# IANCAS
## Bulletin

## Isotopes in water resource management

# Editor: Y. K. Bhardwaj

## *Editorial*

*"Water, water, everywhere, Nor any drop to drink" these words from a poem by S. T. Coleridge very well reflect the water crisis being felt worldwide. The water crisis has been assigned to reasons like climate change, population explosion, groundwater deletion, poor water management, destruction of ecosystem, water pollution, wastage of water and undervaluation of this precious resource. Human beings are directly or indirectly responsible for all these reasons. It has been realized that immediate intervention in form of proper and efficient management of water can contribute significantly in alleviating the water scarcity. Conventional methods like water harvesting, adopting water-smart irrigation & industrial practices, water metering etc. have been fast put into practice to mitigate water scarcity. But there is still need of better scientific approach for assessment, exploration and utilization of water resources for better water management.*

*Use of stable and radioisotopes for water resource management is comparatively new technique. Isotopic investigations have been used for determination of: age of water aquifers, recharge source of water bodies, sub-ground movement of water etc. This bulletin is guest edited by Dr. U. K. Sinha an acclaimed expert in the field of applications of isotopes for hydrological investigations. It covers various aspects of isotope applications in water management.*

*I sincerely thank Dr. U. K. Sinha for agreeing to be the guest editor of this bulletin and taking time from his busy schedule to edit the bulletin.*

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# FOCUS
**Dr. P.K. Pujari**
Director, Radiochemistry & Isotope Group
&
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The Department of Atomic Energy (DAE) has been serving its motto, "Atoms in the Service of the Nation", by delivering the benefits of nuclear science and technology to National Security, Energy Security, Food Security, Water Security and Health Security. Water security is the ability to access enough quantity of water to sustain and enhance food production, sanitation and health as well as meeting industrial demands. Although 70% of earth is covered with water; only 0.007% of it is accessible as fresh water. Thus water is an increasingly precious resource, if not managed judiciously, could pose burden on economic growth as well as danger to human health and the environment. Great strides continue to be made in improving availability of limited freshwater to a humongous world population. It is imperative that best methods are put into practice for exploration, utilization and management of water.

Within the realm of the evolving disciplines of environmental sciences, the application of isotope based methods and techniques are being increasingly adopted in view of their inherent advantages. Both stable as well as radioactive isotopes have found extensive use for investigation of various aspects of assessment, development and management of water resources. In last few decades environmental isotopes investigations have provided insight into the processes governing water cycles and effect of climatic conditions on water cycles over a period of time. Applications include tracing the evolution of water from its origin due to precipitation, its recharge processes and ending in an aquifer. Special emphasis is on studying processes at atmosphere-biosphere-land interfaces, since these are the sites of major changes in isotope composition. Isotopes have also been used for determining the origin of specific solutes in ground water. The list of stable isotopes that have vital implications for water resource management has grown in recent years. Unlike stable isotopes that provide insight into geochemical processes in aquifers, the radioisotopes are primarily employed for determining age of water in aquifers. Data obtained gives idea of the residence time of water in an aquifer once it has passed through the unsaturated zone. Ground waters dating can be done by using radioisotopes, although stable isotopes and can also be used for some dating applications. Isotope techniques provide invaluable information on the sources, movement and quantity of water in different environments, including rivers and lakes. They are particularly effective in investigating water reserves below the earth's surface, or ground water, Isotope hydrology provides insights into water's behavior and helps to build the foundations for rational utilization of this precious resource.

It gives me immense pleasure that Indian Association of Nuclear Chemists and Allied Scientists (IANCAS) is bringing out this thematic bulletin consisting of six articles, on various aspects of isotopes in water resource management. The bulletin articles will give a glimpse of the advanced research being carried out by various established research groups of prestigious Indian institutions in the field. I thank all the authors, Dr. Y.K. Bhardwaj. Editor of IANCAS Bulletin and specially. Dr. U.K. Sinha, IRAD, BARC the Guest Editor for devoting his valuable time in bringing out this important thematic bulletin.

(Dr. P.K. Pujari)

# IANCAS Executive Committee (2018-2021)

# Isotopes in water resource management

# Guest Editor

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# Guest Editorial

## Dr. Uday K. Sinha

Access to safe freshwater is considered a basic human right. However, in many parts of the world, surface water and groundwater resources are at risk because of indiscriminate use, rapidly growing populations, increasing agricultural demands and the threat of pollution. These risks are often compounded by a lack of understanding about the local conditions governing the occurrence, distribution and movement of surface and groundwater resources. It has consequently attracted a wide scale international attention of UN Agencies and related international/regional governmental and non-governmental organizations.

Isotope studies applied to a wide spectrum of hydrological problems related to both surface and groundwater resources as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, often referred to as "Isotope Hydrology". It is an emerging discipline with expanding investigation tools for many environmental problems. Improved measurement of naturally occurring isotopic abundances (i.e. relative number of atoms of an element with different numbers of neutrons in the nucleus) in waters followed by microchip design advances in mass spectrometry has immensely increased the utility of isotope techniques in the hydrological investigations. Its impact on subsurface hydrogeology is very significant because of the innate difficulty of imaging subsurface processes with traditional hydrometric tools. It is now possible, for example, to utilize isotopes as conservative tracers of delineating groundwater flow paths, for estimating solute exchange from one phase of a system to another, for determining extents of chemicals reactions in the subsurface, for identifying source regions in watersheds, for identifying recharge areas of aquifers, and for estimating its subsurface residence times. The climatic and hydrologic diversity in India provides unlimited opportunities for application of isotope techniques; be it in arid zones, Himalayan mountainous region, coastal areas, alluvial deposits and hard rock of peninsular India.

The main aim of this bulletin is to provide review of basic principles and practical applications with some illustrative examples. Conclusions, inferences as well as recommendations from the investigations will facilitate the groundwater planners to undertake proper water resources development and management strategies, which in turn can provide benefit to the society. The topics covered in this bulletin include use of isotopes to understand land–atmosphere–biosphere interactions, rivers and surface water, development of deep groundwater resources, urbanization and water resources management, artificial recharge, contamination problems and research frontiers.

This bulletin is designed to be self-sufficient reference material for scientists and engineers involved in research and/or practical applications of isotope hydrology as an integral part of the investigations related to water resources assessment, development and management. Additionally the contents can fulfill the need for basic knowledge in other disciplines of the Earth Sciences dealing with water in general.

# Isotopes in Hydrology: Fundamentals and Applications

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## ABSTRACT

*Isotope Hydrology, an interdisciplinary field is a comparatively young scientific discipline, which evolved around since 1950s, when it was first realized that the methods of nuclear physics and chemistry for the detection of isotopes could have valuable applications in hydrology as well. The conventional tools of isotope hydrology are the isotopes of the constituent elements of the water molecule ($H_2O$) itself, i.e., the isotopes of hydrogen and oxygen. Next addendum were the solutes and isotopes of elements of solutes and their chemistry, which includes radiocarbon ($^{14}C$), that enabled water dating via the decay of $^{14}C$ in the carbon dissolved in the waters. Later on, many more methods were added in isotope hydrology including, injected radioactive tracers and some non-isotope (environmental tracers) methods i.e. dissolved noble gases etc. Therefore, in broader sense, the isotope hydrology may be defined as the application of "environmental isotopes and tracers to study the source, origin, distribution and dynamics of water in various components of hydrosphere".*

*The oceans are the ultimate source of all fresh waters on the earth. Evaporation at ocean surface forms clouds and then it moves to continent side owing to pressure difference created by unequal heating of atmosphere and condensation at higher altitudes again forms liquid water. This traversing path of water molecules in the hydrological cycle is accompanied with variation in isotopic composition at every stage. The various natural phenomena leave their signature on the water molecules. In isotope hydrological investigations this signature is decoded by measuring the isotopic composition of water samples and the type of processes the molecules have undergone is deciphered. The extent of such variation depends on meteorological conditions such as temperature, humidity, state of equilibrium of the process, amount and intensity of rainfall and geographic locations such as northern or southern hemisphere, latitude, altitude etc. This article gives an overview of basis of application of environmental isotopes in hydrology and future prospects.*

## Introduction

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

For acquiring better quality of water, we need the continuation and extension of hydrological research. In this respect, the development and practical implementation of isotope methodologies in water resources management has proved to be very important. Isotope studies applied to a wide spectrum of hydrological problems, related to both surface and

groundwater resources, as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, often referred to as "Isotope Hydrology". Isotopes (stable and radio) of both environmental as well reactor produced are routinely used as tracers in hydrology for various hydrological investigations e.g., aquifer-aquifer interconnection, surface water-groundwater interconnection, source of groundwater salinity and pollution, origin of geothermal waters, efficacy of artificial recharge, dynamics in lakes, source of recharge & estimation of recharge to the groundwater etc.

The selection of a tracer whether radio or stable isotope or both depends on the problem under investigation. Generally, if the area under investigation is large, stable isotopes are the choice. The stable isotopic composition of water is modified by meteoric physico-chemical processes leading to characteristic isotopic signature of precipitation and recharge waters in a particular environment at a specific site. This signature then serves as a natural tracer for the origin of groundwater at that site. The fundamental concepts of tracer methodology indicate that a tracer should have the same physical and chemical behavior as the traced material. Water would be the ideal tracer for tracing water in the hydrological cycle. But the pertinent question is how to distinguish and detect the water tracer in the hydro system. The isotopes come to our help here. Chemically water molecule ($H_2O$) is made up of two atoms of hydrogen and one atom of oxygen. Hydrogen and Oxygen have three naturally occurring isotopes namely $^1H$, $^2H$, $^3H$, $^{16}O$, $^{17}O$ and $^{18}O$. Though a number of isotopic species of the water molecule are possible, $H_2^{16}O$, $HD^{16}O$, $H_2^{18}O$ with natural abundances, 997, 680 ppm (99.76%), 320 ppm and 2040 ppm respectively and are more relevant to the isotope hydrology because of their higher abundance. $H_2^{17}O$ has a very low (370 ppm) abundance in nature and is not of much significance in hydrology as we get same information as from $H_2^{18}O$ (2040 ppm). In meteoric waters even at global scale, isotopic variation of a few ppms only is observed.

Routinely measuring such a small differences in absolute abundances is not easy and requires some rather sophisticated mass spectrometric equipment. Further, the data sets so generated from different laboratories will suffer from tremendous problems in comparing. The good thing about these data is the information of variation of the stable isotope compositions with respect to a standard is good enough for isotope hydrologists rather determining their absolute values. Generally, the stable isotopes are measured as the ratio of the two most abundant isotopes of a given element.

The universally accepted standard for reporting stable isotope compositions of natural waters for hydrogen and oxygen isotopes is the standard Mean Ocean Water (SMOW). It is a logical and natural choice for the standard since all fresh water on the planet is derived from the oceans, which represents 97.2 % of the water in the hydrosphere and they being a very large water body, there is no appreciable change in their isotopic composition with time. Isotopic concentrations are expressed as the difference between the measured ratios of the sample and the reference over the measured ratio of the reference. Mathematically, the error between the apparent and true ratios is cancelled. The universally accepted way to report the isotopic compositions of natural water is in per mil (parts per thousand) deviations ($\delta$) from the SMOW as shown below:

$$\delta(\permil) = \left( \frac{R_x}{R_s} - 1 \right) \times 1000$$

where R denotes the ratio of heavy to light isotope (e.g. $^2H/^1H$ or $^{18}O/^{16}O$) and $R_x$ and $R_s$ are the ratios in the sample and standard respectively. The present day Isotope Ratio Mass Spectrometer can measure the $\delta$ value with a sensitivity of about 1‰ for deuterium and 0.1‰ for oxygen-18. Considering that the normal range of variations of D and $^{18}O$ in nature are approximately –500 to +100‰ and –60 to +10‰ respectively and that the relative variation of D is about 8 times that of $^{18}O$, the sensitivities obtainable in mass spectrometers are more than adequate for most purposes. For other isotopes standards are listed below (Table 1).

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

| Isotope | Ratio | % natural abundance | Reference (ppm) (Abundance ratio) | Commonly measured phases | Application in hydrology |
|---------|-------|---------------------|-----------------------------------|--------------------------|--------------------------|
| $^2H$ | $^2H/^1H$ | 0.015 | VSMOW (155) | $H_2O, CH_4$ | Origin of water |
| $^{13}C$ | $^{13}C/^{12}C$ | 1.11 | VPDB | $CO_2$, Carbonates | Source of carbonates, Groundwater Dating |
| $^{15}N$ | $^{15}N/^{14}N$ | 0.366 | Air $N_2$ (3677) | $N_2$, $NH_4NO_3$, N-organics | Pollution marker |
| $^{18}O$ | $^{18}O/^{16}O$ | 0.204 | VSMOW (2005) | $H_2O$, $CO_2$, $SO_4^{2-}$, $NO_3^-$ | Origin of water |
| $^{34}S$ | $^{34}S/^{32}S$ | 4.21 | CDT | $SO_4^{2-}$ Sulphides, $H_2S$, S-organics | Origin of salinity, Redox condition of aquifer |
| $^{37}Cl$ | $^{37}Cl/^{35}Cl$ | 24.23 | SMOC (0.324) | Saline waters | Source of pollution |
| $^{87}Sr$ | $^{87}Sr/^{86}Sr$ | 07.00 | USGS *Tridacna, Sea Water* | Solution | Provenance of water |
| $^{11}B$ | $^{11}B/^{10}B$ | 80.1 | NISTRM 951 - (A Sodium borate) | Solution | Source of pollution |

The traversing path of water molecules in the hydrological cycle is accompanied with variation in isotopic composition at every stage, termed as isotope fractionation. The various natural phenomena leave their signature on the water molecules. If this signature is decoded by measuring the isotopic composition then the type of processes the molecules have undergone, can be deciphered. The two main physical processes responsible for the formation of precipitation in a hydrological cycle are evaporation and condensation. Both of the processes contribute in the variation of isotopic composition of the water molecules. The extent of such variation depends on meteorological conditions such as temperature, humidity and state of equilibrium of the process etc. Isotope fractionation is the partial separation of isotopes of an element between two or more chemical species or phases. This causes change in isotopic composition of the element in two reservoirs.

**Mechanism of Isotope fractionation**

The two basic mechanisms are: *Equilibrium isotope fractionation,* which is due to differences in bond *energies* of isotopes in compounds and *Kinetic isotope fractionation,* which is due to differences in average *velocity* or *reaction rates* of different isotopes. Both depend only on the *mass* of the isotope and are called *mass dependent fractionation*; both will fractionate, say $^{18}O/^{16}O$ about twice as much as $^{17}O/^{16}O$.

*Equilibrium isotope fractionation*

It controls the distribution of isotopes in the case that a system approaches thermodynamic equilibrium. Isotopes distribute themselves among compounds in a way that minimizes the energy of the system. The sensitivity to mass comes in through the vibrational modes of inter-atomic bonds. It should be noted that isotope fractionation will only occur in systems in which there is both an isotope effect and a reaction that does not proceed to completion. Thus, even in the presence of an isotope effect, there will be no isotope fractionation if all the reactant goes to a single product because all the atoms have reacted and thus the ratio of the heavy to light isotope must be the same in the product as it was in the reactant. The magnitude of an isotope effect is expressed as an isotope fractionation factor ($\alpha$). This is defined as the ratio of the heavy to light isotope in the product divided by the ratio of the heavy to light isotope in the reactant.
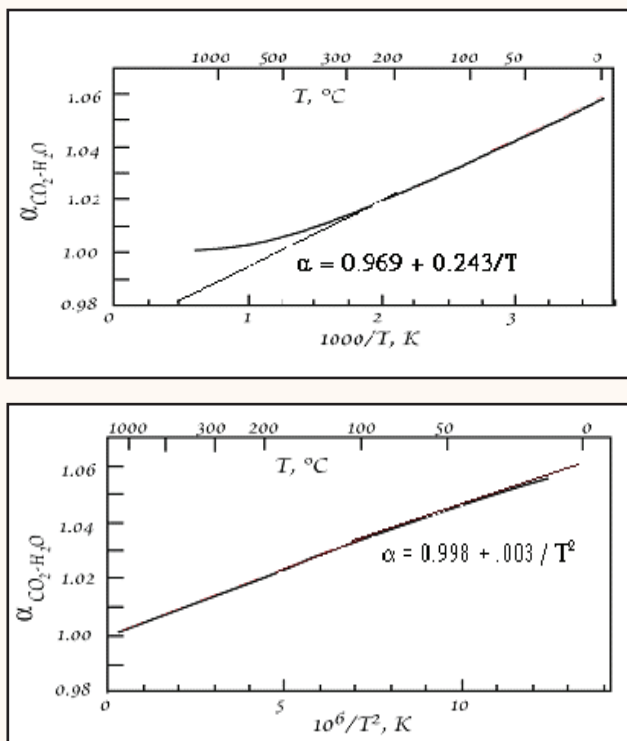
**Fig. 1: Dependence of isotope fractionation factor ($\alpha$) on temperature**

*Temperature dependence of equilibrium isotope effects*

The equilibrium fractionation factor ($\alpha$) decreases with increase of temperature. Figure 1 shows calculated value of $\alpha^{18}O$ for $CO_2 - H_2O$ system, with $1/T$, $1/T^2$; Up to ~ 200 $^0C$, $\alpha$ is linear with $1/T$, for higher temperatures it has linear relation with $1/T^2$.

*Kinetic isotope fractionation effects*

Kinetic isotope effects occur in fast, incomplete, or unidirectional processes like evaporation, diffusion, and biological reactions. Consider an ideal gas, every molecule has, on an average, the same kinetic energy ($E = 1/2\ mv^2$).Then molecules with light isotopic species will diffuse faster in the gas phase. Kinetic fractionation effects can be much larger than equilibrium fractionations. Equilibrium fractionation factors depend on the imbalance between forward rate constants and reverse rate constants for different isotopes, but kinetic factors depend only on the forward rates. Both rates are likely to be faster for light isotopes, so reverse reaction diminishes the fractionation.

Of all the various reasons for isotopic fractionations, the most important, from the point of view of hydrology is the higher volatility of the lighter $H_2^{16}O$ compared to the heavier species. The fractionation factors for all processes, where the process proceeds slowly enough that equilibrium conditions are practically established at the interface of the two phases, the fractionation factor $\alpha$ is simply the ratio between the vapor pressure of lighter component (p) and the heavier component ($p^1$) ($P^1 < P$). It is also defined as the ratio between the isotopic compositions in the liquid phase and the vapor phase. At t =25$^o$C $\alpha$ are as follows:

$$\alpha_D = \frac{P(H_2^{16}O)}{P^1(HDO)} = \frac{(D/H)_{Water}}{(D/H)_{Vapor}} = 1.079$$

$$\alpha^{18}_O = \frac{P(H_2^{16}O)}{P^1(H_2^{18}O)} = \frac{(^{18}O/^{16}O)_{Water}}{(^{18}O/^{16}O)_{Vapor}} = 1.0094$$

The above equations indicate that the vapor is depleted by ~8% in deuterium and ~0.9% in oxygen–18 relative to liquid water. Fractionation factors are temperature dependent and decreases with increase in temperature and have a range of 1.106 to 1.029 for deuterium and 1.0111 to 1.0033 for oxygen respectively from 0$^0$C to 100$^0$C.This leads to the important conclusion that in the normal range of temperatures in hydrological investigations, the enrichment or depletion is unidirectional. The vapor is always depleted in heavy isotopes relative to the liquid and the condensate is always enriched in heavier isotopes relative to the vapor. Condensation is an equilibrium process and occurs at 100% relative humidity where as evaporation normally occurs under non-equilibrium conditions and is controlled by kinetic isotope effect. The exact fractionation value depends on factors such as relative humidity and turbulence at the air-sea interface. The kinetic evaporation effect is bigger than the subsequent equilibrium condensation effect. Isotope values of atmospheric moisture originate from both equilibrium and kinetic effects.

**History of Isotope Standards**

In the early days of stable isotope studies, oxygen and hydrogen isotopes were reported relative to the

oxygen and hydrogen isotope value of seawater. The H and O isotope values of seawater are not perfectly uniform in the world's oceans. The $\delta^{18}O$ value ranges from $-1.5‰$ in Antarctic Bottom Water (ABW) to $+0.5‰$ in North Atlantic Deep Water (NADW). In marginal marine environments like the Baltic Sea, $\delta^{18}O$ may be as low as $-5$ to $-7‰$, whereas in hot arid regions like the Red Sea, values as high as $1.8‰$ are found. In practice nobody had ever used seawater as a genuine laboratory standard. Instead, NBS -1 (Potomac River water) was used, and Harmon Craig defined SMOW relative to NBS-1. This prompted the International Atomic Energy Association to prepare a large aliquot synthetic water standard with an isotope value close to seawater. The new standard was called Vienna SMOW, and all modern O and H isotope measurements are made relative to this standard.

**The Global Meteoric Water Line (GMWL)**

In 1961, Harmon Craig published his GMWL that defines the relationship between $\delta^{18}O$ and $\delta D$ of global precipitation (Craig 1961) as shown in Fig. 2. He proposed the relation;

$$\delta D = 8\delta^{18}O + 10 \text{ SMOW}$$

This is now updated by Rozanski et al. (1993) as;

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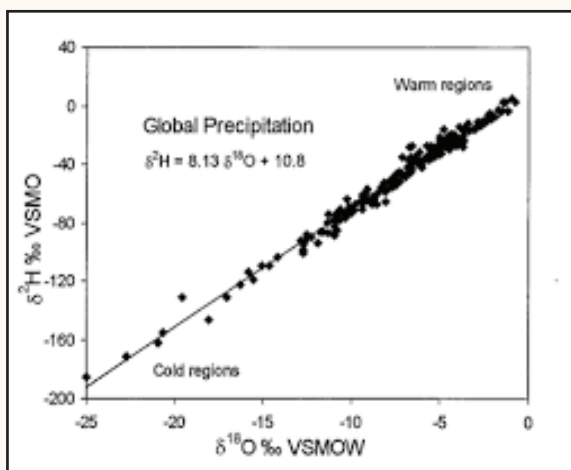


Fig. 2: Correlation between $\delta^{18}O$ and $\delta D$ values of global precipitation

This GMWL is actually made up of many local MWL and is only an approximation for what is going on. It was quickly recognized that cold regions have

low $\delta^{18}O$ values and warm regions have high $\delta^{18}O$ values. This fact has led to a substantial increase in our understanding of the hydrological cycle.
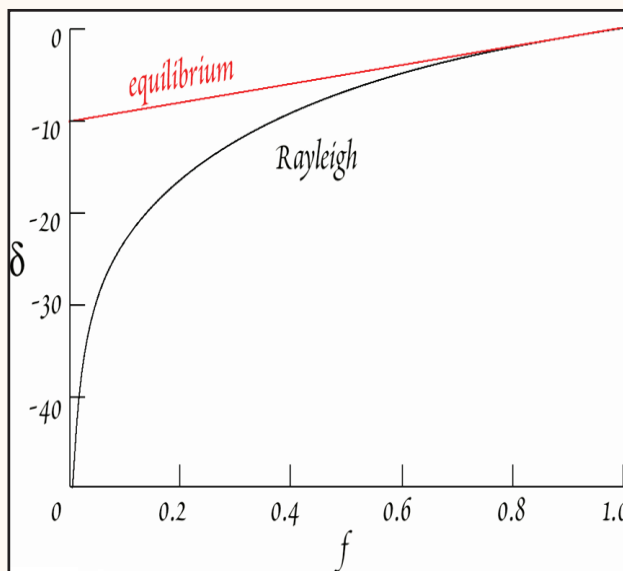


Fig. 3: Fractionation of isotope ratio during equilibrium and Rayleigh condensation. $\delta$ is ‰ difference between the isotopic compositions of the initial vapor and when fraction f of the vapor remains

**Rayleigh condensation**

*It is expressed as $R = R_o\ f^{(\alpha-1)}$,* where Ro is the *vapor's* initial isotope ratio value and R is the value after a rainout event. The fraction *f* is the residual *vapor* reservoir in the cloud. The fractionation factor $\alpha$ is for equilibrium water-vapor exchange at the prevailing in-cloud temperature. Equilibrium condensation is generally the case in clouds, where humidity = 100 %. In a Rayleigh function, $\alpha$ is expressed as product-reactant (i.e. $\alpha_{l-v}$). In the case of $^{18}O$, this would be $\alpha^{18}O_{l-v} = 1.0094$ at 25°C, but will increase as the temperature drops (Fig. 3).

