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Tracing the Sources of River Waters Using Stable Isotopes ($\delta^{18}O$ and $\delta^{2}H$) in Two Mountainous Watersheds, Southern Western Ghats, India

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Abstract

Stable isotopes of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) are useful tools to characterize and monitor the hydrological processes in aquatic ecosystems.The present study uses $\delta^{18}O$ and $\delta^{2}H$ data from two small catchment rivers such as the east-flowing Bhavani river and the west-flowing Thuthapuzha River in southern Western Ghats to get an insight into the water cycle dynamics and sources of water.The Bhavani River drains through the semi-arid, lee-ward side of the Western Ghats and shows a markedly depleted isotopic composition as compared to the Thuthapuzha River which drains through the humid, windward side of the Western Ghats. The isotopic systematics are strongly influenced by the southwest monsoon (SWM) and the northeast monsoon (NEM) rainfalls. However, during the pre-monsoon (PRM) season, the isotopic composition in these river waters is governed mainly by the baseflow and evaporative processes. Both the river basins experience a higher vapour recycling effect in their headwaters. The NEM rainfall contains a considerable amount of recycled vapour, which is evident from the observed high d-excess values. Whereas the SWM rain events show the dominance of the original sea moisture source. There is a distinct difference in the isotopic ratios and d-excess values between the SWM (d-excess: Bhavani River 10.29 ± 1.29‰; Thuthapuzha River 10.52 ± 2.78‰) and the NEM (d-excess: Bhavani River 15.15 ± 0.92‰; Thuthapuzha River 12.67 ± 4.49‰) seasons, with the predominance of lighter isotopes in the latter period. In general, the seasonal and spatial differences in isotopic composition in the Bhavani River ($\delta^{18}O$: PRM−5.42 ± 1.76‰; SWM−4.16 ± 0.77‰; NEM -4.73 ± 0.76‰) and the Thuthapuzha River ($\delta^{18}O$: PRM −4.26 ± 0.67‰; SWM −2.54 ± 0.76‰; NEM −2.68 ± 0.96‰) indicate that precipitation (atmospheric source) as the major source of water in the monsoon (SWM and NEM) season, while the base flow contribution from groundwater has a major stake in PRM season.

Keywords: Stable Water Isotopes, d-excess, Climate Gradient, Base Flow Discharge, Western Ghats, Southwest India.

Introduction

The Western Ghats, a 1600km long mountain range on the western side of Peninsular India located close to the Arabian Sea,is a very important geomorphological feature hosting one of the most important biodiversity hotspots in the world (Gadgil *et al.*, 2011; Lambs *et al.*, 2011; Mohan and Krishnakumar 2011). It acts as a source and lifeline of many major and minor rivers in India (Jain *et al.*, 2007). The Western Ghats is often referred to as the water tower of peninsular India, as it ensures water and food security to a plethora of plants and animals (Ramachandra *et al.*, 2016). The Western Ghats receive much higher levels of precipitation than the adjoining regions of peninsular India and as a result, the natural biota of the region exhibits a high level of endemicity (Subramanyam and Nayar, 2001). The forest cover in the Western Ghats along with the soil and precipitation characteristics act as a life-supporting system by storing water in the sub-surface zones during monsoon and releasing it to the streams during the non-monsoon periods,thereby catering to the needs of the dependent biota and also humans.More than 245 million people in the peninsular Indian states depend onthe Western Ghats rivers for their survival (Naniwadekar and Vasudevan, 2014). Even though human occupation in the Western Ghats dates back many centuries, large-scale deforestation and destruction of forests are more recent phenomena(Chandran, 1997; Subramanyam and Nayar, 2001). The population explosion coupled with the accelerated pace of deforestation due to unplanned and skewed developments in this ecologically fragile region has adversely affected the water resources potential of the area. As a result, most of the perennial channels become dried up, springs disappeared, and water quality worsened, leading to declining in the quality of life of the people (Adam *et al.*, 2018). The expected increase in human pressure in the coming years, along with the adversities of climate change will undoubtedly lead to further degradation of this crucial life support system of South and Central India (Mathew *et al.*, 2022; Latha *et al.*, 2023).

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All these points to the imminent need for indepth-studies on the various environmental components of the life sustaining ecosystems of the Western Ghat mountain ranges. Among the different components, the chemical characterization of river water sources needs urgent attention because apart from the sustenance of life on earth, they also provide environmental connectivity between the hydrological and the geochemical cycles. Again, within the geochemical environments, stable isotopes in water have the remarkable ability to capture changes in the physico-chemical conditions of an environment (Gat, 1996; Rozanski *et al.*, 1993). Stable isotopes in water offer insights into water cycle dynamics and they are easy to sample and analyze for detailed investigations. Different watersources may have distinct signatures and hence can be used as a tool to characterize and monitor hydrology of tropical watersheds. The stable isotopes of water such as oxygen (^{18}O) and hydrogen (^{2}H) are powerful, well-established and efficient tools in the field of hydrology and are widely used to investigate the basic hydrological processes. Various meteorological and catchment scale processes like identifying the different sources to runoff, flow path, evaporation and evapotranspiration processes, surface-ground water interaction, mixing of large rivers, determination of the water balance of lakes, residence time in the watershed and information on climate change can be obtained through stable isotope studies of water (Craig, 1961; Dansgaard, 1964; Gat, 1996; Wu *et al.*, 2019; Bhagat *et al.*, 2021). The ^{2}H and ^{18}O isotopes are extensively used as an ideal indicator in water cycle research due to their capacity to respond sensitively to environmental changes, reflecting isotope fractionation in the process of water phase transformation (Bowen *et al.*, 2007; Joel, 2010). Some of the previous studies suggested that the changes in the atmospheric processes and moisture sources have prominent bearings on the stable isotopes of water (Yu *et al.*, 2016) and the characteristic isotopic signatures of waters are determined by these important influencing factors. The influence of local temperature, latitude and elevation on the distribution of precipitation isotopes is well known (Dansgaard, 1964; Friedman *et al.*, 1964; Gat, 1996). The importance of these climate and geographical factors are summarized as the temperature effect, the latitude effect, the elevation effect, the rainfall effect, the continental effect, and the seasonal effect (Rozanski *et al.*, 1993; Gat, 1996; Poage *et al.*, 2001; Jodar *et al.*, 2016). It is also reported that the rainfall amount effect is the key factor which controls the isotopic systematics in the tropics (Bowen and Ravenaugh, 2003; Rahul and Ghosh, 2019; Ohwoghere-Asuma *et al.*, 2021; Rizvi *et al.*, 2023).

