Isotopic characterization of dual monsoon precipitation – evidence from Kerala, India

C. Unnikrishnan Warrier*, M. Praveen Babu, P. Manjula, K. T. Velayudhan, A. Shahul Hameed and K. Vasu

Isotope Hydrology Division, Centre for Water Resources Development and Management, Kunnamangalam P.O., Kozhikode 673 571, India

The stable isotopes oxygen-18, deuterium and the radioactive isotope tritium of the precipitation samples collected from Kozhikode, Kerala were analysed from 2005 to 2007 for the isotopic characterization of the rainfall derived from two monsoons in the region. The isotopic composition varied from $\delta^{18}O$ = –1.33‰ and δD = –3.9‰ in August 2005 to $\delta^{18}O$ = –5.6‰ and δD = –33.42‰ in June 2007 for the southwest monsoon (June to September) and from $\delta^{18}O$ = – 5.92‰ and δD = –31.43‰ in October 2007 to $\delta^{18}O$ = –8.64‰ and δD = –53.2‰ in November 2007 for the northeast monsoon (October to January) samples. In addition to the two monsoon derived rainfalls, the region also receives pre-monsoon showers (March to May), whose isotopic composition varies from $\delta^{18}O$ = –1.54‰ and δD = –15.85‰ in April 2007 to $\delta^{18}O$ = –10.26‰ and δD = –70.92‰ in April 2005. The tritium content of rainwater was higher in the northeast monsoon period compared to the southwest monsoon period. The tritium level in precipitation was below 5 TU for most of the samples. The rainfall during southwest and the northeast monsoons shows two distinct isotopic signatures which cannot be totally ascribed to the difference in vapour sources but also to the difference in rainout histories of the air masses before reaching Kozhikode. Pre-monsoon rains in Kozhikode lacked any distinct isotope signatures. The tritium level in precipitation supports our observations. Excess tritium in northeast monsoon rains may be due to their origin from higher latitude.

Keywords: *d*-excess, Kerala, monsoon, stable isotopes, tritium.

PRECIPITATION is one of the many manifestations of water in all its forms in the earth atmosphere system. Since precipitation is the primary source of water on land, the formation and spatial variations of precipitation are of much importance for a hydrologist. Precipitation is the expression of meteorological processes at the ground surface and its study must first involve a consideration of the processes in the atmosphere, which causes the formation of clouds. Spatial distributions of stable isotopes of oxygen and hydrogen in precipitation are powerful tracers for identifying the processes leading to it. Spatial and temporal variations in the isotopic composition of precipitation are due to isotopic fractionation occurring during the advection of the water vapour, condensation of vapour into rain and evaporation during downfall from cloud level to ground level[1]. The isotopic composition of local precipitation is primarily controlled by regional scale processes like the trajectories of the water vapour transport over the continents and the average rainout history of the air masses giving precipitation at a particular place[2].

It is well established that stable isotopes of oxygen (oxygen-18, ^{18}O) and hydrogen (deuterium, D) in water are useful to investigate groundwater recharge[3–5], to study the effects of evaporation on groundwater systems[6,7], to study groundwater and surface water interaction[8]. The variations in stable isotopic composition of water bodies have been explained in terms of variations from the World Meteoric Water Line (WMWL)[9]. Therefore, for hydrological studies using the stable isotopes of oxygen and hydrogen, prior knowledge of the isotopic characteristics of precipitation in the region under investigation is essential. The International Atomic Energy Agency (IAEA) in cooperation with the World Meteorological Organization (WMO) is measuring isotope ratios in precipitation at numerous monitoring stations worldwide, which includes a few stations in India. The deuterium excess[1] (*d*-excess) of rainfall is extensively used to identify the origin of vapour source of precipitation[10,11]. The results of stable isotopic composition and the tritium content of precipitation collected from Greece showed non-homogeneous spatial distribution of the average *d*-excess which indicates the differences in origin and history of water vapour masses[12]. They also reported seasonal differences in tritium content of precipitation. The stable isotopic compositions of precipitation from eight meteorological stations along with selected groundwater samples in Saudi Arabia were studied by Alyamani[13] and found that the monsoon-derived rainfall plays a crucial role in the alluvial aquifer recharge. In the Indian context also, the isotopic composition of precipitation was being used for various environmental applications like identifying the monsoon processes, different moisture sources contributing to precipitation, its influences in the recharge, etc. Factors controlling the stable isotopic composition of

*For correspondence. (e-mail: warrieruk@rediffmail.com)

rainfall in New Delhi were analysed by Datta *et al.*[14] They found that even though long-term values agree with the WMWL, the short-term features were found to follow an evaporative line probably due to evaporation and subsequent enrichment during the fall. The available regional maps of amount weighted monthly isotopic data of precipitation from the Global Network of Isotopes in Precipitation (GNIP)/IAEA database was used to discern and describe the hydrological processes responsible for giving characteristic regional distribution of $\delta^{18}O$ and *d*-excess for different seasons over the Indian subcontinent[15]. The base line data on the isotopic composition of precipitation in Kolkata was used to delineate the sources of vapour generating the rains during both the summer and winter monsoons at Kolkata[16].

