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The Local Meteoric Water Line in the Pampean Plain of Córdoba, Argentina

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Abstract: *Stable isotopes are very useful to trace groundwater from their recharge origin as precipitation. This is due to the conservation of the meteoric signal during its subsurface flow. Thus, is very important to have a local meteoric line (LML) in every world region to more accurately adjust the interpretations of hydrological relationships and processes like recharge areas, evaporation, water mixtures and probable isotopic exchanges with rocks and sediments. The objective of this work is to analyze the isotopic composition of precipitations in the dry sub-humid sector of the Pampa plain of Córdoba, its connection with the meteorological conditions and the temporal variations to improve the comprehension of the input function to the regional hydrological systems. The isotopic values were evaluated and the arithmetic and weighted averages were calculated. The local meteoric line was defined using a least square regression. Precipitation in the South of Cordoba province is characterized by average values of* $\delta^{18}O$ *and* $\delta^{2}H$ *of -4.7 ‰ and -23.5 ‰. The obtained local meteoric line is represented by the equation* $\delta^{2}H = 8.3\ \delta^{18}O + 15.2$ *‰ considered representative of the sub-humid-dry sector of the Pampean plain. From September to April, in which the most important precipitations and the highest temperatures occur, is where the most enriched precipitation falls and with the highest deuterium excess values. From May to August, the period in which the lowest precipitation amounts and the lowest temperatures are recorded, the precipitation is more isotopically impoverished showing the lowest "d" values. The observed variations in "d" reveal different origins of the air masses that originate the precipitations, mainly recycled steam linked to the jet stream in low layers, and also the influence during some months of the ENSO phenomenon and the ITZC variation. For the hydrological studies in the Pampean plain of the province of Cordoba, this local meteoric line is a very important basis to compare with the isotope composition of the different hydrological systems for the understanding of the recharge areas, water mixtures, the hydrodynamic and even chemical relationships in the different hydrological environments.*

Keywords*: chemistry, isotopes, precipitation, Pampean plain.*

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I. Introduction

When a hydrogeological model is needed, a detailed analysis of precipitations is important since they are, in general, the main water source of rivers and aquifers. Variations in the chemistry and stable isotope composition of precipitations depend on many factors including seasonality, moisture source, precipitation amount and meteorological conditions during evaporation, condensation and precipitation[1,2,3]. As was stated by Clark (2015) the use of stable isotopes to trace groundwater from their recharge origin as precipitation is based on a conservation of the meteoric signal throughout its subsurface flow. In this way one can distinguish recharge at different elevations, different seasons or different climates.

Isotopic measurements in precipitations allowed the construction of a global meteorological line (GML) to which the diverse hydrological processes that act in surface and groundwater can be associated (Global Network for Isotopes in Precipitation-GNIP)[4,5]. Although the GML is very useful, it is better to have a local meteoric line (LML) in every world region to more accurately adjust the interpretations of hydrological relationships and processes like recharge areas, evaporation, water mixtures and probable isotopic exchanges with rocks and sediments (figure 1). These aspects may allow us to understand the hydrological systems behavior and became a basis to evaluate their sustainable management.

Taking into account that precipitations must be monitored in isotope studies, Argentina has a National Collector Network of stable isotopes in precipitations. The different stations were coordinated since 1978 by the Institute of Geochronology and Isotopic Geology (INGEIS) and for the last 3 years by the Coastal Geology

Center of the National University of Mar del Plata. Several of these stations are part of the global network (Global Network for Isotopes in Precipitation-GNIP)[6,4,5].