**Rainout**

The only way to produce precipitation is by cooling an air mass. This occurs by adiabatic expansion (no loss of enthalpy) as warm air rises to lower pressures, or by radiative heat loss. When the dew point is passed, water vapor condenses to maintain thermodynamic equilibrium, and it will rain or snow. As an air mass leaves its source (usually in the subtropics) it cools as it rises above the continents or as it moves to higher latitudes. This cooling induces precipitation that distills the heavy isotopes from the water vapor
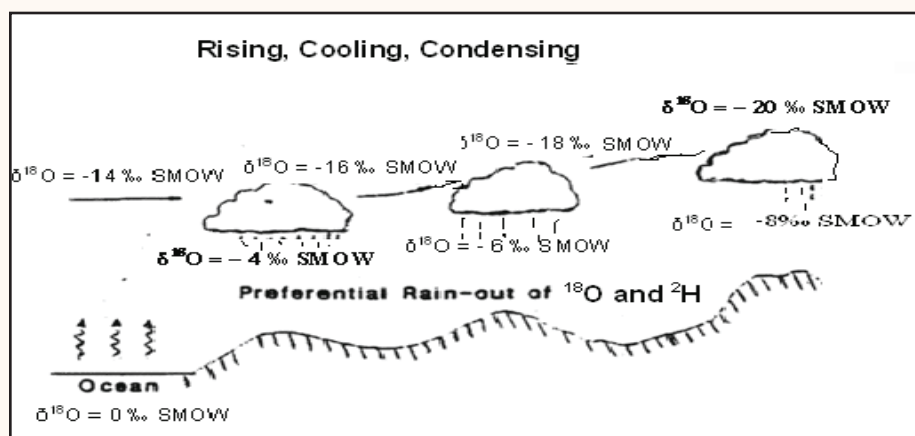
**Fig. 4: Cartoon depicting progressive depletion in heavy isotope by rainout effect**

in the air mass. The remaining vapor becomes progressively depleted in $^{18}O$ and $^2H$ according to a Rayleigh-type condensation. Precipitation with relatively high isotope values (compared to the air mass vapor) falls from the clouds. As precipitation continues however, the water vapor remaining attains lower and lower values resulting in precipitation attaining lower and lower values. This results in the so-called continentality effect and orographic effect that produces precipitation with very low values at high latitudes and altitudes respectively (Fig. 4). The relationship between isotope values and temperature allow us to estimate seasonal variability, altitude, latitude and paleoclimatic effects.

For condensation to occur, cooling must take place. Cooling can take place by;

1) Lifting over a mountain range.
2) Warm moist air rising.
3) Warm moist air ramped over cold dry air.
4) Air mass warms over lake or ocean and is then lifted and cooled over land (lake effect).
5) Air mass moves to center of the continent during the winter (cooling it).

Controls on the isotope value of precipitation are;

1) Isotope value of source
2) Rate of evaporation of source
3) Isotopic evolution of air mass
4) Relative humidity during precipitation (raindrops may evaporate or gain mass as they fall).

5) At high latitudes the amount effect becomes less pronounced as evaporation is lessened.

**Isotopic equilibrium in water-vapor exchange**

The difference in vapor pressure between $H_2^{18}O$ and DHO leads to their differential evaporation rates. During equilibrium fractionation this leads to $\sim 8$ times the decrease in Deuterium compared to $\delta^{18}O$ in the vapor at $25^0C$ and this ratio increases with decrease in temperature as the equilibrium fractionation factor for D/H fractionation is more sensitive to temperature in compare with $^{18}O/^{16}O$ fractionation which is expected looking at the % mass difference between the pairs. For e.g., at 25 °C the ratio of $\delta D_{vapor}/\delta^{18}O_{vapor}$ is 8.17, which rises to 8.77 at 10 °C and to 9.13 at 0 °C.

**Humidity and kinetic (non-equilibrium) evaporation**

The rate of evaporation determines how close to equilibrium a water-vapor pair can be. The faster the evaporation, lesser the opportunity for exchange between the two phases. Increased evaporation therefore results in an increased kinetics or non-equilibrium isotope effect. Kinetic effects are related to humidity, surface temperature, wind speed (actually shear at the water surface) and salinity. At low humidity, water-vapor exchange is minimal; therefore evaporation is a non equilibrium process. Researchers found that the $\delta^{18}O$ and $\delta D$ values of surface water become progressively higher as evaporation proceeds.

## Deuterium excess "d-excess" in meteoric waters

Under conditions of 100% humidity, the vapor is in isotopic equilibrium with seawater and in theory the first rain should plot on a MWL through seawater on the $\delta D$ v $\delta^{18}O$ plot. It doesn't, however, because of the diffusion related to the kinetic isotope effect, which is a function of relative humidity difference between the bulk atmosphere and the boundary layer. When humidity is low ($h = 50\%$) the vapor is strongly depleted of the heavier isotopic molecules and precipitation plots above seawater, and even above the GMWL. When humidity is ~85%, precipitation plots very close to the global meteoric water line are obtained. Accordingly, global atmospheric water vapor forms with an average humidity of about 85%, and produces precipitation on a line that is displaced from seawater by +10‰ for $\delta D$. Craig's meteoric water line for global precipitation, therefore, has a deuterium excess of 10‰. The d-excess stems from differences in the kinetic isotope fractionation effect between isotopic molecules containing D, and those containing $^{18}O$. Dansgaard proposed in 1964 the use of the value, d, to characterize the deuterium excess in global precipitation (Dansgaard 1964). The value d is defined for a slope of 8, and is calculated for any precipitation sample as: $d = \delta D - 8\delta^{18}O$

The correlation between temperature and $\delta^{18}O - \delta D$ controls the position of precipitation on the meteoric water line. From this correlation we can derive isotope effects due to seasons, altitude, latitude, continentality and paleoclimates. The GMWL slope is 8.2, but it can be affected by the evaporation of rain as it falls. In arid environments, the slope of the meteoric water line is much less than 8 and typically in the range of 3-5 which is a characteristic of evaporating water. However, the evaporation of falling rain increases the humidity in the air column. This increase in humidity also increases the slope.

## Geographical parameters affecting isotopic values of precipitation

The isotopic composition of rainwater are related with the geographical parameters such as Latitude effect, Altitude effect, Continental effect, Seasonal variations, Amount effect and Paleoclimates. Considering the complexity of hydrological cycle, it may be surprising that $^{18}O$ and $^2H$ behave at all predictably.

### *Latitude Effect*

Approximately 65% of the world's water vapor originates between $30^0N$ and $30^0S$ latitudes. Pole ward transport of vapor is associated with rainout and a resultant decrease in available moisture. Isotope values of precipitation collected at mid-latitude continental stations are in general lower than coastal or marine stations located at the same latitude (Fig. 5). This is especially clear in the Northern Hemisphere. There is a strong vertical gradient in isotope values of atmospheric vapor that results in a tendency to observe lower values at higher altitudes.
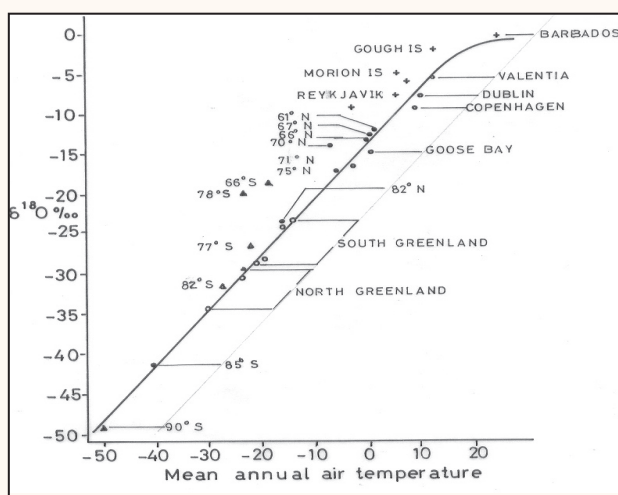


**Fig. 5: Latitude effect on isotope values of precipitation**

### *Altitude effect*

In general, the distribution of $\delta$ values mimics the topography, with mountain chains showing up clearly low values of heavier isotopes at higher altitudes. This is called the altitude or orographic effect. Any time a vapor mass gets pushed up a hill, the air will cool adiabatically (through expansion) resulting in precipitation. The lower temperatures at higher altitudes result in low $\delta$-values. This decrease in $\delta$-value is about $-0.15$ to $-0.5$‰ per 100m rise in altitude for $\delta^{18}O$ and about $-1$ to $-4$‰ for $\delta D$ (Fig. 6). This effect has been used to determine areas of recharge in hydrological studies.

**Fig.6: Altitude effect- δ¹⁸O values in precipitation decrease with increasing altitude**

*Continental Effect*

Lower value of heavier isotopes in rain waters is observed as it moves away from the coastline. This is called the continental effect (Fig. 7). The same mechanism is responsible for both effects (altitude & continental)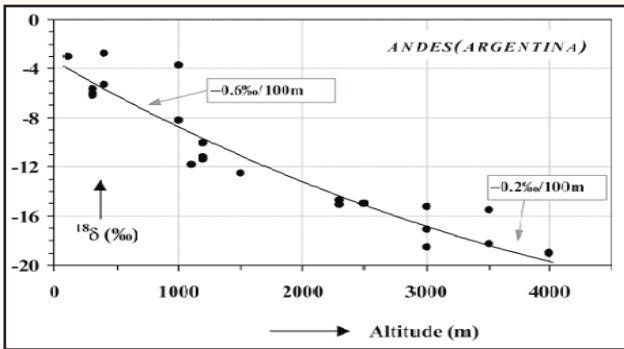, i.e., gradual removal of moisture from air masses that move inland, or are orographically lifted, coupled with preferential removal of heavy isotopes during condensation. This implies that the ocean is a major source of water vapor over the continents. Such an assumption might however, not always be correct. Large inland water bodies such as lakes or empirics seas could impart a significantly different isotope value upon the vapor derived from the ocean.
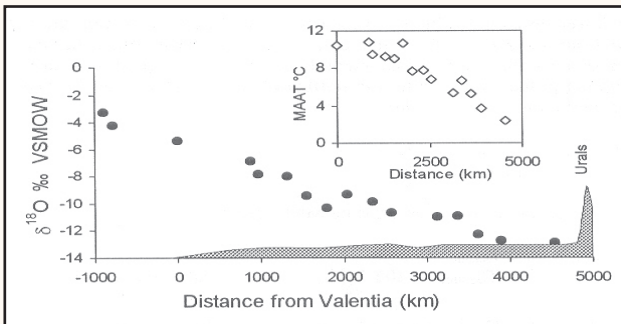


**Fig. 7: Continental effect on isotopic composition of precipitation**

*Seasonal variation*

Seasonal effects are generally coupled with continental effects such that high latitude mid continental sites has highly variable $\delta^{18}O$ and $\delta D$ values seasonally (Fig. 8). This variation provides a convenient way to estimate seasonal timing of recharge, circulation of groundwater, and the general effect of a precipitation event on a watershed. The regular variation from low δ-values in the winter to high in the summer at mid to high latitudes is due to several factors. Seasonal temperature variation- influences the amount of moisture in the atmosphere and the Rayleigh distillation of that moisture. Seasonal variation in evapo-transpiration induces seasonal changes in the atmospheric water balance. The figures below show that seasonal effects are more pronounced at northern hemisphere observation stations compared to that of southern hemisphere because of higher continentality (lower coastal influence).
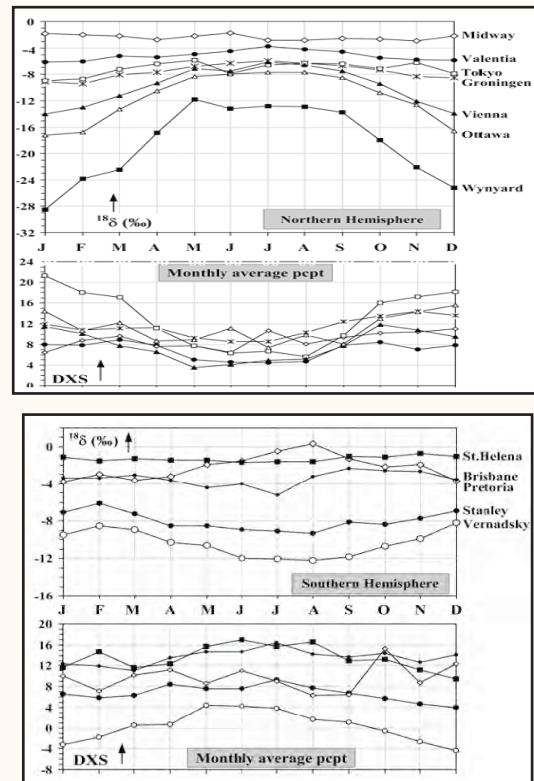




**Fig 8: Seasonal variation in isotopic composition of precipitation**

*Amount effect*

The observation of considerably depleted water during the event of heavy rains is known as amount effect. During the periods of heavy rains more of the water is squeezed from the atmospheric vapor (clouds) by rapid condensation resulting in less isotopic separation between vapor and water formed. In addition, owing to high humidity the degree of secondary evaporation also reduces .The net result of these two phenomena is depleted rain waters (Fig. 9).

Time sequence of the isotopic composition of precipitation during showers; examples are shown for two cases of convective storms: **A)** rain intensity in mm/2 hours (Mook et al., 1974); **B)** cumulative rain over variable periods.

**Fig. 9: Amount effect- δD and δ¹⁸O values decrease with increasing intensity and duration of rainfall, A) individual rain event and B) cumulative values**

*Paleoclimatic effect*

Paleoclimatic meteoric waters can have entirely different isotopic signatures. It may not fall along modern GMWL. The rainwaters of wet period would be highly depleted compared to that of arid period which could be enriched. Even the evaporated paleoclimatic waters can be distinguished from modern day waters as the starting isotopic composition of the paleo-waters would be different.

**Importance of δD - δ¹⁸O relationships in hydrological studies**

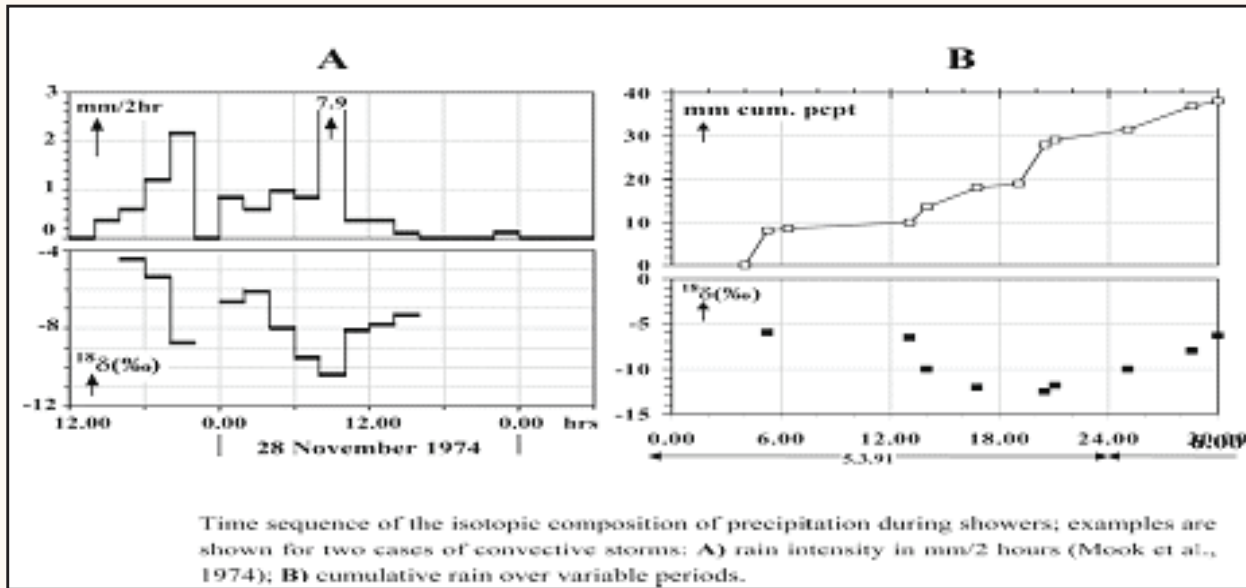The observation that isotopically depleted waters are associated with cold regions and enriched waters from that of warm regions was recognized as a tool for characterizing groundwater recharge environments, and is now the basis of groundwater provenance studies. The δD - δ¹⁸O relationships of water samples from a study area are of great importance to isotope hydrology. The method provides a clue as to whether a given groundwater body is receiving or from an evaporating body such as a lake or a reservoir. During evaporation also the linear correlation between δD - δ¹⁸O in the remaining liquid fraction is conserved and evaporating waters show lower slopes of the order of 3 to 5.In geothermal exchange, only 18O content is modified, as at high temperature water gets enriched in 18O with the oxygen in the hot rocks,

which have usually a higher 18O compared to water. The intersection of the geothermal δD-δ¹⁸O line with meteoric line represents their source of recharge. The conditions under which the δD-δ¹⁸O line deviates from slope 8 are depicted in the figure 10.
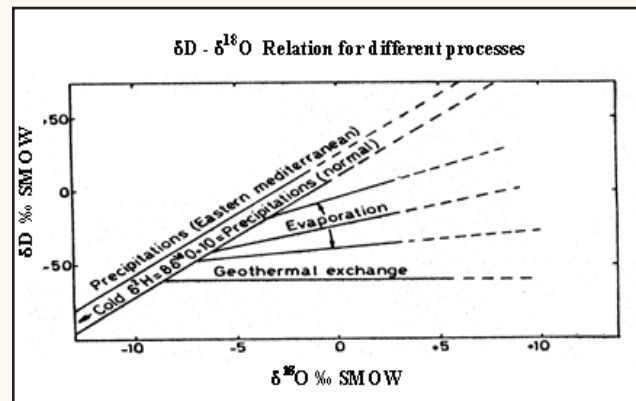


**Fig. 10: δ²H and δ¹⁸O correlations under different conditions**

**Radioisotopes in hydrology**

*Tritium (T or ³H):*

Hydrogen has three isotopes, two stable (¹H and ²H), and one radioactive (³H). The radioactive isotope tritium (³H) can be used for dating very young groundwater (less than 50 years).Natural tritium is created in the upper atmosphere from the cosmic bombardment of nitrogen with fast neutrons. Tritium then combines with oxygen to produce tritiated water

(³HHO) and enters the hydrologic cycle. Tritium decays to a rare, stable isotope of helium (³He) by beta (β⁻) emission. Lithogenic tritium is produced by the showering of lithium present in rocks by neutrons produced during the spontaneous fission of uranium and thorium. This process is limited by the amount of lithium in rocks. In most cases, lithogenic production is negligible compared to other sources. The lithogenic tritium enters the groundwater directly. Natural production of tritium in the atmosphere is very low. Due to the advent of thermonuclear technology, this production in the atmosphere has been supplemented by anthropogenic production (Fig. 11). Beginning in the 1950's, large amounts were produced from the atmospheric testing of thermonuclear bombs. The production of tritium and its decay in equation are shown as below;

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

$$^{3}H \rightarrow {}^{3}He + \beta^{-}$$
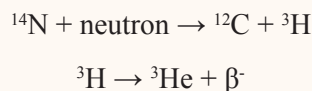
Concentrations of tritium decreased after 1963 because of the Soviet-American treaty banning above-ground testing. Since anthropogenic tritium is also currently produced by releases from nuclear power plants, present day concentrations of tritium in the atmosphere have not returned to natural concentrations, but levels have gradually decreased since the 1960's as the tritium continues to decay. All atmospheric tritium, whether cosmogenic or anthropogenic, is rapidly incorporated into water molecules and falls in meteoric precipitation to enter the hydrologic cycle.
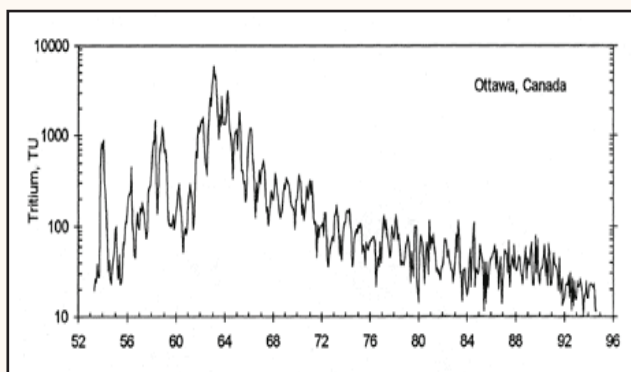


**Fig. 11: Tritium distribution in precipitation at Ottawa, Canada (Clark and Friz 1997)**

## Measurement Techniques

Tritium concentrations are represented in tritium units (TU). One tritium unit is equal to one molecule of ³H per $10^{18}$ molecules of ¹H and has an activity of 0.118 Bq/kg (3.19 pCi/kg).Tritium is typically measured by a liquid scintillation counter. The sample is mixed with a scintillation mixture of a solvent, emulsifier, and solute. Tritium emits beta decay electrons, which excites the solvent. The solvent transfers its energy to the solute, which emits light photons. The light pulses are detected and counted.

### *Carbon-14*

Carbon has three isotopes, two stable and one cosmogenic. Natural variation of the two stable isotopes of carbon can be useful for understanding food webs and carbon cycling in ecosystems. Carbon-14, a cosmogenic isotope with a half life of 5730 years, is useful for age dating as well as for tracing hydrologic processes, such as groundwater flow and ocean circulation. ¹⁴C is created when cosmic rays in the Earth's atmosphere cause some of the atoms in the upper atmosphere to fly apart into pieces. Neutrons that come from these fragmented molecules run into other molecules, causing chemical reactions. When a neutron reacts with a ¹⁴N (nitrogen) atom, the result is ¹⁴C, shown below.

$$^{14}N + neutron \rightarrow {}^{14}C + proton$$
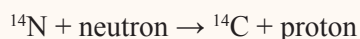
Much ¹⁴C has been added to the atmosphere due to the nuclear bomb tests from the 1950s and the use of nuclear power. Thus produced ¹⁴C, reacts with atmospheric oxygen to produce $CO_2$ which enters hydrological cycle as bicarbonate ($HCO_3^-$), either by reacting with moisture as

$$CO_2 + H_2O \rightarrow + H_2CO_3$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+$$
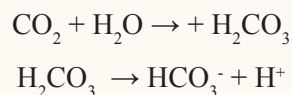
or through photosynthesis enters into the plants. Plant respiration releases $CO_2$ in root zone, which reacts with water to produce bicarbonate ($HCO_3^-$). The later contribution is 2-3 order higher compared to the first process.

There are two types of counting C-14 in the system, viz., gas counting and liquid scintillation counting. In gas counting, a carbon containing sample is converted to methane or $CO_2$, which is used to fill a proportional gas counter. The decay of a ^{14}C atom triggers an electrical discharge in the gas, which is electronically detected. The rate at which the decay occurs depends on the number of ^{14}C atoms present in the sample gas. In the case of liquid scintillation counting, a sample of Ba/Sr $CO_3$ is precipitated in the field and converted in to $CO_2$ which is absorbed in an organic solvent (Carbasorb) mixed with scintillator and counted in LSC.A sample of carbon is converted to benzene, mixed with special organic compounds and placed in a transparent container. The benzene is produced as follows: $CO_2$, obtained by burning the sample, reacts with metallic lithium to form lithium carbide. The lithium carbide is hydrolyzed to acetylene, which is subsequently converted to benzene by catalytic trimerisation. The solution emits a pulse of light whenever a ^{14}C atom decays due to beta-decay, and the light pulse is detected by sensitive photomultiplier tubes placed close to the container. Accelerator Mass Spectrometry (AMS) is typical method of analysis for small samples that have very low levels of [14]C. Carbon from the sample is converted into graphite. This graphite is then loaded into the sample chamber of the AMS where it is ionized. These ions are then separated and analyzed for [14]C.

**Isotopes of dissolved components**

Besides stable isotopes D and 18O which were discussed in the last lecture, there are other stable isotopes which could be used for hydrological studies. Some of them are carbon-13, nitrogen-15 and sulfur-34. These occur as dissolved compounds, carbon-13 as carbonates, Nitrogen-15 as nitrates and sulfur-34 as sulfates. This lecture deals with introduction to the use of these stable isotopes in hydrology.

*Carbon-13*

Determination of ^{13}C of dissolved carbonate in water helps in understanding geochemical evolution of groundwater. This is of particular importance for interpreting of carbon-14 data. The $\delta^{13}C$ of soil $CO_2$ in most temperate and humid climates fall between –21 to 26 ‰. In arid zones, enriched values can be found because of special plant assembalges and the increased importance of atmospheric $CO_2$ which has a $\delta^{13}C$ = -7 ‰. Water which passes through the unsaturated zone towards the water table will become saturated with this $CO_2$ and its dissolved inorganic carbon will reflect the composition of recharging water. Modification of ^{13}C contents of aqueous carbonate after the infiltration could occur through number of processes, the most important of which are carbonate mineral dissolution or precipitation reaction and biological processes.

During the geological periods in the past, the terrestrial surfaces have been covered by ocean and as a result marine carbonate sequences as well as metamorphic carbonate (modified marine carbonate) are found in all continents. Marine carbonates have ^{13}C values close to 0 ‰ with reference to PDB. (The universally accepted carbon isotope standard is PDB. The PDB originates from the calcium carbonate of the rostrum of a cretaceous belemnite collected in the Peedee formation of South Carolina in USA). Similarly the $\delta^{13}C$ of metamorphic carbonate sequences are close to 0 ‰, unless magmatic $CO_2$ played a role in their formation. In such cases ^{13}C values between –5 to –2 ‰ could be expected. These values are considerably enriched in ^{13}C with respect to biogenic sources such as soil $CO_2$. As a result carbonate dissolution will bring about an enrichment in ^{13}C in the dissolved aqueous carbon. Primary carbonates are free of radiocarbon and hence their dissolution causes a decrease in the ^{14}C activity of the DIC. Carbon-13 analysis of groundwater in combination with geochemical considerations could be used to assess the magnitude of this dilution in the ^{14}C activity and to correct the ^{14}C dates.