The humid tropical forests which are localized in the Western Ghats mountain ranges play a crucial role in controlling the regional moisture dynamics and thus the monsoon rainfall. The rivers originating from the Western Ghats are generally rain-fed and many of them are shrunken to rivulets during the summer season.As a result of the altitude of the Western Ghats, the coastal hills are one of the wettest parts of the Indian subcontinent. The mountain ranges of Western Ghats act as a critical climate barrier which leads to a non-uniform distribution of moisture over the Indian subcontinent. There exists a substantial difference in precipitation seasonality and aridity between the windward and leeward sides of the Western Ghats. Gonfiantini *et al.* (2001) revealed that there is a relatively higher input of lighter isotopes to groundwater and surface water at high altitudes than on the lower elevations in the windward side. However, the relationship between the climate and the isotopic variations in precipitation of the windward and leeward sides of the Western Ghats is not yet fully addressed. The basins of humid tropical rivers originating from the Western Ghats Mountain ranges are one of the major regions that support higher degree of rock-water interaction (Gurumurthy *et al.*, 2012), and water vapour recycling (Tripti *et al.*, 2016). Further, in recent years the southern Western Ghats is under the threat of climate change effects which is evidenced from the frequent flood and drought events since 2018 (Ali and George, 2022; Jennifer *et al.*, 2022; Pramanick *et al.*, 2022). All these hydrology-related parameters need to be thoroughly investigated to formulate a climate adaptation strategy for the study area in particular and the southern Western Ghats in general, as the region acts as a gateway of Indian Summer monsoon.

In the present study, we have attempted to document the spatio-temporal variations of stable isotopic compositions of the river waters of two tropical montane rivers – the west flowing (draining windward side of the Western Ghats) Thuthapuzha River and east flowing (draining the leeward side of the Western Ghats) Bhavani River - that are flowing through distinct climate gradients and geologic settings across the southern Western Ghats. The study not only deals with the importance of Western Ghats in governing the water isotopic characteristics and the possible controlling factors in water cycle dynamics but also unfolds clues on the sources of water (atmospheric/groundwater) in these rivers.

Study Area

Among the two rivers considered for the present study (Bhavani River: 10° 55′53″N - 11° 44′58″N and Thuthapuzha River: 76° 05′00″E - 77° 41′10″ E) (Fig. 1a), the Bhavani River is 217 km long and originates from the Nilgiris hills of Western Ghats. It enters from the Silent Valley National Park of Kerala State and then flows through the western parts of Tamil Nadu and joins with the Cauvery River near Bhavani Town (PWD, 2002). The Bhavani River Basin (BRB) spreads over an area of 6200 km^2. The river is the largest tributary of the Cauvery River and drains nearly 8% of the total area of the Cauvery River Basin (Varunprasath and Daniel, 2010). The yearly precipitation of the Upper Bhavani Basin (4100km^2) is mainly contributed by SWM (1600mm), but in the Lower Bhavani Basin (2100 km^2), most of the rainfall occurs from the northeast monsoon (NEM).The basin experiences a composite climatic condition due to the rain shadow effect of the Western Ghats Mountain ranges (Anandakumar *et al.*, 2007). The area is covered with crystalline rocks mostly of Archaean age. The deposits of alluvial materials are noticed in the foothills and stream channels (Anand *et al.*, 2020). The major rock types in the Bhavani basin are hornblende-biotite gneiss, charnockites and granites (Anandakumar et al., 2007). The upper catchment area of the Bhavani Basin is prone to rampant soil erosion due to the undulating topography, steepness of the slope, the friable nature of the soils, and heavy and erratic rainfall (Narayanaswamy *et al.*, 1957). The Bhavani River Basin exhibits a variety of land use categories which include evergreen to semi-evergreen forests, deciduous forests in the sub-humid zone and dry deciduous vegetation in the semi-arid lower Bhavani region. The lower reaches are highly irrigated and cultivated (Fig. 1b).

The Thuthapuzha River originates from the Anginda peak in the Nilgiri Hills of the Western Ghats and flows through the tropical evergreen forests and mountainous terrains of the Silent Valley National Park in Kerala. It is a 100 km long, 6^{th}-order tributary of the west-flowing Bharathapuzha River and has a basin area of 1018 km^2

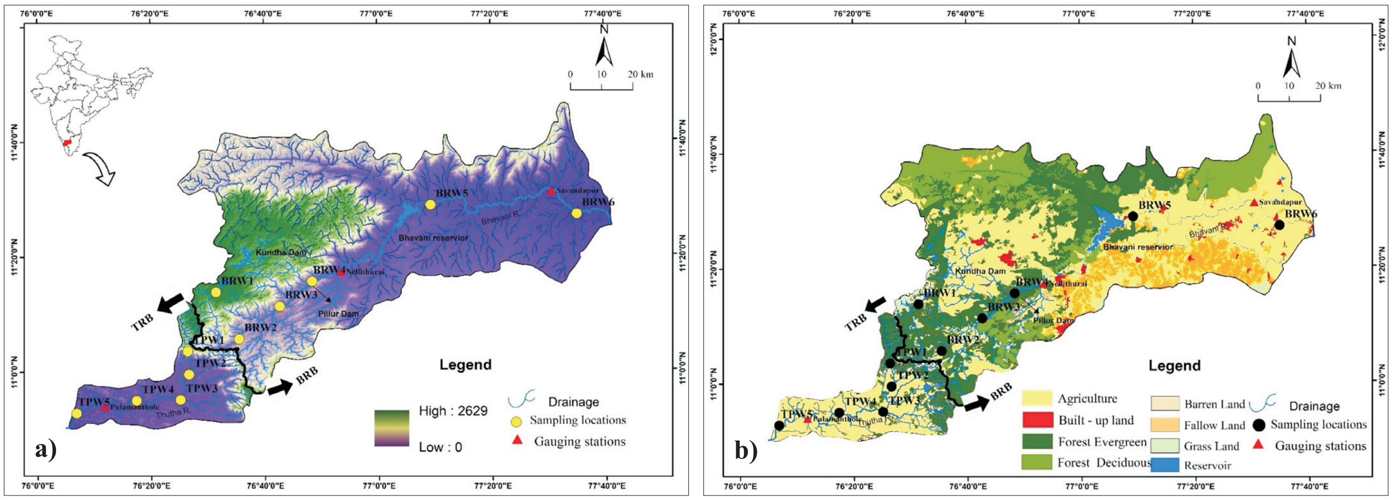

Fig. 1. (a) Location map of the study area showing drainage characteristics and topography, (b) Land Use-Land Cover map of the study area. (TRB: Thuthapuzha River Basin; BRB: Bhavani River Basin).

