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Articles

Isotopic composition of precipitation in Valle de Querétaro, Mexico

Composición isotópica de la precipitación en el Valle de Querétaro, México

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Abstract

Stable isotopes monitoring of rainfall in México has been limited. This study presents the characterization of the isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Excess-d) of meteoric water that occurred in the Querétaro Valley from September 2017 to July 2021. Laser water isotope analyzers Picarro L2110-i and Los Gatos Research LWIA-45EP were used to carry out the stable isotope analyses. The local meteoric water line was obtained using a least squares regression of the isotope data, $\delta^2\text{H} = 7.65 \delta^{18}\text{O} + 6.97$. This line has a slope and an intercept lower than the World Meteoric Line (LMM). The data show that the Local Meteoric Line has a lower slope and intercept than the LMM, due to secondary evaporation of small rainfall (< 30 mm per month). This collector forms part of the National Network for Monitoring the Isotope Composition of Rain that the Mexican Institute of Water Technology installed in various physiographic provinces of the country.



Keywords: Rain, stable isotopes, meteorological line of Querétaro, Secondary evaporation, national network for monitoring the isotope composition of rain.

Resumen

El uso de los isótopos estables del agua para determinar la relación entre la precipitación y la recarga/descarga del agua subterránea ha sido limitado en México. Una de las principales limitaciones es la falta de monitoreo de los isótopos estables de la lluvia. Este estudio presenta la caracterización de la composición isotópica ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Exceso-d) del agua meteórica ocurrida en el Valle de Querétaro de septiembre de 2017 a julio de 2021. Los análisis de isótopos estables se realizaron en el laboratorio de hidrología isotópica del Instituto Mexicano de Tecnología del Agua (IMTA), utilizando analizadores láser Picarro L2110-i y Los Gatos Research LWIA-45EP. Por medio de una regresión lineal de mínimos cuadrados de los datos isotópicos se determinó la línea de agua meteórica del valle de Querétaro (LAMVQ), $\delta^2\text{H} = 7.65 \delta^{18}\text{O} + 6.97$. Esta línea tiene una pendiente y un intercepto menor al de la línea meteórica mundial (LMM). Los datos mostraron que los valores de la pendiente, del intercepto y del exceso de deuterio (d) dependen de la cantidad de lluvia. La LAMVQ tiene una pendiente e intercepto menor al de la LMM debido a evaporación secundaria de las precipitaciones pequeñas (< 30 mm mensual). Este colector forma parte de la Red Nacional de Monitoreo de la Composición Isotópica de la Precipitación Pluvial (RENIP), que el IMTA instaló en diversas provincias fisiográficas del país.



Palabras clave: lluvia, isótopos estables, línea meteórica de Querétaro, evaporación secundaria, Red Nacional de Monitoreo de la Composición Isotópica de la Precipitación.

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Introduction

The stable isotopes of hydrogen and oxygen of the water molecules from precipitation are a useful tool, for studying the origin and dynamics of surface and groundwater (Bowen & Good, 2015; Eastoe, Hess, & Mahieux, 2015; Ouyse, Wehncke, & Carrillo-Rivera, 2018; Sánchez-Murillo *et al.*, 2019). The International Atomic Energy Agency in conjunction with the World Meteorological Organization, implemented the Global Network of Isotopes in Precipitation in order to characterize the isotopic variability in precipitation on a global and regional scale ((Schotterer, Oldfield, & Froehlich, 1996). The network began operating since 1960, collecting isotopic and meteorological data to this day. Two stations operated in



Mexico, one in the city of Chihuahua and the other in the city of Veracruz, from 1962 to 1988.

The use of water isotopes to determine the relationship between precipitation and groundwater recharge/discharge has been limited in Mexico. One of the main limitations is the lack of monitoring of the stable isotopes of rain. Some recent studies have been carried out on the subject, however, information is still lacking in many areas of the country. One of these studies was carried out by Aguilar-Ramírez, Camprubí, Fitz-Díaz, Cienfuegos-Alvarado and Morales-Puente (2017) in the center-northeast of the Sierra Madre Oriental. The collection of rain was the rainy season of 2012, between the months of July and October.

The Local Meteoric Water Line that they determined was $\delta^2\text{H} = 8.15 \cdot \delta^{18}\text{O} + 15$. The slope (8.15) and the intercept (15) of the equation are higher than the values of the World Meteoric Line (8, 10). This is likely due to the fact that the sampling was carried out only in the rainy season. A sampling in the dry season is recommended, to verify if these values are maintained or decreased.

Another of the studies was carried out by Cejudo, Acosta-González and Leal-Bautista (2021), in the Yucatán peninsula (Campeche, Quintana Roo and Yucatán). The study period spanned from November 2018 to November 2019. The Regional Meteoric Water Line they found was $\delta^2\text{H} = 7.803 \cdot \delta^{18}\text{O} + 12.075$. According to Putman, Fiorella, Bowen and Cai (2019), to define a Local Meteoric Line at least four years of observations are required. In the case of the Yucatan peninsula, more years of monitoring are required for a better definition of the Meteoric Line.



Examples in Mexico of the application of stable isotopes of rainwater are the Meteoric Water Line of Mexico City (Cortés & Farvolden, 1989; Cortés, Durazo, & Farvolden, 1997), which helped to determine the origin of groundwater salinity (Ortega-Guerrero, Cherry, & Aravena, 1997) and study the hydrogeology of the deep aquifer (Morales-Casique, Escolero, & Arce, 2014), the Meteoric Water Line of Quintana Roo, which helped to interpret the paleo-climatic information of the stalagmites of the Río Secreto caves (Lases-Hernandez, Medina-Elizalde, Burns, & DeCesare, 2019), and the Meteoric Water Line of Baja California Sur, which allowed to determine the sources of recharge of coastal aquifers (González-Hita, Mejía-González, Martínez-Cardeteño, Aparicio-González, & Flores-Mañón, 2021).