*Nitrogen-15*

Nitrogen is a biologically active element and participates in a multitude of reactions that are important to life and that affects water quality. Isotopic fractionation between various N bearing compounds provides the basis of nitrogen-15 as a tool in isotope hydrology. Isotopic composition of fertilizers is near zero owing to the synthesis of nitrogen from air ($\delta^{15}N$ = 0). (Atmospheric nitrogen is used as reference

standard). Nitrates from uncultivated soil have $^{15}N$ values 2 to 4 ‰ while for cultivated soils it ranges from 4 to 8 ‰.Nitrates coming from oxidation of organic matter, from sewers or agricultural manure are enriched due to volatilization of ammonia which favors $^{14}N$.Denitrification proceeds with a series of intermediate steps involving nitrogen oxides in presence of bacteria thiobacillus denitrificans. During denitrification enrichment of $\delta^{15}N$ of the remaining nitrate takes place.

## *Sulfur-34*

Sulfur has 4 stable isotopes- $^{32}S$, $^{33}S$, $^{34}S$ and $^{35}S$ with natural abundances 95.0, 0.76, 4.22, and 0.014 % respectively. Normally only $^{34}S$ is measured as very little additional information is gained using the other isotope pairs. The stable isotopic content of aqueous sulfur compounds (chiefly $SO_4^{-2}$, $H_2S$, $HS^-$) may provide information on the origin of the sulfur compound and the kind of redox reaction involving sulfur. The $\delta^{34}S$ of sulfates of modern oceanic water is constant at +20 ‰ with respect to CDT (The accepted reference standard for $^{34}S$ is CDT which is the triolite phase of Canon Diablo Triolite). However the $\delta^{34}S(SO_4^{-2})$ of evaporites which possibly represent the sulfates in the ocean when they were deposited, vary with age. The $\delta^{34}S$ of sulfates of precipitation falls in the range of +3.2 to 8.2 ‰ in non industrialised areas and values upto 15.6 ‰ in industrialized areas. Groundwater may contain sulfate derived from precipitation, from oxidation of sulphide minerals or organic sulfur or from dissolution of evaporite minerals. Sulfur isotope variation in the subsurface could occur due to bacterial reduction of sulfate to $H_2S$ or oxidation of sulfides to sulfates (Kinetic effect) and chemical exchange reactions (between sulfates and sulfides).

The principal organism which transforms sulfate to $H_2S$ is the sulfate reducing bacteria belonging to the genera Desulfovibrio and Desulfatomaculum. When the product $H_2S$ is continually extracted from the system- for instance by degassing of precipitation of iron sulfides, the bacteria continues to reduce

sulfate until no more sulfate is available. The $\delta^{34}S$ of the residual sulfate increases with decreasing sulfate concentration. The isotope variation of sulfur compounds could thus be used to identify origin of groundwater and to study its geochemical and hydrological history.

## *Chlorine-37*

As chloride seldom participates in biological reactions there is less fractionation of $^{37}Cl$ compared to $^{34}S$, $^{15}N$ etc. Its conservative inorganic nature leaves only physical processes for isotope fractionations. Even over a wide range of crustal temperatures and pressures, ionic chloride is relatively stable in aqueous solutions. However chloride movement through these environments can be fractionating. The most important fractionating processes seem to be physical mechanisms such as ion filtration, diffusion, geothermal boiling, brine evaporation and salt deposit formation. However, little work has been done to constrain the relative importance of these processes in fractionating $^{37}Cl$.Much effort has been expended in trying to identify the origin of chloride in sedimentary basin brines and brines from crystalline shield environments.

## Applications in water resources management

Study of the isotopes of oxygen and hydrogen in water, or of elements contained in dissolved salts, which have the same behavior as water enable exact recording of phenomena affecting the occurrence and movement of water in all its forms. Isotopic methods are normally used in conjunction with conventional hydrological, hydrogeological and geochemical or water-chemical techniques, so as to provide additional and valuable information for solving hydrological problems. In recent years, in hundreds of difficult cases, isotopic methods have provided definite, satisfactory results. Useful stable isotope tracers and information they provide for water quality and environment (Table 2).The isotopic techniques can be employed in order to study the following aspects related to water resources management.

**Table 2: Isotopes and their interpretation**

| Tracer type | Interpretive value |
|---|---|
| $\delta^{18}O$ and $\delta^2H$ of water | Ideal conservative tracer of water sources and mixing; useful for quantifying flow contributions from different tributaries and groundwater; sensitive indicator of evaporation |
| $\delta^{18}O$ and $\delta^{15}N$ of $NO_3$ | Quantify $NO_3$ from different sources (fertilizer, wastewater, wetlands, atmospheric deposition, etc.); role in the production of algae and degree of recycling; evidence for denitrification, assimilation, and nitrification |
| $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ of Particulate organic matter | Information on sources of POM; information about the source of the C, N, and S – and the biogeochemical reactions that cycle the elements – even after incorporation into algal biomass; quantify algal vs terrestrial contributions to biomass |
| $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ of Dissolved organic matter | Information on sources of DOM; information about source of C, N, and S – and biogeochemical reactions that cycle the elements – even after incorporation into biomass; quantify algal vs terrestrial contributions to biomass; evidence for degradation of organic matter |
| $\delta^{13}C$ of Dissolved Inorg. Carbon | Information on sources of DIC, evidence for in situ algal productivity, evidence for degradation of organic matter, degree of gas exchange with atmosphere, nitrification |
| $\delta^{18}O$ of Dissolved Oxygen | Information about the ratio of productivity to respiration in the water column, source of the $O_2$, degree of gas exchange with atmosphere, biological oxygen demand (BOD) mechanism |
| $\delta^{34}S$ and $\delta^{18}O$ of $SO_4$ | Quantify sulfate from different sources (soil, wastewater, wetlands, atmosphere, etc.), source of algae, and extent recycling |
| $\delta^{18}O$ of $PO_4$ | Quantify phosphate from different sources; information about the extent of algal production, recycling of material within the river reach, and P limitation |
| $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ $\delta^2H$ and $\delta^{18}O$ of Biota (algae, invertebrates, fish) | Information on geographic origin of biota; information about the source of the C, N, and S – and the biogeochemical reactions that cycle the elements – even after incorporation into biomass; quantify algal vs terrestrial contributions to biomass; trophic structure; food chain base |

**Surface Water**

- Hydrographs separation
- River discharge measurements
- Dynamics of lakes and reservoirs
- Water balance
- Leakage through dams,
- Sedimentation rate
- Evaporation/Evapotranspiration
- Surface water and groundwater interaction
- Sources and tracing of pollutants
- Snow and glacial melt runoff

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

**Applications in Meteorology**
- Variability of environmental conditions/ climate change
- Movement of clouds and variability in precipitation
- Environmental pollution and mechanism
- Prediction of arrival and retreat of monsoon

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# Application of Isotopes in Groundwater Recharge Studies

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## 1. Introduction

Stable and radioactive isotope techniques are cost effective tools in hydrological investigations and assessments, and are critical in supporting effective water management. Isotopes help in understanding various hydrological processes. In the developed countries, meteorologists, hydrologists, and hydro-geologists commonly use environmental isotopes in the study of water. The use of isotopic techniques has greatly increased in India, but still it requires momentum and training of the field persons in this subject. Study of the isotopes of oxygen and hydrogen in water, or of elements contained in dissolved salts, which have the same behavior as water, enable exact recording of phenomena affecting the occurrence and movement of water in all its forms. In the past few decades, sophisticated nuclear-hydrological instrumentation have been developed to measure accurately both radioactive as well as stable isotopes and accordingly various nuclear methods have been evolved. It is therefore, now very easy to solve many hydrological problems related to planning of water resources, agriculture, industry, and habitation using isotope techniques, which were very difficult, sometimes impossible to tackle in the past.

The use of isotopes in hydrology started in early 1950's with the application of radiocarbon dating technique for determining the age of groundwater. After that, the application of isotopes is being successfully used to find the effective solutions of various hydrological problems in the developed countries. Later on the International Atomic Energy Agency (IAEA), Vienna, Austria, an independent intergovernmental organization with in the United Nations System, took a leading role in the development and use of isotope techniques in hydrology. Presently, isotope techniques are used frequently in the developed countries while their use in the developing counties is increasing slowly.

In groundwater, isotopes are commonly employed to investigate:

- Sources and mechanisms of groundwater recharge;
- Groundwater age and dynamics;
- Interconnections between aquifers;
- Interaction between surface water and groundwater;
- Effectiveness of artificial recharge measures Groundwater salinization; and
- Groundwater pollution.

### Application of isotopes in groundwater management

Isotopes are being used extensively for studying the soil moisture variation and its movement; recharge through unsaturated zone; origin, age, occurrence and distribution of groundwater in a regional recharge mechanism, determination of groundwater flow direction and velocity; interconnections and interaction between aquifers; and identification of recharge areas and sources. Isotopes can also be applied to study surface water and groundwater interaction; tracing sources of pollutants including sea water intrusion and salinization mechanism.

Isotopic methods are normally used in conjunction with conventional hydrological, hydrogeological and geochemical or water-chemical techniques, to provide additional and valuable information for solving hydrological problems. In recent years, a number of complex groundwater problems have been resolved successfully using isotopic methods.

### Groundwater Recharge

Several methods, such as, water balance, pumping tests, chemical mass balance, artificial or environmental tracers and hydraulic interpretations of the soil moisture movement below the active

roots in the unsaturated zone are used to estimate groundwater recharge. The hydraulically based methods, though highly developed in theory and practice, are hampered by the complex relationship between hydraulic conductivity and hydraulic gradient in the unsaturated zone. Tracer techniques have the advantage that old soil water can be differentiated from relatively fresh water. A rather recent method of estimating groundwater recharge is to use radioactive / stable isotopes as tracers. The methodology of using artificial as well as environmental isotope tracers for estimating percolation rate and groundwater recharge is discussed here.

### Artificial Radioactive Isotope Tracers (Tritium tagging) for Estimating Groundwater Recharge

Artificial radioactive isotopes (produced in laboratory or reactor), can be used as water tracers to estimate groundwater recharge. The advantage of artificial tracers over environmental tracers is that they are injected in a controlled way and their concentrations are high enough to be easily detected. The disadvantage is that it is non-natural, which means it may be environmental hazardous and that experiments can only be made at specific points and at specific times.

The most commonly used artificial tracer isotope for groundwater studies is tritium ($^3H$) as HTO, which is applied below the root zone or in the groundwater depending on the purpose of the study.

Artificial radioactive isotope tracer method, also known as, *Tritium tagging technique* was developed by Zimmermann et al. (1967a,b), Blume et al. (1967) and Munnich (1968a,b) with the assumption that the movement of soil moisture in a unsaturated zone is similar to piston type flow. Any water applied to the ground surface, either from precipitation or from irrigation, infiltrates and percolates by pushing equal amount of water beneath it further down. The amount of moisture content of the last layer in the unsaturated zone is added to the groundwater as recharge. Blume et al., (1967) suggested to introduce/inject the tracer below the ground surface (preferably below the root

zone); otherwise, it may be lost by evaporation or evapotranspiration.

The field experiments of Zimmermann et al. (1967a and 1967b) and Blume et al. (1967), showed "piston flow" type behavior of soil moisture in nearly homogeneous soils. In heterogeneous soils, infiltrating water moves along a range of different pathways and causes a considerable dispersion of the tracer. This means that the soil moisture profile may change shape, but no newly percolated water bypasses water that has previously percolated below the root zone. In the above-mentioned experiments, the broadening of the peak of the injected tracer was of the same magnitude as expected by molecular diffusion only (NIH, 209; NIH, 2000).

In addition, experiments conducted in the alluvial tracts of north India by Bahadur et al. (1977) showed broadening of the tracer peak not comparable to the spread by molecular diffusion. It means that if the flow is slow, the lateral mixing, mostly from molecular diffusion, in rather homogeneous soils between moisture packets having different flow velocities is quite effective, thus indirectly counteracting vertical dispersion.

In the course of water infiltration, an injected or environmental tracer is carried along with the soil water. The position of the peak tracer concentration can be monitored in the soil profile. From the temporal displacement of the tracer, percolation rate or moisture flux, and the groundwater recharge can be estimated, provided the measurements are taken below the root zone so that all water movements are directed downwards. Zimmermann et al. (1967a) used deuterium and tritium as tracers and called the method of tracing the peak as "tracer tagging" technique. The principle of how percolation rates are determined from tracer monitoring is illustrated in Fig.1.

Shortly after the tracer injection, the peak concentration, which is at depth $z_1$, moves down and is found at depth $z_2$ after a certain time. Provided no vertical mixing takes place during the downward movement, the mean moisture flux, q at the lower
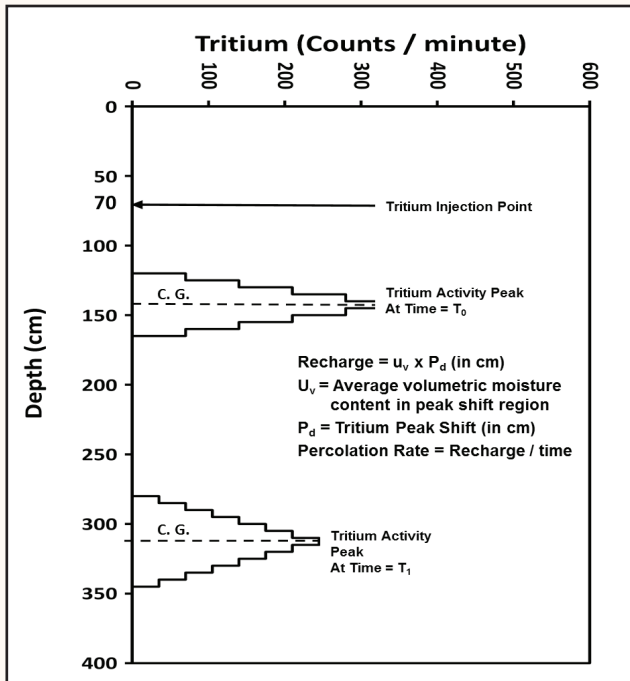
**Fig. 1: Shifting of injected tritium with respect to the movement of infiltrated water**

depth $z_2$ over the time period, $\Delta t$, between the two observations is,

$$q = \theta_v (z_2 - z_1)/ \Delta t$$

where, $\theta_v$ is the average volumetric moisture content between the two depths at the time of the first observation after reduction of eventual residual moisture content, that is, interstitial water or water that adheres to the soil particles. This residual moisture content is generally negligible, except for very fine soils.

If the experiment is for a full season or full year, the moisture flux corresponds to the recharge over a season or year, although the particular soil water particles do not reach the groundwater during the particular year when the observations are made.

This method has been used in India for groundwater recharge in various parts of Ganga Plains (NIH, 1999; NIH, 2000; Samadder et. al., 2011)

*Environmental Tritium Technique*

Tritium released from thermonuclear explosions in the atmosphere, made possible a way of estimating groundwater recharge. Before 1952, the tritium concentration in precipitation was low, but after thermonuclear testing began in the atmosphere in 1952, tritium concentrations in precipitation suddenly increased and reached a record-high concentration in 1963-64 in the northern hemisphere. In India, the peak concentration of bomb-derived tritium in 1963 was more than 1000 TU. The fact that water originating from precipitation before 1952 has lower tritium concentration than the precipitation after 1952, has been successfully used for tracing groundwater.

Munnich et al. (1967), Sukhija and Shah (1976) in India, and Andersen and Sevel (1974) in Europe have used bomb-released tritium for the evaluation of groundwater recharge in Europe and India, respectively. An example of tritium concentration in soil profile is given in Fig. 2.
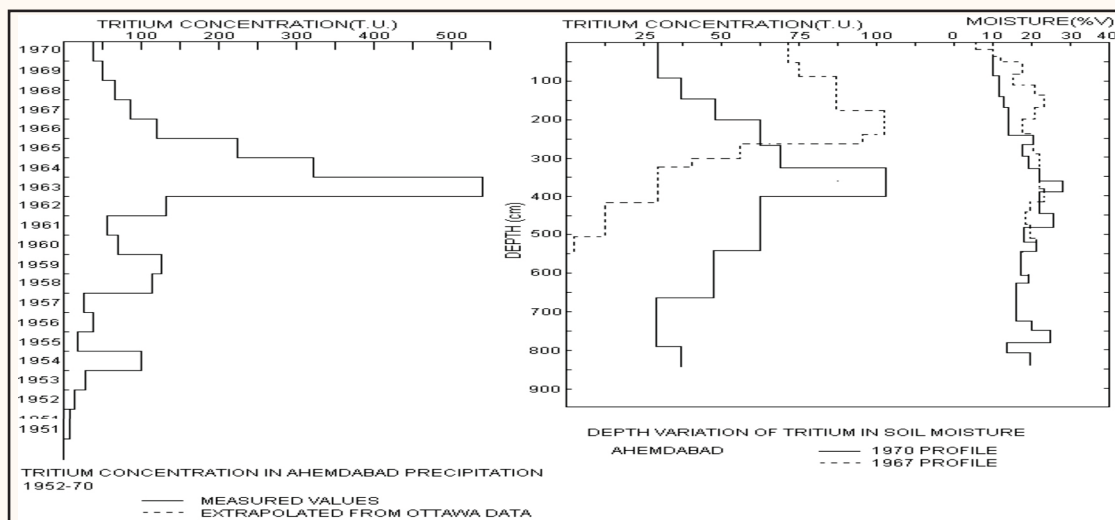


**Fig. 2: Tritium concentration (without decay correction) in precipitation at Ahmedabad (1952-1970). (Source: Sukhija and Shah, 1976)**

In this method, the assumption that the amount of water from the soil surface to the soil depth, where the 1963-64 tritium peak is located, is the measure of recharge from that time until the time of investigation. In the other method, the tritium concentration of the water lost as evaporation of surface runoff as well as of the water percolating below the root zone is, at any time, assumed to equal the concentration of the precipitation. The accumulated percolation, R, which will contribute to groundwater recharge, is simply given by,

$$R = P*(M_s / M_p)$$

where, `P` is accumulated rainfall since the beginning of the bomb tests, $M_p$ is the total amount (per unit area) of tritium in the precipitation, and $M_s$ is the amount of tritium found in the soil above the depth where the tritium concentration is at pre-1952 level. The method can be adjusted to be applied from the peak concentration time instead of from 1952, that is, from 1964.

### *Environmental Stable Isotopes Technique*

The stable isotopes $^{18}O$ and D ($^2H$) in precipitation are being used for a long time as potential tracers for natural waters yet they have been little exploited for measuring percolation. The flux of HDO and $H_2{}^{18}O$ from an open water body to the atmosphere is relatively low as compared to the flux of the lighter $H_2{}^{16}O$ because of the lower vapor pressure of the former species, which causes fractionation in evaporation and condensation processes. In cold climate, seasonal stable isotopic composition of precipitation is rather well reflected in soil moisture, whereas, in semi-arid climate, the isotope picture of soils is rather complex due to strong fractionation caused by high evaporation rates from the soil.

Soil water infiltrated during two periods with a time span of a year can be identified within a soil profile based on stable isotopic composition of either deuterium ($^2H$ or D) or oxygen-18(Fig. 3). Therefore, the total amount of percolated water during the year can be estimated simply by totaling the amount of soil water between the two depths where the soil water

from the two periods is found. Reduction should be made for eventual residual water.
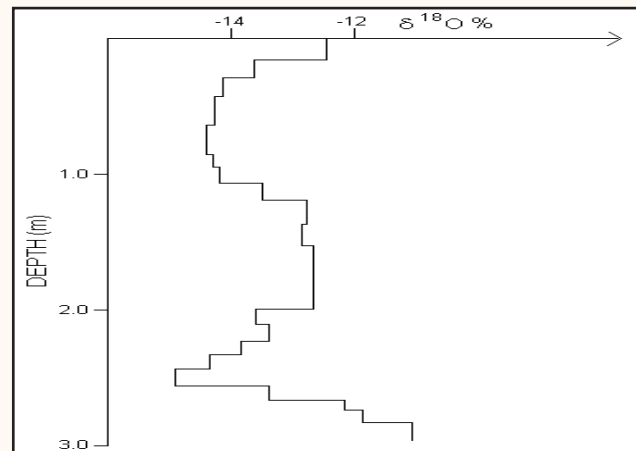


**Fig. 3: Oxygen-18 profiles in soil moisture patterns indicating infiltrated water in different years**

Mathematically expressed, the annual percolation, R, which will later contribute to groundwater recharge, is

$$R = \int_{z_1}^{z_2} \theta_v \, dt$$

where $z_1$ and $z_2$ are the identified depths and $\theta_v$ is the volumetric soil moisture content after reduction of eventual residual water. The method cannot be applied in areas where the groundwater level is shallow during some periods of the year.

The method was first applied to estimate the recharge to groundwater in sand dunes with depth fluctuations in deuterium in soil moisture profiles (Thoma et al., 1979). The seasonal variations of $\delta^{18}O$ in precipitation have been traced in the soil moisture and estimates of groundwater recharge and rates of moisture movement were estimated for Swedish glacio-fluvial deposits and moraine formations (Saxena, 1984). Now, this technique is used wherever the measurement of stable isotopes is possible.
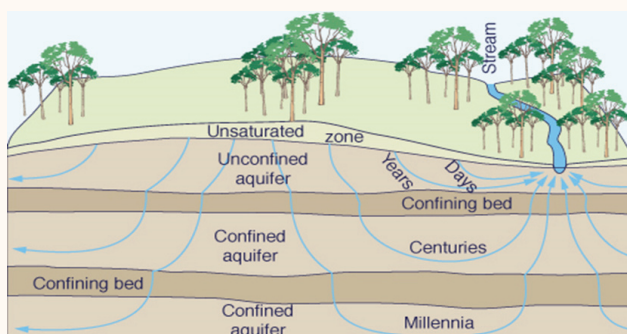
### Recharge Zones and Sources to Aquifers/Springs

### *Recharge Zones of Deeper Aquifers*

Until the end of $20^{th}$ century, groundwater was mostly abstracted from the shallow aquifers and was believed to be safe, free from pathogenic bacteria and from suspended matter. However, with the increase in

population and urbanization, and due to technological advancement, the stress on deeper aquifer has increased, mostly because the shallow aquifers have either drying-up or been contaminated. In fact, the deeper aquifers are not only catering the present need of fresh water at present but also these will be the only potential source of fresh water in future. The deeper aquifers for which recharge zones may be located at far-flung areas (Fig. 4), may suffer adversely by the various anthropological activities that may either reduce the recharge area or contaminate the recharge source. Once the recharge zones are identified, these can be protected from the anthropogenic activities.



**Fig. 4: Representation of recharge and discharge zones in confined aquifers**

Environmental isotopes like $^3H$, $^{14}C$, $^2H$, and $^{18}O$ are used to identify the recharge zones and recharge sources of aquifers and springs. Geohydrological details like groundwater level conditions, geological cross sections etc., and water quality data like major and minor ion chemistry, physico-chemical parameters etc., are used as supporting tools. Groundwater samples are collected from different aquifers for the measurement of $^3H$, $^{14}C$, $^2H$, and $^{18}O$. The dating of groundwater using $^3H$ and $^{14}C$ provide information of recharge zones, groundwater flow velocity and flow pattern while the $\delta D$ and $\delta^{18}O$ analysis help in understanding the contribution of different recharge sources and also to pinpoint the most important recharge source.

### Recharge Zones of Springs

In order to identify the recharge zones of springs, the water samples of springs are collected along with precipitation samples from different altitude. The $\delta D$ and $\delta^{18}O$ of samples are analyzed along with

environmental tritium of spring water. The altitude effect in the study area is established. The $\delta D$ vs $\delta^{18}O$ plot is used to determine the isotopic value of spring water. If the sample data fall on the evaporation line, then the line is extended back to get the real isotopic value of spring water if it would have not been subjected to evaporation. After determining the isotopic value of spring water (either $\delta D$ or $\delta^{18}O$), the altitude of the recharge area is determined using the altitude effect equation (Shivanna, 2008).

### Recharge Sources / Surface Water and Groundwater Interaction

In regions where direct and rapid infiltration of rain occurs, the composition of the groundwater will have isotope ratio as that of the precipitation or slightly enriched due to evaporation effect during the process of infiltration as when evaporation precedes, the heavier isotope gets enriched in water phase. The analyses of stable isotopic composition together with that of groundwater dating using radioisotopes gives a reliable 'fingerprint' to identify each group of water of different sources. Water infiltrated at higher altitude and is transmitted over long distances will show depleted $\delta^{18}O$ and low tritium compared to water infiltrated from local precipitation.

One of the important uses of isotopic characterization of waters is to study the surface water and groundwater interaction. It is because the surface water, particularly rivers originating at the higher altitude, normally has different stable isotopic composition than that of groundwater recharged by infiltration of local precipitation where the surfacegroundwater relation is under investigation.

In the areas near to bank of the river or lake, there are two possible sources of recharge to groundwater, viz. infiltration of local precipitation and infiltration of river/lake 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* (most common value of the source water) of these two potential sources of recharge and the difference between these indices. An estimate of the isotopic indices of the surface water body is made

because of isotopic values measured at different times and especially at different stages/discharge to ascertain whether there are any significant variations in stable isotopic composition with stage/discharge. If variations are evident, then the mean value weighted for various stages/discharges is used. The preferable approach is to sample groundwater close to the river where piezometer indicates river water as the source of recharge. The estimation of the index for groundwater generated by infiltration of local precipitation is based on measurements of groundwater away from the influence of the river. 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 isotopes, $^{18}O$ and D ($^2H$) are utilized for determining the contribution of groundwater to the surface water or vice-versa. If $R_1$ and $R_2$ are the isotopic composition of the groundwater and the surface water body, respectively and $m_1$ and $m_2$ are the fractions of groundwater and surface water, respectively in the admixture, while $R_{am}$ is the isotopic composition of the admixture, then the isotopic balance and mass balance equations can be written as,

$$m_1 R_1 + m_2 R_2 = R_{am} \text{ and } \quad m_1 + m_2 = 1$$

From the above two equations, we have

$$m_2 = (R_{am}\ R_1) / (R_2\ R_1)$$

Therefore, by knowing the value of $R_1$, $R_2$, and $R_{am}$, the fraction of surface water mixed with groundwater can be evaluated.