In the province of Córdoba (Argentina), the Research Hydrogeology Group (Geology Department of the National University of Río Cuarto) has strategically located three precipitation collectors (figure 2): a) Canals Station: 33°33'44.56" S, 62°53'6.23" W, it is located 126 meters above sea level (m.a.s.l) in the occidental humid plain of the province and it operates since 2012. b) Río Cuarto Station: 33°7'4 " S, 64°19'46" W, 434 m.a.s.l. It is considered the most representative station since it is located in the dry sub-humid plain, the largest in the province. Also, it covers the longest time operation period (2006-2019). c) Alpa Corral station: 32°41'25.32" S, 64°43'20.66" W, 823 m.a.s.l. It is located in the Comechingones Mountains and has been operating since 2014. In all these stations the precipitation samples are being collected monthly for stable isotope analysis to have information along a transect in the south of the province to investigate possible changes in isotope precipitation values. In this paper only the information of Rio Cuarto station is showed. In the province of Córdoba, surface water and especially groundwater are important supply sources for all urban and rural activities[7,8]. It is known that precipitations are the main source of water supply to surface water and groundwater systems. Therefore, knowing the temporal changes in precipitation isotopic signature is essential to establish recharge areas, evaporation processes and water mixtures. This information will be important to establish the basic guidelines for water sustainable use.

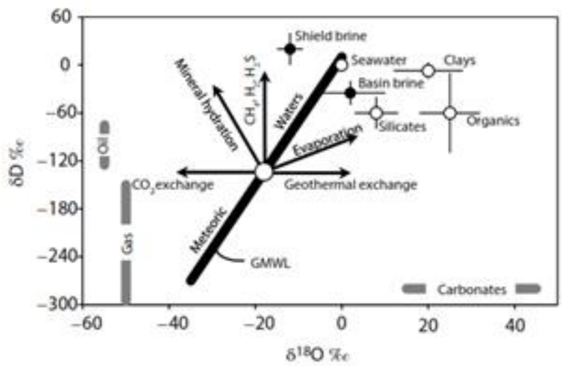

Figure 1. $\delta^{18}O$ and $\delta^{2}H$ ranges for major crustal reservoirs and different exchange mechanisms for the modification of the isotopic composition of meteoric waters (Source: Clark, 2015).

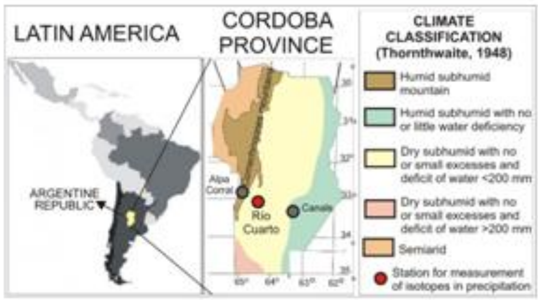

Figure 2. Location of stations for measurement of isotope in precipitations stations.

Objective

The objective of the work is to analyze the isotopic composition of precipitations in the dry sub-humid sector of the Pampa plain of Córdoba province and its connection with the meteorological conditions (precipitation and temperature) and the temporal variations to improve the comprehension of the input function to the regional surface water and groundwater systems.

Study Area

Geologic and climatic characteristics: The study area is located in the Pampean plain, one of the greatest plains worldwide, in the South of Cordoba province. The area exhibits a smoothly undulated relief and it is characterized by outcropping sedimentary formations of Quaternary age. Two large environments may be distinguished: fluvio-aeolian and fluvial. The first one presents a pattern whose most outstanding features are constituted by very fine silty sand dunes (loessical deposits) from the Upper Holocene superimposed on fluvial deposits. The second is linked to the Quaternary activity of the Rio Cuarto River, determining fluvial geoforms associated with different hydrodynamic stages (different levels of terraces, meandering paleochannels, channel bars, spills, among others) where coarser sediments domain.

In the studied area there is a climatic variability[9] and therefore different possibilities of water supply to rivers, lakes and aquifers[10,11].The Argentine climate is governed by four action centers, permanent or semi-permanent, two high pressure (the Atlantic and Pacific anticyclones) and two low pressure (the cyclones of the northwest and the southern depressions). Due to the latitude in which the province of Córdoba is located it has a temperate climate with Mediterranean characteristics. The climatic variations in the province occur depending on the relief changes, the air masses origin and local meteorological processes. According to Capitanelli (1979) the temperature (T) regime is characterized by a rigorous winter (with T <10ºC, between June and August) and a moderately warm "thermal summer" (with T> 20ºC, between October-November and March-April), with major frosts from May to September. The average temperature in the region is 16.5ºC (max. = 25ºC and min. = 10ºC).