(Chethan and Vishnu, 2018). On its course, the river flows through the Palakkad and Malappuram districts of Kerala and finally joins the Bharathapuzha River near Pallippuram. Four tributaries are draining into the Thuthapuzha River, namely – the Kunthipuzha, the Kanjirapuzha, the Thuppanadpuzha and the Nellipuzha. Due to the presence of the less disturbed Silent Valley Reserve Forests to a greater part of the upper reaches of the basin, the Thuthapuzha River Basin (TRB) experiences a high amount of rainfall and contributes approximately 42% of the total rainfall in Bharathapuzha River Basin (Nikhil Raj and Azeez, 2009). The basin experiences a humid tropical climate and exhibits a wide disparity in the rainfall with an average of 2362mm (Warrier and Manjula, 2014). Rainfall in the Thuthapuzha watershed is dominated by SWM and nearly 75% of the total rainfall is received during SWM. It is reported that the Thuthapuzha River basin consists of Precambrian crystalline rocks -charnockite, charnockitic gneiss, khondalites and migmatites (Ravindrakumar and Chacko, 1994). Laterite capping with a maximum thickness of 20 m is also observed over a major part of the study area along its western part. Four kinds of soils are observed in the Thuthapuzha Basin - lateritic, riverine alluvium, forest loam and brown hydromorphic soil. In the Thuthapuzha River Basin, the majority of the area is used for agricultural activities and forests cover constitutes only 19.49 % of the total area (Fig. 1b).

Materials and Methods

A total of 33 river water samples were collected from the Bhavani (n=18) and the Thuthapuzha (n=15) rivers. The sampling was carried out during Pre-monsoon (PRM), Southwest monsoon (SWM) and Northeast monsoon (NEM) seasons in the year of 2019. The river water sampling was mainly concentrated along the master channel of both the Bhavani and Thuthapuzha Rivers. Dry and clean high-density polyethylene bottles were used for water sample collection and the bottles were rinsed two to three times with the water from the sampling site and then the actual sampling for the present study was carried out. The altitude of each sampling location was determined using GPS. The collected water samples were filtered with 0.45 µm membrane filters before analysis. The sample bottles were tightly packed in order to avoid isotopic fractionation through evaporation process. The oxygen and hydrogen isotopic ratios in the water samples were analyzed using a Triple Water Isotope Analyser (TWIA-45 EP) instrument (Los Gatos Research), enabled with Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) technique, at the National Centre for Polar and Ocean Research, Goa. The water samples were introduced in TWIA-45EP instrument through PAL, HTC-xt auto-injector (CTC Analytics) equipped with a heated (≈85 °C) injector block (LGR) (Berman *et al.*, 2013). Samples were added to the injector block using Hamilton 1.2 µL, zero dead volume syringes and were evaporated for the analysis of isotopic ratios. The measured isotopic ratios from the instrument were processed in the LGR post-analysis software to obtain the final data of δ^2H and $\delta^{18}O$ in the water sample. The stable isotopic composition for δ^2H and $\delta^{18}O$ is expressed in per mil (‰) with respect to the Vienna Standard Mean Ocean Water (VSMOW). The analytical precision of the measured standard is found to be better than ±0.13‰ (n=5) for δ^2H and ±0.06‰ (n=5) for $\delta^{18}O$.

The multivariate statistical method was used to study the factors controlling the distribution of river water stable isotopes using the statistical software package SPSS version 16. Principal component analysis (PCA) was performed to classify river water samples and to identify the relation between the isotopic systematics and river water samples. A correlation matrix, using several parameters such as elevation, distance from the source, distance from Bay of Bengal and distance from Arabian Sea was performed to explore the altitude and continental effects in controlling the distribution of river water stable isotopic composition in the Bhavani and the Thutathupzha River Basins.

Results

$\delta^{18}O$ and δ^2H Composition in River Water

The $\delta^{18}O$ and δ^2H isotopic compositions in the water samples of the Bhavani and Thuthapuzha Rivers during Pre-monsoon (PRM), South-West monsoon (SWM), and North-East monsoon (NEM) seasons are presented in Table 1 and their variations along the river channels together with the d-excess values are depicted in Fig.2. The results show significant seasonal variability in both the rivers. The Bhavani River accounts for an average $\delta^{18}O$ value of −5.42±1.76‰ (range: −8.65 to −3.78‰) in PRM season. However, the $\delta^{18}O$ compositions are slightly enriched in the SWM

Table 1: Isotopic composition of water samples of the Bhavani River, along with the calculated mean values and standard deviation during pre-monsoon (PRM), southwest monsoon (SWM), and northeast monsoon (NEM) seasons

Sample Name	Elevation	PRM			SWM			NEM		
	(m)	δ^2H (‰)	δ^{18}O (‰)	d-excess (‰)	δ^2H (‰)	δ^{18}O (‰)	d-excess (‰)	δ^2H (‰)	δ^{18}O (‰)	d-excess
BRW1	2272	-23.51	-4.93	15.91	-24.95	-4.61	11.95	-24.22	-5.11	16.64
BRW2	529	-31.56	-5.94	15.98	-15.53	-3.08	9.10	-14.55	-3.65	14.62
BRW3	464	-25.52	-5.10	15.31	-18.16	-3.42	9.23	-17.59	-4.05	14.79
BRW4	415	-52.58	-8.65	16.65	-23.89	-4.30	10.49	-23.71	-4.76	14.36
BRW5	241	-19.16	-3.78	11.05	-29.30	-5.12	11.70	-29.73	-5.71	15.93
BRW6	163	-24.05	-4.14	9.08	-26.30	-4.45	9.28	-26.45	-5.13	14.56
Min.		-52.58	-8.65	9.08	-29.30	-5.12	9.10	-29.73	-5.71	14.36
Max.		-19.16	-3.78	16.65	-15.53	-3.08	11.95	-14.55	-3.65	16.64
Average		-29.40 ± 12.04	-5.42 ± 1.76	14.00 ± 3.14	-23.02 ± 5.19	-4.16 ± 0.77	10.29 ± 1.29	-22.71 ± 5.65	-4.73 ± 0.76	15.15 ± 0.92

(−4.16±0.77‰; range: −5.12 to −3.08‰) and NEM (−4.73±0.76‰; range: −5.71 to −3.65‰) samples.Like the case of δ^{18}O, δ^2H values also show a similar trend among the different seasons. The average δ^2H values of the Bhavani River water for PRM, SWM, and NEM are −29.40±12.04‰ (−52.58 to −19.16‰), −23.02±5.19‰ (−29.30 to −15.53‰) −22.71±5.65‰ (−29.73 to −14.55‰), respectively. The variations in the isotopic (δ^2H, δ^{18}O) values are quite different in the PRM season compared to the other two seasons. But, among the monsoons, SWM exhibited slightly enriched values in all the sampling stations of the Bhavani River than the NEM.