**Effectiveness of Artificial Recharge Measures**

Management of depleting groundwater table in the urban areas and in semiarid/arid regions has drawn the attention of water resources managers. This situation is also common in areas where surface water bodies such as rivers, canals and natural or artificial lakes/reservoirs do not exist. In order to mitigate the increasing shortage of groundwater, artificial recharge of groundwater by making earthen bunds, through injection wells or roof top rainwater harvesting programs have been given priority by many organizations and individuals. However, the effectiveness of these programs has not been assessed at the desired scale as it is difficult using conventional techniques. Isotope techniques have the potential to assess the effectiveness of these programs using environmental isotopes.

The effectiveness of artificial recharge measures can be studied with the use of environmental isotopes (either $\delta D$ or $\delta^{18}O$ and $^3H$, if required) provided the artificially recharged water has different isotopic composition then the natural recharge. However, if the same water is used for artificial recharge through prolonged infiltration by constructing earthen bunds, the isotopic composition of ponded water is changed due to evaporative enrichment (Kumar et.al. 2009). The isotopic indices ($\delta D$ or $\delta^{18}O$) of precipitation, groundwater (without artificial recharge component), and surface water being used for artificial recharge are determined and then the isotopic composition of the groundwater (from the study area) are determined at different time intervals (minimum monthly frequency). The use of two component model can reveal the percentage of mixing of artificially recharged water at different time. If the groundwater samples are collected from different locations around the site/s of artificial recharge, then the effect and extent of recharge (%) can be determined in different directions. $^3H$ values of groundwater can confirm the recent recharge due to artificial measures.

For example, the contribution of rainfall ($m_p$) or channels ($m_{ch}$) in groundwater can be determined using the following relation based on $\delta^{18}O$ values of end members.

$$m_p = (\delta^{18}O_{gw} - \delta^{18}O_p) /(\delta^{18}O_{ch} - \delta^{18}O_p) \text{ or } m_{ch}$$

$$= (\delta^{18}O_{gw} - \delta^{18}O_{ch}) /(\delta^{18}O_p - \delta^{18}O_{ch})$$

$^3H$ values of groundwater can confirm the recent recharge due to artificial measures.

## Conclusion

When estimating natural ground water recharge, it is essential to proceed from a good conceptualization of different recharge mechanisms and their importance in the study area. The choice of methods should, besides this conceptualization, be guided by the objectives of the study, available data and possibilities to get supplementary data. Of course economy also must be considered. Since all available methods are affected with substantial uncertainty, it is desirable to apply more than one method based on independent input data.

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# Revelations of Rainfall Contribution in the Bhagirathi River near Gomukh, Western Himalayas, India by oxygen-18 isotope

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## Abstract

*Gomukh is the snout of Gangotri Glacier located at an altitude of 4000 m in the Himalayas. The snow and glacier fed river known as Bhagirathi emerges out from this place and Bhagirathi is one of the two headwater streams of the river Ganga. The conventional hydrological investigations concluded that there is no contribution of rainfall in the discharge of Bhagirathi River at Bhojwasa near Gomukh. In order to understand the reality, snow, ice, river discharge and rainfall samples were collected for stable isotope ($\delta^{18}O$) analysis along with other hydrometeorological data during ablation period (May to October) for 2004 and 2005 at Bhojwasa, 3 km downstream of Gomukh. The variation in river isotopic composition ($\delta^{18}O$) with time shows the varied percentage of snow, glacier and rain contribution in the flow of Bhagirathi River during the ablation period. The discharge of Bhagirathi River shows positive correlation with temperature but negative correlation with rain event. The enriched $\delta^{18}O$ values of river flow (-12‰ to -13.0‰) from May to June and its depletion afterwards reveals that snowmelt dominates the river discharge during May and June while ice/glacier melt dominates in the subsequent months of ablation period. The contribution of rain was found maximum up to 40% of the total discharge of river on the day of rainfall. The complete hydrograph separated out for three rain events occurred in July and September, 2005 revealed the rain contribution to the tune of 14% to 15% of the total river discharge. The contribution of the total rainfall occurred during the ablation period was estimated to be only 3% of the total discharge. But the conventional hydrologists did not satisfied with our findings till it was physically clarified to them that the melting of snow and glacier/discharge of the river is strongly temperature dependent and the melting of snow and glacier decreases drastically due to decrease in atmospheric temperature during rain event even after the direct rainfall and rainfall runoff contribution. This fact clearly explains the phenomenon of decrease of overall discharge of snow and glacier fed rivers during the rainfall at higher altitudes or near snouts.*

*Keywords: Discharge, snow, ice and rain contribution, stable isotopes, Bhagirathi River*

## Introduction

The snow and glacier melt runoff contributes significantly to all north India Himalayan rivers during summer when demand of water increases for hydropower, drinking and irrigation etc. Due to lack of information on hydrological processes of snow/glacier regime and assured availability of melt water, water resources management policies at lower reaches of the glacier fed rivers are often formulated without considering the impact of snow and glacier on river hydrology [1]. Depending upon the prevailing climatic conditions, the melt water contribution from the glaciers to Himalayan Rivers starts in May, after depletion of accumulated seasonal snow due to rise in atmospheric temperature. Usually the melt contribution from the glaciers starts in summer months after melting of seasonal snow and continues till October [2]. Precipitation in the form of snow occurs only during October to March, when the primary source of moisture is related to the winter monsoon and western disturbances. During maximum snow accumulation period snowline comes down to about 1500m in the western Himalaya and to about 3000 m in the eastern Himalayas. The south-west monsoon also plays an important role during the ablation period of Himalayan glaciers [3]. Generally, the contribution of snow and glacier melt runoff into annual flow of the different Himalayan rivers have been studied on meso-scale covering large areas, considering the glaciers and seasonal snow cover area as a single unit [4-5]. For the few glaciers of Himalayan region, runoff and sediment load transportation studies have been carried out by various workers [6-10]. Therefore, it becomes essential to understand the contribution of snow and glacier melt to the river in headwater region along with the impact of rainfall on river discharge. But it is difficult to understand the different components of river discharge using the conventional techniques. A group of scientists was working on Bhagirathi River for more than a decade for measuring river discharge and other associated hydrological and meteorological parameters using conventional techniques near Gomukh and concluded that the river does not receive any contribution due to rainfall in the area. The strong support for their argument was the discharge-time and rainfall plot which indicated the decrease of discharge with the rainfall event. Therefore, we decided to use stable isotope of oxygen-18 to understand the reality.

Few studies in Ganga, Brahmaputra and Indus basins have been conducted based on stable and radioisotopes to understand the hydrological process in the Himalayan region. Ramesh and Sarin [11] observed that $\delta D$ and $\delta^{18}O$ value of these rivers fall on Global Meteoric Water Line (GMWL) and estimated the altitude effect in $\delta D$ and $\delta^{18}O$ using river isotopic data. Bartarya et al. [12] proposed an equation with a slope of ~7.1 and intercept of ~15 for Gaula basin of the Kumaun Himalayas based on randomly selected individual storm events. Pande et al. [13] based on $\delta^{18}O$-$\delta D$ and d excess of the headwaters of the Indus and its tributaries inferred the source of precipitation and altitude effect. Dalai et al. [14] studied the isotopic composition of Yamuna River and its relationship with water chemistry. Nizampurkar et al. [2] have studied the climatic changes and ice dynamics of Dokriani Glacier by dating the ice and measuring the isotopic composition of snow and ice. Studies based on $\delta^{18}O$ in snow/ice and ice core from the Tibetan (Xizang) Himalaya have addressed the seasonal relationship between $\delta^{18}O$ in snow/ice and air temperature and moisture sources [15-17]. The status of studies show that the estimation contribution of snow, ice and rain in the river discharge in the headwater region has been not studied. In this study, the stable isotope data generated for the years 2004 and 2005 were used to understand the contribution of snow and glacier melt in Bhagirathi River. This study was the first modest attempt through which the rain contributions of different water sources, namely, rain, snow and glacier were estimated using the isotopic techniques in Bhagirathi River near Gomukh the origin of Ganges.

## Study Area

Gangotri glacier is the largest glacier in the western Himalayas. The study area falls in Uttarkashi District of Uttarakhand State (U.K.) between latitude 30° 43'N and 31°01'N and between longitudes 79° 0'E and 79°17'E (Fig. 1).

The proglacial melt water river, known as the Bhagirathi River emerges from the snout of the Gangotri Glacier at an elevation of 4000 m. The
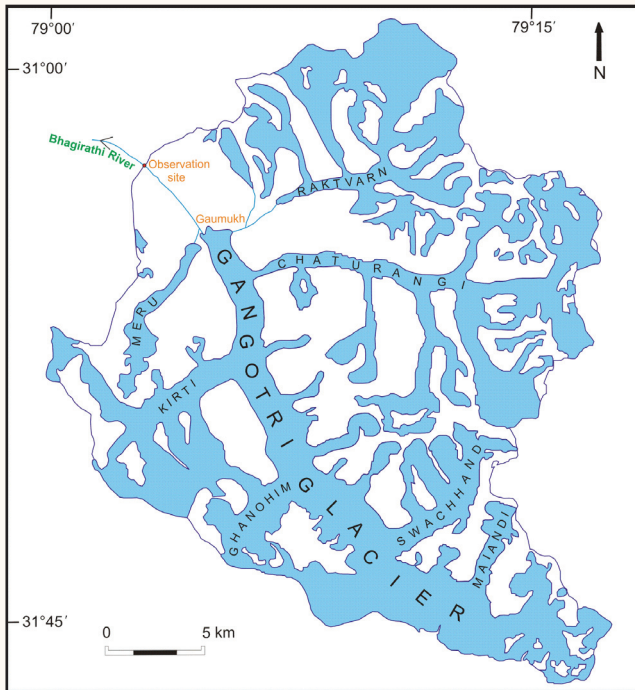
**Fig. 1: Location map of study area**

melt water is drained through a well defined single terminus of the glacier, known as Gomukh (the mouth of a cow). Gomukh is considered as the origin of the Ganga River. The main Gangotri Glacier (length: 30.20 km; width: 0.2 - 2.35 km; area: 86.32 km$^2$) forms the trunk part of the Gangotri Glacier system. The major glacier tributaries of the Gangotri Glacier system are Raktvarn Glacier (area: 55.30 km$^2$), Chaturangi Glacier (area: 67.70 km$^2$), Kirti Glacier (area: 33.14 km$^2$), Swachand Glacier (area: 16.71 km$^2$), Ghanohim Glacier (area: 12.97 km$^2$), Meru Glacier (area: 6.11 km$^2$), Maindi Glacier (area: 4.76 km$^2$) and a few others having a glacierized area of about 3.08 km$^2$ in total. The total catchment area up to the sampling location is about 556 km$^2$. Out of this a total area of 286 km$^2$ is glacierized [2]. The elevation range of the Gangotri Glacier varies from 4000 to 7000m and the elevation of the study area up to the gauging site lies between 3800 and 7000m.

**Sample collection and measurement techniques**

In order to measure the discharge of the river and weather parameters, a hydrometeorological observatory was established near Bhojwasa by National Institute of Hydrology, Roorkee. To monitor the water level data, an automatic water level recorder was installed in the stilling well constructed near the right bank of river. To measure the $\delta^{18}O$ of rainfall, integrated monthly and ten-day samples were collected during ablation period of years 2004 and 2005 using an ordinary rain gauge. From the integrated samples, 20 ml water sample was collected for stable isotopic analysis ($\delta^{18}O$) measurements. Diffusive and evaporative losses from rain gauges were avoided by collecting the water daily in a double lid plastic container while evaporation from storage containers was avoided by sealing the outer cap with paraffin. Discharge samples were collected from the flowing portions on ten-day basis for the years 2004 and on daily basis for the year 2005. Water sampling from standing water was avoided because the isotopic composition is affected by evaporation of standing water.

Snow and ice samples were collected from the Gangotri glacier. Few snow samples were collected in sealable plastic bags or containers. In order to avoid sublimation, re-crystallization, redistribution, melting and rainfall on snow, which alter the isotopic composition of snow and ice, the snow sampling was carried out just after every local snowfall. Once, the snow was melted in containers, the water samples were transferred to plastic bottles. The collected samples were analysed by Stable Isotope Ratio Mass Spectrometer (SIRMS) at the Nuclear Hydrology Laboratory, National Institute of Hydrology, Roorkee. Particularly, the Dual Inlet Isotope Ratio Mass Spectrometer was used for measuring oxygen and hydrogen isotopes ratios. The $CO_2$ equilibration method was used to determine $\delta^{18}O$, while $H_2$ equilibration method with Hokko beads was used for determining $\delta D$ following standard procedure [18, 19]. The measurement precision for $\delta^{18}O$ was ±0.1 ‰ and for $\delta D$ was ±1‰. All the $\delta D$ and $\delta^{18}O$ isotope data reported in this article correspond to VSMOW.

**Results and Discussion**

*River Discharge, Rain and Air Temperature Relationship*

The recording of the discharge of Bhagirathi River at gauging site revealed that the discharge of the river remains more or less in the range of 8.0 to 10 m$^3$/s in the months of May/first week of June (Fig 2). As
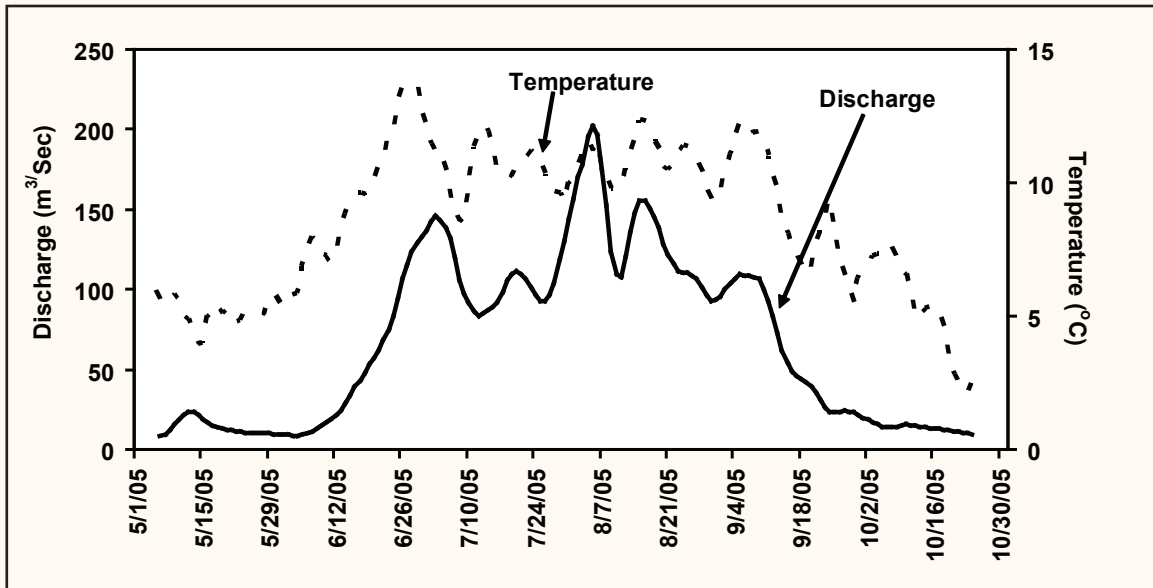
**Fig. 2: Variations of discharge with temperature in Bhagirathi River at gauging site near snout**

temperature starts increasing, discharge starts rising and higher discharge (100-180 m³/s) was recorded in the months of July/August when temperature reaches a maximum of 10°C to 12°C (Fig 2). This feature of discharge and temperature shows strong correlation between air temperature and discharge of the Bhagirathi River. The recession of discharge starts in the month of September and quickly reaches to the tune of 10.0 m³/s as it was observed during the initial part of May. A sharp decrease in air temperature was recorded in the months of July, August, and September whenever heavy rain event occurs (Fig. 2 and 3). It was observed that whenever there is a sharp decline in air temperature due to cloudy weather conditions and raining, the river discharge also declines abruptly instead of increasing (Fig. 3).
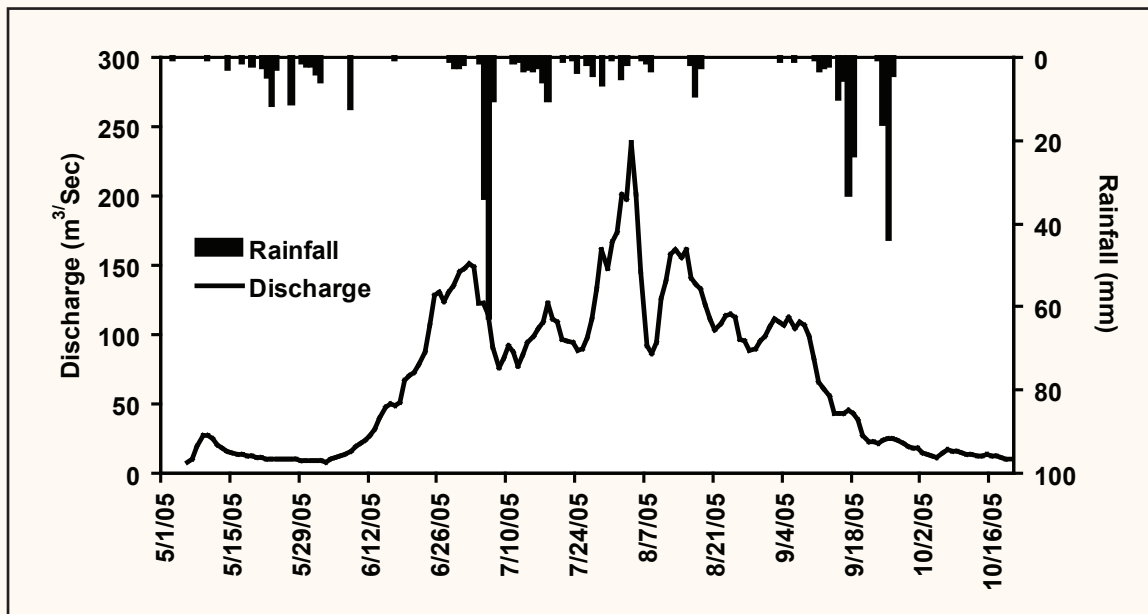


**Fig. 3: Variation of river discharge with rainfall during ablation period in the year 2005**
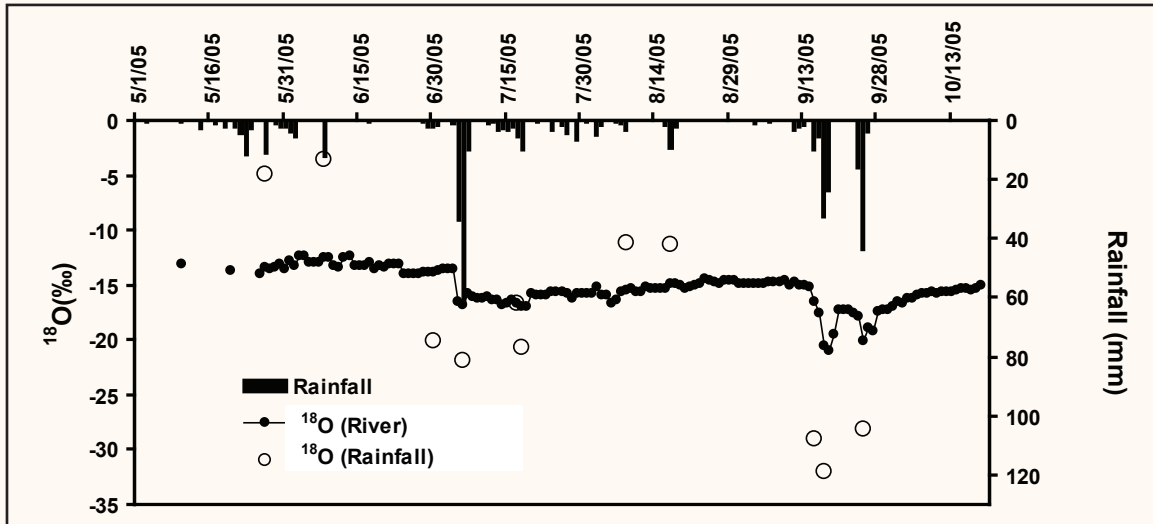
**Fig. 4: Variation of δ¹⁸O in Bhagirathi River & rainfall with time during ablation period in year 2005**

The decreasing trend of river discharge with rain events apparently indicates as if there is no effect of rainfall on river discharge. Therefore, it becomes difficult to estimate the impact of rain on discharge in case of snow and glacier fed rivers at higher altitudes using the conventional techniques. It also posed a problem in estimating the contribution of rain to the discharge of Bhagirathi River to the group of scientists from NIH, Roorkee working for more than a decade and they concluded that there is no contribution of rainfall in the discharge of Bhagirathi River near Gomukh. Consequently, isotopic signatures of river and rainfall were employed to understand the reality. The abrupt change in isotopic composition of river after the rain events is only possible due to runoff generated by concurrent rain joining the river (Fig. 4).

While the decrease in river discharge might be due to cloudy weather conditions during rainfall results in sudden decline of atmospheric temperature. It clarifies that the decline in atmospheric temperature reduces the melting of snow and ice greatly which declines overall discharge of the river while it includes the runoff contributed by rain, direct rainfall on river surface along with snow and glacier melt runoff.

**Isotopic Composition of Rainfall**

Isotopic values of rainfall ($\delta^{18}O$) measured for the years 2004 and 2005 reveal significant variation in isotopic composition of precipitation during ablation period. The maximum depleted rainfall in terms of oxygen isotope ($\delta^{18}O$) observed in the month of September during the years 2004 and 2005 are -23.8‰ and -30.3‰, respectively. Similarly, the maximum enriched $\delta^{18}O$ in rainfall observed in the month of June 2004 and 2005 are -1.7‰ and -3.6‰, respectively (Fig 5).



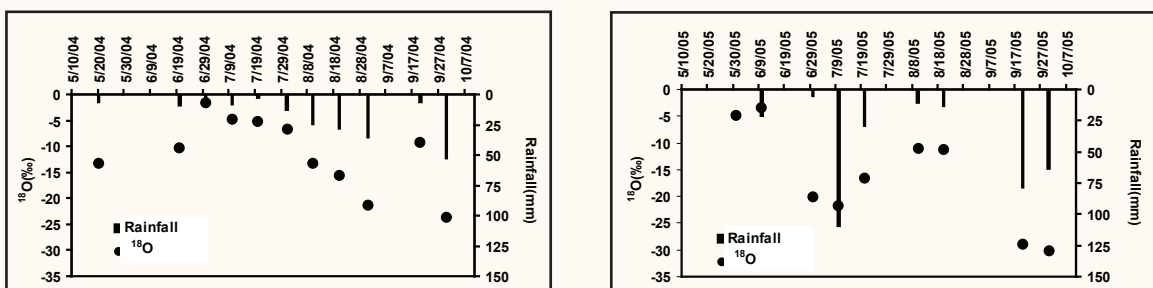**Fig. 5 : Variation of δ¹⁸O values in precipitation during ablation period in year 2004-2005**

However, it was noticed that rainfall bears enriched values of $\delta^{18}O$ in the months of May and June compared to $\delta^{18}O$ values in July to September. The different isotopic signatures of rains during premonsoon (May and June) and monsoon seasons (July, August and September) reveals that source of moisture for precipitation in the months of May and June is different than that occurs in the months of July, August and September. The depleted isotopic signature of rains in July, August and September become unique feature and important for various hydrological studies. The depleted $\delta^{18}O$ values of rains in July, August and September confirm that precipitation during these month occurs due to SW Monsoon vapours which depletes due to the continental and altitude effects while the source of moisture during summer months may be dominated by local evapotranspiration. The isotopic enrichment of pre-monsoon rains (May and June) may also be enriched due to secondary evaporation of rain drops during fallout process.

**Isotopic composition of Snow and Ice**

The isotopic signature of the fresh snow and surface ice samples collected from different altitudes in the accumulation and ablation zones of the Western Himalayan glaciers by various workers and under the present study from Gomukh snout are presented in Table 1 and Table 2.

