JOURNAL OF
ENVIRONMENTAL HYDROLOGY

The Electronic Journal of the International Association for Environmental Hydrology
On the World Wide Web at http://www.hydroweb.com

VOLUME 19 2011

ISOTOPIC COMPOSITION OF RAINWATER IN THE SUBTROPICAL ISLAND OF TENERIFE, CANARY ISLANDS

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The results of the most extensive study of stable isotope composition carried out on single precipitation events in a weather station located in La Laguna, Tenerife, Canary Islands are presented. During the year 2007 to 2009, individual precipitation samples have been collected and analyzed for the composition of $\delta^{18}O$ and $\delta^{2}H$, within the Global Network of Isotopes in Precipitation (GNIP) project. The data display a wide range of values, from -9.3‰ to -1.4‰ for $\delta^{18}O$ and from 6.8‰ to -57.8‰ for δD. The weighted-mean values of all the data are -4.34‰ for $\delta^{18}O$ and -18.9‰ for δD. On the basis of 42 precipitation event samples, the local meteoric water line (LMWL) was established as $\delta^{2}H= 7.6\cdot\delta^{18}O+13.7$, which coincides with previous work in this region. Precipitation amount effect was investigated, finding a good correlation with mean precipitation intensity (MPI), calculated as the ratio between total precipitation and the total days of event duration. No significant relation between rainfall $\delta^{18}O$ and $\delta^{2}H$ and surface temperature has been found, according to subtropical island environment. However, the base and the top cloud temperatures, calculated from local atmospheric soundings, show a better correlation due to the fact that the cloud temperature is more likely a better representation of the actual temperature of the precipitation. Finally, the source and pathway of water vapor was analyzed using five-day isentropic back-trajectories. The preliminary results suggest that the $\delta^{18}O$ lower values are associated with events derived from the east and after a Sahara invasion event, or with long path trajectories from northwest. The higher values are relative to events derived from the northwest and with short pathways.

INTRODUCTION

Stable isotopes ratios of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) of atmospheric precipitation are an important tool for hydrological, climatological and meteorological applications (IAEA, 1981; Rozanski et al., 1993). Hydrological studies on a regional scale, give important information on the mean recharge elevation, quantification of water resources for their effective management, water–rock interactions, transit time, etc. Isotope hydrology can provide such information because the spatial and temporal variations in the isotopic composition of precipitation are due to isotopic fractionation occurring during the evaporation of seawater and condensation during the advection of water vapour (Dansgaard, 1964). Therefore, the isotope composition of local precipitation is primarily controlled by regional scale processes: it is greatly influenced by the provenance of wet air masses, the trajectories of the water vapour transport over the continents, their possible partial condensation in continental areas (Merlivat and Jouzel, 1979) and in general the average rain-out history of the air masses (Rozanski et al., 1982).

The isotopic composition of hydrogen and oxygen in the water is expressed in δ notation, where

$$\partial_{sample} = \left[\frac{R_{sample} - R_{VSMOW}}{R_{VSMOW}}\right] x1000$$

with R as the ratio of the heavy to the light isotope ($^{18}O/^{16}O$ or D/H) in the sampled water (R_{sample}) or in the Vienna Standard Mean Ocean Water, V-SMOW (R_{VSMOW}).

In precipitation, these quantities follow the so-called meteoric line equation

$$\partial^{2}H = 8\partial^{18}O + d$$

The parameter d, termed "deuterium excess" (d-excess) (Dansgaard, 1964), depends among others, on the location. The worldwide mean of d-excess was first reported by Craig (1961) to be 10‰. The d value in precipitation reflects the evaporation condition where the moisture comes from (Jouzel et al. 1982; Armengaud et al. 1998). Under dry climate condition, the kinetic fractionation will be intensified during evaporation, and d in the following precipitation will be high. Under humid climate condition, the kinetic fractionation in evaporation will be much diminished, resulting in low d in the following precipitation (Merlivat and Jouzel 1979).

Numerous studies have identified relationship between precipitation isotopes and temperature (Craig, 1961; Dansgaard, 1964), amount of precipitation (Dansgaard, 1964), altitude (Poage and Chamberlain, 2001; Gonfiantini et al., 2001), latitude (Dansgaard, 1964; Fricke and O'neil, 1999) and history of the air mass and/or the source of the rainfall (Lawrence et al., 1982; Zhongfang et al., 2008). For these reasons the isotopic hydrology can contribute to reveal the mechanisms that are being altered as consequence of the climate change. According to the information of the Intergovernmental Group of Experts on the Climate change (IPCC, 2007), the subtropical region on Canary Islands is a very sensitive zone to climate changes, which turns it into an ideal emplacement for the study of such changes. In addition, in spite of being a slightly studied region (with regard to others) from the meteorological point of view, it is a zone with a crucial importance to understand dynamics and thermodynamic atmospheric, for its coincidence in latitude with the descending branch Hadley's cell, that originates a thermal vertical typical structure from the surface up to the tropopause, the islands turn into an emplacement favored for the study of the atmosphere from different perspectives.

