Oxygen and Hydrogen Isotope Systematics for Hydrological Applications

R.D. Deshpande[*]
Physical Research Laboratory, Navrangpura, Ahmedabad, Gujarat India 380 009

Abstract

The study of oxygen and hydrogen isotopic composition of water is a powerful tool to trace the origin and movement of water (and vapour) throughout the hydrological cycle. As H_2O molecules travel through hydrological cycle, various isotopic molecular species, having different isotopic combinations of oxygen (^{18}O and ^{16}O) and hydrogen (^{1}H and ^{2}H or D) in them are differentially partitioned between vapour, liquid and solid phases, imparting distinguishable isotopic signature to all the three phases. This partitioning of isotopes of the same element between two different phases is referred to as isotope fractionation, which is governed primarily by temperature (in case of thermodynamic equilibrium between two phases in contact) and relative humidity (in case of diffusive evaporation). The oxygen and hydrogen isotopic composition is usually expressed in terms of its δ values in per mil (‰ = per thousand) units, which is nothing but per mil deviation of isotope ratios ($^{18}O/^{16}O$ and $^{1}H/^{2}H$ or D) of sample from an international standard reference material.

It is primarily because of the isotope fractionation that various water sources (sea water, atmospheric moisture, rainwater, river water, surface water, groundwater, snow and glaciers), at different geographical locations, have characteristic long terms average isotopic composition ($\delta^{18}O$ and δD) with typical seasonal variations governed by local hydrometeorological and geohydrological processes. The isotope fractionation changes the isotopic composition of a given water source in a predictable manner depending on the extent to which the fractionating process (e.g. evaporation, condensation, rainout, sublimation, vapour deposition etc) has proceeded. Therefore, during a phase change process, it is possible to quantitatively estimate the flux of H_2O molecules across the boundary between the two phases. The isotopic composition of a given H_2O reservoir (e.g. atmospheric moisture, groundwater, river water, sea water) can also change due to mixing of another H_2O flux, of different isotopic composition. In such cases of mixing, no isotopic fractionation is involved, but H_2O flux associated with this mixing process can be estimated quantitatively by isotopic mass balance. Thus, oxygen and hydrogen isotopic composition can be advantageously used as a tool to (i) characterize various H_2O reservoirs within hydrological cycle; (ii) understand subtle hydrometeorological and hydrogeological processes (phase change or mixing); and (iii) quantitatively estimate the fluxes across various reservoir boundaries.

This article discusses some of the fundamental concepts of oxygen and hydrogen isotope systematics and general thumb rules based on which oxygen and hydrogen isotopes are applied in hydrological studies.

---

[*] For Correspondence: desh@prl.res.in

1. Introduction

Among various isotopes used as tracers in hydrology, stable isotopes of oxygen (^{16}O and ^{18}O) and hydrogen (^{1}H and ^{2}H, also known as deuterium; D) are the most important since these isotopes form integral parts of a water molecule. As H_2O molecules travel through hydrological cycle, various isotopic molecules, having different isotopic combinations of oxygen (^{18}O and ^{16}O) and hydrogen (^{1}H and ^{2}H or D) in them are differentially partitioned (fractionated) between vapour, liquid and solid phases, imparting distinguishable isotopic signature to all the three phases. Therefore, oxygen and hydrogen isotopic composition of H_2O molecules forms a powerful tool to trace the origin and movement of water (and vapour) throughout hydrological cycle. Isotope tracing can provide useful insights, in particular, about those subtle hydro-meteorological and hydro-geological processes which can not be studied with common hydrometric approach of measuring volumes or fluxes (rainfall, groundwater level, river water level, reservoir level, river discharge etc).

Detailed understanding of such subtle processes is very important in the present times where hydrological cycle is simultaneously influenced by three forcing factors. These forcing factors are: (i) engineered interventions (construction of dams and inter-basin transfer, rain water harvesting and artificial groundwater recharge, etc); (ii) global climate change due to emission of green house gases and atmospheric aerosols; and (iii) natural climatic variability. The combined hydrological consequences of these three forcing factors are not yet understood very clearly even as extensive monitoring, documentation and research efforts are going on, collectively, under the aegis of the Intergovernmental Penal on Climate Change (IPCC).

Beyond purely academic perspectives, it is also important to fill the existing knowledge gap to more efficiently manage the already stressed water resource scenario of the country and meet the increasing water demand for agricultural, industrial, domestic and livestock requirements (Gupta and Deshpande, 2004; Rakesh Kumar et al., 2005). In such a situation, improved understanding about water related natural processes and their monitoring using isotope approach can be useful to strengthen the water resource development and management strategy and possibly help foresee the undesirable hydrological consequences of global changes based on which appropriate mitigation strategy can be advocated.

Importance of water isotope applications in hydrological investigations have been discussed at length in vast literature based on studies in different parts of the world (Araguas-Araguas et al., 1998; Clark and Fritz, 1997; Dincer et al., 1974; Gat and Matsui, 1991; Gonfiantini, 1986; Kendall and McDonnell, 1998; Rozanski et al., 1993; Salati et al., 1979). Several Indian case studies have also been reported over the last few decades (Bhattacharya et al., 2003; Bhattacharya et al., 1985; Chandrasekharan et al., 1992; Dalai et al., 2002; Das et al., 1988; Datta et al., 1994; Datta et al., 1996a; Datta et al., 1996b; Datta et al., 1991; Deshpande et al., 2003; Deshpande et al., 2011; Deshpande et al., 2010; Gupta and Deshpande, 2003, 2005a, b; Gupta et al., 2005; Krishnamurthy and Bhattacharya, 1991; Kumar et al., 1982; Kumar et al., 2010; Maurya et al., 2011; Navada et al., 1993; Navada and Rao, 1991; Nijampurkar et al., 2002; Pande et al., 2000; Rai et al., 2009; Ramesh and Sarin, 1992; Sarin et al., 1992; Sengupta and Sarkar, 2006;

Shivanna et al., 2004; Shivanna et al., 2008; Sukhija et al., 1998; Warrier et al., 2010; Yadav, 1997). However, even as of today, the isotope application has been the domain of a few leading research institutions in the country, well conversant with this isotope systematics and analytical techniques.

Considering its proven potential as evident from above references, application of oxygen and hydrogen isotopes in hydrological studies should be treated as a useful and necessary tool rather than a fashion or fancy. Realizing the need and potential application of oxygen and hydrogen isotopic monitoring of water sources, a multi-institutional collaborative National Programme on isotope fingerprinting of waters of India (IWIN) is currently underway in which some of the important central agencies, are also participating and getting familiarised with isotope applications ((Deshpande et al., 2011; Deshpande and Gupta, 2008; Deshpande and Gupta, 2009).

With a view to disseminate the working knowledge about oxygen and hydrogen isotope systematics, and highlight and facilitate its practical applications in hydrology, fundamental concepts and general thumb rules are discussed in the following.

2. Isotopes of Oxygen and Hydrogen

The basic fact-sheet of the isotopes of oxygen and hydrogen is given in *Table 1*. The oxygen has three natural stable isotopes (^{16}O, ^{17}O, ^{18}O). The most abundant oxygen isotope (^{16}O) is a principal isotope i.e. formed during stellar evolution, directly by stars that were made exclusively of hydrogen. Most ^{16}O is thus, synthesized at the end of the helium fusion process in stars. Other isotopes of oxygen are secondary isotopes, meaning that their nucleosynthesis requires seed nuclei. The oxygen has fourteen radioactive isotopes but all of them decay in less than 123 seconds with ^{15}O having the longest half-life of 122.24 s; and ^{12}O having the shortest half-life 580×10^{-24} s. The hydrogen has two natural stable isotopes (^{1}H - Protium and ^{2}H - Deuterium) and one natural radioactive isotope (^{3}H - Tritium). There are synthetic radioactive isotopes of hydrogen ^{4}H to ^{7}H with half-lives in the range of 10^{-22} s.

Since oxygen and hydrogen together form a water molecule, isotopes of oxygen and hydrogen are collectively referred to as water isotopes in some literature.

3. Isotopic Molecular Species of Water (isotopologues)

A water molecule is formed by combination of two hydrogen atoms (any two of the two stable isotopes; ^{1}H and D) and one oxygen atom (any one of the three stable isotopes ^{16}O, ^{17}O, and ^{18}O). Thus, 9 possible combinations of these 2 isotopes of hydrogen and 3 isotopes of oxygen are possible, which gives rise to following 9 isotopic molecular species, also referred to as water isotopologues. These 9 possible isotopic molecules of water are: (1) $^{1}H_2{}^{16}O$; (2) $^{1}H_2{}^{17}O$; (3) $^{1}H_2{}^{18}O$; (4) $^{1}HD^{16}O$; (5) $HD^{17}O$; (6) $HD^{18}O$; (7) $DD^{16}O$; (8) $DD^{17}O$; (9) $DD^{18}O$. The four most abundant isotopic molecules of water are given in *Table 2* along with their relative abundance and molecular masses.

Any water or vapour reservoir is basically composed of the above nine isotopologues, with minor variation in relative abundance of these isotopologues, caused by their differential partitioning in two phases during phase change processes within hydrological cycle. Consequently, different hydrological resources (vapour, rain, groundwater, river water, snow, and glacier) have only slightly different isotope abundance ratios ($^{18}O/^{16}O$, $^{17}O/^{16}O$ or D/H). For example, surface water of Arabian Sea may have $^{18}O/^{16}O$ ratio of 0.002006 and that of Himalayan snow may have this ratio of 0.001960. The differences in abundance ratios in various reservoirs are so small that expressing the isotopic composition of various reservoirs in terms of abundance ratios is not practical. Therefore, instead of expressing the isotopic compositions in terms of absolute abundance ratios, it is expressed in terms deviation of abundance ratio from an international standard reference material. The conventional way of expressing isotopic composition is discussed in the following.

