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Stable isotopic (δ^2H, δ^{18}O) monograms of winter precipitation events and hydro-climatic dynamics in Central Mexico

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A R T I C L E I N F O

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A B S T R A C T

The unusual winter storm event of March 2016 brought excess rainfall in the Central part of Mexico and this study attempts to determine the moisture sources by characterizing the rainwater isotopes (δ^{18}O, δ^2H) and understanding their monthly spatial variations. Rainwater samples from six different stations (Agua Blanca, Molango, Mexico City, Pachuca, Tula and Tulancingo) of Mexico were sampled in March, April and May 2016. Enriched isotopic signatures in Tulancingo during March exhibited a mixture of moisture sources in which the predominant source was from the North followed by the Gulf of Mexico, while the depleted isotopic levels in Pachuca and Tula moisture from the recycling of inland vapour. However, the isotopic characterization in the month of April presented no much variations in δ^{18}O values irrespective of the station (−2.31 to −2.56‰), signifying that the prime moisture source is mainly from the inland sources and migrated from the central parts to the Gulf of Mexico. In contrast, the inland migration of the vapour source from Gulf of Mexico was witnessed in May with both the continental and the amount effect. However, the enriched δ^{18}O values in Tulancingo and Agua Blanca in May were found to be −0.84‰ and −1.44‰ respectively, with significant lesser *d*-excess values.

1. Introduction

Winter storms are weather systems typically dominated by precipitation formed at low temperatures i.e. snow, sleet and frozen rain. These storms, accompanied by high winds and frigid temperatures last from few hours to several days (Stevenson, 2016; McGrane et al., 2017). Winter storms form in various ways with three contributing factors in common, viz., cold air, moisture and the lift (Grossman and Betts, 1990). The collision of warm air with cold air or airflow along the mountainside or of a lake typically provides the lift (Serreze, 1995; Masselink et al., 2015). Favourable conditions for the formation of winter storms namely low temperatures and humidity in the atmosphere are present in high altitudes and latitudes, mainly among the mountainous areas of the Northern and Southern Hemispheres, viz. North America, Greenland, Europe and Russia. In North America, the winter storms occur predominantly in the eastern part, where warm air masses from the Gulf of Mexico ride over the cold air masses from Canada (Gay and Davis, 1993; Wagner et al., 2010). Winter storms primarily happen in the winter season, while they can also occur during the summer season in some continental regions

Abbreviations: AMSL, Above Mean Sea Level; GCMWL, Gulf Coast Meteoric Water Line; GMWL, Global Meteoric Water Line; GOM, Gulf of Mexico; LMWL, Local Meteoric Water Line; NAM, North American Monsoon.

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In Mexico, the winter storm season spans between October and May, but most active from December to March. During the winter season, the axis of the high-pressure area located near the USA moves southward, and subsequently towards north of Mexico (Cavazos and Hastenrath, 1990). Among the polar air invasions that typically take place in the coastal plains of Gulf of Mexico during the cold season, only 20% are strong enough to affect the interior parts of central Mexico (Hill, 1969) with adequate rain for several days. However, most often, the continental polar masses that penetrate up to the central part of Mexico are generally dry (Domínguez, 1940). The occurrence and intensity of cold fronts and winter storms in Mexico are primarily controlled by ENSO (El Niño Southern Oscillation), NAO (North Atlantic Oscillation), AO (Arctic Oscillation) and the PNA (North American Pacific Pattern). Climatic records indicate higher frequency of winter storms ($n = 30$) during the years 2013–2016, where neutral ENSO winters exerted more control over El Niño and La Niña winters ensuring substantial impacts in the northern regions of the country (SMN, 2016).

Isotopes serve as a potential tools in determining moisture sources and regional dynamics of climate (Friedman, 2002; Aggarwal et al., 2004). They are also used to trace the recent and previous quaternary climatic settings leading to paleo-climatic interpretations (Schmidt et al., 2007; Chidambaram et al., 2020; Rodriguez-Espinosa et al., 2020). However, the interpretation of isotopic data becomes more complex when the raindrops equilibrate with the surrounding atmosphere after the process of condensation (Stewart, 1975; Good et al., 2014). The situation is even more complex under extreme precipitation events viz., tropical cyclone, hurricane, etc. as it depends on diverse factors viz. intensity of source vapour, the impact of sea spray, mixing of vapour, humidity, temperature and other processes (Gedzelman, 2002; Fudeyasu et al., 2008). The kinetic fractionation of $\delta^{18}O$ is significantly influenced by the variations in humidity and wind speed when compared to $\delta^{2}H$ (Lachniet, 2009).

Numerous studies have modelled the rainout process during its migration towards inland (Vuille et al., 2005; Lachniet et al., 2007) to determine the influence of southern oscillations/El Nino on the isotopic signatures in the tropical rain events (Vuille, 2003; Lachniet et al., 2007), dynamics of monsoonal vapour circulations (Johnson and Ingram, 2004; Vuille et al., 2005) and the changes in isotopic nature of precipitation. Warburton et al. (1993) and Gedzelman (2003) have used isotopic signatures to determine the trajectory of meteorological phenomena of cold fronts or winter storms that cross certain areas. Hu and Dominguez (2015) established two major sources of moisture for Central America, i.e. the enriched vapour from the Caribbean and GOM and the depleted vapour from the Gulf of California and Pacific. Isotopes studies in the groundwater and rainwater from Central Mexico (Cortes and Farvolden, 1989; Edmunds et al., 2002; Peñuela-Arévalo and Carrillo-Rivera, 2013; Rodriguez-Espinosa et al., 2020), and Yucatan Peninsula (Cejudo et al., 2021; Lases-Hernandez et al., 2019) provided information on the recharge regions and also aided in deriving the meteoric waterline for the respective regions. Depleted isotopic nature of the precipitation samples were observed in regions dominated by tropical storm (Lawrence and Gedzelman, 1996; Perry et al., 2003). Isotopic characterization of tropical cyclones was attempted by few researchers (Fudeyasu et al., 2008; Good et al., 2014) in the Gulf of Mexico (Lawrence and Gedzelman, 1996; Lawrence, 1998) and during the hurricane Olive (Lawrence et al., 2001). Variations in isotopic signatures due to the change in moisture sources in North America (Wright et al., 2001; Liu et al., 2011) and Asia were also documented (Chidambaram et al., 2009b; Xie et al., 2011; Tang et al., 2015). Sea surface temperatures near the Gulf of California influenced the $\delta^{18}O$ values of rainwater in the nearby regions of Baja California (Wright et al., 2001). Likewise, studies on the $\delta^{18}O$ values of rainfall in Western America showed that advection travel and source are largely responsible for isotopic variations (Friedman, 2002; Strong et al., 2007). Henceforth, the transport of atmospheric moisture, geographic location, seasonal fluctuation in climate are the principal factors governing the isotopic composition of rainwater. The frequency of winter storms has been increasing globally and the present investigation would fill the gap in understanding their spatial dynamics and provenance provide necessary evidences for atmospheric scientists by enhancing the precision of climate related findings.

