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Moisture sources and spatio‑temporal variation of isotopic signatures in Iraqi precipitation

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Abstract

Precipitation represents the input to the hydrological system, and it is the source or recharge for surface water reservoirs and groundwater aquifers. Stable isotopes (${}^{2}H$ and ${}^{18}O$) were measured for the period from 2011 to 2020 for 240 precipitation samples in all 16 Iraqi provinces distributed throughout the country. These isotopic results of the precipitation were adopted to produce for the first time a unified Iraqi Local Meteoric Water Line (LMWL), $(\delta^2H = 7.66 \delta^{18}O + 14.19)$. The d-excess values (14.19) fall between the value of the global meteoric water line (GMWL) (10) and the east Mediterranean meteoric water line (22). This is due to the continental effect with less humidity and higher temperature than the Mediterranean area. The study showed a weak positive correlation between the stable isotope values and the ambient air temperature and a weak negative correlation between relative humidity and the precipitation amount. This is mainly due to the variation in moisture sources and the amount of precipitation. The efect of altitude was refected in the isotope signatures of precipitation. The altitude gradient of δ^{18} O in precipitation was estimated to be – 0.5‰ per 100 m elevation. The results indicated the influence of ambient temperature, spatial deviation of the precipitation amount, and relative humidity levels. Additionally, the sources of moisture for the rainfall events were also deduced using the HYSPLIT backward trajectory model. The Mediterranean Sea and the Black Sea moistures have been identifed as the two major moisture source regions.

Keywords Meteoric water line · Deuterium · Oxygen-18 · Moisture source · Deuterium excess

Introduction

Freshwater scarcity poses signifcant threats to humanity today. Iraq, as an arid to semi-arid country, is seriously affected by water scarcity. Efforts must be stepped up to protect existing water resources, fnd new sources of sustainable water, and improve water resource management strategies.

The application of environmental isotope techniques plays an essential role in the assessment, management, and protection of water resources. Stable environmental isotopes are a powerful tool to study the sources of water bodies, allowing a better appraisal of their capacity and more rational exploitation. Stable isotopes of water are intrinsic to the water molecule and do not react with rock matrix at environmental temperatures (Aggarwal et al. [2005\)](#page-10-0). Accordingly, stable isotopes of hydrogen and oxygen $(^{2}H$ and ^{18}O) can provide a unique fngerprint of a water resource (Cejudo et al. [2020](#page-10-1)). These distinct characteristics help to evaluate the sources and potential risk of contamination, as well as to investigate the transport and fate of contaminants (Panda et al. [2022](#page-11-0)). The isotopes are also used to study the paleoclimatic conditions during the time of recharge.

The isotope techniques were adopted to monitor water resources globally (Noble and Ansari [2019;](#page-11-1) Ansari et al. $2020a$). A linear relationship was established between δ^2 H and δ^{18} O values in meteoric water (δ^2 H = 8 δ^{18} O + 10), and this regression line is referred the Global Meteoric Water Line (GMWL) (Craig [1961](#page-10-3)). The frst study on the isotopic composition of atmospheric waters in the Mediterranean region was established by Gat and Carmi ([1970](#page-10-4)). Recently, several regional efforts had brought out local meteoric water lines (LMWL) for a few countries in the region (Table [1](#page-1-0)). Further, few isotopic studies on the precipitation in diferent regions of Iraq have derived linear regression lines and they

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Table 1 Review of previous studies to obtain local meteoric water line equation

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are used to describe the association of the rainwater to the groundwater for diferent places in the country. The studies exhibited variations in isotopic signatures spatially.

This study was aimed at integrating data from the analysis of several rainwater samples collected over a period of ten years along with the data collected from other published literature. The data thus integrated will be focused on developing a regional meteoric water line for the country. Though local meteoric water lines prevail for a few provinces, the derived line will serve as the frst Iraqi Meteoric Water Line (IMWL). The line thus derived will serve for the hydrological studies and studies relating to surface water and groundwater dynamics. In addition, the study evaluated the effects of ambient temperature, elevation, and relative humidity on the measured values of the stable isotopes of hydrogen and oxygen $(^{2}H$ and ^{18}O). Further, the study was conducted to determine the sources of moisture for the precipitation during the study period.