The exceptions correspond to higher altitudes in mountains. Precipitations in the plain come mainly from the Atlantic anticyclone, 70% corresponding to frontal processes, that is, with the intervention of more than one air mass[9]. Of the total annual rainfall, 82% is concentrated in spring-summer.

In the plain, the climate varies (figure 2) from humid-subhumid to subhumid-dry. The former is characterized by a mean anual precipitation (MAP) in the order of 950-850 mm and null to small water deficiency. The latter shows a MAP between 850 and 600 mm, with nulls to small water excesses and water deficit in general less than 200 mm in the central sector, to slightly greater than 200 mm in the south west of the province. This climatic features explain the influence of the warm and humid air from the Atlantic Ocean. To this general behaviour it can be added some changes generated by the action of El Niño-Southern Oscillation (ENSO), the South Atlantic Convergence Zone (ZCAS), the Jet Stream in Low Layers (LLJ), the Mesosystems, Circulation of the Oestes, among many others[12]. The mountains and the piedmont show greater rainfall variability due to the combination of geomorphological factors like altitude and exposure[9,13].

II. Material And Methods

Daily records of precipitations and temperatures are available from the Climatological Station of the Faculty of Agronomy and Veterinary (UNRC) which is located in the same city where monthly precipitation samples are being collected. The monthly integrated precipitation water samples were collected in PET bottles of 100 mL and sent to the laboratory. The isotopic analysis (δ^2H and δ^{18}O) were made until 2014 in the INGEIS Stable Isotope Laboratory by mass spectrometry (IRMS) and laser spectroscopy. From 2014 to the present the measurements are being made by laser spectroscopy (Los Gatos Research inc. (OA-ICOS: Off-Axis Integrated Cavity Output Spectroscopy) in the Laboratory of Stable Isotopes of the National University of Mar del Plata (UNMdP) which maintains cross-checks of analytical quality with IAEA (International Atomic Energy Agency). The results are expressed as isotopic deviations (δ), in ‰ according to the equation: $\delta = 1000\ (Rs - Rp) / Rp$ being R the isotopic ratio (^{2}H/^{1}H, ^{18}O/^{16}O) of the international reference (Rp) and of the water sample (Rs). The reference used is Vienna Standard Mean Ocean Water (V-SMOW)[14] which has the value $\delta_{V\text{-}SMOW} = 0$ ‰. The uncertainties for δ^{18}O, in both laboratories, are ± 0.2 ‰ by IRMS and ± 0.3 ‰ by laser spectroscopy. Uncertainties are ± 0.2 ‰ and ± 0.3 ‰ for δ^{18}O by IRMS and laser spectroscopy. The uncertainty for δ^2H is ± 1.0 ‰. The isotopic values were evaluated and the arithmetic and weighted averages were calculated[15]. The weighted averages were calculated based on the precipitation amount fallen in the sampling month and in each calendar year individually. Prior to these calculations, a careful evaluation of the data was carried out, which consisted of the purification of the anomalous values[15] evidenced by inconsistencies in ^{18}O, ^{2}H and excess deuterium ("d") values, which may be linked to sampling contingencies or very scarce rainfall volumes. The smaller precipitation amounts are more likely to have a lower d-excess due to re-evaporation of raindrops below the cloud-base or biases in the sampling method[16]. For example, the samples corresponding to June and July 2006 and August 2007 were discarded because the precipitation amount was very low (few mm). The differences between the arithmetic mean and the weighted average are generally not significant in stations with uniform rainfall distribution; however, weighted averages are more appropriate as input functions when studying hydrological systems, since they eliminate the afore mentioned effects[15]. The local meteoric line was defined using a least square regression which gives equal weighting to all data points regardless of the precipitation amount they represent. Two methods have been used to determine the LML: the ordinary least squares regression (OLSR) and the reduced major axis (RMA) regression, sometimes incorrectly called the orthogonal regression[17]. RMA regression is considered more representative of the isotope precipitation variations in an area since it takes into account the uncertainty of the independent and dependent variables, while the OLSR only considers the uncertainty in the independent variable. In the study of precipitation processes, the relationship between δ^2H and δ^{18}O is properly described by OLSR or RMA, which fully considers variability in d excess. However, when the LML is used to interpret groundwater or surface water data, the use of these regressions can introduce some undesired effects. This is because small precipitation amounts, which may have undergone enrichment by evaporation processes and are not so relevant for aquifer or river supply, have the same influence on the LML slope. While the use of weighted or monthly average values slightly reduces this effect, it does not eliminate it. As a consequence, when analyzing precipitation data, some authors choose to exclude small rain events or low value d excesses to reduce its effect on the line. Other authors generate new formulas that eliminate these biases[17]. Finally, a statistical analysis was carried out to obtain the main statistics parameters of precipitation, temperatures and isotope values, using the SPSS software (v.11). The June 2006-February 2019 period was selected to analyze and compare temporal variations of meteorological and isotopic information in Rio Cuarto station.