**Table 1. $\delta^{18}O$ values of snow measured under different studies**

| Location | Altitude (m) | $\delta^{18}O$ (‰) | Investigators |
|---|---|---|---|
| Chhota Shigari | 4050 to 4750 | -5 to -9 | Nizampurkar et al.[2] |
| Dokriani | 4695 | -4.5 to -7.2 | |
| | 4695 | -5.0 to -23.0 | Nizampurkar and Rao[20] |
| Gomukh near Bhojwasa | 3800 | -11.6 | Present Study |
| | 3800 | -13.9 | |
| | 3800 | -9.7 | |
| | 3800 | -10.1 | |
| | 3800 | -11.7 | |
| | 3800 | -4.0 | |
| | 3800 | -14.0 | |

**Table 2. $\delta^{18}O$ values of ice/glacier reported by various investigators**

| Location | Altitude (m) | $\delta^{18}O$ (‰) | Investigators |
|---|---|---|---|
| Rohtang | 3748 | -18.1 | Pande et al.[13] |
| Balacha La | 4650 | -15.9 | |
| Thanglang La | 5210 | -24.7 | |
| Zozilla | 3540 | -12.2 | |
| Khardung La | 5629 | -17.2 | |
| Khardung La | 5649 | -15.3 | |
| Dokriani | 4836 | -11 to -15.2 | Nizampurkar et al.[2] |
| Chhota Shigri | 4100 to 4600 | -6 to -11 | Nizampurkar and Rao[20] |
| Changme Khangfu | | -12 to -17 | |
| Gomukh | 4000 | -18.5 | Present Study |
| | 4000 | -13.37 | |
| | 4000 | -18.1 | |
| | 4000 | -14.5 | |
| | 4000 | -13.5 | |
| | 4000 | -15.0 | |
| | 4000 | -14.4 | |

The results clearly indicate that the fresh snow bears more enriched isotopic signature than the glacier. This is possible as glacier is formed from the snow that occurs at higher altitude and it also takes several decades in transformation from snow to ice. Based on [32]Si and ^{210}Pb radioactivity, the age of Nehnar, Chhota Shigri and Dokriani glaciers is calculated to be about 500 years, 250 years and 400 years respectively[4]. The depleted $\delta^{18}O$ of these dated glacier snouts revealed that these region were having cooler atmosphere by few degree during their formations.

## Isotopic Composition of Discharge

The spatial and temporal variations in the isotopic composition of river mainly depend upon the number and type of its sources. The variations in the observed $\delta^{18}O$ reflect the variable contributions from isotopically different sources, which can be evaluated if isotopic indices of the sources are known. However, the river isotopic characterisation and its utility in studying hydrograph separation and river-aquifer interactions depend greatly on the spatial and temporal variations of isotopic compositions.

The $\delta^{18}O$ values of river water during pre-monsoon (April to June) vary between -12‰ and -13‰. The $\delta^{18}O$ values further depletes slowly in the month of July with an abrupt depletion in the order of -17‰ in the first week of July (Fig. 4). The depleted $\delta^{18}O$ signatures continue in the remaining months of August and September with slight enrichment and abrupt depletion. The abrupt depletion of $\delta^{18}O$ in July and September is triggered with a heavy rainfall event. It has been observed that the isotopic values of river initially follow the $\delta^{18}O$ values of snow as shown in Table 1 (-4.0‰ to -14.4‰ for samples collected in the month of May and June). It suggests that snowmelt dominates in the river discharge at initial stage (during May and June). Due to melting of snow in initial phase, the glacier/ice gets exposed below the snow line and starts melting subsequently. The melting of glaciers bears depleted isotopic signatures; hence the depletion in isotopic composition of river starts from the last week of June/first week of July. It clearly indicates that glacier melt runoff dominates in the river discharge during the month of July and August.

## Hydrograph Separation

The hydrograph of Bhagirathi River at Gomukh site comprises of multiple peaks. The variation in discharge occurs due to variations in climatic conditions which affects the contribution of different components to river discharge. To separate out the rainfall contribution in Bhagirathi River, the isotopic composition of river water and observed rainfall were studied. The $\delta^{18}O$ of river was found isotopically different during pre and post event of rainfall. The pre-event river $\delta^{18}O$ represents the combined signature of snow and glacier melt while post-event river represents mixed signatures of rain, snow and glacier melt components. The significant variation in $\delta^{18}O$ of river due to south-west monsoon rains was observed during July and September 2005 (Fig. 4). The isotopic composition of pre-event river (-14‰ to -16‰) was found sharply depleted to -20‰ due to mixing of much depleted rain (-30.3‰). The proportion of the two components in total discharge of the river can be separated out using two components model. The water mass balance equation can be written as:

$$Q_t = Q_{sm} + Q_r \qquad (1)$$

Where Q is discharge component and subscripts t, sm and r represent total river flow, snow/ice melt and rain contribution, respectively. Similarly, the isotopic mass balance equation can be written as

$$\delta_t Q_t = \delta_{sm} Q_{sm} + \delta_r Q_r \qquad (2)$$

Where $\delta = [(R_{sample}/R_{std}) - 1] * 10^3$ ‰

By substituting $Q_r = Q_t - Q_{sm}$ and rearranging Eq. (2), one gets

$$Q_{sm} = Q_t(\delta_t - \delta_r)/(\delta_{sm} - \delta_r) \qquad (3)$$

Using the Eq. (3), the runoff component can be separated out.

In order to separate out rainfall generated runoff component, different events of precipitation were selected during the years 2004 and 2005. In the month of August 2004, large variation in isotopic composition of river was recorded at the time of rainfall. The $\delta^{18}O$ of rainfall occurred between 21st to 31st August 2004 was found -21.5‰, pre-storm river -15.5‰ and river during rainfall -17.9‰ (Fig. 4). The two components model shows the maximum runoff
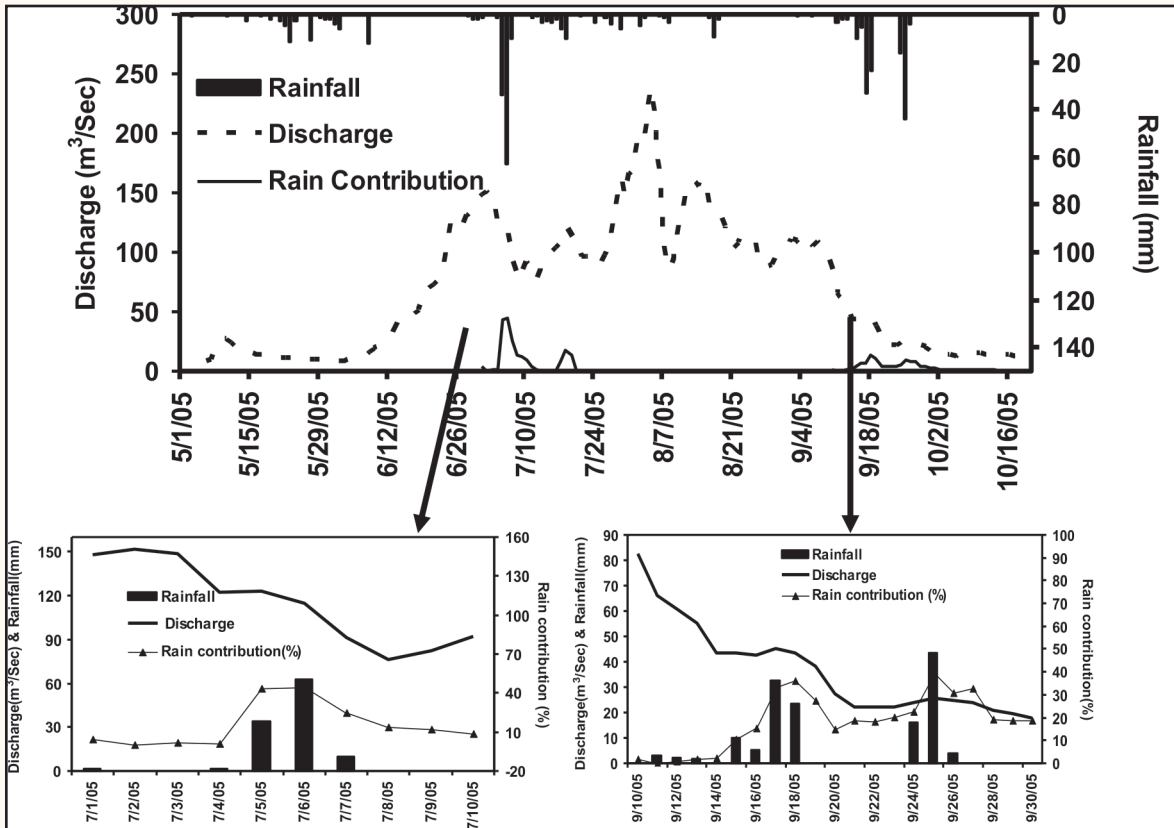
**Fig. 6: Rainfall contribution in Bhagirathi River using two component model for different rain events occurred during ablation period of the year 2005**

contribution of the order of 40% in river discharge. Similarly, three rain events were monitored in the months of July and September 2005 (Fig 6). The maximum rainfall contribution to the tune of 40% was computed for the rain occurred in the month of July, up to 30% in case of rainfall occurred in the third week of September while up to 40% in case of rainfall occurred during the last week of September. The extent of change in isotopic composition of river was found to be a function of proportion of rainfall contribution to the river discharge at gauging site during the rainfall above 20 mm (Fig. 4).

In order to estimate the total contribution of a rainfall event to the river discharge, daily sampling was carried out and isotopic composition was measured. Hydrograph separation was carried out on daily basis for the month of July, August and September in the year 2005, which revealed the rain contribution in the order of 14% to 15% of the total river discharge for each storm (Fig. 6).

Similarly, the rainfall contribution of all the rain events occurred during ablation period of the year 2005 was computed, which comes out to be an aggregate of 3% of the total discharge of river.

**Conclusion**

The variation in $\delta^{18}O$ of river discharge with time clearly indicates the varied contribution of snow, ice and rain to river due to variation in weather conditions during ablation period. Isotopic signature of river shows that snowmelt dominates in river discharge up to June while glacier melt during the later period. The maximum contribution of rainfall to river discharge is estimated up to 40% during the day of rainfall. While, the contribution of individual rain event estimated to vary from 14% to 15% of river discharge. But the total contribution of all rain events during an ablation period was found limited to only 3% of the total discharge of the river Bhagirathi at Bhojwasa gauging site. The isotopic signatures of rain and river (pre and post event of rainfall) revealed

that the discharge of the Bhagirathi River near snout decreases during rainfall due to considerable decrease in snow and glacier melt runoff as a result of decrease in atmospheric temperature during rainfall.

The depleted $\delta^{18}O$ signature of rain in July, August and September becomes unique and important for various hydrological studies. The present study reveals that stable isotopes are very useful in segregating the different components of river discharge near snout while conventional techniques have limitations. The long-term data of $\delta^{18}O$ of river near snout would be useful to study the impact of climate change on melting of Himalayan glaciers.

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# Climate Change studies and moisture prediction through water stable isotopes proxies

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## 1. Introduction

After the development of mass spectrometry in the 1960s, stable isotopes in solid and liquid precipitation ($\delta$D, $\delta$18O) is being used as a tracer to identify the origins of precipitation & transportation in the hydrologic cycle, in the climate change studies as a proxy data for temperature, relative humidity, and precipitation. This is due to the different nature of heavy and light isotopes species during the fractionation processes during phase change which traces behind its original signature. Because of these characteristics, natural paleoclimatic archives, i.e., deep ice cores, well-preserved lake sediments, undisturbed corals, tree rings, stalagmites, and groundwater preserve the climatic signal of the past variations in the hydrologic cycle and in meteorological conditions. The most well-known application of stable water isotopologue is the reconstruction of past climate using temperature and isotope in the polar ice cores. Furthermore, the spatial and temporal distribution of modern meteoric water isotope indicates a close relationship with meteorological variables through the Global Meteoric Water Line (GMWL) but also depends on various meteorological parameters, i.e., temperature, amount of precipitation, the source of moisture and teleconnection of moisture through the atmospheric circulation pattern [1,2]. Tritium, a radioactive isotope of Hydrogen integrated naturally as well as anthropogenically in the hydrologic cycle is very useful for tracing and dating. Tritium is naturally produced in the stratosphere through the interaction of Nitrogen atom with the cosmic radiation at the average rate of 3200 atoms m-2 s-1 [3] and bears the half-life of $12.32 \pm 0.02$ years [4]. Here, we are discussing a brief theoretical background of stable water isotopes and the application water stable and unstable isotopes in the precipitation as well as in the hydrologic cycle.

## 2. Theoretical Background

Deuterium ($^2$H or D) and $^{18}$O are heavier compared to the $^1$H and $^{16}$O and $^{17}$O which means that heavier molecule will prefer to stay with the stronger bond during the phase change process. Because of the homogeneous nature of ocean water, it is considered as a referencestandard to measure the stable water isotopes of hydrogen and oxygen in precipitatin [5,6].

The delta value is defined as

$$\delta\ (‰) = \left(\frac{Rx}{Rstd} - 1\right) * 1000.$$

Where R denotes the ratio of $^{18}$O/$^{16}$O, $^{17}$O/$^{16}$O and D/H respectively. Positive and negative values signify the enrichment and depletion of the heavy isotopic species relative to their standards respectively. Variation in the bond strength of H and O, isotopes of hydrogen shows higher variability compared to the Oxygen with the fact that hydrogen exhibits weaker bond strength and is easily to break. The breaking of the bond during the phase changing process leads to the fractionation which is further dependent on the rate of chemical reaction and equilibrium conditions. The isotopic species removed from the system at every instant and are in thermodynamic equilibrium condition follow the distillation process known as Rayleigh distillation.

$$R = Ro * f^{(\alpha-1)}$$

Where R is a final isotopic ration of vapor, $R_o$ is initial vapor isotopic ratio, f is remaining vapor fraction and $\alpha$ is fractionation factor.

## 3. Water stable Isotopes in the Hydrologic cycle:

### Effect on precipitation

The global relationship between $\delta$D and $\delta^{18}$O was first shown by Craig [6] (1961) using surface water and precipitation. The observed relationship

of δD and δ<sup>18</sup>Ofalls on the slope and intercept of 8 and 10 respectively (δD =8*δ<sup>18</sup>O + 10, called Global Meteoric Water Line-GMWL. In this study, we have used theGNIP Database [7] and subsets the data only for Delhi, which receives ample amount of rainfall especially during the Indian Summer Monsoon (ISM) and has clear seasonal variation in meteorological parameters. Precipitation samples were calculated for the period 1962 to 2012 for the entire year. δ<sup>18</sup>O and δD show a clear seasonal cycle where δ<sup>18</sup>O and δD range from -15‰ to 6‰ and -130‰ to 50‰ respectively (fig.1). Figure 1(c) clearly shows the linear relationship between δD and δ<sup>18</sup>O at Delhi. The lower slope and intercept of Delhi shows the dominance of evaporative and dry conditions throughout the year. The most depleted δD and δ<sup>18</sup>O values are during the

ISM while the most enriched values are from the pre-monsoon season. The higher range of δD and δ<sup>18</sup>O for Delhi is interesting and further tempted to conclude that Delhi receives dominated dry season with high temperature {fig.1(c), fig.2} followed by wet and humid season (during ISM and western disturbances in winter time).

**Temperature Effect**

Dansgaard [1] (1964) first showed a strong correlation among δ<sup>18</sup>O and temperature on a global scale (0.7/ºC). The correlation among temperature and stable isotopes in precipitation is very important in the estimation of paleo temperature changes and also to validate the accuracy of the global circulation model (GCM) output. Figure 2 shows the monthly variation of water stable isotopic parameters (δD and δ<sup>18</sup>O) and temperature. The temperature shows a clear seasonal cycle where its monthly amplitudinal variations are narrower compared to the δD and δ<sup>18</sup>O which is due to the interdependency on various meteorological conditions. The study has shown that the 'temperature effect' varies for individual stations and further it was summarized [8] that the temperature effect at individual stations showed the long-term annual temperature coefficient values ranged from 0.25 to 1.10‰. Datta et al. (1991) [9short-term features can be seen following an evaporation line. Rainfall in the monsoon months (June-September]also reported the temperature effect for New Delhi and argued that the temperature effect differed with the monthly rainfall and indicated that the temperature–δ<sup>18</sup>O relationship shows large variations that depend on time and location.

*Amount Effect*

This effect (fig. not shown) was first observed by Dansgaard in1964 [1] where he found the interesting correlation between the monthly precipitation amount and its isotopic composition. This is mainly due to the rain-out process, deep convective clouds, isotope exchange and partial evaporation of raindrops below the cloud base, and alteration in vapor isotopic composition at source region [10]. This effect was furthermore studied in the Southeast Asian and western
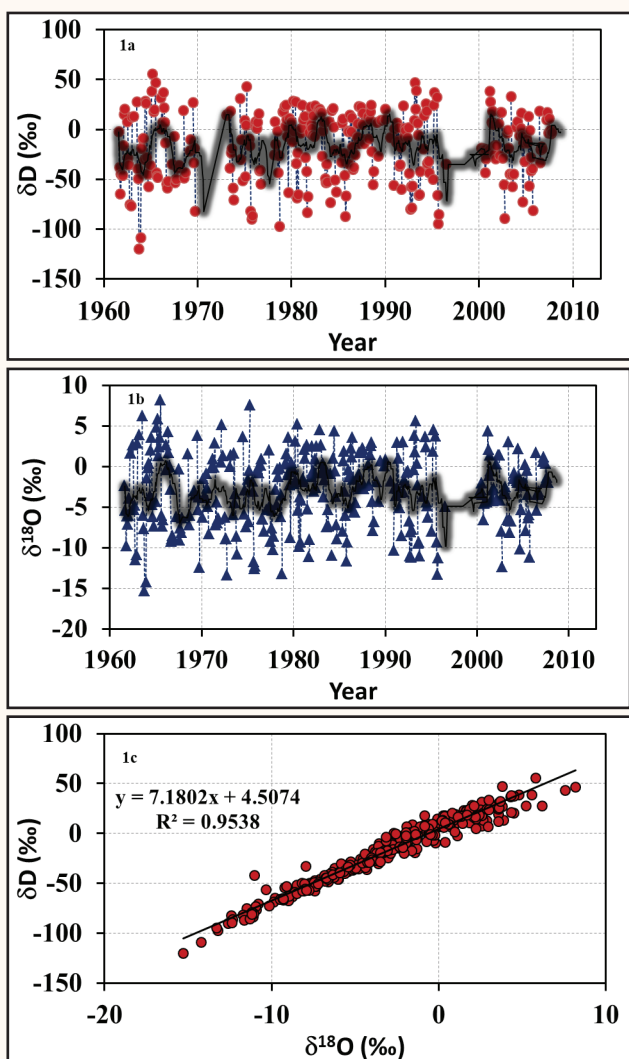


**Fig.1: (a and b) Time series annual variation of δD, and δ<sup>18</sup>O (c) Linear regression between δD and δ<sup>18</sup>O for Delhi since 1962**

Pacific regions and found that seasonal isotopic variation of precipitation was mainly temperature driven. The same effect was also reproduced through the modeling studies [11,12]. Interestingly the coefficient of the amount effect of $\delta^{18}O$ over Panama ranged from –1.63 to –2.47 /100 mm [13].

### Altitude and Latitude Effect

Correlation and relationship between $\delta^{18}O$ and altitude (fig not shown)were first observed in Switzerland where it was found that a decrease in $\delta^{18}O$ with altitude (0.26/100 m) and also others various European regions (0.16 –0.40 /100 m) [14].
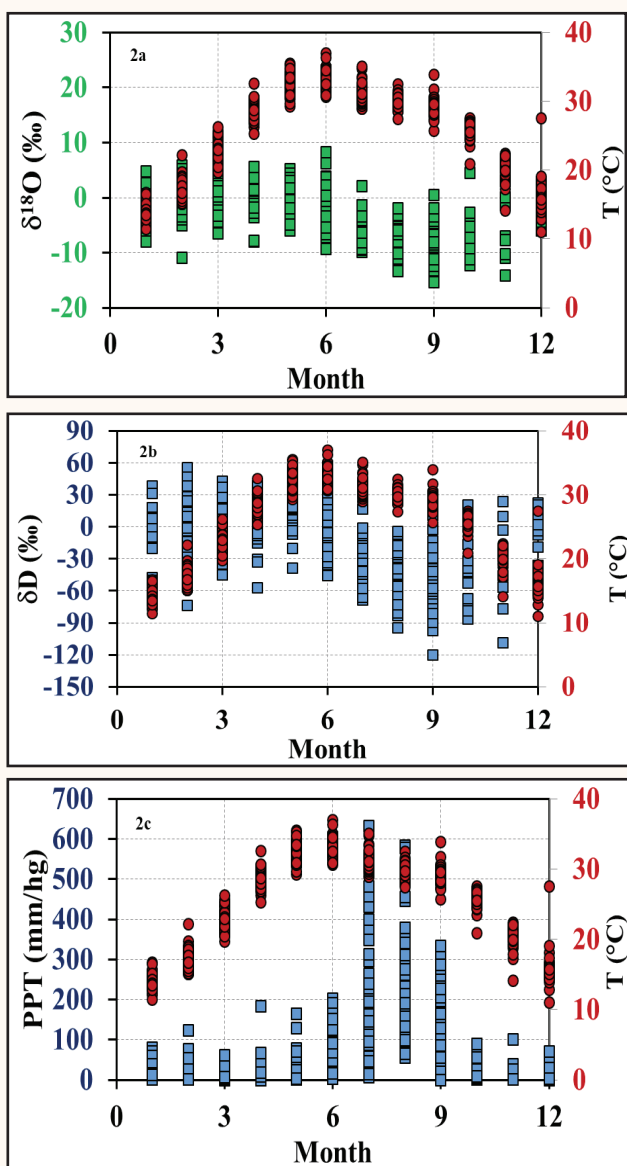


Fig. 2: Averaged monthly variation of (a) $\delta^{18}O$ (b) $\delta D$ and (c) precipitation (PPT) with temperature (T) for Delhi during 1962-2012. Larger PPT was observed during the period of July and August (Indian summer monsoon)

Furthermore, it was reported that [15] the $\delta^{18}O$ bears larger in the rainy (0.23–0.26 /100 m in a rainy year) compared to the dry season 0.11–0.16 /100 m. The altitude effect was studied and reported throughout the mountain with their consistent gradient except for the Himalayas due to its complex terrain and topographic conditions [16]. Interestingly, it was observed that the $\delta^{18}O$ global distribution of precipitation is tightly bounded with latitude and altitude the through the following equation, $\delta^{18}O_{ppt} = -0.0051(|LAT|2) + 0.1805(|LAT|) - 0.002(|ALT|) -5.247$[17].

Latitude effect can be understood with the fact that the major source of global water is tropical where a major percentage of evaporative flux is generated there due to high solar radiation and further leads to the pole ward transport of vapour where it gets progressively depleted due to rain-out effect (Rayleigh distillation effect) (Fig.3). This pole ward transport of vapour plugged with the gradual rain out process resulting into the total reduction of precipitation amount in the atmosphere as well as gradual depletion of heavier isotopes in the vapour and precipitation respectively.
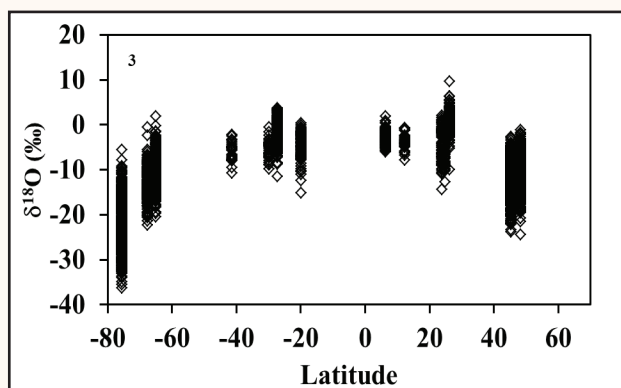


Fig. 3: Latitude effect with $\delta^{18}O$ where higher latitude receives more depleted signal due to progressive depletion

### Bomb Peak in Precipitation

Apart from the natural formation of Tritium at the upper atmosphere, a vast amount of anthropogenic tritium was also injected into the atmosphere produced during 1950s-1960s due to nuclear test (fig.7). Due to these tests, a huge amount of "tritium peak" (or "bomb peak") was integrated into the hydrologic cycle and measured in the in precipitation [7]. In case of Delhi, more than 1100 TU (tritium unit) was recorded in the 1960s especially at the latitude range of 40° N to

50°N (fig 7b) tested mainly by USA and USSR. This elevated peak gradually decreases in precipitation due to radioactive decay and dilution effect together with effective Nuclear Test Ban Treaty in 1963.



