Spatial and temporal variation in precipitation isotopes at 2 locations in southwest Spain

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ABSTRACT

The δ^2H and $\delta^{18}O$ composition of 77 precipitation samples collected between January 2014 and April 2019 from two sites across the Guadalquivir Basin, SW Spain, were analyzed. Sampling was performed within intervals of at least 14 days basis if rain occurred but frequently intervals were longer according to the rainfall incidence. Precipitation weighted averages and local meteoric water lines are presented for use in hydrological applications. δ^2H and $\delta^{18}O$ values show a remarkably high variability attributed to the influence of Atlantic and Mediterranean vapor sources. Precipitation weighted average d-excess values of 12.5-13 ‰ confirm the Western Mediterranean influence. Temperature and amount effects were found to be weak but significant influence of secondary evaporation for single rainfall events during summer was identified by reduced d-excess values and enriched isotopic signatures plotting close or below the Global Meteoric Water line (GMWL). Isotopic signatures of both sites are very similar in general and any temperature related urban effects of Seville city compared to the rural site Doñana could not be identified with the present data.

INTRODUCTION

Precipitation is an essential component of the global water cycle, constituting a crucial factor for wetlands, for irrigation as well as for industrial and domestic uses in arid and semi-arid regions. The study of the isotopic composition of stable isotopes as an environmental tracer in atmospheric precipitation is an efficient means to improve the current knowledge of the local and global water cycle (Dansgaard, 1964). δ^2H and δ18O values of modern precipitation are valuable tools for understanding regional climate dynamics and moisture sources and for tracking changes in atmospheric circulation on modern and quaternary time scales (Clark and Fritz, 1997).

The relationship between δ^2H and $\delta^{18}O$ in precipitation at a global scale, is called global meteoric water line (GMWL) (Craig, 1961) but due to the site specific regional scale processes it varies in space. Therefore, the understanding of the local water cycle benefits significantly from the determination the local meteoric water line (LMWL) specific to a study area which may show a clear deviation from the GMWL (Gammons et al., 2006; Simpkins, 1995).

The local isotopic signatures of precipitation are mainly controlled by regional scale processes, such as vapor origin and trajectory, rainout history and meteorological conditions such as humidity and temperature (Rozanski et al., 1982). The regional environmental background refers to the source of precipitation vapor. Local geographical factors represent the various climatic factors during precipitation, including rainfall, temperature, and relative humidity. Analysis of δ^2H and

$\delta^{18}O$ is mostly used in a local area, so the local geographical factors should be considered predominantly.

Among the local geographic factors, the temperature effect and the rainfall amount effect may constitute important control on the isotope signatures. The temperature effect consists in its positive correlation with stable isotopes contents in precipitation as a consequence of a higher energy level leading to the transfer of heavier isotopes into the vapor phase. The slope of the stable isotopes in precipitation versus temperature is important because it can be used to estimate paleo temperature changes and to validate the accuracy of Global Climate Model outputs (Ichiyanagi, 2009). Dansgaard (1964) showed a strong correlation between the annual mean $\delta^{18}O$ and temperature on a global scale, with an average change of 0.7‰/°C. Rozanski et al. (1992) showed that the long-term annual temperature effect averaged only in European stations was around 0.60‰/°C. When sampled on an event or daily basis, the correlation between precipitation isotopes and temperature from the mid-latitudes is weaker compared with monthly or annual timescales (Baldini et al., 2010). Seasonal variations are observed, where seasonal variations of temperature are well pronounced. A remarkably temperature effect has been discerned mainly in high and mid-high latitude continents (Dansgaard, 1964). In order to study the effect of temperature on precipitation, $\delta^{18}O$ is generally selected as an indicator due to its higher temperature sensitivity of the fractionation process as a consequence of the higher mass difference (Zhang and Wu, 2007).

The negative correlation of isotope content in precipitation with the rainfall is called the rainfall amount effect and is related to the fact that the content of heavy isotopes decreases with the progress of precipitation. Nonetheless, the amount of this change at a specific site is related to rainfall, temperature, relative humidity and other conditions which explains the large variability of isotope signatures of individual precipitation events and even during single precipitation events. A monthly amount effect has been observed in low-mid latitude oceans, islands, and monsoon areas (Dansgaard, 1964).

Also secondary evaporation below the clouds may play a significant role in affecting isotopic signatures and d-excess. The preferential evaporation of the light isotopes during the secondary evaporation process leads to heavy isotopes enrichment and d-excess decrease. Meng and Liu (2010) divided precipitation data according to different rainfall amounts. They analyzed the composition of isotopes in different precipitation ranges and concluded that rainfall is more affected by secondary evaporation when rainfall is low leading to lower d-excess values for low precipitation events. Cortecci et al. (2008) compared isotopic precipitation signatures of an urban and a rural site in Bologna (Italy). They showed that precipitation in the urban center of Bologna undergoes appreciable isotopic effects due to secondary evaporation during falling. As a consequence, the resulting $\delta^{2}H$-$\delta^{18}O$ meteoric line has a notably lower slope and $\delta^{2}H$-intercept different from that of precipitation in the peripheral non-urban area.