The objectives of the study were: 1) The characterization of the isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Excess-d) of the meteoric water that occurred in the Valley of Querétaro from September 2017 to July 2021, 2) Determine the Meteoric Water Line of the Valley of Querétaro, and 3) Identify the processes that control the slope and intercept of the Meteoric Line.

Study area



The Querétaro Valley is located in the Central part of the Physiographic Province called the Trans-Mexican Volcanic Belt (INEGI, 1997) (Figure 1). This Valley is the product of a series of events that took place from the end of the Cretaceous to the beginning of the Tertiary, including the Laramide Revolution, which caused the dislocation and folding of marine sedimentary rocks, giving rise to the formation of mountain ranges and faults. Subsequently, new fractures and faults originated pillars and rifts associated with volcanic activity, which were filled with alluvial sediments, lava flows and volcanoclastic deposits (Conagua, 2015).



Figure 1. Location of the Querétaro Valley.

It is an extensive valley with an elongated shape in a north-south direction, with topographical forms of mountain ranges, hills and plains with altitudes between 1 800 and 2 390 m (INEGI, 1997). The most important elevation is the Cimatarío (2 390 m).



Climatic Characteristics

The predominant climate is semi-dry-semi-warm, the average annual temperature is 19 °C, and the average annual rainfall is 549 mm (INEGI, 1997). Precipitation is most abundant from June to October, that is, typically of summer (Reyna, 1970). Sometimes a less humid period occurs in the middle of the rainy season, which is known as the midsummer drought (Reyna, 1970). Figure 2 and Figure 3 show, respectively, the behavior of the temperature and the mean monthly precipitation.

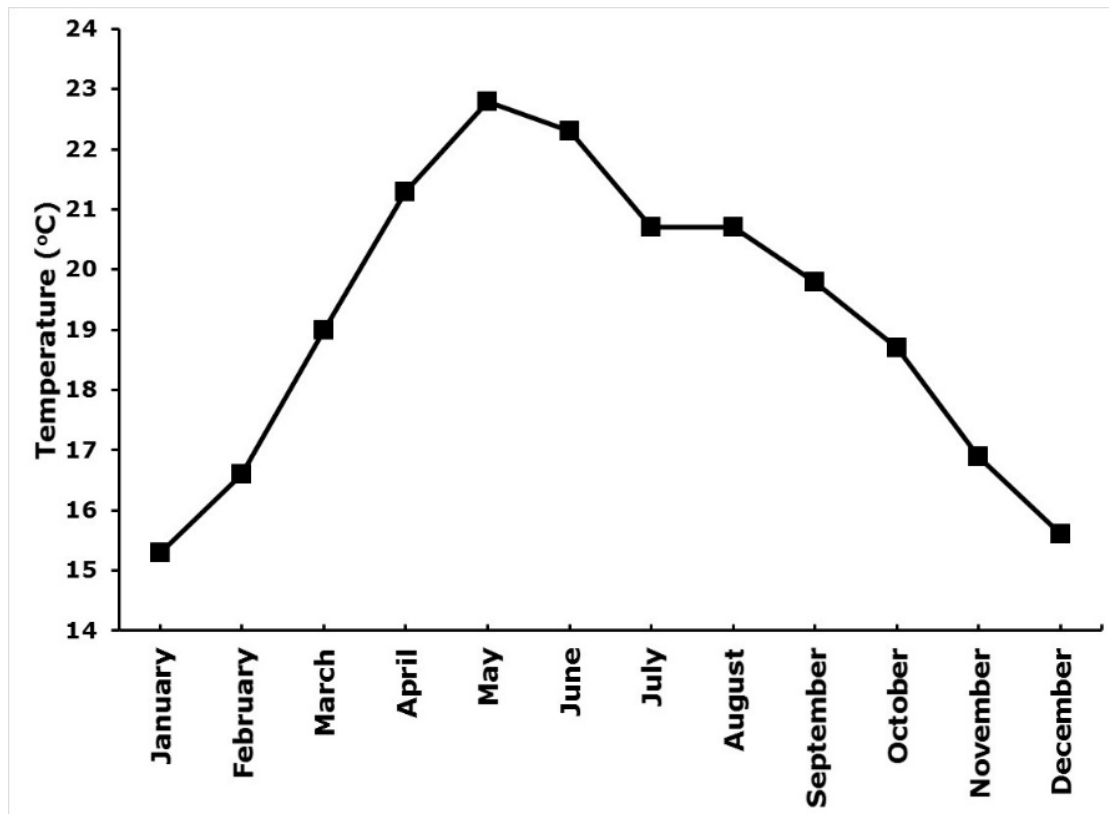


Figure 2. Average monthly temperature of the Querétaro Valley, 1951-2010. Source: SMN (2011).