Table 1. The fact sheet of isotopes of oxygen and hydrogen (Compiled from (CRC, 1980) and other literature).

Name (Symbol)	Oxygen (O)	Hydrogen (H)
Atomic number	8	1
Standard Atomic Mass	15.9994(3) g/mol	1.00794(7) g/mol
Chemical Series	Non-metals, chalcogens	non-metals
Group, period, block	16, 2, p	1, 1, s
Electronic configuration	$1s^2\ 2s^2\ 2p^4$	$1s^1$
Stable isotopes and their Natural abundance	^{16}O: 99.762% ^{17}O: 0.038% ^{18}O: 0.200%	^{1}H: 99.985% ^{2}H (or D): 0.015%
Isotopic mass	^{16}O: 15.9949146 u ^{17}O 16.9991315 u ^{18}O 17.999160 u	^{1}H (Protium): 1.00782503 u ^{2}H (Deuterium): 2.01410177 u
Abundance ratio	$^{18}O/^{16}O = 0.002004171$ $= 2004.17\times 10^{-6}$	$^{2}H/^{1}H = 0.0001500225$ $= 150 \times 10^{-6}$
Radioactive isotopes	Oxygen has fourteen radioactive isotopes from ^{12}O to ^{15}O and from ^{19}O to ^{28}O All radioactive isotopes have half-life less than 3 minutes	Hydrogen has one radioactive isotope ^{3}H (tritium) With half-life of 12.32(2) years, which β- decays to ^{3}He.

Table 2. The four most abundant isotopologues of water and their molecular masses.

Isotopologue	$H_2{}^{16}O$	$H_2{}^{18}O$	$H_2{}^{17}O$	$HD^{16}O$	$D_2{}^{16}O$
Relative natural abundance	99.78%	0.20%	0.03%	0.0149%	0.022 ppm
Molecular mass	18	20	19	19	20

4. Expressing Isotopic Composition

Isotopic compositions are normally expressed in δ–notation, as deviations of heavy to light isotopic ratios relative to an international standard of known composition, in units of parts per thousand or per mil (denoted as ‰). The isotopic composition in terms of δ values can be calculated using following equation.

$$\delta(\text{in ‰}) = \left[\frac{R_{\text{Sample}}}{R_{\text{S tan dard}}} - 1\right] \times 1000 \qquad (1)$$

In the above equation, R_{sample} and R_{standard} denote the ratio of heavy to light isotope (e.g. $^{18}O/^{16}O$ or D/H) in the sample and standard respectively. The oxygen and hydrogen isotopic compositions are normally referred to as δD and $\delta^{18}O$. Both, δD and $\delta^{18}O$ values, are usually reported relative to an international standard reference material such as SMOW (Standard Mean Ocean Water; (Craig, 1961b) or the equivalent VSMOW (Vienna-SMOW; (Gonfiantini, 1978)).

The SMOW defined by Craig (1961b) never existed physically. It was hypothetical water calibrated relative to the isotopic content of NBS-1, a sample from the Potomac River catalogued by former NBS. The $^{18}O/^{16}O$ ratio in SMOW was 1.008 times that in NBS-1 and the $^{2}H/^{1}H$ ratio in SMOW was 1.050 times that in NBS-1. Subsequently, the IAEA prepared the standard water from distilled sea water that was modified to have an isotopic composition close to SMOW. This reference was identified as VSMOW (Vienna Standard Mean Oceanic Water). The values of measured abundance ratios ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) in SMOW and VSMOW are given in *Table 3*.

Table 3. Measured abundance ratios in international standard reference material

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

To understand how δ values are calculated from ratios, one can do the following simple exercise. If the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios in a sample are given to be 0.0020104 and 0.00015735 respectively, its oxygen and hydrogen isotopic compositions ($\delta^{18}O$ = 2.59‰ and δD = 10.27‰) with respect to VSMOW can be easily calculated using Equation (1) and the isotopic ratios for VSMOW, as given in *Table 3*.

In addition to the commonly used SMOW and VSMOW, there are two more international standard reference materials, namely, SLAP (Standard Light Antarctic Precipitation) and GISP (Greenland Ice Sheet Precipitation). The oxygen and hydrogen isotopic compositions of SLAP and GISP are given in *Table 4*.

Table 4. The oxygen and hydrogen isotopic compositions of SLAP and GISP

Standard Light Antarctic Precipitation (SLAP)	**Greenland Ice Sheet Precipitation (GISP)**
$\delta^{18}O_{SLAP}$ = –55.50‰ VSMOW	$\delta^{18}O_{GISP}$ = –24.76‰ VSMOW
δD_{SLAP} = –428.0‰ VSMOW	δD_{GISP} = –189.5‰ VSMOW

5. Isotope Fractionation

During any phase change process, the heavier (e.g. $H_2{}^{18}O$ and $HD^{16}O$) and lighter ($H_2{}^{16}O$) isotopologues of water are differentially partitioned between the two interacting phases due to the differences in physical properties of various isotopologues. Consequently, the heavy and light isotopes are also differentially partitioned betweens two phases. This differential partitioning of isotopes between the two phases is known as the isotope fractionation. Fractionation can, thus, be visualized as ratio (Phase 1/Phase 2) of isotope abundance ratio (heavy/light) between the two phases. Some times the term isotope discrimination is also used to convey the isotope fractionation, although fractionation is more commonly used.

The isotope fractionation takes place due to the fact that although chemical properties of various isotopologues of water are identical, their physical properties (bond strength, rotational, vibrational and translational frequencies, density, vapour pressure, collision frequency etc) are different due to their mass differences. Though difference in physical properties of various isotopologues is very small, it is large enough to cause the measurable difference in the abundance ratio of these isotopes in the two phases, using sensitive mass spectrometers.

The mass differences between isotopologues of water directly influence their mobility, diffusive velocity, collision frequency and binding energy. Two important controlling factors for fractionation, namely, temperature and diffusive velocities are discussed in the following.

5.1 Effect of temperature

At a given temperature, all isotopologues have similar kinetic energy ($kT = ½mv^2$; where k = Boltzmann constant, T = absolute temperature, m= molecular mass, v = average molecular velocity). Since heavier isotopologues have higher mass, their velocity is smaller and consequently their mobility is less at molecular level. Thus, heavier isotopologues have lower velocity compared to lighter isotopologues. Due to their lower velocity, collision frequency of heavier isotopologues is smaller. Due to smaller collision frequency, rate of chemical reaction is smaller for heavier isotopologues whereas lighter isotopologues react faster. In case of equilibrium conditions, this mass dependent velocity differences affect the equilibrium fractionation in an indirect way, via its effect on bond strength and not directly as in case of diffusivity related fractionation (see section 5.2).

Due to their mass difference, the heavier isotopologues have greater binding energy compared to lighter isotopologues. The difference in the strength of bonds formed by the light versus heavier isotopes of a given element is the basis for isotope fractionation. This difference in binding energy can be understood with a simple potential energy distribution model of the relationship between potential energy of a molecular bond and inter-atomic distance for heavy and light isotopes of a molecule. The two oppositely charged particles in a molecule experience competing forces. One of these is the repulsive force which rapidly increases with decreasing distance ($\sim 1/r^{13}$). Another is the attractive force which increases less rapidly with decreasing distance ($\sim 1/r^2$ in ionic crystals; $\sim 1/r^7$ between uncharged particles). Balanced by these two competing forces, the two particles will be located at an ideal inter-atomic distance from each other depending on the net attractive force between the two. Therefore, it will require additional energy either to push the atoms together or separate them. The energy required to break apart the molecules is referred to as dissociation energy (also known as binding energy or bond strength) and differs for isotopically different molecules. The heavier isotope will have stronger bond and require more energy to dissociate compared to lighter isotope.

Even at absolute zero temperature (-273.15°C) particles will have certain minimum energy called zero-point energy which decides three modes of motion of a molecule –rotation (of the molecule around certain molecular axes), translation (displacement of the molecule as a whole) and vibration (vibrations of the atoms in the molecule with respect to each other). The zero-point energy for lighter isotopes will be more than heavier isotopes. The heavier particle has smaller zero-point energy and is located deeper in the potential energy well than the lighter particle. Consequently, the heavier particle requires more energy to escape from the potential energy well, or in other words has greater binding energy. Thus, heavier isotopes get preferentially enriched in the phase in which their binding energy is higher.

With increase in temperature, relatively smaller energy is required for breaking the bond, and hence bonds can break more easily at higher temperature than at lower temperature; thought bonds of lighter molecules continue to break more easily compared to heavier irrespective of temperature. Thus, with increasing temperature, fractionation continues but magnitude of fractionation decreases. In other words, at higher temperature the substance is less fractionated compared to at lower temperature.

From the perspectives of statistical mechanics, strong temperature dependence of fractionation can also be understood in terms of partition function (Q) which describes the statistical properties of a system in thermodynamic equilibrium. The partition function is a function of temperature of the system, mass of the molecule, symmetry of the molecule and the summation of energy states from zero-point energy to the energy of dissociated molecule. The dissociation energy of a molecule is related to its partition functions which are based on three molecular movements (rotational, translational and vibrational) or energy frequencies. The partition function can be defined for each of these three molecular movements, and is given by:

$$Q = \sigma^{-1} m^{3/2} \sum e^{-E/kT} \qquad (2)$$

In Equation(2), s is a symmetry value; m is mass; E is the energy state (Joul.mole^{-1}), k is the Boltzmann constant (JK^{-1}) and T (K) is the temperature in Kelvin.