A monsoon is traditionally defined as a seasonal reversing wind accompanied by changes in precipitation patterns. The seasonal reversal of temperature and pressure gradients and the associated changes in the wind circulation patterns caused by the annual northward and southward motion of sun forms the causative mechanism of the monsoon[17]. The monsoons greatly help in sustaining life on earth. The monsoons affect a vast area of the globe – from Africa across Asia to the Pacific; northern China and the Himalayas to north Australia; and even Mexico and parts of Central America – directly influencing the lives of over half the world's population.

Kerala is situated at the southwest corner of the Indian peninsula. The state extends from 8.2°N to 12.8°N parallel and 74.8°E to 77.5°E meridian, covering an area of ~ 38,800 km^2. Kerala is bounded by Arabian Sea on the west and Western Ghats skirts it on the east, forming a continuous chain, that physiographically separates it from the rest of the country. The coastline is 580 km long. The maximum east–west width is 120 km. Averaged over the entire state, Kerala gets an annual average rainfall of 3000 mm spread over 126 rainy days[18]. Kerala is under the influence of dual monsoon system namely the southwest monsoon (summer monsoon) and the northeast monsoon (winter monsoon).

The unique position of Kerala in the Indian subcontinent places it directly across the path of the maritime air blowing from the Indian Ocean and Arabian Sea in the northern hemispheric summer[18]. The north–south oriented Western Ghats intercept this southwest monsoon current. The moist air undergoes orographic uplift on the windward slopes and gives rise to copious rains. The first outburst of southwest monsoon over the Indian subcontinent takes place over Kerala, it starts mostly by the first week of June and extends up to September. The heaviest rainfall is observed in June and July. The southwest monsoon contributes about 65% of the annual rainfall[18]. The timely onset, optimum duration and reasonable strength of the southwest monsoon are of vital importance to the life and economy of Kerala and to the entire south Asian region. There is a progressive increase in rainfall latitudinally from south to north. During the northeast monsoon period, the pressure and wind patterns change with the withdrawal of the southwest monsoon from the subcontinent. The pressure gradient is reversed with high pressure to the north and low pressure to the south. The wind therefore blows in the opposite direction, from land to the sea[18]. The northeast monsoon is thus more or less dry, giving rise to only small amount of precipitation. The northeast monsoon starts by October and extends up to January, however rainfall is rarely noticed in December and January. Sandwiched between the two are the pre-monsoon rains (March–May) with irregular pattern. The pre-monsoon showers vary highly in both amount and time. Significant pre-monsoon showers are usually observed in April and May. Usually scanty rainfall is observed in March.

In the southern Indian Peninsula, the major sources of moisture for the southwest monsoon are the northern Indian Ocean and the Arabian Sea[19] whereas the southern Indian Ocean, Bay of Bengal and the continental vapour sources supply moisture to the northeast monsoon to provide precipitation in the eastern and southeastern part of the Peninsula[18,20]. The precipitation arising from these two monsoons is expected to show distinctive isotopic signatures depending on its moisture sources and other local effects. In this study, isotopic compositions of the precipitation samples collected from the Kozhikode station of Kerala (Figure 1) during 2005–07 covering southwest, northeast and pre-monsoon periods are presented and discussed. Even though the isotopic characteristics of monsoon-derived rainfalls[14–16] of the Indian Peninsula have been extensively studied, the isotopic characterization (including the radioactive isotope tritium) of the rainwater collected covering the southwest, northeast and the pre-monsoon periods has not been much reported from a south Indian station. In the Indian context, there is a knowledge gap in the understanding of the isotope characteristics of the southwest, northeast and the pre-monsoon rains, especially in the southern part of the Indian Peninsula. This work is an attempt towards generating and discussing stable isotope (oxygen-18 and deuterium) and environmental tritium data of these seasonal rainfalls in this region. It may help in closing the existing gaps in the understanding of the isotopic systematics of monsoon derived precipitation.

Study area

The precipitation samples were collected from the Centre for Water Resources Development and Management (CWRDM) at Kunnamangalam (long. 75°52′15″E, lat. 11°17′07″N) of Kozhikode district, Kerala (Figure 1).

Kozhikode receives good amount of rainfall with an annual average value of around 3090 mm (1979–2007). The year 2005 had normal rainfall (3100 mm), whereas the next two years had higher rainfall than the average

value. In 2006, the rainfall (3990 mm) was 29% and in 2007 (4645 mm), it was 50% more than the average. During this study period (2005–07), the annual average rainfall was much higher (3910 mm) than the long-term average value of 3090 mm. The southwest monsoon contributed about 75% of the rainfall whereas the northeast monsoon and pre-monsoon rain contributed the rest (Figure 2). The mean monthly temperature of the location varies from 26.2°C in July to 29.9°C in April. The highest temperature of about 35°C was observed in April and the lowest temperature of about 20°C in December. The mean monthly humidity of 72% is noticed in January, whereas June and July show the highest mean monthly value of 86% (CWRDM, unpublished data).