Prior to this work, modern rainwater isotope data has been scarce for Canary Island. However it can be found some hydrogeology studies performed in this archipelago showing the variance of oxygen ($\delta^{18}O$) and hydrogen (d^2H) from precipitation and groundwater sources. These studies have been made by Gonfiantini, 1973; Gonfiantini et al., 1976; Custodio et al., 1987; Gasparini et al., 1987,1990; Veeger, 1991; Herrera and Custodio, 2000; Herrera, 2001; Custodio and Manzano, 2000; Muñoz, 2005. The first meteoric water line in Tenerife was established in 1973 by Gonfiantini, who made use of a limited set of groundwater samples. The obtained line was: $\delta^2H = 6{,}57 \cdot \delta^{18}O + 6{,}75$. Later, with new obtained data, Custodio calculated and represented a new line adopting a slope of 8. That way, the additive term will be deuterium excess. The meteoric line was: $\delta^2H = 8 \cdot \delta^{18}O + 15$. The average value for the deuterium excess obtained in 2008 by Custodio and Jiménez-Martínez is +14‰. Deuterium excess values observed in the Islands may be due to the proximity of the African continent, which results in a dryer atmosphere in the Archipelago. The variance of the altitude gradient was -0,22‰/100m and -0,19‰/100m for $\delta^{18}O$ and δ^2H, respectively (Gonfiantini, 1973) in Tenerife Island. In Gran Canaria, Gonfiantini (1976) calculated $\delta^{18}O$=-0,13‰/100m and δ^2H=-1‰/100m for the North of the island. The studies performed in the South shown -0,25‰/100m and -1,2‰/100m for $\delta^{18}O$ and δ^2H. In Fuerteventura Island, values for $\delta^{18}O$ - 0,27 to -0,32 ‰/100m have been found (Herrera, 2001).

The objectives of the present study are (1) to provide an isotope database of precipitation in Tenerife in order to assist in hydrologic and atmospheric research for this region; (2) to document the seasonal and spatial variability in the stable isotopic composition of the precipitation in semi-tropical coastal region where temperatures changes are minimal; (3) to analyses isotopic variation of precipitation with different source region of vapour as well as to different trajectories of precipitating air masses.

EXPERIMENTAL SECTION

Study area

The Canary Islands, which are located west of North Africa (Figure 1a), are under the direct influence of the trade wind belt, making the climate very stable all year. Usually, the Azores high acts as a shield, preventing Atlantic lows from affecting the area south of 30ºN. In autumn and winter, when the anticyclone is at its weakest, low-pressure systems occasionally reach the Canaries. In spring, the anticyclone begins to strengthen, and in summer it reaches the maximum strength stage and latitudinal position, reinforcing the intensity of the trade winds (Font, 1956). Owing to the quasi-permanent subsidence conditions over the Canary Islands, an inversion layer remains below 2000 m.a.s.l. (meters above the sea level) throughout the year, resulting in a strongly stratified low troposphere. Moreover the islands are surrounded by a cold current named the Canaries Current, coming from the north as a derivation of the Gulf Stream. The average trade winds blow mainly against the north side of the islands, advecting wet and fresh air, which can rise over the island slopes, often leading to condensation and cloud growth that is usually obstructed by the typical vertical stratification structure. Rainy events only happen when disturbances break the inversion layer, either at surface (Atlantic lows) or at upper levels (troughs). Most of the typical rainfall situations cannot be detected at surface level, and are only evident when upper levels are analyzed. Island-averaged precipitation regimes similarly show a strong seasonality with maximum monthly rainfall between 30 and 100 mm during autumn and winter and relatively dry or even rainless months from April-May to September (García Herrera et al., 2001). Relief is the main