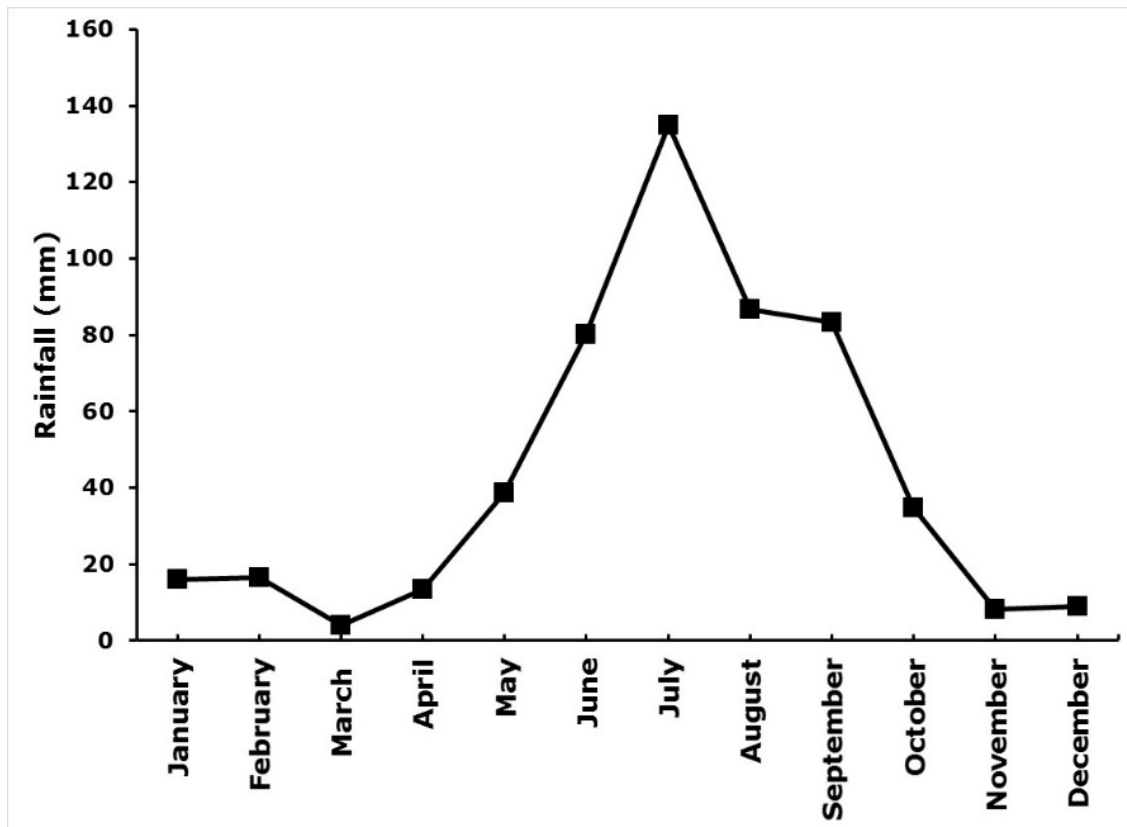


Figure 3. Mean monthly precipitation of the Querétaro Valley, 1951-2020. Source: SMN (2011).

Methodology



Rain samples were collected from September 2017 to July 2021 accumulated monthly, using a RS2 PALMEX rainwater collector (Figure 4) which allows monthly samples to be taken without evaporation or fractionation (IAEA, 2002). Samples were filtered using 0.45 μm cellulose membranes, and stored in high-density polyethylene bottles with polyseal and conical insert caps.



Figure 4. Rainwater collector RS2 PALMEX.

Stable isotope analyzes were performed in the isotope hydrology laboratory of the Mexican Institute of Water Technology (IMTA), using



laser water isotope analyzers Picarro L2110-i and Los Gatos Research LWIA-45EP. The analytical precision is ± 0.5 ‰ for $\delta^2\text{H}$ and ± 0.13 ‰ for $\delta^{18}\text{O}$.

The collector is located in the facilities of the National Meteorological Service of Querétaro whose coordinates are (20° 34' 13" North, 100° 22' 11" West) and altitude 1820 meters above sea level.

Results

The rain samples collected from September 2017 to July 2021 were determined for their stable isotope content. The values of $\delta^{18}\text{O}$ ‰ (VSMOW) and $\delta^2\text{H}$ ‰ (VSMOW) are shown in Table 1. The $\delta^{18}\text{O}$ values span from -0.5 ‰ to -15.5 ‰, with an average of -7.77 ‰. The $\delta^2\text{H}$ values range from 0.3 ‰ to -111.8 ‰, with an average of -52.5 ‰.

Table 1. Monthly isotopic composition of precipitation in the Querétaro Valley in the period September 2017- July 2021.

COLECTOR	LATITUD N	LONGITUD W	ALTITUD (msnm)	FECHA DE MUESTREO	$\delta^{18}\text{O}$ (‰) VSMOW	$\delta^2\text{H}$ (‰) VSMOW	Exceso-d	Precipitación (mm)
QUERETARO	20.56342	-100.36944	1,902	Septiembre.2017	-11.27	-78.1	12.1	105
QUERETARO	20.56342	-100.36944	1,902	Febrero.2018	-2.90	-20.0	3.2	7.68
QUERETARO	20.56342	-100.36944	1,902	Abril.2018	-1.35	-6.9	3.9	4.19
QUERETARO	20.56342	-100.36944	1,902	Mayo.2018	-3.16	-12.3	13.0	57.29
QUERETARO	20.56342	-100.36944	1,902	Junio.2018	-12.33	-89.0	9.6	229.31
QUERETARO	20.56342	-100.36944	1,902	Julio.2018	-3.13	-17.90	7.1	41.22
QUERETARO	20.56342	-100.36944	1,902	Agosto.2018	-7.30	-51.70	6.7	101.93
QUERETARO	20.56342	-100.36944	1,902	Septiembre.2018	-7.80	-51.30	11.1	98.51
QUERETARO	20.56342	-100.36944	1,902	Octubre.2018	-7.61	-49.70	11.2	28.64
QUERETARO	20.56342	-100.36944	1,902	Noviembre.2018	-9.09	-62.60	10.1	44.71
QUERETARO	20.56342	-100.36944	1,902	Mayo.2019	-0.5	0.30	4.0	23.75
QUERETARO	20.56342	-100.36944	1,902	Junio.2019	-9.3	-58.90	15.5	141.13
QUERETARO	20.56342	-100.36944	1,902	Julio.2019	-6.6	-38.30	14.1	43.32
QUERETARO	20.56342	-100.36944	1,902	Agosto.2019	-15.5	-111.80	12.0	75.0
QUERETARO	20.56342	-100.36944	1,902	Octubre.2019	-13.2	-96.20	9.6	122.27
QUERETARO	20.56342	-100.36944	1,902	Noviembre.2019	-8.9	-65.30	5.6	0.63
QUERETARO	20.56342	-100.36944	1,902	Diciembre.2019	-7.5	-48.18	12.1	2.79
QUERETARO	20.56342	-100.36944	1,902	Enero.2020	-7.5	-47.50	12.1	13.97
QUERETARO	20.56342	-100.36944	1,902	Febrero.2020	-8.4	-50.40	16.7	44.71
QUERETARO	20.56342	-100.36944	1,902	Mayo.2020	-5.4	-31.50	11.9	23.75
QUERETARO	20.56342	-100.36944	1,902	Junio.2020	-5.1	-27.90	13.1	154.06
QUERETARO	20.56342	-100.36944	1,902	Julio.2020	-10.41	-77.6	5.7	62.04
QUERETARO	20.56342	-100.36944	1,902	Agosto.2020	-11.62	-83.9	9.1	78.95
QUERETARO	20.56342	-100.36944	1,902	Septiembre.2020	-7.19	-50.2	7.3	49.61
QUERETARO	20.56342	-100.36944	1,902	Octubre.2020	-6.18	-48.8	0.6	9.08
QUERETARO	20.56342	-100.36944	1,902	Enero.2021	-6.43	-44.40	7.0	17.47
QUERETARO	20.56342	-100.36944	1,902	Mayo.2021	-4.72	-23.60	14.2	84.54
QUERETARO	20.56342	-100.36944	1,902	Junio.2021	-13.61	-95.40	13.5	43.32
QUERETARO	20.56342	-100.36944	1,902	Julio.2021	-11.55	-83.00	9.4	83.84

