Factors controlling the stable isotopic composition of recent precipitation in Spain

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Abstract. Composite monthly samples of precipitation were collected for the period 2000-2004 at 16 meteorological stations included in the "*Red Española de Vigilancia de Isótopos en la Precipitación*" (REVIP), the Spanish Network for Isotopes in Precipitation. Oxygen-18 and deuterium results were used to review previous maps showing the spatial distribution of isotope contents over the Iberian Peninsula. Long-term mean weighted values of $\delta^{18}O$ over the Iberian Peninsula range from ca. -4.0 ‰ in stations from Andalusia to ca. -10.0 ‰ in the stations located in the northern plateau. The $\delta^{2}H$-$\delta^{18}O$ relationship of the long-term weighted means is in good agreement with the GMWL, showing d-excess values only slightly above 10‰, indicating the relevance of air masses of Atlantic origin, as the main source of water vapour over the Iberian Peninsula. The spatial distribution of $\delta^{18}O$ y $\delta^{2}H$ in precipitation over the Iberian Peninsula can be explained by a simple multiple regression model, based on two geographic factors: latitude and elevation. This polynomial model reproduces reasonably well the observed spatial distribution of the stable isotope composition of precipitation over Spain, facilitating the use of stable isotopes as a tool to trace the origin of surface and ground waters. Differences between measured and predicted $\delta^{18}O$ values with both global and local scale models are explained by other regional and local factors that influence the isotopic composition of precipitation.

1. Introduction

The study of the spatial and temporal changes of the isotopic composition of atmospheric water vapour, precipitation, surface water and groundwater, and the understanding of the processes controlling its spatial variability, have greatly contributed to a better knowledge of the water cycle in the last decades. Environmental isotopes have contributed to make more precise quantitative assessments of the water fluxes occurring within the different components of the hydrologic cycle at local, regional and global scale and to gain a better understanding of the governing processes. The importance of these achievements has been shown in many studies directed to the assessment of water resources and the quality of these resources, research programmes in global change, studies of ecosystems, regulatory developments and quality control in human diet.

Research on the atmospheric part of the hydrologic cycle (precipitation and surface waters) was initiated in the early 1950s. Isotope monitoring of precipitation at global scale was launched in the 1960s under the auspices of a joint collaboration between the IAEA and WMO under the programme Global Network for Isotopes in Precipitation (GNIP). In Spain, the *Centro de Estudios y Experimentación de Obras Públicas* (CEDEX) maintained the operation of the meteorological station of Madrid - Retiro since 1970, as well as some other stations with a shorter record since 1980, until the *Red Española de Vigilancia de Isótopos en la Precipitación* (REVIP) was created in 2000. Nowadays REVIP is managed by the *Centro de Estudios y Técnicas Aplicadas* (CETA-CEDEX), in collaboration with the Spanish Meteorological Survey (INM).

A first study of the factors controlling the isotopic composition of precipitation and groundwater in Spain covering the national territory in the Iberian Peninsula [1] provided a general framework for the interpretation of isotopic analyses for hydrogeology and related fields in this country. The lack of systematic isotope analyses of samples collected in meteorological stations evenly distributed through the whole national territory was pointed out though. More recently, CEDEX has presented an assessment of the results of the first two years of operation of REVIP [2], including information on the isotope variability of precipitation and water vapour, and also including samples collected in stations located in the Balearic and Canary islands. This paper presents the first analysis of the information gathered during the first five-year period of the Spanish Network, which is the result of the collaboration between the Geological Survey of Spain (IGME) and CEDEX.

2. *The Spanish Isotope Network: REVIP*

2.1. Objectives and design of REVIP

Main objectives of REVIP, the Spanish Network of Isotopes in Precipitation, are: 1) to study the meteorological and geographic factors controlling the isotopic composition of precipitation; 2) to define a simple model to assess and predict the local isotope index of precipitation over the entire country as a tool to trace the origin of surface water and ground waters; 3) to enhance the practical applications of stable isotope tracing to hydrological problems; 4) to provide information for the assessment of climatic changes; and 5) to contribute to the efforts of the IAEA to provide a better coverage of the GNIP network.