Sampling sites and isotope analysis

Iraq can be divided into four topographical zones, namely, a desert and plateau in the west, mountains in the north, and sedimentary plain in the central and the southern regions. Two great international rivers extend from the north to the south of Iraq (Tigris and Euphrates). Population distribution, agriculture, and industrial activities are all distributed along these two river basins and their tributaries. Main topographic features along with spatial distribution of precipitation, and location of sampling stations are shown in Fig. [1.](#page-2-0)

Iraqi climate varies according to areas, such as temperate climate in the north, subtropical climate in the east and southeast, and continental desert climate in the west and southwest. The annual average precipitation ranges from 900 mm in the northeastern part to less than 50 mm in the southwestern part. Precipitation in Iraq occurs mainly during the winter which is characterized as the cold season (December to April) while it rarely rains during other months. However, most of the precipitation occurs in the northern area which is noted in the higher altitude. The relatively low temperature in this region assists in frequent precipitation and also favors a higher amount of precipitation. During the sampling period, rainfall varied from 0.2 to 90.17 mm/d (mean: 14.6 ± 14.9 mm/d).

Samples were collected for the period 2011–2020 based on the rain events, from 16 out of the 18 Iraqi provinces (with the exception of Babil and Dohok). However, some stations were ignored due to security issues related to sampling and feld measurements.

Stable isotopes (2 H and 18 O) were measured using liquid water isotope analyzer Model DLT-100 from LGR Company-USA and reported as (δ^2 H and δ^{18} O) in ‰ (per mil or ppt) relative to a VSMOW standardization.

A total of 240 rainwater samples were analyzed for their stable isotope abundance as follows: 58 samples from the northern area (Erbil, Sulaimaniya, Mosul, Kirkuk, and Saladin), 18 samples from the western area (Anbar), 120 samples from the central part of Iraq (Baghdad, Diala, Karbala, Najaf, and Kut), and 44 samples from the southern area of Iraq (Basra, Misan, Diwaniya, Muthana and Thiqar). Baghdad, the capital of Iraq, constituted 38% of the collected

Fig. 1 Map of Iraq showing the main topographic features, the spatial distribution of precipitation, and the selected sampling stations in Iraq

samples, while stations Thiqar, Kirkuk, Wasit, and Karbala, each represented 1% of the collected samples. This inhomogeneity in the spatiotemporal distribution of the samples might have an adverse efect on the statistical evaluation of the obtained results. However, few samples were excluded from the analysis (26 samples), especially those collected from the central and the southern region during the spring seasons. The amounts of precipitation recorded in these locations were less than 20 mm. Their isotope concentration may have been afected by partial evaporation of the falling droplets, thus, leading to the enrichment of heavy isotopes in the rainwater (Gat and Carmi [1970\)](#page-10-4).

In addition to isotopes, pH and electric conductivity (EC) of the water samples were also measured. Meteorological data including ambient temperature, relative humidity, and precipitation amount were obtained from the meteorological services in Iraq. The location of the sampling stations and the annual precipitation weighted average of the measured values of δ^{18} O and δ^2 H together with other specifications of the collected samples are presented in Table [2](#page-3-0). Measurements were conducted at the Iraqi Ministry of Science and Technology, Environment and Water Directorate.

Results and discussion

Stable isotope variability in precipitation

The results indicate that during the study period from 2011 to 2020 (December to April), the precipitation $\delta^{18}O$ values ranged from $- 13.4\%$ to 7.3% (mean: $- 3.6 \pm 3.4\%$); while the δ^2 H values ranged from -95.4% to 47.5‰

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(mean: $-14 \pm 24.7\%$) (Table [2\)](#page-3-0). The time series analysis of isotopic values during the precipitation period (December – April) shown as the monthly weighted $\delta^{18}O$ and δ^2H in Baghdad city indicates that enriched isotopic values were characteristic of precipitations in March; conversely depleted values were found in February.

By and large, the observation was that the isotopic values were gradually depleting from December to February, contrariwise, it was detected to have enriched in March. These variations in isotopic content could be considered a regional phenomenon and are controlled by meteorological factors, such as rainfall amount, temperature, and relative humidity (RH). It is noted that from December to February, the precipitation amount and RH values were seen to be gradually increasing; while the temperature was more or less the same which has caused the gradual depletion in the isotopic content in the region. Albeit, during March, the temperature was observed to be relatively higher; RH was low and the amount of rainfall was also low, which has caused enrichment in the isotopic values during this month.

