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Role of Stable Isotopes in Groundwater Resource Management

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15.1 Introduction

Isotopes are the naturally occurring substances found on the Earth. Hydrogen, carbon, nitrogen, oxygen, and sulfur are the most important elements of the hydrological and geological systems. Elements having the same number of protons with a different number of neutrons are called isotopes. The element can have two, three, or more stable naturally occurring isotopes (Sinha et al. 2019). The movement of water can be traced by the abundance of hydrogen and oxygen isotopes (Sinha et al. 2019; Gupta and Goel 2021). An element can have both stable as well as radioactive isotopes. Stable isotope does not undergo any radioactive decay because their nuclei are always stable (Guay et al. 2006; Sinha et al. 2019; Gupta and Goel 2021).

Precipitation forms an important component in the hydrologic cycle and plays a vital role to replenish the groundwater sustainably (Wan et al. 2012; Khairul Nizar et al. 2018). Precipitation is classified as rain, freezing rain, snow, snow pellets, hail, and ice pellets (Patel and Shah 2008). The study of precipitation is of much significance from a hydrological perspective (Warrier et al. 2010), and the process which controls the temporal and geographic disparity of isotopic composition of precipitation always play a significant role in isotope hydrology (Gupta and Deshpande 2003). "Isotopic fractionation" leads to the geographical and temporal disparities in the isotopic composition of precipitation. Therefore, for a particular environment of precipitation, the unique isotopic signature provides information on the provenance of groundwater. The ^2H or D and oxygen ^{18}O help track the movement of water in the hydrologic cycle. These two isotopes of water are also called "water isotopes"

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(Clark and Fritz 1997; Gupta 2011; Cayuela Linares et al. 2018; Valdivielso et al. 2020). Oxygen and hydrogen isotopes of precipitations are the important tracers of hydrological processes for understanding the source of vapor, locally recycled vapor, rainout history, condensation temperature, relative humidity, etc. (Gupta and Deshpande 2003; Srivastava et al. 2015). The difference between the compositions of water isotopes can be explained using Global Meteoric Water Line (GMWL). Global Network of Isotopes in Precipitation (GNIP) has been jointly established by World Meteorological Organization (WMO) and International Atomic Energy Agency (IAEA). This organization conducts isotopic studies of $\delta^{18}O$ and $\delta^{2}H$ for precipitation at various monitoring stations worldwide including stations in India. The database maintained by the GNIP network is available at the website http://isohis.iaea.org (IAEA/WHO 2004; Deshpande 2006; Deshpande and Gupta 2008).

The Indian monsoon is considered a major factor in the atmosphere-ocean circulation system. The oceanic moistures sources generated from the Bay of Bengal (BOB) and the Arabian Sea chiefly contribute to the rainfall in the Indian sub-continent. The southwest monsoon from June to September is influenced by the Arabian Sea and the Indian Ocean in the southern Indian peninsula. BOB, Indian Ocean, and continental vapor play an important role in the contribution of moisture for the precipitation during the northeast monsoon (Berkelhammer et al. 2012; Roxy et al. 2015; Saravanan et al. 2019). However, there is a major gap in the availability of stable isotopic data of precipitation in India as a result of limited stations.

15.2 Background

15.2.1 Isotope Systematics

The isotope partitioning, which is also known as isotope fractionation, results from the differences in mass numbers of the molecules. The disparities that occur in the number of neutrons of an element are responsible for the different mass number of the same element. Heavy water ($^{2}H_2\,^{16}O$) with a mass number of 20 and normal water ($^{1}H_2\,^{16}O$) having a mass number of 18 represent the example of this situation. Water molecules travel through different domains of the hydrological cycle having different isotopic combinations that may get partitioned (fractionated) among the three phases of matter (Nisi et al. 2014).

The ratios of the two isotopes are considered for the stable isotopic studies of water using ^{1}H and ^{2}H, and ^{16}O and ^{18}O (Clark and Fritz 1997). The relative difference in the ratio of heavy isotope to the more abundant, light isotope of a sample to a reference is measured, as the absolute abundance ratio is not ordinarily determined for natural water. This difference (δ) is expressed as Eq. 15.1 (Gonfiantini 1981):

$$\left\{ \delta = \frac{R_{sample} - R_{reference}}{R_{reference}} \right\} \tag{15.1}$$

where R represents the ratio of isotopes. In the case of water, it can be $^{2}H/^{1}H$ or $^{18}O/^{16}O$.

The isotopic composition of a water sample is analyzed by considering Vienna Standard Mean Ocean Water (V-SMOW) as a reference (Clark and Fritz 1997). Since small differences occur between the samples and reference value, the δ value may be expressed as part per thousand or permil (‰) differences (Gonfiantini 1981) as given in Eq. 15.2. Equation 15.2 has been further modified as Eqs. 15.3 and 15.4 when the relative difference of ratio is considered in permil (‰).

$$\delta(‰) = \delta \times 1000 \tag{15.2}$$

$$\delta(‰) = \frac{R_{sample} - R_{reference}}{R_{reference}} \times 1000 \tag{15.3}$$

$$\delta(‰) = \frac{R_{Sample} - R_{VSMOW}}{R_{VSMOW}} \times 1000 \tag{15.4}$$

where the δ (‰) is the isotope ratio relative to a standard, R represents the ratio of isotopes, R_{VSMOW} is the ratio of the isotopes used in international standards (Gonfiantini 1978).

A positive [(+ve) sign] with δ values gain by the above equation elucidates that there is an increase of massive (heavier) isotope (i.e. ^{18}O) over the second (^{16}O) to a standard. The negative [(-ve) sign] of δ values represents the other situation (Clark and Fritz 1997).

15.2.2 Isotope Fractionations

The disparities between the velocity and bond strength between isotopes lead to isotopic partitioning or fractionation. It is also described as differential partitioning of isotopes between the two phases of liquid or vapor or solid (Kumar 2013). Sometimes isotopic partitioning is described as "isotope discrimination." The fractionation factor, "α," is characterized as the isotope proportions, which is expressed as Eq. 15.5 (Clark and Fritz 1997).

$$\left\{\alpha = \frac{R_{reactant}}{R_{product}}\right\} \tag{15.5}$$

where $R_{reactant}$ and $R_{product}$ represent the isotopic ratios of reactant and product, respectively.

For instance, in the case of a water–water vapor system, Eq. 15.5 can be written as follows (Eq. 15.6).

$$\left\{\alpha = \frac{\left(O^{18}/O^{16}{}_{water}\right)}{\left(O^{18}/O^{16}{}_{vapour}\right)}\right\} \tag{15.6}$$

Reactant and product interact for a longer time during the isotopic equilibrium establishment process. In a nonequilibrium state, rapid temperature change or addition or removal of product or reactant takes place. In the case of diffusive fractionation, the product under isotopic equilibrium disseminates slowly from the product reservoir. Equilibrium and kinetic fractionations describe these three types of fractionation processes (Araguas-Araguas et al. 2000; Chacko et al. 2001).