With the data, the graph of the relationship $\delta^{18}\text{O}$ ‰ (VSMOW) versus $\delta^2\text{H}$ ‰ (VSMOW) was elaborated (Figure 5). Using a linear least squares regression of the isotopic data, the Meteoric Water Line of the

Queretaro Valley was determined, $\delta^2\text{H} = 7.65 \delta^{18}\text{O} + 6.97$, with $r^2 = 0.9829$.

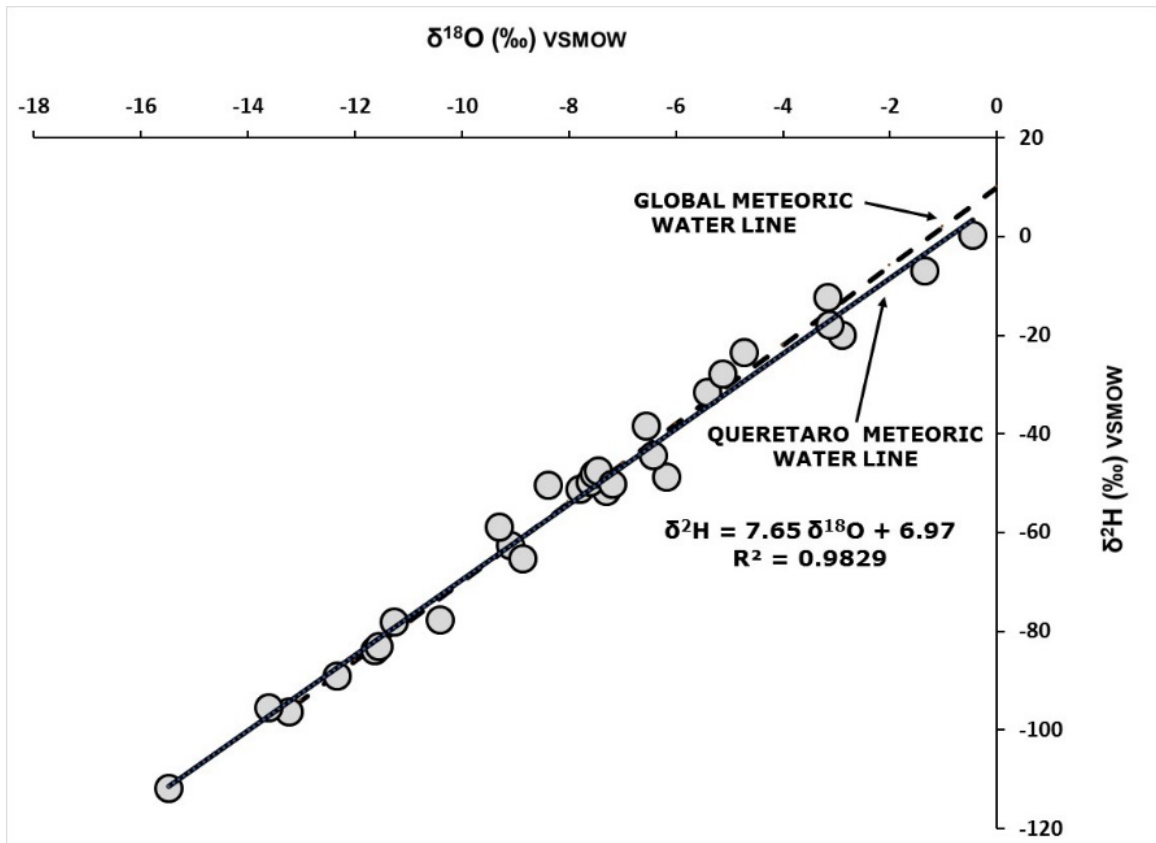


Figure 5. Meteoric Water Line of the Valley of Querétaro

Discussion

Dry season

During the period from December to mid-May, the little precipitation that occurs is affected by secondary evaporation. It is also known as "evaporation under the cloud", because it is the evaporation suffered by raindrops on their descent from the clouds to the ground. Descending in a column of dry air occurs kinetic fractionation of raindrops (Stewart, 1975; Dansgaard 1964). Fractionation produces enrichment of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Peng, Mayer, Harris, & Krouse, 2007). When the rain is very intense or lasts for a long time, the air under the clouds becomes saturated and the secondary evaporation process stops.

