrichment run, 500 g of initially distilled sample, with sodium peroxide as electrolyte, is taken in a cell and is electrolytically reduced to about 12 g. For this, a total charge of 1450 Ampere hours are passed over a period extending more than 7 days. The electrolysed samples are transferred into glass flasks, neutralised with lead chloride and distilled to get the final sample ready for LS counting.

#### LIQUID SCINTILLATION COUNTING SYSTEM

The enriched samples are counted in a liquid scintillation spectrometer. The counter is a micro processor controlled and provided with a refrigerated sample chamber. Low background of 2.5 cpm or less may be achieved by careful selection of operational parameters is a special feature of the system.

Generally 8 ml of the sample is mixed with 14 ml of an universal scintillator in a 24 ml capacity polyethylene vial. The vial contents are hand-shaken well to give a homogeneous gel. The vial is wiped with a moist tissue to remove any static charge on it and is introduced into the counter.

A set of samples comprising of unknown samples interspered with background and standard samples (two or three each) and the sealed spectrometer standard are supplied with the instrument. Background and standard samples are identical to unknown samples, prepared with tritium free water and tritiated water of known concentration respectively. The standard is a dilution of NBS which can be obtained from IAEA. The spectrometer standard helps to monitor the performance and long term stability of the counter.

Each sample is counted for a fixed duration (say 30 min) at a time and the whole set is cycled repeatedly many times till the end of the counting episode. In this way each sample is counted for a required duration (say 500 min.). The cycling helps in averaging

any changes taking place to the sample (loss of weight), shift in counter background etc. which may affect the sample count rate when the counting lasts over a few days. This also helps in discarding any particular value which is not acceptable statistically without losing the entire data on a sample.

#### CALCULATION FOR TRITIUM CONCENTRATION

Low concentrations of tritium are expressed in Tritium Ratio (TR) which represents one tritium atom in 10 atoms of H or an activity of 0.118 Bq. Kg. (3.19 p Ci Kg ) in water. The low concentration of tritium can be enriched by using the tritium enrichment unit which consists electrolytic cells of specific volume for the enrichment of tritium using the distillation under controlled conditions.

For a set of cells with uniformly developed cathode surfaces, the enrichment factor Z (final tritium concentration/initial tritium concentration) is calculated from two or three spiked cells with samples of known tritium concentration included in the run. It is calculated with the application of enrichment parameter E as defined below,

$$E = \frac{W_0 - W}{W_e} \times \frac{\ln Z}{\ln (W_0/W)}$$

Where  $W_0$  ,  $W$  and  $W_e$  are initial and final weight of the sample and the theoretical weight of sample electrolysed respectively.

The tritium concentration of a sample on counting date is calculated as,

$$T_c = T_{cs} \times \frac{N}{N_s} \times \frac{1}{Z}$$

Where  $T_c$ ,  $T_{cs}$  are tritium concentrations in TR and  $N$  &  $N_s$  are net count rates for sample and standard respectively.

The standard error could be evaluated from:

$$\sigma(c) = \sqrt{\sigma^2(N) + \sigma^2(Z) + \sigma^2(Tcs)U^{1/2}}$$

Other non- poison errors (e.g. weighing error) could be identified and added.

The measurement of  $^{14}\text{C}$  activities are also performed by beta counting by converting the carbon species (precipitation obtained from the water sample) into either  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_6$  (for gas counting) and  $\text{CH}_4$  (for liquid scintillation counting) using standard methods, i.e., originally benzene was synthesized using an aluminum catalyst to activated with de-boron gas which would trimerize acetylene to benzene on the catalyst. This technique produce pure benzene with 50% chemical yield. Noakes (1980)<sup>(78)</sup> improved this method by eliminating the use of di-borane gas which was chemically unstable and explosive - A vanadium pentoxide catalyst was used in place of the original catalyst for which the chemical yields for benzene were as high as 96 % .

Results of carbon-14 activity are expressed in percent with respect to so called 'modern carbon' which is supposed to represent the specific activity of the atmospheric before any significant dilution by fossil fuel combustion has occurred (i.e.  $13.56 \pm 0.07$  dpm. g of carbon). For practical purpose, the activity of modern carbon is 0.95 of the specific activity of the carbon of the oxalic acid supplied by the National Bureau of standards (Washington, D.C., U.S.A.) which is on the point of being exhausted.

## 5.0 REVIEW OF THE STUDIES CARRIED OUT IN INDIA:

### 5.1. USING ENVIRONMENTAL STABLE ISOTOPES

The ratio of D/H and  $^{18}\text{O}/^{16}\text{O}$  are measured by using mass spectrometers and compared with ocean water as standard (SMOW). Mass spectrometric facilities are available at NGRI, Hyderabad; Hydrology and Tracer Section, Isotope Division, BARC, Bombay and Physical Research Laboratory, Ahmedabad as national facilities which are exclusively used for nuclear hydrological studies. Mass spectrometric facilities are also available with Defence Laboratory, Jodhpur, Nuclear Research Laboratory, IARI, New Delhi, Atomic Minerals Division, Hyderabad and ONGC, Dehradun for the measurement of stable isotopes mass ratios.