**Fig.4: Variability of Tritium concentration (a) During 1962-2012 (b) at different latitudes**

## 4. Variability in moisture sources and isotopic characterization of rain water in Western Himalaya: a case study from upper Chandra basin

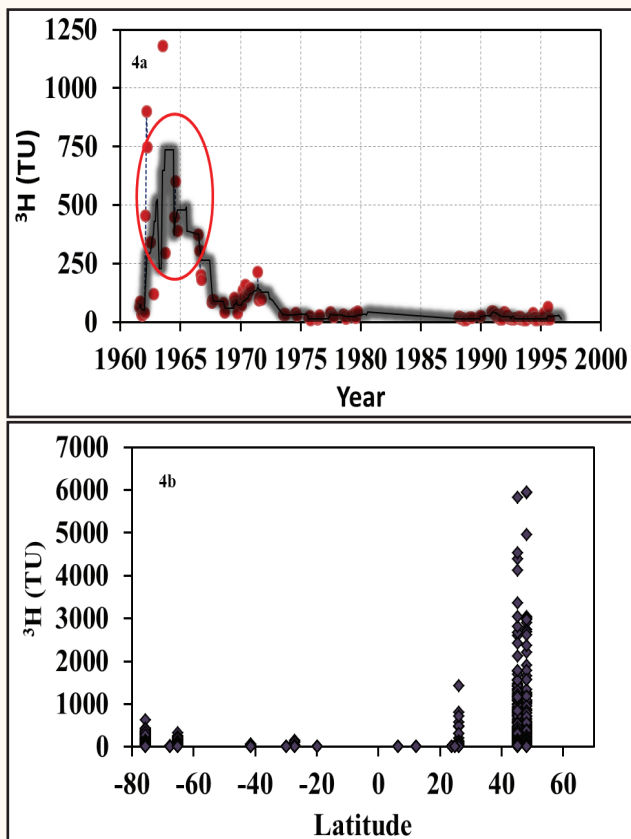Recent published article (Kumar et al., 2018) defined the LMWL for the Upper catchment of Chandra basin in western Himalaya with help of rain water samples collected during each rain event for whole season (June, July, August, September and October) at Chhota Shigri base station, expressed as $\delta D = 7.95\delta^{18}O + 21.4$ (n = 35, $r^2$ = 0.98). This relationship is similar in slope but high in deuterium intercept to the LMWL of western Himalaya ($\delta D = 7.95\delta^{18}O + 11.51$) (Kumar et al., 2010) and global meteoric water line (GMWL): $\delta D = 8\delta^{18}O + 10$ (Craig., 1961); $\delta D = 8.20 \pm 0.07\delta^{18}O + 11.27 \pm 0.65$ (Rozanski

et al., 1993). LMWL from this study is also similar in slope and intercept to the LMWL line of the Middle Himalaya ($\delta D = 8.9\delta^{18}O + 22.26$) (Tian et al., 2005) and to the Mediterranean meteoric water line (MMWL) ($\delta D = 8\delta^{18}O + 22$) (Gat and Carmi, 1970). The high intercept is due to the process of mixing of air moisture from different sources in different season (Tian et al., 2005) which is confirmed with d-excess variation Fig. 5(b).To trace the origin of moisture source Dansgaard (1964) defined parameter deuterium excess (d-excess = $\delta D - 8\delta^{18}O$) which is nothing but the intercept of the best fit line of regression between $\delta D$ and $\delta^{18}O$. Similarly, present study used d-excess to distinguish moisture sources in different season where it was found that south west monsoon is dominant only for the short stretch during summer (low d-excess; <20%) while the remaining period in winter is contributed by westerly (high d-excess; >25%) (Fig.5b). This finding is in line with the previous study at Chhota Shigri glacier where it is reported that south west monsoon accounts for only 21% of the annual precipitation while rest part of the year is influenced by mid-latitude westerly which governs 79% of total precipitation (Azam et al., 2014). The pattern of d-excess shifting along with the season, leads to high intercept between $\delta D - \delta^{18}O$ regression line Fig. 5(a). Its low (<15%) and high value (15% - 24%) shift is the signature of active period of south west monsoon and westerly, respectively (Jeelani et al., 2013, Tian et al., 2005).
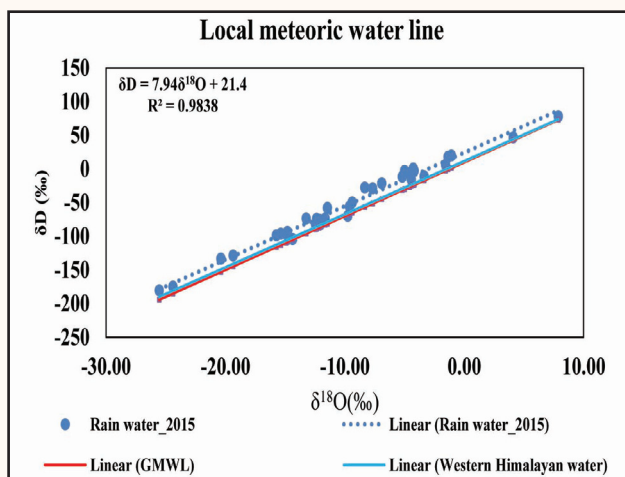


**Fig. 5a: Regression line (blue dot line) between $\delta^{18}O$-$\delta D$ value of rain water samples (n=35) at Chhota Shigri glacier in Western Himalaya during entire ablation season**
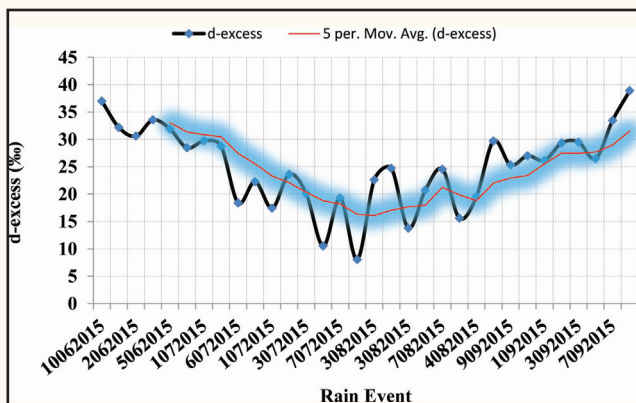
**Fig. 5b: d-excess variation in rain water samples collected at base station of Chhota Shigri glacier (CS) during June to October 2015**

## 5. Conclusion

Water stable isotopic ratio of hydrogen and oxygen is an important tool in the hydrologic cycle to understand the source of precipitation as shown by the case study from upper Chandra basin. Further, recycling of moisture during their transportation and admixture of different air masses during their path can be observed in this case study. The comparative isotopic studies show that stable water isotopes are interlinked with various meteorological parameters and therefore can be used to infer the past climate reconstruction through the help of well preserve ice cores, lake sediment core as stalagmites

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# A review on the techniques to determine recharge prospects of fresh groundwater resources along the mountain front

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## *Abstract*

*Mountain front recharge (MFR) plays an important role to recharge the basin aquifers of mountain front (MF) in arid and semi-arid regions. In general, it depends upon the precipitation characteristics of mountain. There are two methods like mountain centered and basin centered generally considered to estimate MFR. These methods altogether avoid of considering the complexities of hydrology above the MF. Subsequently, hydrology above the MF is an area suitable for significant scientific advancement. Thus, in a complete perspective MFR would investigates the entire mountain block (MB) system and the hydrological processes occurring in the highest peak slopes to deepest depth of circulating groundwater. Important aspects of MF include rainfall pattern, vegetation-controlled evapotranspiration, snow melting, surface runoff, infiltration of water derived from the fractured or faulted bed rock and flow of water along the mountain stream channels and underlying MB. This paper first defines some key terms, then reviews methods of estimating MFR in arid and semiarid regions, and finally addresses some of the future directions for MFR research.*

*Keywords: Mountain front recharge; Geophysics; Hydrochemistry; Remote sensing; Mountain block*

## 1. INTRODUCTION

Groundwater is an indispensable natural resource and plays a promising role to meet the domestic, industrial as well as crop water requirements due to its desirable high quality, particularly in semi-arid regions. Thus, natural groundwater recharge rates have to be quantified for the proper management of the resource. Mountain contribution to annual river basin discharge is about four times that of the basin floor [1]. The term mountain front recharge (MFR) in complete perspective investigates the hydrological processes occurring in the highest peak slopes to deepest depth of circulating groundwater which, comprises of the water from adjacent stream channels and the underlying mountain block (MB). It also includes water from precipitation, melting of snow, surface runoff and through fractures and faults as well as evapotranspiration. The water of MB, enters into the adjacent basin through either focused or diffuse surface and subsurface components, termed as MFR [1].

Several authors have tried to define the term mountain front (MF) but still a clear and transparent definition of MF is lacking. The main ambiguity is; whether the MF is a strict line or a narrow zone? As that of the regions affected by sea water intrusion along the coastal aquifer.

If it is considered as a line then several naturals' line can be taken into consideration like vegetation boundaries, soil boundaries (e.g. the edge of bare rock), slope boundaries, mountain bounding faults or even the snow line. According to Ruxton and Berry [2] there are 3 alternative MF boundaries are given as in figure 1.
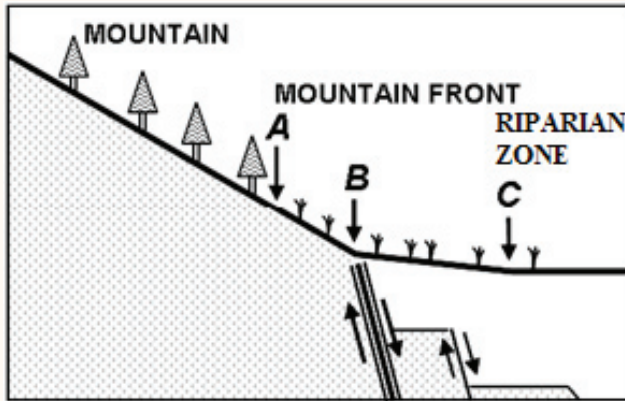


**Fig. 1: Schematic view of naturally occurring lines and potential mountain front boundaries [3]**

i. The region where there is a reflection of change in vegetation (Figure 1, A).
ii. The region where the mountain abuts the piedmont, often corresponding to a change in soil type and presence of the mountain bounding faults (B).
iii. And the plinth angle where the piedmont meets the edge of the basin floor (C).

Whereas, when the MF considered as a narrow zone between the mountain and basin floor, technically any boundaries as described in above figure 1 can be considered as MF zone. But, to study MFR in arid and semi-arid regions like the present study area, the piedmont zone (the region between B and C: figure 1) is the best definition of MF. The riparian zone (RZ) can be defined as the interface between land and a river or stream (Figure 1). The term MFR refers to the total amount of water enters into the basin aquifer of both MB and MF. In other way, it can be defined as the contribution of mountain to recharge the aquifers at the MB as well as MF (Figure 2). On the basis of definition, MFR can be categorized into 2 forms like recharge at the MF zone (direct MFR) and the subsurface water from the MB recharged to the basin aquifer (Indirect MFR). The direct (near surface) and indirect (sub-surface) leads to focused and diffused path of recharge for each and gives rise to four different components of MFR [3] (Figure 3).

**A.** Focused near surface component (FS): The recharge along the MF from the surface stream runoff (FS1, easy to measure) and shallow subsurface water transmitting through streambed sediments (FS2, difficult to measure).

**B.** Diffuse near surface component (DS): Surface flow along the steep front slopes and however subsurface flow (through the thin soil layer) which originates from the small catchments directly above the MF.

**C.** Focused subsurface component (FR): In this component the groundwater water flows along the bed rock openings such as faults, fractures due to tectonic activity or manmade consequences, joints and pipes like lava tunnels, tubes and dissolved openings in carbonates or other rock formations to the MB and basin aquifers.
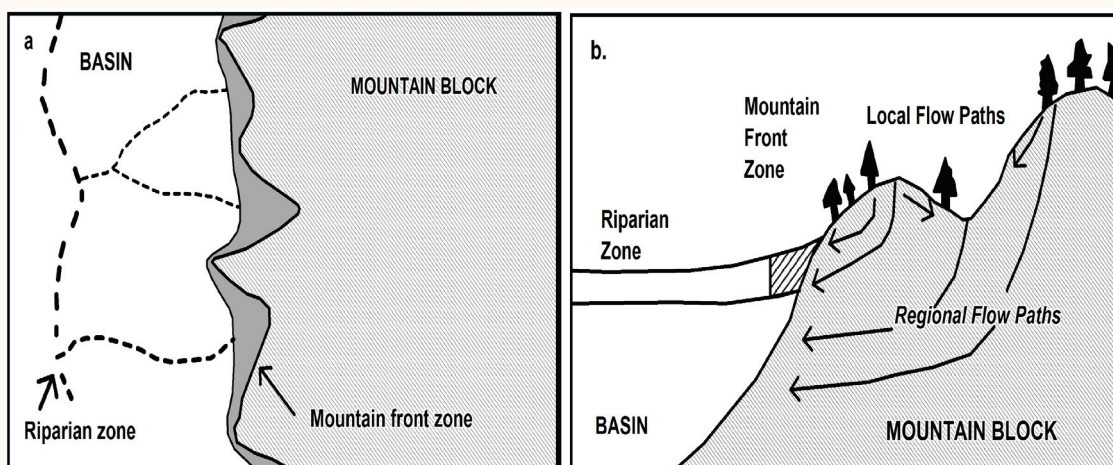


Fig. 2: Schematic diagram showing four hydrologically distinctive units of the landscape in map view (a) and in cross-section (b) The cross section also shows various groundwater flow paths in the MB {modified from Toth [4] and Keith [5]}
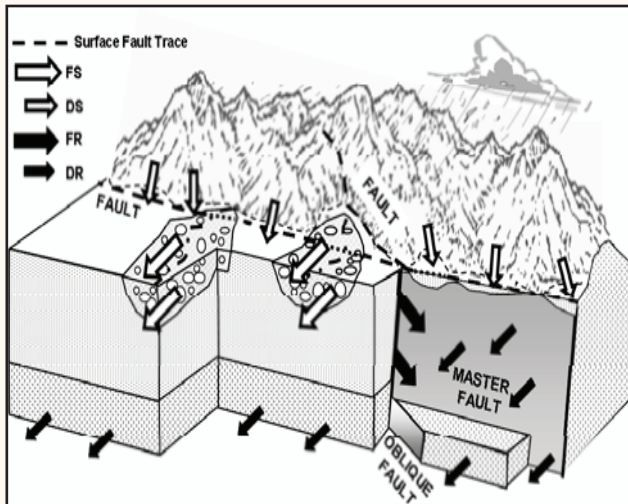
**Fig. 3: Schematic diagram illustrating MFR components. FS = focused near-surface recharge, DS = diffuse near-surface recharge, FR = focused subsurface recharge, DR = diffuse subsurface recharge [3]**

*D) Diffuse subsurface component (DR):* Groundwater transmitted through the contact between the MB bedrock and the basin aquifer sediments.

Based on the definitions of the above components: MFR1=(FS1+FS2) +DS+FR+DR

## 2. ESTIMATION METHODS

Several techniques have established for the quantification of groundwater recharge along the arid and semi-arid regions, each with significant uncertainties [6,7,8&3] and it includes environmental tracers, physical and empirical methods and numerical models. Literature on different techniques for groundwater recharge studies have been highlighted in the due course of this study.

### 2.1. GEOPHYSICAL APPROACH

Resistivity survey technique has been applied to identify the hydrogeological structure of aquifers by incorporating inferred resistivities [9-11]. Resistivity survey adopting Wenner configuration was used to identify the groundwater recharge zone in Seethanagaram, India and inferred that groundwater potential is at deeper zones (50–70 m) with good yield [12].

The procurement of geotechnical and hydrological subsurface information to assist in foundation design

and groundwater resource development in Nigeria has attempted by Amigun et al. [13] by using VES method. Nejad et al. [14] used resistivity survey by Schlumberger configuration in Curin basin, Iran to determine the subsurface layering and aquifer characteristics. Several authors have been using the electrical resistivity method in groundwater studies, to achieve multiple objectives such as water quality assessment and groundwater potential zone delineation [15], saline water intrusion, recharge identification, aquifer parameter determination [16], and protective capacity assessment of vadose zone material [17, 18].

Resistivity data integrated with remote sensing and GIS techniques for the delineation of groundwater potentiality along the numerous regions of the world [19] in both hard rock and sedimentary aquifers.

### 2.2. REMOTE SENSING

Remote sensing is reinforced by GIS due to the fact that the recharge is a process which is dependent on number of collaborative factors, that can be operated in the GIS platform. Several studies, by the authors like as Teeuw [20], Edet et al. [21] and Travaglia and Ammar [22], show that these recharge factors vary from one study to the other, in fact, none includes a complete list of them. All the above described studies include digital elevation model (DEM) technique for the procurement of the slope of the study area, which plays an important role in delineating the groundwater flow direction and the artificial recharge sites [23-25].

The multiple thematic layers like geomorphology, lithology, land-use and spatial maps like rainfall and water level of an area can be spatially integrated to identify the groundwater recharge potential zones. Several researches have attempted these methods to identify the groundwater recharge potential zone [26], identification of artificial recharge sites [27, 28] and for the spatial analysis of groundwater potential zones [30].

Few other studies by Vaidyanathan [30], Das et al. [31], Kumar and Tomas [32] and Pratap et al. [33] have targeted groundwater prospects by considering

the geomorphological aspects derived from satellite images. Studies have also attempted to select suitable sites for artificial recharge as well as recharge structures [24,34] by adopting this technique. Deepesh et al. [35], Prabir et al. [36], Cheng et al. [37] have incorporated this technique to groundwater potential zones by using integrated selected thematic layer on the basis of weighted linear combination and ranking technique in GIS environment. Recently, remote sensing and GIS techniques adequately employed to identify the characteristics of the surficial features of the earth like lineaments, drainage etc. and also to examine the groundwater recharge [38, 39].

A GIS based study was done by Chidambaram et al. [40] on the water table fluctuation (WTF) in the coastal alluvial aquifers of Pondicherry to understand the spatial variations of recharge along with the rate of discharge and recharge. The weighted overlay analysis in GIS platform helps in determining the groundwater potentiality, which works on the principle of assigning ranks and weights to the thematic map by analyzing its significance to influence the groundwater recharge process of that region.

## 2.3. HYDROMETEOROLOGY

Large-magnitude rise of water table in response to rainfall has been related to various fractured rock regions around the world [41, 42]. Gburek and Folmar [41] observed several meters of water table rise over a few hours. Rodhe and Bockgård [42] noted similar response in granite aquifer wells of central Sweden which is overlaid by till of 10m thickness and moves rapidly through the porous medium. The aquifers in Ontario responds significantly to the rainfall events in a variable manner i.e. the water level rises in a rate of 1.0–3.0 m at one well over a few hours, while nearby, whereas in the nearby wells the rate of rise is less than 1.0 m [43]. In each of these cases, the response could be indicative of actual recharge (water table rise), or a hydraulic effect due to mechanical loading, air entrapment or a combination of these [44].

Healy and Cook [45] and Healy [46] have started a revision of recharge estimation methods based on the relationship between WTF and specific yield, which has gained its importance when examined with the

response to individual storms in shallow aquifers [8]. The analysis of the WTF helps to identify recharge of the basis using extensive time series data, the variations in groundwater recharge resulting from changes in land use or climate change [47]. Park and Parker [48] have developed analytical solutions to improve the WTF method, by taking the different variables into consideration, that is intervening in the recharge phenomenon.

## 2.4. HYDROCHEMICAL ASPECTS

The chemical characteristics of groundwater have a significant role in understanding groundwater flow condition of a region. The major ions and heavy metals are enormously used to determine the origin of groundwater and its source of recharge, geochemical evolution, residence time as well as the definition of recharge zones [49]. The variation in groundwater chemistry is mainly influenced by the chemistry of recharge area as well as the various geochemical processes. Thus, the major ions vary spatially and temporally and provide information regarding the aquifer heterogeneity and connectivity and also the reason behind the hydrochemical variation and source of recharge [50, 51]. Hydrogeochemical techniques have been adopted to determine the source of origin / recharge of groundwater using different methods.

### 2.4.1. STATISTICS

The technique cluster analysis helps in sorting a set of individual samples into smaller groups for correlation or identification of location [52]. Multivariate statistical data are broadly used to depict and estimate groundwater [53] along with groundwater quality [54, 55] and it is useful for substantiating sequential and spatial variations caused by natural and human factors linked to recharge.

Another method to develop an evolution model is making predictions about the processes along the flow direction using thermodynamic calculations and hydrochemical modelling [56].

### 2.4.2. ISOTOPES

Stable isotopes of water ($\delta^{18}O$, $\delta^2H$) have been used since the pioneering work of Craig [57] and

Dansgaard [58] to trace the water cycle (Figure 4). Stable isotopes are employed as tracers to comprehend hydrogeological processes such as precipitation, groundwater recharge, groundwater-surface water interactions and basin hydrology [59]. Stable isotopes help in determining source of recharge, origin of groundwater, its flow pattern and also in pollutant transport [60] (Figure 5). The recharge mechanism can be delineated with the comparison of $\delta^{18}O$ and $\delta^2H$ of precipitation and groundwater [61, 62].

Mostly old water in the aquifers of arid and semi-arid region, due to the lower recharge rate, is rarely flushed out. Thus, several researchers have estimated the past as well as recent recharge rates and also the age of the groundwater by using environmental isotopes with $^{14}C$ [63, 64], $^{36}Cl$ [65] or noble gases [66].

The assessment of age range of residence of tracers is a very important technique to obtain the recharge rates as well as the age of the groundwater in arid and semi-arid region [67, 68]. The time ranges of the tracer used in determining the recharge rates is given in the following figure 6.

Some authors have also studied d-excess for the identification of the meteoric water source and to define the seasonal recharge of groundwater and to understand the pre-recharge fractionation [70, 71]. Studies have also been carried out in sedimentary aquifers to estimate the groundwater recharge by using chloride, deuterium and oxygen – 18 profiles [72, 73].
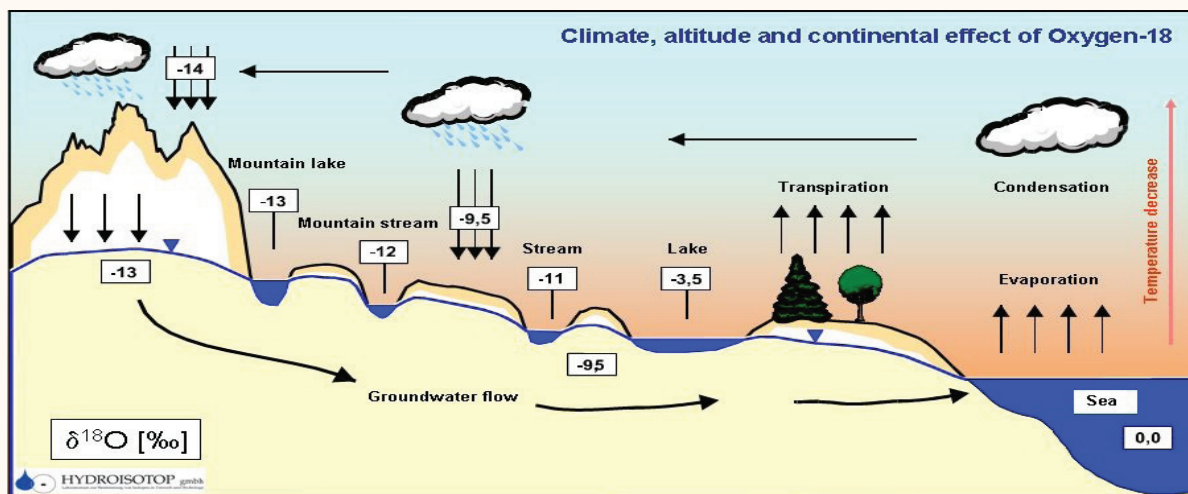


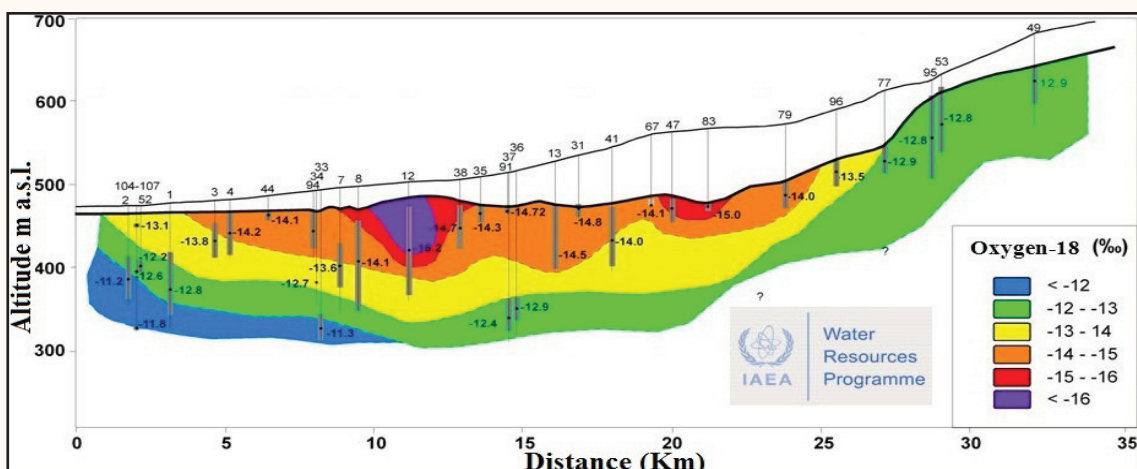Fig. 4: Hydrological cycle with $\delta^{18}O$ (‰ VSMOW) contents [69]



Fig. 5: Santiago de Chile: Isotopes help to define sources of recharge, groundwater origin, flow patterns and pollutant transport [74]
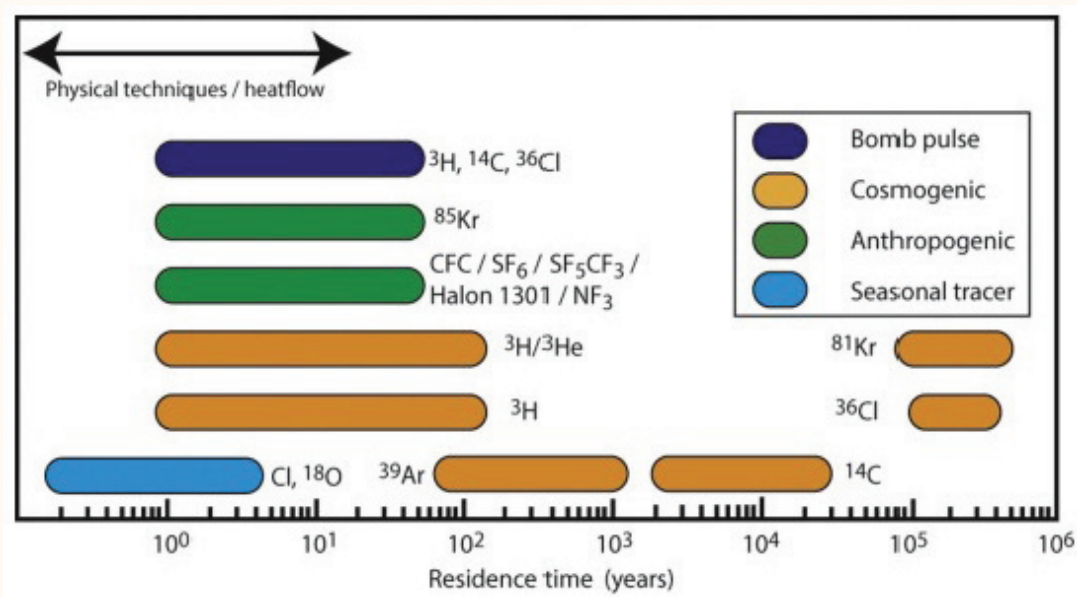
**Fig. 6: Approximate residence time range of tracers used in determining recharge rates [68]**

Tritium is used as a tool for dating the age of water [75]. Nevertheless, the presence of tritium itself specifies the presence of "young" water (i.e. less than about 50-60 years old) due to recharge. At the same time, the absence of thermonuclear tritium should not be misunderstood as an absence of modern recharge, just older than about 60 years [76].