Table 2 presents three ranges of precipitation, their average values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, the slope and intercept of the correlation $\delta^{18}\text{O}$ - $\delta^2\text{H}$, and the excess of deuterium (d). The table shows that the values of the slope, intercept, and d-excess depend on the range of precipitation. Rain greater than 70 mm has the highest slope and intercept values. As precipitation decreases, the slope values decrease from 8.21 to 7.22, and the intercept values decrease from 13.26 to 2.94. This trend indicates

that the isotopic composition of light rain is affected by secondary evaporation.

Table 2. Values of $\delta^{18}\text{O}$, $\delta^2\text{H}$, Excess-d, and correlation parameters $\delta^{18}\text{O}$ - $\delta^2\text{H}$, for different ranges of precipitation.

Precipitation range mm	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	$\delta^{18}\text{O} - \delta^2\text{H}$		Deuterium Excess d
			Slope	Intercept	
0-30	-5.42	-36.2	7.22	2.94	7.16
30-70	-7.69	-50.6	7.89	10.07	10.92
> 70	-9.98	-68.7	8.21	13.26	11.14

During evaporation there is an excess of deuterium (H^2) relative to ^{18}O in the vapor. This is due to the difference in the weight of a water molecule containing deuterium ($\text{H}^1\text{H}^2\text{O}^{16} = 19 \text{ g / mol}$) and one containing oxygen-18 ($\text{H}^1\text{H}^1\text{O}^{18} = 20 \text{ g / mol}$). The excess deuterium (d) is defined as $d = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$. The value of the d-excess of the Global Meteoric Water Line (GMWL) is 10 (Dansgaard, 1964).

After evaporation of surface water (or a raindrop), the remaining water will have deuterium excess values lower than 10, while the vapor produced will have deuterium excess values greater than 10, in a process as shown in Figure 6 (Victoria, Martinelli, Mortatti, & Richey, 1991). That is, evaporation decreases deuterium excess, while recycled moisture increases it (Froehlich *et al.*, 2008).



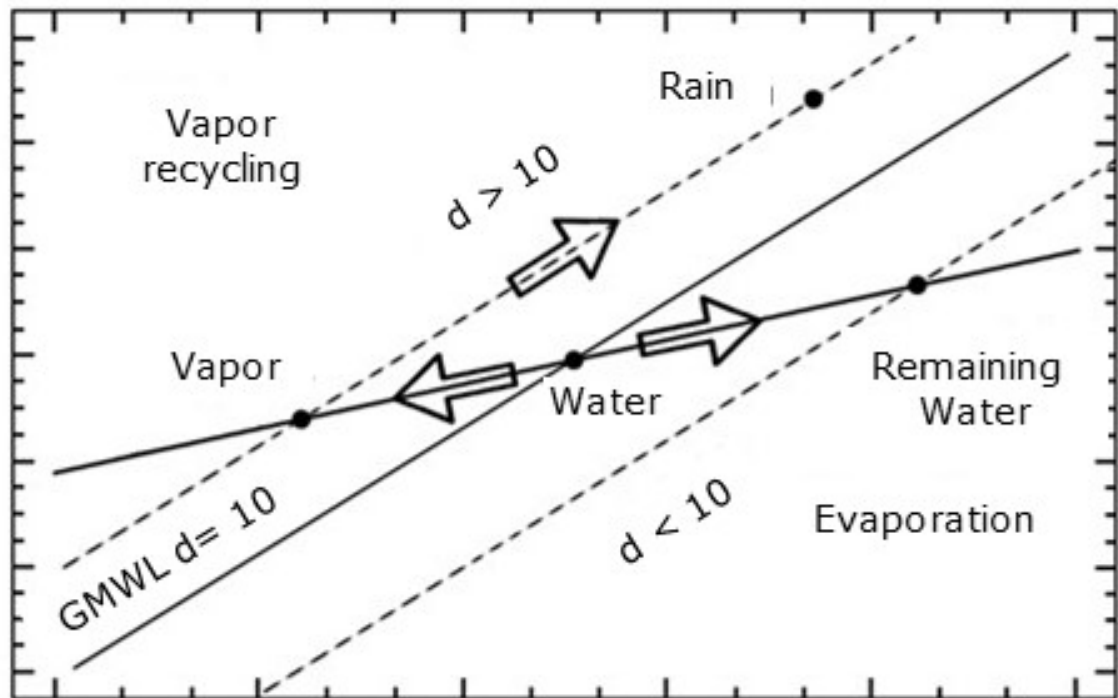


Figure 6. Isotopic evolution of water subjected to evaporation (Victoria *et al.*, 1991; ©The Royal Swedish Academy of Sciences. Used with permission).

As can be seen in Table 2, the deuterium excess of the precipitations smaller than 30 mm is smaller than the GMWL value ($d_{<30\text{mm}} = 7.16 < d_{\text{GMWL}} = 10$), which indicates that they evaporated. The excess- d of the precipitations greater than 30 mm is similar to the GMWL value, which indicates that these samples did not evaporate.

Figure 7 and Figure 8 show that values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are enriched in the dry season, and depleted in the rainy season.