REVIP consists of 16 meteorological stations where composite monthly samples of precipitation are collected and analysed following the protocols established by the IAEA for GNIP. Particular care was taken in the design of REVIP in order to have wide geographic (N-S and E-W, different physiographic setting and topographic height) and climatic (stations representative of semiarid and humid areas, continental and littoral, Atlantic and Mediterranean) coverage. All main River Basin Districts defined at national level are represented in REVIP (Fig. 1). Table 1 presents the main geographic, meteorological and summary isotope characteristics of the REVIP stations for the period 2000-2004.

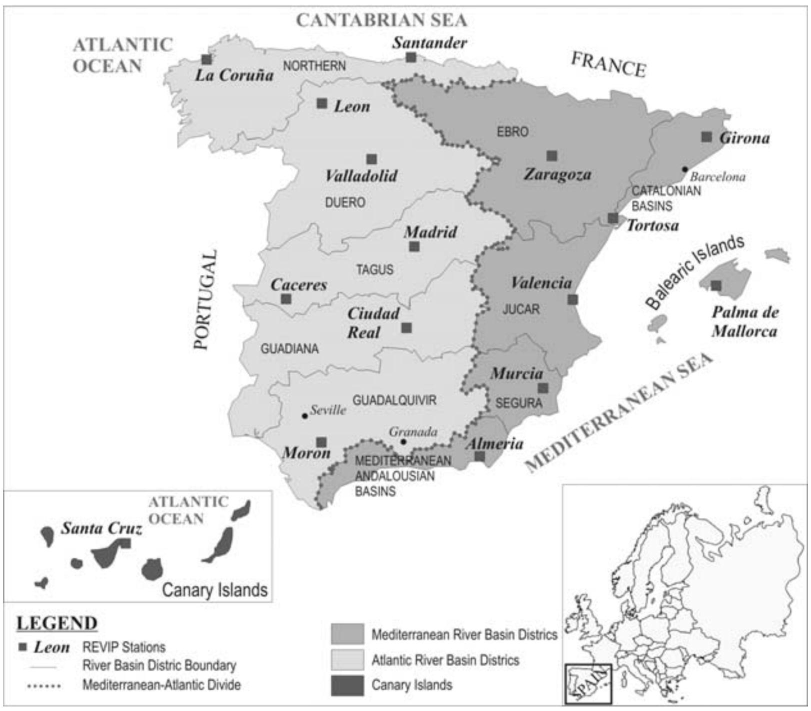

FIG. 1. Meteorological stations included in REVIP and GNIP database (operative since 2000).

TABLE 1. Meteorological data and weighted mean ($\delta^{18}O$, $\delta^{2}H$, and d-excess) for REVIP stations during the 2000-2004 period.

