A comparative study on isotopic composition of precipitation in wet tropic and semi-arid stations across southern India

C UNNIKRISHNAN WARRIER* and M PRAVEEN BABU

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

**Corresponding author. e-mail: warrier@cwrdm.org*

Isotopic composition of monthly composite precipitation samples from Kozhikode ($n = 31$), a wet tropic station and Hyderabad ($n = 25$), a semi-arid station across southern India were studied for a period of four years from 2005 to 2008. During the study period, the Kozhikode station recorded an average rainfall of 3500 mm while the Hyderabad station showed an average rainfall of 790 mm. The average stable isotope values in precipitation at the Kozhikode station were $\delta^{18}\text{O} = -3.52\text{‰}$, d-excess = 13.72‰; $\delta^{18}\text{O} = -2.94\text{‰}$, d-excess = 10.57‰; and $\delta^{18}\text{O} = -7.53\text{‰}$, d-excess = 13.79‰, respectively during the pre-monsoon (March–May), monsoon (June–September) and post-monsoon (October–February) seasons. For the Hyderabad station, the average stable isotope values were $\delta^{18}\text{O} = -5.88\text{‰}$, d-excess = 2.34‰; $\delta^{18}\text{O} = -4.39\text{‰}$, d-excess = 9.21‰; and $\delta^{18}\text{O} = -8.69\text{‰}$, d-excess = 14.29‰, respectively for the three seasons. The precipitation at the two stations showed distinctive isotopic signatures. The stable isotopic composition of precipitation at the Hyderabad station showed significant variations from the global trend while the Kozhikode station almost followed the global value. These differences are mainly attributed to the latitudinal differences of the two stations coupled with the differences in climatic conditions.

1. Introduction

Isotope hydrology has proven itself as a powerful tool for hydrological investigations. 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 (Fontes 1980; IAEA 1981; Mazor 1991; Mathieu and Bariac 1996; Clark and Fritz 1997), to study the effects of evaporation on groundwater systems (Gonfiantini 1986; Hendry 1988), to study groundwater and surface water interaction (Krabbenhoft *et al* 1990), to identify the source and to elucidate the possible mechanism of saline water intrusion (Kulkarni

et al 1997; Saravana Kumar *et al* 2009). 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 (Clark and Fritz 1997). The variations in stable isotopic composition of water bodies have been explained in terms of variations from the Global Meteoric Water Line (Craig 1961). 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.

Keywords. Stable isotopes; d-excess; Kozhikode; Hyderabad; India.

The deuterium excess (d-excess, Dansgaard 1964) of rainfall is extensively used to identify the origin of vapour source of precipitation (Rozanski *et al* 1982; Kondoh and Shimada 1997). The results of stable isotopic composition and the tritium content of precipitation samples 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 (Argiriou and Lykoudis 2006). The stable isotopic compositions of precipitation from eight meteorological stations along with selected ground-water samples in Saudi Arabia were studied by Alyamani (2001) and found that the monsoon-derived rainfall plays crucial role in the alluvial aquifer recharge. In the Indian context also, the isotopic composition of precipitation has been widely applied for various environmental applications like identifying the monsoon processes, for characterising different moisture sources contributing to precipitation (Kumar *et al* 2010; Unnikrishnan Warriar *et al* 2010), its influences in the recharge, etc. Datta *et al* (1991) found that even though long term stable isotope values in precipitation values at New Delhi agree with the Global Meteoric Water Line, the short term features were found to follow an evaporative line probably due to evaporation and subsequent enrichment during the fall. Deshpande *et al* (2003) used the available regional maps of amount weighted monthly isotopic data of precipitation from the GNIP/IAEA (Global Network of Isotopes in Precipitation/International Atomic Energy Agency) database to discern and describe the hydrological processes responsible for giving characteristic regional distribution of $\delta^{18}\text{O}$ and d-excess for different seasons over the Indian subcontinent. 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 (Sengupta and Sarkar 2006). In the present study, the variations in isotopic composition of precipitation of Hyderabad and Kozhikode, two stations across southern India are compared and discussed. This study attempts to apply stable isotope techniques (δD and $\delta^{18}\text{O}$) to understand the variations in precipitation patterns at the two locations.

2. Study area

Kerala is one of the southern states of India and is situated at the southwest corner of the Indian peninsula. The state extends from 8.2° – 12.8°N parallel and 74.8° – 77.5°E meridian, covering an area of $\sim 38,800\text{ km}^2$. It is bounded by Arabian Sea on the west while 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 with a maximum east-west width of 120 km. Averaged over the entire state, Kerala gets an annual average rainfall of 3000 mm spread over 126 rainy days (Menon and Rajan 1989). Kerala is under the influence of dual monsoon system namely the southwest monsoon (summer monsoon) and the northeast monsoon (winter monsoon).