The d-excess of precipitation was seen to vary widely and it ranged from $- 14.8$ to 35.3‰ (mean: $14 \pm 7.7\%$). It was established that precipitations during January and February months had comparatively higher d-excess; while lower d-excess values were observed in March (Fig. [2](#page-4-0) and Table [3](#page-5-0)). This variability of d-excess in rainwater could be attributed to changes in moisture source (continental and marine), rainfall break, and RH variability in the region.

Relationship between δ²H and δ¹⁸O, and deuterium **excess**

The regression line obtained between δ^2 H and δ^{18} O of rainwater of a region is known as LMWL, representing the meteorological and geographical state of that region. The relationship between δ^2 H and δ^{18} O for the collected data during the study period from 2011 to 2020 throughout the 16 Iraqi provinces illustrates a linear regression line (Fig. [3\)](#page-5-1), referred to as the Iraqi meteoric water line (IMWL), with a slope of 7.66 \pm 0.2 and y-intercept, or d-excess of 14.19 ± 1.06 at a confdence level of 95%, showed to be consistent with precipitation that was observed regionally (Nir [1967;](#page-11-2) Kattan [1997](#page-10-7)).

The Iraqi Meteoric Water Line (IMWL), according to this study, is as follows:

 δ^2 H = (7.66 \pm 0.2) δ^{18} O + (14.19 \pm 1.06)

The IMWL has a gentler slope and higher intercept compared to the GMWLs of Craig [\(1961\)](#page-10-3) and Rozanski et al. (1993) (1993) , δ^2 H = $8\delta^{18}$ O + 10 and δ^2 H = $8.2\delta^{18}$ O + 11.27, respectively. This gentler slope of the IMWL would indicates the prevalence of secondary sub-cloud evaporation (raindrop

Fig. 2 Time series analysis of $\delta^{18}O$, δ^2H , and d-excess value in rainwater in Baghdad along with rainfall amount, relative humidity, and temperature

evaporation at the time of descent) in the region. Ansari et al. ([2020a\)](#page-10-2) have observed that an increase in atmospheric temperature, reduction in precipitation amount, decline in vapor pressure, and lower RH could reduce the slope of the meteoric water line. In the study area, the rainfall amount was low; temperature was high, and RH was low, causing the lower slope of LMWL in the region.

Deuterium excess or d-excess, was calculated using the same Craig equation, i.e. $(d$ -excess = $\delta^2H - 8\delta^{18}O$). It could be defned as the deviation of the derived meteoric water line from that of the GMWL (Dansgaard [1964](#page-10-19)). It can be used to identify humidity source regions, which may vary seasonally. Accordingly, low d-excess values refect slow evaporation due to the high humidity region; while high values refect rapid evaporation due to low humidity (Clark & Fritz [2013](#page-10-20)).

It is worth noting that Nir ([1967](#page-11-2)), showed that the d-excess is+22‰ for the Mediterranean area. However, for a region like Iraq with less humidity, high evaporation rate, higher mean temperature than the Mediterranean area, and differing moisture sources, the $14.19 \pm 1.06\%$ would appear to be logical, especially when compared with results

Table 3 Monthly mean δ^{18} O and d-excess value in rainwater along with rainfall amount, relative humidity and temperature (*this data has been used for time series analysis in Fig-2*)