The partition functions are defined for each isotopic molecular species in a given isotope exchange reaction at a given temperature. Since translational and rotational frequencies for isotopic species are nearly identical, it is only the differences in vibrational frequencies which cause effective partition of isotopes in two phases. The total partition function ratio for light and heavy isotopes is given by:

$$\left(\frac{Q^*}{Q}\right)_{total} = \left(\frac{Q^*}{Q}\right)_{trans} \times \left(\frac{Q^*}{Q}\right)_{rota} \times \left(\frac{Q^*}{Q}\right)_{vibra} \qquad (3)$$

In Equation(3), * indicates heavy isotope.

The equilibrium fractionation, defined as ratio of isotope abundance ratio of one phase to another, is then nothing but the ratio of partition functions for heavy to light molecular species in one phase to another, as given by:

$$\frac{(\text{isotope abundance ratio})_x}{(\text{isotope abundance ratio})_y} = \frac{\left(Q_x^* \big/ Q_x \right)}{\left(Q_y^* \big/ Q_y \right)} \qquad (4)$$

5.2 Effect of diffusive velocities

In addition to the differences in bond-strength which cause isotope fractionation under equilibrium conditions, differences in diffusive velocities of molecules is another physical parameter which causes isotope fractionation particularly in case on systems not in equilibrium. Isotope fractionation due to difference in diffusive velocities corresponds to the ratio of diffusive velocities which in turn relate to the reduced mass of the isotopic molecule. A system in which a gas or solute diffuses through another medium, the mass of the medium also needs to be taken into account by incorporating reduced mass instead of just molecular mass of the species which is diffusing. The reduced mass is the effective inertial mass of the molecule in a two component system (e.g. diffusion of water vapour through air). The reduced mass μ is given by:

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} \qquad (5)$$

In Equation(5), m refers to molecular mass of various isotopic species, M refers to the molecular mass of the medium through which diffusion occurs and μ is the reduced mass.

The fractionation due to differences in diffusive velocities can then be calculated using following equation:

$$\text{Diffusive Fractionation} = \frac{v^*}{v} = \frac{\sqrt{\frac{kT}{2\pi m^*}}}{\sqrt{\frac{kT}{2\pi m}}} \sqrt{\frac{\mu}{\mu^*}} \qquad (6)$$

In Equation(6), v is the molecular velocity of isotopic molecule, μ refers to the reduced mass, k is Boltzmann constant, T is absolute temperature and * refers to heavy isotopic molecular species.

5.3 Equilibrium and Kinetic Fractionation

The isotope fractionation can occur due to: (i) physicochemical reactions under equilibrium condition; (2) physicochemical reactions under non-equilibrium condition; and (3) molecular diffusion. In the first case, reactant and product interact for sufficiently long duration so that isotopic equilibrium is established. In the second case, sudden change in temperature or addition or removal of product or reactant prevents the isotopic equilibrium in a given physicochemical reaction. In the third case, product under isotopic equilibrium is slowly diffusing out of the product reservoir but the product reservoir may remain in isotopic equilibrium with large reservoir of reactant. Although these three types of fractionating processes are known to occur, for all practical purposes, fractionations are conveniently grouped in to two major classes namely, equilibrium and kinetic. Isotopic fractionation can occur during: (i) equilibrium isotopic exchange reactions and (ii) non-equilibrium (kinetic) processes.

5.3.1 Equilibrium Fractionation

Equilibrium exchange reactions involve thermodynamic equilibrium between the two phases during a phase change process during which redistribution of the isotopes between the two phases (products and reactants) takes place. When forward and backward rates of phase change reaction are equal the thermodynamic equilibrium is said to have been attained. The equilibrium fractionation is primarily governed by the binding energy of the isotopologues in two phases. Since the binding energies depend on temperature, the equilibrium fractionation depends on temperature. The heavier isotopologues, gets concentrated in the phase in which they have greater binding energy. As a 'rule of thumb', among different phases (vapour, liquid, solid) in which H_2O can exist, the denser the phase, the more it tends to be enriched in the heavier isotopes (D and ^{18}O).

The natural example of an equilibrium fractionation is vapour to liquid phase change in cloud, where liquid phase remains in contact with surrounding vapour and is believed to have attained the isotopic equilibrium with vapour phase, before it rains out from the cloud.

5.3.2 Non-equilibrium or kinetic fractionation

In systems out of equilibrium, forward and backward reaction rates are not identical, and isotope reactions become unidirectional and irreversible. This can happen due to sudden change in temperature or sudden addition or removal of product or reactant. Under these circumstances, relative amount of the reactant or product suddenly changes and hence the two can not attain thermodynamic equilibrium with each other. Isotope fractionation due to such reactions is called non-equilibrium or kinetic fractionation. Although this is a non-equilibrium fractionation, it still strongly depends on temperature, like equilibrium fractionation.

Natural example of this type of fractionation is sudden uplift of warm vapour loaded air mass and resultant cloud burst; immediate removal of vapour emanating from water bodies (lakes, flowing rivers, surface water spread for irrigation etc) due to strong winds etc.

5.3.3 Diffusive fractionation

Fractionation due to differences in diffusive velocities is a variant of the non-equilibrium or kinetic fractionation. In this case, different isotopic molecules diffuse out of the bulk reservoir, with different diffusive velocities. Actually, the reservoir from which the molecules diffuse out should become progressively enriched in molecules with lower diffusive velocities (see section 5.2). However, if the system, from which molecules are diffusing out, is being continuously replenished while in equilibrium with parent reservoir, it is possible to establish a steady-state diffusion regime such that steady state is maintained in isotopic composition of the bulk reservoir from which molecules are diffusing out. In other words, even though outgoing flux has different isotopic ratio than the bulk reservoir, isotopic composition of the bulk reservoir remains the same. Unlike the kinetic fractionation caused by sudden temperature change or sudden addition / removal of mass, which has strong temperature dependence, the diffusive fractionation is strongly governed by diffusive velocities and has only slight temperature dependence, which is for all practical purposes can be ignored in actual calculations of fractionation factors. The diffusive fractionation is also referred to as transport fractionation in some literature.

Natural scenarios where diffusive fractionation occurs are evaporation from open water body and diffusion of vapour from surface of water to air above.

In isotope hydrology, the most accepted model for non-equilibrium evaporation from a water body involves diffusion of water vapour across a hypothetical microns thin boundary layer over the liquid water interface. The boundary layer has virtually 100% water saturation. This layer is in isotopic equilibrium with the underlying water column. Between the boundary layer and the mixed atmosphere above is a transition zone through which water vapour is transported in both directions by molecular diffusion. It is within the transition zone that non-equilibrium fractionation arises due to the fact that diffusive velocity of ${}^{1}H_2{}^{16}O$ in air is greater than that of ${}^{2}H^{1}H^{16}O$ or $H_2{}^{18}O$.

The vapour over ocean is isotopically depleted with respect to ocean water and the total fractionation is the sum of: (i) the equilibrium fractionation between ocean water and thin boundary layer; and (2) the diffusive fractionation between boundary layer and mixed atmospheric air above.

6. Terminologies symbols related to Isotope Fractionation

There is considerable variety in the terminologies, symbols and approaches that can be used to express the same phenomenon - fractionation. Therefore, it is important to be familiar with different approaches of expressing fractionation.

The isotope fractionation is mathematically expressed by the ratio of abundance ratios of the heavy/light isotope for reactant and product ($\alpha = R_{reactant} / R_{product}$ or $R_{product} / R_{reactant}$) and is referred to as the fractionation factor (α). For example, in case of water-vapour system in equilibrium, the fractionation factor is given by;

$$^{18}\alpha\,(\text{water} - \text{vapour}) = \frac{\left[\dfrac{^{18}O}{^{16}O}\right]_{\text{Water}}}{\left[\dfrac{^{18}O}{^{16}O}\right]_{\text{Vapor}}} \qquad (7)$$

The definitions of both the terms α and δ involve the abundance ratios for heavy to light isotopes. Therefore, α and δ are related by following equation.

$$\alpha_{x-y} = \frac{1+\frac{\delta_x}{1000}}{1+\frac{\delta_y}{1000}} = \frac{1000+\delta_x}{1000+\delta_y} \qquad (8)$$

The isotope fraction effects are usually very small in magnitude and therefore fractionation factor α (= $R_{reactant}/R_{product}$ or $R_{product}/R_{reactant}$) always has values very close to unity. However, depending on (i) whether product becomes isotopically depleted or enriched compared to reactant, during the fractionation process; and (ii) the way in which the fractionation factor is expressed (i.e. $R_{reactant}$ / $R_{product}$ or $R_{product}/R_{reactant}$), the fractionation factor (α) can be slightly greater or smaller than 1. For example, the $^{18}O/^{16}O$ ratio in water is always greater than that in vapour in equilibrium with it, and hence value of $^{18}\alpha$ expressed as R_{water} / R_{vapor} will be greater than 1 (e.g. 1.00937 at 25°C; (Majoube, 1971)). However, if expressed as R_{vapor} / R_{water}, value of $^{18}\alpha$ will is 0.990717. Similarly, the $^{18}O/^{16}O$ ratio in water is always smaller than that in ice in equilibrium with it, and hence the value of $^{18}\alpha$ expressed as R_{water} / R_{ice} will be less than 1 (e.g. 0.996905 at 0°C; (Majoube, 1971; O'Neil, 1968)). However, if expressed as R_{ice} / R_{water}, value of $^{18}\alpha$ will is 1.00310. Craig and Gordon (1965) had introduced a convention of using different symbols to clarify how the fractionation factor has been expressed [$\alpha^* > 1$ and $\alpha^+ < 1$ such that $\alpha^* = 1/\alpha^+$] (Gat, 1996). However, this convention was not adopted by successive researchers. Instead, various researchers adopted their own styles and specified it in their papers.