The precipitation samples for Kozhikode station were collected from Centre for Water Resources Development and Management (CWRDM) at Kunnamangalam (long. $75^{\circ}52'15''\text{E}$, lat. $11^{\circ}17'07''\text{N}$ and elevation $\sim 70\text{ m}$ above MSL) of Kozhikode district, Kerala. Kozhikode receives good amount of rainfall with an annual average value of around 3090 mm (1979–2007). During this study period (2005–2008), the annual average rainfall was slightly higher (3508 mm) than the long-term average value of 3090 mm. The southwest monsoon contributed about 75% of the rainfall while the northeast monsoon and pre-monsoon rain contributed the rest. 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 the month of April and the lowest temperature of about 20°C was noticed in the month of December. The mean monthly humidity of 72% is noticed in the month of January while the month of June and July shows the highest mean monthly value of 86% (CWRDM unpublished data).

The Hyderabad samples were collected from the Mandal Revenue office, Moinabad (lat. $17^{\circ}19'91.1''\text{N}$, long. $78^{\circ}17'23.3''\text{E}$ and elevation $\sim 560\text{ m}$ above MSL). A location map showing both the sampling stations is given in figure 1. Hyderabad is the capital of the state of Andhra Pradesh and is one of the fastest growing cities in India. Hyderabad spreads around an area of $\sim 625\text{ km}^2$, with an estimated population of 6.7 million (Buechler *et al* 2002). The mean monthly temperature of the Hyderabad varies from 22.6°C in January to 32.3°C in May. The mean monthly vapour pressure of 15.3 hPa is noticed in the month of February while the month of January showed the highest mean monthly value of 42.2 hPa (www.isohis.iaea.org). Hyderabad city is having a long term (1901–1970) annual average rainfall of 785 mm and a potential evapotranspiration of 1525 mm with a water deficiency of 810 cm. Mean aridity index of the city is 53.2 and the region falls under semi-arid climate (Katiyar 1990). Hyderabad shows persistency of its climate, in a period of 70 years from 1901–1970, it showed semi-arid climate for 57 years, dry subhumid climate for 9 years and arid climate for 4 years (Katiyar 1990). However, perceptible

Figure 1. Location map showing both the sampling stations.

change in monsoon patterns is noticed in Hyderabad for the last 25 years (Kadorkar 2009). During this study period (2005–2008), the annual average rainfall of Hyderabad station was 790 mm, a value close to that of the long term average annual rainfall of 785 mm.

3. Methodology

Monthly composite precipitation samples from both the stations were collected from 2005 to 2008 following the norms suggested by IAEA (www.isohis.iaea.org). For stable isotopes, the samples were taken in a clean polythene 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.

The stable isotopes were analyzed using Isotope Ratio Mass Spectrometer (FINNIGAN DELTA Plus XP) at the Isotope Hydrology Division of CWRDM. The oxygen isotope ($\delta^{18}\text{O}$) was

analysed using $\text{CO}_2\text{--H}_2\text{O}$ equilibration method. The hydrogen (δD) analyses were performed by the $\text{H}_2\text{--H}_2\text{O}$ equilibration technique using platinum catalyst supported on a hydrophobic material (Epstein and Mayeda 1953). All the measurements were carried out against secondary laboratory standards that are periodically calibrated against the international isotope water standards recommended by the IAEA (V-SMOW, GISP and SLAP). The analytical reproducibility of the results is 0.08‰ for $\delta^{18}\text{O}$ and 1‰ for δD .

4. Isotope systematics

The isotopic results are reported as δ units, i.e., the deviation of the isotope ratio from that of the international standard V-SMOW (Gonfiantini 1978). The δ being defined by

$$\delta = \left[\frac{(R_{\text{Sample}} - R_{\text{VSMOW}})}{R_{\text{VSMOW}}} \right]$$

where R_{Sample} and R_{VSMOW} are the ratio of the less abundant heavier isotope of interest to the most abundant isotope ($^{18}\text{O}/^{16}\text{O}$ or D/H in the case of ^{18}O and ^2H) of the sample and standard respectively. The values are reported in permil (‰) to make the result appear significant and for the ease of comparing the results.

$$\delta (\text{‰}) = \left[\frac{(R_{\text{Sample}} - R_{\text{VSMOW}})}{R_{\text{VSMOW}}} \right] \times 10^3.$$

Stable isotope variations result from isotope fractionation, which occur during physical and chemical processes. In 1961, Craig published his findings that in spite of all the complexities of the various processes in the hydrological cycle, the $\delta^{18}\text{O}$ and δD in fresh waters correlate on a global scale and the isotopic compositions of meteoric waters behave in a predictable manner. Craig's 'Global Meteoric Water Line' (GMWL) defines the relationship between $\delta^{18}\text{O}$ and δD in world-wide fresh surface waters. The GMWL defined by Craig (1961) can be represented by the following equation.