### 2.4.3. HEAVY METALS

Several researchers have studied the presence of heavy metals in groundwater and its influence to understand the groundwater flow condition and its source of recharge. Few of that are listed in the table 1.

Heavy metals are released from various sources related to natural weathering, industrial, domestic and agricultural activities, which adversely affect environment [77]. The heavy metals infiltrate into the surface water from natural and anthropogenic sources. They generally come from the disseminated elements on the bed sediments during the flow of aqueous solution [78]. 90% of heavy metals in surface water is adsorbed on the suspension and then undergoes sedimentation to bottom sediments [79]. Thus, while the surface water penetrates into subsurface and recharge the groundwater, leads to elevated quantity of heavy metals to that aquifer.

Continuous accumulation of the elements may raise the level of concentration from micrograms per liter (ppb) to milligrams per liter (ppm) [80, 81].

Although there are number of environmental tracers used to identify and estimate the source of groundwater recharge but most of them infiltrate into the groundwater from multiple sources (Table 2).

The contamination of water with potentially toxic heavy metal is a significant environmental issue in both developed and developing countries [93]. Heavy metals released into the water by the weathering process of crust materials [94]. Several heavy metals from agricultural, industrial, domestic and urban wastes may infiltrate into the aquifer through leaching [92]. Due to infiltration/recharge, groundwater contamination occurs largely, thus affecting the drinking water supply of rural and urban areas [95]. The anthropogenic sources such as infiltration from land-use, urban sewage and contaminated water in contact with heavy metals may cause adverse health effects if the water consumed by human beings [96]. Disposal of domestic and municipal sewage, industrial wastes and the chemicals used for agriculture contributes continuous accumulation of heavy metal in groundwater [97].

**Table 1: Studies to identify the sources of recharge by using heavy metals**

| Sl. No | Study | Authors | Year |
|---|---|---|---|
| 1 | Assessment of concentrations of trace elements in ground water and soil at the Small-Arms Firing Range, Shaw Air Force Base, South Carolina | Landmeyer | [82] |
| 2 | Ground Water Recharge Using Waters of Impaired Quality | Clare | [83] |
| 3 | Ba/Sr, Ca/Sr and $^{87}Sr/^{86}Sr$ ratios in soil water and groundwater: implications for relative contributions to stream water discharge | Land et al. | [84] |
| 4 | Identifying and quantifying urban recharge: a review | Lerner | [85] |
| 5 | Groundwater recharge and agricultural contamination | Böhlke | [86] |
| 6 | Geohydrologic framework of recharge and seawater intrusion in the Pajaro Valley, Santa Cruz and Monterey Counties, California | Hanson | [87] |
| 7 | Groundwater recharge history and hydrogeochemical evolution in the Minqin Basin, North West China | Edmunds et al. | [88] |
| 8 | Groundwater flow understanding: from local to regional scale. | Rivera and Guerrero | [49] |
| 9 | Interaction between different water bodies in a small catchment in the Paris basin (Brévilles, France): Tracing of multiple Sr sources through Sr isotopes coupled with Mg/Sr and Ca/Sr ratios. | Brenot et al. | [89] |
| 10 | Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water | Shotyk et al. | [90] |
| 11 | Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water-supply wells. | Ayotte et al. | [91] |
| 12 | A comparison of forest and agricultural shallow groundwater chemical status a century after land use change | Kellner et al. | [92] |

**Table 2: Possible sources of environmental tracers (source: [85])**

| Group of marker species | Potential sources of solutes | | | | | |
|---|---|---|---|---|---|---|
| | Atmosphere | Geological | Agriculture | Mains water | Sewage | Industrial and materials commercial sites |
| Major cations and anions | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| N-species ($NO_3$, $NH_4$) | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Other minor ions | ✓ | ✓ | ---- | ✓ | ✓ | ✓ |
| Heavy metals | ---- | ✓ | ✓ | | ✓ | ✓ |

## 3. MFR ESTIMATION

Mountains are considered as the important source of recharge, since it gets greater amount of rainfall due to orographic effects. The MFR is defined as the amount of water contributed by mountains to the adjacent basin aquifer. Keith [5] has defined the term MFR as recharge to a basin aquifer at the margin of aquifers parallel to the mountain area. It has two components (1) subsurface inflow from the adjacent mountains; and (2) infiltration from streams near the MF [98].

Several previous worldwide studies are available, which have focused on the response of stream flow to the precipitation in humid regions to understand the hydrological processes in the mountains [99]. A few of these also carried out in arid and semi-arid regions [100].

Estimation of MFR has been conducted by several researchers in Tucson Basin of Arizona by comparing the geochemical and isotopic characteristics of mountain precipitation with the groundwater at MF, subtracting ET from the mountain precipitation, chloride mass balance method and determining the empirical relationship existing between the MFR and mountain precipitation. It is inferred that the MFR mainly occurs through (a) the beds of losing streams [101]; (b) the high-permeability montane recharge zones at the interface between crystalline rock of basin-bounding mountains and alluvium in the MF zone [102]; (c) as underflow from adjacent basins [103]; and (d) by infiltration of irrigation and sewage effluent continuously discharged into the Santa Cruz River from multiple waste-treatment facilities [103].

In order to get a clear idea of MFR, some of the hydrologists used major ions as environmental tracer [104] stable isotope, tritium, chloride (e.g. chloride mass balance: CMB) and chloride-36 [105]. The chlorides in semi-arid regions provide better information regarding past climate change as well as the land-use change [105-107]. The increase of MFR in a region is considered as the consequence of land use / cover changes [106].

A pre-monsoon (PRM) data was utilized to identify the process of recharge in MF and RZ [108] along the foothills of Courtallam, Tami Nadu, India. Later northeast monsoon (NEM) water level in conjunction with rainfall and stable isotopes of selected locations along the same region were attempted by Banaja et al. [109] to understand the aquifer response to rainfall. Resistivity survey also carried out by Banaja et al. [110] to delineate the groundwater potential zone along the MF as well as RZ of Couratallam foothills for the establishment of possible well sites. Hydrochemical investigation using PRM data has been carried out along the foothills of Courtallam by Banaja et al. [111] to understand the predominant processes along the MF as well as RZ.

## 4. FR PERSPECTIVES

Generally, MFR studied in one of these two perspectives: (1) The traditional basin-centered view (2) The mountain-centered view (Figure 7)

The basin-centered perspective there should be a boundary condition for the basin aquifers and thus, for this purpose the MF used to be taken as boundary condition to avoid the hydrological complexities above the MF. Hydrochemistry is one of the important basin centered approach to characterize the source and nature of groundwater of the basin.

The mountain-centered methods include the rainfall intensity above the mountains and are considered to be affecting mostly the MFR rates but it does not account the subsurface hydrologic configuration of the mountains. The examples of this method include (1) Comparison of hydrochemical characteristic as well as isotopic behavior of mountain precipitation to that of groundwater of the MF aquifers. (2) The empirical relationship between the precipitation and water level fluctuation and correlate it with the MFR (3) Subtraction of estimated evapotranspiration from the precipitation etc.
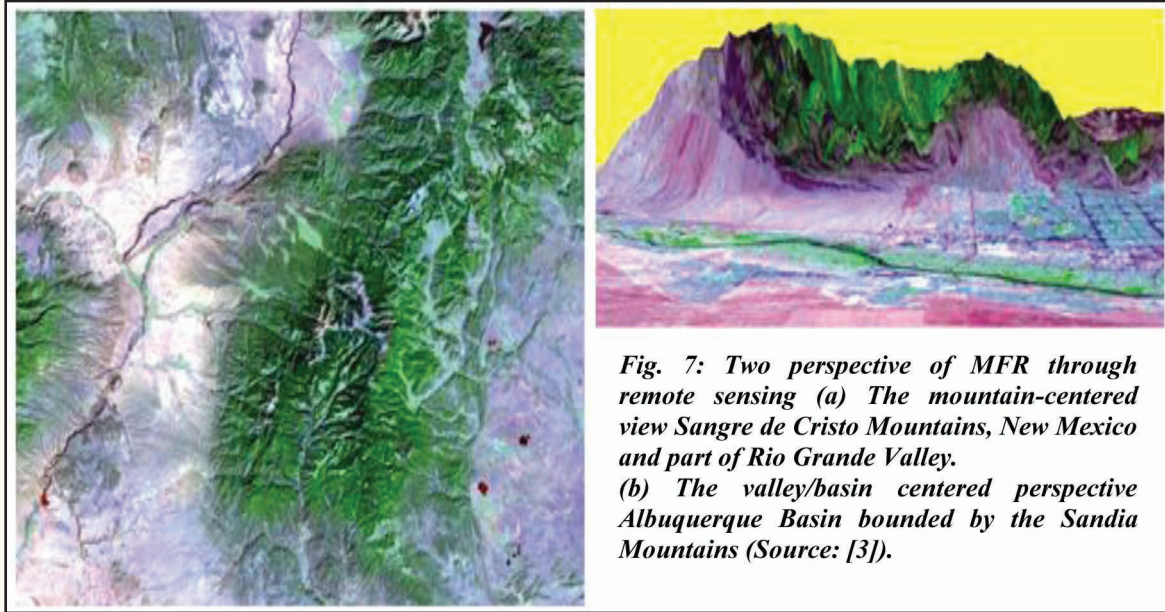
*Fig. 7: Two perspective of MFR through remote sensing (a) The mountain-centered view Sangre de Cristo Mountains, New Mexico and part of Rio Grande Valley.*
*(b) The valley/basin centered perspective Albuquerque Basin bounded by the Sandia Mountains (Source: [3]).*

## 5. Application of Stable isotopes - Case study

Courtallam is located in the northwestern part of Tirunelveli District, Tamilnadu, with an area of 1789 $Km^2$ and falls in between the latitude of 8.834° to 9.328° and longitude of 77.155° to 77.527° (Fig. 8a). These cities offer various facilities for tourists such as hotels, restaurants in addition to buildings and agricultural areas. The mountain front areas are mainly used for agricultural purposes and pastures whereas the hills are dominated by forests. Courtallam has an arid to semiarid climate. The mean air temperature reported by Central Groundwater Board [112] varies from 28 to 37°C.

Courtallam is a hard rock terrain and the major lithological formations includes Charnockite, and Fissile Hornblende Biotite Gneiss (FHBG). There are five major land-use / land-cover patterns were observed i.e. agricultural land, water bodies, waste land, forest and build-up land [109]. About 60% of total area covered with agricultural lands followed by forest (17%) and waste-land (14%). Courtallam is drained by the River Chittar and extends south and north of it to form a part of Chittar, Vaippar and Tamiraparani river basin (Fig 8b). Pediplains are the most prominent geomorphic feature observed along the mountain front. Few places piedmont zone,

structural hills and denudational hills are also found (Fig. 8b).

The region receives normal average rainfall of 917.88 mm/year as reported by CGWB [112]. Out of which 70% is contributed by northeast monsoon and rest by southwest monsoon and few summer showers. Ground water generally occurs under phreatic conditions in the weathered mantle and under semi-confined conditions in the fissured and fractured zones at deeper levels [112]. In the study area, depth to water table varies between 2.1 and 16 m below ground level (bgl) during pre-monsoon while between 0.91 and 16 mbgl during post-monsoon. There are four major types of soils observed in this area i.e. i) Deep Red soil ii) Black Cotton Soil iii) River Alluvium [110]. Deep Red soil are found in Sivakasi, Tenkasi, Senkottai and Sankarankoil blocks and it is suitable for cultivating coconut and palmyrah trees. The Black Cotton Soil is found in Tirunelveli, Palayankottai and Sankarankoil blocks, and it is suitable for cultivating Paddy, Ragi, and Cholam etc. The River alluvial soils occur along the river courses of Tamrabarani and Chittar River covering in the blocks Tirunelveli and Palayankottai and it is suitable for cultivating Groundnut, Chillies and Cumbu.
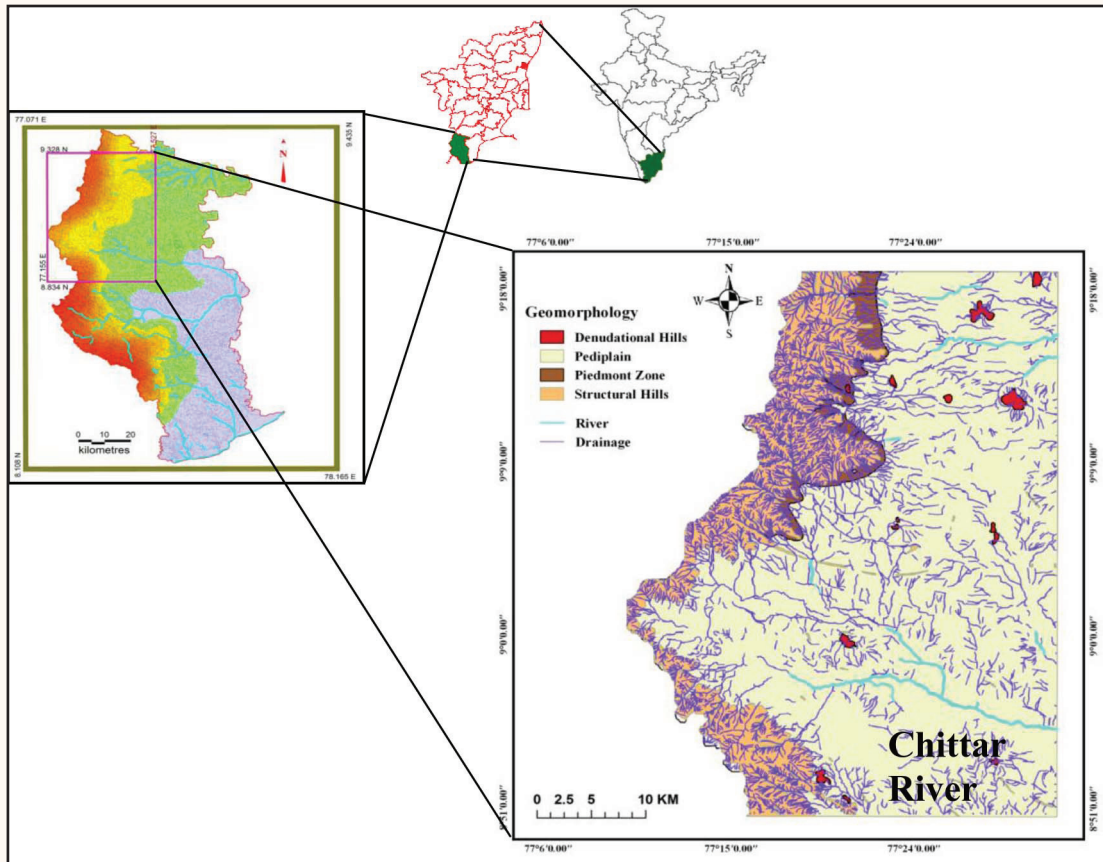
**Fig. 8: Location map of the study area (a) Elevation map (b) Geomorphology, River and Drainage map**

## 6. ENVIRONMENTAL ISOTOPES

Selected samples of PRM season analysed for stable isotopes to understand the nature and source of recharge in both MF and RZ.

Isotopic composition of groundwater of the study area ranges from -2.5 to -12.6‰ for $\delta^{18}O$ and from -91.2 to -15.5‰ for $\delta D$. The local meteoric water line (LMWL), for SWM of Tamil Nadu [113] as well as global meteoric water line (GMWL) by [114] were also plotted in figure 9. Samples fall into two broad clusters, Cluster- A (along with the MF) below the LMWL and Cluster-B (along with the RZ) around the LMWL. A surface water sample which is the representative of waterfalls originating from mountains of the Courtallam region was also plotted in figure 9. Rainwater samples were collected during SWM, was also plotted in the figure 9.

Group A samples can be further categorized into 3 groups, $a_1$: (sample no's. 5, 20, 22, 23 and 41) falling near the rainwater sample, $a_2$: (sample no's. 1, 4 16 and 42) falling below the rainwater sample and $a_3$: (sample no's. 11 and 18) falling above the LMWL (Fig 1). Group ($a_1$) reflects significant impact of local rain events while, group ($a_2$) samples fall below the LMWL and away from the rainwater indicating previous rain events as the source of recharge to these samples. This region also gets significant rainfall during NEM which is characterized by depleted values while isotopic composition of summer monsoon is slightly enriched. In addition to temperature (seasonal effect), amount of precipitation also controls the isotopic composition of the rainwater. The 2015 NEM reported a higher amount of precipitation than the 2016 NEM as observed from the rainfall and water level of this region. The depletion in isotope values of NEM can be attributed to both high amount of rainfall as well as depleted source moisture (Lee and Fung 2008; Deshpande et al. 2003; Sengupta and Sarkar 2006). Group ($a_2$) samples reflect the fact that in addition to local rainfall, the contribution of runoff from high

altitudes of the mountain as subsurface also plays a significant role in aquifer recharge [118,119]. Group (a₃) plot above the LMWL is possibly indicating the influence of rain events occurring at high elevation areas under different wind speeds and temperature conditions [120,121,122].

The group B samples can be further categorized into 3 groups; b₁: (sample no's 2, 7, 33, 35 and 45) falling along the LMWL, b₂: (sample no's 3, 6, 21, 25, 28, 29 and 32) fall in a cluster below b₁ group samples and below the LMWL. The b₃: (sample no's 9, 13, 15, 17, 24, 26, 27 and 30) forming a separate cluster above the LMWL but depleted than b₁ and b₂. Group b₁ plots on the LMWL indicating the recharge is directly from local precipitation [123]. The group b₂ falls below LMWL indicates the recharge is from local evaporated water bodies like open water, i.e., tank/river, agricultural lands and different monsoonal sources. The group b₃ indicates that the source of moisture to these waters is different from foothill samples. A possible source would be recirculated air moisture or a combination of recirculated moisture with monsoonal sources [118,119 122].

Generally, the samples of MF are belonging to modern water or recent recharged type (by considering the tritium values of these locations) as represented in
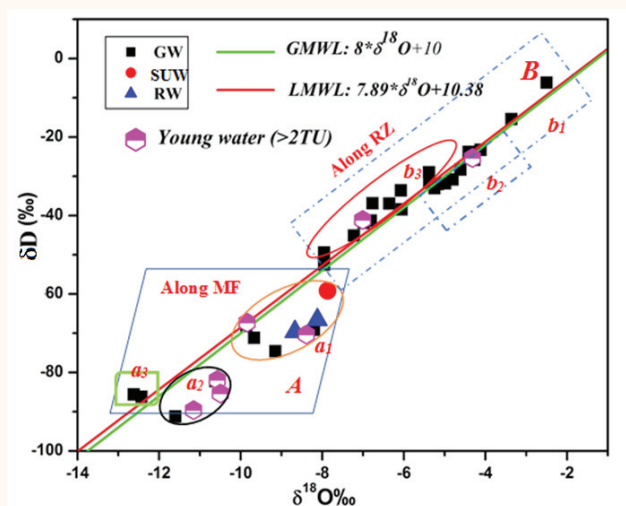


**Fig. 9: Plot of δD vs. δ¹⁸O. LMWL represents the local meteoric water line for rain water samples of south west monsoon in Tamilnadu by Chidambaram et al. (2009). GMWL represents the global meteoric water line by (Craig 1961; Rozanski et al. 1993). GW: groundwater; SUW: surface water; RW: rain water.**

the figure 9. However, it is also interesting to note a few representations of younger water in RZ. This substantiates the fact that there is an inflow of water along the flow direction from MF aquifers to RZ aquifers due to variations in slope gradient and these locations are getting recharged from the foothill aquifers.

## 5. CONCLUSION

MFR plays a significant role for the efficient management of groundwater resource in basin aquifers of arid and semi-arid regions. Thus, the techniques to estimate MFR should be enhanced and upgraded for an effective management of the water resource. As discussed earlier traditionally MFR is estimated by basin-centered approaches which consider the data available in the basin with certain considering the hydrology of MB as well as MF. The estimation of MFR by mountain centered view adopts the consequent equation from the local instrument deployed in the mountain watershed which could not be followed in a global trend if the climate, vegetation or land-use changes because of lack of accuracy. Thus, apart from the traditional basin centered and mountain centered approaches the  new techniques like remote sensing for accessing evapotranspiration, snow cover and land use/cover , DEM and GIS  are all essential to enhance both understanding and characterization of MFR. Geophysical techniques for illustrating geology of the MB and MF as well as the variation of subsurface formation, geochemical and paleo-hydrology approaches (especially environmental tracers) for characterizing water flow paths, source of recharge and residence time distributions, field-sampling and long-term observations of water level fluctuation in accordance to the variation in rainfall pattern are also required to unravel the complexity of MB hydrologic systems to estimate the MFR.

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# Application of stable water isotopes in karst hydrogeology in snow and glacierized catchments of Kashmir Himalayas, India: A review

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## Abstract

*The development of isotope hydrology in Kashmir Himalayas is briefly reviewed. Annual and monthly variabilities of $\delta^{18}O$ and $\delta^2H$ relationships, the altitude effect, the temperature effect and amount effects were calculated. The studies suggested that the western disturbances (WDS) dominantly contribute greater than 70% to the water resources of the Kashmir Himalayas, while as Indian summer monsoons (ISM) contribute less than 30%. It was reported that the depleted isotopic values were observed in the headwaters of the streams/tributaries and enriched values at lower elevations. The stable water isotopic studies of karst springs have suggested that the flow in springs and streams is predominantly controlled by melting of winter snowmelt. The glacier melt contribution to the streams and springs is generally very low. The studies have summarized that the changing climate has a significant effect on the annual discharge of karst springs and isotopic composition of the glaciers. The longer mean residence time (MRT) of stream water was ascribed to complex topography and shorter mean residence time of groundwater is attributed to the significant karstification in the region.*

*Keywords: Kashmir Himalayas, isotope hydrology, karst, stable water isotopes*

## Introduction

Kashmir Valley formed by the bifurcation of Higher Himalayan range west of Ravi, occupies an oval shaped depression between Pir Panjal range to the southwest and much sheared ranges of north Kashmir to the north east located between Latitude 33° 00′ and 34° 30′ N and Longitude 74° 00′ and 75° 30′ E. The average length of Kashmir valley is 140 km and width 40 km, covering an area of 5200 km², with an average elevation of 1850 m [(amsl Fig. 1)]. In Kashmir Valley, the carbonate rocks (Syringothris and Triassic Limestone) provide a significant source of clean and fresh water to the local population in the form of karst springs [1]. It is understood that the karst geo ecosystems are greatly fragile environments that are suffering a progressive degradation caused by human activities [2]. Urbanization, deforestation and quarrying in catchments have disturbed and partially or totally demolished the karst landscape causing variation of the surface and underground drainage system and deterioration in the water quality [3,4].
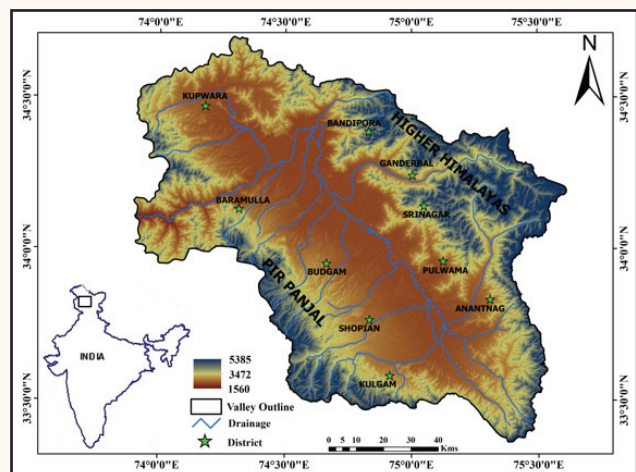


Fig. 1: Kashmir Valley showing altitude and drainage

Keeping in view these facts, it is vital to understand the catchment areas of the karst springs and demarcate the potential recharge sites/areas to prevent and preserve these recharge areas for any contamination to occur. Delineation of recharge areas of karst springs, also referred as capture zones, is critically very important for protection of spring water resources [5], particularly in karst terrains where the aquifers are prone to a greater range of environmental impact problems [6]. Due to numerous meteorological and physiographical effects, the meteoric water at a specific location has atypical isotopic signature that serves as a basis for demarcating the recharge areas of groundwater/spring water. For understanding, the components and mechanism of groundwater recharge, stable water isotopes have been widely used as tracers to recognize the recharge areas [7]. Temporal fluctuations in stable water isotopic values have been used to quantify infiltration rates and categorize primary recharge seasons [8].The meteoric stable water isotopic signature of the groundwater is altered considerably by isotope exchange between groundwater and minerals at elevated temperature. However, at low temperature exchange is low in liquid systems [9]. In carbonate reservoirs at high temperatures, the degree of disequilibrium is high, which yields enriched $^{18}O$ waters. However, in low temperature environments, increased fractionation may yield $^{18}O$-depleted waters [10].Temporal temperature variations and high relief in Kashmir Himalayas produce substantial spatial and temporal variations in the stable isotope composition of oxygen and hydrogen in precipitation, which therefore may serve as an ideal tracer of groundwater/spring water. The present study is proposed to give a brief review on the development of isotope hydrology in Kashmir Himalayas since last 15 years.