NGRI has carried out integrated geohydrological investigations in the lower Maner basin in Andhra Pradesh by analyzing the water samples for D/H and  $^{18}\text{O}$  and  $^{16}\text{O}$  ratios. D and  $^{18}\text{O}$  values of 1977 precipitation. Samples showed a linear correlation while the results obtained from lakes, Maner rivers, its tributaries and dug wells provide very interesting information regarding evaporation effect and interrelationship of precipitation, surface and sub surface water. Isotope balance studies showed that the Masueancha stream, the only perennial tributary to the Maner, in the basin, is sustained during summer season mainly through the contribution from lake water. Ground water isotopic data revealed that the recharge to phreatic aquifers in different geological units of the basin is mainly due to direct percolation of the precipitation ( B.Kumar et al ).<sup>(79)</sup>

The NGRI, Hyderabad in collaboration with Central ground Water Board have carried out various studies like delineation and interconnections between aquifers and identification of recharge zones etc. in the Vedavati river basin in Tamil Nadu and Kerala,

Union Territory of Pondichery, Pambar Manimuttar river basins in Ramanathanpuram district and Neyveli area in South Arcot district in Tamil Nadu.

Isotope Division of BARC has used stable isotopes extensively in the study of (i) seepage from Chilla Hydel Channel UP, (ii) source of recharge to the groundwater in Jalore area of Barmer Distt., Rajasthan, (iii) salinization of groundwater in coastal Minjur aquifer near Madras, in Midnapore district of West Bengal, and (iv) salinization of groundwater in some parts of Haryana<sup>(80)</sup>, (v) interconnection between aquifers in Cauvery delta, (vi) surface water and groundwater interaction along river Ganga, (vii) origin of isothermal water, (viii) mixing of deep hot waters with shallow cold waters in Jatapai (MP) and (ix) hot spring in some parts of Bihar, W. Bengal and Orissa.

Physical Research Laboratory group have carried out the studies of D and O<sup>18</sup> isotopic ratios in groundwater as well as waters of rivers, lakes and hot springs etc. taken from a variety of locations in India. The groundwaters showed a large continental effect (isotopic variation of distance from coast) both in western and eastern sectors. Studies showed the most depleted <sup>18</sup>O values in the subcontinent in the high altitude lakes in Bhutan followed by Upper reaches of Ganga at Devprayag and Rishikesh, obviously due to melt waters of Himalayan glaciers<sup>(81)</sup>.

Defence Laboratory, Jodhpur and Nuclear Research Laboratory, IARI, New Delhi have also carried out studies like recharge to groundwater and period of recharge of deep groundwater bodies in Rajasthan and studies of evaporation from root zone in the areas near Delhi.

Groundwater pollution and dynamics of geothermal waters have also been studied by BARC using artificial and environmental isotopes including stable isotopes.

Studies on snow and glacier were probably carried out in India during as early period as Mughal period or earlier, but, systematic studies started with snow surveys by Dr. Church in 1947. Bahadur et al.<sup>(82)</sup> Ü. During 1969, the Indian National Committee in International Hydrological Programme appointed high level Committee on snow, Ice and Glaciers. Some studies like glacier mass balance, thermal profiling of ice body, hydrometeorological body observations, glacier dynamics, artificial melting of snow and ice, geomorphological and also the isotopic investigations were conducted and reports, papers, technical notes etc. on physical description, approach to the glacier, geological and geomorphological information, monitoring of meteorological parameters and advancement, recession of snout of the glaciers along with the mass balance and ice movement conducted by the conventional methods started coming up by a number of organisations like Geological Survey of India (GSI) and Department of Science and Technology (DST) etc.

At present, a number of organisations, departments and academic institutions like India Meteorological Department (IMD), snow and Avalanche Study Establishment (SASE), Mineral Development and Exploration Division of Geological Survey of India (GSI), Survey of India (SOI), Department of Science & Technology (DST), Central Water Commission (CWC), National Remote Sensing Agency (NRSA), Physical Research Laboratory (PRL), and National Institute of Hydrology, Bhabha Atomic Research Centre (BARC) are involved in snow cover mapping and snow pack studies for determination and modelling of the water equivalent, runoff due to snow melt and impact of changing behavior of the glaciers on runoff processes.



Indian contribution have been mostly around the Himalaya, which contains nearly trillion cubic metre of water in its glaciers comparable to the total ground water resource of the country. Nijampurkar et al.<sup>(83)</sup> dated the glaciers with environmental isotopes. The possibility of study the receding behavior by isotopic technique was suggested. A review of the isotopic technique for snow and glacier hydrology has been made by Bahadur<sup>(84)</sup> and Jain et al.<sup>(85)</sup>, Nijampurkar<sup>(86)</sup> has also reported the investigations of Himalayan glaciers using radioactive and stable isotopes. It was reported that study of radioactive tracers can provide quantitative estimates in understanding the behavior of glaciers in the past. Nijampurkar and Rao<sup>(87)</sup> carried out the studies pertaining the dynamics of the glacier ice, past accumulation rate of ice, climatic variations and chemical pollution using stable isotopes, natural and artificial isotopes and chemical tracers. Nijampurkar et al.<sup>(88)</sup> reviewed the glaciological studies in Himalayan using radioisotopes.