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10. \quad (1)$$

The intercept of the above equation (1) was subsequently confirmed by Yurtsever and Gat (1971) and more recently by Rozanski *et al* (1993) who obtained the following equation (2) by considering all the isotopic results obtained by IAEA, from the WMO collection stations using the mean arithmetic values.

$$\delta\text{D} = (8.17 \delta^{18}\text{O} \pm 0.06) + (10.35 \pm 0.65). \quad (2)$$

Kumar *et al* (2010) developed meteoric water line for India using hydrogen (D/H) and oxygen ($^{18}\text{O}/^{16}\text{O}$) isotopic ratios in precipitation collected from several locations in India during the period 2003–2006. They also developed regional or Local Meteoric Water Line (LMWL) for different zones in India. The Indian Meteoric Water Line (IMWL) developed by them is given in equation (3) below.

$$\delta\text{D} = (7.93 \pm 0.06) \times \delta^{18}\text{O} + (9.94 \pm 0.51). \quad (3)$$

The IMWL differs slightly from the GMWL in its slope and intercept. Various studies have also developed LMWLs for several Indian regions (Deshpande *et al* 2003; Unnikrishnan Warriar *et al* 2010). The LMWL provides a baseline for groundwater investigations of a region, which differs from the global line owing to the variations in climatic and geographic parameters. The deuterium

excess (d-excess) of precipitation (Dansgaard 1964) can also provide valuable information on the moisture sources of precipitation. The d-excess defined as $d = \delta\text{D} - 8\delta^{18}\text{O}$, 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. Evaporation from continental surface water bodies at low humidity can produce vapour mass with high d-excess (Clark and Fritz 1997).

5. Results and discussions

5.1 Stable isotope variations

The stable isotope results and the monthly precipitation for the study period at the two locations are given in table 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 airmasses giving precipitation at a particular place (Rozanski *et al* 1982). Stable isotope content of precipitation at the two stations showed significant variations. The Oxygen-18 content in precipitation ranged from $\delta^{18}\text{O} = -1.16\text{‰}$ in April 2008 to $\delta^{18}\text{O} = -10.76\text{‰}$ in October 2008 at the Kozhikode station and from $\delta^{18}\text{O} = -0.03\text{‰}$ in May 2008 to $\delta^{18}\text{O} = -11.43\text{‰}$ in October 2005 for the Hyderabad station. The LMWL of Kozhikode and Hyderabad stations were constructed (figure 2a and b) and are compared with the GMWL (Rozanski *et al* 1993) and IMWL (Kumar *et al* 2010). The $\delta^{18}\text{O}$ and δD in precipitation at both the stations were fairly correlated. The LMWL of the Kozhikode station showed slope and intercept close to that of the global and Indian values while the intercept at the Hyderabad station were much lower than that of the global and Indian values. The modification of the stable isotopic signatures due to the secondary evaporation from the falling raindrops is the reason for the lower intercept at Hyderabad station. The difference in altitude can also influence the stable isotopic composition of two locations. The altitude of the Kozhikode and Hyderabad stations are 70 m above MSL and 560 m above MSL, respectively. Among the three seasons, only the monsoon samples can be considered for determining any altitude effects as the pre-monsoon rainfall at Hyderabad station is prone to significant secondary evaporation and the post-monsoon rains at the two stations are having different origins. The observed decrease in $\delta^{18}\text{O}$ with altitude between the two stations is 0.31‰ per 100 m during the monsoon season.

Table 1. Isotope results and monthly rainfall at Kozhikode and Hyderabad during 2005–2008.