Station	Long (º)	Lat (º)	Elevation (m.a.s.l.)	Mean annual rainfall (mm)	Mean annual temp (ºC)	Relative humidity (%)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	d (‰)
1. Atlantic basin									
1.a. Island									
Santa Cruz de Tenerife	16 14 56 W	28 27 18 N	36	239.7	22.0	63	-1.74	-8.3	5.7
1.b. Coastal									
La Coruña	08 25 10 W	43 22 02 N	57	1070.7	15.0	77	-5.58	-36.0	8.6
Santander	03 47 59 W	43 29 30 N	52	1003.4	14.8	75	-5.79	-33.4	13.0
1.c. Continental									
Morón	05 36 57 W	37 09 30 N	88	570.4	18.2	61	-4.77	-27.7	10.4
Cáceres	06 20 22 W	39 28 20 N	405	577.6	16.3	58	-6.53	-42.9	9.4
Ciudad Real	03 56 11 W	38 59 22 N	627	413.9	16.0	63	-7.63	-50.9	10.2
Madrid	03 40 41 W	40 24 40 N	667	471.8	15.2	57	-6.80	-47.1	7.0
Valladolid	04 46 27 W	41 38 40 N	735	466.8	12.9	65	-7.93	-54.6	8.6
León	05 39 07 W	42 35 10 N	913	539.2	11.0	68	-9.02	-63.5	8.7
2. Mediterranean basin									
2.a. Island									
Palma de Mallorca	02 37 35 W	39 33 18 N	3	440.2	18.7	70	-5.57	-34.4	10.1
2.b. Coastal									
Almería	02 23 17 W	36 50 35 N	21	184.6	19.3	66	-4.81	-27.7	10.8
Valencia	00 22 52 W	39 28 48 N	13	509.3	18.9	65	-4.73	-27.3	10.5
Tortosa	00 29 29 W	40 49 14 N	48	584.9	18.1	63	-5.04	-30.8	9.5
2.c. Continental									
Murcia	01 10 10 W	38 00 10 N	62	290.8	18.9	59	-5.70	-36.7	8.9
Zaragoza	01 00 29 W	41 39 43 N	247	367.5	15.9	62	-6.31	-42.0	8.5
Gerona	02 45 37 W	41 54 05 N	129	622.0	15.0	72	-5.66	-37.3	7.9

2.2. Sampling and analytical methods

REVIP sampling programme is organized according to the protocols issued by the IAEA: monthly collection of precipitation samples and compilation of the isotope ($\delta^{18}O$, $\delta^{2}H$) and meteorological data in a database maintained by CEDEX. Deuterium and oxygen-18 analyses have been undertaken at CEDEX Isotope Hydrology Laboratory using a double-inlet IRMS, Delta Plus Advantage, following the usual procedures for deuterium and oxygen analysis and referring the results to the VSMOW–SLAP scale. The uncertainty is ±0,1‰ for $\delta^{18}O$ and ±1,0‰ for $\delta^{2}H$.

3. Patterns of the isotopic composition distribution of precipitation in Spain

Previous studies on the isotopic composition of precipitation at a global scale have shown the relationship between the degree of depletion in heavy isotopes and latitude, altitude, continentality, and intensity of precipitation [3-5]. The multiple interplay of these factors is favoured at local scale in Spain, due to the great variety of geographic and climatologic features, such as: 1) interplay of several oceanic and continental air masses, but mainly of Atlantic and Mediterranean origin; 2) topographic elevations of more than 3,000 m.a.s.l. are found both in the Iberian Peninsula and in the Canary Islands; and 3) the presence of an extensive plateau, with a mean elevation between 700 and 900 m a.s.l. in the innermost part of the Iberian Peninsula.

The LMWL for Spain, for the 2000-2004 period, basically coincides with the Global Meteoric Water Line, when all stations are considered together, giving a general indication about the overall quality of the results of REVIP. The partitioning of isotopes between stations located on cold (León, Valladolid, Madrid) and warm regions (Tenerife, Valencia, Almería) in Spain is clearly observed, shown the relevance of temperature as the main factor controlling the isotope composition of precipitation at the latitude of the Iberian Peninsula [6]. Deuterium-excess values are only slightly above +10‰ (Table 1), indicating the relevance of air masses of Atlantic origin as the main source of water vapour over the Iberian Peninsula.

A summary statistical analysis of the results obtained from the REVIP for the period 2000-2004 is presented in Figs. 2a and 2b. Depletion in $\delta^{18}O$ and $\delta^{2}H$ is shown for the Mediterranean stations as the latitude increases (left side of the plots). A similar tendency is seen for the Atlantic stations as the latitude, altitude and continentality increase (right side of the plots). However, two stations located at the Northern most part of Spain (La Coruña and Santander) make this trend to reverse due to their location at the coast and consequently at a lower altitude, showing that elevation also is an essential factor controlling isotope composition in the stations located on the Atlantic coast.