Even though there are few studies documenting the synoptic evolution and societal impacts of winter storms, the present work highlights the isotopic characteristics of winter storm that extremely impacted Mexico in March 2016. Additionally, in this study we have also attempted to determine the source of moisture for the months of April and May (2016) to document the dynamics of winter and normal precipitation episodes.

2. Materials and methods

2.1. Study Area

The study areas (Agua Blanca, Molango, Mexico City, Pachuca, Tula and Tulancingo) in Central Mexico (Fig. 1) are located about ~400 km from the Gulf of Mexico coast and ~ 500 km away from the Pacific coast. Additionally, the sampling stations are inland to the west of the semi-permanent anticyclone region of the North Atlantic (Bermuda-Azores) and their seasonal shifts determine the climate of almost entire Mexico (Jauregui, 1979). Distinct characteristics of the sampling stations namely altitude (AMSL), wind velocity (km/h), humidity (%), climate, average temperature (°C/year) and precipitation (mm/year) are presented in Table 1.

The climatic pattern of the sampling stations is mainly described by considering the various air mass movements that determine the rainfall distribution over the region. Mexico is influenced by the cold winds traversing from NE to SW or from east to west at high altitudes that collects the moisture from the Gulf of Mexico (Garcia et al., 1964). At the beginning of autumn, precipitation increases due to the influence of the tropical hurricanes from both the Gulf of Mexico and the Pacific Ocean. However, during the cold half of the year, both the high-pressure subtropical belt and the trade zone move southward, dominating the winds of the west in the north and the upper atmosphere of Central Mexico. In the winter, the jet stream from the west moves to the south and it passes north of Mexico City eventually allowing the winds in the high troposphere over the capital to traverse from the west or SW with robust intensity. During this period, the polar air masses descend from North America and imparts lower temperature in Central Mexico (Krumm,

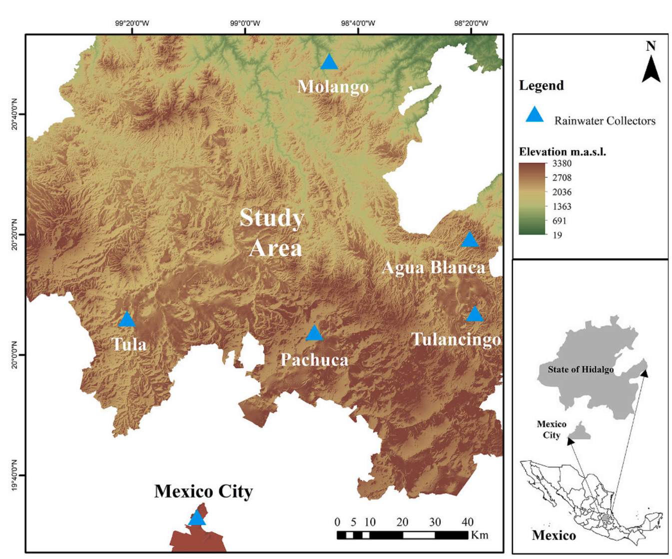

Fig. 1. Study area map of the rainwater sampling locations in Central Mexico, Mexico.

Table 1
Physical and climatological characteristics of the sampling locations in Central Mexico.

Location	Altitude (masl)	Average temperature (°C/year)	Average rainfall (mm/year)	Latitude	Longitude	Climate
Agua Blanca	2100	14.2	1061	20.3465°N	−98.3595°W	Cold-temperate
Molango	1620	17	1438	20.7908°N	−98.7288°W	Warm-temperate
Mexico City	2240	16	893	19.4873°N	−99.1236°W	Temperate subhumid
Pachuca	2382	15.5	574	20.1011°N	−98.7591°W	Semi-arid
Tula	2020	17.6	438	20.0522°N	−99.3442°W	Semi-arid
Tulancingo	2181	14	532	20.0905°N	−98.3691°W	Temperate semi-dry

1954). At the peak winter season, the passage of the high trough western wind currents renders large temperature fluctuations in the study area. The influence of this phenomenon causes a well-marked discontinuity of the temperature, due to the advection of cold air (Elder, 1959).

2.2. Sampling

Monthly composite precipitation samples were acquired from six sampling stations using rainwater collectors in March, April and June during the year 2016 following IAEA guidelines (www.isohis.iaea.org). The rainwater collectors composed of a plastic recipient (~ 5 L) fixed with a glass funnel of 20 cm diameter that reached up to the bottom of the container. Additionally, a long narrow tube attached to the top of the recipient was also installed (length ~ 10 cm and diameter ~ 2 cm) to balance the pressure (Ansari et al., 2020). The monthly rainwater samples were procured in clean high-density polyethylene bottles of 60 mL capacity by filling to the maximum level leaving only a little space for thermal expansion and were closed tightly to avoid isotope exchange with air moisture. Medicinal paraffin oil was added to the rainwater collectors to avoid evaporation of the sample.

2.3. Analytical procedures and estimation of stable isotopes ($\delta^{18}O$ and δ^2H)

Stable isotope measurements ($\delta^{18}O$ and δ^2H) were performed using a Continuous Flow Isotope Ratio Mass Spectrometer (Finnigan DeltaPLUS XP) at the Isotope Hydrology Division of Centre for Water Resources Development and Management, Kerala, India. Estimation of $\delta^{18}O$ was carried out using the CO_2-H_2O equilibration method (Epstein and Mayeda, 1953) and δ^2H analyses were carried out by the H_2-H_2O equilibration technique incorporating a platinum catalyst supported on hydrophobic material. The results are reported in δ-notation and expressed in units of parts per thousand (denoted as ‰). The δ values were calculated using (Coplen, 1996):

$$\delta(‰) = \left(\frac{R_x}{R_s} - 1\right) \times 1000$$

where R denotes the ratio of heavy to light isotope (e.g. $^2H/^1H$ or $^{18}O/^{16}O$), while R_x and R_s are the ratios in the sample and standard respectively. Laboratory standards were periodically calibrated against the Vienna Standard Mean Ocean Water (V-SMOW), Greenland Ice Sheet Precipitation (GSIP) and Standard Light Antarctic Precipitation (SLAP). The analytical reproducibility of the measurements was 0.08‰ for $\delta^{18}O$ and 0.8‰ for δ^2H (2σ criteria). Deuterium excess (*d*-excess) defines the relative humidity and evaporation of precipitation in each area (Clark and Fritz, 1997) and was estimated using the formula $\delta^2H - 8 \times \delta^{18}O$ (after Dansgaard, 1964). *d*-excess values <10‰ indicate evaporative enrichment, whereas values >10‰ denote contribution of recycled moisture (Gonfiantini, 1978; Clark and Fritz, 1997; Wassenaar et al., 2009). Statistical tests namely correlation and principal component analysis were performed using STATISTICA (version 12) for the entire dataset to understand the consistency and associations of climatological parameters with the isotopic values in the sampling locations.