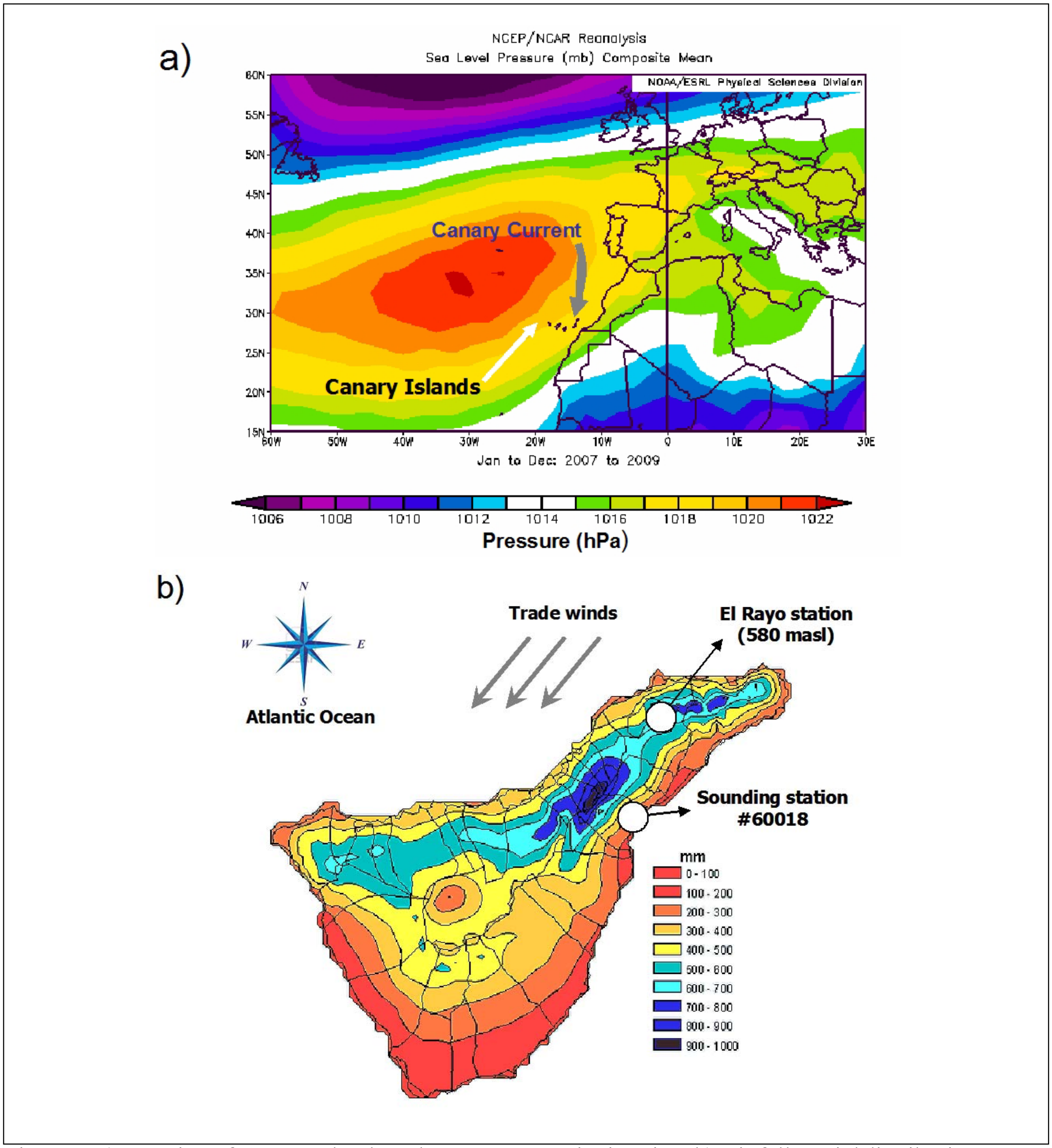

Figure 1. a) Location of Canary Islands and average synoptic situation; b) rainfall spatial distribution at Tenerife island (mm/year) according to CIATFE (Consejo Insular de Aguas de Tenerife) and location of sampling site and sounding station.

factor that affects the local rainfall distribution, as can be seen in the distribution of precipitation for Tenerife Island (Figure 1b). In general, precipitation increases across the archipelago from east to west.

The measurements station is located in the Aguere Valley (El Rayo, 28.5ºN, 16ºW) 580 m.a.s.l. in the NE of Tenerife (Figure 1b). This valley is a natural pathway of the oceanic air that blows north-to-south along the gap between the 'Mercedes' and 'Esperanza' mounts. Aguere station is close to La Laguna (city) and directly exposed to the NW airflow predominant in the valley (trade winds channelled from the ocean). Its relative humidity is very high during all year and the precipitation is very scarce or inexistent during the summer months.

The radiosonde data are obtained from Sounding Station #60018 (Güimar: 28.321ºN, 16.381ºW, 105 m.a.s.l.) 20 km away from El Rayo station (Figure 1b). Radiosonde are launched twice a day at 0000 UTC and 1200 UTC by the Territorial Meteorology Centre of Western Canaries belonging to the AEMET (Agencia Estatal de Meteorología) in Tenerife, using the Vaisala ‘‘DigiCORA Unmanned Sounding System AUTOSONDE’’ with a RS80 sonde-probe-sounding.

Sample collection

Monthly stable isotopes data are the most commonly available and the most of the studies about its contribution in meteorological, climatological and hydrological subject have been carried out on this time basis. However, event-base data, due to their temporal resolution, allow a better investigation of specific aspects, such as local relationships with temperature, precipitation amount, source region and vapour transport pathways, etc. Forty two event-based precipitation samples were collected between 2007 and 2009. Cases with precipitation below 2 mm were not taken into consideration, as isotope compositions in too small samples are modified by evaporation in raindrops during precipitation. Events being able to be registered of one or more days, using collection devices built according to an IAEA design to minimize re-evaporation and consequent sample enrichment. These samples are sent later to the laboratory of isotopic hydrology of the International Atomic Energy Agency (IAEA) in Vienna, where the stable isotope analysis are currently being performed using their normal methods and procedures. The results of isotope composition are expressed as per mille deviations from the internationally accepted V-SMOW standard (Gonfiantini, 1978). The mean weighted $\delta^{18}O$ and $\delta^{2}H$ composition of rainfall was determined according to Yurtsever (Yurtsever et al., 1981) by the following equation:

$$R_{MW} = \sum_{i=1}^{n} P_i \partial X_i / \sum_{i=1}^{n} P_i \tag{1}$$

where P_i is the precipitation events, n is the number of events and δX_i refers to either $\delta^{18}O$ or $\delta^{2}H$ composition of the precipitation events.

RESULTS AND DISCUSSION

Local Meteoric Water Line (LMWL)

The collected precipitation events samples of El Rayo ranges from -9.3‰ to -1.4‰ for $\delta^{18}O$ and from 6.8‰ to -57.8‰ for δD. Mean isotope values of El Rayo precipitation are -3.55‰ and -13.1‰ for $\delta^{18}O$ and δD respectively. The weighted-mean values of all the data, calculated according to equation (1), are -4.34‰ for $\delta^{18}O$ and -18.9‰ for δD. The most ^{18}O-depleted value ($\delta^{18}O$=-9.29 and δD=-57.85) corresponds to rain collected when the precipitation occur after a Saharan invasion event.