Since values of α are very close to 1 and differ only at 4th decimal place, another numerical term ε [$= (\alpha - 1) \times 1000$] is defined to comprehend the fractionation in a manner corresponding to the definition of δ. The term ε is referred to as “fractionation” rather than “fractionation factor”. Some times ε is also referred to as the “enrichment factor” or just “enrichment”. The +ve values of ε convey enrichment of heavier isotopes and –ve values of ε convey depletion. It must, however, be noted that in some literature $\alpha - 1$ is not multiplied by 1000.

The terms α and ε are related to the abundance ratios for heavy to light isotopes and can be expressed by following equation.

$$\varepsilon_{x-y} = (\alpha - 1).10^3 = \left(\frac{R_x}{R_y} - 1\right).10^3 \qquad (9)$$

To convey the fractionation which occurs under non-equilibrium conditions, often some prefix or subscript is used such as Δε, ε_{kin}, α_{kin} etc.

Based on the definition of δ, another term isotope separation (Δ) is also used to convey the difference in isotopic composition of any two substances, such that:

$$\Delta_{x-y} = \delta_x - \delta_y \qquad (10)$$

In view of this multitude of expressions, one needs to be careful while using the equations presented in different papers, for their calculations.

7. Calculating the Values of Fractionation Factors

7.1 Equilibrium fractionation factor

In principal, the equilibrium fractionation factor can be theoretically calculated from partition functions using Equations(2), (3) and (4), provided sum over the all energy states (which involves probabilistic statistical mechanics) can be accurately ascertained. Several researchers have experimentally determined the values of equilibrium fractionation factors for different phases of water (solid, liquid and vapour), at different temperatures, by controlled experiments (Arnason, 1969; Craig and Gordon, 1965; Kakiuchi and Matsuo, 1979; Majoube, 1971; O'Neil, 1968; Suzuoki and Kumura, 1973). These values may differ slightly from one another due to differences in experimental setups.

Based on the regression of most of the experimental values reported in literature, following equations for determining the equilibrium fractionation factor (α) between the liquid and vapour phase, at a given temperature (K) is proposed by Horita and Wesolowski (1994) for oxygen (Equation (11)) and hydrogen (Equation (12)) isotopes.

$$10^3 \ln \alpha_{(l-v)}(^{18}O) = 6.7123\left(\frac{10^3}{T}\right) - 1.6664\left(\frac{10^6}{T^2}\right) - 7.685 + 0.35041\left(\frac{10^9}{T^3}\right) \quad (11)$$

Equation(11) is valid from 0°C to the critical temperature of water (374.1 °C) within ±0.11(1σ).

$$10^3 \ln \alpha_{(l-v)}(D) = 1158.8\left(\frac{T^3}{10^9}\right) - 1620.1\left(\frac{T^2}{10^6}\right) + 794.84\left(\frac{T}{10^3}\right) - 161.04 + 2.9992\left(\frac{10^9}{T^3}\right) \quad (12)$$

Equation(12) is valid from 0°C to the critical temperature of water (374.1 °C) within ±1.2(1σ) (n = 157).

The fractionation terms in Equations (11) and (12) is expressed as $10^3 \ln\alpha$ because of the fact that trend line between α and absolute temperature has a polynomial form which produces a linear graph when $\ln\alpha$ is plotted against the inverse of temperature. However, $\ln\alpha$ is nearly zero, so multiplying by 1000 (i.e. $10^3 \ln\alpha$) offers a quantity which corresponds to δ in per mil units. The values of $10^3 \ln\alpha$, fractionation factor α, and enrichment ε calculated using Equations (11) and (12) for a range of temperatures are given in *Table 5*.

From the forgoing one can notice that various terms (fractionation factor α, enrichment ε, isotopic composition δ, isotope separation Δ and $10^3 \ln\alpha$) express the isotope fractionation and can be interchangeably used in calculations, after proper conversion. However, fractionation factor α (or $10^3 \ln\alpha$) is the only fundamental parameter which is derived theoretically or experimentally. All other terms involve mathematical approximations and can slightly differ numerically. These differences can be ignored when fraction effect is small. However, when fractionation is large these numerical differences are pronounced and can yield erroneous results. In such case it may be necessary to use $10^3 \ln\alpha$ instead of ε in the calculations.

Table 5. Values of $10^3 ln\alpha$, fractionation factor α, and enrichment ε calculated using Equations (11) and(12).

Temp. °C	$10^3 \ln\alpha^{18}$	$^{18}\alpha$	$^{18}\varepsilon$	$10^3 \ln\alpha^2$	α^2	ε^2	$\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}}\right)$
0	11.75	1.0118	11.82	105.96	1.1118	111.78	9.0
5	11.19	1.0113	11.25	99.00	1.1041	104.06	8.8
10	10.67	1.0107	10.73	92.54	1.0970	96.96	8.7
15	10.18	1.0102	10.24	86.55	1.0904	90.40	8.5
20	9.73	1.0098	9.78	80.97	1.0843	84.34	8.3
25	9.30	1.0093	9.35	75.79	1.0787	78.74	8.1
30	8.90	1.0089	8.94	70.96	1.0735	73.54	8.0
40	8.17	1.0082	8.20	62.24	1.0642	64.21	7.6
50	7.51	1.0075	7.54	54.61	1.0561	56.13	7.3
60	6.93	1.0069	6.95	47.90	1.0491	49.07	6.9
70	6.40	1.0064	6.42	41.98	1.0429	42.88	6.6
80	5.92	1.0059	5.93	36.74	1.0374	37.42	6.2
90	5.48	1.0055	5.49	32.07	1.0326	32.59	5.9
100	5.08	1.0051	5.09	27.90	1.0283	28.29	5.5

7.2 Kinetic fractionation factor

Calculating the values of kinetic fractionation factor, either theoretically or experimentally, is not as straight forward as calculating equilibrium fractionation factor. This is because the two possible scenarios, (see section 5.3.2 for temperature change or addition / removal mass; and section 5.3.3 for diffusion) are difficult to experimentally evaluate and requires to be modelled separately. The most useful and exhaustive model for estimating isotope fractionation during evaporation is that proposed by Craig and Gordon (1965), which is based on Langmuier linear resistance model for evaporation and has stood the test of the time (Craig and Gordon, 1965; Gat, 1996). In addition, isotope effects during diffusive evaporation for surface water bodies have been experimentally and theoretically examined by other workers (Clark and Fritz, 1997).

It is important to understand why humidity is so critical in determining the kinetic fractionation factor. Using molecular masses of various isotopic molecular species of water (m: $H_2{}^{18}O$ = 20; $HD^{16}O$ =19; $H_2{}^{16}O$ =18) and that of air (M: 28.8 for 79% N_2 and 21% O_2) in Equations(5) and (6), one can calculate kinetic fractionation factors for oxygen and hydrogen, due to diffusion of vapour from microns thick boundary layer at the air-water interface into well mixed atmospheric air above. This calculation yields kinetic fractionation factor $^{18}\alpha_k = 1.0323$ and $^{2}\alpha_k = 1.0166$. These fractionation factors translate into $\Delta\varepsilon^{18} = 32.3‰$ and $\Delta\varepsilon^2 = 16.6‰$. Such extreme fractionation is never observed in nature because these theoretical calculations are based on dry air, with humidity = 0. In nature, however, relative humidity is rarely close to 0 therefore, relative humidity needs to be incorporated in the calculation of fractionation factor. The isotopic enrichment ($\Delta\varepsilon$) of evaporating water due to kinetic fractionation at relative humidity (h; fractional) can be approximated by the two empirical relationships that ignore all other controlling factors except the humidity (Gonfiantini, 1986).

$$\Delta\varepsilon^{18}O_{(bl\text{-}v)} = 14.2\times(1-h)\,‰ \qquad (13)$$

$$\Delta\varepsilon^{2}H_{(bl\text{-}v)} = 12.5\times(1-h)\,‰ \qquad (14)$$

These equations provide only approximate value of enrichment because other factors such as surface temperature, wind speed, salinity of water etc are ignored.

It is seen from the above equations that relative magnitude of kinetic fractionation for oxygen isotopes is greater than that for hydrogen isotopes, whereas in case of equilibrium condition fractionation for oxygen is lower than that for hydrogen.

The total fractionation between water column and open air is the sum of the enrichment factor for equilibrium water vapour exchange ($\varepsilon_{l\rightarrow v}$) and the kinetic factor ($\Delta\varepsilon_{bl\text{-}v}$). For ^{18}O, this would be:

$$\delta^{18}O_l - \delta^{18}O_v = \varepsilon^{18}_{(l-bl)} + \Delta\varepsilon^{18}_{(bl-v)} \qquad (15)$$

The RHS in Equation (15) indicates the total fractionation (equilibrium + kinetic) during evaporation. Because the boundary layer is at 100% saturation, $\varepsilon^{18}O_{l\rightarrow bl}$ corresponds to equilibrium fractionation between water and vapour. Under conditions of 100% humidity (h = 1), the vapour is in isotopic equilibrium with seawater ($\Delta\varepsilon^{18}O_{bl\text{-}v} = 0$). When humidity is low the vapour is strongly depleted in ^{18}O compared to D, resulting in excess deuterium over ^{18}O.

The kinetic fractionation can also occur during vapour deposition (vapour to solid condensation) under supersaturated condition, due to differences in diffusive velocities through air layer supersaturated with vapour. The kinetic fractionation factor in such cases can be estimated using following equation (Jouzel and Merlivat, 1984):

$$\alpha_{kin} = \frac{S_i}{\left[\alpha_{equ}\times\frac{D}{D'}\times(S_i-1)\right]+1} \qquad (16)$$

In Equation(16), D and D’ refers to diffusive velocities of light and heavy isotope, S_i refers to saturation index (actual vapour pressure/ saturation vapour pressure) which in such cases is <1.