3. Results and discussion

3.1. Climatological parameters

Stable isotope values and precipitation data of the sampling locations are presented in Table 2, while the calculated mean monthly figures of $\delta^{18}O$, δ^2H, *d*-excess, humidity and temperature are denoted in Table 3. The sampling station, Tula presented the maximum and minimum precipitation of 2760 mm (May) and 50 mm (March) respectively during the study period. High humidity and temperature were recorded at Molango during May. April had the lowest humidity at Tula (41.69%) and the lowest temperature was observed at Mexico City during March (15 °C). In general, the temperature gradually increased from March to May, but a minor drop in humidity (3.5% to 1.03%) was witnessed during April. In general, the enriched isotopic values were observed in Tulancingo in May, and the depleted values were observed at Pachuca during March.

3.2. The Global Meteoric Water Line (GMWL)

There are three main factors responsible for the changes in isotope signatures of rainwater, namely i). dry atmosphere leading to the evaporation of falling raindrop (Dansgaard, 1964), ii) A regional continental effect (Kurita et al., 2009; Chidambaram et al., 2009), and iii) Seasonal variation in moisture source. The variation of the slope in the meteoric water line is mainly due to the evaporation process succeeding condensation and variation in the atmospheric humidity at the cloud boundary (Lambert and Aharon, 2010). The plot of $\delta^{18}O$ vs δ^2H values shows that most of the samples fall along the GMWL (Fig. 2). The local meteoric water line (LMWL) established by several researchers is mentioned in Table 4, which infers that all the slope values and some intercept values of the precipitation of the study area are similar to GMWL, indicating that the primary source signature (i.e. ocean) is not modified significantly. The samples representing the month of March deviate from the GWML, especially in Tula and Tulancingo sites (Fig. 3), probably indicating different moisture source to the rain events (SMN, 2016). The plot of the samples of April presents a very narrow range of values and are more enriched than those of March. A wide range of isotopic composition was observed in the samples of May and they fall along the GMWL. Wagner and Slowey (2011) reported that $\delta^{18}O$ of GOM varied from −1.0‰ to 0.5‰ in August and −1.4‰ to 1.2‰ in May as the enrichment of isotopes are directly related to salinity of the waters. The evaporation of the falling droplets depends on the temperature and relative humidity and this process alters the slope of the meteoric water line (Gat, 2000; IAEA, 1992). The meteoric water lines derived for rainwater samples collected along the coastal region are referred as Gulf Coastal Region (GCMWL) and was studied on both weekly and monthly basis by Lambert and Aharon (2010);

$$\delta^2H = (7.11 \pm 0.19)\ \delta^{18}O + (19.52 \pm 0.88) : \text{weekly trend}$$

$$\delta^2H = (7.03 \pm 0.39)\ \delta^{18}O + (8.97 \pm 1.79) : \text{monthly trend}$$

The study indicated that the weekly trends have larger variations in *d*-excess values signifying minor dissimilarities in precipitation episodes. While, monthly isotopic compositions of rainwater reflected the

Table 2
Monthly rainfall, $\delta^{18}O$, $\delta^{2}H$, d-excess, humidity and temperature recorded in each sampling location during March, April and May 2016.

Locations	Date of sampling	Rainfall (mm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	D_{excess} (‰)	Humidity (%)	Temp (°C)
Agua Blanca	Mar 2016	385	−2.77	−10.31	11.85	58.92	17.37
Molango	Mar 2016	1500	−2.22	−12.20	5.56	51.80	19.64
Mexico City	Mar 2016	65	−3.26	−15.23	10.86	46.18	15.27
Pachuca	Mar 2016	160	−5.19	−29.38	12.14	50.48	16.03
Tula	Mar 2016	50	−3.70	−26.72	2.88	45.20	16.15
Tulancingo	Mar 2016	1140	−2.90	−26.34	−3.14	58.90	17.37
Agua Blanca	Apr 2016	1500	−2.56	−13.53	6.95	56.00	19.90
Molango	Apr 2016	1510	−2.31	−7.18	11.30	52.83	21.50
Pachuca	Apr 2016	645	−2.38	−10.62	8.42	47.87	18.63
Tula	Apr 2016	390	−2.39	−9.61	9.51	41.69	18.19
Tulancingo	Apr 2016	2170	−2.55	−10.02	10.38	56.00	19.89
Agua Blanca	May 2016	830	−1.44	−6.57	4.95	61.42	21.52
Molango	May 2016	2235	−2.66	−12.86	8.42	62.69	22.84
Mexico City	May 2016	950	−2.44	−13.29	6.23	48.03	20.17
Pachuca	May 2016	2170	−3.41	−18.67	8.61	56.31	20.12
Tula	May 2016	2670	−4.70	−26.70	10.90	52.10	20.40
Tulancingo	May 2016	1130	−0.84	−0.10	6.62	61.41	21.50

Table 3
Minimum, maximum, mean and standard deviation values of $\delta^{18}O$, $\delta^{2}H$, d-excess, rainfall, humidity and temperature in the sampling locations of Central Mexico.