The work carried out in India, by using of environmental radioisotopes include dating of ice samples to obtain glacier flow rates by monitoring of beta-activity and measurement of Lead-210, Silicon-32.

## 5.2. USING ENVIRONMENTAL RADIOACTIVE ISOTOPES

Tritium ( $^3\text{H}$ ) and Carbon-14 ( $^{14}\text{C}$ ) are produced by cosmic radiations and introduced by thermonuclear explosion in the atmosphere. These are injected in the hydrological cycle by natural process. Measurement of very small quantity of these two radioactive isotopes is very tedious. At present, three institutes, namely BARC, Bombay; NGRI, Hyderabad, and PRL Ahmedabad have such facilities in India.

The tritium ( half life 12.23 years) used to determine the age of ground water ranging up to 100 years. The carbon-14 ( half life 5700 years) is used to determine the age of ground water ranging up to 50,000 years. The Tata Institute of Fundamental Research (TIFR) group<sup>(89)</sup> and PRL<sup>(90)</sup> group of scientists had carried out the chronological studies in Gujarat and Maharashtra using tritium and carbon-14. The TIFR group<sup>(91-93)</sup> had introduced the use of silicon-32 , for the age detection of ground water. Silicon-32 (half life only 500 years) is used to determine the age of ground water ranging up to 1000 to 2000 years. In fact, it was a long felt need to find out an environmental isotope for the determination of the age of water between the range of 100 years (T) and 5,000(<sup>14</sup>C) and therefore, <sup>32</sup>Si had filled this gap. However, <sup>32</sup>Si age dating is very complex and also the half-life is uncertain. Its recent estimate is about 100 years.

The PRL and TIFR group of scientist have also determined the regional flow velocities and residence times using environmental tritium carbon-14 and silicon -32 in different aquifers at various places in the country.

Environmental tritium and radio-carbon studies were also carried out in Vedavati River basin, situated partly in Karnataka and partly in Andhra Pradesh, to determine the general recharge conditions of the aquifers and interconnections of ground water bodies and age of ground water. About 40 samples of ground water were analyzed and found that the water bodies are not interconnected and groundwater belongs to an age of 25 years except at few places.

The NGRI has also carried out the recharge measurement studies using environmental tritium technique at three sites in Lower Maner basin falling in Karimnagar district of Andhra Pradesh. The

recharge to ground water through soil profiles in granitic and sedimentary terrains were calculated using the 1963 peak in tritium introduced by atomic bomb testing in atmosphere and also by using the integrated tritium method (Sukhija)<sup>(93)</sup> groundwater dating using radiocarbon and recharge studies using environmental tritium in various parts of Gujarat and Maharashtra.

BARC<sup>(94)</sup> has carried out studies of recharge to groundwater and dating of deep groundwaters in Rajasthan. Study of seepage from tail race tunnel at the Salar hydroelectric project interconnection of aquifers in the Cauvery delta in Tamil Nadu have also been carried out by Hydrology and Tracer Section of BARC, Bombay<sup>(95)</sup> using environmental isotopes. BARC has also carried out studies of ground water salinity and recharge in Madinapore, West Bengal and in coastal Orissa using environmental tritium and Carbon-14.

PRL scientists<sup>(96-99)</sup> have carried out radiocarbon dating of groundwater to estimate regional aquifer transmissivity in Watrak Shedi sub basin ( of Sabarmati Basin ) for a group of aquifers between 30-80 m. depth. The value of transmissivity, 7640 m<sup>2</sup>/day estimated by this method was found to be in fair agreement with the values obtained by pumping test.

## 6.0 GAPS AND FUTURE PROSPECTS IN INDIA

The Tarai and Bhawer belt has unaccounted flowing wells but due to lack of knowledge about the extent of water availability from these sources, the judicious planning for the use of water has not been possible so far. Isotope techniques employing environmental stable isotopes, (<sup>18</sup>O, <sup>2</sup>H), can be used for the identification of the recharge zone and evaluation of water available round the year in order to plan the future schemes to utilize the water.

The study of water balance and sedimentation rates in natural lakes in India using isotopes have not been attempted so far. Information is also required on the recharge zone and sources of supply of water to the lakes. Isotope techniques using environmental stable and radioactive isotopes can be used with advantage for obtaining above information for carrying out water balance and taking necessary measures for maintaining environmentally sound eco system and taking steps for maintaining ecological balance of the region. Water balance study of artificial lakes at the dam site has not been done.

Rivers are important source of water supply for various uses and the management of river water has to be planned judiciously. Since surface water and groundwater are two elements of the same system, the understanding of interaction between surface water and groundwater form a very important element of estimation of water availability and programme of proper planning for various uses. The information on surface water and groundwater interaction can be obtained with advantage by the use of stable isotope and artificial radioisotopes.