Period of collection	Kozhikode				Hyderabad			
	δD (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	Rainfall (mm)	δD (‰)	$\delta^{18}O$ (‰)	d-excess (‰)	Rainfall (mm)
April 2005	−70.92	−10.26	11.16	158.8	NA	NA	NA	NA
May 2005	−3.89	−1.89	11.23	95.2	NA	NA	NA	NA
June 2005	−9.44	−2.63	11.60	857.6	−12.25	−2.71	9.43	59
July 2005	−10.53	−2.70	11.07	897.4	−11.03	−2.37	7.93	306
August 2005	−3.9	−1.33	6.74	210.2	−33.47	−5.08	7.17	127
September 2005	−7.38	−2.08	9.26	419.6	−19.12	−3.83	11.52	198
October 2005	−38	−6.25	12	216.2	−77.82	−11.43	13.62	305
November 2005	−48.2	−7.90	15	178.6	NA	NA	NA	0
December 2005	−52.08	−7.90	11.12	52.8	NA	NA	NA	0
March 2006	−16.37	−3.79	13.95	48.6	−76.47	−11	11.53	19
April 2006	−15.3	−2.61	5.58	48.8	−20.07	−2.57	0.49	56
May 2006	−9.01	−3.12	15.95	662.4	−75.15	−9.26	−1.23	36
June 2006	−6.78	−2.56	13.70	1006.6	NA	NA	NA	52
July 2006	−2.53	−1.61	10.35	632.6	−14.14	−2.79	8.18	57
August 2006	−6.62	−2.10	10.18	483.6	−35.71	−5.42	7.65	135
September 2006	−29.6	−4.83	9.04	680.2	−35.74	−5.36	7.14	188
October 2006	−42.99	−6.85	11.81	281.4	NA	NA	NA	14
November 2006	−38.86	−6.72	14.86	147.4	NA	NA	NA	0
April 2007	NA	NA	NA	155.6	−66.48	−8.55	1.92	35.4
May 2007	−29.14	−5.11	11.74	34.2	−68.59	−8.17	−3.23	12
June 2007	−33.42	−5.60	11.38	936.9	−43.66	−7.03	12.58	195
July 2007	−3.58	−1.79	10.74	1383	−24.10	−3.87	6.86	23
August 2007	−10.43	−2.88	12.58	712	−23.98	−3.79	6.34	128
September 2007	−20.19	−3.73	9.64	711	−32.56	−4.91	6.72	153
October 2007	−47.19	−7.97	16.60	333	NA	NA	NA	26
November 2007	−53.2	−8.64	15.92	78	NA	NA	NA	8
February 2008	NA	NA	NA	3.8	−26.53	−4.93	16.03	56
March 2008	NA	NA	NA	165	42.25	5.32	−2.81	141
April 2008	3.66	−1.16	12.95	88.4	NA	NA	NA	0
May 2008	−6.76	−2.59	14	72	5.90	−0.03	6.14	40
June 2008	−8.52	−2.76	13.56	828	−2.05	−1.31	8.43	46
July 2008	−10.85	−2.82	11.71	594	−9.28	−2.11	7.6	76.2
August 2008	−11.41	−2.81	11.07	294	−12.86	−3.3	13.54	269
September 2008	−31.89	−4.90	7.31	441	−61.78	−9.66	15.5	208
October 2008	−66.36	−10.76	19.72	579	−61.27	−9.31	13.21	34
November 2008	−44.62	−6.85	10.18	38	NA	NA	NA	35

NA – Not available.

5.2 Deuterium excess

The d-excess of precipitation varied from 5.58‰ in April 2006 to 19.72‰ in October 2008 for the Kozhikode station and from −3.23‰ in May 2007 to 16.03‰ in March 2008 for the Hyderabad station (table 1). The d-excess of precipitation of the Hyderabad station were lower than that of the Kozhikode station for most of the period. Both the stations receive a small amount of pre-monsoon rains in the March–May period. Among the two stations, the Hyderabad samples are showing lower d-excess in most cases during this season including negative values in some cases (table 1). The

negative d-excess is an indication of excessive secondary evaporation of raindrops during its fall beneath the cloud base (Clark and Fritz 1997). The Hyderabad samples are more prone to secondary effects because of the difference in climatic conditions existing in the two stations (table 2).

5.3 Seasonal variations

5.3.1 Pre-monsoon season

The seasonal average values of $\delta^{18}O$, δD and d-excess of precipitation at Kozhikode and Hyderabad stations are given in table 3. During

the pre-monsoon period (March–May), the average $\delta^{18}\text{O}$ at Kozhikode and Hyderabad stations were -3.81‰ and -5.88‰ , respectively indicating depletion of stable isotopic composition at Hyderabad. The d-excess values at the two stations during this season were 12.06‰ and 2.34‰ , respectively. The pre-monsoon rains in both the locations draw most of its moisture from the continental sources. Due to the latitudinal difference of the two stations, the precipitation at the Hyderabad station is expected to be more depleted than that of the Kozhikode station. This will cause the surface water sources and other moisture sources at

Hyderabad to be depleted in comparison with that of the Kozhikode station. The evaporating moisture from these sources and the subsequent precipitation at Hyderabad during the pre-monsoon period is thus depleted than that of the Kozhikode station.

The difference in climatic regimes in both the station is also having significant influence in determining the isotopic signature of the precipitation during the pre-monsoon season. Due to the differences in the amount of precipitation, temperature and humidity between the two stations (table 2), the precipitation at Hyderabad station will undergo significant secondary evaporation beneath the cloud base during its fall. This effect will enrich the isotopic content of precipitation, changes its actual isotopic signature and lowers its d-excess. This effect is the reason for the low d-excess (2.34) of precipitation at Hyderabad station especially during the pre-monsoon period. The stable isotopic composition of precipitation at this station especially during pre-monsoon season would have been more depleted in the absence of this effect. In the case of Kozhikode, the possibility of secondary evaporation of the pre-monsoon rains is limited as it belongs to a wet tropic station situated about 15 km away from the coast. Most of the pre-monsoon rains at Kozhikode are not influenced by secondary evaporation. The relatively enriched $\delta^{18}\text{O}$ value of the pre-monsoon rains at Kozhikode suggests that it may have some marine moisture contribution especially in the month of May.

Figure 2. The Local Meteoric Water Line of (a) Kozhikode and (b) Hyderabad.

5.3.2 Monsoon season

Monsoon derived rainfall is the most characteristic feature of the climate in the Indian

Table 2. Average monthly rainfall, temperature and vapour pressure at two stations.