	March (n = 6)				April (n = 5)				May (n = 6)			
	Min	Max	Mean	Std. Dev	Min	Max	Mean	Std. Dev	Min	Max	Mean	Std. Dev
Rainfall (mm)	50	1500	550	619	390	2170	1243	721	830	2670	1664	785
$\delta^{18}O$ (‰)	−5.19	−2.22	−3.34	1.03	−2.56	−2.31	−2.44	0.11	−4.70	−0.84	−2.58	1.38
$\delta^{2}H$ (‰)	−29.38	−10.31	−20.03	8.38	−13.53	−7.18	−10.19	2.28	−26.70	−0.10	−13.03	9.25
d-excess (‰)	−3.14	12.14	6.69	6.10	6.95	11.3	9.31	1.70	4.95	10.90	7.62	2.12
Humidity (%)	45.20	58.90	51.90	6.0	41.69	56	50.88	6.12	48	62.7	57	5.9
Temperature (°C)	15.30	19.60	17	1.5	18.19	21.5	19.62	1.30	20.1	22.8	21.1	1.1

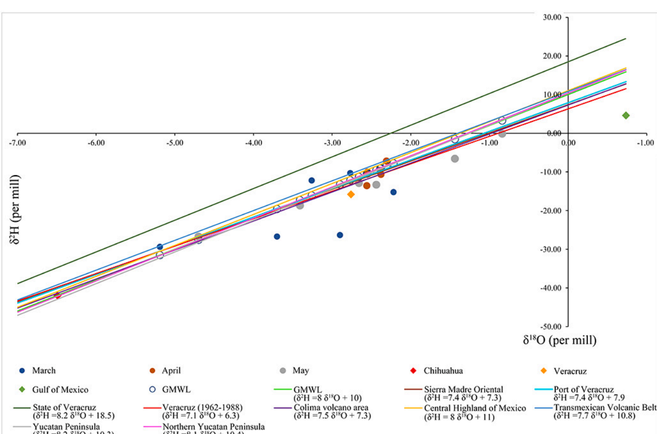

Fig. 2. Isotope values of $\delta^{18}O$ plotted against $\delta^{2}H$ and compared with GMWL. The isotope values of nearby regions Veracruz (WISER GNIP –IAEA database), Chihuahua (Issar, 1985) and Gulf of Mexico (Yobbi, 1992) are plotted for comparison.

average values of the events, where minor intense rain events could have been masked. The continental low latitude locations had a difference in $\delta^{2}H$ signature of −3.56% between the winter and summer precipitations (Dansgaard, 1964) but the difference is found to be higher in the $\delta^{2}H$ values of the present study especially Tula, Pachuca and Tulancingo. The variations are probably due to the fact that the study period was within three months of winter season and the region had been experiencing extreme events due to the cold fronts no. 45 and 46. The slope of GCMWL was found to be <8 and moderate than the GMWL (Lambert and Aharon, 2010).

The isotope values of the present study were also compared with the reported rainwater composition of the adjacent regions namely

Table 4
The LMWL derived by different authors for the regions nearby the study area.

S. No.	Location	Equation	Reference
1	Sierra Madre Oriental	$\delta^{2}H = 7.4\ \delta^{18}O + 7.3$	Quezadas et al., 2015
2	Port of Veracruz (2007 to 2012)	$\delta^{2}H = 7.4\ \delta^{18}O + 7.9$	Quezadas et al., 2015
3	State of Veracruz	$\delta^{2}H = 8.2\ \delta^{18}O + 18.5$	Goldsmith et al., 2011
4	Veracruz (1962–1988)	$\delta^{2}H = 7.1\ \delta^{18}O + 6.3$	Lachniet, 2009
5	Colima volcano area	$\delta^{2}D = 7.46\ \delta^{18}O + 8.9$	Hartsough, et al., 2008
6	Central Highland of Mexico	$\delta^{2}H = 8\ \delta^{18}O + 11$	Cortés et al., 1997
7	Transmexican Volcanic Belt	$\delta^{2}H = 7.7\ \delta^{18}O + 10.8$	Quezadas et al., 2015
8	Yucatan Peninsula	$\delta^{2}H = 8.2\ \delta^{18}O + 10.3$	Cejudo et al., 2021
9	Northern Yucatan Peninsula	$\delta^{2}H = 8.1\ \delta^{18}O + 10.4$	Socki et al., 2002

Chihuahua, Veracruz and seawater value of GOM. A comparison of the isotope values of the current study with the different local meteoric water lines of region (Table 4), shows that the samples fall between the MWL of the Trans Mexican volcanic belt and Veracruz (1962–1988). The samples of Mexico City, Pachuca and Agua Blanca collected during the month of March were observed to align with the Trans Mexican Volcanic belt MWL, but the samples of Molango, Tulancingo and Tula were noted to have different isotopic composition probably due the influence of winter storm events during this period. It is interesting to note that the samples representing the month of May were noted to be adjacent to the Veracruz (1962–1988) MWL, indicating GOM moisture sources. The samples collected during the month of April were predominantly oriented to the central Highland of Mexico MLWL. The average value of GOM signatures was found to be more enriched and isotopic values of

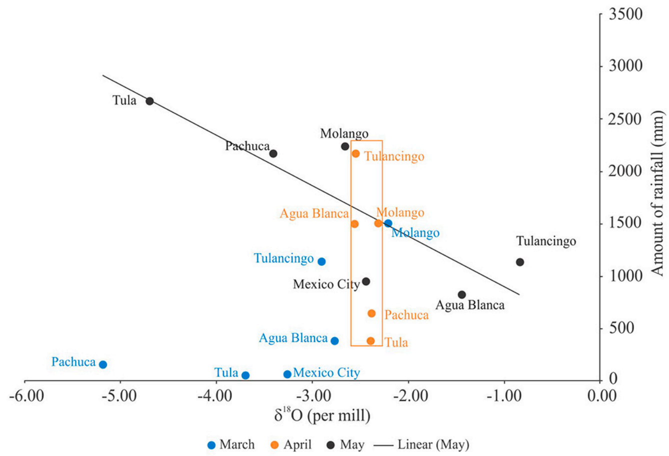

Fig. 3. The comparison of $\delta^{18}O$ values to the total monthly rainfall observed during the period of study in each sampling location.

Chihuahua were more depleted than all the samples collected during the period of study.