The construction of dams in mountainous region with basaltic foundation pose a problem of seepage and leakage through the foundation of the dam and bed of the reservoir. The use of environmental stable isotopes and artificial radioisotopes, along with the dyes can provide a very useful tool for handling such problems.

None of the methods can solve the technical problems of measurement parameters of snow cover independently, while water equivalent of a large representative area is considered. Isotopic technique is a new technique as compared to the conventional techniques for the measurement of water equivalent of snow, ice and

glacier. The snowmelt-runoff studies ,in India, started a decade before. But, they are limited to develop satisfactory forecasting models. Combination of two or more techniques: airborne gamma technique and automatic reporting type snow gauges (as ground devices) using the gamma or cosmic radiation absorption technique ,will help to provide better solution. Fully automatic system on snow cover and water equivalent is the necessity of the time for monitoring the temporal changes of these parameters of a particular course/catchment or representative basin. Efforts made to incorporate the nuclear isotopic techniques in last few years, are just the beginning, and, would need coordinated efforts of the organisations working in this field to develop and apply such forecasting and mass balance models to Indian snow fed catchment ,which may bring them to an operational level

Glacier and seasonal snow covers are important source of water in high altitude region specially in northern India. The evaluation of water equivalent of snow and snow and glacier melt are important element of water resources estimation. Isotopic snow gauges have been used for estimation of point water equivalent of snow. Environmental gamma ray has also been used with advantage for this purpose abroad. Possibility of that in Indian terrain use to be explored.

In Northern part of the country, there are large areas where problems of salinity being experienced specially, in areas where old waters of the saline nature are available. This situation has been experienced in Uttar Pradesh, Punjab, Haryana and in Northern Rajasthan. The dating of deeper saline water and tracing out the saline zone using suitable radioisotopes can help in taking necessary safety precautions to save the deeper aquifers from the further salinization.

The other important investigations are related to thermal waters. The use of environmental stable and artificial radioisotope can provide the valuable information in this field also.

The National Institute of Hydrology has recently initiated studies in the area of nuclear application to hydrology. The study programme relate to the identification of recharge zone, surface water and groundwater interaction, lake water balance and sedimentation, soil moisture movement and recharge to groundwater, stream flow measurement in mountainous rivers and leakage/seepage from dams and irrigation works. The programme of the Institute is examined and recommended by a Working Group constituted for this purpose.

In order to give a boost and to have a coordinated effort, for planing activities in the area of application of nuclear techniques to water and related agricultural areas by the various organizations, there is a need to have proper expertise and advanced facilities / instrumentation for the use of environmental isotopes in the country specially in a institute like National Institute of Hydrology, Roorkee.

LIST OF THE VARIOUS ORGANIZATIONS, INSTITUTES ENGAGED IN THE USE OF ISOTOPES FOR HYDROLOGICAL STUDIES IN INDIA

1. Bhabha Atomic Research centre, Trombay, Bombay
2. National Geophysical Research Institute, Hyderabad
3. Physical Research Laboratory, Ahmedabad
4. Nuclear Research Laboratory, Indian Agricultural Research Institute New Delhi.
5. Central Water and Power Research Station (CWPRS), Pune
6. UP Irrigation Research Institute, Roorkee
7. UP Ground Water Department, Lucknow
8. Defence Laboratory, Jodhpur
9. Haryana State Minor Irrigation Tube well Corporation , Karnal, Haryana.
10. Irrigation and Power Research Institute, Amritsar.
11. Maharashtra Engineering Research Institute ( MERI), Nasik, Maharashtra.
12. Water Resources Development and Training Centre and Department of Hydrology, University of Roorkee, Roorkee
13. Centre for Water Resources Development and Management (CWRDM), Calicut, Kerala.
14. Ground Water Survey and Development Agency, Maharashtra
15. Department of Chemistry , IIT Kanpur
16. National Institute of Hydrology, Roorkee.

## REFERENCES

1. Lal, D., V. N. Nijampurkar and S. Rama (1970), "Silicon-32 hydrology", Isotope Hydrology 1970 (Proc. Symp. Vienna, 1970), IAEA, Vienna (1970) 847
2. Loosli, H.H. and H. Deschger (1979), "Argon-39, carbon-14 and krypton-85 measurement in groundwater samples", Isotope Hydrology 1978 (Proc.Symp. Neuberberg, 1978) Vol.II, IAEA, Vienna (1979) 931
3. Giauque, W.F. and H.L. Johnston (1929), "An isotope of oxygen, mass 18", J. Arn. Chem.Soc. 51, 1436
4. Mecke. R. and W.N.J. Childs (1931), "The atomic weight of oxygen", Z. Phys.68, 362
5. Nier, A.O. (1950), "A redetermination of the relative abundance of the isotopes of carbon, nitrogen, oxygen, argon and potassium", Phys. Rev. 77, 789
6. Urey, H.C., F.G. Brickwedde and G.M. Murphy,(1932a),"A hydrogen isotope of mass 2", Phys. Rev. 39, 1645
7. Urey, H.C., F.G. Brickwedde and G.M. Murphy,(1932b), "Hydrogen mass 2 and its concentration", Phys. Rev.40, 145.
8. Rankama, K., (1954), "Isotope Geology", Pergamon Press, Oxford, 490p.
9. Craig, H., (1961), "Standard for reporting concentrations of deuterium and oxygen -18 in natural waters", Science 133, 1833
10. Craig, H., (1961), 'Isotopic variation in meteoric waters ',science, V. 133, pp. 1702-1703.
11. International Atomic Energy Agency, (1969), "Environmental Isotope Data No.1 World Survey of Isotope Concentration in Precipitation (1953-1963), Technical Reports Series No.96, IAEA, Vienna