Month	Hyderabad			Kozhikode		
	Rainfall (mm)	Temperature (°C)	Vapour pressure (hPa)	Rainfall (mm)	Temperature (°C)	Vapour pressure (hPa)
January	8	22.6	42.2	2	28	25.9
February	42	25.4	15.3	6	28.8	27.3
March	31	28.6	16.3	22	29.7	29.4
April	9	31.4	19.7	73	30.3	30.9
May	43	32.3	22.2	335	29.2	31.1
June	81	29.4	24.7	687	27.3	29.8
July	170	27.1	25.8	608	26.6	27.9
August	256	26.1	26.2	396	26.7	29.1
September	96	26.4	26.2	181	27.4	29.4
October	97	26.0	23.7	311	27.6	28.2
November	15	24.3	19.6	125	28.2	27.9
December	26	23.2	17.5	58	27.4	25.6

Source: International Atomic Energy Agency.

subcontinent. The southwest monsoon period from June to September is the principal rainy period at both the locations. During this period, Kerala receives copious amount of rainfall while Hyderabad receives only moderate amount of rainfall. During the southwest monsoon period, the average $\delta^{18}\text{O}$ at Kozhikode and Hyderabad stations were -2.94‰ and -4.39‰ , respectively. The d-excess values at the two stations during this season were 10.57‰ and 9.21‰ , respectively (table 3). The average $\delta^{18}\text{O}$ of precipitation at the Hyderabad station during the southwest monsoon period were about 1.4‰ depleted than that at the Kozhikode station. This is due to the latitudinal difference and the differences in climatic conditions of the two stations. Kerala, situated at the southern tip of the Indian subcontinent is positioned directly across the path of the maritime air blowing from the Indian Ocean and Arabian Sea during the northern hemispheric summer (Menon and Rajan 1989). 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 and it starts mostly by the first week of June. This first condensate behaviour of the rain is the reason for the Kozhikode station to show comparatively enriched isotopic composition. In contrast, the moisture input for monsoonal precipitation at Hyderabad advects into the region from the western coast north of Kozhikode and travels longer distance through continent before shedding its drops at Hyderabad. During its journey to Hyderabad, it acquires vapour from continental sources and the precipitation at Hyderabad is having significant continental vapour contribution. The rainout effect and the continental vapour contribution make the precipitation at Hyderabad comparatively depleted than Kozhikode. However, in Hyderabad, due to lower amount of rainfall and lower humidity, there is a possibility that the falling raindrops may

undergo evaporation beneath the cloud base. The possibility of secondary evaporation of the falling rain may enrich the samples and mask the actual depletion to a smaller extent.

5.3.3 Post-monsoon season

During the post-monsoon period (October to February) the pressure and wind patterns in the region 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 (Menon and Rajan 1989). This causes the Indian winter monsoon also called the northeast monsoon causing rains in some parts of India especially in coastal Tamil Nadu. The northeast monsoon is more or less dry and gives rise to only lesser amount of precipitation. Among the two stations studied, Kozhikode station is under the influence of dual monsoon precipitation while there is not much influence of northeast monsoon in Hyderabad. Average $\delta^{18}\text{O}$ in precipitation during the post-monsoon period was -7.53‰ and -8.69‰ , respectively at Kozhikode and Hyderabad stations. The d-excess of precipitation were 13.79‰ and 14.29‰ respectively at the two stations. The post-monsoon rains at Hyderabad station was 0.93‰ depleted than the Kozhikode station. The northeast monsoon travels over large landmasses before reaching Kerala resulting in large rainout effects. These winds by the time it reaches the southern tip of India must have shed most of its vapours and get recharged from the oceanic sources of Bay of Bengal causing heavy rains along coastal Tamil Nadu. These winds then cross over Tamil Nadu and reach the Kozhikode station. Unnikrishnan Warriar *et al* (2010) suggested that the slightly higher amount of tritium observed in northeast monsoon rains at Kozhikode may also be due to picking up of tritium by the

Table 3. Average and weighted average of $\delta^{18}\text{O}$, δD and d-excess at two stations.

Season	Kozhikode			Hyderabad		
	δD (‰)	$\delta^{18}\text{O}$ (‰)	d-excess (‰)	δD (‰)	$\delta^{18}\text{O}$ (‰)	d-excess (‰)
Average						
Pre-monsoon	-18.46	-3.81	12.06	-44.66	-5.88	2.34
Southwest monsoon	-13.00	-2.94	10.57	-25.89	-4.39	9.21
Post-monsoon	-46.45	-7.53	13.79	-55.21	-8.69	14.29
Weighted average						
Pre-monsoon	-16.80	-3.85	13.99	-42.13	-5.42	1.24
Southwest monsoon	-12.89	-2.99	11.00	-26.24	-4.51	9.87
Post-monsoon	-48.57	-8.00	15.21	-51.35	-8.27	14.80

northeast monsoon winds from nuclear reactors in Tamil Nadu during its journey to Kozhikode. The northeast monsoon at Kozhikode is having depleted isotopic signatures owing to its complex rainout histories and picking moisture from continental vapour sources during its journey to Kozhikode.

