Mapping Oxygen-18 in Meteoric Precipitation over Peninsular Spain using Geostatistical Tools

José E. Capilla[1], Javier Rodriguez Arevalo[2], Silvino Castaño Castaño[3], María Fé Díaz Teijeiro[2], Rut Sanchez del Moral[3] and Javier Heredia Diaz[3]

Abstract Rainfall isotopic composition is a valuable source of data to understand and model the complexity of hydrological systems. The identification of water recharges origins, water flow trajectories and pollutants movement in the hydrologic cycle can greatly benefit from this information. It is also very useful in other environmental forensic applications. However, its use has been strongly limited by the availability of data. A major challenge is to extend sparse measurements of stable isotopes data to surrounding geographic areas taking into account other secondary variables as latitude, altitude and climate related parameters.

In Spain the network REVIP, made up by 16 nodes, maintained by governmental agencies, provides continuous recorded data of O-18 in meteoric precipitation since the year 2000. So far, only regression models have been proposed to map stable isotopes against latitude and altitude. Yet, these maps maintain small residuals at the network nodes that are possibly caused by local features of climatic events. There is an ongoing effort to improve these maps including the identification of relevant climatic parameters and the application of geostatistical techniques.

This paper describes the application of a regression kriging methodology to map O-18 over peninsular Spain using REVIP data. A previous regression has lead to a normalized stable isotope concentration variable independent of latitude and altitude. Then, a structural analysis of this variable and an ordinary kriging has allowed to map O-18 in a grid of 5000x5000 m. Results confirm the dependency of O-18 with latitude and altitude, show a good fitting of a variogram exponential model to the normalized variable, and provide an exact reproduction of isotopic contents at the nodes changing previous maps over large areas of the peninsula. These differences extend mainly to the NW and SW areas of Spain, and might be showing the influence of climatic events characteristic of these areas.

---

[1] Research Institute of Water and Environmental Engineering; Universitat Politécnica de Valencia, Spain, jcapilla@upv.es

[2] Centro de Estudios y Experimentación de Obras Públicas (CEDEX), Spain, Javier.Rodriguez@cedex.es

[3] Instituto Geologico y Minero de España (IGME), Spain, s.castano@igme.es

Introduction

Oxygen-18, as well as other stable environmental isotopes data, provides very useful information in different fields as paleoclimatology, paleoceanography, other paleosciences, climate change and forensic applications of environmental interest. In the field of hydrology, these isotopes allow to trace water origins and understand water dynamics (recharge areas, residence time in aquifers, etc.) to understand and model the complexity of water resources systems and the hydrological cycle. Oxygen-18 is an environmental isotope and belongs to a subset of isotopes, both stable and radioactive, which are the object of isotope geochemistry. It is frequently referred to as Oxygen-18, O-18, ^{18}O or Ω. In order to represent the contents of ^{18}O in a water samples, the ratio O-18/O-16 represented by $\delta^{18}O$ and given in Equation (1) is used.

$$\delta^{18}\mathrm{O} = \left(\frac{\left(\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}} \right)_{\text{sample}}}{\left(\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}} \right)_{\text{standard}}} - 1 \right) \times 1000 \, {}^{o}/_{oo} \qquad (1)$$

The quotient $(^{18}O/^{16}O)_{\text{standard}}$ in Equation (1) refers to a known isotopic composition (Vienna Standard Mean Ocean Water, VSMOW). The possibility of characterizing geographically the distribution on $\delta^{18}O$ in precipitation opens a huge potential in the field of hydrology. The goal of this paper is to map this distribution over peninsular Spain using Geostatistical tools.

Oxygen-18 in rainfall

There is clear evidence that $\delta^{18}O$ decreases as Latitude and Altitude increase, and toward the continental interior. These trends are modified by local climatic conditions which are highly variable in time and space. Some important facts regarding the index $\delta^{18}O$ in precipitation to understand these trends are:

- O-16 preferential evaporation from seawater.
- The surface ocean contains greater amounts of O-18 around the subtropics and tropics where there is more evaporation, and lesser amounts of O-18 in the mid-latitudes where it rains more.
- Heavier water molecules (holding O-18 atoms) tend to condense and precipitate first. The water vapor heading from the tropics to the poles gradually becomes more and more washed-out of O-18.

- Isotopically heavier precipitation occurs as rain (typically ~ -3‰ - 0‰), while snow is dramatically lighter (~ -20‰).
- O-18 contents get lighter with increasing latitude; get lighter toward the continental interior; and use to show sharp changes in the mountain areas, where apart from temperature / elevation effects, the windward side of a range receives precipitation enriched in O-18 because of the rainout effect.