In the Thuthapuzha River, the δ^{18}O recorded an average value of −4.26±0.67 (−5.34 to −3.66‰) during PRM season which is slightly heavier than the PRM δ^{18}O compositions of the Bhavani River. The average values in the SWM and NEM are −2.54± 0.76‰ (−3.23 to −1.27‰) and −2.68±0.96‰ (−3.60 to −1.29‰), respectively (Table 2). The δ^2H during PRM accounts for an average of −23.56±5.22‰ (range: −32.20 to −19.12‰) which is markedly lighter than SWM (avg.: −9.77±3.36‰; range: −12.26 to −4.14‰) and NEM (avg.: −8.76±3.42‰; range: −11.41 to −3.34‰) seasons. The Thuthapuzha River also showed a distinct seasonal pattern as that of the Bhavani River with respect to its isotopic composition during the PRM. The SWM and NEM seasons exhibit almost similar isotopic compositions with a slight enrichment of lighter isotopes in the latter.

Fig.2a shows the spatio-temporal variability of isotopic composition in the Bhavani and Thuthapuzha Rivers. It is clear from the figure that in general the upstream samples are isotopically depleted to significant levels than the downstream samples. Rain gauge measurements show that on an average 70% of the rainfall occurs during SWM followed by the NEM season. The PRM season contributes only very minimal rainfall in the study area. During PRM season, the Pillur Dam (BRW4) in the Bhavani River exhibits the lowest δ^{18}O value. Thereafter, an enrichment of heavy isotopes is observed (BRW5 and BRW6) (Fig. 2a) and this may be due to increased evaporation in the semi-arid climate prevailing in the area.

During the SWM, the δ^{18}O values of the Thuthapuzha River are more enriched (−2.54± 0.76‰) compared to the Bhavani River (−4.16± 0.77‰). During this season, the river flow is maximum in both rivers. In the SWM season, the headwaters of both the Bhavani and Thuthapuzha Rivers experience isotopically lighter values and the values get progressively enriched in downstream. In the NEM, the average δ^{18}O composition at Thuthapuzha River and Bhavani River water is −2.68 ± 0.96‰ and −4.73 ± 0.76‰, respectively. The mean annual δ^{18}O and δ^2H values were −4.77±1.24‰ and −25.04±8.37‰ for the Bhavani River and −3.16±1.10‰ and −14.03±7.95‰ for the Thuthapuzha River. In a previous study (Achyuthan *et al.*, 2010), it is reported that Cauvery River recorded a δ^{18}O value of−2.77‰ at the source and −2.28‰ in the downstream reaches. However, the recent study by Bhagat *et al.* (2021) reported much more depleted isotopic compositions in the Cauvery River −3.6±1.1‰ during pre-monsoon, −4.7±0.8‰ during monsoon and −6.2±2.0‰ during post monsoon seasons.

Bivariate Plots of δ^{18}O and $\delta^2 H$

The bivariate plots depicting the inter-relationship existing among δ^{18}O *and* δ^2H of the river water samples of the Thuthapuzha River and Bhavani River are shown in Fig. 3. Studies show that different climatic and geographic conditions can influence the

Table 2: Isotopic composition of water samples of the Thuthapuzha River along with the calculated mean values and standard deviation during pre-monsoon (PRM), southwest monsoon (SWM) and northeast monsoon (NEM) seasons

Sample Name	Elevation	PRM			SWM			NEM		
	(m)	δ^2H (‰)	δ^{18}O (‰)	d-excess (‰)	δ^2H (‰)	δ^{18}O (‰)	d-excess (‰)	δ^2H (‰)	δ^{18}O (‰)	d-excess (‰)
TPW1	109	-19.12	-3.73	10.73	-12.26	-3.23	13.54	-11.11	-3.60	17.70
TPW2	65	-22.92	-4.29	11.44	-11.38	-2.82	11.15	-10.51	-3.35	16.31
TPW3	49	-19.81	-3.66	9.45	-11.87	-2.90	11.32	-11.41	-3.03	12.82
TPW4	23	-32.20	-5.34	10.49	-9.20	-2.48	10.63	-7.43	-2.13	9.58
TPW5	11	-23.74	-4.26	10.32	-4.14	-1.27	5.98	-3.34	-1.29	6.96
Min.		-32.20	-5.34	9.45	-12.26	-3.23	5.98	-11.41	-3.60	6.96
Max.		-19.12	-3.66	11.44	-4.14	-1.27	13.54	-3.34	-1.29	17.70
Average		-23.56± 5.22	-4.26± 0.67	10.49 ± 0.72	-9.77 ± 3.36	-2.54 ± 0.76	10.52 ± 2.78	-8.76 ± 3.42	-2.68 ± 0.96	12.67 ± 4.49

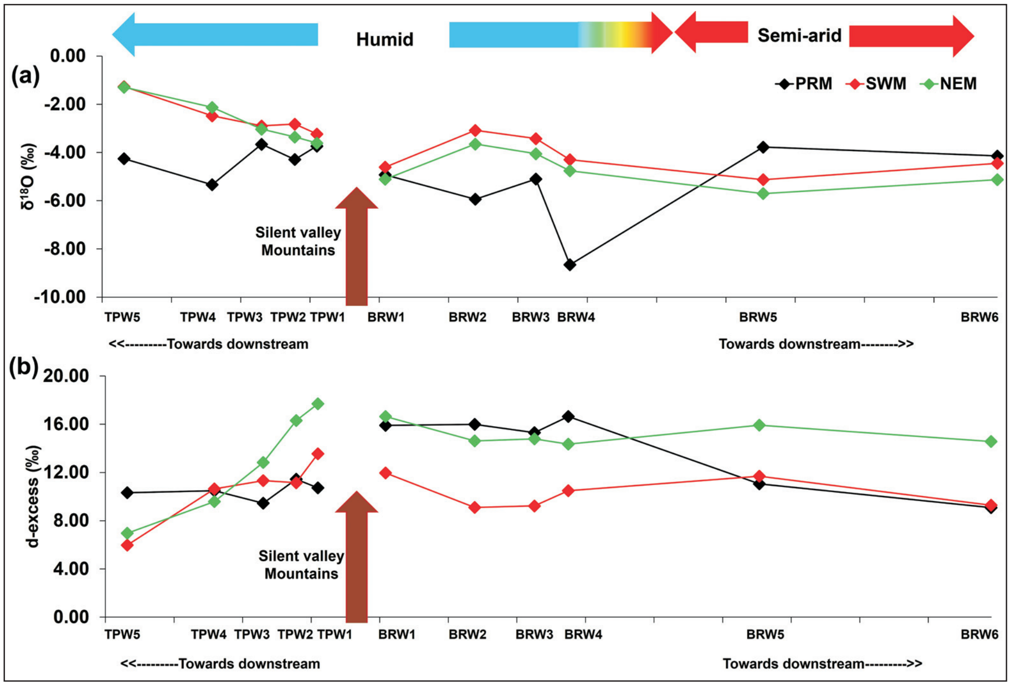

Fig. 2. Spatio- temporal variability of (a) stable isotopes of oxygen and (b) d-excess in Bhavani River and Thuthapuzha River during pre-monsoon (PRM), southwest monsoon (SWM) and northeast monsoon (NEM) seasons.