8. Rayleigh Distillation

The rain (or snow) is prodiced when an air mass containing vapour cools. The cooling occurs by (i) adiabatic (without loss of heat) expansion as the warm air rises to lower pressure; or (ii) radiative loss of heat. When the temperature of the air parcel drops below the dew point (temperature at which relative humidity is 100%) vapour condenses in to liquid (rain) or snow (solid), in order to maintain the thermodynamic equilibrium at that temperature. The vapour and condensate remain in an intimate contact at a given temperature in the cloud. If the temperature drops further, condensation of vapour proceeds further and if temperature increases, the evaporation of liquid or snow occurs. The first condesantes are tiny particles which float and remain in close contact with vapor under equilibrium. When tiny particles coalesce and sufficiently massive particle is formed, it begins to fall under gravity. This is how we receive rain on ground.

During equilibrium condensation at prevalent in-cloud temperature, isotopic molecular species (see section 3) differentially partition between vapor and liquid (or solid) phase such that more condensed phase is always enriched in heavier isotopes and vapor is depleted in heavier isotopes. Thus, with progressive rainout along the wind trajectory from marine vapor source region into continental interiors, the remaining vapor becomes progressively more and more depleted in heavier isotopes. At every stage of rainout, the condensate is always enriched in heavier isotopes compared to vapor. Since vapor is progressively depleted at successive stage of rainout, the resultant rain at succesive stage is also isotopically depleted.

One can model isotope evolution during rainout according to Rayleigh distillation equation:

$$R = R_0 f^{(\alpha - 1)} \qquad (17)$$

The Rayleigh equation gives isotopic ratio (R) of a vapour reservoir progressively diminishing in its mass due to outflux by condensation, at an instance when residual fraction (f) of the original reservoir with isotope ratio (R_0) has diminished from initial value $f = 1$ to a value $f < 1$, with α being the equilibrium fractionation factor at temperature at which condensation takes place. The Rayleigh equation can also be expressed in the form of δ-notation, in which R and α are translated into δ and ε respectively.

$$\delta = \delta_0 + \varepsilon \ln f \qquad (18)$$

In Equation (18), δ refers to instantaneous isotopic composition of progressively diminishing vapor reservoir at an instance when residual fraction (f) of the original reservoir with isotopic composition δ_0 has diminished from initial value $f = 1$ to a value $f < 1$, with ε being equilibrium enrichment at temperature at which condensation takes place.

The Equation (18) is useful for theoratical estimation of isotopic variation at succesive stages of condensation or evaporation under equilibrium condition. However, in natural situations, the application of Rayleigh equation is more complex due to the fact that non-equilibrium fractionation effects are involved (mainly during evaporation) and the mass and the isotopic composition of residual vapor reservoir may be altered due to addition of secondary vapor flux by evapotranspiration.

The effect of the admixture of evapotranspiration flux on the isotopic composition of the downwind atmospheric vapour and subsequent precipitation depends on the details of the evapotranspiration process. Transpiration returns precipitated water essentially un-fractionated back to the atmosphere, despite the complex fractionation in leaf water (Forstel, 1982; Zimmermann et al., 1967). Thus transpiration, by returning vapour mass with isotopic composition R_V (= R_l/α) in the downwind direction, in a way restores both the vapour mass and the heavy isotope depletion caused by the rainout in such a way that the next rainout event is not as depleted as it would have been without the transpiration flux. Under such circumstances, the change in the isotopic composition along the air mass trajectory is only due to the fraction ‘f_{net}’, representing the net loss of water from the air mass, rather than being a measure of the integrated total rainout. This causes apparent reduction in the downwind isotopic gradient. The evaporated water, on the other hand, is usually depleted in heavy species relative to that of transpired vapour, thus restoring the vapour mass to the downwind cloud but reducing its isotopic composition. This may cause apparent increase in the downwind isotopic gradient.

9. Global Meteoric Water Line (GMWL)

Craig (1961a) for the first time showed that in spite of the great complexity in different components of the hydrological cycle, $\delta^{18}O$ and δD in fresh surface waters (representing precipitation) correlate on a global scale. The regression line between $\delta^{18}O$ and δD is referred to as meteoric water line. Craig's global meteoric water line (GMWL) defines the relationship between $\delta^{18}O$ and δD in global meteoric water (i.e. derived from precipitation) as:

$$\delta D = 8 \times \delta^{18}O + 10 \ \left(‰ \ \mathrm{SMOW}\right) \qquad (19)$$

It must be noted that Craig’s GMWL is based on fresh surface water and not the actual precipitation.

Improving the precision of the Craig’s GMWL, Rozanski et al.(1993) compiled the isotope data of precipitation from 219 stations of the IAEA/WMO operated Global Network for Isotopes in Precipitation (GNIP). This refined relationship between ^{18}O and D in global precipitation (*Figure 1*) is given by:

$$\delta D = 8.17\left(\pm 0.07\right) \times \delta^{18}O + 11.27\left(\pm 0.65\right) \ \left(‰ \ \mathrm{VSMOW}\right) \qquad (20)$$

The $\delta^{18}O$-δD regression equation of *Rozanski et al.*(1993) is based on actual precipitation whereas that of *Craig* (1961a) was based on fresh surface waters.

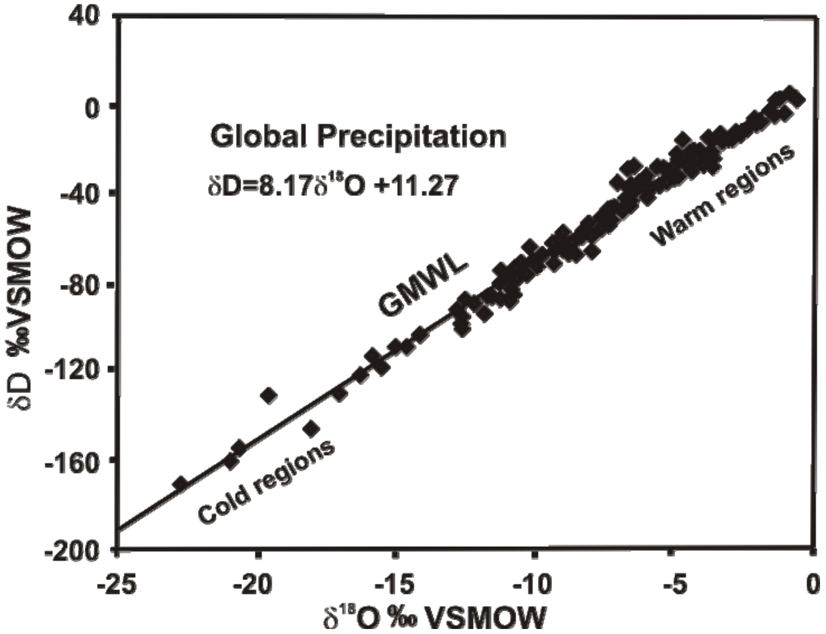

Figure 1. The linear regression line between δ^{18}O and δD of global precipitation samples. Data are weighted average annual values for precipitation monitored at 219 stations of IAEA/WMO global network. Redrawn from Rozanski et al (1993).

The GMWL indicates that the isotopic composition of meteoric waters behave in a fairly predictable fashion. The GMWL is average of many local or regional meteoric water lines, which may differ somewhat in slope and intercept from each other due to varying climatic and geographic parameters. A Local Meteoric Water Line (LMWL) can differ from global line in both slope and deuterium intercept. Nonetheless, GMWL provides a reference for interpreting the hydrological processes and provenance of different water masses.

There are specific reasons why the slope of the GMWL is around 8 and deuterium intercept is around 10. Further, the δ^{18}O-δD regression lines for local precipitation (LMWL) and for any other H_2O reservoir can differ from GMWL in slope and intercept. This deviation of slope and intercept from that of GMWL provides important insights about the hydrometeorological processes operating in a given geographical region or at a given time.

In order to understand why the slope of GMWL is around 8 and what does it signify, the following exercise may be necessary.

Analogous to Equation(18), following two equations can be set up for oxygen and hydrogen isotopes.

$$\delta^{18}O = \delta^{18}O_0 + \left({}^{18}\varepsilon \times \ln f \right) \qquad (21)$$

$$\delta D = \delta D_0 + \left({}^{2}\varepsilon \times \ln f \right) \qquad (22)$$

By eliminating the term ln f, following equation can be derived:

$$\delta D = \delta^{18}O \times \left(\frac{^{2}\varepsilon}{^{18}\varepsilon} \right) + \left[\delta D_0 - \delta^{18}O_0 \times \left(\frac{^{2}\varepsilon}{^{18}\varepsilon} \right) \right] \qquad (23)$$

Equation (23) is a straight line (y = mx+c) in the coordinates of δ^{18}O and δD, which is nothing but the GMWL. It can be noticed by comparing Equations(19) or (20) with (23) that the slope of the regression lines correspond to ratio $\left({}^{2}\varepsilon / {}^{18}\varepsilon \right)$ i.e. the ratio in which ^{18}O and D are partitioned between vapour and liquid phases during condensation. From *Table 5* it is seen that at 25°C temperature the ratio $\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}} \right)$ has a value of 8.1, nearest to the slope of GMWL. This, however, is just a close approximation. In fact, the ratio $\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}} \right)$ varies only narrowly between 8 at 30 °C and 9 at 0°C (see *Table 5*. Therefore, the slope 8 of GMWL only signifies the ratio of fractionation for hydrogen and oxygen under equilibrium condition which is around 8. It is important to understand that the slope 8 of GMWL does not signify condensation temperature of ~25°C, but it conveys that the condensation is largely under equilibrium.