In the case of Hyderabad, there is not much influence of northeast monsoon. During this season most of the rainfall is believed to be caused by the depressions originating from the Bay of Bengal and are characterized by very rapid downpour. The isotopic signatures of rain during this season is highly depleted and have high d-excess (e.g., $\delta^{18}\text{O} = -11.43\text{‰}$, d-excess = 13.62, October 2005) The post-monsoon rains at Hyderabad are mostly caused by the cyclones originating from Bay of Bengal and travels greater distance through land before reaching the station. The precipitation arising from cyclonic storms are expected to have depleted isotopic signatures (Lawrence and Gedzelman 1996). Studies have also revealed that surface water of Bay of Bengal is more depleted compared to that of the Arabian Sea (Delaygue *et al* 2001; Deshpande *et al* 2003). Also, by the time these vapours reach this station, it might have acquired vapour contribution from continental sources. The heavy rains characteristic of this season may also reduce the possibility of secondary evaporation of falling rains which are usually noticed in this region. These factors may be the reason for highly depleted isotopic signatures and higher d-excess (avg. 14.29) of rains at Hyderabad during this season. The isotope values of precipitation at Hyderabad in the month of February ($\delta^{18}\text{O} = -4.93\text{‰}$, d-excess=16.03, February 2008) suggest that there may be an influence of western disturbance during this period. However, during the present study, the number of samples collected during the post-monsoon season was less (only three samples) and hence more detailed investigation is needed for further understanding on this matter.

5.4 Amount effect

The term amount effect was coined by Dansgaard (1964) who found a strong negative correlation between $\delta^{18}\text{O}$ and monthly rainfall, with heavy rainfall resulting in more negative $\delta^{18}\text{O}$ for some 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– $\delta^{18}\text{O}$ diagram of Kozhikode and Hyderabad stations considering entire samples covering all the three seasons is shown in figure 3(a and b) respectively. The precipitation amount (monthly total) and monthly

Figure 3. Amount of rainfall– $\delta^{18}\text{O}$ diagram of (a) Kozhikode and (b) Hyderabad stations.

$\delta^{18}\text{O}$ of rainfall for both the stations are not well correlated with correlation coefficient for amount *vs.* $\delta^{18}\text{O}$ ($R^2 = 0.102$ and $R^2 = 0.021$) respectively for both the stations. The relationship between the amount and $\delta^{18}\text{O}$ of rainfall at the Kozhikode and Hyderabad stations were:

$$\delta^{18}\text{O} = 0.002P_m - 5.6, \quad R^2 = 0.102 \quad (\text{all seasons}) \quad (4)$$

$$\delta^{18}\text{O} = -0.006P_m - 4, \quad R^2 = 0.021 \quad (\text{all seasons}) \quad (5)$$

The average rate of depletion in $\delta^{18}\text{O}$ was $+0.2\text{‰}$ per 100 m for Kozhikode (equation 4) and 0.6‰ per 100 m for the Hyderabad station (equation 5). The ‘positive’ amount effect observed at the Kozhikode station resembles the results obtained by Yadava *et al* (2007) who noticed similar positive slope for monthly weighted average $\delta^{18}\text{O}$ and monthly total amount of rainwater samples collected from Mangalagangothri, Mangalore in Karnataka. They explained the ‘positive slope’ observed in the Mangalagangothri station in the following manner. In the location most rain events in September and October are lower in amount and also isotopically depleted compared to those of the preceding months with higher amount and enriched isotopic signatures. When monthly values are plotted, the low rainfall, depleted isotope ratios plot on the lower left of the graph and the high rainfall in the preceding months with enriched values plot on the top right, with a distribution in between and

shows an apparent positive slope. The same explanation holds good for the Kozhikode station also as most rain events in this station during October and November are lower in amount and also isotopically depleted compared to the heavy rains received during the southwest monsoon period from June to September.

The amount effect observed during different seasons at the Kozhikode station is given below

$$\delta^{18}\text{O} = -0.013P_m - 2.3, \quad R^2 = 0.006 \text{ (pre-monsoon)} \quad (6)$$

$$\delta^{18}\text{O} = -0.0001P_m - 2.7, \quad R^2 = 0.185 \text{ (monsoon)} \quad (7)$$

$$\delta^{18}\text{O} = -0.004P_m - 6.7, \quad R^2 = 0.374 \text{ (post-monsoon)} \quad (8)$$

The average rate of depletion in $\delta^{18}\text{O}$ is 1.3‰, 0.01‰ and 0.4‰ per 100 mm of precipitation respectively for the pre-monsoon (equation 6), monsoon (equation 7) and post-monsoon period (equation 8). The amount effect obtained for the Hyderabad station is given below.

$$\delta^{18}\text{O} = 0.150P_m - 11.83, \quad R^2 = 0.404 \text{ (pre-monsoon)} \quad (9)$$

$$\delta^{18}\text{O} = -0.010P_m - 2.5, \quad R^2 = 0.149 \text{ (monsoon)} \quad (10)$$

$$\delta^{18}\text{O} = -0.010P_m - 7.04, \quad R^2 = 0.204 \text{ (post-monsoon)} \quad (11)$$

The pre-monsoon samples at Hyderabad showed an apparent positive slope with an enrichment of 15‰ for $\delta^{18}\text{O}$ per 100 mm of precipitation (equation 9). The reason for the positive slope may be the excessive secondary evaporation of the low intensity rains during the pre-monsoon season. The amount effect during the monsoon and post-monsoon period is 1‰ for $\delta^{18}\text{O}$ per 100 mm of precipitation (equations 10 and 11).