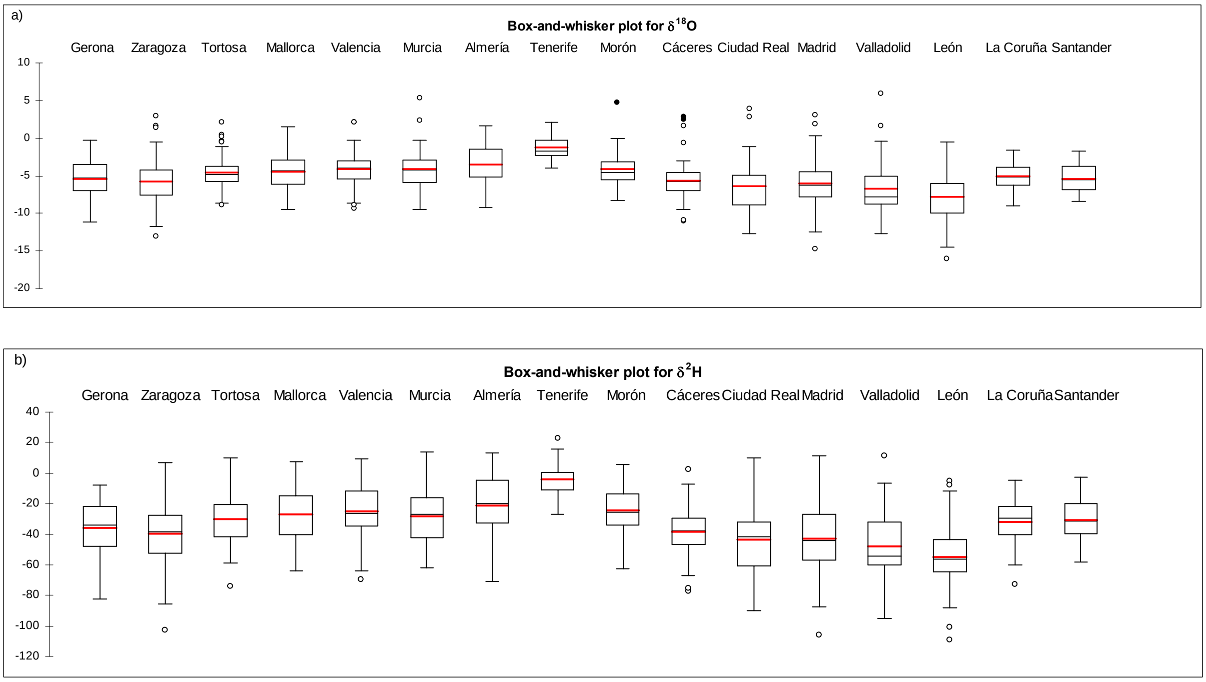

FIG. 2. (a) Box-and-whisker plots for $\delta^{18}O$. (b) Box-and-whisker plots for $\delta^{2}H$. Monthly averages for all REVIP stations during the 2000-2004 period are used.

4. Derivation of a model for the latitude and elevation dependance of $\delta^{18}O$

In this study, the model approach used in [7-8] was adopted to predict the spatial distribution in the isotopic composition of recent precipitation in Spain. A first approximation of the spatial variation in $\delta^{18}O$ in REVIP stations is presented in Fig. 3a, using the long/term isotope compositions of global precipitation from the IAEA/GNIP database and the equation that describes $\delta^{18}O$ as a function of latitude and altitude determined in [7]. Fig. 3b shows that the isotope composition of REVIP stations are more positive than those for GNIP stations located at similar latitudes, particularly in the case of REVIP coastal stations (elevation < 200 m). These differences may derive from the influence of the positive $\delta^{18}O$ signature that the warm Gulf Stream may imprint to European precipitation, as suggested in [8].