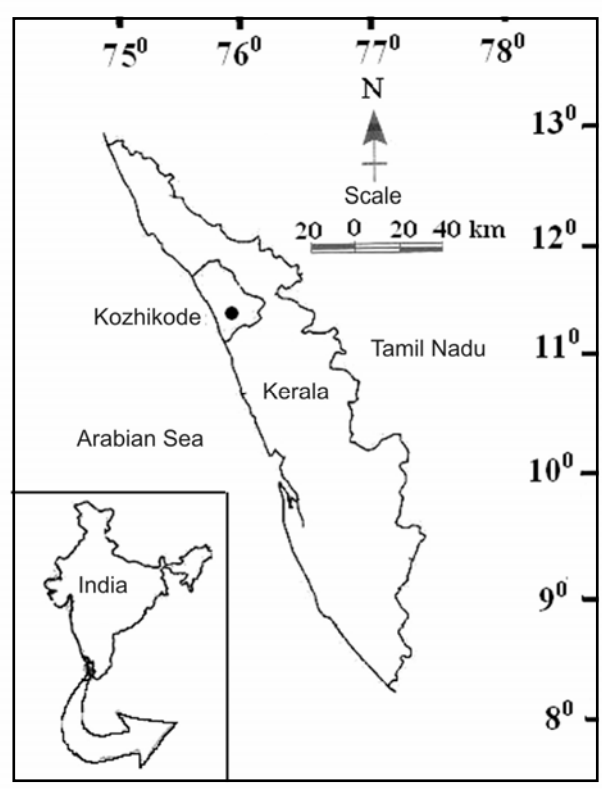

Figure 1. Location map of Kozhikode.

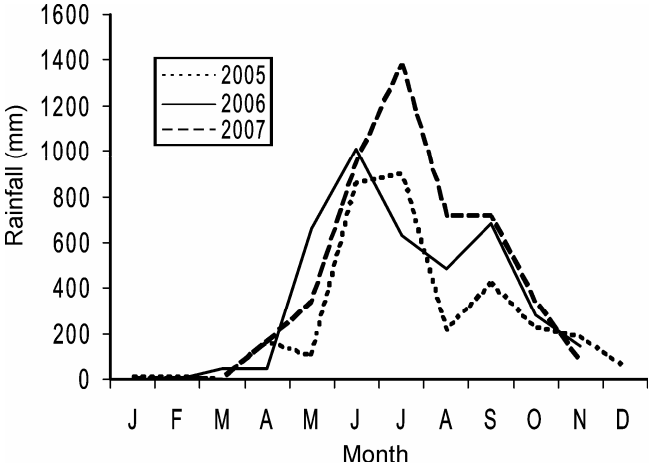

Figure 2. Monthly variation of rainfall in Kozhikode.

Isotope systematics

The stable isotopic results of hydrogen and oxygen are reported as δ units, i.e. per mil (‰) deviation of the isotope ratio from the international standard Vienna Standard Mean Ocean Water (V-SMOW)[21], δ being defined by

$$\delta(‰) = [(R_{\text{sample}} - R_{\text{VSMOW}})/R_{\text{VSMOW}}] \times 10^3. \quad (1)$$

Stable isotope variations result from isotope fractionation, which occur during physical and chemical processes. Evaporation and condensation of water are some of the physical processes, which could lead to isotopic fractionation. The isotopic composition of precipitation in clouds is primarily determined by equilibrium fractionation process. In a given region, the isotopic composition of the condensing parent vapour and temperature are the two major factors that determine the stable isotopic composition of precipitation. The meteoric history of the original air mass and its modification by upwind loss by precipitation coupled with contributions due to evapotranspirational recycling influences the composition of the condensing vapour. The isotopic composition of precipitation is thus highly variable in space and time due to these effects, which occur during the various processes in the hydrological cycle. In 1961, Craig[22] published his findings that in spite of all these complexities of the various processes in the hydrological cycle, the δ^{18}O and δD in freshwater correlate on a global scale and isotopic compositions of meteoric waters behave in a predictable manner. Craig's 'Global Meteoric Water Line' (GMWL) defines the relationship between δ^{18}O and δD in worldwide fresh surface waters. The global meteoric water line defined by Craig can be represented by the following equation.

$$\delta D = 8\delta^{18}O + 10. \quad (2)$$

The slope 8 of GMWL is due to the ratio of the enrichment factor ε of D and ^{18}O (8.2 at 25°C) during condensation, which is largely an equilibrium process[4]. The global atmospheric water vapour forms with an average humidity just slightly greater than 85%, and kinetic fractionation which occurs during evaporation under ~85% humidity produces precipitation on a line that is displaced from seawater by 10‰ for δD[4]. The intercept of the eq. (2) was subsequently confirmed by Yurtsever and Gat[23] and more recently by Rozanski *et al.*[9] who obtained the following equations by considering all the isotopic results obtained by the IAEA, Vienna from the WMO collection stations.

$$\delta D = (8.17\delta^{18}O \pm 0.06) + (10.35 \pm 0.65). \quad (3)$$

When only the mean arithmetic values are used and when the weighted mean values are used, then

$$\delta D = (8.20\delta^{18}O \pm 0.07) + (11.27 \pm 0.65). \quad (4)$$

Even though the GMWL is global in application, it is an average of many regional or Local Meteoric Water Lines (LMWL), which differ from the global line due to varying climatic and geographic parameters[15]. LMWL provide the baseline for groundwater investigations in a region. The position of meteoric waters on this line is controlled by a series of temperature-based mechanisms that drive the rainout process. This includes vapour mass trajectories over continents, rising over topographic features, moving to higher latitudes and seasonal effects. Each has a characteristic effect on the stable isotopic composition of precipitation.