The study site is mainly influenced by the North Atlantic Oscillation (NAO), being the dominant mode of interannual atmospheric variability in the Northern Hemisphere, and a clear influence on the isotopic composition of rainfall was previously established (Baldini et al., 2008). For the nearby Mediterranean region, the Western Mediterranean Oscillation index, an index measuring the difference between the standardized atmospheric pressure recorded at Padua (45.40°N, 11.48°E) in northern Italy, and San Fernando, Cádiz (36.28∘N, 6.12∘W) in Southwestern Spain (Martin-Vide and Lopez-Bustins, 2006) has being explored as another source of variability. (Celle-Jeanton et al., 2001) established a relationship between the isotopic content of precipitation and the origins of air masses for the Western Mediterranean basin defined as the Western Mediterranean Waterline (WMWL) with d-excess of 14‰ which falls between the Atlantic (10‰) and the Eastern Mediterranean (22‰). Monthly weighted time series between 1985 and 1991 of Western Mediterranean data from Barcelona, Gibraltar, Tunis and Genoa revealed a much higher temporal variability for the Barcelona station which was attributed to almost equal influence of the Atlantic and the Mediterranean vapor origin whereas Genoa and Gibraltar are influenced mainly by only one vapor source, Mediterranean or Atlantic, respectively (Celle-Jeanton et al., 2001). A detailed analysis (Moreno et al., 2014) based on single event sampling between 2010 and 2012 in north-east Spain confirmed the high variability of $\delta^{18}O$ signatures compared to other Mediterranean locations documented by Celle-Jeanton and Travi (2001).

The Spanish network for isotopes in precipitation (Red Española de Vigilancia de Isótopos en la Precipitación, REVIP) provides composite monthly samples of precipitation collected since 2000 at 16 meteorological stations. The stations have a wide geographic distribution, and are located in the main hydrographical basins, in areas representative of the different climatic zones in Spain (Teijeiro et al., 2007). The nearest long term Global Network of Isotopes in Precipitation site is located in the village Morón de la Frontera, representing the only station of the Guadalquivir basin at a distance of about 130 km to the Atlantic Ocean. This study therefore adds useful information providing data directly measured at the coast line and in a mayor urban area.

This study reports time series of $\delta^{2}H$, $\delta^{18}O$ and deuterium excess (d-excess or d) in precipitation over a four to five-year period at two sites in southwestern Spain with at least biweekly intervals. A local meteoric water line and precipitation weighted average values are established which can be used for hydrological studies in the region or at a Mediterranean scale. Furthermore, the seasonal behavior of the isotopes as well as secondary evaporation effects are described and the importance of temperature and amount effects on the isotope composition as well as possible urban influence is investigated.

STUDY AREA

1.1. Geographical location

Stable isotopes of water were sampled at two sites located in the southwest of the Iberian Peninsula, in the Region of Andalusia (Fig. 1). Site 1 is in Seville city on the roof of the North Tower at Plaza de España, Latitude: 37° 22' 41'' N, Longitude: 5° 59' 17'' W and an altitude of about 31 m.a.s.l. Site 2 is located in a coastal dune of the Doñana National Park at the province of Huelva, at the Atlantic coast (rural area), Latitude: 37° 01' 19'' N, Longitude: 06° 33' 18'' W and an altitude of about 38 m.a.s.l.