III. Result And Discussion

For the 2006-2019 temperature series of Rio Cuarto city, the average annual temperature (AAT) is 16.5°C, with a minimum of 15.4°C registered in 2007 and a maximum of 17.5°C (in 2018). The temporal variation in precipitations (figure 3) shows an alternation of humid and dry cycles, with an average annual precipitation of 755 mm. The years 2006, 2007, 2008, 2012, 2015 and 2016 stand out as the most humid with an annual precipitation greater than 800 mm. The driest were the years 2009, 2010, 2013 and 2018, with values lower than 610 mm. The period of highest precipitations is spring summer. Then, the climate is characterized by a marked seasonality (figure 4), with a warmer and more humid period that extends from September to April (spring-summer) and a cooler and drier season from May to August (autumn-winter).

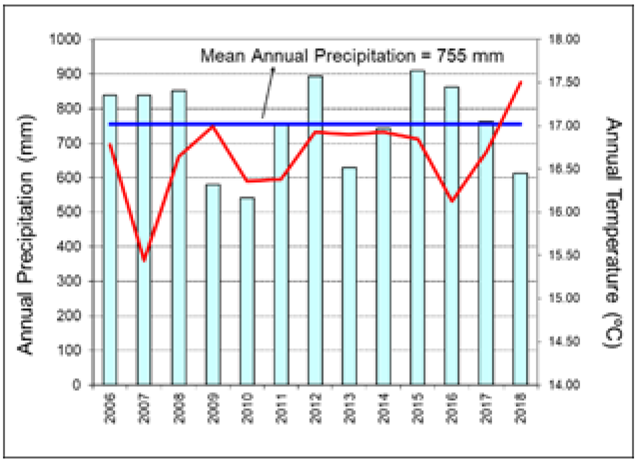

Figure 3. Annual chronological precipitation line.

In this region, more than 80% of the days are windy, with a maximum wind concentration at the end of winter and spring. Winds from the north-northeast, south and southeast prevail, with average speeds that exceed 10 km/h in the majority of months with blasts of more than 100 km/h. The annual average potential evapotranspiration is 827 mm, which determines a deficit soil water balance (~ 40 mm). The monthly water balance shows water excesses up to 75 mm between April and May and between October-November, especially during the more humid years (2006-2008, 2012 and 2015-2016). It should be noted that from these total water excesses a percentage of them will supply the surface runoff and the rest will recharge the aquifers[10].