deviations in the slope and intercept of the water line compared to the Global Meteoric Water Line (GMWL) (Smith *et al.*, 2021). The majority of the river water samples in both the BRB and the TRB fall above the GMWL with a few sample plots falling below or on the Local Meteoric Water Line (LMWL). Linear regression analysis is used to derive the River Water lines (RWLs) for the BRB and the TRB. The RWL for Bhavani and Thuthapuzha Rivers is given by the equations $\delta^2H = 6.52*\delta^{18}O+6.09$ ($R^2=0.93$, n=18) and $\delta^2H = 6.80*\delta^{18}O+7.43$ ($R^2=0.88$, n=15), respectively (Fig. 3). The isotopic composition of the Bhavani River displays a mixed/overlapped sample distribution in the three seasons (PRM, SWM and NEM) whereas the Thuthapuzha River displays a distinguishable seasonal pattern during the non-monsoon (PRM) and monsoon (SWM and NEM) seasons. The slope, as well as the intercept of the RWL displayed by the river water samples was significantly different to that of the GMWL, and it is evident that the slope of the Bhavani (6.52) and the Thuthapuzha (6.80) Rivers is lower than that of GMWL (8) and LMWL (7.6) because of the local variation in moisture sources as well as evaporation effects (Craig, 1961). The lower values of slopes and intercepts of bivariate plots (Fig. 3) indicate that the Bhavani and the Thuthapuzha Rivers are affected significantly by the kinetic isotope fractionation due to evaporation.

Deuterium Excess (d-excess)

The d-excess, obtained for river water samples of the three seasons of the BRB varied between 9.08‰ and 16.65‰ in the PRM; 9.10‰ and 11.95‰ in the SWM and 14.36‰ and 16.64‰ in the NEM (Table 1). The d-excess values estimated for TRB during PRM, SWM and NEM seasons range from 9.45 to 11.44‰, 5.95 to 13.54‰ and 6.96 to 17.70‰, respectively (Table 2). The d-excess in the two rivers exhibits marked spatial and temporal variations (Fig. 2b). The variation of seasonally averaged d-excess values in the three seasons of the two river basins is given in Table 1-2. From the distribution of d-excess, it is revealed that the values were consistently higher than 10‰ in PRM and NEM seasons compared to SWM season. In terms of seasonal distribution, the highest seasonal average d-excess values in BRB

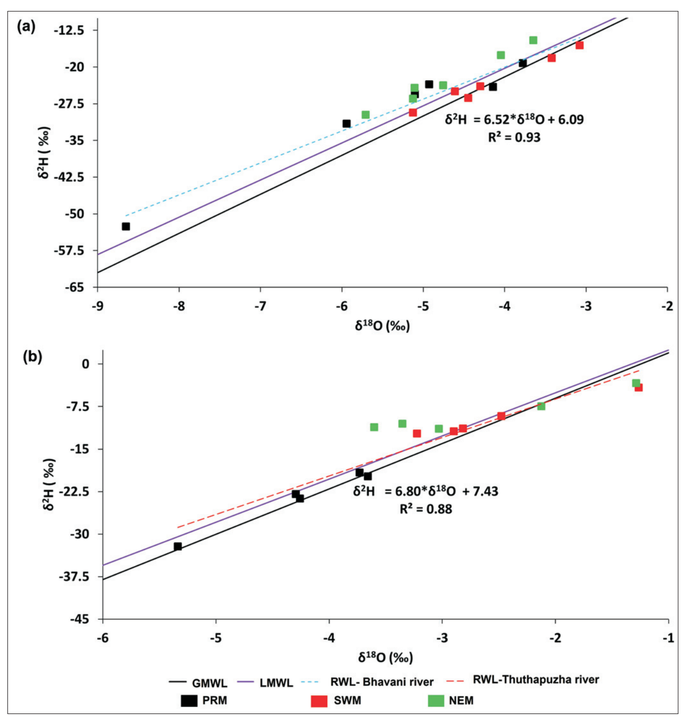

Fig. 3. Relationship between $\delta^{18}O$ and δ^2H values of river water samples. The Global Meteoric Water Line (GMWL) is plotted with the equation $\delta2H = 8 * \delta^{18}O + 10$ (Craig, 1961), the Local Meteoric Water Line (LMWL) is plotted with the equation $\delta2H = 7.6 * \delta^{18}O + 10.4$ (Warrier *et al.*, 2010) and the River Water Line (RWL, equation given) of (a) Bhavani and (**b**) Thuthapuzha Rivers.

are recorded for the NEM season (avg. 15.15±0.92‰) followed by PRM season (14.00± 3.14‰). The lowest seasonal average d-excess is observed for the SWM season (avg. 10.29 ±1.29‰). In the case of TRB, d- excess was the highest in the NEM (avg. 12.67±4.49‰) and the lowest during PRM seasons. The PRM (10.49±0.72‰) and SWM (10.52±2.78‰) seasons showed almost similar values.

During the PRM season, the Thuthapuzha River showed almost the same d-excess in its entire course indicating the dominance of both continental moisture recycling process (over the Western Ghats) and the Rayleigh distillation process of moisture originated from the Arabian Sea. The majority of the river water samples in the SWM season are characterized by an enriched stable isotope composition with lower d-excess, which is similar to that of the original monsoonal moisture source (d-excess = 10‰). The Bhavani and the Thuthapuzha Rivers showed higher d-excess value during NEM season compared to the other seasons.

Principal Component Analysis

Principal Component Analysis (PCA) was performed in order to explore the altitude and continental effects in controlling the distribution of river water stable isotopic composition in the Bhavani and Thutathupzha River Basins. The distribution of the principal component (PC) loading in space (with respect to sampling stations) is shown in the scatter plot of PC1 vs PC2 (Fig. 4). This was performed to determine the dominant controls governing the isotopic systematics of the river water in the study area. The season-wise analysis of the components PC1 versus PC2 indicates that the river water samples fall into two distinct groups (Fig. 4). The first group falls in the negative loading sector of the PC1 while the second group in the positive loading sector (Fig. 4). During SWM and NEM seasons, all the Thuthapuzha River water samples fall on the positive loading sector of the PC1 and PC2, whereas all the Bhavani River samples (except BRW2) falls in the negative loading sector. The PRM season shows a different trend compared to SWM and NEM seasons. It can be inferred that the majority of the samples in the first group during the monsoon season lie close to the Arabian Sea and the second group lies the sub-humid to semi-arid part of the study area.