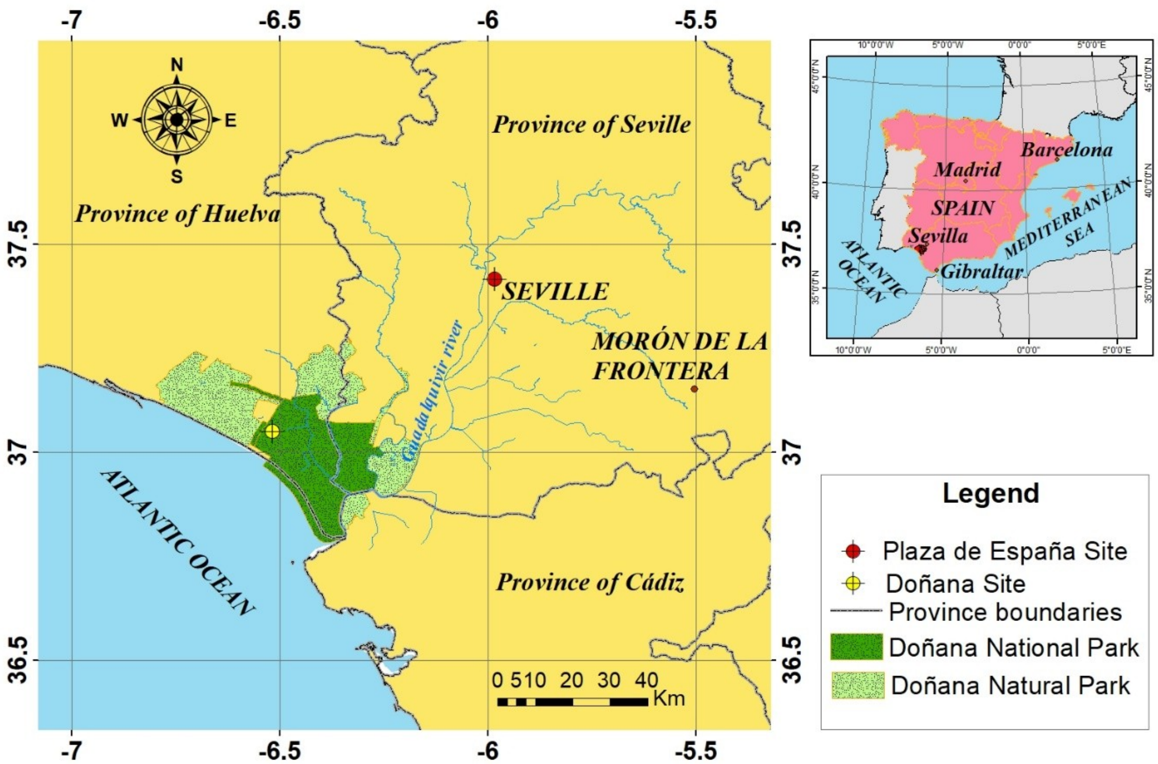

Figure 1. Study area.

1.2. Climate

The climate at the Doñana National Park is sub-humid Mediterranean, which is affected by the Atlantic influence, dry summers and humid winters (Custodio et al., 2009). In Doñana, the average rainfall, which occurs between October and March, is between 500 and 600 mm with a great interannual variability, between 250 and 1100 mm. The average annual air temperature is about 18 °C in the center of the National Park and there are around 3,000 hours of sunshine per year (Manzano et al., 2005).

Seville city has a Mediterranean climate, featuring very hot, dry summers and mild winters with moderate rainfall. The annual average temperature is 25.4°C during the day and 13°C at night (with an annual average of 19.2°C). Precipitation varies from 500 to 600 mm per year, with frequent torrential rain. December is the wettest month, with an average rainfall of nearly 100 mm. On average there are 50.5 days of rain (Kottek et al., 2006).

2. METHODS

2.1. Rainfall sampling and analyses.

Samples of rainwater for stable isotopes (δ^2H and $\delta^{18}O$) analysis at the two sites were collected in a 5-L polyethylene bottle between January 2014 and April 2019 in the Doñana National Park and in Seville city (Plaza de España). In total, 77 rainwater samples were collected with 40 rainwater samples from Plaza de España, from January 2014 to June 2018, and 37 rainwater samples in Doñana, from February 2016 to April 2019 (supplemental material). Sampling was performed within intervals of at least 14 days basis if rain occurred but frequently intervals were longer according to the rainfall incidence. In case of high intensity rainfall events leading to complete filling of the rainwater collector, sampling was performed after the respective event to avoid losing precipitation of subsequent events. Therefore, the individual samples represent averaged precipitation weighted results of cumulated rainfall for the period since the previous sampling date.

The samples were collected by attaching a funnel to a high-density polyethylene bottle (5L) containing paraffin oil to prevent evaporation and the respective accumulated sample volume was registered for each sampling event. Samples were collected without air bubbles in polyethylene bottles and conserved immediately at 4°C in the refrigerator until isotopic analysis in the laboratory. In both sampling sites, some rainwater samples were taken 2 times on the same day for double checking. In which the results showed similar isotope values, and, in this case, we used the average of both samples. Meteorological data were taken from nearby official meteorological stations, la Rinconada for the Plaza de España site and Almonte for the Doñana site.

The analyses of the stable isotopes ($\delta^{18}O$ and δ^2H) of water were carried out in the laboratory of the Center of Hydrogeology of the University of Malaga with a Laser spectroscopy system (Model L1102-i, PICARRO™). All data are refered to V-SMOW and expressed as delta per mil (‰).

Statistical parameters of the regression lines were calculated as follows:

Residual mean square: $$RMS = \frac{\sum_{i=1}^{N} (Y_i ¿ - \hat{Y})^2}{N-2} ¿ \quad (1)$$

where Y is the measured and $\hat{Y}$ the fitted value, Subscript i is the value enumerator and N is the number of measured Y values.