The intercept of GMWL on the other hand signifies the non-equilibrium fractionation during formation of vapour. If only equilibrium fractionation was prevalent in nature, the intercept of the δ^{18}O-δD regression should have a value of 0. This is because, under equilibrium condition (such as during condensation of vapour in cloud), $\delta D_0 = \delta^{18}O_0 \times \left(\frac{^{2}\varepsilon}{^{18}\varepsilon} \right)$ and therefore, GMWL should have intercept value of 0 and should have passed through origin $\left[\delta D_0 - \delta^{18}O_0 \times \left(\frac{^{2}\varepsilon}{^{18}\varepsilon} \right) = 0 \right]$. However, the GMWL has an intercept of ~10, which signifies that original vapour parcel is formed under the condition in which $\left(\frac{10^3 \ln\alpha^2}{10^3 \ln\alpha^{18}} \right)$ is considerably different from 8, which means that kinetic fractionation is effective during evaporation from the oceans. The evolution of δ^{18}O and δD values of meteoric waters begins with evaporation from the oceans, where the rate of evaporation controls the water - vapour exchange and hence the degree of isotopic equilibrium. Increased rates of evaporation impart a kinetic or non-equilibrium isotope effect to the vapour. Kinetic effects are influenced by surface temperature, wind speed (shear at water surface), salinity and, most importantly humidity. At lower values of humidity, evaporation becomes an increasingly non-equilibrium process.

9.1 The deuterium excess (*d*-excess)

The observed intercept of the GMWL was advantageously used by Dansgaard, (1964) to define a parameter (*d*-excess), which can be calculated for individual pair of δ^{18}O and δD using following equation.

$$d\text{-excess} = \delta D - 8 \times \delta^{18}O(‰) \qquad (24)$$

The basic premise behind defining such a parameter is that whenever kinetic fractionation is involved, the net ratio of fractionation for deuterium to oxygen is different from 8. This is because, unlike equilibrium fractionation, the magnitude of kinetic fractionation for oxygen is more than that for hydrogen $\left[\frac{\Delta\varepsilon^{2}H_{(bl\text{-}v)}}{\Delta\varepsilon^{18}O_{(bl\text{-}v)}} \approx 0.88\right]$(see Equations (13) and (14)). Since ^{18}O is more fractionated compared to ^{2}H due to kinetic fractionation during evaporation, the liquid phase is relatively more enriched in ^{18}O compared to ^{2}H. Consequently, the resultant vapour is relatively more enriched in ^{2}H compared to ^{18}O, due to kinetic effects. These isotope imprints of kinetic evaporation can be easily detected in the *d*-excess. The average *d*-excess of meteoric waters is ~10‰. As a thumb rule, the *d*-excess of water decreases if it undergoes kinetic evaporation and consequently the *d*-excess of resultant vapour correspondingly increases.

It is must be understood that deuterium excess (*d*-excess) and the deuterium intercept of δ^{18}O-δD regression lines are two different parameters and should not be confused while interpreting the data set. While deuterium intercept is the property of a dataset under investigation the *d*-excess can be calculated for individual pair of δ^{18}O-δD. Therefore, based on *d*-excess, individual sample can be separately interpreted whereas intercept is not useful for individual sample. In fact, a set of samples defining a regression line intercept can have very different *d*-excess values.

The *d*-excess as defined above represents the excess δD than 8 times δ^{18}O for any water or vapour sample. Since magnitude of equilibrium fractionation for D is about 8 times that for ^{18}O, any value of δD in vapour, in excess of 8 times δ^{18}O signifies the effect of kinetic fractionation due to evaporation. As mentioned earlier, the intercept (~10‰) of GMWL also signifies the kinetic fractionation during evaporation but the difference between intercept and *d*-excess is that the intercept of a meteoric or any other water line is valid for an entire dataset whereas, the *d*-excess parameter can be calculated for a single water sample whose δD and δ^{18}O values are known.

As the evaporation proceeds, because of relatively higher enrichment of ^{18}O in the residual water, the *d*-excess of the evaporating water body decreases and that of the resulting vapour increases. Therefore, if the original water was meteoric in origin, the residual water not only gets enriched in heavier isotopes but also shows progressively lower *d*-excess values as the evaporation proceeds i.e. its position on the δ^{18}O – δD plot will be below the Local Meteoric Water Line. The resulting vapour on the other hand shows the opposite effect. Further, since condensation is an equilibrium process (with slope ~8), it does not significantly alter the *d*-excess until significant rainout occurs from the same vapour parcel. Thus, *d*-excess provides an additional handle on identifying vapours of different histories and their mixing. Due to the effect of evaporation, most meteoric and subsurface processes shift the $\delta^{18}O$–δD signatures of water to a position below the LMWL. It is rare to find precipitation or groundwater's that plot above the LMWL, i.e., showing higher *d*-excess. However, in low-humidity regions, re-evaporation of precipitation from local surface waters and/or soil water/ water table creates vapour masses with isotopic content that plots above the LMWL. If such vapours are re-condensed in any significant quantity before mixing with the larger tropospheric reservoir, the resulting rainwater will also plot above LMWL, along a condensation line with slope ~8. It is however, important to recall that recycling of water back to the atmosphere in the form of vapour from soil moisture by plant transpiration is a non-fractionating process that does not affect the *d*-excess.

A small fraction of rain percolates down through the soil layer eventually to become groundwater. For many ground waters, their isotopic composition has been shown to equal the mean weighted annual composition of precipitation (Bhattacharya et al., 1985; Douglas, 1997; Hamid et al., 1989; Krishnamurthy and Bhattacharya, 1991) (Rank et al., 1992). However, significant deviations from precipitation are also found in several cases. Such deviations from local precipitation are more pronounced in arid zones due to extensive evaporation from the unsaturated zone or even evaporative losses from water table (Allison et al., 1984; Dincer et al., 1974). Considering that only a small percentage of precipitation actually reaches the water table in most situations, the meteoric signal in ground water can get significantly modified. Isotope variations in precipitations get attenuated and seasonal biases in recharge are imparted to the newly formed ground water. This bifurcation of the hydrological cycle between precipitation and surface water on one hand and groundwater on the other hand, ends where groundwater discharges and rejoins surface runoff in streams and rivers. Thus, oxygen and hydrogen isotopes can play a significant role in quantifying relative contribution of groundwater to stream flow and in understanding the hydraulic processes operating in a catchment area.

10. Interpretative Significance of slope, intercept and *d*-excess

In order to understand the interpretative significance of various isotopic parameters it is necessary to visualize how various theoretical concepts and equations discussed in the forgoing can be practically used and how it would manifest in the data under a given hypothetical condition.

For example, let us begin with tropical ocean surface water with isotopic composition of $\delta^{18}O = 0‰$ and $\delta D = 0‰$. This is indeed a very close approximation to real situation. Suppose evaporation is taking place at 25 °C temperature and under the relative humidity of 85%. Using Equations (11) and (12) one can calculate $^{18}\varepsilon$ and $^{2}\varepsilon$ values (9.37‰ and 79.3‰ respectively) for 25 °C. Using Equations (13) and (14) one can also calculate $\Delta^{18}\varepsilon$ and $\Delta^{2}\varepsilon$ values (2.13‰ and 1.88‰ respectively) for relative humidity of 85%. The effective total fractionation ($\varepsilon + \Delta\varepsilon$) can be calculated as the sum of the two types of fractionations, as given in the RHS of Equation (15). Thus the approximate isotopic composition of ocean vapour can be estimated as $\delta^{18}O = -11.5‰$ and $\delta D = -81.21‰$. Using the Rayleigh distillation equation in δ notations, as given in Equation (18), one can compute the evolution of the isotopic composition of vapour as it rains out progressively. Correspondingly, one can also estimate the instantaneous isotopic composition of rain in equilibrium with vapour at each stage. The evolution of isotopic composition of vapour and rain, as a function of fraction of original vapour remaining at successive stage of rainout, is shown in *Figure 2*. Important point to be noticed here is that with successive rainout, both the vapour and the rain diminishes in its heavier isotope content as reflected in progressively decreasing $\delta^{18}O$ and δD values. It is also seen that the *d*-excess also decreases with progressive rainout.

This example is just for visualization of isotopic variations. In reality, situations are more complex than simple addition of equilibrium and kinetic fractionation. Formation of atmospheric vapour is a more complex process involving mixing between evaporated water vapour and residual atmospheric water vapour following condensation and rain over sea (Craig and Gordon, 1965). According to the Craig and Gordon (1965) model mass is conserved such that net evaporation equals net precipitation and the mean isotopic composition of outgoing oceanic vapour equals the global mean for precipitation.

As an example, the effect of relative humidity on isotopic evolution of water during evaporation is shown in *Figure 3*. The isotopic evolution of a hypothetical water sample ($\delta^{18}O = -4‰$ and $\delta D = -22‰$; *which is also the mean global precipitation value according to Craig and Gordon (1965) Model*) on the GMWL, as it evaporates under two different Rh regimes (100% and 10%), but at the same temperature (30ºC), can be computed using Equations (11), (12), (13), (14), (15) and (18). As shown in *Figure 3*, the water evolves along a line with very low slope and intercept values in case of 10% Rh. However, in case of 100% Rh, water evolves along a line which has slope value slightly greater than GMWL. This simple exercise conveys why lower slope value of any data set is usually ascribed to evaporation.

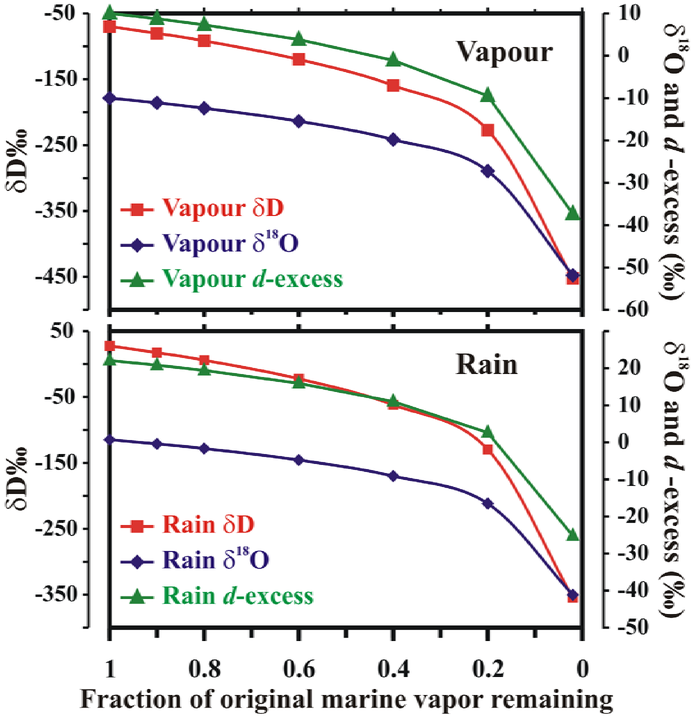

Figure 2. Isotopic evolution of vapour and rain as a function of fraction of original marine vapour remaining at successive stages of rainout.