12. International Atomic Energy Agency, (1970), "Environmental Isotope Data No.2 World Survey of Isotope Concentration in Precipitation (1964-1965)", Technical Reports Series No.117, IAEA, Vienna
13. International Atomic Energy Agency, (1971), "Environmental Isotope Data No.3 World Survey of Isotope Concentration in Precipitation (1966-67)", Technical Reports Series No.120, IAEA, Vienna
14. International Atomic Energy Agency, (1973), "Environmental Isotope Data No.4, World Survey of Isotope Concentration in Precipitation (1968-1969)", Technical Reports Series No.147, IAEA, Vienna
15. International Atomic Energy Agency, (1975), "Environmental Isotope Data No.5, World Survey of Isotope Concentration in Precipitation (1970-1971)", Technical Reports Series No.165, IAEA, Vienna
16. International Atomic Energy Agency, (1979), "Environmental Isotope Data No.6, World Survey of Isotope Concentration in Precipitation (1972-1975)", Technical Reports Series No.192, IAEA, Vienna
17. Gat, J.R., Gofiantini, R., Tongiorgi, E. (1968), 'Evaporation from lakes', Guidebook on nuclear techniques in , technical report series no. 91, p. 175, IAEA , Vienna.
18. Dinçer, T., (1968), "The use of oxygen-18 and deuterium concentrations in water balance of lakes", Water Resour. Res.4, 1289
19. Friedman, J., D.R. Norton, D.B. Carter, and A.C. Redfield, (1956), "The deuterium balance of Lake Maracaibo", Limnol. Oceanogr. 1, 239
20. Friedman, I. and A.C. Redfield, (1971), "A model of the hydrology of the lakes of the Lower Grand Coulee, Washington"
21. Gat, J.R., (1970), "Environmental isotope balance of Lake Tiberias", Isotope Hydrology 1970 (Proc. Symp. Vienna, 1970), P.109, IAEA, Vienna
22. Merlivat, L., (1970), "Etude quantitative de bilans de lacs a l' aide des concentrations en deuterium et oxygene-18 dans l' eau", Isotope Hydrology 1970 (Proc. Symp. Vienna 1970), p.89, IAEA, Vienna.

23. Zimmerman, U. and D. Ehhalt,(1970), "Stable isotopes in the study of the water balance of Lake Neusiedl, Austria", Isotope Hydrology 1970 (Proc. Symp. Vienna 1970) p. 129, IAEA Vienna.
24. Fontes, J.Ch. and R. Gonfiantini,(1967), "Comportement isotopique an course de l'evaporation de deux bassins sahariens", Earth Planet. Sci Lett. 3. 258
25. Gat, J.R. and Y. Levy,(1978), "Isotope Hydrology of inland subkhas in the Bardawil drea, Sinai", Limnol, Oceanogr. 23.
26. Friedman, I, G.I. Smith and K.G. Hardcastle, (1976), "Studies of quanternary saline lakes - II. Isotopic and compositional changes during desiccation of the brines in Owens Lake, California, 1969-1971", Geochim. Cosmochim Acta 40, 501.
27. Davis, G.H., B.R. Payne, T. Dinçer, T Florkowski, and T. Gattinger,(1967), "Seasonal variations in the tritium content of groundwaters of the Vienna Basin, Austria", Isotopes in Hydrology (Proc. Symp. Vienna, 1966), IAEA, Vienna(1967) 451.
28. Bakalowicz, M., B. Blavoux and A. Mangin,(1974), "Apports du tracage isotopique naturel a la connaissance du fontionnement d'un systeme karstique - teneur en O de trois systemes des Pyrenees, France", J. Hydrol. 23 (1974) 141.
29. Eberentz, P.,(1975), "Apport des methodes isotopiques a la connaissance de l'aquifere karstique", Universite paris VI, These 3eme cycle
30. International Atomic Energy Agency,(1981), "Stable Isotope Hydrology Deuterium and Oxygen-18 in the Water Cycle", Technical Reports Series No.210, IAEA, Vienna
31. Friedman, I. and J.R. O'Neil,(1977), "Compilation of stable isotope fractionation factors of geothermal interest", US Goel. Survey, Prof. Paper 440-KK
32. Abernethy, C.L.,(1980), "Problems of soil erosion and sedimentation in the context of population growth and economic development", Proc. IAHR/UNESCO Seminar on Hydraulics Research and River Basin Development, Nairobi, September 1980.