Coefficient of determination (R-squared): $$R^2 = \frac{\sum_{i=1}^{N} (Y_i ¿ - \hat{Y})^2}{\sum_{i=1}^{N} (Y_i ¿ - \hat{Y})^2 + \sum_{i=1}^{N} (Y_i ¿ - \overline{Y})^2 ¿ ¿} ¿$$

(2)

where $\overline{Y}$ is the average of all Y values.

Calculation of local meteoric water lines was based on data covering entire years ranging from February 2014-February 2018 for Plaza de España and February 2016- February 2019 for Doñana.

RESULTS AND DISCUSSION

$\delta^{18}O$, $\delta^{2}H$ and D-excess results

Precipitation weighted mean values and standard deviations of both sites are compiled in Table 1 and are in agreement with data of the nearby stations Morón de la Frontera and Gibraltar (Teijeiro et al., 2007). High d-excess values of 12.6-13 ‰ point to an important western Mediterranean influence beside the Atlantic vapor source.

Table 1. Precipitation weighted $\delta^{18}O$ and $\delta^{2}H$ mean values and standard deviations for the stations Doñana and Plaza de España.

Stations	$\delta^{18}O$ mean	$\delta^{18}O$ st. dev.	$\delta^{2}H$ mean	$\delta^{2}H$ st. dev.	d-excess
Doñana	-4.57 ‰	1.98	-23.89 ‰	14.18	13.0 ‰
Plaza de España	-5.20 ‰	1.96	-28.63 ‰	15.07	12.6 ‰

The standard deviations of Table 1 show a very high temporal variability which may be related to the influence of both, Atlantic and Mediterranean vapor sources origins. Nonetheless, these standard variations are not in agreement with (Celle-Jeanton et al., 2001) who report these high variabilities only for Barcelona, whereas the nearby Gibraltar station showed much less variability which was attributed to a domination of the Atlantic vapor source.

Time series plots of $\delta^{2}H$, $\delta^{18}O$, d-excess, temperature and precipitation for individual samples are shown in Figure 2. A seasonal fluctuation of $\delta^{2}H$, $\delta^{18}O$ behavior is evident with more depleted values in winter and isotope enrichment during the warm season. Large precipitation events are more likely to be seen between October and April and are almost absent in July and August. Isotope ratios of the warm season show the expected increase in comparison with winter values, but due to the lack of precipitation in July and August there is no clear peak. Since precipitation samples are covering at least 2 weeks, one sample normally represents several rain events which reduces the variability of isotopic signatures, typically observed between single events, due to their specific conditions defined by temperature, rain intensity or vapor source. Nonetheless, some samples, for example these ones indicated by circles in Figure 2, represent only one single rain event and therefore show a larger variability. D-excess values are anticorrelated with isotopic enrichment and decrease during the summer months, indicating evaporation effects due to higher temperatures and smaller precipitation amounts, which leads to reduced d-excess values (Meng and Liu, 2010).