Month	$d^{18}O$	d-excess	P (mm)	Temp	RH(%)
$Dec-10$	-4.34	19.09	17.6	15.1	54.9
$Jan-11$	-3.15	18.15	6.1	14.8	57.3
Feb-11	-8.51	16.50	24	14.3	57.3
$Mar-11$	-1.545	2.795	7.3	31.3	38.3
$Dec-11$	-2.64	8.026	5.5	12.8	55
$Jan-12$	-2.07	6.93	2.9	11.2	60.5
Feb-12	-0.66	-6.35	2.2	11	57
$Mar-12$	-2.49	10.47	6.9	29	53.7
$Nov-12$	0.67	5.84	$\sqrt{2}$	14	42
$Dec-12$	-6.30	20.50	35.4	14	54
$Jan-13$	-4.40	17.50	7.6	12	61
Feb-13	-0.46	15.38	6	22	53
$Mar-13$	2.71	6.12	1.6	27	40
$May-13$	-8.34	8.42	9	34	44
$Oct-13$	0.05	15.59	46	42	35.5
$Nov-13$	-9.22	21.64	68	28	55
$Dec-13$	-2.15	11.72	10.8	20	43
$Jan-14$	0.01	14.13	4.9	11.5	59
Feb-14	-1.99	18.13	9.1	14	55
Mar-14	0.22	8.795	5.1	29.5	41.5
Feb-15	-5.50	23.17	42.3	15	54
$Oct-15$	-4.69	15.70	91.2	27	43
$Nov-15$	-3.41	13.02	1.7	19.5	47
$Dec-15$	-1.72	13.63	11	15	44.5
$Jan-16$	-0.12	13.40	14.3	16	55
Feb-16	-0.75	12.23	29.2	19	74
$Dec-16$	-0.84	5.23	12	12.6	54.5
$Jan-17$	-4.09	16.96	9	20	78
Feb-17	-2.06	23.08	8	13	75
$Mar-17$	-0.21	16.89	10	19	39.5
Feb-18	-3.61	14.27	4.8	18	62
Apr-18	-0.96	8.65	31	30	27
May-18	-2.35	9.72	10	35	33
Nov-18	-3.84	17.51	14.3	18.7	86
Dec-18	0.52	14.59	15.2	17	45
$Jan-19$	-2.98	15.46	34.5	15	83
Feb-19	-3.91	20.04	2.9	14.5	81.5
Mar-19	-2.34	14.05	21.2	29	55
Apr-19	-4.65	17.25	27.7	35	40
$Jan-20$	-5.47	17.56	1.3	12	60
Feb-20	-3.25	16.49	60	22	83

obtained from neighboring countries (Kattan, [1997](#page-10-7); Saad et al. [2005](#page-11-3)), this trend was comparable to the results of Syria and Lebanon.

Calculations showed higher d-excess values (14–25‰) during precipitation incidents that occurred in October and

Fig. 3 Relationship between δ^2 H and δ^{18} O for precipitation in Iraq, and relation with LMWL and GMWL

May and mainly in the northern part of Iraq. During both these periods, the temperature ranged from 8–22 °C. This is very close to the d-excess value of the eastern Mediterranean due to the seasonal cold winds in Iraq from the Mediterranean, carrying much of snow and rain, creating high humidity conditions. On the other hand, precipitations occurring during the spring season (March–April) are characterized by low d-excess values of 8–12‰, similar to the d-excess of the global meteoric water line. The ambient temperature in this season was seen to be relatively high and ranged from 22–44 °C, and precipitations resulted from cloudy Atlantic winds passing through the middle of Africa and Saudi Arabia. This moisture source controls rain events in Kuwait (Hadi et al. [2016\)](#page-10-6) and the central and southern parts of Iraq. Accordingly, there is a negative trend between temperature and d-excess values (Fig. [4\)](#page-5-2). However, no regression equation could be developed with an adequate confdence level because of the extensively scatted points in the plot. This scattering is mainly due to the mixing of the two diferent sources of precipitation and refects a wide spatial variation for the season.

Fig. 4 Relationship between the d-excess and the ambient air temperature

The relation between $\delta^{18}O$ and d-excess was evaluated to be able to understand the infuence of secondary sub-cloud evaporation in isotopic variability owing to the rain droplet evaporation causing a strong inverse correlation between δ^{18} O and d-excess. Generally, high wind velocity, low RH, and scanty rainfall cause raindrop evaporation; hence, there is a strong inverse correlation existing between d-excess and δ^{18} O (Ansari et al. [2020a\)](#page-10-2). In the region, a moderate correlation (r^2 =0.3) was estimated between the δ^{18} O and d-excess (Fig. [5](#page-6-0)). It showed that signifcant rain droplet reevaporation persisted during precipitation (Modon Valappil et al. [2022\)](#page-10-21); hence, the isotopic content was found to be enriched in the region.

Efect of ambient air temperature and humidity

Ambient temperature varies among Iraqi provinces. It is cold and dry in the mountainous area in the north (e.g., Sulaimania); while it is hot and humid in the south (e.g., Basra). The relation between ambient temperature and the concentration of $\delta^{18}O$ (Fig. [6](#page-6-1)) showed that the results were scattered along the trend line with a low correlation coefficient $(r^2=0.01)$ and a positive slope. This relationship leads to the inference that a very minor variation in isotope signatures could be associated with the change in temperature and vice versa.