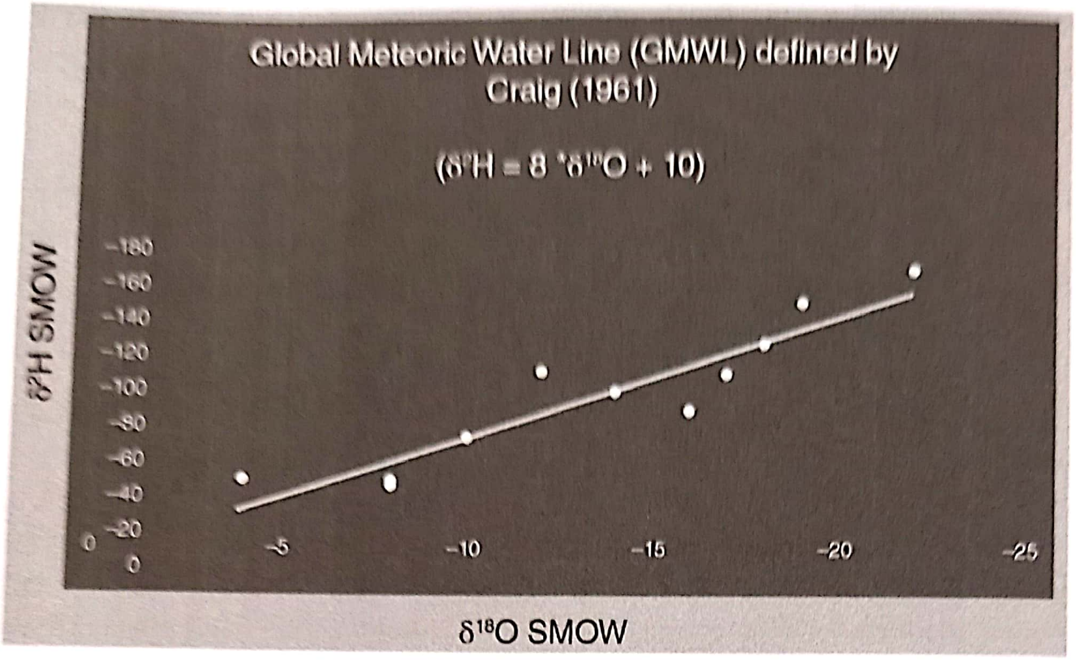

Figure 15.1 Global meteoric water line. *Source:* Adapted from Craig (1961).

15.2.2.1 ^{18}O and D in Precipitation

The stable isotopic composition of precipitation is controlled by parent vapor and temperature. It may also show higher variations due to evapotranspirational reprocess (Warrier et al. 2010). Based on the empirical observations, Craig (1961) correlated $\delta^{18}O$ and $\delta^{2}H$ in fresh water on a worldwide scale. The $\delta^{2}H$ and $\delta^{18}O$ are the potential tool to decipher the recharge processes and identify the diverse source of hydrological processes (Scholl and Murphy 2014; Oiro et al. 2018; Yeh and Lee 2018; Yang et al. 2019). It is known as the "Global Meteoric Water Line (GMWL)" that describes the relationship between $\delta^{18}O$ and δD in global fresh surface waters (Figure 15.1). The GMWL is expressed as Eq. 15.7.

$$\delta D = 8\delta^{18}O + 10 \tag{15.7}$$

The slope '8' in Eq. 15.7 is the ratio of isotopic equilibrium fractionation factors for D and ^{18}O (at 25 °C) during the equilibrium condensation. The "D" enrichment in water is approximately "8" times greater than that of ^{18}O. The "intercept" 10 is a function of meteorological conditions in nonequilibrium evaporation of the ocean surface from where the precipitation begins (Clark and Fritz 1997).

The intercept of Eq. 15.7 has been further confirmed from several studies (Yurtsever and Gat 1981; Rozanski et al. 1993). They used all the isotopic results acquired by the "GNIP" program jointly initiated by IAEA, Vienna, and WMO. Those observations were given in Eq. 15.8.

$$\delta D = \left(8.17\delta^{18}O \pm 0.06\right) + \left(10.35 \pm 0.65\right) \tag{15.8}$$

Equation 15.8 was obtained by using the mean arithmetic values. When the weighted mean values were used, Eq. 15.9 was generated (Yurtsever and Gat 1981; Rozanski et al. 1993).

$$\delta D = \left(8.20\delta^{18}O \pm 0.07\right) + \left(11.27 \pm 0.65\right) \tag{15.9}$$

Deshpande et al. (2003) and Warrier et al. (2010) proposed the "Local Meteoric Water Line" for various parts of Indian regions. Kumar et al. (2010) provided an Indian Meteoric Water Line (IMWL) through the isotope ratios of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) in natural waters based on data from several stations in India. In addition, the "Regional Meteoric Water Line" (RMWL) for the different zones of the country like the southern part, western Himalayas, and the northern part of the country were also given by them. The IMWL made by them can be expressed as Eq. 15.10.

$$\delta D = \left(7.93 \pm 0.06\right)\delta^{18}O \pm \left(9.94 \pm 0.51\right) \tag{15.10}$$

The IMWL discussed in Eq. 15.10 is having a slight difference in slope and intercept compared to GMWL. IMWL has a great significance and it gives a baseline for groundwater investigation of a particular region. It differs from GMWL based on the disparities in climatic conditions and geographic constraints (Kumar et al. 2010).

15.2.2.2 Deuterium Excess

Deuterium excess is defined as the excess deuterium that cannot be accounted for kinetic fractionation between "water" and "vapor." ^{18}O and ^{2}H concentrate in a liquid phase, whereas ^{16}O and ^{1}H enter into the vapor phase based on the difference in mass number. The water vapor gets enriched in ^{16}O and ^{1}H and the remaining liquid water with ^{18}O and ^{2}H during the process of evaporation. Humidity, wind speed, salinity, and temperature are the important parameters that control the process of kinetic fractionation (Urey 1947; Clark and Fritz 1997). Among them, humidity is the most important parameter.

In the GMWL equation proposed by Craig (1961), the deuterium excess has a value of ~10 which represents the evaporation with ~ 85% of relative humidity. In regional precipitation, the value of deuterium excess is greater than 10 when the humidity is low (Gat and Carmi 1970). When the humidity (h = 50%) is low, the vapor is strongly depleted and the Local Meteoric Water Line (LMWL) plot would be above the GMWL, whereas when humidity is 85% (h = 85%), the precipitation plot is close to the GMWL (Clark and Fritz 1997).