**Variation of stable water isotopes in precipitation, streams, snow, glaciers and karst groundwater**

Applications of stable isotopes of oxygen and hydrogen has tremendous significance in water resources development and management, their spatial and temporal variation in precipitation, surface water, groundwater is essential for any hydrological study. Jeelani et al [11-16]and Bhat et al [12]analyzed the stable water isotopes of precipitation in across

Kashmir valley [16] and different watershed [11-15]. They observed the stable isotopic variation of $\delta^{18}O$ and $\delta^2H$ ranged from -2.1 to -10.6‰ [12], -12.98to -0.58‰ [13], 1.7 to -11.1‰[14], -15.6 to -0.1‰ [16] for $\delta^{18}O$ and –12.59 to -60.6 [12], -74.5‰-11.1‰ [13],29 to -67‰[14], -112 to 0.3‰ [16]for $\delta^2H$ respectively. The samples were depleted in $\delta^{18}O$ and $\delta^2H$ at higher elevation and enriched during summer [(11-16, Fig.2)].

The stable isotopic composition showed very good correlation with temperature and precipitation [11-16]. The temporal variations in stable water isotopes of precipitation with depleted and enriched $^{18}O$ and $^2H$ in January-May and July-November except August was ascribed to the temporal changes in ambient temperature, precipitation, the source of moisture and air mass trajectory (Fig.2).The sharp depletion of $^{18}O$ in precipitation along with the decrease in d-excess in August confirm the maximum intrusion of southwest monsoons into the valley [16]. The studies summarized that the stable water isotopes of precipitation are strongly influenced by the basin relief and meteorology [11-15]. Jeelani et al [13, 15] calculated the mean altitude gradient of precipitation as 0.23‰ and 1.2‰per 100 m change in elevation and –0.15‰ and –1.16‰per 100 m change in elevation for $\delta^{18}O$ and $\delta D$ based on amount weighted mean precipitation isotopic composition.
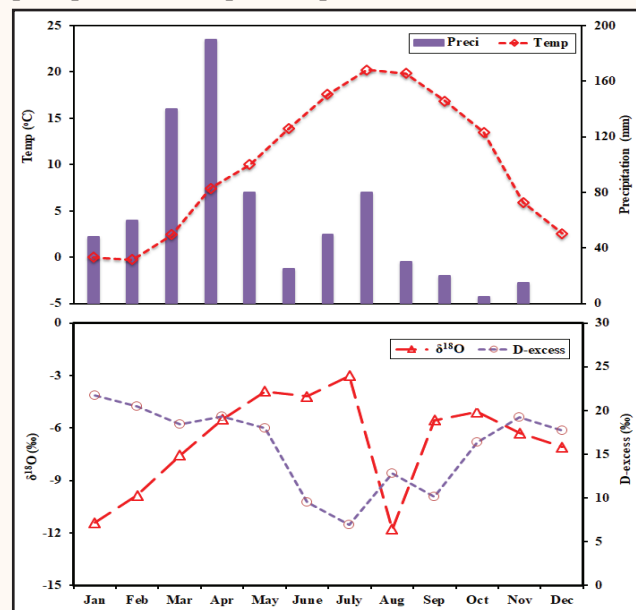


**Fig. 2: Temporal variation of δ$^{18}$O and d-excess in precipitation along with average temperature and precipitation amount in Kashmir Himalayas**

Jeelani and Deshpande [17] studied the isotopic fingerprints of precipitation associated with western disturbances and Indian summer monsoons across the Himalayas. In this study, heavier isotopic values were observed in most of the samples in Jammu, whereas lighter values were observed in the majority of the samples in Uttarakhand. Precipitation at Jammu seems to have undergone intense evaporation while that from Uttarakhand suggest normal Rayleigh fractionation of the air mass as it moves from the source region to the precipitation site and/or orographic lifting. In this study, it was also observed that the d-excess of rainfall in Kashmir has a distinctly higher median value of 18‰ compared to other precipitation sites with a median of 9-12‰. Using discrete isotopic values, the regions receiving precipitation from two different weather systems (western disturbances and Indian summer monsoons) have been identified. These results are very helpful in applying stable water isotopic data to solve hydrological, glaciological and paleo-climatic problems.

Jeelani et al [11, 13, and 14] studied the stable isotopic variation in stream waters in Kashmir Himalayas. The overall $\delta^{18}O$ composition of the stream waters ranged between -11.56‰ -6.92‰ and -5.9 to -11.4‰ [14]. In these studies, it was observed that the streams with their catchments at higher altitudes were more depleted than at lower elevations [11, 13, and 14]. Temporally the streams were most $^{18}O$ and $^2H$ depleted in May and least $^{18}O$ and $^2H$ depleted in September (Fig.3).



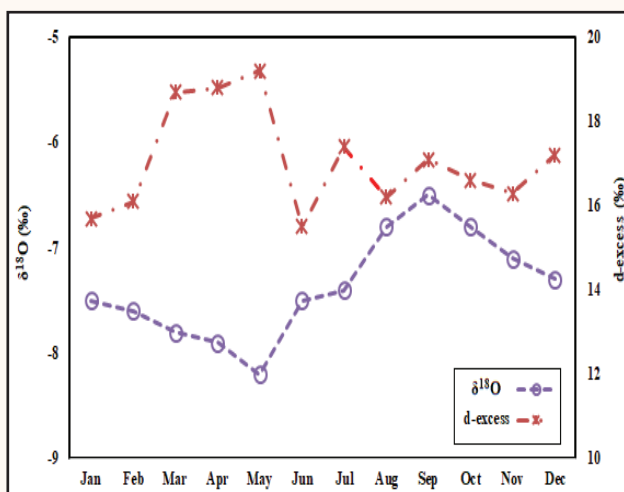**Fig. 3: Mean temporal variation of $\delta^{18}O$ and d-excess in stream waters of Kashmir Himalayas**

Jeelani et al [18] estimated snow and glacier melt contribution to streams in a mountainous catchment using stable water isotopic approach. The study suggested that the stream flow in the spring season is controlled by the snow melt released from low altitudes and becomes isotopically depleted as the melt season advances.

Jeelani et al [14] observed that snow samples taken from the winter-accumulated snowpack's along various transects covered a wide isotopic range, from -5.9 to -11.4‰ in $\delta^{18}O$ and -29.1 to -73.6‰ in $\delta^2H$, with an average of -8.6 and -48‰. Isotopic composition of snow packs showed a substantial correlation ($R^2=0.80$, p=0.005) with altitude. The vertical isotopic gradient of snowpacks ranged from -0.23 to-0.33‰ for $\delta^{18}O$ and -1.5 to -2.9‰ for $\delta^2H$ per 100 m increase in altitude. The vertical isotopic gradient of snowpack's (in ‰/100 m) was slightly higher in Kuthar basin ($\delta^{18}O$: -0.33 and $\delta^2H$: -2.9) than in Bringi ($\delta^{18}O$: -0.23 and $\delta^2H$: -2.1) and Liddar ($\delta^{18}O$: -0.24 and $\delta^2H$: -1.5) basins. The observed isotopic altitude gradient of snowpack's is high erthan that of precipitation in Kuthar and Liddar basins and lower than that of precipitation in Bringi basin. The $\delta^{18}O$-$\delta^2H$ relationship shows that all the snow pack samples fall above the GMWL and close to the LMWL. The LMWL ($\delta^2H = 7.6$ (± 0.2) × $\delta^{18}O$ + 15 (± 1.5); $R^2 = 0.95$) determined for snow packs shows higher slope and higher intercept than LMWL of precipitation, which designates lower condensation temperature and recycled moisture.

Jeelani et al [14] studied the temporal variation of glacier melt in Kashmir valley. It was observed the variation of $\delta^{18}O$ (and $\delta^2H$) was large during the start of melting season ($\delta^{18}O$: -7.1 to-11.3‰ and $\delta^2H$: -34 to -65‰) and lower in peak melting season ($\delta^{18}O$: -12 to -14.9‰ and $\delta^2H$: -68to -102‰). Monthly isotopic values of glacier melt were enriched in May and depleted in September (Fig.4). A substantial correlation ($R^2 = 0.75$; p= 0.002) was observed between the isotopic values of glacier melt and altitude. The estimated vertical isotopic gradient for the glaciers ranged from -0.59 to -0.68‰ for $\delta^{18}O$ and -3 to -4.2 ‰ for $\delta^2H$ per 100 m increase in elevation, which is higher than the vertical isotopic gradients of

snow packs and precipitation in the Liddar basin. Sheshram glacier exhibited lower vertical isotopic gradient ($\delta^{18}O$:-0.68‰/100 m and $\delta^2H$: -4.2‰/100 m) than Kolahoi glacier ($\delta^{18}O$: -0.59‰/100 m and $\delta^2H$: -3‰/100 m). The $\delta^{18}O$-$\delta^2H$ regression equation ($\delta^2H$ = 7.4 (±1) × $\delta^{18}O$ + 13.1 (±1.7);$R^2$ = 0.84) determined for glacier melt displays higher slope than LMWL indicating limited evaporation.

Lone et al [20] evaluated the sensitivity of two glacier-fed basins of western Himalayas to changing climate using stable water isotopes and remote sensing. It was observed that the glacier samples collected from Suru basin were more depleted in $^{18}O$ and $^2H$ (-10.9 to -16.2% and -73 to -128%) than the glaciers of Liddar (-8.2 to -14.9% and -52 to -102%). The d-excess values of the glacier samples in Suru basin were lower (13.5–21.6%) than the glaciers of Liddar basin (17–28%).

Jeelani et al., [11, 20 and 22] studied the stable isotopic variation in karst spring water. The mean annual $\delta^{18}O$ values of the spring waters ranged from -7.48‰ to -9.01‰. It was observed the springs located at the lowest elevation exhibits the most depleted mean annual $^{18}O$ composition and the springs at higher elevations exhibit the least depleted mean annual $^{18}O$ composition [11, 20 and 22]. The oxygen isotope composition of springs was almost similar to that observed in the streams (Fig. 4).
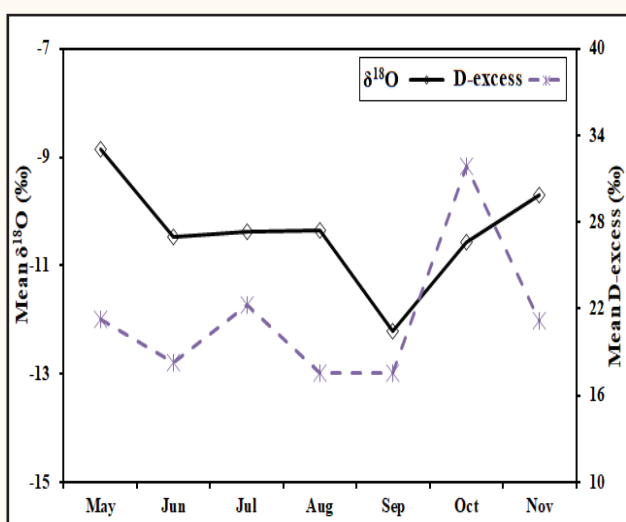


Fig. 4: Plot showing the mean temporal variation of $\delta^{18}O$ in glaciers of Kashmir Himalayas

It was observed the spring water samples were most depleted in heavier isotopes in May and enriched in September. D-excess and $^3H$ corroborate with the stable isotope results that the spring flow in spring season (May) and autumn (September) is dominantly controlled by the melting of winter snowmelt [11, 20 and 22]. The results showed that unlike $\delta^2H$, the $\delta^{18}O$ value in the karst spring waters decreases in January suggesting in to $\delta^{18}O$ shift [20].The karst spring samples fall above LMWL [11] and GMWL indicating the $\delta^{18}O$ shift due to the interaction of groundwater with the host carbonate rocks during its traverse [20]. It was also postulated spring waters bear the isotopic signatures of winter and summer precipitation, which suggests the melting of winter snow melt dominantly controls the flow of springs.

Jeelani et al [15, 18] studied the applications of water isotopes to identify the sources of groundwater recharge in karstified landscapes of western Himalaya. The $\delta^{18}O$ and $\delta^2H$ values of groundwater exhibited a narrow spatial and temporal variation in comparison to precipitation and ranged from –6.8 ‰ to –10 ‰ and –58‰ to –38‰, with an average of –8‰ and–46‰ [15] and -9.3 to -6.8 ‰ and -57 to -43 ‰, with an average of -8.4 and -50 ‰ [18]. The most depleted stable water isotopic values were observed in karst springs and most enriched stable isotopic values were observed in shallow groundwater samples [15].
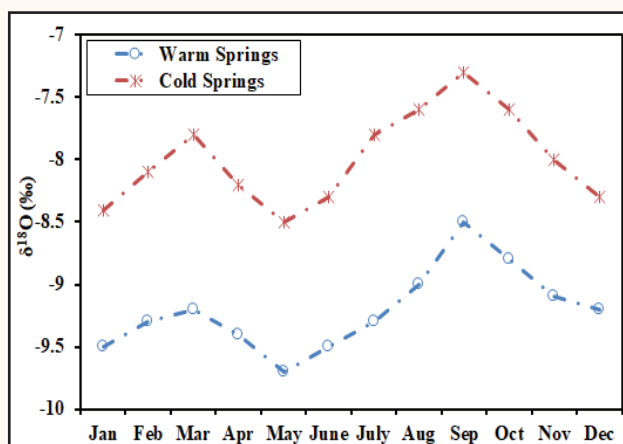


Fig. 5: Temporal variation of $\delta^{18}O$ in Warm and Cold springs of Kashmir Himalayas

The results suggest that the groundwater with most depleted isotopic values have recharge areas at higher altitudes, whereas the groundwater with less

depleted isotopic values has recharge areas at lower elevations [15, 18].This type of hydrogeology is anticipated within the mountainous catchments with heterogeneous secondary permeability. Groundwater did not show temporal variation except in March/April and September. The heavier isotopic values in March/April and September in groundwater may be attributed to the onset of melting (recharge from enriched snowmelt at lower altitudes) and enriched precipitation (recharge from enriched rain). The depleted values in May/June/July (when the discharge of springs is higher) may be ascribed to the melting of accumulated winter precipitation with lighter isotopic values at higher altitudes. Highly depleted isotopes in groundwater in August suggest the recharge from depleted precipitation and glacier melt [18]. Insignificant snow melting and/or glacier melting due to sub-zero ambient temperature and no rainfall during winter (when the spring discharge is minimum) designated the contribution of stored water of the aquifer to stream flow, and the isotopic signature in winter with least spatial variability is therefore a true representative of base flow in mountainous catchment [18].
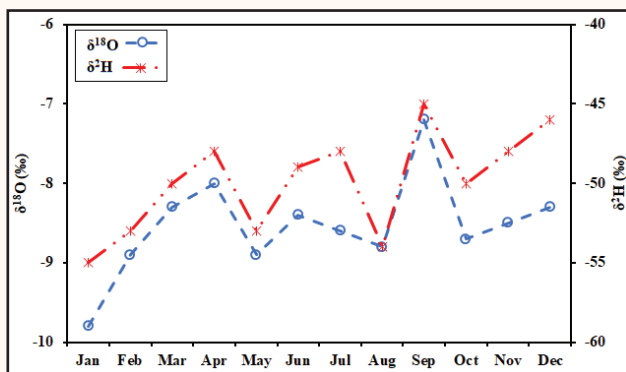


**Fig. 6: Temporal variation of $\delta^{18}O$ and $\delta^2H$ in groundwater of Kashmir Himalayas**

## Sources of streams and karst groundwater

Precise monitoring and proper description of hydrological processes in snow and glacier-dominated basins are challenging but vital for sustainable water-resource management. Stable isotopes have been used to recognize the areas contributing precipitation to groundwater, to comprehend the recharge mechanisms and to identify the sources and origin of surface water

and groundwater. Jeelani et al [13] suggested that the winter precipitation (snow) dominantly contributes the annual stream flow with average snowmelt contribution of about 29%in early spring, 66% in late spring, and 61% in summer while the base flow contribution is found in the order of40% in an autumn season. The application of tracer-based two- and three-component mixing models in Karst springs[22] suggested that the snowmelt predominantly contributes to the spring flow (55–96%), followed by glacier melt (5–36%) and rain (4–34%). Jeelani et al [18] exhibited that the snowmelt contributed a substantial proportion (5–66 %) to stream flow throughout the year with the maximum contribution in spring and summer seasons (from March to July). The study also postulated that in 2013 a large and persistent snowpack contributed considerably (~51%) to stream flow in autumn (September and October) as well. The average annual contribution of glacier melt to stream flow is little (~5 %). However, the monthly contribution of glacier melt to stream flow reaches up to 19 % in September during years of the less persistent snowpack.

## Local Meteoric water line and sources moisture in precipitation

In Kashmir Himalayas, stable water isotopic studies of oxygen and hydrogen in precipitation can be dated a few years back [11]. Since then, precipitation sampling and studies on precipitation in different regions of Kashmir northwestern Himalayas was carried out [12-22]. These studies contributed a lot to understanding the distribution characteristics of stable isotopes in precipitation in Kashmir Himalayas. The local meteoric water line, $\delta^2H = 7.7 \times \delta^{18}O + 11.1$, was obtained towards south Kashmir [12] suggesting a significant secondary evaporation effect on falling rain droplets from cloud base. Jeelani et al [13] established the LMWL for the south Kashmir, based on amount weighted monthly samples as$\delta^2H = 7.59 (\pm 0.32) \delta^{18}O + 11.79 (\pm 2.07) (R^2 = 0.96)$ with lower slope and intercept than GMWL, and LMWL for the western Himalayas indicating the effect of evaporation and/or different sources of moisture. The seasonal regression lines indicate the effect of evaporation with lower slopes and intercepts except in winter. The LMWL based on event-wise precipitation samples obtained

in three glacierized basins [14] is $\delta^2H = 7.1(\pm0.25) \times \delta^{18}O+12$ $(\pm1.2)$ $(n=115, R^2 =0.96, p=0.008)$. The LMWL shows lower slope and higher intercept than the global meteoric water line. The regression line of precipitation from October to May showed lower slope and higher intercept than the GMWL, whereas the regression line of precipitation from June to September showed lower slope and lower intercept than the GMWL.
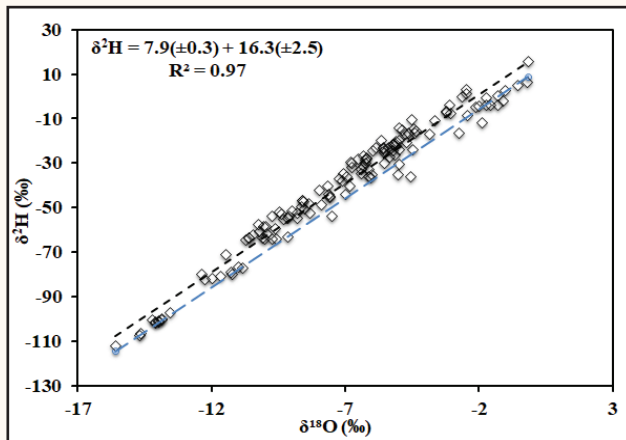


**Fig. 7: Local Meteoric Waterline of Kashmir Himalayas**

Jeelani et al [16] calculated the LMWL for the whole Kashmir valley as $\delta^2H=7.97(\pm0.3) \times \delta^{18}O+16.3(\pm2.5)$ $(n=229, R^2 =0.97, p=0.05)$ (Fig.7)

The higher intercept of the regression equation indicates the dominant contribution of precipitation from western disturbances. The study suggested that the southwest monsoons enter the Kashmir Valley from southwest through the mountainous passes.

The study also summaries that the Kashmir Valley receives heavy precipitation (>71 %) from October to May, when western disturbances are active. However, 29 % of the rainfall from June to September could be due to southwest monsoons, when they are active in most parts of India.

**Mean recharge elevation and spring catchments**

Stable water isotopes have been widely used to as a significant tool in demarcating the recharge areas of aquifers. Bhat et al [12] used stable water isotopes and hydrochemistry to delineate the recharge areas and distinguish the source of karst springs. With the help

of the local vertical isotopic gradient of precipitation ($\delta^{18}O=-0.27‰$ per 100 m increase in elevation), the mean elevation of precipitation that recharged the aquifer was estimated that ranges between 2500 and 2900 m, amsl. Jeelani et al [14] used isotopic data to estimate the mean recharge altitude of the springs in different basins. The mean recharge altitude ranges from 1,800 to 2,000 m amsl for springs in Bringi basin, 3,400 to 3,700 m amsl for springs within Liddar basin, and 2,400–2,700 m amsl for springs located in Kuthar basin. Based on the local vertical isotopic gradient of oxygen the mean altitude of the recharge by rainfall infiltration was estimated which lies between 2600 m and3300 m amsl [11]. The karst and alluvial springs were found to be recharged from higher altitudes and the hard rock controlled springs at lower elevations.

**Mean residence time of streams and karst groundwater/springs**

The stable isotopes have been widely used to identify and/or distinguish the source and pathways of streams and groundwater recharge and to estimate the mean residence time of water in catchments. Jeelani et al [13] studied the mean residences time of stream water and postulated that the mean stream residence times (MRT) of stream waters ranged from 6 to 12.4 months. The longer MRT of stream waters in some catchments is ascribed to larger area and complex topography of Kashmir Himalayas.

Shah et al [23] estimated the mean residence time of karst groundwater in mountainous catchments of the western Himalayas using multiple approaches (Tritium method, the sine wave model and tracer tests). High tritium values were observed in winter precipitation and low values in summer precipitation. The variation of tritium in karst springs was similar to that of the streams, whereas glacier melt showed lower tritium values. The MRT of cold karst springs was shorter than that of warm karst springs. The tracer breakthrough curves (TBC) retrieved for different springs suggested a short travel time for groundwater and possibly conduit flow. Deterioration of water quality and variation in flux magnitude were postulated as two main practical consequences of the short travel time of karst groundwater in the region.

## Lake water budget

Isotopic studies of oxygen and hydrogen played a very important role to determine the lake inflow, studying hydrodynamics of Lake water system and identifying the mixing between different hydrological components. Saleem and Jeelani [24] used the geochemical, isotopic and hydrological mass balance approaches to constrain the lake water-groundwater interaction in Dal Lake, Kashmir valley. Isotopic composition of $\delta^{18}O$ and $\delta D$ indicates that water in the different basins of the lake is significantly influenced by evaporation and shows evaporative enrichment. The groundwater generally shows an average stable isotopic signal of the local precipitation indicating active recharge with an annual average of 10%. The total volume of water in lake varied from $79.11 \times 10^6$ $m^3$ to $56.78 \times 10.^6$ $m^3$. The stable isotopic approach suggested groundwater (flux) contributes major component (23–40%) to lake water budget. It was found that the average groundwater inflow to Dal Lake was $32 \times 10^3$ $m^3$ $day^{-1}$ in winter months and $508 \times 103$ $m^3 day^{-1}$ in summer month with an annual average of $276 \times 10^3$ $m^3$ $day^{-1}$. Uncertainty in precipitation (10%) and evaporation (10%) measurements suggests that groundwater inflow rates may increase or decrease 17 and 14%.

## Climate change impact on glaciers

Stable water isotopic studies played an important role to comprehend and to explore the long-term climatic and hydrological signals under changing climate. It was observed by Lone et al [19] that the temporal changes in weather pattern strongly influence the isotopic composition of the glaciers with progressive decrease and increase in $\delta^{18}O$ and $\delta^2H$ with the increase in ambient temperature and rainfall. The results designate that during the sunny days of August and September, the glaciers are melting at higher altitudes (3900–4172 m) in the accumulation zone, reflecting that the glaciers in Liddar basin are not the perfect sites for paleoclimatological studies.

## Conclusion

In this paper, observational studies of stable water isotopes in different hydrological components were reviewed. The relationships among temperature, precipitation, and stable water isotopes have been used as proxies to understand atmospheric circulation. The stable water isotopic studies of karst springs have revealed that flow in springs is dominantly controlled by melting of winter snow melt. The studies perceived that the changing climate has a significant effect on the annual discharge of karst springs and stable isotopic composition of glaciers. It was also reported that the depleted isotopic values being observed in the headwaters of the streams/tributaries and enriched values at lower elevations. The longer mean residence time of streams, (MRT) was attributed to complex topography. Deterioration of water quality and variation in flux magnitude were postulated as two main practical consequences of the short travel time of karst groundwater.

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