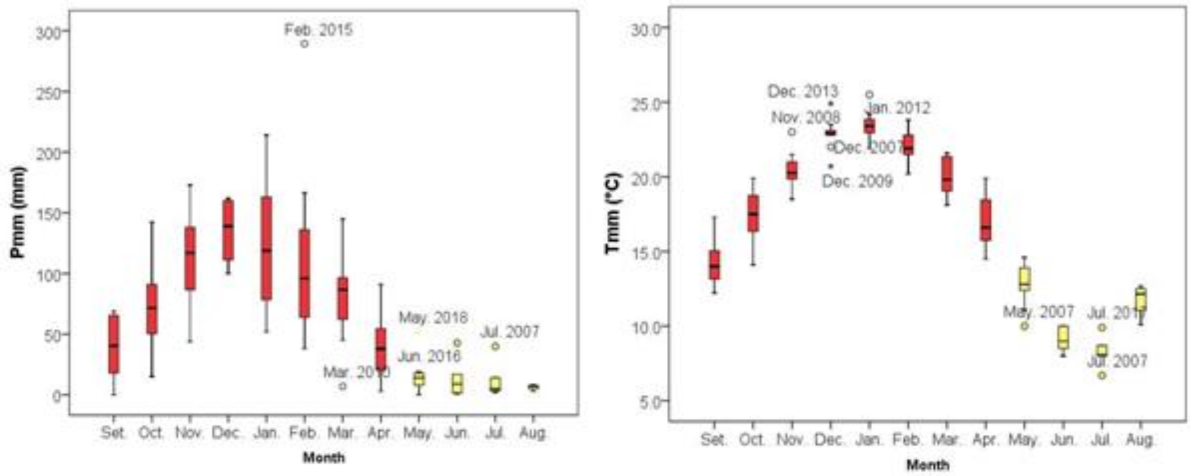

Figure 4. Monthly distribution of precipitations and temperatures Rio Cuarto city series 2006-2018.

Variability of the isotope composition in precipitations

The arithmetic average of $\delta^{18}O$ and $\delta^{2}H$ in precipitations for the analyzed period (2001-2019) results in the order of -4.9 ‰ and -25.4 ‰, respectively, similar to the weighted average ($\delta^{18}O$ = -4.7 ‰; $\delta^{2}H$ = -23.5 ‰). The most enriched precipitation appears between August and January, being the Spring the season with the most positive values, with maximum values in October (+ 3.00 ‰ in $\delta^{18}O$ and +24.7 ‰ in $\delta^{2}H$, figure 5 and tables 1 and 2). On the other hand, the most negative isotope values were recorded from February to July, being July (full winter) the month where the most impoverished precipitation occurs with minimum of up to -11.4 ‰ for $\delta^{18}O$ and up to -84.0 ‰ for $\delta^{2}H$ (figure 5 and tables 1 and 2). In this way, a typical "seasonal effect"[1] taking place in this region would explain the differences between seasons. However, as can be seen, the most positive isotope values do not coincide with the warmest and most rainy months. This displacement would be explained by the "amount effect"[1] that impoverishes the summer rainfalls taking into account that in this season the highest and most intense rainfalls occur. It should be clarified that in order to sustain the "amount effect", it is necessary to have isotopic measurements in a daily way so as to be able to distinguish variations associated with high intensity storms produced by convective events.

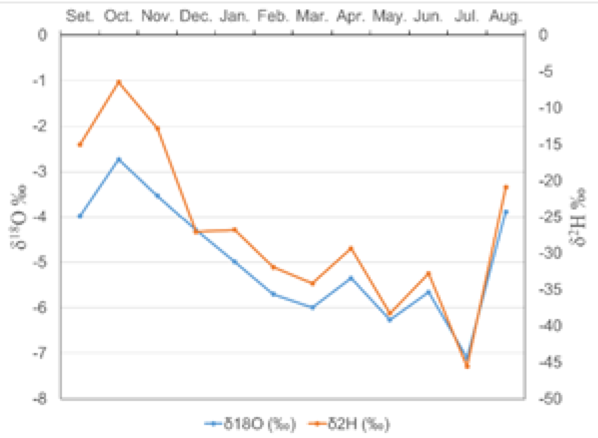

Figure 5. Annual variations in $\delta^{18}O$ and $\delta^{2}H$

The isotopic composition of the 114 precipitation samples recollected during the period 2006-2019 is shown in the conventional diagram $\delta^{2}H$ vs. $\delta^{18}O$ (figure 6). It can be observed that precipitation isotope values are aligned on a straight with a specific slope and y-interception that defines the local meteoric line. The LML was defined by means of the ordinary linear regression (OLSR: $\delta^{2}H = 8.0\ \delta^{18}O + 13.7$ ‰) and by means of the reduced major axis regression (RMA: $\delta^{2}H = 8.3\ \delta^{18}O + 15.2$ ‰), resulting both lines very similar and slightly displaced in relation to the GML.