Dansgaard (1964) studied the characteristics of the d-excess at global precipitation, expressed by Eq. 15.11.

$$d = \delta D - 8\delta^{18}O \tag{15.11}$$

Deuterium excess always provides valuable information about the moisture sources in the precipitation and the evaporation (Clark and Fritz 1997).

15.2.2.3 Continental Effect

Topographic condition in landmasses controls the rainout situation. Extreme temperature variation affects the isotopic composition in precipitation. The coastal precipitations are isotopically enriched with a minor range of $\delta^{18}O$ (−0‰ to −5‰), whereas the colder inner continental province receives isotopically depleted precipitation with strong seasonal differentiation. There is a strong seasonal variation in the temperature at continental regions which refers to a reflection of distance from moderating marine influences and latitude (Wolf et al. 2020; Saranya et al. 2021).

15.2.2.4 Seasonal Effect

Strong seasonal variation controls the water isotopes of precipitation due to seasonal variation of temperature. The values are found depleted in the colder months than the summer months suggested that there is a latitude variation from 0.5 ‰ per degree celsius in high latitude stations to 0 ‰ per degree celsius in tropical ocean islands (IAEA 1983; Ala-aho et al. 2018; Dublyansky et al. 2018; Vasil'chuk et al. 2022). Rozanski et al. (1993) also discussed the variations of $\delta^{18}O$ in a highly continental station and the sub-tropical region as a result of strong seasonal variation in temperature.

15.2.2.5 Latitude Effect

Precipitation at higher latitudes tends to have more negative $\delta^{18}O$ values as the air masses come to the inland, the vapor gets constantly depleted in the heavier isotopes due to the rainout effect process from the cloud during moisture transport from the tropics to the poles. The global study of $\delta^{18}O$ in precipitation demonstrated a relatively flat gradient over the tropic's regions. This gradient increases poleward with some distortion because of the continental effect and ocean currents (Yurtsever and Gat 1981; Clark and Fritz 1997; Kern et al. 2020; Leketa and Abiye 2020; Laonamsai et al. 2021; He et al. 2021). Rozanski et al. (1993) found that there is a (-0.6‰) latitude effect of $\delta^{18}O$ for continental stations of North America and Europe and (-2‰) $\delta^{18}O$ for the colder Antarctic regions.

15.2.2.6 Altitude Effect

Temperature change with altitude is called the "wet adiabatic lapse rate." At higher altitude having low average temperature, precipitation is isotopically depleted that varies from -0.15 ‰ to 0.5 ‰ per 100 m rise in altitude for ^{18}O and from −1 to −4‰ for ^{2}H. The altitude effect is also known as the "alpine effect" or "elevation effect." The altitude effect has great significance in groundwater recharge studies (IAEA 1983; Clark and Fritz 1997; Kern et al. 2020).

15.2.3 Methodology and Precautions in the Collection of Rainwater Samples

Appropriate sample collection techniques are important in any environmental study. In the case of isotope hydrological studies, enough precautions are needed during the collection of precipitation samples. To acquire dependable isotope data, it is fundamental that the standard testing system ought to be pursued. When the isotope technique is applied to a region to examine the various hydrological processes, all the accessible hydrological and meteorological data can also be obtained and this helps in fixing the sampling points and their intervals. Monitoring programs for precipitation are combined monthly like 12 samples per year. Daily samples of rain gauges are poured into a monthly sample bottle and are sealed and the accumulative amount can be noted for the weighting calculations (Clark and Fritz 1997; Krajcar Bronić et al. 2020; Wenninger 2020).

15.2.3.1 Rainwater Collection Techniques

Rainwater samples can be collected on a daily or weekly or monthly basis for isotopic studies using a specially designed rainwater collector. Rainwater collections on monthly basis are generally followed. In a monthly composite precipitation methodology, the accumulated precipitation for one full month period is collected. A thin layer of paraffin or silicon oil of about 2 mm thickness should be poured into the rainwater collector for preventing the loss of water through evaporation, which floats over the sample (Clark and Fritz 1997). Samples were collected from the specially designed collector instrument suggested by IAEA. The rainwater collector instrument contains 20 L polyvinyl chloride (PVC) carboy with a specially designed nylon cap consisting of two holes. These two holes have been further fixed with a plastic funnel (6 m long and 20 cm in diameter) and a 10-mm-thick PVC tube. A 6-mm plastic hosepipe inserted through a polymer cork and tightly fitted inside the funnel into the container up to the base. Paraffin oil of about 2 mm thickness should be poured into the rainwater collector apparatus before sampling so that it can form a layer of paraffin floating over water to protect it from evaporation. The instrument should be washed properly after collecting the sample and must be poured with paraffin oil into the collector before starting next month's sampling. A "separating funnel" should be used for separating water from the paraffin layer at the end of each month. Precipitation samples could have been taken in clean polythene (Torson) bottle of 60 mL capacity by filling up to the maximum level leaving only a little space for thermal expansion. The bottle must be closed tightly to avoid isotope exchange with air moisture.

15.2.3.2 Principle of Isotope Ratio Mass Spectrometer

Isotope Ratio Mass Spectrometer (IRMS) is specially designed to measure the mass differences of a molecular compound. The basic concept of IRMS is that the beam of the charged molecules can be produced by the thermal ionization of a solid source (solid sample) or by ionizing a gaseous sample. Source design generally depends on the isotopes of interest. IRMS can measure even a very small fraction of isotopes of $^{2}H/^{1}H$ and $^{18}O/^{16}O$. Oxygen-18 and deuterium (D) analysis of water samples can be done by equilibration methods. The analysis of oxygen isotopes ($^{18}O/^{16}O$ ratio) can be performed by CO_2–H_2O equilibration method, whereas deuterium analysis can be performed by H_2–H_2O equilibration method using platinum as a catalyst (Clark and Fritz 1997; Kaklamanos et al. 2020). Table 15.1 shows the different standards for the del (δ) value suggested by IAEA for V-SMOW.

15.2.4 Application of Isotopes in Water Resource Management

There are various applications of the environmental isotope in groundwater resource management as follows:

- Interconnections between surface and groundwater
- Tracking sources of groundwater recharge
- Groundwater age or groundwater dating
- Source and mechanism of groundwater pollution
- Sanitary landfills
- Agriculture watersheds
- Groundwater salinization

Table 15.1 Norms suggested for δ value by IAEA for V-SMOW (Vienna-SMOW, SLAP, and GISP agencies).

		Delta (δ) value for V-SMOW	
S. No.	**Norms**	**δ^2H (‰)**	**$\delta^{18}O$ (‰)**
1	V-SMOW	0	0
2	Standard Light Antarctic Precipitation (SLAP)	δ^2H_{SLAP} = -428.0 ‰ VSMOW	$\delta^{18}O_{SLAP}$ = -55.50 ‰ VSMOW
3	Greenland Ice Sheet Precipitation (GISP)	δ^2H_{GISP} = -189.5 ‰ VSMOW	$\delta^{18}O_{GISP}$ = -24.78 ‰ VSMOW

Source: Adapted from Gonfiantini (1978).