Correlation analysis was performed for the factor loadings of the river water samples with the variables – elevation, distance from the source, distance from Bay of Bengal (BoB), and distance from Arabian Sea (AS) (Table 3). The factor loadings of the Bhavani River water samples were strongly correlated with the variables, distance from the origin, distance from AS and distance from BoB during the SWM season as compared to the NEM and PRM seasons. In Thuthapuzha, the factor loadings were found to be highly correlated with the variables elevation, distance from the origin and distances from the AS and BoB during the SWM and NEM seasons as compared to the PRM season.

Discussion

Isotopic Systematics and Climate Influence

A seasonal evaluation of the isotopic values of the Bhavani and Thuthapuzha Rivers shows that the values are in general more depleted in PRM season than the rest of the seasons. The inter comparison of isotopic values between the Thuthapuzha River and

Fig. 4. Scatter plot showing the spatial patterns of the principal component loadings for pre-monsoon (PRM), southwest monsoon (MON) and northeast monsoon (NEM) samples of Bhavani and Thuthapuzha Rivers.

the Bhavani River reveals slightly heavier PRM isotopic values in the former than the latter. Among the two river basins, the TRB is located close to the Arabian Sea, and which could make the TRB waters slightly heavier than the BRB during the PRM season. In the Bhavani River, isotopically more depleted values are recorded in the upstream stations, whereas the downstream counterparts are characterized by comparatively heavier isotopes. This indicates that during PRM season, the evaporation process is active as the river passes through the semi arid-arid area, a process also observed earlier (Bhagat *et al.*, 2021).

During SWM and NEM seasons, the downstream samples of the Bhavani River and the Thuthapuzha River experience isotopically depleted values. This could be the result of precipitation from water vapour originating from recycled or re-evaporated rainfall (vapour from canopy interaction, falling rain or ponds and wetlands) (Gat, 2000; Tripti *et al.*, 2016).The headwater regions of the study area are characterized by the presence of tropical evergreen forests and moist deciduous forests with high humidity levels and low temperatures (Gat, 2000; Lambs *et al.*, 2012). The presence of evergreen forests at the higher altitudinal slopes of the Western Ghats favours vapours to undergo evapotranspiration under suitable high humid conditions (Lambs *et al.*, 2011; Tripti *et al.*, 2016). The average isotopic value of $\delta^{18}O$ at BRB during the SWM season was 1.6‰ enriched than that of TRB.

Table 3: Correlation analysis between the Principal Component (PC) scores and climatic and topographic variables of Bhavani and Thuthapuzha Rivers

Variables	PRM		SWM		NEM	
	PC1	PC2	PC1	PC2	PC1	PC2
	Bhavani River					
Elevation	-0.07	0.67	-0.25	0.71	-0.25	0.79
Distance from the origin	0.55	-0.82	-0.28	-0.94	-0.35	-0.76
Distance from AS	0.58	-0.81	-0.38	-0.91	-0.45	-0.72
Distance from BoB	-0.58	0.81	0.35	0.92	0.42	0.72
	Thuthapuzha River					
Elevation	0.51	0.57	-0.82	0.22	-0.90	0.33
Distance from the origin	-0.34	-0.48	0.97	0.05	0.99	-0.02
Distance from AS	0.35	0.41	-0.97	-0.15	-0.99	-0.08
Distance from BoB	-0.34	-0.34	0.95	0.28	0.97	0.19

Values in bold – Statistically significant at alpha = 0.05

It is observed that there is a relatively higher input of lighter isotopes to river water on the lee-ward side (eastern side) of Western Ghats Mountain ranges and enrichment of heavier isotopes on the lower elevations of the windward side due to continental effect (Gat, 1996). This is perhaps the reason for the comparatively enriched isotopic composition in TRB than that of the BRB which drains the leeward side of the Western Ghats. The continental effect and the continental vapour contribution make the precipitation in the uplands of the BRB comparatively depleted in isotopic composition than the TRB.

Among the monsoon rainfall events, the $\delta^{18}O$ values are slightly depleted in both the Bhavani and Thuthapuzha Rivers (-0.14‰ and -0.57‰ respectively) during the NEM season than the SWM season. The Bay of Bengal caused about 1‰ depletion in $\delta^{18}O$ of its surface waters compared to the Arabian Sea because of the high-water discharge from the Himalayan rivers (Prell *et al.*, 1980; Duplessy and Ganseen, 2001). As a consequence, the moisture derived from the Bay of Bengal also became slightly depleted in $\delta^{18}O$ compared to the Arabian Sea moisture (Deshpande *et al.*, 2003). Therefore, the isotopic signature from the corresponding moisture source is inherited by the precipitation and causes depletion in the isotopic composition of surface water. All the NEM samples of the BRB shows depleted isotopic values compared to the SWM samples. But in the case of Thuthapuzha River, the upstream samples show depleted isotopic composition than the downstream samples. Further in the downstream, isotopic compositions have almost similar values during both the monsoon seasons due to the influence of moisture contribution from the nearby Arabian Sea source.

The plots of $\delta^{18}O$ *vs* $\delta^{2}H$ show that the river water in both the BRB and the TRB are of meteoric origin, as the corresponding samples lie on or above the LMWL (Fig. 3). During the PRM season, the upstream samples of the Bhavani River fall above the LMWL whereas the downstream samples fall below the line indicating evaporative enrichment in the downstream. In the SWM season, upstream samples fall on the LMWL suggesting that the isotopic values were not modified by evaporation and reflect the influence of the SWM. In contrast, downstream sample points lie below the LMWL indicating that these samples have undergone some amount of evaporation kinetics and the influence of SWM is comparatively less. During the NEM season, all the sample points lie above the LMWL demonstrating the influence of NEM throughout the basin. In the TRB, all the PRM samples fall below/close to LMWL, indicating that the basin experiences a certain extent of evaporative fractionation (Joshi *et al.*, 2018). In TRB, all the sample points (except one) fall above and/or the LMWL indicating that the TRB is influenced by both SWM and NEM seasons.

Factors Controlling Isotopic Variability

Vapour Recycling

The headwater samples of the Bhavani River Basin showed higher d-excess values (d-excess > 11‰) (Fig. 2b) compared to the downstream samples during the PRM season. This could be the result of precipitation of water vapour originating from recycled or re-evaporated rainfall (Gat, 2000) and baseflow contributions. The downstream semi-arid part of the BRB exhibits lower d-excess indicating relatively less recycling and possible higher evaporation from agricultural lands and areas with less vegetation, on the original moisture source in the BRB. The SWM season is characterized by an average d-excess value of 10‰ in both BRB and TRB, indicating the dominance of the contribution of rainwater from the original sea moisture source. It is reported that due to the rainout effect, water in the humid tropical basins of Western Ghats displays sea source moisture signatures at the onset of SWM, and as the monsoon intensifies; the moisture source is dominated by higher vapour recycling effect (Tripti *et al.*, 2018).