Table no 1. Statistics of the monthly distributions of $\delta^{18}O$ (‰)

month	N	Min.	Max.	Mean	Standard deviation
Set.	9	-6.40	-2.20	-3.98	1.48
Oct.	11	-5.80	3.00	-2.73	2.70
Nov.	13	-6.10	-0.90	-3.53	1.85
Dec.	10	-7.10	-0.77	-4.29	2.00
Jan.	12	-6.90	-2.00	-4.99	1.41
Feb.	12	-9.60	-4.00	-5.70	1.61
Mar.	8	-8.70	-3.50	-5.99	2.09
Apr.	12	-10.20	0.00	-5.35	2.73
May.	10	-10.90	-3.00	-6.26	2.40
Jun.	5	-7.80	-2.50	-5.66	2.36
Jul.	4	-11.40	-4.60	-7.10	3.07
Aug.	4	-7.00	0.20	-3.88	3.07

Table no 2. Statistics of the monthly distributions of $\delta^{2}H$ (‰)

month	N	Min.	Max.	Mean	Standard deviation
Set.	9	-39.90	0.00	-15.04	12.89
Oct.	11	-30.00	24.70	-6.43	16.86
Nov.	13	-33.30	7.70	-12.79	13.73
Dec.	10	-47.00	-0.60	-27.06	14.49
Jan.	12	-42.50	-3.50	-26.79	10.73
Feb.	12	-62.00	-15.00	-31.92	12.49
Mar.	8	-54.60	-14.10	-34.13	15.62
Apr.	12	-65.10	0.00	-29.34	19.52
May.	10	-78.00	-16.00	-38.27	21.58
Jun.	5	-50.10	-7.60	-32.80	17.91
Jul.	4	-84.00	-24.30	-45.58	27.36
Aug.	4	-47.40	8.00	-20.90	23.20

Taking into account the total precipitation samples significant variations in excess deuterium ("d") values were identified, which would indicate different air masses origin and especially in the moisture content. 82.5% of the treated samples have "d" values greater than 10 ‰, which would indicate that precipitation is originated from recycled steam from air masses with moisture contents below 85%. The 14.0% of the samples have "d" values less than 10 ‰, that is, they could be originated from air masses with humidity higher than 85%, indicating kinetic fractionation processes. Only 3.5% have "d" values equal to 10 ‰, which would indicate evaporation processes in the air mass. The high percentage of rainfall with "d"> 10 ‰ gives a typical signature to the precipitations, which then is reflected in the groundwater isotopic signature of the south of the Cordoba plain[13]. Temporal variations over a calendar year show in general that the largest "d" values appear between September and April while the minor "d" values appear between May and August (table 3 and figure 7), indicating different air masses origins, mainly recycled steam linked to the jet stream in low layers (Low Level Jet), as well as the ENSO phenomenon and the variation of the ITZC[18].