15.2.4.1 Interconnections Between Surface and Groundwater

The demand for freshwater resources has been increased due to the rapid growth of population, industrial development, and agricultural activities. The relationship between surface water (such as lakes, rivers, and streams) and groundwater can be well established using stable isotopes tracers. Isotopic compositions of groundwater are generally controlled by meteorological processes. Both environmental isotopes, stable isotopes and radioactive isotopes, are used as a tracer in hydrological investigations and provide essential information for the better management of water resources (Clark and Fritz 1997, Archana et al. 2014; Yang et al. 2019; Jung et al. 2020). Stable isotopic data can be well used to assess the relative proportions of surface water and precipitation in recharge. In arid and semiarid regions, due to the evaporation in surface water bodies, the stable isotope compositions of groundwater are useful in the detection of different recharge components. River water can also show a seasonal variation in stable isotope composition). In arid regions, river water may be enriched in δD and $\delta^{18}O$ compared to the groundwater, and then the fractionations of river water in groundwater can be evaluated based on differences in the isotopic composition of the mixing components (IAEA 2011). Therefore, the mechanism of stable isotope exchange in their composition can be well understood by surface and groundwater interactions.

15.2.4.2 Tracking Sources of Groundwater Recharge

It has been challenging for the hydrologist to track the sources of recharge to aquifers and the relative contributions from multiple sources. The rate of pumping has been increased in the past years which affects the declination of head and recharge changes. Therefore, it is indeed to understand the qualitative and quantitative characterization of groundwater recharge to ensure the sustainable development and management of groundwater resources (Zongyu et al. 2011; IAEA 2011). In the past years, stable and radioactive isotopes have been applied successfully to understand the problems related to groundwater recharge and delineation of flow systems. In addition, the advancement of nanotechnology imparts the novel tracers being used for groundwater dynamics (Cook and Herczeg 2000; Geyh et al. 2008; Kinzelbach et al. 2002; Warsi et al. 2020). The isotopic composition of groundwater can be evaluated based on the isotopic composition of recharge, and if the recharge is obtained through the direct infiltration of precipitation, then the groundwater will reflect the isotopic composition of that precipitation; and if it is through surface water instead of precipitation, it will reflect the mean isotopic composition of the contributing river or lake. Tritium is produced naturally by cosmic radiation and over the past three decades, the presence of thermonuclear tritium (^{3}H) was used as clear evidence for active recharge. In the arid and semiarid regions, isotope techniques constitute virtually the only approach for the identification and quantification of groundwater recharge (Clark and Fritz 1997; IAEA 2011; Aggarwal et al. 2021).

15.2.4.3 Groundwater Age or Groundwater Dating

Groundwater age means groundwater residence time, which means the length of time from which the water has been isolated from the atmosphere or the average travel time between the point of recharge and the point of discharge. Groundwater dating means estimating the groundwater age by using different methods. Radioactive isotopes play an important role in the estimation of groundwater age. Tritium (^{3}H) and carbon-14 (^{14}C) are the most well-known radioisotopes that are used in groundwater dating. In the confined aquifers, recharge is usually occurring in a horizontal or lateral gradient age which means the age increases with distance from the area of recharge. In addition to the unconfined aquifers, recharge is usually occurring in a vertical gradient of groundwater ages which means increasing the age with depth (Clark and Fritz 1997; IAEA 2011; Gupta 2011; Chacha et al. 2018; Ju et al. 2020).

15.2.4.4 Source and Mechanism of Groundwater Pollution

Stable isotope can also be helpful in the estimation of the source and mechanism responsible for groundwater pollution. Groundwater isotopes such as δ^{18}O and δ^2H, when used in combination with hydrochemical data, are very useful in characterizing and delineating various sources of groundwater contamination, which is rather difficult to ascertain from hydrochemical data alone (Datta et al. 1996). Pollution that occurs based on anthropogenic resources has a great influence on groundwater resources management. Stable isotopes of groundwater (δ^{18}O and δ^2H) are important in tracing the pathways of pollutants in aquifers and also their spatial and temporal variations. In addition, the sources of nitrate and sulfate pollution can be identified with the measurement of concentration and stable isotope composition of sulfate and nitrate. Chemical and isotopes tracers are the best tools to provide a better understating of groundwater origin (IAEA 2011; Vitvar et al. 2005; Rizvi and Mohammed-Aslam 2019; Mohammed-Aslam and Rizvi 2020)

15.2.4.5 Sanitary Landfills

Municipal garbage dumps were unlined and sited with little regard to the local hydrogeology and the consequences are that leachate and gas migration is now threatening groundwater resources. Environmental isotopes in conjunction with geochemistry play an important role in the identification of the migration of leachate from the older, non-engineered sites or modern landfills, identification of leachate contamination zone, and siting of new facilities to demonstrate the security of groundwater from contamination (Sinha et al. 2012; Aljaradin and Persson 2014; Ahamad et al. 2019; Madon et al. 2020).

15.2.4.6 Agriculture Watersheds

The use of excess fertilizers and pesticides can deteriorate the quality of groundwater and surface water in agricultural watersheds, and the predominance of the septic systems and municipal waste dumps adds a further complication to understanding the sources and pathways of the contaminant zones (Madhav et al. 2021). This can be well understood with the help of environmental isotopes with the recharge origin and mixing in groundwater, to determine the sources of nitrate and ammonium from fertilizer, to determine the fate of chlorocarbons pesticides, to determine the sources of salinity and oxidation processes, etc. (Clark and Fritz 1997; Bohlke 2002; IAEA 2013; Rizvi and Mohammed-Aslam 2018; Rizvi and Mohammed-Aslam 2019).

15.2.4.7 Groundwater Salinization

Saline groundwater is mainly dominated by chloride salts with sulfates and other anions in minor constituents. Sodium chloride salinity is dominated in the coastal areas where the groundwater is affected by seawater intrusion. Isotope techniques can be used in the measurement of the sources where salinization occurs in groundwater. Isotope techniques can be used to distinguish the leaching of salts by percolating water, the intrusion of saltwater bodies such as seawater, brackish surface water, or brines, and the concentration of dissolved salts through evaporation (Clark and Fritz 1997; IAEA 2011; Han et al. 2011; Han et al. 2014; Etikala et al. 2021).