A second approximation was attempted in order to better assess the combined influence of both latitude and elevation on the composition of precipitation over Spain. The equation that describes the $\delta^{18}O$ values as a function of latitude and altitude, represented in Fig. 4a, was derived using the same two-step approach used in [7]: first the dependence on latitude was obtained for all REVIP stations except Tenerife (Canary Islands) which belongs to a different climatic region, and later the effect of elevation was quantified. Adding the two equations, the combined dependence of isotope composition on latitude and elevation can be described as follows:

$$\delta^{18}O = -0.0131LAT^2 + 0.9507LAT - 0.0034ALT - 22.253 \quad (1)$$

where LAT is the latitude in decimal degrees and ALT the elevation of the sampling station in metres. Equation 1 provides a good first-order estimate of observed $\delta^{18}O$ in Spain (r^2 = 0.92; Fig 4b). The highest difference between measured and modelled data is found for Madrid-Retiro station. This positive residual (Fig. 5) may be explained as a consequence of the effect of higher evaporation rates of falling raindrops, since this is the REVIP station with the lowest mean annual relative humidity (Table 1).

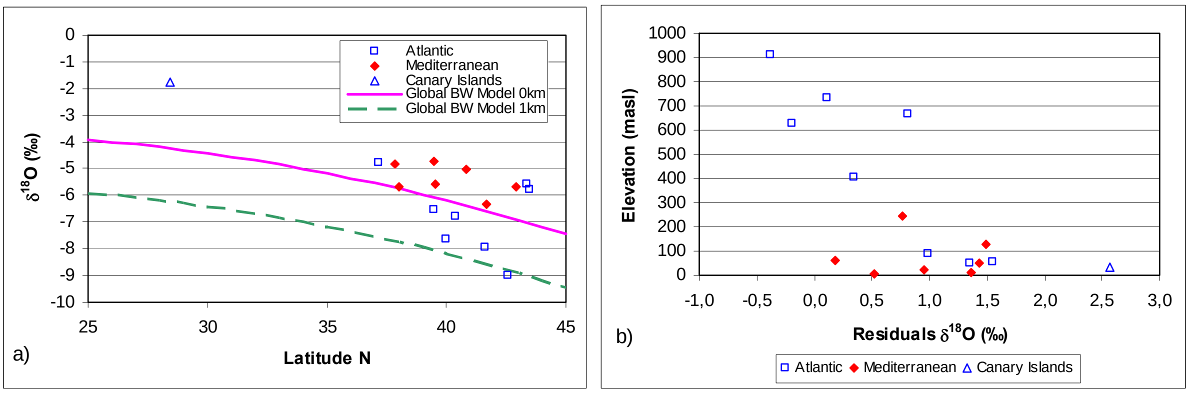

FIG. 3. (a) Global model lines obtained for 0 and 1 km elevation for the $\delta^{18}O$ contents of meteoric precipitation with increasing latitude and elevation for GNIP stations (Bowen and Wilkinson model [7] referred to as global BW model), and comparison with REVIP stations. (b) Residuals between measured isotope values of REVIP stations and global BW model $\delta^{18}O$ versus elevation.