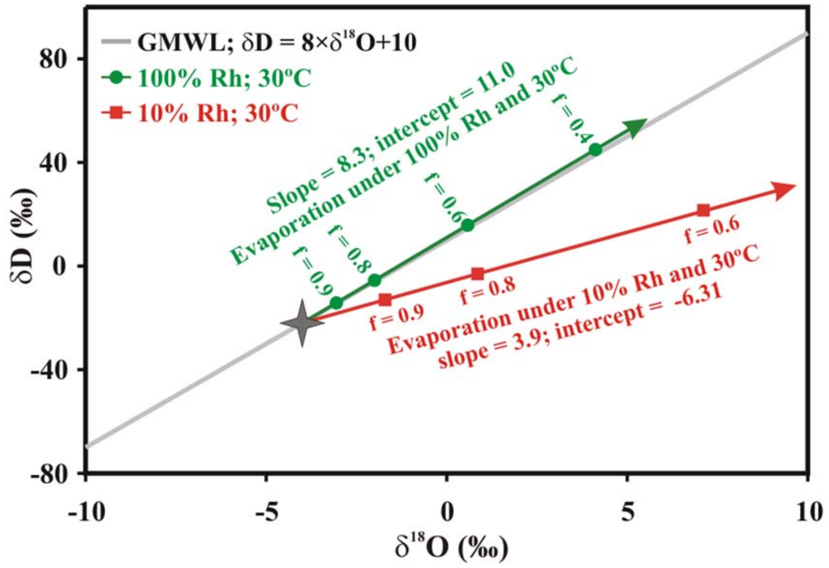

Figure 3. Isotopic evolution of water ($\delta^{18}O$ = –4‰ and δD = –22‰ under different relative humidity conditions but at the same temperature.

These simple fractionation processes are at the core of some of the interpretative aspects.

The slope and intercept of δ^{18}O-δD regression lines for a set of samples and *d*-excess of individual water sample can provide some useful hydrological insights. If the slope of δ^{18}O-δD regression line for a set of samples is less than that of GMWL it is an indication that the water under consideration has undergone certain degree of evaporation. Lower the slope greater the evaporation. The intersection point of LMWL and GMWL is indicative of the average isotopic composition of precipitation at that location. Intersection point of LMWL and δ^{18}O-δD regression line for groundwater is indicative of the average isotopic composition of the surface water from which the groundwater is recharged.

The intercept of the δ^{18}O-δD regression line can provide useful hydrological insights, only if the slope of the regression line is ~8. If the slope is much different from ~8 the intercept can not be assigned any interpretative significance. If the slope of LMWL is ~8 and intercept is >10‰ it is an indication that precipitation is derived from vapour which is produced by kinetic evaporation under considerably lower relative humidity. For example, the Eastern Mediterranean Water Line (EMWL) defined by Gat and Carmi (1970) has slope = 8, but intercept = 22.

The *d*-excess is the most useful parameters in deriving hydrological insights from water isotope data. Lower than average *d*-excess of a rainwater sample could be due to evaporation from falling raindrops or it could as well signify considerable rainout from original marine vapour parcel. Higher (than average) *d*-excess in a particular rainwater sample signifies either formation of marine vapour parcel under lower (than average) relative humidity (for e.g. from Mediterranean Sea) or contribution of recycled vapour from continental areas for that particular event. It may be possible to rule out one the two possible interpretations in case of both high or low *d*-excess values if the *d*-excess value of a sample is interpreted in combination with δ^{18}O or δD values. For example, if lower *d*-excess values are associated with significantly higher δ^{18}O values, it indicates the evaporation from falling rain drops because, as discussed earlier, evaporation causes decrease in *d*-excess and increase in δ^{18}O or δD values. On the other end, considerable rainout from a given vapour parcel results in progressive decrease in both *d*-excess and δ^{18}O.

References

Allison, G. B., C. J. Barnes, M. W. Hughes, and F. W. J. Leaney, 1984, Effects of Climate and Vegetation on Oxygen-18 and Deuterium Profiles in Soils, Isotope Hydrology 1983, IAEA Symposium 270: Vienna, IAEA, p. 105-123.

Araguas-Araguas, L., K. Froehlich, and K. Rozanski, 1998, Stable isotope composition of precipitation over Southeast Asia: Journal of Geophysical Research, v. 103, p. 28721-28742.

Arnason, B., 1969, Equilibrium constant for the fractionation of deuterium between ice and water: J. Phys. Chem., v. 73, p. 3491-94.

Bhattacharya, S. K., K. Froehlich, P. K. Aggrawal, and K. M. Kulkarni, 2003, Isotope variation in Indian monsoon precipitation: records from Bombay and New Delhi: Geophys. Res. Lett., v. 30, p. 2285, doi:10.1029/2003GL018453, 2003.

Bhattacharya, S. K., S. K. Gupta, and R. V. Krishnamurthy, 1985, Oxygen and hydrogen isotopic ratios in groundwaters and river waters from India: Proc. Indian Academy of Sciences (Earth and Planetary Science), v. 94, p. 283 – 295.

Chandrasekharan, H., K. S. Sunandra Sarma, D. K. Das, D. Datta, P. Mookerjee, and S. V. Navada, 1992, Stable isotope contents of perched water under different land use and salinization conditions in the canal command of Arid western Rajasthan: Journal of Arid Environments, v. 23, p. 365–378.

Clark, I. D., and P. Fritz, 1997, Environmental Isotopes in Hydrogeology: Boca Raton, Lewis, 328 p.

Craig, H., 1961a, Isotopic variations in meteoric waters: Science, v. 133, p. 1702-1703.

Craig, H., 1961b, Standards for reporting concentrations of deuterium and oxygen-18 in natural waters: Science, v. 133, p. 1833.

Craig, H., and L. I. Gordon, 1965, Deuterium and oxygen-18 variations in the ocean and marine atmosphere, *in* E. Tongiorgi, ed., Stable isotopes in Oceanography Studies and Paleotemperatures: Pisa, Italy, Report CONS. Naz. delle Ric. Lab. di Geol. Nucl., p. 9-130.

CRC, 1980, CRC handbook of chemistry and physics: Boca Raton, Florida, CRC Press, Inc.

Dalai, T. K., S. K. Bhattacharya, and S. Krishnaswami, 2002, Stable Isotopes in the Source Waters of the Yamuna and Its Tributaries: Seasonal and Altitudinal Variations and Relation to Major Cations: Hydrological Process, v. 16, p. 3345-3364.

Dansgaard, W., 1964, Stable Isotopes in Precipitation: Tellus, v. 16, p. 436–438.

Das, B. K., Y. P. Kakar, M. H., and W. Stichler, 1988, Deuterium and oxygen-18 studies in groundwater of the Delhi area, India: Journal of Hydrology, v. 98, p. 133-146.

Datta, P. S., S. K. Bhattacharya, P. Mookerjee, and S. K. Tyagi, 1994, Study of groundwater occurrence and mixing in Pushkar (Ajmer) valley, Rajasthan, with d18O and hydrochemical data.: Journal Geological Society India, v. 43, p. 449–456.

Datta, P. S., S. K. Bhattacharya, and S. K. Tyagi, 1996a, 18O studies on recharge of phreatic aquifers and groundwater flow-paths of mixing in the Delhi area: Journal of Hydrology, v. 176, p. 25-36.

Datta, P. S., D. L. Deb, and S. K. Tyagi, 1996b, Stable isotope (^{18}O) investigations on the processes controlling fluoride contamination of groundwater: Journal of Contaminant Hydrology, v. 24, p. 85–96.

Datta, P. S., S. K. Tyagi, and H. Chandrasekharan, 1991, Factors controlling stable isotopic composition of rainfall in New Delhi, India: Journal of Hydrology, v. 128, p. 223-236.

Deshpande, R. D., S. K. Bhattacharya, R. A. Jani, and S. K. Gupta, 2003, Distribution of oxygen and hydrogen isotopes in shallow groundwaters from Southern India: influence of a dual monsoon system: Journal of Hydrology, v. 271, p. 226-239.

Deshpande, R. D., M. Dave, S. R. Laxmi, and S. K. Gupta, 2011, IWIN National Programme: New Hydrological Insights: Fourteenth ISMAS Symposium cum Workshop on Mass Spectrometry, p. 95-108.

Deshpande, R. D., and S. K. Gupta, 2008, National Programme on Isotope fingerprinting of waters of India (IWIN), *in* A. K. Singhvi, A. Bhattacharya, and S. Guha, eds., Glimpses of Geosciences Research in India, the Indian Report to IUGS, p. 10-16.

Deshpande, R. D., and S. K. Gupta, 2009, IWIN National Programme for Isotopic Characterization of Indian Hydrological Cycle: Preliminary Results: 11th ISMAS Triennial Conference of Indian Society for Mass Spectrometry, p. 95-107.