33. Wiebe, K. and L. Drennan,(1973), "Sedimentation in reservoirs, in Fluvial Processes and Sedimentation", Proc. Hydrology Symposium, University of Alberta, Edmontono, May 8 - 9: 539-561
34. Lomenick, T.F. and T. Tamura,(1965), "Naturally occurring fixation of cesium-137 on sediments of lacustrine origin", Soil Sci. Soc. Am. Proc.29: 383-386.
35. Rogowski, A.S. and T. Tamura,(1965), "Movement of Cs by runoff, erosion and infiltration on the alluvial Captina silt loam", Health Phys. 11:1333-1340.
36. Ritchie, J.C., P.H. Hawks and J.R. McHenry,(1975), "Deposition rates in valleys determined using fall-out cesium-137", Geol.Soc.Am. Bull. 86:1128-1130.
37. Baltakmens, T. and L.P. Gregory,(1977), "Profiles of Sr and Cs concentrations in selected New Zealand soils and their bearing on milk contamination levels",. N.Z. J. Sci.20: 425-431.
38. Wiebe, K. and L. Drennan,(1973), "Sedimentation in reservoirs, in Fluvial Processes and Sedimentation", Proc. Hydrology Symposium, University of Alberta, Edmonton, May 8-9: 539-561.
39. Sly, P.G.,(1978), "Sedimentary processes inlakes, in Lakes: Chemistry, Geology and Physics", A. Lerman (Ed.), Springer - Verlag, New York
40. Simpson, H.J., C.R. Olsen, R.M. Trier and S.C. Williams,(1976), "Man-made radionuclides and sedimentation in the Hudson river estuary", Science 194: 179-183.
41. McHenry, J.R. and G.D. Bubenzer,(1982), "Field erosion estimated from Cs activity measurements", Proc. Conference Am. Soc. Agri. Engrs., Univ. of Wisconsin - Madison, June 27-30, Paper No.82-2034.
42. Wischmeier, W.H. and D.D. Smith,(1962), "Soil loss estimation as a tool in soil and water management planning", Int. Assoc. Sci. hydrology Comm. on Land Erosion, Publ. 59: 148-159.
43. Wischmeier, W.H. and D.D. Smith,(1965), "Rainfall-erosion losses from cropland east of the Rocky Mountains", USDA Handbook 282.
44. Beck, H.L., 1966. Environmental gamma radiation from deposited fission products, 1960-1964, health Phys. 12:313-322.

45. McHenry, J.R., Ritchie, J.C. and Gill, A.C., 1973. Accumulation of cesium-137 in soils and sediments in selected watersheds, Water Resour. Res.9:676-686.
46. Ritchie, J.C., McHenry, J.R., Gill, A.C., 1972. The distribution of Cs in the litter and upper 10 centimeters of soil under different cover types in northern Mississippi, Health Phys. 22:197-198.
47. Baltakmens, T. and Gregory, L.P., 1977. Profiles of <sup>90</sup>Sr and <sup>137</sup>Cs concentrations in selected New Zealand soils and their bearing on milk contamination levels. N.Z. J. Sci. 20:425-431.
48. Garland, J.A., 1979. Resuspension of particulate matter from grass and soil, Report AERE-R-5492.
49. Campbell, B.L., Loughran, R.J. and Elliott, G.L., 1982. Caesium-137 as an indicator of geomorphic processes in a drainage basin system, J. Aust. Geog. Studies 20:49-64.
50. Brown, R.B., Cutshall, N.H. and Kling, G.F., 1981a. Agricultural erosion indicated by Cs redistribution: I. Levels and distribution of Cs activity in soils, Soil Sci. Soc. Am. J. 45: 1184-1190.
51. Ritchie, J.C., McHenry, J.R. and Gill, A.C., 1974, Fallout Cs in the soils and sediments of three small watersheds, Ecology (US) 55:887-890.
52. McCallan, M.E., O'Leary, B.M. and Rose, C.W., 1980. Redistribution of caesium-137 by erosion and deposition on an Australian Soil, Aust. J. Soil Res.18:119-128.
53. Ritchie, J.C., McHenry, J.R., Gill, A.C. and Hawks, P.H., 1972a. Fall-out Cs in reservoir sediments, Health Phys. 22:96-98.
54. Loughran, R.J., Campbell, B.L. and Elliott, G.L., 1982. The identification and quantification of sediment sources using <sup>137</sup>Cs, in Recent Developments in the Explanation and Prediction of Erosion and Sediment Yield, Proc. Exeter Symposium, July 1982, IAHS Publ. No.137:361-369.