The best fit line of the δD and $\delta^{18}O$ content of precipitation is named meteoric water line. Craig (1961) after a global survey of stable isotope contents in precipitation proposed a Global Meteoric Water Line (GMWL), which was later modified by Rozanski et al. (1993) and expressed as:

$$\delta D(‰) = 8.17\delta^{18}O(‰) + 10.35 \text{ (n=206, } r^2\text{=0.98, significant at 0.05 level)} \tag{2}$$

The regression line equation for El Rayo data, which represent the Local Meteoric Water Line (LMWL, Figure 2), is

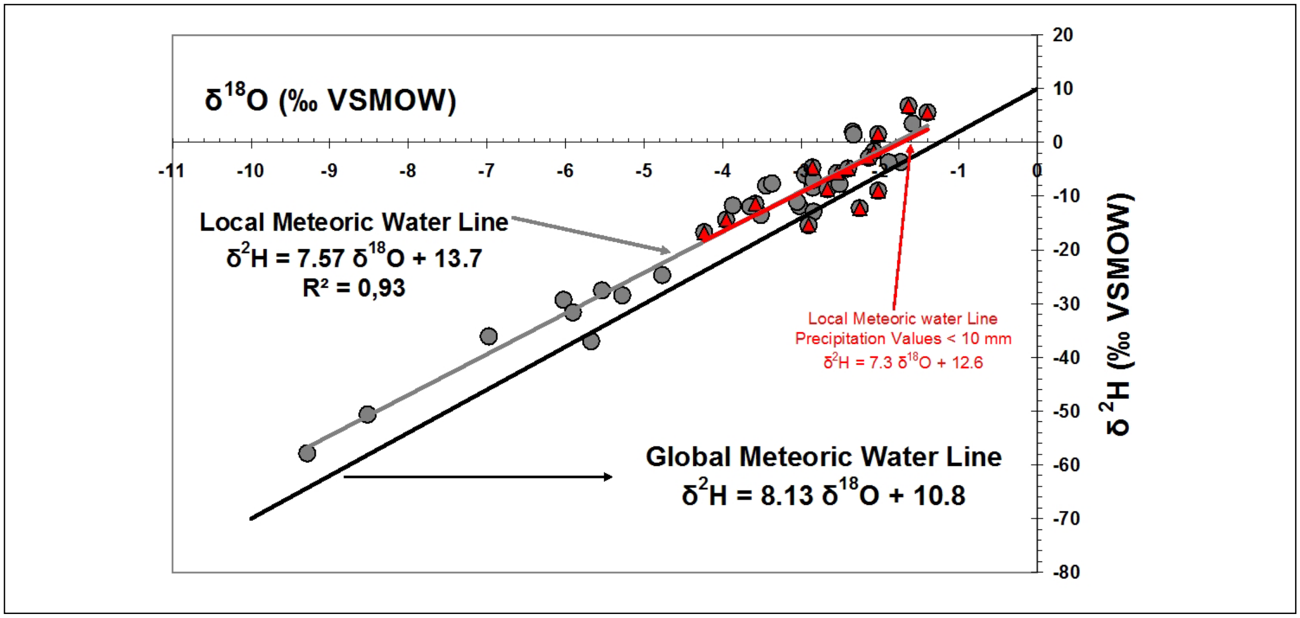

Figure 2. Scatter plot of äD and ä^{18}O values of event precipitation collected in La Laguna. The local meteoric water line is based on a linear regression of 42 groups of isotopic data and the global meteoric water line is that of Rozanski et al. (1993). In red color it is represented a scatter plot and regression line for event with precipitation amount less than 11 mm (12 group of isotopic data).

$$\delta D(‰) = 7.57 \cdot \delta^{18}O(‰) + 13.7 \quad (n=42;\ r^2=0.93) \tag{3}$$

Deviations of slope and interception (deuterium excess parameter defined as the difference δD - 8xδ^{18}O) of the equation from GMWL (Craig, 1961) reflected the specific regional atmospheric circulation patterns, regional water vapor sources and evaporation modes. The LMWL obtained from El Rayo station shows deviations from a GMWL and it is very close to obtained from Mediterranean region with Atlantic-derived precipitation (Araguás-Araguás et al., 2005; Diaz-Teijeiro et al., 2009) indicating the significance of the North Atlantic as a moisture source for Canary Island precipitation. Also, it must be taken into consideration the largest kinetic evaporation effect in the relatively dry marine environment in the Saharan belt, which is the same effect to explain the greater deuterium excess observed in rainfall originated in the Mediterranean area (Herrera et al., 2003).

The slope slightly lower than 8 (7.6) can be attributed to varying conditions in the source areas for the vapour and/or enhanced evaporation of raindrops in a relatively dry atmosphere below the cloud base (Araguás et al., 2000). On the other hand, the evaporation during sample collection can affected the isotopic composition and changes the slope of LMWL to low values. Most of these are associated with very small precipitation volumes for which evaporation in the sampler or storage bottle was more likely. In order to investigate this point, data with precipitation amount less than 10mm has been represented (red line in Figure 2). The LMWL found with this 15 pair of isotopic data do not show significant differences, indicating that the event samples with low amount of precipitation were not subject to evaporation during sample collection.