It is reported that air masses from the Bay of Bengal draw moisture from depleted east oceanic and continental sources, giving rise to higher d-excess values (Lambs *et al.*, 2011) during NEM. This suggests that, the rain during the NEM season generally has a considerable influence on the recycled vapour which is demonstrated in terms of the observed high d-excess values. The d-excess values in the Thuthapuzha River during the NEM season are relatively lower compared to the Bhavani River, indicating that the degree of vapour recycling in the NEM season is relatively higher in the larger Bhavani basin compared to the smaller Thuthapuzha Basin. Thus, the water vapour recycling effect is found to have a significant effect on the oceanic moisture source carried by the seasonal winds in these tropical river basins of the Western Ghats that are subjected to the present study.

Altitude and Continental Effects

In the Bhavani River, the factor loadings varied seasonally and the maximum correlation is observed during SWM season (Table 3). The PC1 was not significantly correlated with any of these parameters during the different climatic seasons. The highest correlation of PC2 of river water was the distance from the origin (-0.94) followed by distance from BOB (0.92) and distance from AS (-0.91). All these correlations were found to be statistically significant at alpha = 0.05. During the NEM season, the correlation coefficient values decreased to −0.76, −0.72 and 0.72 respectively for distance from the origin, distance from AS and distance from BOB. In the PRM season, comparatively lower values of correlation coefficients with elevation (0.67) were exhibited for PC2 (Table 3). Among the continental and altitude effects, the former is the more pronounced driver in depleting the heavier isotopes during rainout events. The river water exhibited maximum continental effect during the SWM season. The correlation of the parameters during the different seasons indicates that the elevation effect has a moderate contribution to the isotopic composition while the continental effect/distance effect is more pronounced in the BRB.

In the case of Thuthapuzha River, the highest correlation of PC1 of river water was found to be distance from AS (-0.97) followed by distance from the origin (0.97), distance from BOB (0.95) and elevation (-0.82). The observed correlations were found to be statistically significant at alpha = 0.05. The NEM season also shows the same trend of correlation indicating that the distribution of $\delta^{18}O$ and $\delta^{2}H$ across the Thuthapuzha River Basin is controlled mainly by the altitude effect (Dansgaard, 1964; Rozanski *et al.*, 1993) of the Western Ghats orographic barrier together with the continental effect (Deshpande *et al.*, 2003; Tripti *et al.*, 2016) of the region. During the PRM season, the highest correlation between PC1 and PC2 was found to be with elevation (0.51 and 0.57). While for both PC1 and PC2, it was found to be devoid of any correlation with the other corresponding variables. Precipitation during PRM season is derived from continental/local sources; hence, the lack of progressive depletion in stable isotopic ratios on the basis of the continental/altitude effect is predictable. The river water exhibited maximum continental and altitude effects during SWM and NEM seasons.

Sources of Stream Water

The results of the HYSPLIT simulations (Fig. 5a-g) show the influence of different moisture sources for precipitation over the study area. From the back trajectory analysis, it is clear that three major sources namely local vapour, vapour from the AS and vapour from the BoB determine the nature and characteristics of precipitation in the area. In the SWM season (June-September), the moisture has covered the Arabian Sea, peninsular India and further proceeded through the north western coastal region. The windward side of the Western Ghats (TRB) is influenced by the moisture which originated essentially from the Arabian Sea during the SWM. It is also clear from back trajectory analysis that the stations along the leeward side of the Western Ghats (BRB) are influenced by moisture sources from the Bay of Bengal during the NEM (October-December). In the TRB, both SWM and NEM are significant; however, the river flow is at its maximum during the SWM. The BRB experiences marked variations – the western part of the basin (Nellithurai gauging station) is influenced by the SWM whereas the eastern part (Savandpur gauging station) is fed mainly by NEM, even though the total quantity of NEM precipitation is comparatively less. In addition to this, local moisture recycling also has a profound effect in contributing to rains in the area. During the PRM season, the amount of rainfall is minimal and the moisture source for the precipitation is essentially from the continental sources. Both Bhavani and Thuthapuzha Rivers experience lean flow during the PRM season and whatever fraction of water in the channel is presumed to be contributed from the groundwater sources as baseflow (Bhagat *et al.*, 2021). The groundwater isotopic data of Gayathri *et al.* (2023) was examined to test this view for the Upper Bhavani region. Table 4 shows the isotopic data summary for the river waters of the Thuthapuzha and the Bhavani Rivers along with the open well and bore well data for the Upper Bhavani River Basin.

The groundwater data collected from the Upper Bhavani River Basin during the PRM season showed an average $\delta^{18}O$ value of −4.60±0.83‰ for the Open well and −5.61±0.72‰ for the Bore well (Table 4). The groundwater samples displayed an average d-excess value of 14.31±2.25‰, similar to the value of the river water (14.00±3.14‰) (Gayathri *et al.*, 2023). This indicates that during PRM, the rivers are fed essentially by the local groundwater sources that are generally lighter in isotopic composition, compared to the precipitation received from the moisture sources. Further, it is well known that the Western Ghats act as a water tower for the rivers during dry months (Viviroli *et al.*, 2007). In both the BRB and the TRB, the annual runoff is higher in the SWM and NEM seasons. The runoff in the PRM season is characterized by reduced stream flow. It is evident that precipitation is the major source governing the isotopic composition during SWM and NEM seasons. But, during the PRM season, mountainous areas receive much less precipitation and the bulk of the river flow is from groundwater sources as base flow.

Conclusions

The seasonal and temporal variations in the stable isotopic (δ^2H and $\delta^{18}O$) composition in the Bhavani and Thuthapuzha Rivers which link the humid western and semi-arid eastern climatic conditions are addressed in this paper. A relatively higher input of lighter isotopes to river waters on the eastern side of Western Ghats and enrichment of heavier isotopes on the lower elevations of the windward side noticed in this study points to the rainout effect to which the region is subjected. The significant contribution by the baseflow of groundwater and the evaporative process controls the isotopic composition during the pre-monsoon season. The river water shows a depleted isotopic composition during NEM compared to SWM seasons. The isotopic systematics of these river basins depend mainly on various factors like water vapour evaporation from the inland sources, moisture source of the monsoon precipitation, the continental effect and the difference in basin size. The enrichment of isotopes in the western part of the Western Ghats, (*i.e.* the Thuthapuzha River Basin) compared to the eastern part (*i.e.* the Bhavani River Basin) could be explained in terms of the influence of moisture source from the nearby Arabian Sea. The higher d-excess in BRB during NEM season (ranges from 14.36 - 16.64‰) compared to SWM season, indicates the involvement of NEM rains that undergo a series of evaporation-condensation cycles in the larger basins. The majority of the Thuthapuzha River samples also show higher d-excess values during NEM season. Thus, the water vapour recycling effect is found to have dominant control over the oceanic moisture source carried by the seasonal winds in these tropical river basins of the Western Ghats. The inter-relationship existing among the different seasons indicates that the elevation effect has a moderate role in contributing to the observed isotopic composition while the continental effect/distance effect has more pronounced effect, especially in the Bhavani River Basin. The absence of seasonal monsoon contribution and low rainfall facilitated by the local moisture sources points to the pronounced effect of groundwater