55. McHenry, J.R., Ritchie, J.C. and Gill, A.C., 1973. Accumulation of cesium-137 in soils and sediments in selected watersheds, *Water Resour. Res.* 9: 676-686.
56. McHenry, J.R. and Ritchie, J.C., 1977a. Estimating field erosion losses from fall-out cesium-137 measurements, *Proc. Symposium Erosion and Solid Matter Transport in Inland Waters*. Paris, 1977, IAHS Publ. No.122:26-33.
57. Ritchie, J.C., McHenry, J.R. and Gill, A.C., 1973. Dating recent reservoir sediments, *Limnol. Oceanogr.* 18:254-263.
58. Ritchie, J.C., Hawks, P.H. and McHenry, J.R., 1975. Deposition rates in valleys determined using fall-out cesium-137, *Geol. Soc. Am. Bull.* 86: 1128-1130.
59. Stichler, W., A. Herrmann (1977) 'Variations of Isotopes in Snow Covers as Input of Temperate Glaciers', *Z. Gletscherkde. Glazialgeol.* Vol. 13, p.181.
60. Krouse, H.R., J.L. Smith (1973) 'Oxygen-18/Oxygen-16 abundance variations in Sierra Nevada, Seasonal Snow pack and their use in Hydrological Research', *The Role Of Snow and Ice in Hydrology (Proc. Symp. Brandff, 1972)*, UNESCO-WMO- IAHS, Paris, p.24.
61. Herrmann, A., M. Lehrer, W. Stichler (1981) 'Isotope input into runoff system from melting snow covers', *Nord. Hyd.* Vol.12, p.309.
62. Dansgaard, W., S.J. Johnsen, H.B. Clausen, N. Gundestrup (1973) 'Stable isotope glaciology', *Medd. Om Greenland* 1972 , p.1.
63. Merlivat, L., J. Ravoire, J.P. Vergnaud, C. Lorius (1973) 'Tritium and deuterium content of the snow in Greenland', *EarthPlanet. Sci. Lett.* 19 ,p.235.
64. Merlivat, L., J. Jouzel, J. Robert, C. Lorius (1977) 'Distribution of artificial tritium in firn samples from East Antarctica, Isotopes and Impurities in Snow and Ice', (Proc. Symp. Grenoble, 1975), Paris, IAHS Publ. No. 118 p.138.

65. Moser, H., W. Stichler (1975) 'Deuterium and oxygen-18 contents as index of the properties of snow blankets', Snow Mechanics (Proc. Symp. Grindelwald, 1974), IAHS Publ. No. 114 p.122.
66. Friedman, I., G.I. Smith, (1972) 'Deuterium content of snow as an index to winter climate in the Sierra Nevada area', Science 176 , p.790.
67. Judy, C. et al. (1970) 'Deuterium Variations in an Annual Snowpack ', Water Research ,vol. 6, Feb. 1970.
68. Moser, H., W. Stichler (1970) 'Deuterium Measurements Snow Samples from the Alps' Proc. IAEA ,Symposium on Use of Isotopes in Hydrology, March 9-13th, Vienna, pp.43-57.
69. Bahadur, J. (1976) 'Altitude Variation in Deuterium Concentration of Water Samples of Central Himalayas', Ind. J. Met. hydrol. geophys, Vol.27, No.1, pp.55-58.
70. Ambach, W. et al. (1976) ' Deuterium, Tritium and Gross-beta-activity investigations on Alpine Glaciers ', J. Glaciology, Vol. 17, p.383.
71. Friedman, I., (1953), 'Deuterium content of natural waters and other substances ' Geochem Acta 4, 89.
72. Coleman, M. L., (1982), 'Water with zink for hydrogen isotope analysis Analytical Chem. 54, (6) p. 993.
73. O' Neil, J. R. and S. Epstein (1966), 'A method for oxygen isotope analysis of milligram quantities of water and some of its applications', J. Geophys. Res., 71, pp 4955
74. Dugan, J. P. (1985), 'Guanidine hydrochloric method for the determination of water oxygen isotope ratios and oxygen-18 fractionation between CO<sub>2</sub> and water at 25 °C', Anal. Chem., 57, pp 1734
75. O' Neil, J. R., L. H. Adami and S. Epstein, (1975), 'Revised value for <sup>18</sup>O fractionation between CO<sub>2</sub> and H<sub>2</sub>O at 25 °C', J. Res. U. S. Geol. Surv., 3, pp 623