The deuterium excess values show an increase of 3‰ with respect to GMWL and vary by as much as 15‰. The weighted-mean value for deuterium excess is 14.7‰. This value is very similar to some data reported from other investigation in Canary Islands and that attribute to the environmental dryness in spite of treating itself about the Atlantic Ocean (Custodio et al., 1987; Marrero et al., 2007; Jiménez-Martínez et al., 2008; Díaz-Teijeiro, 2009).

Amount Effect and Humidity

The apparent correlation between the amount of monthly precipitation and its isotopic composition was first observed by Dansgaard (Dansgaard, 1964) and named the "amount effect". The amount effect has been attributed to a number of factors: 1) the isotopic value of the condensate in a cloud decreases as cooling and ''rainout'' proceeds; 2) smaller raindrops equilibrate to a larger degree with the water vapor and temperature conditions below the cloud; and 3) small raindrops evaporate more than larger raindrops on their way to the land surface. Figure 3a illustrates this relationship for El Rayo data. The regression lines in this figure mean that $\delta^{18}O$-values change by -3.96‰ and δD-values by -28.6‰ per 100 mm of rainfall. It also can be seen that the isotopic composition for high amount of precipitation shows much larger scatter than that for low amount of precipitation. Some studies carried out in eastern Canary Islands (Fuerteventura and Gran Canaria) on the isotopic content of meteoric waters (Gasparini et al., 1990, Herrera, 2001) found out that on having increased the quantity of rainfall, the isotopic variation of $\delta^{18}O$ is stabilized near to -4 ‰ values. Considering that the precipitation patterns in eastern Canary Islands are characterized for event of very scarce precipitation, it can be seen similar results in Figure 3 than those obtained with events with low precipitation amount (red squares; precipitation <11mm).

Rozanski (Rozanski et al., 1993) offered additional explanations for the amount effect, including the higher rain intensity and greater extent of rainout in convective clouds and different water vapor isotopic compositions due to different source regions. The inverse relationship between precipitation $\delta^{18}O$ (δD) values and precipitation intensity (PI) have been investigated by several authors (Miyake et al., 1968; Yapp, 1982). The mean intensity precipitation (MIP) for each precipitation event was calculated, dividing the isotopic composition between the total days of event duration. The representing versus $\delta^{18}O$ (δD) values can see in Figure 3b. In this case it was found a more marked correlation, with linear correlation coefficients relatively high. Although there is a good correlation between the $\delta^{18}O$ (δD) in precipitation and the MPI, such a result do not imply that the MPI is a main and direct control factor of impacting the variation of the isotopic composition in precipitation, because $\delta^{18}O$ (δD) in precipitation and the MPI in atmosphere change together under the same circulation background and are governed by some similar geographical and meteorological factors.

Related to the amount effect and with atmospheric humidity condition, some investigators have looked correlation between the $\delta^{18}O$ (δD) in precipitation and total precipitable water (PW) (Zhang et al., 2010; Yoshimura et al., 2010). Precipitable water in atmosphere is defined as the height of liquid-water column transformed by all vapor in a vertical air column. The value of PW stands for the total vapor in atmosphere and reflects the humid condition in whole atmosphere. In the Figure 3c it is represented the correlations between $\delta^{18}O$ and δD with PW, calculated from atmospheric sounding at Tenerife station. In this case it can be seen that there is a similar correlation that with precipitation amount, with very similar linear correlation coefficients.

Correlation with the temperature

The stable water isotopes in precipitation have long been known to correlate with temperature, as a result of temperature-dependent distillation processes in the atmosphere (Craig, 1961; Dansgaard, 1964). This correlativity was most significant in the interior of continent. However, at the moist tropical island stations where the vapour source region essentially coincides with the region of precipitation, the isotopic content of precipitation correlates poorly with temperature,