Tritium, the radioactive isotope of hydrogen, emits low energy (18 keV) beta radiation and has a half-life of 12.32 years. The tritium (T) content in precipitation is expressed in tritium units (TU). One TU equals one ^{3}H atom in 10^{18} ^{1}H atoms ($T/H = 10^{-18}$), which is equivalent to an activity of 0.11919 Bq/kg. Tritium exists in the environment due to continuous natural production in the atmosphere by cosmic ray interactions with various atmospheric components. It is also produced artificially as a consequence of thermonuclear tests, operation in nuclear reactors especially those using heavy water as moderator[24], nuclear power plants and other industrial outputs like manufacturing of tritiated paints and liquids used in illuminating dials and signals. In the early sixties, the atmospheric nuclear tests resulted in an increase in tritium concentrations in the atmosphere and in precipitation up to 1000 times (about 5000 TU) in northern hemisphere in 1963 (ref. 25). After the nuclear test ban, tritium activity started decreasing more or less exponentially and today it has reached the values of the pre-test era[24,25] though regional increase in tritium concentrations in precipitations has been noticed at places near nuclear reactors and other nuclear installations like nuclear power stations, nuclear fuel-reprocessing facilities, etc. Higher concentration of tritium in precipitation collected from Thessaloniki station compared to other stations in Greece is probably due to emissions from nuclear power stations of the neighbouring countries[12]. In the northern hemisphere, summer precipitation is expected to have slightly more tritium than the winter precipitation[25]. This is due to the onset of intense mixing across the tropopause or more specifically due to sudden upward shifts of the tropopause level in high latitudes during springtime[26]. Such upward shifts of the stability regions would leave high concentrations of tritium behind in the troposphere to be mixed into the moist layer and precipitated. Due to the reasons explained here, the tritium concentration in rain increases towards mid and high latitudes. Such seasonal differences were noticed in precipitation in Greece[12] and in precipitation samples collected from locations across Croatia and Slovenia[27]. The moisture evaporating from ocean is low in tritium content[28]. Oceanic and coastal stations thus show considerably lower concentration than the continental stations. This is due to the water vapour exchange between atmosphere and the sea surface[26]. Similar differences were reported in the mean tritium content of precipitation samples collected from maritime and continental stations located in Croatia and Slovenia[27].

Methodology

Monthly composite precipitation samples (except in few cases) from 2005 to 2007 were collected following the norms suggested by IAEA (www.isohis.iaea.org). For stable isotopes, the samples were taken in a clean polythene (Tarson) bottle of 60 ml capacity by filling to the maximum level leaving only a little space (for thermal expansion) and closing the bottle tightly to avoid isotope exchange with air moisture. For the analysis of tritium, 500 ml of each samples was also collected separately.

The stable isotopes were analysed using continuous flow isotope ratio mass spectrometer (FINNIGAN DELTA^{PLUS} XP) at the Isotope Hydrology Division of CWRDM. The oxygen isotope ($\delta^{18}O$) was analysed using the CO_2–H_2O equilibration method[29]. The hydrogen (δD) analyses were performed by the H_2–H_2O equilibration technique using platinum catalyst supported on a hydrophobic material. All the measurements were carried out against laboratory substandards that are periodically calibrated against the international isotope water standards recommended by IAEA (V-SMOW, Greenland Ice Sheet Precipitation (GISP) and Standard Light Antarctic Precipitation (SLAP)). The analytical reproducibility of the results is 0.08‰ for $\delta^{18}O$ and 0.8‰ for δD. Tritium was analysed using ultra low level liquid scintillation counter (Wallac, Quantulus-1220) also housed at the Isotope Hydrology Division of CWRDM. The pre-distilled water samples were electrolytically enriched before counting using 250 ml capacity electrolytic cell after adding 0.5 g of sodium peroxide as electrolyte.

Results and discussions

As part of this study, 29 precipitation samples during 2005–2007 were analysed for stable isotopes (δD and $\delta^{18}O$) and the radioactive isotope tritium. The results of the stable isotope and tritium analyses along with the rainfall data of the sampling location are given in Table 1.

Stable isotope analysis

The $\delta^{18}O$–δD scatter diagram of Kozhikode is given in Figure 3. LMWL of Kozhikode was drawn which is

Table 1. Stable isotopes, tritium and monthly rainfall of Kozhikode during 2005–2007