Table 4: $\delta^{18}O$ (‰) composition of the surface water sources of Thuthapuzha and the Bhavani Rivers along with the open well and bore well isotopic data for the Upper Bhavani River Basin [pre-monsoon (PRM), southwest monsoon (SWM) and northeast monsoon (NEM)]

Sample	$\delta^{18}O$ (‰)			Reference
	PRM	SWM	NEM	
Bhavani river	-5.42± 1.76	-4.16± 0.77	-4.73± 0.76	Present study
Thuthapuzha river	-4.26± 0.67	-2.54± 0.76	-2.68± 0.96	Present study
Thuthapuzha river	-3.54	-4.32	-4.23	Warrier and Manjula, 2014
Thuthapuzha (Groundwater)	-3.70	-3.98	-3.83	Warrier and Manjula, 2014
Cauvery river	-2.77 (at the source) and -2.28 (downstream)			Achyuthan *et al.*, 2010
Cauvery river	-3.6±1.10	-4.7±0.80	-6.2±2.00	Bhagat *et al.*, 2021
Bore well (Upper Bhavani)	-5.61±0.72	-5.97±1.21	-5.74±0.36	Gayathri *et al.*, 2023
Open well (Upper Bhavani)	-4.60±0.83	-5.19±1.03	-4.67±0.52	Gayathri *et al.*, 2023

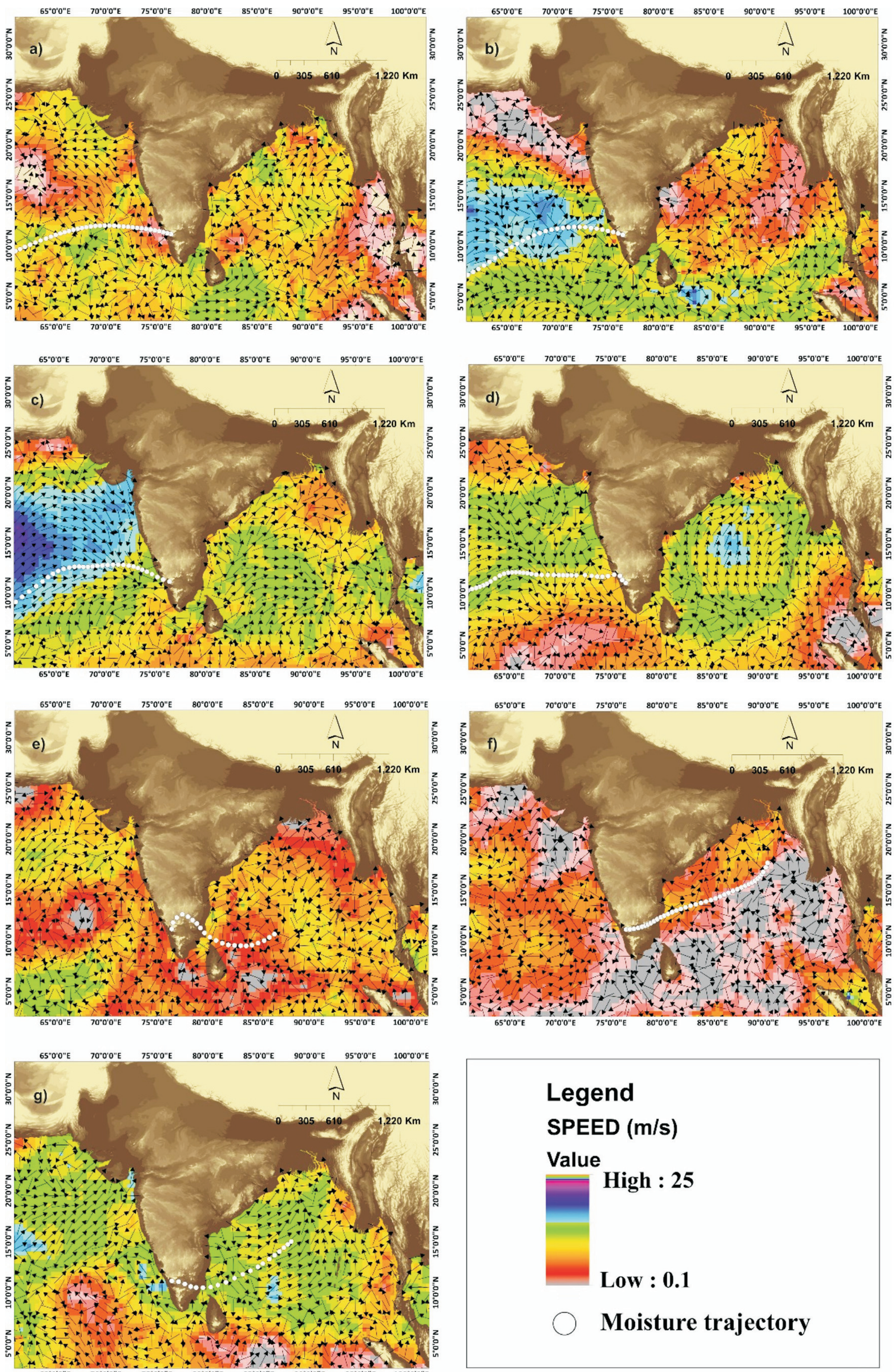

Fig. 5. The sketches of air mass trajectories with regional wind vectors demonstrating how moisture is added/subtracted to a particular airmass from the adjacent Arabian sea and Bay of Bengal during its travel to the study area during (a) June (b) July (c)August (d) September (e) October (f) November and (g) December.

in maintaining the river flow and controlling the isotopic composition during the PRM season.

Authors' Contributions

VTR: Design of Study, Data Preparation, Writing-Original Draft. **GJA**: Design of Study, Data Preparation, Writing-Original Draft. **RKS:** Data Analysis and Interpretation. **BLR:** Stable Isotope Analysis. **KS:** Data Analysis and Interpretation. **DP:** Conceptualization, Supervision, Editing and Reviewing. **KSN:** Conceptualization, Editing and Reviewing

Conflict of Interest

The authors declare no known competing financial interests that could have appeared to influence the work reported in this paper.

Availability of Data and Material

The data that support the findings of this study are available within the manuscript and any additional information will be provided upon reasonable request.

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