3.3. Amount effect

Long term observations on monthly precipitation isotopic composition were carried out to study the amount effect in diverse locations namely Hong Kong, New Delhi and Guam (Rozanski et al., 1993), western USA (Lechler and Niemi, 2011) and also in Central Mexico (Lachniet et al., 2012). The $\delta^{18}O$ isotope values for the three months were compared with the amount of rainfall (Fig. 3) in the sampling stations. Precipitation records of Mexico indicate that March 2016 was the sixth rainiest month in the country since 1941 with an average of about 28.6 mm of rainfall that is 85% higher than the usual average of 15.4 mm during the period 1941–2015. However, Pachuca, Tula and Mexico City experienced a lesser rainfall with depleted isotope signatures. Henceforth, the spatial distribution of stable isotopes in precipitation cannot be easily understood from the idea of Rayleigh distribution as the role of surface water interaction is more significant (Lee et al., 2007) above the oceans in the mid and low latitudinal regions. Precipitation also occur due to the presence of water vapour formed from the release of latent heat (Lawrence et al., 2001) and the variation in the amount of evaporation and precipitation governs the atmospheric circulation which is thus reflected in the isotopic values of the components. Tropical storms and topographical conditions result in an isotopic shift ensuing in sudden enrichment of isotopes, this effect is noted in samples collected from elevations >1000 m AMSL (Quezadas et al., 2015). Further, depletion of the isotopes ($\delta^{18}O$ and $\delta^{2}H$) are also noted due to the increase in the amount of rainfall and due to precipitation from clouds of higher atmospheric levels, especially during intense storm events (Dansgaard, 1964). It is interesting to note that the samples from Agua Blanca, Tulancingo and Molango showed enrichment even though the locations received a higher amount of rainfall during this period. The residence time of vapour in the atmosphere also influences the isotopic values of the precipitation (Breitenbach et al., 2010; Aggarwal et al., 2012). The saturation vapour pressure of heavy isotopes is less and do not evaporate as fast as in normal rain event (Lawrence and Gedzelman, 1996). Lawrence (1998) inferred that the isotope value of precipitation in a normal rain event is more enriched than that of an extreme high rain event. The altitude, thickness of the clouds relative longevity and rain shields lead to depleted values in the extreme events like hurricanes. The isotope ratios are also influenced by the diffusive isotope exchange and evaporation of in-flowing vapour and sources (Lawrence, 1998; Partin et al., 2012).

Irrespective of the rainfall amount only a minor variation of $\delta^{18}O$ was observed during April. The rain events during May indicated depletion of $\delta^{18}O$ with the increase in the amount of rainfall, reflecting the amount effect. Hence the amount effect was clearly witnessed only during the month of May. Extremely low $\delta^{18}O$ values (−5.19‰) are observed in regions with greater precipitation (Table 3; Fig. 3). The monthly changes in temperature are generally correlated with the $\delta^{18}O$ values of precipitation in the mid-latitude regions (35°N - 55°N) (Rozanski et al., 1993). The study area falls between 19°N and 20°N, where the studies indicate that at latitudes <35°N amount effect plays a significant role in determining the isotopic values (Dansgaard, 1964) as the temperature does not cause drastic variation (Quade, 2003).

3.4. d-Excess

d-Excess values in precipitation are mainly governed by relative humidity, wind speed, and temperature and it generally plays a key role in determining the primary vapour source (Gimeno et al., 2012; Jouzel et al., 2013). The average *d*-excess values in each sampling locations during the study period are listed in Table 3. The $\delta^{18}O$ values of the samples were compared to the *d*-excess values to determine the fractionation process. A *d*-excess value of 10‰ is assigned to the evaporation of seawater at a specific relative humidity (80%) and standard temperature (25 °C) (Dansgaard, 1964; Merlivat and Jouzel, 1979). Low-pressure precipitations or rain events due to convective process result in a *d*-excess value of <10‰ (Guan et al., 2013); and rain events from frontal events and those derived from more than a single condensation and/or due to recycled moisture results in a *d*-excess value of >10‰ (Clark and Fritz, 1997; Wassenaar et al., 2009; Guan et al., 2013). In the Yucatan peninsula of Mexico, *d*-excess values were greater than 10‰ during November to March (Cejudo et al., 2021) probably due to the mixing of air masses from variable sources that resulted in a wide range of *d*-excess values and fluctuating isotopes signatures (Li, 2015).

In the present study, almost all the rainwater samples presented depleted isotope values during March 2016 due to the unusual rains because of the interaction with the winter storm composed of moistures from the Pacific and cold fronts No. 45 and 46 (a total of 50 cold fronts were recorded in 2016), and these precipitation episodes contributed nearly 69.2% of rains during 7–12 March 2016 (SMN, 2016). This has resulted in a drastic variation in their *d*-excess values reflecting the changes in the moisture sources due to convective process. Conversely, lesser *d*-excess values during the month of May in the samples of Mexico City is due to the convective process, while the lesser *d*-excess values in the samples of Tulancingo (−3.14‰) is due to the higher humidity and increased amount of rainfall (Fig. 4), indicating the evaporative water source. The sub-cloud evaporation might have also led to low *d*-excess values as this process can be enhanced if a relatively dry air mass

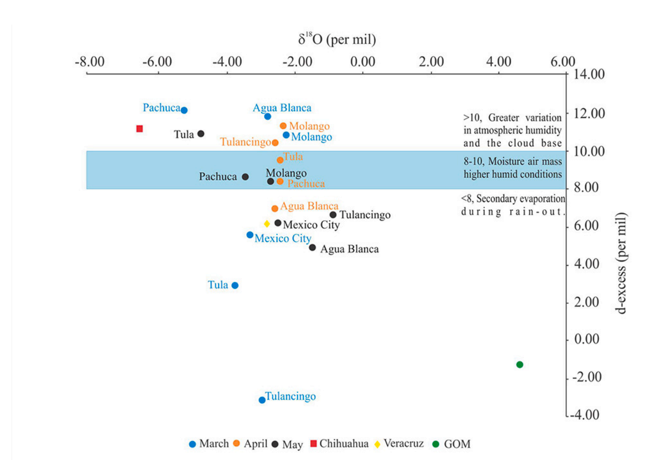

Fig. 4. The distribution of samples with respect to $\delta^{18}O$ and d-excess in the rainwater samples collected during the monthly campaign in Central Mexico.

persisted (Munksgaard et al., 2015) during March. The *d*-excess values of Pachuca are close to the reported values of Chihuahua during this period probably due to rainfall caused from the condensation of recycled moisture (Salati et al., 1979). The rainwater isotopically re-equilibrates or evaporate partially during its descent (Gat, 1996; Lee and Fung, 2008). Since, Agua Blanca is about 120 Km away from the coast, exchange of rain with vapour from spray or rapid evaporation process and higher wind speed might result in an increase of *d*-excess values, during March (Lawrence and Gedzelman, 1996). The climatic records of Agua Blanca show that the higher windspeed was observed during the month of March which generally reduces during the subsequent months. Values of *d*-excess in the month of April ranged between 6.95 and 11.3‰ and the summer precipitations during this time presented $\delta^{18}O$ values > −4‰ (Eastoe and Dettman, 2016). Additionally, similar *d*-excess values in the month of April specify that there had been no major changes in the moisture sources of the region and variation in the isotopic signatures are mainly due to the rain-out process. A clear negative relationship was observed between $\delta^{18}O$ and *d*-excess in the samples collected during May. Higher d-excess values are also reported if the relative humidity of the vapour sources at the cloud base is <60% (Merlivat and Jouzel, 1979). Tulancingo, is 140 Km from the coast and presented higher *d*-excess value during April probably due to significant evaporation at the source due to sea spray and greater wind speed (Gedzelman, 2003). The climatic records of Tulancingo indicate lesser windspeed during the month of March that eventually increases in April. Similarly, high *d*-excess is typical of areas, where evaporation from large surface bodies such as the Mediterranean Sea (Gat, 1996) or the Great Lakes in North America (Gibson et al., 2005). Major vapour sources governing the precipitation and their isotopic signatures of North America depend on the directions of GOM vapour migration, the geographical location with respect to the distance from the source and mountainous regions, which arrests the eastward migration of vapour from the Pacific Ocean. Apart from these factors, the latitude and the altitude of the location also governs the isotopic signatures (Colville and Meyers, 1965).