Year	Period of collection	Rainfall (mm)	δD (‰)	δ^{18}O (‰)	*d*-excess (‰)	^{3}H (TU)
2005	01.04.05 to 30.04.05	158.8	–70.92	–10.26	11.16	6.11
	01.05.05 to 30.05.05	95.2	–3.89	–1.89	11.23	4.16
	01.06.05 to 30.06.05	857.6	–9.44	–2.63	11.6	5.8
	01.07.05 to 30.07.05	897.4	–10.53	–2.7	11.07	4.07
	01.08.05 to 30.08.05	210.2	–3.9	–1.33	6.74	1.19
	01.09.05 to 30.09.05	419.6	–7.38	–2.08	9.26	3.44
	01.10.05 to 30.10.05	216.2	–38	–6.25	12	4.04
	01.11.05 to 30.11.05	178.6	–48.2	–7.9	15	2.94
	01.12.05 to 30.12.05	52.8	–52.08	–7.9	11.12	2.22
2006	01.03.06 to 30.03.06	48.6	–16.37	–3.79	13.95	3.04
	01.04.06 to 30.04.06	48.8	–15.3	–2.61	5.58	2.97
	01.05.06 to 30.05.06	662.4	–9.01	–3.12	15.95	2.5
	01.06.06 to 30.06.06	1006.6	–6.78	–2.56	13.7	2.91
	01.07.06 to 30.07.06	632.6	–2.53	–1.61	10.35	2.86
	01.08.06 to 30.08.06	483.6	–6.62	–2.1	10.18	2.81
	01.09.06 to 30.09.06	680.2	–29.6	–4.83	9.04	3.02
	01.10.06 to 30.10.06	281.4	–42.99	–6.85	11.81	6.36
	01.11.06 to 30.11.06	147.4	–38.86	–6.72	14.86	
2007	01.04.07 to 30.04.07	155.6	–15.85	–1.4	–4.65	1.82
	01.05.07 to 30.05.07	334.2	–29.14	–5.11	11.74	2.25
	01.06.07 to 30.06.07	936.9	–33.42	–5.6	11.38	BDL
	01.07.07 to 15.07.07	893.6	–3.58	–1.79	10.74	0.65
	15.07.07 to 30.07.07	489.6	NA	NA	NA	NA
	01.08.07 to 15.08.07	500	–9.66	–2.92	13.7	0.77
	15.08.07 to 30.08.07	212	–12.23	–2.77	9.93	–
	01.09.07 to 15.09.07	316.4	–25.1	–4.19	8.42	BDL
	15.09.07 to 30.09.07	395.2	–16.26	–3.36	10.62	–
	01.10.07 to 15.10.07	77.1	–2.05	–2.08	14.59	3.81
	15.10.07 to 30.10.07	255.8	–60.8	–9.75	17.2	–
	01.11.07 to 15.11.07	78	–53.2	–8.64	15.92	1.96

NA, Not available; BDL, Below detectable level.

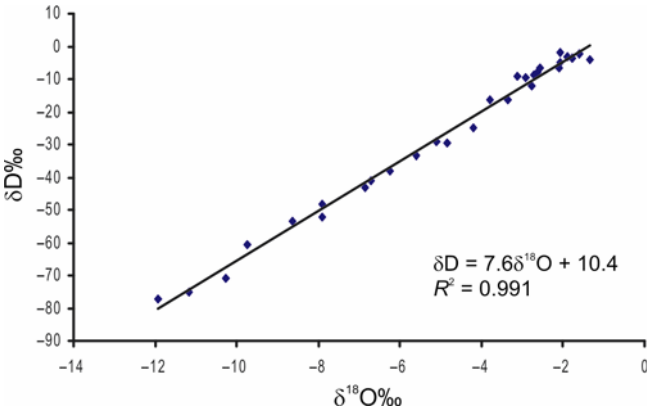

Figure 3. Local meteoric water line of Kozhikode.

the best-fit line passing through all the points. The δ^{18}O and δD of precipitation in Kozhikode station are fairly correlated ($R^2 = 0.991$, $n = 28$).

LMWL gives the relationship

$$\delta D = (7.6\ \delta^{18}O \pm 0.13) + (10.4 \pm 0.81). \quad (5)$$

Both the slope and intercept of the LMWL are close to that of the GMWL defined by Craig[22]. The local trend of stable isotopic signatures of Kozhikode almost follows the global trend.

The variations in δ^{18}O and δD of precipitation at Kozhikode during the study period are shown in Figure 4 *a* and *b* respectively. There is significant variation in the δD and δ^{18}O values obtained for samples collected during southwest, northeast and the pre-monsoon periods. There is considerable enrichment in both D and ^{18}O in the southwest monsoon samples compared to the northeast monsoon samples. This suggests the difference in vapour sources of the two monsoons. It is also noticed that δ^{18}O and δD signatures of both southwest and northeast monsoon samples showed uniform trend in all the three years (2005–07) indicating the constant nature of their vapour sources. The pre-monsoon showers lack any distinct isotopic signatures.

Amount effect

The term amount effect was coined by Dansgaard[1] who found a strong negative correlation between δ^{18}O and

monthly rainfall, with heavy rainfall resulting in more negative $\delta^{18}O$ for many of the global stations. The amount effect can possibly be explained on the basis of different amounts of removal of water from the atmosphere. The amount of rainfall–$\delta^{18}O$ and amount of rainfall–δD diagram of the Kozhikode station are shown in Figure 5 *a* and *b* respectively. The precipitation amount and $\delta^{18}O/\delta D$ of the rainfall in Kozhikode are not well correlated with correlation coefficient for amount versus δD slightly better ($R^2 = 0.16$) than for $\delta^{18}O$ ($R^2 = 0.13$). Kozhikode receives most of its rains during the southwest monsoon period where the rains represent the first condensate. The poor correlation of the amount and $\delta^{18}O/\delta D$ of the rainfall in Kozhikode indicate that the region receives a continuous supply of moist air masses since the southwest monsoon currents move across extended marine regions before reaching Kozhikode.