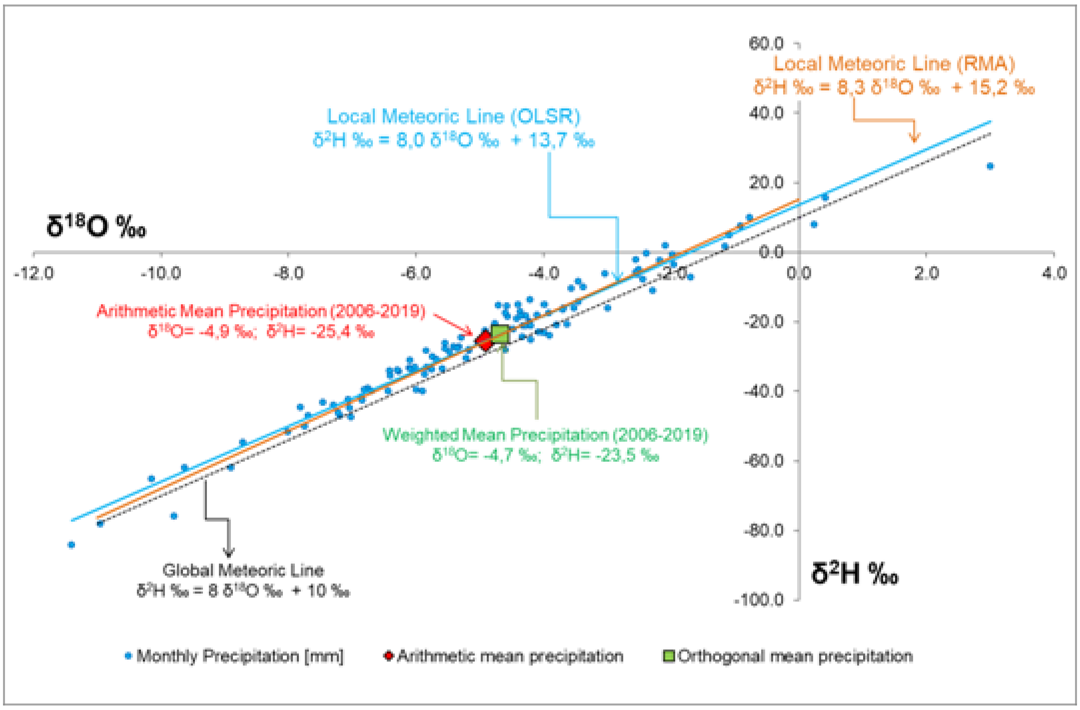

Figure 6. δ^2H *vs.* $\delta^{18}O$.

Table no 3. Statist of the excess deuterium (d) of precipitation discriminated by month

month	N	Min.	Max.	Mean	Standard deviation
Set.	9	11.50	20.10	16.79	2.73
Oct.	11	0.70	22.60	15.28	6.60
Nov.	12	11.20	18.80	15.55	2.20
Dec.	9	7.20	16.60	12.56	3.48
Jan.	11	8.80	16.10	12.69	2.28
Feb.	11	8.60	17.10	13.19	2.88
Mar.	8	7.60	18.00	13.88	3.08
Apr.	12	0.00	17.90	13.44	5.21
May.	10	2.60	16.90	11.83	4.58
Jun.	5	9.80	14.00	12.22	1.61
Jul.	4	7.00	13.60	11.23	2.93
Aug.	4	6.10	13.20	10.08	3.25

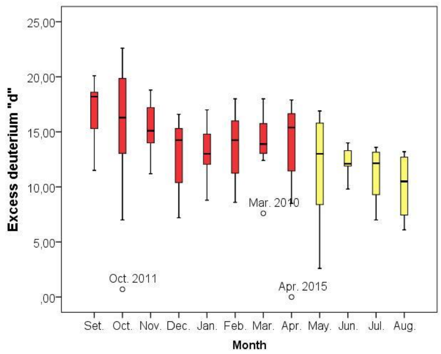

Figure 7. Annual variations in excess deuterium

IV. Conclusion

Precipitation in the south of Córdoba province is characterized by a distinctive isotopic composition with average values of $\delta^{18}O$ and δ^2H of -4.7 ‰ and -23.5 ‰. The obtained local meteoric line is represented by the equation $\delta^2H = 8.3\ \delta^{18}O + 15.2$ ‰ considered representative of the sub-humid-dry sector of the Pampean plain, so it can be extrapolated to a large area in the province of Córdoba that does not has isotope precipitation information.

From the isotope point of view a seasonal effect was observed. The period from September to April, in which the most important precipitations and the highest temperatures occur, is where the most isotope enriched precipitation occurs ($\delta^{18}O$ of up to + 3.00 ‰ and δ^2H of up to +24.7 ‰) and with the highest deuterium excess values. From May to August, the period in which the lowest precipitation amounts and the lowest temperatures were recorded, the precipitation is more isotopically impoverished (up to -11.4 ‰ for $\delta^{18}O$ and up to -84.0 ‰ for δ^2H) showing the lowest "d" values.

The observed variations in deuterium excess reveal different origins of the air masses that originate the precipitations, mainly recycled steam linked to the jet stream in low layers (82.5% of the rainfall with "d" values less than 10 ‰) and also the influence during some months of the ENSO phenomenon and the ITZC variation.

For the hydrological studies in the Pampean plain of the province of Córdoba, this local meteoric line is a very important basis to compare with the isotope composition of the different hydrological systems for the understanding of the recharge areas, water mixtures, the hydrodynamic and even chemical relationships in the different hydrological environments.

Acknowledgments

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