Deshpande, R. D., A. S. Maurya, B. Kumar, A. Sarkar, and S. K. Gupta, 2010, Rain-Vapor Interaction and Vapor Source Identification using Stable Isotopes from Semi-Arid Western India: Journal of Geophysical Research, v. 115.

Dincer, T., A. Al-Mughrin, and U. Zimmermann, 1974, Study of the infiltration and recharge through the sand dunes in arid zones with special reference to the stable isotopes and thermonuclear tritium: J. Hydrol., v. 23, p. 79.

Douglas, M., 1997, Mixing and Temporal Variation of Ground Water Inflow at the Con Mine, Yellowknife, Canada: An Analogue for a Radioactive Waste Repository: Unpublished thesis, Univ. of Ottawa, Canada.

Forstel, H., 1982, $^{18}O/^{16}O$ Ratio of Water in Plants and Their Environment. In Stable Isotopes, *in* H. L. Schmidt, H. Forstel, and K. Heinzinger, eds., Stable Isotopes, Elsevier, p. 503–516.

Gat, J. R., 1996, Oxygen and Hydrogen Isotopes in the hydrological Cycle: Annual Review of Earth Planetary Science, v. 24, p. 225-262.

Gat, J. R., and I. Carmi, 1970, Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area: J. Geophys. Res., v. 75, p. 3039.

Gat, J. R., and E. Matsui, 1991, Atmospheric water balance in the Amazon basin: an isotopic evapotranspiration model: J. Geophys. Res., v. 96, p. 13179–13188.

Gonfiantini, R., 1978, Standards for Stable Isotope Measurements in Natural Compounds: Nature, v. 271, p. 534–536.

Gonfiantini, R., 1986, Environmental isotopes in lake studies, *in* P. Fritz, and J.-C. Fontes, eds., Handbook of Environmental Isotope Geochemistry, v. 2 The Terrestrial Environment: Amsterdam, The Netherlands, B. Elsevier, p. 113-168.

Gupta, S. K., and R. D. Deshpande, 2003, Synoptic hydrology of India from the data of isotopes in precipitation: Current Science v. 85, p. 1591–1595.

Gupta, S. K., and R. D. Deshpande, 2004, Water for India in 2050: first-order assessment of available options: Current Science, v. 86.

Gupta, S. K., and R. D. Deshpande, 2005a, Groundwater Isotopic Investigations in India: What has been learned?: Current Science, v. 89, p. 825–835.

Gupta, S. K., and R. D. Deshpande, 2005b, Isotopes for Water Resource Management in India: Himalayan Geology, v. 26, p. 211–222.

Gupta, S. K., R. D. Deshpande, S. K. Bhattacharya, and R. A. Jani, 2005, Groundwater δ^{18}O and δD from central Indian Peninsula: influence of the Arabian Sea and the Bay of Bengal branches of the summer monsoon: Journal of Hydrology, v. 303, p. 38-55.

Hamid, S., M. Dray, A. Fehri, J. M. Dorioz, M. Normand, and J. C. Fontes, 1989, Etude des transfers d'eau a I'interieur d'une formation morainique dans le Bassin du Leman-transfer d'eau dans la zone non-saturee: Journal of Hydrology, v. 109, p. 369–385.

Horita, J., and D. J. Wesolowski, 1994, Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature: Geochimica et Cosmochimica Acta, v. 58, p. 3425-3437.

Jouzel, J., and L. Merlivat, 1984, Deuterium and oxygen-18 in precipitation: modelling of the isotopic effects during snow formation: J. Geophys. Res., v. 89, p. 11749.

Kakiuchi, M., and S. Matsuo, 1979, Direct measurements of D/H and 18O/16O fractionation factors between vapor and light water in the temperature range from 10º to 40º: Geochemical Journal, v. 13, p. 307-311.

Kendall, C., and J. J. McDonnell, eds., 1998, Isotope tracers in catchment hydrology: Amsterdam, Elsevier, 839 p.

Krishnamurthy, R. V., and S. K. Bhattacharya, 1991, Stable Oxygen and Hydrogen Isotope Ratios in Shallow Groundwaters from India and a Study of the Role of Evapotranspiration in the Indian Monsoon, v. Spl. Publ. 3, The Geochemical Society, p. 187-193.

Kumar, B., R. N. Athavale, and K. S. N. Sahay, 1982, Stable isotope geohydrology of the Lower Maner Basin, Andhra Pradesh, India: Journal of Hydrology, v. 59, p. 315-330.

Kumar, B., S. P. Rai, U. Saravana Kumar, S. K. Verma, P. Garg, S. V. Vijaya Kumar, R. Jaiswal, B. K. Purendra, S. R. Kumar, and N. G. Pande, 2010, Isotopic characteristics of Indian precipitation: Water Resour. Res., v. 46, p. W12548.

Majoube, M., 1971, Fractionment en oxygene-18 et en deuterium entre l'eau et sa vapeur: Journal of Chemical Physics, v. 197, p. 1423-1436.

Maurya, A. S., M. Shah, R. D. Deshpande, R. M. Bhardwaj, A. Prasad, and S. K. Gupta, 2011, Hydrograph separation and precipitation source identification using stable water isotopes and conductivity: River Ganga at Himalayan foothills: Hydrological Processes, v. 25, p. 1521-1530.

Navada, S. V., A. R. Nair, S. M. Rao, B. L. Paliwall, and C. S. Dashy, 1993, Groundwater Recharge Studies in Arid Region of Jalore, Rajasthan Using Isotope Techniques: Journal of Arid Environments, v. 24, p. 125-133.

Navada, S. V., and S. M. Rao, 1991, Study of Ganga River – groundwater interaction using environmental 18O: Isotopenpraxis, v. 27, p. 380-384.

Nijampurkar, V., K. Rao, M. Sarin, and J. Gergan, 2002, Isotopic study on Dokriani Bamak glacier, central Himalaya: implications for climatic changes and ice dynamics: Journal of Glaciology, v. 48 p. 81-86.

O'Neil, R., 1968: J. Phys. Chem., v. 72, p. 3683-3683.

Pande, K., J. T. Padia, R. Ramesh, and K. K. Sharma, 2000, Stable Isotope Systematics of Surface Water Bodies in the Himalayan and Trans-Himalayan (Kashmir) Region: Proc. Indian Academy of Sciences (Earth and Planetary Science), v. 109, p. 109-115.

Rai, S. P., B. Kumar, and P. Singh, 2009, Estimation of contribution of southwest monsoon rain to Bhagirathi River near Gaumukh, western Himalayas, India, using oxygen-18 isotope: Current Science, v. 97, NO. 2, 25 JULY 240 2009, p. 240-245.

Rakesh Kumar, R. D. Singh, and K. D. Sharma, 2005, Water Resources of India: Current Science, v. 89, p. 794-811.

Ramesh, R., and M. M. Sarin, 1992, Stable Isotope Study of Ganga (Ganges) River System: Journal of Hydrology, v. 139, p. 49-62.

Rank, D., G. Volkl, P. Maloszewski, and W. Stichler, 1992, Flow Dynamics in an Alpine Karst Massif Studied by Means of Environmental Isotopes, Isotope techniques in Water Resources Development, v. Proc. IAEA Symposium 319: Vienna, IAEA, p. 327–343.

Rozanski, K., L. Araguas-Araguas, and R. Gonfiantini, 1993, Isotopic Patterns in Modern Global Precipitation, Climate Change in Continental Isotopic Records, v. 78, American Geophysical Union Monograph, p. 1-36.

Salati, E., A. Dall’olio, M. E., and J. R. Gat, 1979, Recycling of water in Amazon Basin: an Isotopic Study: Water Resour. Res., v. 15, p. 1250-1258.

Sarin, M. M., S. Krishnaswami, J. R. Trivedi, and K. K. Sharma, 1992, Major ion chemistry of the Ganga source waters: Weathering in the high altitude Himalaya: Proc. Indian Academy of Sciences (Earth and Planetary Science), v. 101, p. 89-98.

Sengupta, S., and A. Sarkar, 2006, Stable isotope evidence of dual (Arabian Sea and Bay of Bengal) vapour sources in monsoonal precipitation over north India: Earth and Planetary Science Letters, v. 250, p. 511-521.

Shivanna, K., U. P. Kulkarni, T. B. Joseph, and S. V. Navada, 2004, Contribution of storm to groundwater in semi-arid regions of Karnataka, India: Hydrological Processes, v. 18, p. 473-485.

Shivanna, K., K. Tirumalesh, J. Noble, T. B. Joseph, G. Singh, A. P. Joshi, and V. S. Khati, 2008, Isotope techniques to identify recharge areas of springs for rainwater harvesting in the mountainous region of Gaucher area, Chamoli District, Uttarakhand: Current Science, v. 94, p. 1003- 1011.

Sukhija, B. S., D. V. Reddy, and P. Nagabhushanam, 1998, Isotopic fingerprint of palaeoclimates during the last 30,000 years in deep confined groundwaters of Southern India: Quatern. Res., v. 20, p. 252–260.

Suzuoki, T., and T. Kumura, 1973, D/H and $^{18}O/^{16}O$ fractionation in ice-water systems: Mass Spectrometry, v. 21, p. 229-233.

Warrier, C. U., M. P. Babu, P. Manjula, K. T. Velayudhan, A. Shahul Hameed, and K. Vasu, 2010, Isotopic characterization of dual monsoon precipitation - evidence from Kerala, India: Current Science, v. 98, p. 1487- 1495.

Yadav, D. N., 1997, Oxygen isotope study of evaporating brines in Sambar lake, Rajasthan (India): Chemical Geology, v. 138, p. 109-118.

Zimmermann, U., K. O. Munnich, and W. Roether, 1967, Downward Movement of the Soil Moisture Traced By Means of Hydrogen Isotopes, Isotope Techniques in the Hydrologic Cycle, v. Geophysical Monograph Series 11: Washington D.C., American Geophysical Union, p. 28-36.