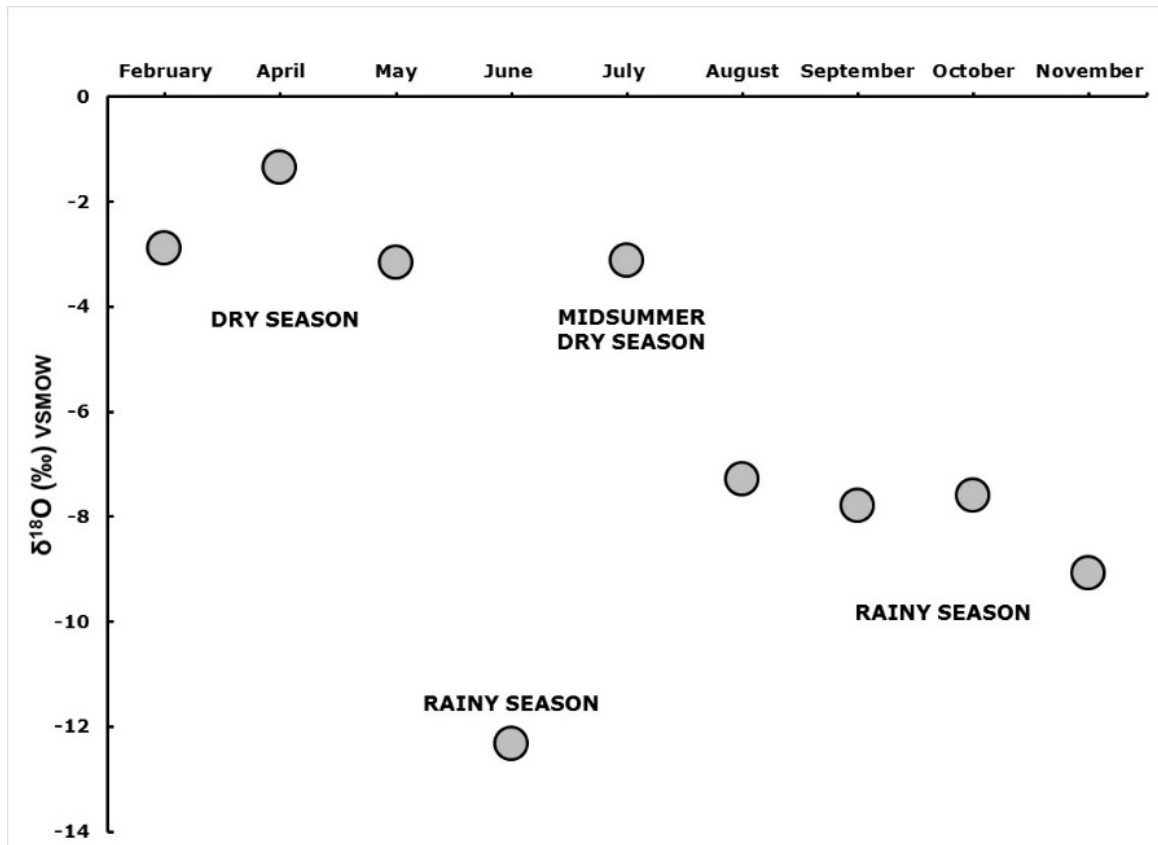


Figure 7. Monthly values of $\delta^{18}\text{O}$ of rainfall during 2018.

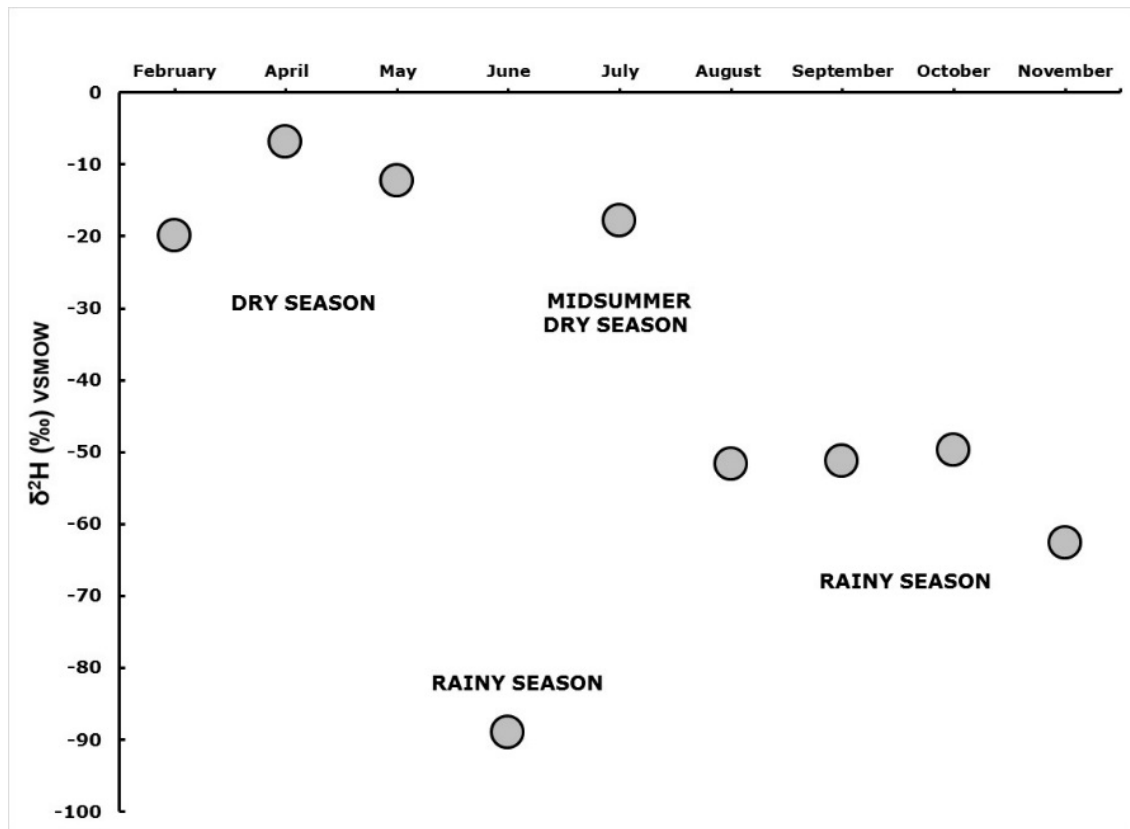


Figure 8. Monthly values of $\delta^2\text{H}$ of rainfall during 2018.