Samples collected from November to February in the northern area had the depleted values of $\delta^{18}O$, due to the low ambient temperature during this season varying from 8–22 °C. During April to May, temperature rises to 22–44 °C, thus, Oxygen-18 enrichment occurs due to the evaporation efect at high temperature. When the temperature is low, the evaporation rate is also low. Albeit, as stated above a very minor correlation was observed between the isotope values and temperature $(r^2=0.01)$, reflecting a lesser infuence on the stable isotope concentrations. The slope of this relation indicated a change of 0.045 ‰ per °C. The northern area showed the highest slope value and the strongest correlation; while the desert area in the west showed the

Fig. 5 Relationship between the d-excess and δ^{18} O

least correlation, attributed to the mutual effect of precipitation amount and humidity on ambient temperature. These results run parallel with the conclusions found in the literature indicating that the temperature efect on stable isotopes concentration is complex due to the source of moisture and their pathways to its fnal destination (Ansari et al. [2020b](#page-10-22)), given that, the changes in the isotope signatures along the pathways are more signifcant than the temperature efect (Jouzel et al. [2000;](#page-10-23) Aggarwal et al. [2004](#page-10-24), [2005](#page-10-0)).

Ambient temperature was thus identifed to have a negative correlation with relative humidity; humidity increased as temperature decreased and vice versa. Apparently therefore, the effect of humidity on isotope values showed a negative correlation (Fig. [7](#page-6-2)). All the same, the correlation was weak for the same reason as that of the effect of temperature on the concentration of the isotopes.

Efect of altitude

Evidently, the altitude effect has been significant in hydrological studies, especially when tracking the origin of

Fig. 6 Relationship between the δ^{18} O concentration with the ambient air temperature

Fig. 7 Relationship between the δ^{18} O concentration with the ambient air relative humidity

Fig. 8 Relationship between the weighted average of δ^{18} O concentration with the altitude of Iraqi provinces **Fig. ⁹**Relationship between the δ18O concentration with the precipi-

groundwater recharge water sources, and the relationship between surface and groundwater. Stable isotope concentration in water has a well-known relation to altitude, measured as meters above sea level, masl (Mook [2001](#page-11-7)). As the altitude increases, temperature reduces, and the isotope values become more depleted.

The weighted mean values were calculated with respect to the precipitation amount. The relation between weighted mean values of $\delta^{18}O$ and the altitude showed a marked depletion in stable isotopes values as altitude increased, with a slope of -0.5‰ per 100 m, with a good correlation coefficient of 0.65 (Fig. [8](#page-7-0)). The water samples from the elevated provinces (>900 masl), showed values of -8‰ for $\delta^{18}O$, while samples collected in the southern province Basra (1 masl) showed values of $\delta^{18}O$ ranging from 1 to -2.5‰. The obtained slope of the $\delta^{18}O$ variation with altitude concur with studies in the literature showing that δ^{18} O reduced from 0.1–0.6 ‰ per 100 m elevations; while deuterium reduced from 1 to 4‰ per 100 m (Mook [2001;](#page-11-7) Clark & Fritz 2013). In addition, the obtained slope per 100 m in this study (-0.5‰) came logically in the middle among the Syrian value (to the west of Iraq) (-0.21‰) (Al-Charideh and Zakhem [2010](#page-10-8)), Lebanies value (North west of Iraq) (-0.23‰) (Saad et al. [2005](#page-11-3)), and the Iranian value (to the east of Iraq) (-0.8‰) (Heydarizad et al. [2021\)](#page-10-25).

Efect of precipitation amount

Most of the precipitation incidents were minor with few exceptions in the central and the northern area of Iraq. A weak negative correlation was observed with $\delta^{18}O$ (Fig. [9\)](#page-7-1) because almost all the precipitation values during the whole study period were relatively lesser with very low intensity. Large precipitation values are characterized by the presence of lesser amounts of heavy isotopes, and accordingly, the negative correlation between δ^{18} O and the precipitation amount was expected as compared with previous studies (Gat et al. [2000;](#page-10-26) Clark and Fritz [2013\)](#page-10-20).

tation amount

Minor precipitation events showed a higher concentration of enriched isotopes due to the partial evaporation of the raindrops. This is especially notable in arid and semi-arid areas, like Iraq (Saravana Kumar and Hadi [2018\)](#page-11-8). According to the obtained equation, the δ^{18} O value reduces by -7.2% per 100 mm increase in the precipitation amount. However, this could accurately be applied in the northern area of Iraq with a more frequent and larger amount of precipitation. In contrast, other areas showed scattered results due to their low amount of precipitation from two moisture sources, as well as from the continental effect. The southern area showed similar scattering behavior as to the effect of precipitation amount from those obtained in Kuwait, which could be due to the similar geographical conditions (Hadi et al. [2016\)](#page-10-6).