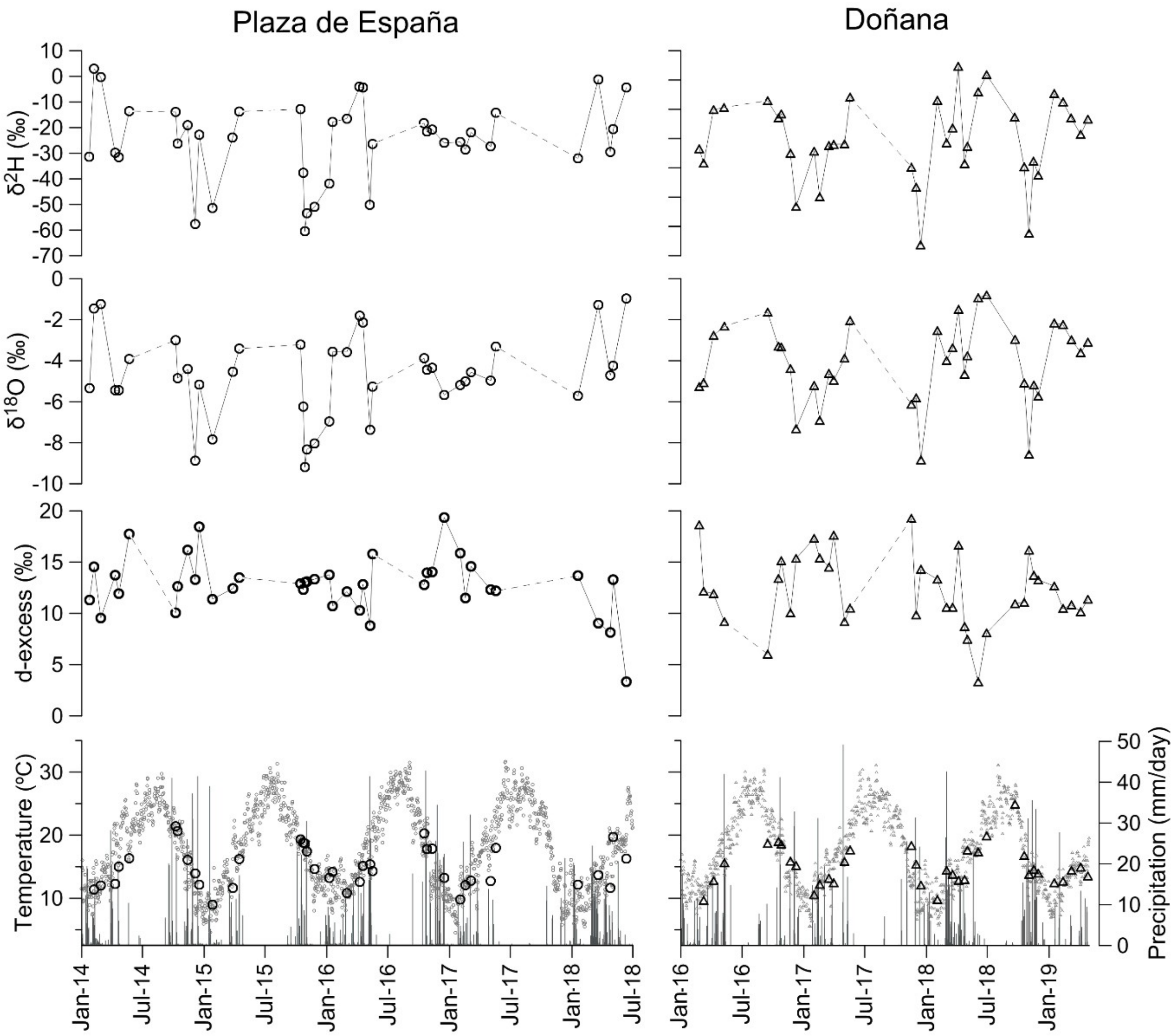

Fig. 2. Values of precipitation, temperature, δ^{18}O, δ^{2}H and d-excess in Plaza de España and Doñana considering all available data. Temperatures at the field sites represented by circles or triangles are averaged for the period since the previous sampling event and weighed by daily precipitation amounts. Precipitation (bars) and temperature (grey dots) were taken from the nearby official meteorological stations, la Rinconada for the Plaza de España site and Almonte for the Doñana site.

Local meteoric water lines (LMWLs)

A bivariate plot of δ^{18}O against δ^{2}H, and the relevant meteoric water lines are presented Figure 3. Most of the analyzed cumulated samples, but especially those of δ^{18}O signatures smaller than -4, plot on the WMMWL indicating d-excess which can be explained by higher degrees of Rayleigh distillation of moisture sourced from isotopically similar marine sources, typical for western Mediterranean semiarid climate conditions.

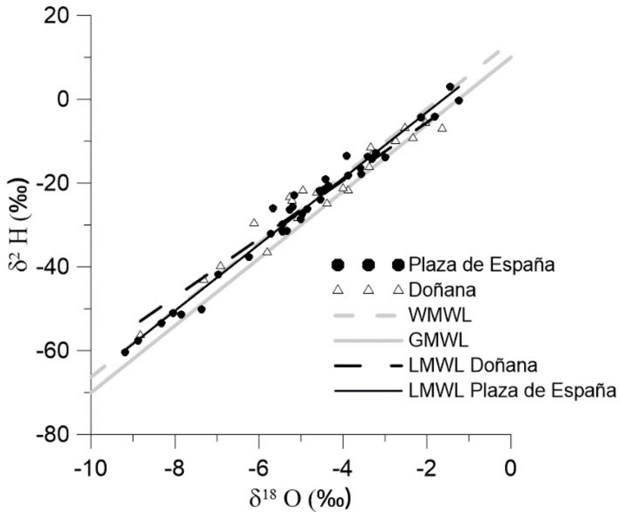

Figure 3. δ ²H versus δ ¹⁸O contents of precipitation. GMWL= Global meteoric water line, WMWL= Western Mediterranean Meteoric WaterLine, LMWL=Local Meteoric Water Lines at Plaza de España (data considered February 2014-February 2018) and Doñana (February 2016- February 2019).

The corresponding equations of the meteoric water lines shown in Figure 3 are compiled in Table 2.

Table 2. Equations of the meteoric water lines.

	Equation	R^2	N
LMWL Plaza de España	$\delta^2H = 7.6 * \delta^{18}O + 10.9$ ‰	0.97	36
LMWL Doñana	$\delta^2H = 7.0 * \delta^{18}O + 8.4$ ‰	0.95	21
GMWL	$\delta^2H = 8.0 * \delta^{18}O + 10.0$ ‰		
WMMWL	$\delta^2H = 8.0 * \delta^{18}O + 13.7$ ‰		

More enriched samples at both sites also plot more closely to or even below the GMWL which points to secondary evaporation at higher temperatures leading to slightly smaller slopes of the LMWL compared to the GMWL. The signatures of both sites are very similar in general. Small differences between the two LMWL with a minor slope at the Doñana site may point to a stronger influence of secondary evaporation at the Doñana site but exclude urban effects. However, due to non-identical sampling periods and times, the available data set does not allow robust conclusions here.