Pérez-Quezadas, Adams, Sánchez-Murillo, Lagunes y Rodríguez-Castañeda (2021) their study of the North American monsoon in the Sonora river basin (northwestern Mexico), also found a correlation between the amount of rainfall and deuterium excess (Figure 9).

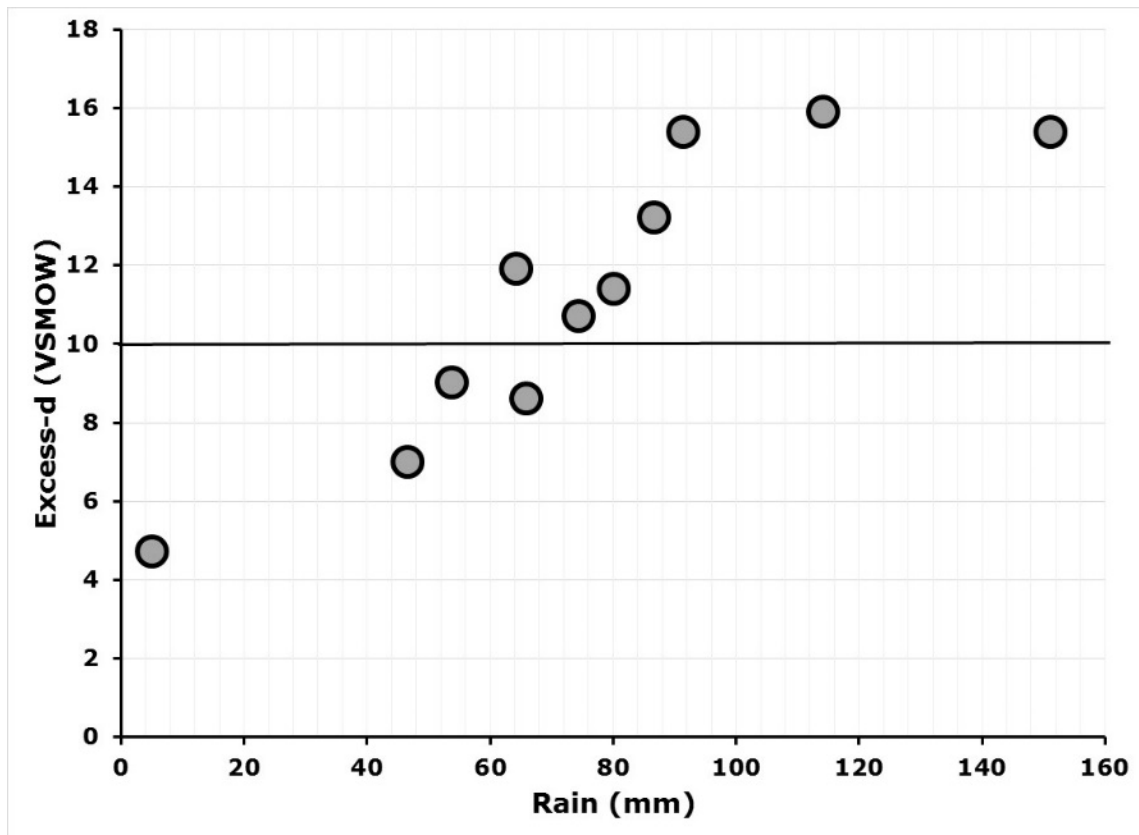


Figure 9. Relationship between the amount of rainfall and deuterium excess in the Sonora river basin (northwestern Mexico) in 2018 (Data obtained from Pérez-Quezadas *et al.*, 2021).

Rainy season

During this season, the northern trade winds that carry moisture from the Gulf of Mexico and the southern trade winds that carry moisture from the Pacific Ocean, converge in the tropic of Mexico, generating updrafts that produce abundant rainfall as the moisture condenses (Jáuregui-Ostos, 2003; Waliser & Jiang, 2014). This region is called the Intertropical Convergence Zone (Figure 10).