Fig. 10 Pearson correlation analysis between meteorological and geographical parameter (Higher positive correlation is indicated by deep blue color with a large circle and negative correlation by deep red color with a large circle). The diameter of the circle is proportional to the R-value)

To understand the infuence of meteorological and geographical factors on the isotopic variability, the Pearson correlation analysis was also performed between the isotopic values of rainwater with meteorological parameters (rainfall amount, temperature, RH) and altitude (Fig. [10](#page-7-2)). The results showed a poor correlation between temperature and $\delta^{18}O$, as well as with RH and $\delta^{18}O$ values. Conversely, a moderate correlation was revealed between δ^{18} O and the amount of rainfall as well as with $\delta^{18}O$ and altitude.

Figure [11](#page-8-0) illustrates the average annual spatial distribution of the weighted values of δ^{18} O and δ^2 H and the calculated values of the deuterium excess. The fgure confrms the previous results where the western arid area shows enriched isotopic concentration while the other regions showed depleted values.

Moisture source analysis

Hybrid Single Particles Lagrangian Integrated Trajectory (HYSPLIT4.0) air mass back trajectory model by NOAA (Draxler and Rolph [2014\)](#page-10-27) was developed for 72 h (in an interval of 3 h) prior to rainfall event during the rainfall days in January 2011, 2015 and 2020 for Central area (Baghdad city), to determine the moisture sources for the precipitation. The elevation of 1500 m above ground level (agl) was considered as the initiation of each trajectory since, 90% of the total rainfall is contributed by low-level clouds and their height (cloud base) varies from 1200 to 1500 m agl, during the rainy season.

By using HYSPLIT back trajectory model, three possible categories of moisture source regions can be deduced

Fig. 11 Spatial distribution of the weighted average values of δ^{18} O and δ^2 H and the calculated values of the deuterium excess

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for the Central area (Baghdad city); the Mediterranean Sea, the Black Sea, and inland (local). In 2011, the majority of the moisture was derived from the northern region, i.e., that is from the Black Sea; insignifcant contribution from the Mediterranean and local inland locations. Meanwhile, in 2015 and 2020, most of the moisture for the precipitation was derived from the Mediterranean Sea; while a minor contribution was discerned from the Black Sea and local inland locations (Fig. [12\)](#page-9-0).

Conclusions

A detailed analysis of the environmental isotopic characteristics of the precipitation in Iraq was conducted to identify the factors responsible for the isotopic variabilities and for the frst time, to derive a unifed Iraqi MWL. The obtained IMWL was $δ²H = 7.66 δ¹⁸O + 14.19$. The d-excess in this Equation (14.19) was lower than that of the Mediterranean

meteoric water line (22) due to the continental effect that characterizes Iraq, i.e., with less humidity and higher temperature than that of the Mediterranean area. The study showed a weak positive correlation between stable isotope values and ambient air temperature and a weak negative correlation between humidity and the precipitation amount. Mainly this could be because of diferent moisture sources and a minor amount of precipitation in the southern region. The altitude effect was observed to significantly influence the isotope signatures of the precipitation. This efect was apparent due to the mutual effects of the variation of ambient temperature, spatial deviation of precipitation amount, and relative humidity levels. The altitude gradient of $\delta^{18}O$ in precipitation was estimated to be − 0.5‰ per 100 m elevation. Further, two major moisture source regions have been deduced, the Mediterranean Sea and the Black Sea which provide a large amount of moisture, thus causing signifcant rainfall in the region.

Fig. 12 Backward wind trajectories analysis during the rainy season (January)

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Declarations

Conflict of interest This manuscript has not been published and is not a consideration for publication elsewhere. We have no conficts of interest to disclose.

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