As illustrated above in Figure 2, the observed wide range of stable isotope compositions of rainwater in one hydrological year is attributed to seasonality. In general, most of the rainfall occurs in cold season between October and April but with high temporal variability regarding the distribution among these months. Figure 4 shows that the cold season leads to more depleted values at both sites. However, cumulative rainfall before 21st of March (winter) may have more enriched isotope signatures than before 21st of December (autumn), which may produce more depleted signatures in autumn than in winter depending on the monthly rainfall distribution during the years as can be observed in the Doñana site.

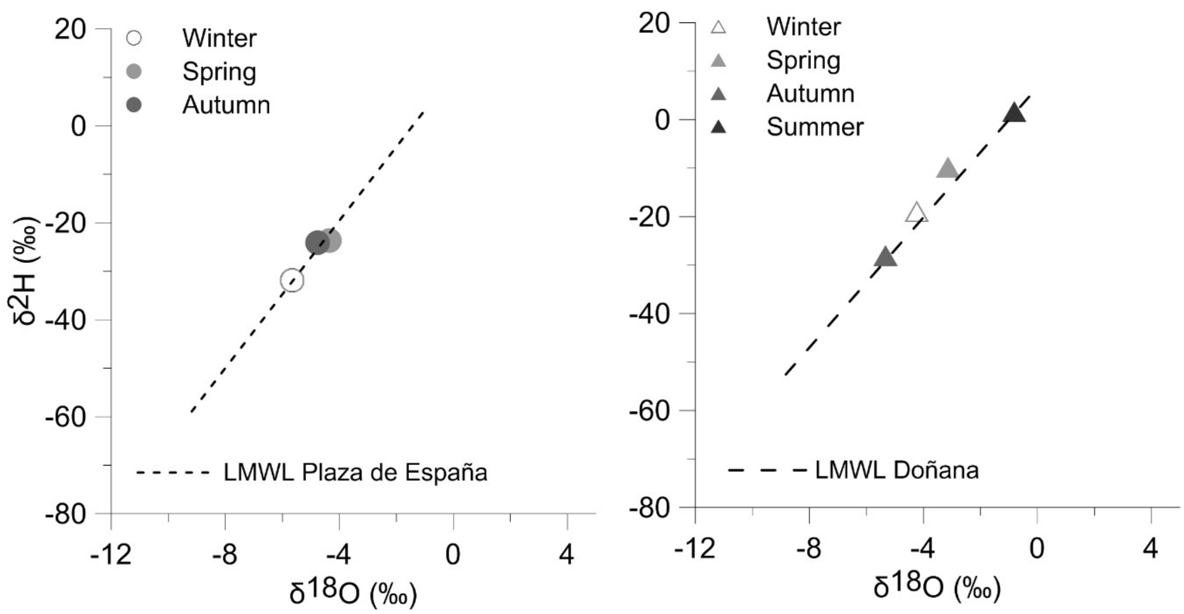

Figure 4. Precipitation weighted average of isotope signatures for different seasons at the two studies sites. No summer rain was collected at Plaza de España.

Effects of temperature on $\delta^{18}O$ and d-excess in precipitation

Figure 5 shows the relationship of $\delta^{18}O$ and d-excess values with temperature and sampled volume for the study period at both locations with the respective regression lines in Table 3. Results show that most rainfall events occur at temperatures below 20°C which is the "colder" season regarding local conditions. Figure 5a indicates weak positive correlations between $\delta^{18}O$ and temperature at both locations although with a large scattering which may be related to the influence of Atlantic and Mediterranean vapor source origin and is also visible in the standard deviations compiled in Table 1. Due to the practical absence of rainfall during the summer months, the major amount of rainfall occurs in a comparatively small range of temperatures at both sites which considerably reduces the importance of temperature compared to other local or regional effects such as vapor source variability. Considering the fact that the sites are located at low-mid latitudes and also close to the ocean which additionally dampens the annual temperature amplitude, the weak relationship is in agreement with general findings that remarkably positive correlation of the temperature effect were been identified mainly in high and mid-high latitude continents (Dansgaard, 1964). Nonetheless, the pronounced variability is not in agreement with Celle-Jeanton et al. (2001) who report this only for Barcelona, whereas the nearby Gibraltar station showed much less variability, which was attributed to a domination of the Atlantic vapor source.

Figure 5c shows a decrease of d-excess with high temperatures which is attributed to secondary evaporation and confirms results discussed above in Figure 2, although the correlation is weak. High temperature rain events above 20 °C show a remarkable decrease of d-excess.