15.3 Utilization of Water Isotopes in Hydrology: A Case Study

15.3.1 Study Site

An investigation has been carried out in the north-western part of the Kalburgi district to get a better understanding of water isotopes ($\delta^{18}O$ and $\delta^{2}H$) of precipitation of different monsoon seasons within the region. The entire region falls under the semiarid provinces of Karnataka State of India (Rizvi and Mohammed-Aslam 2018, 2019). The region is well known for water scarcity (Mohammed-Aslam and Rizvi 2020). This area receives rainfall generally from June till September. The average annual rainfall received by the area is 777 mm, whereas the annual minimum rainfall is 342 mm and the annual maximum rainfall is 1270 mm (CGWB 2012). Therefore, monthly composite precipitations samples (except pre-monsoon (March to May) and post-monsoon (October to February) periods) from 2016 to 2017 were collected. The rainfall collector was fixed at the PWD office, Aland located at latitude $17^{0}34'15''$ N and longitude $76^{0}34'7''$ E, having an elevation of 497 m from the mean sea level (MSL) as shown in Figure 15.2.

15.3.2 Findings and Discussions

Rainfall, wind speed, and relative humidity data were collected from the online portal (https://www.ksndmc.org) of Karnataka State Natural Disaster Monitoring Centre (KSNMDC) for 2016 and 2017. The average annual rainfall of 856.53 mm in 2016 and

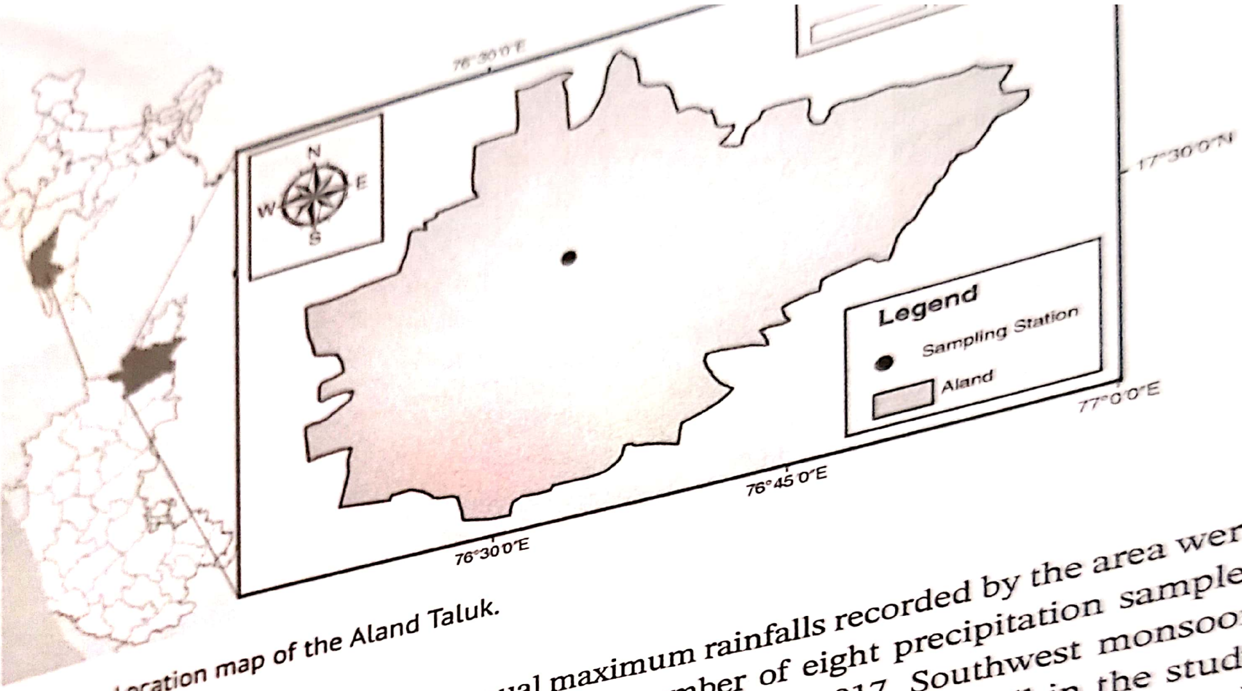

Figure 15.2 Location map of the Aland Taluk.

853.71 mm in 2017 were recorded. The annual maximum rainfalls recorded by the area were 585.50 mm in 2016 and 631.0 mm in 2017. A total number of eight precipitation samples were analyzed for water isotopes ($\delta^{18}O$ and δD) from 2016 to 2017. Southwest monsoon (June to September) is the major contributor (approximately 78%) in rainfall in the study area compared to post-monsoon (October to February) and pre-monsoon (March to May). The mean (monthly) temperature of the area varied from 33.8 °C in April to 23.3 °C in December. The maximum mean (monthly) value of humidity was 77% in September, whereas the minimum was 32% in April. At low humidity, the evaporation from the continental surface body may generate vapor masses with the highest deuterium excess (d-excess) values (Clark and Fritz 1997). The monthly variation of rainfall in the years 2016 and 2017 was shown in Figure 15.3a. Monthly average rainfall data with average relative humidity, wind speed, dew point, and average vapor pressure of the study area are given in Table 15.2.

The mean monthly highest saturated vapor pressure was 52.73 hPa in April, whereas the minimum was in December (28.68 hPa). The actual mean monthly vapor pressure showed from 14.74 in January to 28.29 in June during 2016–2017. The mean monthly "Dew Point Temperature" varied from 12.73 °C in January to 23.09 °C which was the maximum dew temperature in June. The results of the stable isotope analysis with rainfall data of the sampling location are shown in Table 15.3.

Water vapor over the continents and the average rainout history of air masses control the isotopic composition of local precipitation. The LMWL of Aland has been plotted in Figure 15.3b and was compared with GMWL and IMWL proposed by Kumar et al. (2010). The best-fitted regression line, passing through all the points of δ^2H and $\delta^{18}O$ in precipitation, was fairly correlated (R-square = 0.977 and n = 8 with standard error ± 0.46 and ± 1.79, respectively).