3.5. Longitudinal effect

The comparison of $\delta^{18}O$ values with longitude shows that there is depletion in the values during the month of May compared to other months as the vapour moves progressively inland from the coast (Fig. 5), whichis evident in the best-fit lines. This illustration can be interesting as the migration of vapour source is from GOM. Likewise, Wagner and Slowey (2011) observed that the $\delta^{18}O$ of the GOM varied from −1.0‰ to 0.5‰ in August and − 1.4‰ to 1.2‰ in May as the enrichment of isotopes are directly related to salinity of the waters. There is no definite trend observed during March which is due to the possibility of mixing with different sources (NAM, local inland vapour source and GOM) and the vertical mixing of vapour sources that are mainly governed by the shear velocity and directional changes of the wind during convection. The samples of April indicate depletion towards the coast, where $\delta^{18}O$ values are enriched in the inland and depleted in the coast. The variations of $\delta^{18}O$ in the vapour sources are generally due to the advection of moisture sources from different regions (Strong et al., 2007) and it is relatively enriched in the vapours of GOM. The depleted and enriched isotopes values are also governed by the atmospheric circulation; the enriched isotopes are generally isotopes from warmer source (Wright et al., 2001).

3.6. Latitudinal effect

Latitudinal effects of $\delta^{18}O$ values were also studied, and the results revealed a positive trend in Mexico City, Tulancingo, Agua Blanca and Molango, except for two samples from Pachuca and Tula in the month of March (Fig. 6), attesting the fact that the enriched values are observed in the higher latitudes and are depleted progressively as the moisture source migrates towards the south. The moisture source obtained from the evaporation of the sea surface near t Baja California provides the driving force, resulting in the unusual excessive rain events due to Pacific moisture and cold fronts No. 45 and 46. There is no definite trend observed in samples collected during April and the samples representing May show depletion trend with respect to the latitude. This trend is also observed in two different patches which may be due to the geographical position of Mexico City and Tula near a rain shadow region or due to the variation in the mixing proportion of Caribbean and GOM moisture sources (Bryson and Hare, 1974). Studies on $\delta^{18}O$ values in the low latitudes have also revealed that the role of convection process influences the isotopic signature rather than the amount of rainfall (Vimeux et al., 2011; Moerman et al., 2013; Lekshmy et al., 2014). The studies on the isotopic values of precipitation in a mountainous region represent a windward and a leeward side (rain shadow region), which is commonly observed in a region with one dominant direction of the wind (Blisniuk, 2015). However, there still exits a gap in clear documentation of isotopic rain shadows along the leeward side of the tropical mountainous regions (Lachniet et al., 2007). Court (1974) and Lawson and Fairbank (1974) determined that the moisture source from GOM is warm and that of Pacific is dry and mild. The moisture source of precipitation along the central region of Mexico has a great significance due to interplay of these sources along with altitude and rain out effects. The isotopic signatures become more significant especially, during major storm events.

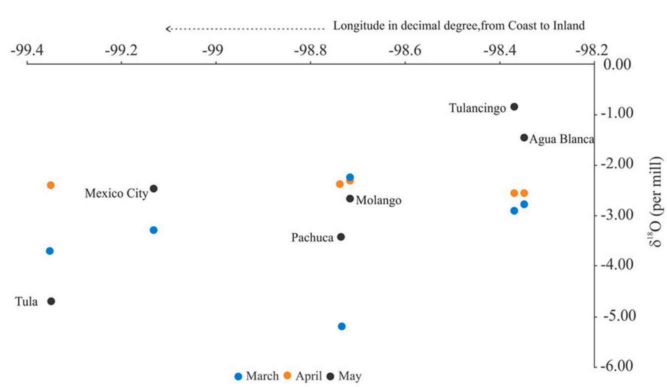

Fig. 5. Longitudinal effect of $\delta^{18}O$ values in the monthly rainwater samples collected during the study period.

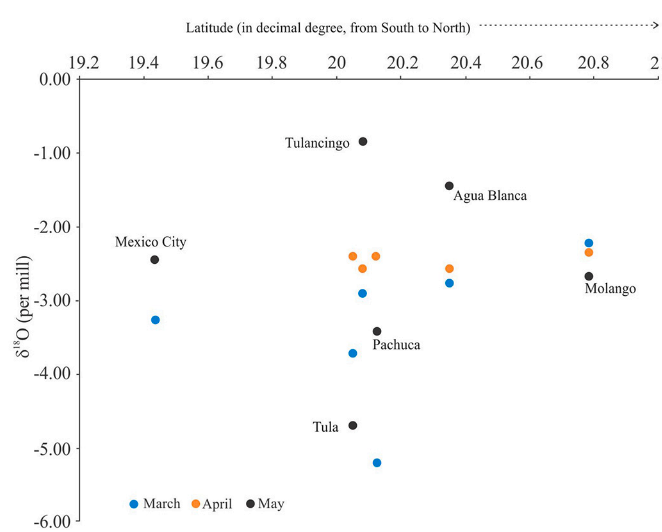

Fig. 6. Latitudinal effect of $\delta^{18}O$ values in the monthly rainwater samples collected during the study period.

4. Statistical assessment

4.1. Correlation analysis

The physiography of the land surface, terrestrial vapour sources and amount of precipitation across the inland also results in the variation of isotope values apart from temperature and humidity (Gedzelman, 2002; Trenberth, 2007). Hence, correlation analysis (Table 5) for the entire dataset was attempted for all the sampling months (March, April and May) to unravel the interrelationship among their geographical position (latitude and longitude), physiography (elevation), climatological (rainfall, temperature and humidity) and isotopic characteristics.