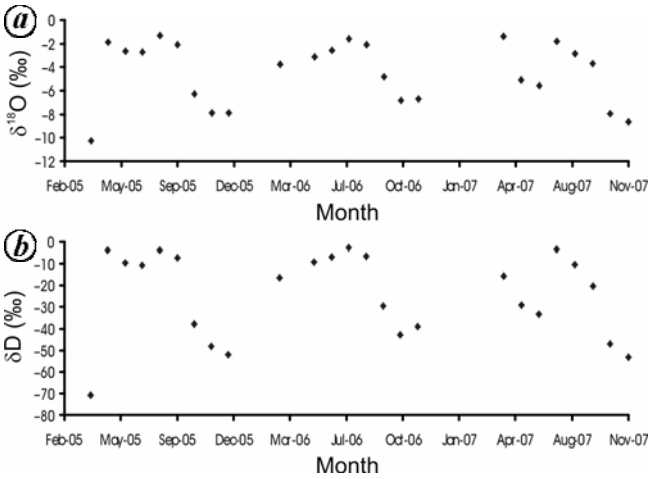

Figure 4. Monthly variations in (***a***) $\delta^{18}O$ of precipitation and (***b***) δD of precipitation in Kozhikode.

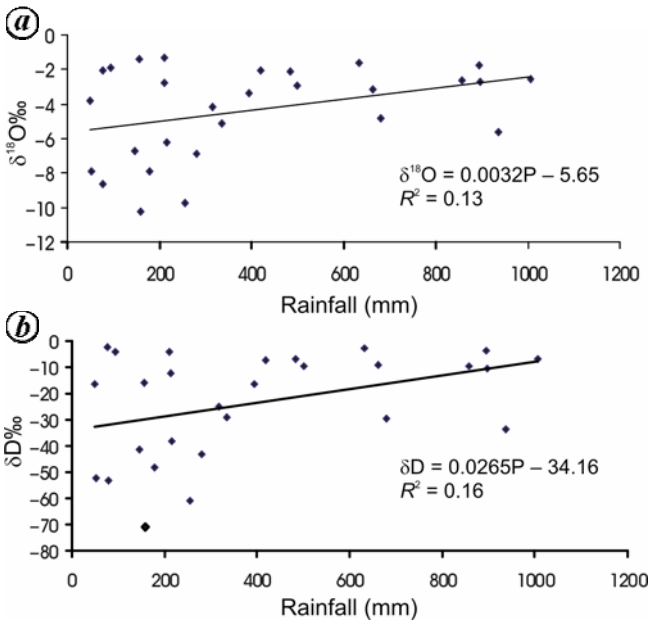

Figure 5. Variation of (***a***) $\delta^{18}O$ as a function and (***b***) δD as a function of monthly amount precipitation.

Deuterium excess (d-excess)

The concept of *d*-excess[1], which is defined as $d = \delta D - 8\delta^{18}O$, of a specific atmospheric precipitation sample is believed to be mainly related to the meteorological conditions at the vapour source region and kinetic fractionation during evaporation of falling rain drops. The deuterium excess of precipitation is primarily governed by the relative humidity of the air mass at its origin and is practically independent of the atmospheric processes[30–32]. Evaporation from continental surface water bodies at low humidity can produce vapour mass with high *d*-excess[25]. The monthly variation of *d*-excess is graphically represented in Figure 6. The *d*-excess value confirms that the vapour sources contributing to precipitation in Kozhikode are of different origin. The marine origin of the southwest monsoon samples is clear from its *d*-excess value of around 10.5. The continental contribution to the northeast monsoon samples is evident from its higher *d*-excess of around 14. However, both the monsoon samples showed uniform trend for all the years confirming their constant source. The pre-monsoon showers in the region show greater fluctuations in *d*-excess probably due to the varying amounts of secondary effects it is undergoing beneath the cloud base which are being controlled by the meteorological conditions and the other local effects.

Seasonal variations

The seasonal and weighted means of $\delta^{18}O$, δD and *d*-excess of precipitations (southwest, northeast and

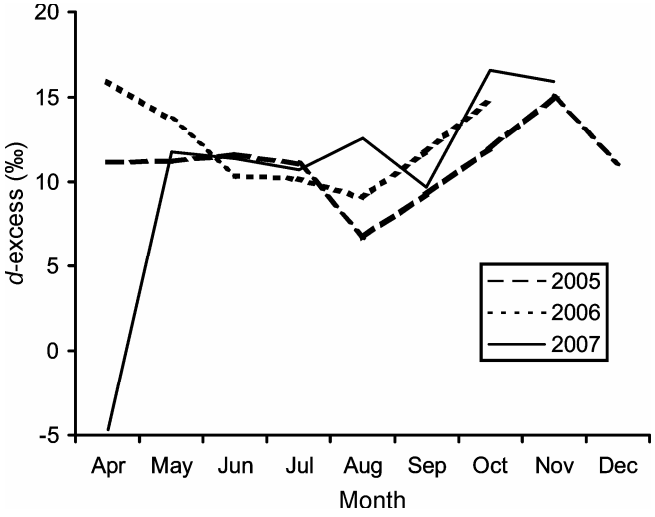

Figure 6. Variation of *d*-excess of precipitation in Kozhikode.