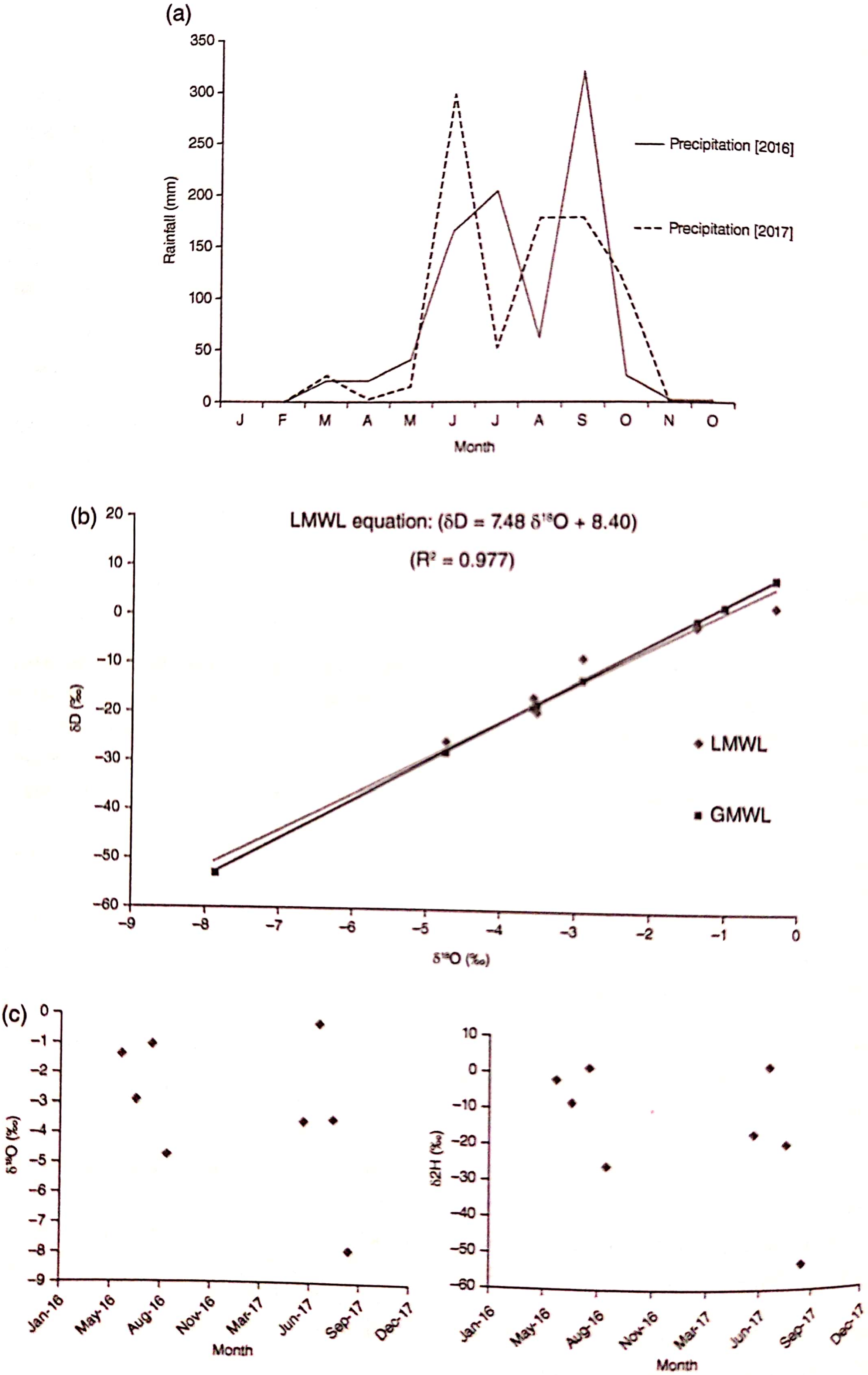

Figure 15.3 (a) Monthly variation of the rainfall in the study region. (b) Local Meteoric Water Line of Aland. (c) Monthly variations of $\delta^{18}O$ and $\delta^{2}H$ in precipitation in Aland.

Table 15.2 Average of meteorological parameters of the region (2016–2017).

						Vapor Pressure (h/Pa)	
Month	**Rainfall (mm)**	**Temperature (°C)**	**Wind Speed (m/s)**	**Dew Point (°C)**	**Relative Humidity (%)**	**Saturated Vapor Pressure**	**Actual Vapor Pressure**
January	0.39	23.9	0.73	12.7	49.58	29.80	14.74
February	0.99	27.4	0.91	13.2	41.73	36.48	15.18
March	22.6	30.2	0.94	14.7	39.18	42.95	16.76
April	12.38	33.8	1.18	15.02	32.41	52.73	17.10
May	27.8	33.8	1.1	20.03	44.57	52.66	23.44
June	228.96	29.3	0.90	23.09	69.51	40.68	28.29
July	126.59	27.7	0.77	22.5	73.27	37.28	27.25
August	118.16	27.4	0.66	22.4	74.47	36.52	27.20
September	245.94	26.8	0.54	22.4	77.21	35.27	27.28
October	67.8	26.2	0.55	20.4	70.45	34.14	24.14
November	1.73	24.4	0.40	15.7	58.74	30.57	18.02
December	1.76	23.3	0.60	14.8	58.68	28.68	16.83

Table 15.3 Stable isotopes and monthly rainfall of the study area from 2016 to 2017.

Year	Month of Collection	Rainfall (mm)	δD (‰)	δ¹⁸O (‰)	d-excess
	June	163.28	−2.1	−1.38	8.94
	July	201.93	−8.54	−2.9	14.66
	August	60.07	1.5	−1.01	9.58
	September	315.30	−25.68	−4.74	12.24
	October	25.25	NA	NA	NA
2017	June	294.64	−16.79	−3.56	11.69
	July	51.26	1.97	−0.32	4.53
	August	176.25	−19.52	−3.51	8.49
	September	176.59	−52.92	−7.87	10.04

The LMWL of Aland gives the relationship which is expressed in Eq. 15.12.

$$\delta D = \left(7.48\ {}^{18}O \pm 0.46\right) + \left(8.40 \pm 1.76\right) \quad \left(R^2 = 0.977, n = 8\right) \tag{15.12}$$

The equation of IMWL with which the results were compared is given as Eq. 15.13.

$$\delta D = \left(7.93\delta^{18}O \pm 0.06\right) + \left(9.94 \pm 0.51\right) \quad \left(R^2 = 0.98, n = 272\right) \tag{15.13}$$

RMWL for the northern, southern, and Himalayan regions were also developed by Kumar et al. (2010) is given as Eq. 15.14.

$$\delta D = \left(7.82\delta^{18}O \pm 0.17\right) + \left(10.23 \pm 0.85\right) \quad \left(R^2 = 0.97,\ n = 62\right) \tag{15.14}$$

The slope of the generated LMWL of Aland (Eq. 15.12) is close to the slope of IMWL (Eq. 15.13), RMWL (Eq. 15.14) and GMWL (Eq. 15.7) respectively. But, the intercept of the LMWL of Aland (Eq. 15.12) is much lower than the intercept of GMWL, IMWL, and RMWL. This condition confirmed that the modifications of water isotopic signatures are due to the "secondary evaporation" from the precipitation.

Monthly variations between $\delta^{18}O$ and δ^2H of precipitation are given in Figure 15.3c, and it indicated that there was a significant variation during the samples collected between southwest monsoons (June to September) for both years. There was no precipitation in the area of study for March to May (pre-monsoon) and October to February (post-monsoon) months. As a result, a correlation for these months was not possible. There was a considerable enrichment in deuterium and oxygen-18 values during southwest monsoon periods between 2016 and 2017. The deuterium (δ^2H) and oxygen-18 ($\delta^{18}O$) signatures of southwest monsoon periods of both years showed a uniform trend indicating the constant nature of their vapor sources. Secondary evaporation always decreases when relative humidity increases (Zongyu et al. 2011).