In March 2016, the amount of rainfall presented positive relationship with $\delta^{18}O$ (humidity, temperature, latitude and longitude indicating the fact that the enrichment of $\delta^{18}O$ takes place with respect to the increase of all these parameters (Table 5). Further, $\delta^{18}O$ shows a positive relationship with $\delta^{2}H$, temperature and rainfall. In contrast, the negative relationship of $\delta^{18}O$ and $\delta^{2}H$ with elevation displays that when there is an increase of elevation, there is depletion of the isotopic values revealing the attitude effect. There is also a reduction in temperature with change in elevation (1390 m AMSL to 2390 m AMSL) that resulted in a negative relationship between these two parameters during March. Additionally, the negative correlation of *d*-excess vs amount of rainfall indicates the variation in moisture source during the period. There have been unusual rain events recorded during March from different sources, where the major predominant vapour source is that of NAM from Baja California. In addition, terrestrial precipitations also receive vapour through transpiration and evapotranspiration that maintains the isotope significance of earlier rain events (Hu and Dominguez, 2015).

Likewise, the amount of rainfall in April presented significant positive correlation with humidity, temperature and longitude demonstrating that the rainfall increases from inland to the coast. This is also supported by the negative relationship of isotope signatures to rainfall and longitude, indicating the rainout process. The *d*-excess values presented a positive relationship to $\delta^{18}O$. Furthermore, the latitudinal extension presented weak positive correlation to the isotope signatures signifying the fact that they are typically enriched in higher latitudes. The correlation matrix of May indicated a similar positive relationship between the amount of rainfall vs *d*-excess and elevation indicating an orographic control. The amount has a negative relationship to latitude and longitudinal as the moisture source migrates from coast to inland.

4.2. Principal component analysis

The data reduction method using principal component analysis was adopted for the monthly data to determine the predominant processes governing the isotopic signatures through factor scores for each location (Table 6). The PCA analysis for March data extracted three factors with a variance of 44% (PCA 1), 28% (PCA 2) and 18% (PCA 3) respectively. Among the three factors, PCA 1 and PCA 3 are observed to influence the isotopic composition, while PCA 1 is represented by the rainfall amount (0.69), $\delta^{18}O$ (0.85), $\delta^{2}H$ (0.75), temperature (0.86) and latitude (0.69). The positive association between enrichment of $\delta^{18}O$ and $\delta^{2}H$ values and rainfall indicate the amount effect. The enriched isotope value during thunderstorms are due to low precipitation efficiency, comparatively with lesser life span and lesser horizontal extent (Lawrence and Gedzelman, 1996) and this effect is observed at Agua Blanca and Molango stations only; that is located in the northern part of the study area. The unusual rain events during this month have been due to the cold front numbers 45, 46 and moisture from Pacific. 70% of the total precipitation of northwestern region of Mexico is contributed by North American Monsoon (NAM) (Douglas and Leal, 2003), and GOM serves as the main moisture source for the NAM. This mixture of sources makes it complex to exactly determine the process and the perfect mixing of atmospheric vapour is very rare (Goessling and Reick, 2012). An attempt to understand the vertical mixing of air masses was attempted by different models (Schmitz and Mullen, 1996; Douglas and Leal, 2003; Van der Ent et al., 2013). PCA 3 denoted significant negative association of rainfall

Table 5
Correlation analysis between the isotopic, climatological and localization characteristics of each sampling location during the study period.

	Rainfall	$\delta^{18}O$	$\delta^{2}H$	d-excess	Hum.	Temp.	Elev.	Lat.	Long.
March 2016 (n = 6)									
Rainfall	1.00								
$\delta^{18}O$	0.66	1.00							
$\delta^{2}H$	–	0.73	1.00						
d-excess	−0.53	–	–	1.00					
Hum.	0.52	–	–	–	1.00				
Temp.	0.90	0.67	–	–	–	1.00			
Elev.	−0.58	−0.76	−0.74	–	–	−0.84	1.00		
Lat	0.69	–	–	–	–	0.90	−0.78	1.00	
Long.	0.54	–	–	–	0.97	–	–	–	1.00
April 2016 (n = 5)									
Rainfall	1.00								
$\delta^{18}O$	−0.55	1.00							
$\delta^{2}H$	–	0.77	1.00						
d-excess	–	0.51	0.94	1.00					
Hum.	0.92	−0.58	–	–	1.00				
Temp.	0.71	–	–	–	0.71	1.00			
Elev.	–	–	–	–	–	−0.77	1.00		
Lat	–	–	–	–	–	0.88	−0.88	1.00	
Long.	0.83	−0.64	–	–	0.96	0.54	–	–	1.00
May 2016 (n = 6)									
Rainfall	1.00								
$\delta^{18}O$	−0.84	1.00							
$\delta^{2}H$	−0.79	0.99	1.00						
d-excess	0.96	−0.88	−0.82	1.00					
Hum.	–	0.54	0.58	–	1.00				
Temp.	–	–	–	–	0.82	1.00			
Elev.	0.66	–	–	0.56	0.50	–	1.00		
Lat	−0.64	–	–	–	−0.66	−0.72	−0.78	1.00	
Long.	−0.87	0.87	0.84	−0.88	–	–	–	–	1.00

Elev.: Elevation; Hum.; Humidity; Lat.: Latitude; Long. Longitude; Temp.: Temperature.

Table 6
Principal component analysis of the isotopic, climatological and localization characteristics of each sampling location during the study period.

	March 2016 (n = 6)			April 2016 (n = 5)			May 2016 (n = 6)	
	PCA1	PCA2	PCA 3	PCA1	PCA2	PCA 3	PCA1	PCA2
Rainfall	**0.69**	0.41	-0.51	**0.96**	0.16	0.18	-0.95	0.31
δ^{18}O	**0.85**	0.10	-0.09	-0.69	0.34	**0.56**	**0.96**	0.23
δ^{2}H	**0.75**	0.07	**0.59**	-0.23	0.22	**0.95**	**0.93**	0.31
d-excess	-0.13	-0.05	**0.94**	0.06	0.11	**0.98**	-0.97	0.14
Humidity	0.20	**0.95**	-0.08	**0.94**	0.31	-0.12	0.37	**0.89**
Temperature	**0.86**	0.36	-0.27	**0.55**	**0.76**	0.35	0.27	**0.85**
Elevation	-0.96	-0.11	-0.12	-0.10	-0.94	-0.03	-0.43	**0.73**
Latitude	**0.69**	0.38	-0.18	0.12	**0.95**	0.26	0.39	-0.92
Longitude	0.18	**0.98**	0.00	**0.92**	0.14	-0.25	**0.92**	-0.07
Variance %	44	26	18	39	30	27.5	55.7	34.9
Agua Blanca	0.46	1.03	-1.26	0.51	0.64	-1.56	1.12	-0.05
Molango	1.71	-0.16	-0.31	-0.02	1.43	1.06	0.38	1.44
Mexico City	-0.38	-0.96	0.86	-	-	-	-0.40	-1.54
Pachuca	-1.25	0.40	-0.28	-0.52	-0.62	0.22	0.57	-0.06
Tula	-0.21	-1.34	0.64	-1.30	-0.50	0.10	-1.50	-0.40
Tulancingo	-0.34	1.03	-1.44	1.33	-0.95	0.62	0.94	0.62