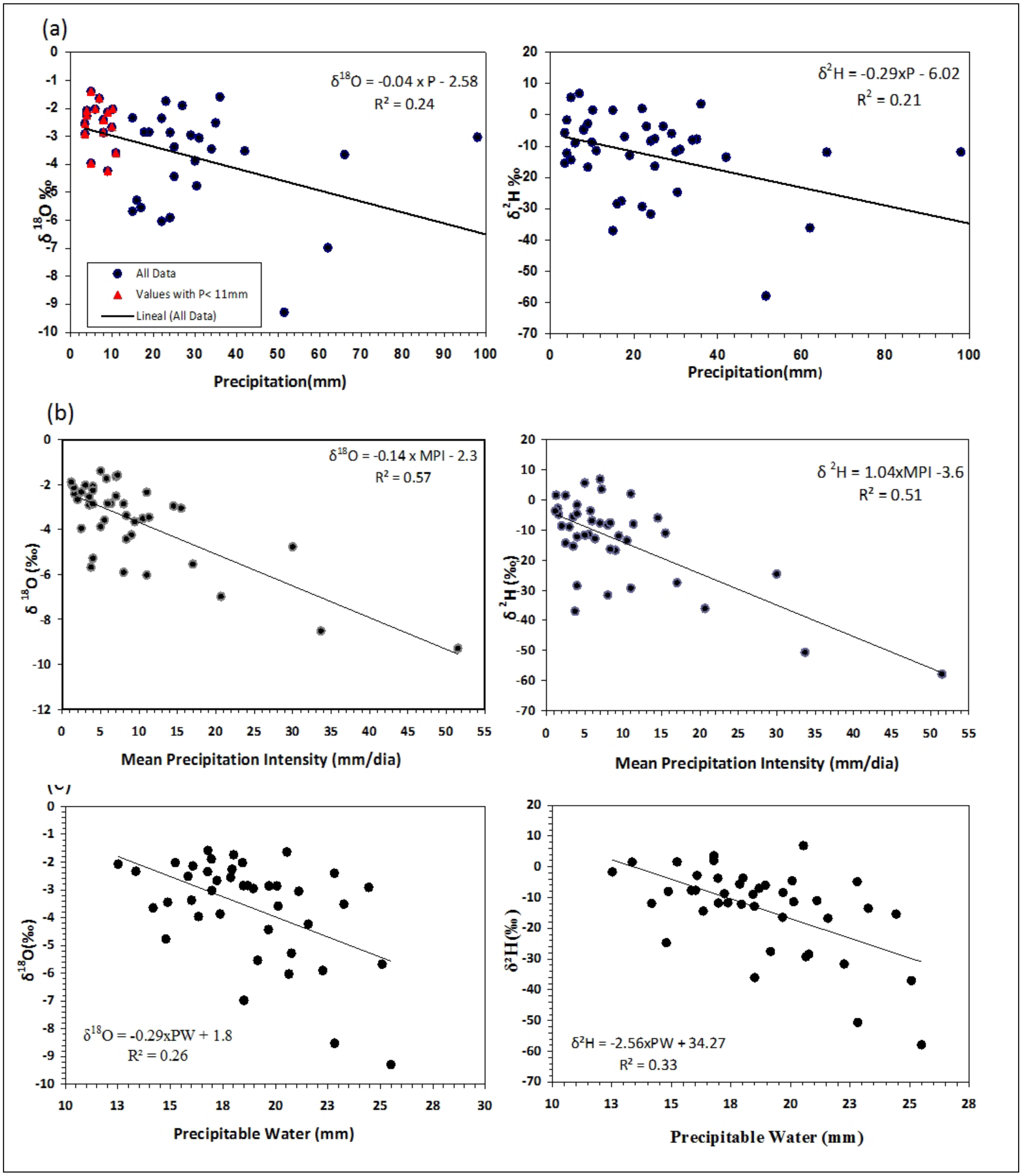

Figure 3. Scatter plot for $\delta^{18}O$ and $\delta^{2}H$ amount effect relationship. (a) dependence of the isotopic content with the rainfall amount; (b) correlation with the Mean Precipitation Intensity (MPI); (c) correlation with Total Precipitable Water (TPW).

being important the correlation with the amount of precipitation. The sharp transition from temperature to precipitation controlled isotopic content occurs at 30° N/S (Bowen, 2008). As corresponding to a subtropical island, the data showed a lack of a clear correlation with surface temperature (Figure 4a), showing high variability in the short range of temperature in which all rainfall events occurs in Canary Island.