15.3.2.1 Estimation of d-excess

Deuterium excess can be used in finding out the sources of vapor, information on moisture sources in precipitation, and evaporation of water bodies. It may also be related to kinetic fractionation (Warrier et al. 2010). Deuterium excess is controlled by the relative humidity of air mass from its origin. Monthly variations of deuterium excess values are shown in Figure 15.4a and Table 15.3. The values of d-excess' were found varying from 8.94‰ in June 2016 to 14.66‰ in July 2016, whereas 11.69‰ in June 2017 to 4.53‰ in July 2017 during southwest monsoon periods. The higher variation in stable isotopes and "d-excess" values were observed in samples of 2017, indicating that the precipitation of this year has contributed to the addition of re-evaporated vapor and moistures from continental sources through inland evaporation as noticed by Warrier et al. (2010).

However, samples taken during southwest monsoon periods showed a uniform trend for both years indicative of their nature of the constant source. Kong and Pang (2012) explained that the deuterium excess study may be useful in the investigation of "moisture recycling processes" in arid regions. The relationship between $\delta^{18}O$ and temperature and $\delta^{18}O$ and humidity has been shown in Figure 15.4b. A poor correlation among these explains the "complex isotopic fractionation" during the rainout process. Such a condition is similar to the explanation given by Kumar et al. (2010) in respect of sources of condensing moisture and their effects.

15.3.2.2 Estimation of the Amount Effect

Dansgaard (1964) explained the term "amount effect" for stable isotopes studied for monthly rainfall. He found that there is an increment in the negative values of oxygen-18 with heavy rainfall for several worldwide stations. The variation between the "amount of rainfall – oxygen-18 ($\delta^{18}O$)" values and "amount of rainfall – deuterium (δ^2H)" values is

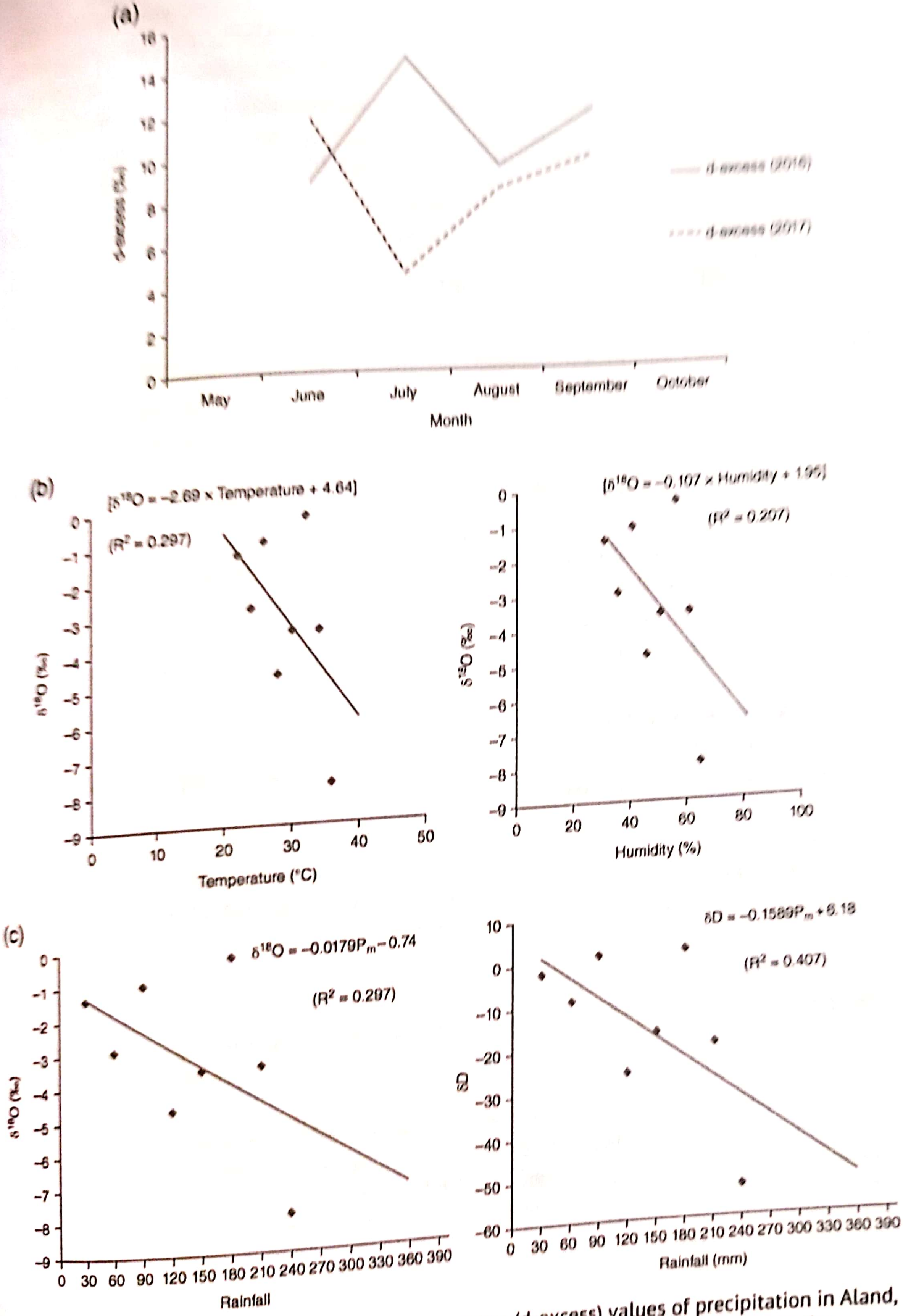

Figure 15.4 (a) Monthly variations of deuterium excess (d-excess) values of precipitation in Aland, (b) plot of $\delta^{18}O$ versus air temperature and humidity of Aland, and (c) variations between the amount of rainfall and $\delta^{18}O$, δD values in precipitation where $\delta^{18}O$ and δD are functions of monthly amount of precipitation in Aland

given in Figure 15.4c considering the monthly precipitation. A poor correlation exists between the monthly amount of precipitation and $\delta^{18}O$, and δ^2H of rainfall in the study region. It was observed that the precipitation versus δ^2H ($R^2 = 0.407$) is slightly better than that of $\delta^{18}O$ ($R^2 = 0.297$). The relationship between the monthly precipitation and $\delta^{18}O$, δ^2H of rainfall of the station at Aland is expressed by the Eqs. 15.15 and 15.16.

$$\delta^{18}O = -0.0179P_m - 0.74 \qquad \left(R^2 = 0.297\right) \tag{15.15}$$

$$\delta D = -0.1589P_m + 6.18 \qquad \left(R^2 = 0.407\right) \tag{15.16}$$

The above equation indicates that the average rate of depletion in $\delta^{18}O$ was 1.79‰ per 100 mm of precipitation, whereas 15.89‰ in δD per 100 mm of precipitation during southwest monsoon (June to September). The rate of depletion of δD in precipitation is higher than the depleting rate of $\delta^{18}O$ per 100 mm of precipitation. The poor correlation obtained by the Eqs. 15.15 and 15.16 indicates the existence of secondary evaporation in the region.