Table 2. Mean and weighted mean of $\delta^{18}O$, δD, *d*-excess and tritium of different seasons

Season	Average rainfall (mm)	Arithmetic mean				Weighted mean			
		$\delta^{18}O$ (‰)	δD (‰)	*d*-excess (‰)	^3H (TU)	$\delta^{18}O$ (‰)	δD (‰)	*d*-excess (‰)	^3H (TU)
SWM	2970	–2.8	–12.1	10.4	2.2	–2.94	–12.84	10.7	2.1
NEM	430	–7.3	–45.4	13.5	3.7	–9.29	–57.04	17.2	3.8
PM	500	–4.3	–24.6	10.1	3.4	–4.43	–24.92	10.5	3.2

SWM, Southwest monsoon; NEM, Northeast monsoon; PM, Pre-monsoon.

pre-monsoon) along with the average amount of precipitation during different seasons of the sampling period (2005–07) are presented in Table 2.

The stable isotope values of southwest monsoon samples varied from $\delta^{18}O = -1.33‰$ and $\delta D = -3.9‰$ in August 2005 to $\delta^{18}O = -5.6‰$ and $\delta D = -33.42‰$ in June 2007 (Table 1). The *d*-excess value ranged from 6.74 (August 2005) to 13.7 (June 2006) with an average value of 10.4 (Table 2). There is a timely variation of isotopic signatures within the southwest monsoon samples, July and August show enriched isotopic values (average $\delta^{18}O = -2.06‰$), whereas June and September show relatively depleted isotopic values (average $\delta^{18}O = -3.58‰$). The precipitation of July and August almost retains its marine identity (average $\delta^{18}O = -2.06‰$ and low average *d*-excess = 10.15) and can be taken as the best representative of southwest monsoon rainfall. June shows a slightly depleted (average $\delta^{18}O = -3.56‰$) isotopic signature with a relatively high average *d*-excess of 12.23. June precipitation seems to have a slight contribution from the reevaporated vapours formed in May at a higher temperature and low humidity with a majority of marine vapour having relatively enriched isotopic value.

The major source of moisture for the southwest monsoon rains in the southern Indian peninsula is the northern Indian Ocean and the Arabian Sea[19]. The relatively enriched isotopic values ($\delta^{18}O > -3‰$) of most of the southwest monsoon samples reveal that the southwest monsoon in Kozhikode derives its moisture from the Arabian Sea branch of southwest monsoon. The marine origin of the vapour source is evident from the average and weighted mean *d*-excess value of the southwest monsoon samples (10.4 and 10.7) and is further confirmed by the relatively low tritium concentration (Table 2).

The stable isotope values of northeast monsoon samples varied from $\delta^{18}O = -5.92‰$ and $\delta D = -31.43‰$ in October 2007 to $\delta^{18}O = -8.64‰$ and $\delta D = -53.2‰$ in November 2007 (Table 1). The *d*-excess value ranged from 11.12 (December 2005) to 15.9 (October 2007) with an average value of 13.5 (Table 2). The high *d*-excess value of northeast monsoon samples is probably due to continental vapour contribution. Most of the northeast monsoon samples have depleted isotopic values ($\delta^{18}O < -6.5‰$) as the northeast monsoon winds originating from the central Asia can draw moisture from depleted continental vapour sources and oceanic sources like South China Sea and Bay of Bengal during its southward journey[11] and the subsequent rainout effect. The continental vapour contribution is evident from the high average and weighted mean *d*-excess values (13.5 and 17.2) of the samples (Table 2).

The difference in the isotopic composition of the precipitation from the southwest and northeast monsoons can also be ascribed to the differences in rainout histories of the two air masses before reaching Kozhikode. The southwest monsoon's first precipitation is on the Kerala coast resulting in enriched isotope values whereas the northeast monsoon travels over large land masses including the Indian peninsula before reaching Kerala resulting in large continental effect.

The study also attempted to characterize the pre-monsoon rains received in the region. For the pre-monsoon rains, stable isotope values varied from $\delta^{18}O = -1.54‰$ and $\delta D = -15.85‰$ in April 2007 to $\delta^{18}O = -10.26‰$ and $\delta D = -70.92‰$ in April 2005 (Table 1). The *d*-excess value of the pre-monsoon rains varied greatly and showed high values of 15.95 in May 2006 and a negative value of –4.65 in April 2007 (Table 1). The negative *d*-excess is an indication of secondary evaporation of the falling raindrops. Partial evaporation of raindrops during their fall, with a non-equilibrium fractionation, may cause enrichment of heavier isotopes in rainfall and a decrease in *d* values during non-monsoon months[14]. The larger variation observed in the stable isotope values and *d*-excess indicates that the pre-monsoon rains in the region have re-evaporated vapour contribution and may be deriving most of its moisture from continental sources through inland evaporation. The negative *d*-excess values however suggest that pre-monsoon rains undergo severe evaporation during its downfall. The continental vapour source of the pre-monsoon showers is further confirmed by its relatively high mean and weighted mean tritium concentrations than southwest monsoon samples. If the precipitation is free from any effects after its formation through the equilibrium condensation from vapour, these samples should give depleted isotopic values with a high *d*-excess. But the fluctuating isotopic values and *d*-excess values of pre-monsoon rains clearly indicate that the pre-monsoon rains are prone to further isotopic modification through non-