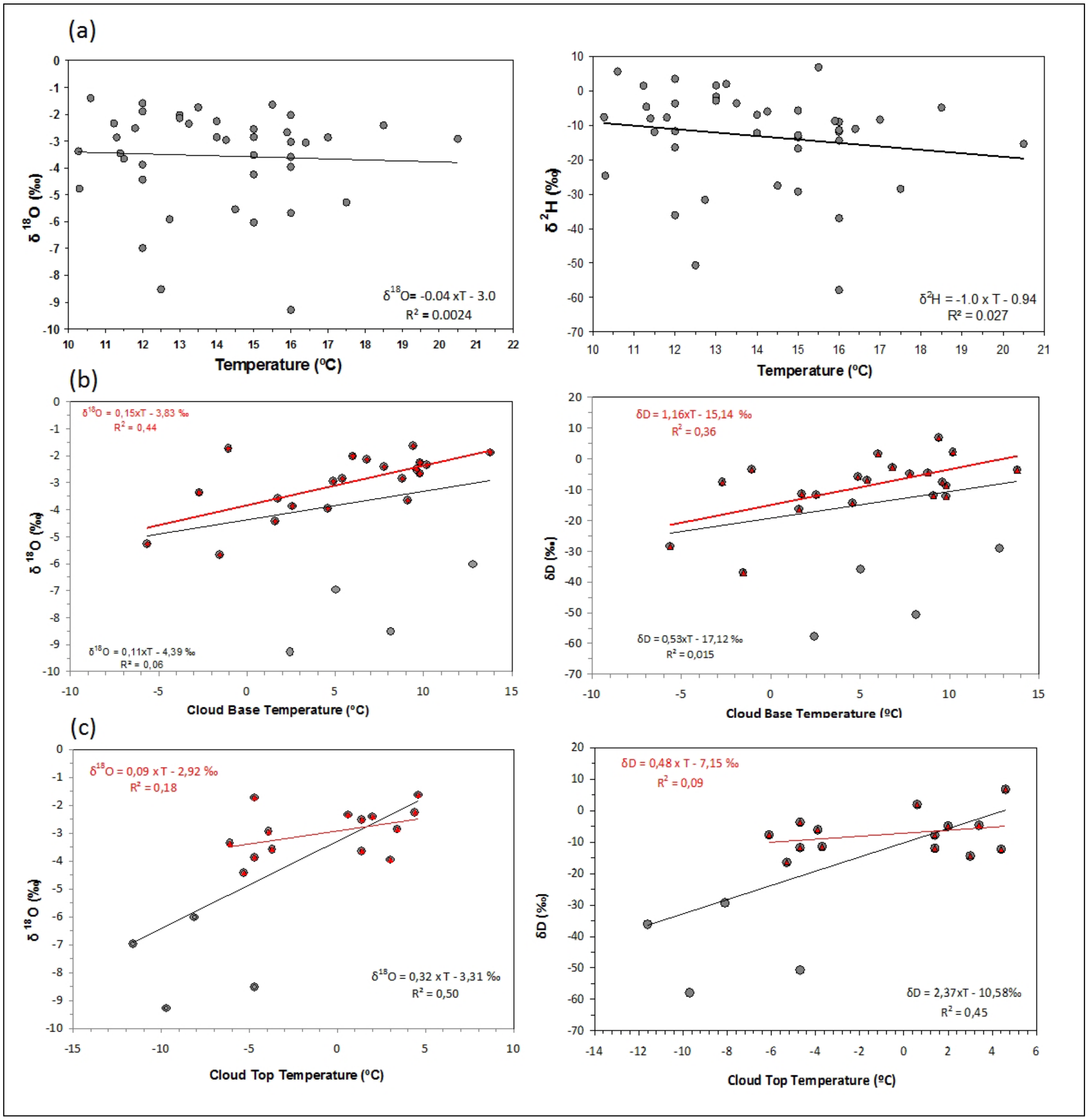

Figure 4. Scatter plot for δ^{18}O-T and δ^{2}H-T relationship. a) correlation with surface temperature; b) correlation with the cloud base temperature; c) correlation with the top base temperature

Some investigations have shown that there is a better correlation with the cloud base temperature (Rindsberger and Magaritz, 1983) and with the cloud top temperature (Suzuki and Endo, 2001) because cloud temperature is more likely a better representation of the actual temperature of the precipitation. In order to verify this point, and using data from a radiosounding Tenerife-Güimar station, cloud base and cloud top temperature have been calculated for each precipitation event in which cloud base and top was perfectly defined. The cloud extension was determinate at the sounding looking level with relative humidity greater than 95%. In precipitation event of several days it has been calculated the average temperature of cloud base and top during this period. The results shown that there is a better correlation using cloud base or cloud top temperature that ground temperature (Figures 4 b,c). Cloud base temperature linear dependence is better if considered $\delta^{18}O$ data higher than -6‰ (red triangle points in Figure 4b), only. It is found a temperature effect of 0.15‰ and R^2=0.44 for $\delta^{18}O$-temperature relation and 1.15‰ and R^2=0.4 for δ^2H-temperature relation. Values of $\delta^{18}O$ under -6‰ are uncommon at these latitudes, so the isotopic composition of precipitation in these events with low isotopic values can be influenced by other factors (vapor sources and source temperatures, air mass trajectories and fallout histories, recycling water, etc.) that will be investigated in detail in future investigations.

Rainfall history and air mass moisture source

The variation of isotopes in precipitation is not only influenced by meteorological factors, but also by moisture sources and transport trajectories (Rozanski et al., 1993; Aravena et al., 1999). In Canary islands, eighty per cent of the synoptic situations that generate rain are related with disturbances at surface (Atlantic lows) or at upper levels (troughs), which allow the arrival to the archipelago of cold and humid air from high latitudes (Font, 1956; García H. et al., 2001; Knippertz, 2003). Nevertheless, important percentage of events that do not answer to these conditions, exist generating episodes that might have its isotopic specific brands. In order to investigated the relation between stable water isotopes in precipitation and origin and transport paths of the air masses, the back-trajectories was calculated using the 5-day HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) 4.0 dispersion model back-trajectories (Draxler and Rolph, 2003; Rolph, 2003), with the FNL meteorological dataset and vertical velocity model. The starting point was set at Tenerife (El Rayo station) and the altitude was fixed at the pressure level where there was the base of the cloud, as it was made previously with temperature.

Figure 5 shows the calculated back-trajectories according to their isotopic composition as it is shown in the graphic legend. The majority of trajectories arriving to Tenerife are derived mainly from northwest and north (American and North Atlantic Sector), corresponding to Atlantic low or