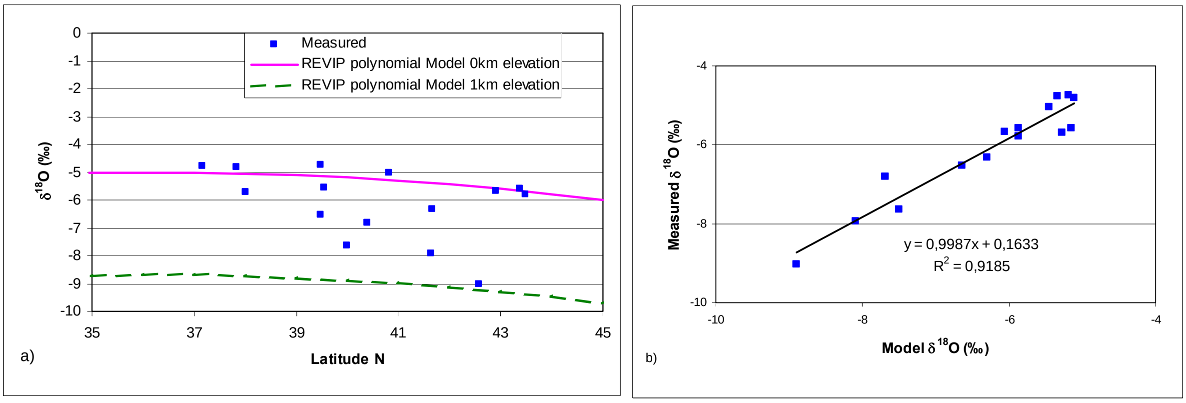

FIG. 4. (a) Local model lines obtained for 0 and 1 km elevation for the rate of depletion in ^{18}O of meteoric precipitation with increasing station latitude and elevation for REVIP stations. (b) Difference between measured and predicted $\delta^{18}O$ by the second-order polynomial for REVIP stations.

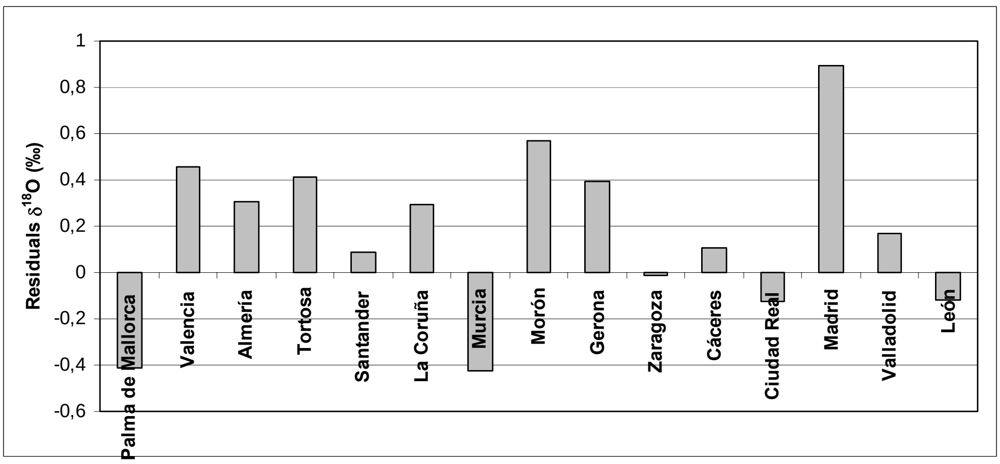

FIG. 5. Residuals between measured isotope values and the REVIP polynomial model $\delta^{18}O$.

5. Conclusions

Oxigen-18 and deuterium analyses are being performed as a contribution to GNIP, for composite monthly samples of precipitation collected at the 16 meteorological stations of the "*Red Española de Vigilancia de Isótopos en la Precipitación*" (REVIP), the Spanish Network for Isotopes in Precipitation. The δ^2H-$\delta^{18}O$ relationship of the long-term weighted means (for the period 2000-2004) is in good agreement with the GMWL, showing d-excess values only slightly above 10‰, indicating the relevance of air masses of Atlantic origin as the main source of water vapour over the Iberian Peninsula.

The spatial distribution of $\delta^{18}O$ y δ^2H in precipitation in Spain can be explained in a simplistic form by a simple multiple regression model, based on geographic factors (latitude and elevation). This model reproduces reasonably well the observed main features of the spatial distribution of the stable isotope composition of precipitation over Spain, facilitating the trace of the source of surface and ground waters.

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