Even though there can be many reasons for not having amount effect, the probable cause in the above cases may be that the Kozhikode station receives most of its rains during the southwest monsoon period where the rains represent almost first condensate behaviour. The absence of amount effect of rainfall in Kozhikode during the monsoon period indicates that the region receives a continuous supply of moist airmasses since the southwest monsoon currents moves across extended marine regions before reaching Kozhikode (Unnikrishnan Warriar *et al* 2010). In the case of Hyderabad station, the rain is undergoing significant secondary evaporation during its fall. This effect may be maximum during the pre-monsoon period

and minimum during the monsoon period. The different extent of secondary evaporation from the falling raindrops during different seasons and the addition of locally evaporated moisture may be the reason for the poor correlation of the Hyderabad samples during the pre-monsoon period.

6. Conclusions

The stable isotopic composition of precipitation of two stations across southern India are discussed and compared. These stations are Kozhikode, a coastal station in Kerala having wet tropic climatic conditions and Hyderabad, a semi-arid continental station in Andhra Pradesh. The following are the major inferences.

- The isotopic composition of precipitation at the Hyderabad station undergoes significant modification due to secondary evaporation during its fall whereas this effect is not significant in the case of Kozhikode.
- Due to secondary evaporation, the isotopic composition of precipitation at Hyderabad station especially during the pre-monsoon rains is not representing its actual isotopic signature but showing a lower depletion than its actual value.
- Most of the precipitation at Kozhikode derives moisture from oceanic sources while the precipitation at Hyderabad receives contribution from continental sources also.
- The proximity of the Kozhikode station to the coast and the first condensate behaviour of the rains make the isotopic composition of precipitation of this station relatively enriched during the southwest monsoon period. The rainout effect and the addition of continental vapours cause the isotopic composition of precipitation at Hyderabad to show comparatively depleted isotopic signatures during this season.
- The northeast monsoon precipitation in Kozhikode is having comparatively depleted isotopic signatures than the southwest monsoon rains since the northeast monsoon currents moves through extended regions before reaching Kozhikode and on its way it picks up moisture from continental sources. The cyclonic nature of rain, distance of the station from moisture source region and the possible contribution from continental sources seem to be the reason for highly depleted isotopic composition of precipitation at Hyderabad during the post-monsoon season.
- The monsoonal precipitation at Kozhikode station is not showing any amount effect possibly because of a continuous supply of moist airmasses in Kozhikode during the southwest monsoon period.

Acknowledgements

This work forms part of the Department of Science and Technology, Government of India sponsored Research Project 'An Investigation on Isotopic Composition of Precipitation, Surface and Subsurface Water and Their Interrelationship'. Dr B Venkateswara Rao and Mr Pavan Kumar are acknowledged for providing rain water samples from Hyderabad and Mr K T Velayudhan for analytical support. The authors are thankful to the Executive Director, CWRDM for the encouragement and permission for publication. We also thank the reviewers for valuable suggestions and constructive comments.