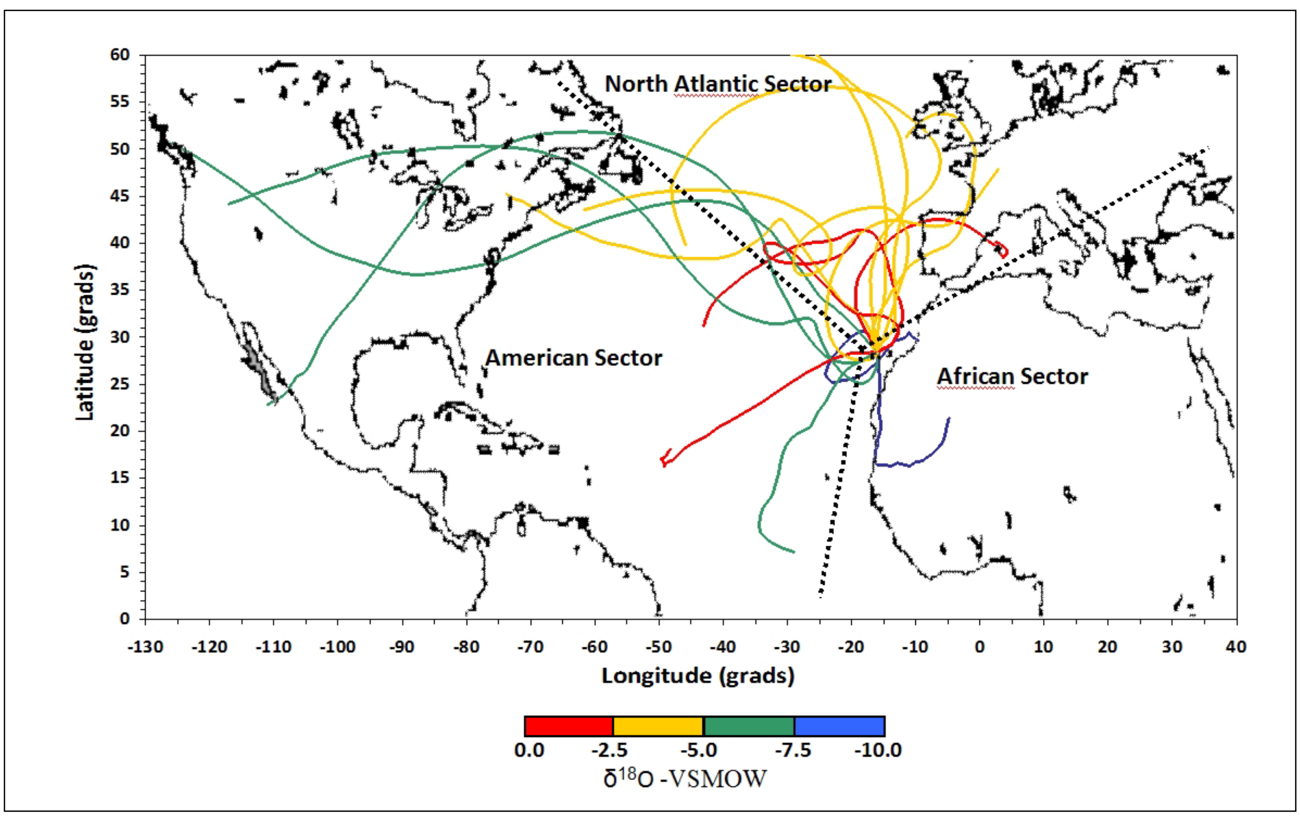

Figure 5. Air mass trajectories are calculated for 150 h before reaching our site.

upper troughs. However, there are some trajectories from southwest and southeast. The most remarkable aspect is that the air masses with the same isotopic composition are similar in every aspect, indicating the similar source and path of water vapor. In general, the most enrichment isotopic composition (red line trajectories) corresponds to back-trajectories with a short path and from different sector (never from African sector), probably indicating a local source of moisture. Sources farther from the sampling location and originating in west areas have depleted isotope values, indicating that significant precipitation has fallen above the ocean, leaving the remaining vapor depleted in ^{18}O and ^{2}H. But the most depleted isotopic composition corresponds with trajectories occurring after an African dust intrusion (blue line trajectories). The arrival of air from the North Africa is a common weather phenomenon in Canaries, mainly during the winter, which has important effects over temperature, humidity and visibility. The importance of dust outbreaks over the Canary Islands and its special isotopic signature makes it necessary to investigate these events in detail in future works.

CONCLUSIONS

This study, about stable isotope composition in rainwater, is one of the most extensive carried out in the Canary Islands and the first based on precipitation events. The relationship found between $\delta^{18}O$ and δD, the LMWL, are in concordance with others LMWL obtained by others investigators, what corroborate that deviations from de GMWL are due to the specific regional meteorological conditions over the region. The relation between rainfall $\delta^{18}O$ and $\delta^{2}H$ and temperature parameters was investigated. No significant relationship was found with the surface temperature, according to subtropical island environment, but it has been found a better correlation between the isotopic composition and the cloud top and base temperature. On the other hand, the relation of the amount of precipitation and $\delta^{18}O$ (δD) is better than with the temperature, which is expected in subtropical islands. It has been obtained a good correlation with the Mean Precipitation Intensity (MPI) calculated as the ratio between total precipitation and the total days of event duration, due to the fact that the isotopic composition in precipitation and the MPI change together. For example, they are governed by similar meteorological factors. Despite not having many data, an important aspect of this study concerns the interpretation of the isotopic composition related to the air mass trajectories. It has been found that lower values of $\delta^{18}O$ are founding after a Sahara invasion event or an event derived from the east or because the air mass trajectories have come a long trajectories from the northwest.

ACKNOWLEDGMENTS

This work has been realized thanks to the financing of the projects of reference PI042005/034 and SolSubC200801000260 of the autonomous Government of Canaries.

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