Figures 5 b plots sample volumes versus δ^{18}O and show a weak negative correlation of more depleted values for higher sample volumes, which may be attributed to the rainfall amount effect leading to a decrease of heavy isotopes with the progress of precipitation. This concurs also with findings of Dansgaard (1964) that amount effects of precipitation are observed in low-mid latitude areas in proximity of the ocean. On the other hand, it may also reflect a temperature effect because higher rain intensity occurs more frequently during the colder season and correlates also negatively with temperature. Based on the fact that our samples represent cumulative rain events, sound conclusions cannot be drawn at this point and additional sampling of individual heavy rain fall events are necessary to clearly identify the amount effect. Figure 5d shows a weak positive correlation of sample volume with d-excess values which is attributed to secondary evaporation when rainfall is low and temperatures are higher and which is also in agreement with observations of other authors (Meng and Liu, 2010). The temperatures indicated by grey colors in Figures 5b and d do no show a clear dependence on the cumulative sample volume. In conclusion and in analogy to the discussion above, also here additional sampling of individual heavy rain fall events are necessary to clearly separate the amount effect from the temperature effect.

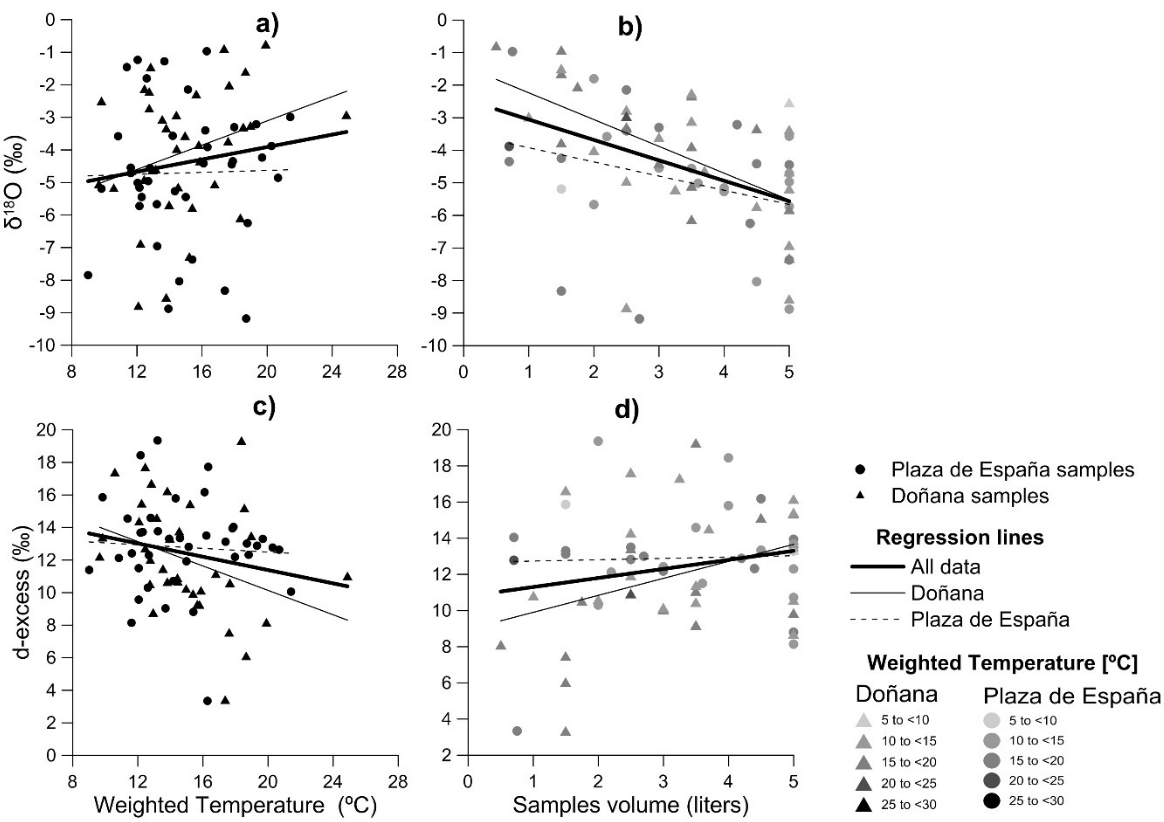

Figure 5. The relationship between δ^{18}O and d-excess with average temperature and sample volume. Rainfall between samples refers to the amount of rainfall registered at the nearby official meteorological stations ("Almonte" for the Doñana site and "La Rinconada" for the Plaza de España site) between two sampling events. Averaged temperature between two sampling events is weighed by daily precipitation amounts.

Table 3. Equations of regression analysis of the respective plots in Figure 5 with R^2 being the coefficient of determination, n the number of samples and **σ^2** the residual mean square.