equilibrium processes such as secondary evaporation beneath the cloud base during its fall through the atmosphere, extent of which is controlled by meteorological conditions and mostly by the amount of rainfall. This is evident from the two extreme conditions as of May 2006 ($\delta^{18}O = -3.12‰$, d-excess = 15.95, rain fall = 662.4 mm) and April 2007 ($\delta^{18}O = -1.4‰$, d-excess = –4.65, rain fall = 155.6 mm). The pre-monsoon rains in Kozhikode do not always represent its actual isotopic signature; rather it shows an acquired secondary isotopic signature, depending on the prevailing meteorological conditions. However, the secondary evaporation of the falling pre-monsoon rain drops from coastal wet tropics like Kerala needs more detailed analysis.

Tritium analysis

The monthly level of natural tritium in precipitation of Kozhikode is presented in Figure 7. The tritium concentration of precipitation in Kozhikode station showed temporal variation. However, it was observed that tritium content in precipitation shows a lower trend during the southwest monsoon period. The tritium level in precipitation was below 5 TU for most of the samples. This result is in accordance with the fact that the tritium level in the region has come down to the values that prevailed in the pre-bomb era. Similar results are reported in precipitation samples collected from most of the stations in Greece[12].

Seasonal mean tritium concentrations, seasonal weighted mean tritium concentration and the average amount of precipitation from these different seasons during the sampling period (2005–07) are presented in Table 2. The seasonal average value of monthly tritium concentration of precipitation was maximum during the northeast monsoon (3.7 TU) and minimum during the southwest monsoon season (2.2 TU), whereas the pre-monsoon rain samples showed values (3.4 TU) which are close to the values for northeast monsoon season. The weighted average of precipitation also follows the same trend (Table 2). The very large amount of precipitation compared to the other two seasons may be the cause of low tritium concentration of the southwest monsoon samples. The relatively low weighted mean of tritium of southwest monsoon rains also confirms that its vapour source is mostly of marine origin[28]. The pre-monsoon showers are seen to have slightly more tritium than the southwest monsoon samples which may be because most of the vapours contributing the pre-monsoon rainfall are derived from continental vapour sources. The northeast monsoon samples showed slightly higher mean and weighted mean of the tritium concentrations than the southwest monsoon samples. The tritium concentrations in rain increases towards mid and high latitudes. The higher tritium concentrations in northeast monsoon rains than the southwest monsoon rains may be due to the northeast monsoon vapours originating at higher latitudes. The northeast monsoon winds originating from central Asia can draw moisture from depleted continental vapour sources as well as oceanic sources like South China Sea and Bay of Bengal[11] during its southward journey and this blend of continental and oceanic vapour sources may govern the tritium concentrations of the northeast monsoon samples. However, it is also possible that the northeast monsoon picks up extra tritium while passing over the Kalpakkam nuclear power station near Chennai on its way to Kozhikode. The power station reactors being of heavy water moderated type may release significant levels of tritium. High tritium content was observed in the surface water in ponds (145–479 TU), canals (62 TU), Bay of Bengal (23 TU) and in the shallow ground water (15–155 TU) in the Kokilimedu[33] (located 80 km south of Chennai) mainly due to effluents from the nuclear power plant situated around 0.5 km of the site. The moisture evaporating from these sources can also contribute to the high tritium content of the northeast monsoon samples. The tritium results also support the stable isotopic observations on the dual monsoon system in Kozhikode.

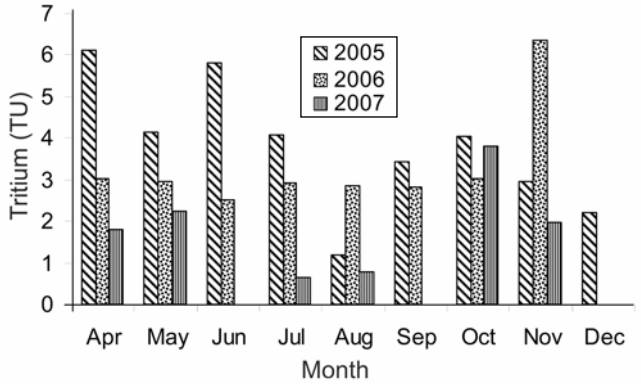

Figure 7. Monthly variations of natural tritium input in precipitation of Kozhikode.

Conclusions

- The local trend of stable isotopic signatures of Kozhikode almost follows the global trend.
- The southwest monsoon and the northeast monsoon show two distinct isotopic signatures.
- The two distinct isotopic signatures of southwest and northeast monsoon rains are not only due to the difference in vapour source but also ascribed to the differences in the rainout histories of the two air masses before reaching the region.
- The pre-monsoon rains in the region lack any distinctive isotopic signature.
- The northeast monsoon samples have a slight excess of tritium because it originates from higher latitude.

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