(−0.51) with δ^2H (0.59) and d-excess (0.94) mainly in Tula and Mexico that represent the rain shadow regions. The d-excess is also governed by the relative humidity, mainly of the season (Merlivat and Jouzel, 1979). This drastic variation may be due to the changes in the fractionation induced by temperature, humidity, amount, rainout is convection process during the period of observation.

The PCA analysis for the data during April month also extracted 3 factors with variances of 39% (PCA 1), 30% (PCA 2) and 27.5% (PCA 3). During this sampling period, significant positive interrelationship was observed between the amount of rainfall (0.96), humidity (0.94), temperature (0.55) and longitude (0.92), whereas the isotopic signatures were negative in PCA 1. The association of these parameters indicate the interplay of tropical air stream from the GOM and the Caribbean Sea, strong westerlies from the Pacific and the Arctic air stream from the north (Bryson and Hare, 1974). The eastern parts of America and Mexico are inferred to be influenced by the tropical air stream. As mentioned earlier, Mexico receives precipitation from two different sources predominantly Pacific and the Gulf of Mexico. The northern regions of Mexico experience precipitation due to northward migration of both the sources and the southern Mexico experience the southward migration of sources especially, $< 20°$N (Harvey, 2001). The westward extension of subtropical high and the position of monsoonal ridge plays a key role in attaining vapour from the GOM and Caribbean (Schmitz and Mullen, 1996; Bosilovich, 2003). NAM precipitation is mainly tropical cyclones from the East Pacific region during the monsoon (Higgins at al., 2003). So, due to this complex nature it is inferred that the shift of the North Atlantic subtropical high and the climatological developments in the monsoonal ridge primarily governs the GOM and the Caribbean Sea sources. Hence, PCA1 is attributed to an increase in amount of rainfall towards the coast with depletion of stable isotope due to rain-out process. This process is represented in Agua Blanca and Tulancingo along the northern regions of the study area. PCA 3 is represented by the positive interrelationship of δ^{18}O (0.56), δ^2H (0.95) and d-excess (0.98) indicating probable local recirculation of evaporated moisture from the inland surface water body. Though studies reveal the significance of the oceanic source for precipitation, the terrestrial input of vapours from the evapo-transpirated soil moisture after the onset of monsoon was inferred to be an important source for convective precipitation (Small, 2001; Bosilovich, 2003; Domínguez et al., 2008). The isotopic signatures of the evapo-transpirated vapour are often complex as it is a mixture of non-fractionated and fractionated process (Yakir and Sternberg, 2000). It estimated that 40% of moisture source for the monsoonal precipitation is contributed by the terrestrial evapotranspiration and evaporation processes (Hu and Dominguez, 2015). This process is represented in Molango, Pachuca, Tula and also in Tulancingo, where the isotopic composition during this period is inferred to be affected by both the processes.

Though two different components were extracted from the May 2016 data set, only one factor (PCA 1) represented the significant relationship of isotope signatures with a variance of 55%. In this case, it is inferred that the isotopic composition of the rain-events during this period is probably governed by a single source which is represented by longitude (0.92). As mentioned earlier, the wet season which prevails from May is predominated by the GOM and Caribbean moisture sources and the remaining period is dominated by the dry westerly upper airflow (Issar, 1985). The Caribbean and GOM sources contribute the NAM by advective transport mechanism from the Yucatan peninsula which was studied during a tropical cyclone (21–26 August 1996) by Hu and Dominguez (2015). Hence, there is depletion in isotope values as it moves inland favouring increased precipitation. This mechanism is a good representation of changes in the atmospheric moisture reflecting the Rayleigh distillation (Rozanski et al., 1993; Araguás-Araguás et al., 1995) which is predominantly observed in the δ^{18}O values of tropical rains (Vuille et al., 2005; Schmidt et al., 2007; Sturm et al., 2007) especially in the regions with orographic barriers. This process reveals the amount effect due to negative association of rainfall and δ^{18}O, δ^2H and the continental effect, as the depletion of the isotope values are observed as it migrates inland from the coast. This effect is observed in samples of Tulancingo, Agua Blanca, Molango and Pachuca.

5. Conclusion

The study on the isotopic signatures of the monthly rain events from different locations of Central Mexico reveals that there is an apparent variation in isotopic composition with respect to geographical locations. The comparison of isotopic composition reveals that they fall in line with GMWL, except for two samples during March due to the unusual rain events and diverse rainfall sources. There is a gradual increase in temperature from March to May; the lesser humidity values are observed during April. The range of stable isotope signatures is greater during March and May, but the values are within a very narrow range during April. The March isotope signatures clearly represent the influences of the winter storm in the Northern part of the study area at Molango and Agua Blanca. The influence of GOM and inland moisture sources were also observed in Tulancingo and southern stations respectively. The longitudinal variation of δ^{18}O indicates mixed moisture sources during March, which depleted towards the coast from inland during April and subsequently enriched during May. The primary moisture source for winter rainfall during March was found to be the NAM and during May it was from the GOM. However, in April the rain shadow regions (Tula and Pachuca) demonstrated isotopic enrichment, as in this case lighter isotopes from the condensate are rapdily evaporated during the process of precipitation at the cloud base and are normally sustained by the drop in humidity levels. In the case of May, inland migration of vapour sources from GOM and Caribbean was demonstrated by the continental and amount effect differences. The PCA study indicates that the isotope values are influenced by different metrological parameters, geographical position and also by the altitude of the location. Further, the influence of these parameter varies with respect to time depending on the source moisture. The present study attests that the climatological and geographical characteristics significantly influence the isotopic signatures of a region. Our results prove to fill the gap in understanding the vital factors and causes, accountable for unusual winter rainfall episodes in Central Mexico.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.atmosres.2021.105744. These data include the Google map of the most important areas described in this article.

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