Relative humidity, precipitation, and temperature are the key factors influencing evaporation below the cloud base. Probably, secondary evaporation can be maximum during northwest and pre-monsoon season due to poor rainfall and minimum during southwest monsoon seasons, when a higher amount of rainfall is received (Zongyu et al. 2011).

15.3.2.3 Estimation of Seasonal Variations

The average and weighted mean values of $\delta^{18}O$, δ^2H, and d-excess of precipitation along with the average amount of rainfall during sampling periods (2016 and 2017) are shown in Table 15.4. The depth of rainfall in the container (rainwater collector) was insufficient to precede the study during March to May and October to February for the analysis of these stable isotopes. Therefore, the only available precipitation samples during southwest monsoon periods (June to September) were used for the study.

Table 15.4 Arithmetic mean and the weighted mean of stable isotopes during 2016 and 2017.

		Arithmetic mean			Weighted mean		
Season/period	**Average rainfall (mm)**	**$\delta^{18}O$ (‰)**	**δ^2H (‰)**	**d-excess (‰)**	**$\delta^{18}O$ (‰)**	**δ^2H (‰)**	**d-excess**
Northeast monsoon	71.51 (mm)	NA	NA	NA	NA	NA	NA
Southwest monsoon	719.66 (mm)	-3.16	-15.26	10.02	-3.67	-18.52	10.79
Pre-monsoon	62.78 (mm)	NA	NA	NA	NA	NA	NA

Note: NA, not available

The stable isotope values of southwest monsoon samples are given in Table 15.4. The δ^{18}O values were found varying from -0.32‰ in July 2017 to −7.87‰ in September 2017. The δD showed the range from −2.1‰ in June 2016 to 1.9‰ in July 2017. The values of d-excess were varying from 4.53‰ in July 2017 to 14.66 in July 2016 with an average value of 10.02‰ (Table 15.4). Timely variation of isotopic occurrence between the samples collected in June and September to the samples collected in July and August were noticed during the southwest monsoon. The values of δ^{18}O during July and August samples showed enriched isotopic values with an average value of -1.93‰ (average $\delta^{18}O_{J,A}$ = -1.93‰), whereas June and September samples were showing relatively depleted isotopic values with an average value of -4.38‰ (average $\delta^{18}O_{J,\,S}$ = -4.38‰). Precipitation taking place in July and August has almost maintained its marine identity with an average value of δ^{18}O (-1.93‰) and the low average value of deuterium excess (9.31‰). This situation may be taken as the best representation of southwest monsoon precipitation, whereas the δ^{18}O values of June and September of precipitation samples have shown slightly depleted isotopic signature with an average value of δ^{18}O (-4.38‰) and relatively high deuterium excess value (10.72‰).

The northern Indian Ocean and the Arabian Sea are the major sources of moisture during southwest monsoon precipitation in the southern part of India and the isotopic values of δ^{18}O in most of the southwest precipitation samples are relatively enriched [($\delta^{18}O_{SW}$ > (-3‰)], as suggested by Warrier et al. (2010), confirming that the rainfall occurring in the region during southwest monsoon periods. The higher value of deuterium excess was noticed in July 2016 (14.66‰) and September 2016 (12.24‰).

Northeast monsoon wind originating from central Asia draws moisture from depleted continental sources and oceanic sources such as the South China Sea and BOB (Deshpande et al. 2003) and is influenced by successive rainout effects. Therefore, it may be a strong reason for very low to no rainfall during the northeast monsoon season in the region as it has to travel over large landmasses (affected by a higher continental effect) before reaching the Aland. Pre-monsoon rain is generally formed by the storm over the BOB, but it is very complicated to predict their arrival and this may be a reason for low to almost no rainfall during this study. However, a detailed study can provide more about the "complex isotopic fractionation" during the rainout process.

15.4 Conclusion

The water isotope characterization of a semiarid region located in a north-western part of Kalburgi District, Karnataka State, during the study period in 2016 and 2017 has been discussed. The LMWL of Aland has been generated and was compared with the GMWL, IMWL, and RMWL. The slope (7.48) of LMWL was almost close (or less than) to the slope of GMWL (evaporation effect), whereas the intercept (8.40) was much lower than the intercept of GMWL, suggesting that the modifications of water isotopic signatures because of "secondary evaporation" from the falling raindrops from the cloud to surface. The deuterium (δ^2H), oxygen-18 (δ^{18}O) signatures, and deuterium excess of southwest monsoon periods of both years show a uniform trend which indicates the constant nature of their vapor sources. The monthly amount of precipitation and δ^{18}O, and δ^2H of rainfall were poorly correlated in the study region. The relationship indicates that the average rate of depletion in $\delta^{18}O$ was 1.7‰ per 100 mm of precipitation whereas 15‰ in δD per 100 mm of precipitation during southwest monsoon periods confirms that the rate of depletion of δD in precipitation was higher than the depleting rate of $\delta^{18}O$ per 100 mm of precipitation. The pre-monsoon and northeast monsoon periods in the region were lacking any distinctive isotopic signature because of very low to almost no rainfall. The nearest LMWL available to the study area is of the Belgaum region given by Kumar et al. (2010) which can be expressed as:

$$\delta D = \left(7.78\delta^{18}O \pm 0.62\right) + \left(11.32 \pm 2.28\right), \qquad \left(R^2 = 0.94,\ n = 12\right)$$

This study would also help open the knowledge gaps in the understanding the characterization of water isotopes of monsoon precipitation in the Indian sub-continent.

15.5 Summary and Conclusions

Environmental isotopes play a vital role in the management of groundwater resources. It has great importance in tracking groundwater resources using stable isotopes of hydrogen and oxygen; groundwater recharge using tritium; groundwater mixing; groundwater dating using tritium, carbon-14, etc. Nowadays, isotope techniques are widely used in groundwater management around the globe. To understand the isotopic variation of any region, continental effect, seasonal effect, latitude effect, and altitude effect should be summarized adequately because these factors always influence the isotopic fractionations. Deuterium excess (d-excess) is useful in finding the vapor sources, formation of moisture sources in precipitation, and evaporation of water bodies. Isotopic variations that occur in the natural waters are important in solving many critical hydrological problems. Among the various environmental isotopes, stable isotopes such as deuterium, oxygen-18, carbon-13, and radioisotopes such as tritium and carbon-14 are important in hydrological studies. Deuterium and oxygen-18 are known as the ideal geochemical tracers of water because their composition does not change with the interaction of aquifer substances. Environmental isotopes are also important in dating younger and older groundwater.

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