Fig 5	All samples	R^2	n	σ^2
a	$\delta^{18}O$(‰)= 0.1*T - 5.82	0.02	74	4.20
b	$\delta^{18}O$(‰)= -0.63*V - 2.42	0.19	62	3.40
c	d-excess(‰)= -0.20*T + 15.48	0.02	74	9.72
d	d-excess(‰)= 0.5*V + 10.80	0.05	62	10.60
	Plaza de España	**R^2**	**n**	**σ^2**
a	$\delta^{18}O$(‰)= 0.01*T - 4.93	0.00	39	4.50
b	$\delta^{18}O$(‰)= -0.44*V - 3.49	0.11	29	3.69
c	d-excess(‰)= -0.06*T + 13.63	0.00	39	8.55
d	d-excess(‰)= 0.07*V + 12.66	0.00	29	9.36
	Doñana	**R^2**	**n**	**σ^2**
a	$\delta^{18}O$(‰)= 0.19*T - 6.39	0.09	35	3.72
b	$\delta^{18}O$(‰)= -0.82*V - 1.41	0.31	33	2.88
c	d-excess(‰)= -0.37*T + 17.64	0.12	35	10.75
d	d-excess(‰)= 0.94*V + 8.96	0.13	33	11.23

To identify potential local effects and spatial variation, the temporal evolution of $\delta^{18}O$ and d-excess of samples representing identical time periods of precipitation at both sites were compared (Figure 6). Results show very similar trends at both sites with exception of the sample of 03/05/2018 where intensive rainfall occurred at different dates at both sites representing different events. Therefore, local effects such as a possible urban influence with a different temperature regime were not identified by constantly more depleted d-excess values at the Plaza de España site.

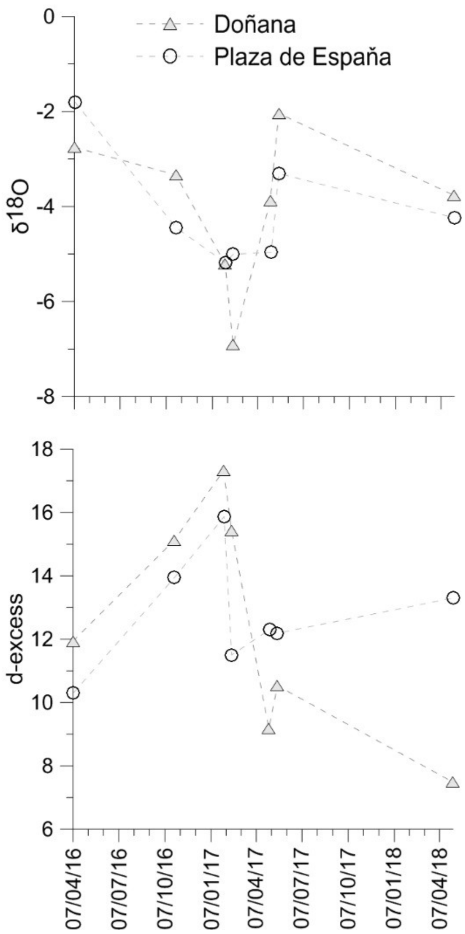

Figure 6. Isotopic variations $\delta^{18}O$ and d-excess at Plaza de España and Doñana sites in samples representing equal periods of rainfall.

Investigations on vapor sources using, the Lagrange Hysplit model were performed but did not lead to any sound conclusions and are therefore not presented here. The model outcome showed a very high sensitivity for the starting day of backward travel simulations and a precise definition of a starting date is not feasible for cumulative rainfall samples.

Conclusions

The study presents stable isotopic signatures of 77 cumulative rain water samples obtained between 2014 and 2019 at two sites in southwest Spain, collected with at least biweekly sampling intervals. Results show 2 additional Local Meteorical Water Lines (LMWL) representative for Southwest Spain which both concur with LMWL of Gibraltar and Morón de la Frontera.

Precipitation weighted average d-excess values of 12.5-13 ‰ point to an important influence of western Mediterranean semiarid vapor source beside the Atlantic influence.

δ^2H, $\delta^{18}O$ values show positive correlations between temperature at both locations although with a large scattering attributed to the variability of Atlantic and Mediterranean vapor source origin. A seasonal fluctuation of δ^2H, $\delta^{18}O$ behavior is evident with more depleted values in winter and isotope enrichment during the warm season.

Results show a trend of more depleted values for higher sample volumes, which may be attributed to the rainfall amount effect leading to a decrease of heavy isotopes with the progress of precipitation. On the other hand, it may also reflect a temperature effect because higher rain intensity occurs more frequently during the colder season and correlates also negatively with temperature.

Evaporation effects of single rainfall events during summer were identified by reduced d-excess values and enriched isotopic signatures below the GMWL.

The signatures of both sites are very similar in general and any temperature related urban effects of Seville City compared to the rural site Doñana could not be identified with the present data.

Acknowledgments

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