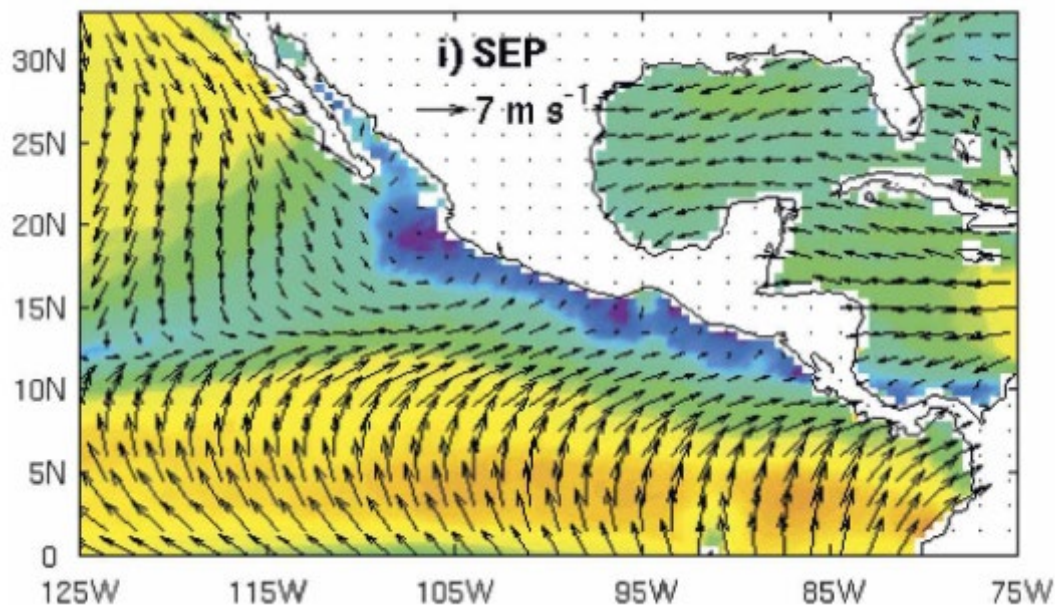


Figure 10. Low-level wind field (m/s) in September (Romero-Centeno, Zavala-Hidalgo, & Raga, 2007; ©American Meteorological Society. Used with permission).

The initial condensation of the marine moisture has values enriched in heavy isotopes (Araguás-Araguás, Froehlich, & Rozanski, 2000). As the marine moisture is transported towards the continent and produces rain, the values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ decrease due to the distillation of heavy isotopes (Rozanski, Araguás-Araguás, & Gonfiantini, 1993). This is known as the continental effect.

The heavy isotopes of rain decrease with altitude. As the vapor masses rise over the mountains, they cool down by adiabatic expansion, condensing and producing rains (Gonfiantini, Roche, Olivry, Fontes, & Zuppi, 2001). When the initial rain occurs, the water molecules containing heavy isotopes preferentially condense, depleting the remaining vapor in heavy isotopes. Consequently, the second rain will be more depleted than the first, and so on (Bony, Risi, & Vimeux, 2008). That is, as the vapor rises and produces rain, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values decrease due to the distillation of heavy isotopes (Scholl, Shanley, Zegarra, & Coplen, 2009; Scholl & Murphy, 2014). This is known as the altitude effect.

Lachniet and Patterson (2009) calculated for the northern region of Central America, the continental effect for $\delta^{18}\text{O}$ which is -0.69‰ per 100 km from the coast. The distance between the Valley of Querétaro and the Gulf of Mexico is ~ 350 kms, therefore the $\delta^{18}\text{O}$ decreases -2.2‰ .

Poage and Chamberlain (2001) calculated, based on a study that covered 68 mountain ranges around the world, the altitude factor for $\delta^{18}\text{O}$. This factor is -2.8‰ per 1 km. The altitude of the Querétaro Valley is 1.85 km, therefore the $\delta^{18}\text{O}$ decreases -5.2‰ .



The average value of $\delta^{18}\text{O}$ of the rainfall in the port of Veracruz is -4 ‰ (IAEA/WMO, 1998).

Adding the effect of altitude and continentality, and assuming that the isotopic content of the initial condensation of the marine vapor is similar to that of Veracruz, the value of $\delta^{18}\text{O} = -4 \text{ ‰} -2.2 \text{ ‰} -5.2 \text{ ‰} = -11.4 \text{ ‰}$. This is the $\delta^{18}\text{O}$ value of the rain at the base of the cloud, in the Querétaro Valley.

Mexico is located between the cyclogenetic regions of the western Atlantic and the northeastern Pacific (Gray, 1979), for which it receives abundant rains from the tropical cyclones that arrive to the country (Breña-Naranjo, Pedrozo-Acuña, Pozos-Estrada, Jiménez-López, & López-López, 2015). Pacific cyclones originate in the Gulf of Tehuantepec (Reyes & Mejía-Trejo, 1991), while those in the Atlantic originate in the Campeche Sound or the Eastern Caribbean. In these synoptic-scale systems, the vapor masses rise to a great height, condensing and producing rains that are highly depleted in heavy isotopes due to the effect of altitude. An example of this was Hurricane Bud and Tropical Storm Carlota, both of which caused heavy rains in the center of the country in June 2018 (SMN, 2018). González-Hita *et al.* (2021) reported for Hurricane Bud, values of $\delta^{18}\text{O} = -13.48$ and $\delta^2\text{H} = -97.8$.

Conclusions

This study presents the characterization of the isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$, Excess-d) of meteoric water that occurred in the Querétaro Valley from September 2017 to July 2021. With the isotopic data the graph of the correlation $\delta^{18}\text{O}$ - $\delta^2\text{H}$ was elaborated, and the Meteoric Water Line of the Valley of Querétaro (LAMVQ) was determined, $\delta^2\text{H} = 7.65 \delta^{18}\text{O} + 6.97$. The LAMVQ has a slope and intercept lower than those of the GMWL.

The data show that the slope and intercept of the correlation $\delta^{18}\text{O}$ - $\delta^2\text{H}$ of abundant precipitation ($>30\text{mm}$) are similar to those of the GMWL. Deuterium excess does not reveal secondary evaporation in these precipitations. On the other hand, the slope and intercept of the correlation $\delta^{18}\text{O}$ - $\delta^2\text{H}$ of light precipitation ($<30\text{mm}$) are lower than those of the GMWL. Excess deuterium shows secondary evaporation in these precipitations. It is concluded that the LAMVQ has a lower slope and intercept than the LMM, due to secondary evaporation of small precipitations. Based on these results, it is speculated that the Meteoric Water Lines of the semi-arid and arid regions of Mexico will be affected by secondary evaporation.

The Meteoric Water Line of the Queretaro Valley can serve as a very important tool to study the origin and dynamics of surface and groundwater. In the specific case of the Querétaro Valley aquifer, it can be useful to determine: 1) the recharge zones; 2) the origin of the nitrate



in the groundwater; 3) the relationship with the Los Apaseos Guanajuato aquifer, and 4) the impact of recharge wells.

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