References

- Argiriou A A and Lykoudis S 2006 Isotopic composition of precipitation in Greece; *J. Hydrol.* **327** 486–495.
- Alyamani M S 2001 Isotopic composition of rainfall and ground water recharge in the western province of Saudi Arabia; *J. Arid Environ.* **49** 751–760.
- Buechler S J, Devi G and Raschid L 2002 Livelihoods and wastewater irrigated agriculture along the Musi River in Hyderabad city, Andhra Pradesh, India; *Urban Agriculture* **8** 14–17.
- Clark I D and Fritz P 1997 Environmental Isotopes in Hydrogeology; Boca Raton, Lewis Publishers, pp. 40–108.
- Craig H 1961 Isotopic variation in meteoric waters; *Science* **133** 1702–1703.
- Dansgaard W 1964 Stable isotopes in precipitation; *Tellus* **16** 436–468.
- Datta P S, Tyagi S K and Chandrasekharan H 1991 Factors controlling the stable isotopic composition of rainfall in New Delhi, India; *J. Hydrol.* **128** 223–236.
- Delaygue G, Bard E, Rollion C, Jouzel J, Stiévenard M, Duplessy J C and Ganssen G 2001 Oxygen isotope/salinity relationship in the northern Indian Ocean; *J. Geophys. Res.* **106**(C3) 4565–4574, doi: 10.1029/1999JC000061.
- Deshpande R D, Bhattacharya S K, Jani R A and Gupta S K 2003 Distribution of oxygen and hydrogen isotopes in shallow groundwaters from Southern India: Influence of a dual monsoon system; *J. Hydrol.* **271** 226–239.
- Epstein S and Mayeda T 1953 Variation of ^{18}O content of water from natural sources; *Geochim. Cosmochim. Acta* **4** 213–214.
- Fontes J Ch 1980 Environmental isotopes in groundwater hydrology; In: *Handbook of Environmental Isotope Geochemistry*; Fritz P and Fontes J Ch (eds) Vol. 1, The Terrestrial Environment (Amsterdam: Elsevier), pp. 75–140.
- Gonfiantini R 1978 Standards for stable isotope measurements in natural compounds; *Nature* **271** 534–536.
- Gonfiantini R 1986 Environmental isotopes in lake studies; In: *Handbook of Environmental Isotope Geochemistry*; (eds) Fritz P and Fontes J Ch (New York: Elsevier) **2** 113–168.
- Hendry M J 1988 Hydrogeology of clay till in a prairie region in Canada; *Ground Water* **26** 607–614.
- International Atomic Energy Agency 1981 *Guidebook on Nuclear Techniques in Hydrology*; Technical Report Series Vienna.
- Kadorkar M S 2009 WWDR3 side publication on Ecosystem Management; United Nations Environment Programme-UNEP, pp. 56–59.
- Katiyar V S 1990 The Indian Monsoon and its Frontiers; (New Delhi: Inter-India Publications), pp. 227–228.
- Kondoh A and Shimada J 1997 The origin of precipitation in eastern Asia by deuterium excess; *J. Japan Soc. Hydrol. & Water Resour.* **10**(6) 627–629.
- Krabbenhoft D P, Bowser C J, Anderson M P and Valley J W 1990 Estimating groundwater exchange with lakes: The stable isotope mass balance method; *Water Resour. Res.* **26** 2445–2453.
- Kulkarni K M, Navada S V, Nair A R, Rao S M, Shivanna K, Sinha U K and Sharma S 1997 Drinking water salinity problem in coastal Orissa, India – Identification of past transgression of sea water by isotope investigation; In: *Isotope Techniques in the Study of Past and Current Environmental Change*, Proc. Intl. Symp. IAEA Vienna, pp. 293–306.
- Kumar B, Rai S P, Saravana Kumar U, Verma S K, Garg P, Vijaya Kumar S V, Jaiswal R, Purendra B K, Kumar S R and Pande N G 2010 Isotopic characteristics of Indian precipitation; *Water Resour. Res.* **46** W12548, doi: 10.1029/2009WR008532.
- Lawrence R J and Gedzelman D S 1996 Low stable isotope ratios of tropical cyclone rains; *Geophys. Res. Lett.* **23**(5) 527–530.
- Mathieu R and Bariac T 1996 An isotopic study on water movements in clayey soils under semiarid climate; *Water Resour. Res.* **32** 779–789.
- Mazor E 1991 Chemical and Isotopic Groundwater Hydrology; The Applied Approach, 2nd edn; Marcel Dekker Inc., New York, 413p.
- Menon P A and Rajan C K 1989 Climate of Kerala; Classic Publishing House Cochin, pp. 5–35.
- Rozanski K, Sonntag G and Munnich K O 1982 Factors controlling the stable isotopic composition of European precipitation; *Tellus* **34** 142–150.
- Rozanski K, Araguas A L and Gonfiantini R 1993 Isotopic patterns in modern global precipitation; *Geophys. Monogr.* **78** 1–37.
- Saravana Kumar U, Suman S, Navada S V and Deodhar A S 2009 Environmental isotopes investigation on recharge processes and hydrodynamics of the coastal sedimentary aquifers of Tiruvadanai, Tamil Nadu State, India; *J. Hydrol.* **364** 23–39.
- Sengupta S and Sarkar A 2006 Stable isotope evidence for dual (Arabian Sea and Bay of Bengal) vapour sources in monsoonal precipitation over north India; *Earth Planet. Sci. Lett.* **250** 511–521.
- Unnikrishnan Warriar C, Praveen Babu M, Manjula P, Velayudhan K T, Shahul Hameed A and Vasu K 2010 Isotopic characterisation of dual monsoon precipitation-evidence from Kerala, India; *Curr. Sci.* **98** 1487–1495.
- Yadava M G, Ramesh R and Pandarinath K 2007 A positive 'amount effect' in the Sahayadri (Western Ghats) rainfall; *Curr. Sci.* **93**(4) 560–564.
- Yurtsever Y and Gat G R 1971 Atmospheric waters; In: *Stable Isotope Hydrology Deuterium and Oxygen-18 in the Water Cycle* (eds) Gat J R and Gonfiantini R, IAEA Technical Report Series Vienna, pp. 103–142.