76. O' Neil, J. R. and L. H. Adami, (1969), 'The oxygen isotope partition function ratio of water and the structure of liquid water', J. Phys. Chem., 73, pp 1553
77. Navada, S. V. and U. P. Kulkarni (1989), 'Measurement of environmental deuterium and oxygen-18 in water samples', Bhabha Atomic Research Centre, Tech. Rep. No. I - 978, p 32
78. Noakes, J. E. and Spaulding, J. d., (1980), 'pulse shape liquid scintillation counting for beta, gamma or beta-gamma counting', in Peng, C, Horrocks, D. L. and Alpen, E. L., eds, Liquid scintillation counting: recent applications and developments, Vol. I, physical aspects: New York, Academic Press, p. 106-117.
79. B. Kumar, Athawale, R. N. and Sahay, K. S. N. 'Use of stable isotopes method in hydrological investigations with special reference to studies in lower Maner Basin, Andhra Pradesh'. Proceedings of the workshop on Nuclear Techniques in Hydrology held at NGRI, Hyderabad, Mar. 19-21, 1980. 1980.
80. Navada S. V. et. al., 'Application of Environmental isotopes in groundwater hydrology', Indian Journal of Earth Sciences, Vol. 13, no. 2-3, 1986, pp. 223-234.
81. Bhattacharya, S. K., S. K. Gupta and R. V. Krishnamurthy, 'Oxygen and hydrogen isotopic ratio in groundwaters and river waters from India', Proc. Indian Acad. Sci. Earth & Planets Sci., Vol. 94, No. 3, 1985, pp. 283-296.
82. Bahadur, J., and R. K. Datta 'Himalayan Glaciology- An Emerging Science', Proc. National Meet on Himalayan Glaciology, 1989, pp. 13-23.
83. Nijampurkar, V. N. and N. Bhandari 'Dating of Glaciers with environmental radioisotopes', Paper presented at the workshop on ICE, Snow and Avalanches at Manali, 18-30 April, 1977.
84. Bahadur, J. 'A review of isotopic techniques for snow and glacier hydrology of mountain watersheds' Proc. of First National Symposium on Seasonal Snow-Cover, 28-30 April, 1983, New Delhi, Vol II, pp. 64-74.

85. Jain S.K. and S.V. Navada 'A short review on the potentialities of the isotope techniques in snow hydrology' Proc. of First National Symposium on Seasonal Snowcover, 28-30 April, 1983, New Delhi, Organised by SASE, Manali, Vol II, pp.144-150.
86. Nijampurkar, V.N. and N. Bhandari 'Investigations of Himalyan Glaciers using radioactive and stable isotopes: A Review, Proc. of First National Symposium on Seasonal Snow-Cover, 28-30 April, 1983, New Delhi, Organised bt SASE, Manali, Vol II, pp.174-179.
- 87 Nijampurkar, V.N and D.K. Rao, 'Partial Scientific report of the Isotopic studies carried out on Chhota Shigri Glacier (H.P.) during the second multidisciplinary Expedition to Chhota Shigri (1987). Multidisciplinary Expedition to Chhota Shigri, July/August 1987, Tech Report No.2, DST, New Delhi, 1988
- 88 Nijampurkar, V.N and D.K. Rao, 'Review of the glaciological studies in Himalays using radioisotopes and chemical tracer, Proce. Nat. meet on Himalayan Glaciology, a DST publication, 5-6 June, 1989, pp.223-244.
89. Rama S.N.I., 'Chronology Guidebook on Nuclear Techniques Hydrlogy, IAEA, Vienna, 1968, pp.167.
- 90 Gupta S.K. and P. Sharma, 'Radio tracer dating of ground waters' An assessment of potentialities and limitations', Proc. of the workshop on Nuclear Techniques in Hydrology held at NGRI Hyderabad, 1980.
91. Lal D. et.al., Silicon-32 hydrology, Proceedings of a symposium on 'Isotope Hydrology 1970', held at IAEA Headquarters, Vienna, Mar. 9-13, 1970.
92. Nijampurkar V.N., 'Application of cosmic ray produced isotope Silicon-32 to hydrology with special reference to dating of groundwaters', Ph. D. Thesis, Unpublished, Bombay University, 1974.
93. Somayajulu B.L.K., 'Cosmic ray produced <sup>32</sup>Si in near coastal waters', Proc. Ind. Acad. Science LXIX, 1969, pp.339.
94. Navada S.V. et.al., 'Potentialities of isotope technique in groundwater recharge studies in Rajasthan - Some field experience', Proc. Symp. on challenging problems of desert environment, 1984.



95. Indian Association of Radiation Protection, 'Bulletin of radiation protection', Vol. No.1, Jan.-March, 1990.
96. Borole, D. V., S. K. Gupta, S. Krishnaswamy, P.S Datta and B.I. Desai, 'Uranium isotope investigations and radiocarbon measurement of river groundwater systems', Sabarmati basin Gujarat, India, Isotope Hydrology, 1978, Vol.1, IAEA, Vienna, 1979, pp.181-201.
97. Gupta S.K. and P. Sharma, 'Environmental radioisotopes in groundwater hydrology', Proc. workshop on isotope hydrology, BARC, Bombay, 1983, pp.56-77.
98. Gupta S.K. and P. Sharma, 'Application of nuclear techniques to groundwater hydrology in India - some case studies', Bhujal News', Vol. 2, No. 3, 1987, pp.5-10.
99. Bhandari, N., S. K. Gupta, P. Sharma, Prem Sagar, V. Ayachit and B.I. Desai, 'Hydrological investigations in Sabarmati and Mahi basins and costal Saurashtra using radio isotopic and chemical tracers', N.Bhandari, HILTECH (Min. of Water Resources, Govt. of India, NIH, Roorkee, 1986, 115 p.