Oxygen-18 data and mapping approaches

Figure (1) shows the Global Network of Isotopes in Precipitation (GNIP) which is managed by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO).

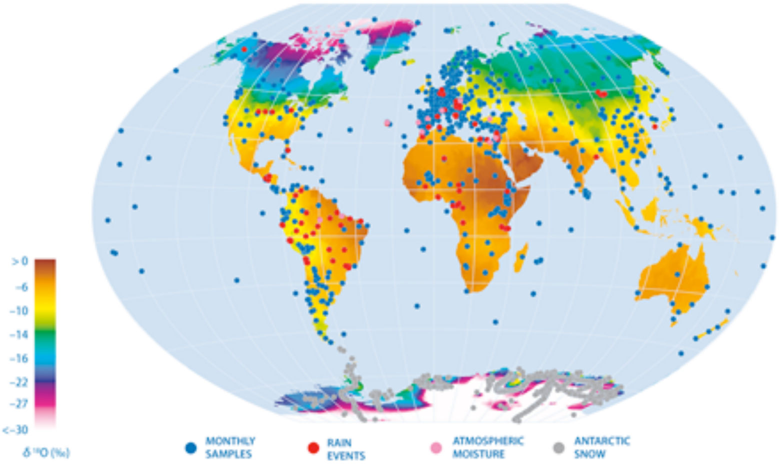


Figure 1. Global Network of Isotopes in Precipitation (GNIP). (Source: www.iaea.org)

As part of GNIP, CEDEX (Centro de Estudios y Experimentación de Obras Públicas, Spain) maintains a sampling program, referred to as REVIP (Red Española de Vigilancia de Isótopos en Precipitación - Spanish Monitoring Network of Isotopes in Precipitation), 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 O-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 $\delta^{2}H$. This network includes 15 stations over peninsular Spain where data have been recorded continuously since 1999.

Base on GNIP data and other surveys, several authors have map $\delta^{18}O$ in precipitation, groundwater and surface water. For this purpose Kendal et al. (2001) compare kriging against an inverse-distance gridding method and found that kriging produces contours that appeared more accurate. However, they chose kriging parameters with the criteria of minimizing artifacts caused by anomalous single-site compositions. No further structural analysis is performed. Bowen (2002) adjusts a second order polynomial to GNIP data, with the form $\delta^{18}O = -0.0051LAT^2 + 0.1805LAT - 0.002\ ALT - 5.247$, and studies possible correlations for "residuals", or better expressed, information not captured by the polynomial. Bowen and Revenaugh (2003) evaluate four interpolation schemes: triangulation, inverse distance weighting, Cressman objective analysis, and previous regression with Latitude and Altitude. Lykoudis et al. (2007) perform a regression against geographical and meteorological parameters, and use of ordinary kriging for residuals. They use an exponential variogram model (with anisotropy). No further details are provided. Bowen et al. (2007), in an attempt to map stable isotope ratios of tap water, used ordinary kriging with a spherical semivariogram (with ArcGIS 9.1). As it can be seen, geostatistical tools, when used, are taken as a "black box" without further data analysis.

Regression–kriging of REVIP data (1999-2007)

After a careful analysis of REVIP data (average annual values of $\delta^{18}O$ for the period 1999-2007) a regression-kriging alternative was chosen to map $\delta^{18}O$ in precipitation over peninsular Spain. The process followed is, in short:

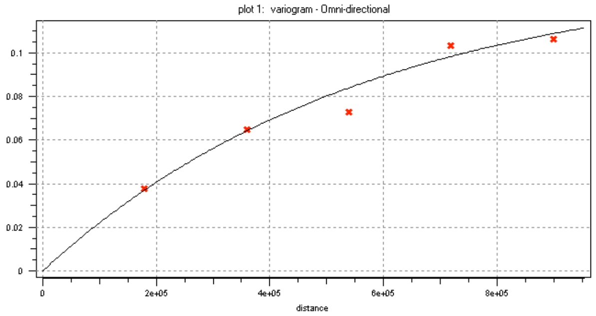
1) Regression for "Sea level stations $\delta^{18}O$" and "Latitude" (8 stations, coef. correlation -0.963): $\delta^{18}O = -0.0488\ Lat - 3{,}4313$

2) Obtaining the no-latitude trend variable by, $\delta^{18}O^* = \delta^{18}O + 0.0488*(Lat-40.41)$, which is referred to null correction at "El Retiro, Madrid" station (Lat 40.41N).

3) Regression "$\delta^{18}O^*$" with "Altitude", (Coef. correlation -0.9631), $\delta^{18}O^* = -0{,}00324651*Alt - 5.26139$

4) Obtain a standardized variable by discounting latitude and altitude influence: $\delta^{18}O^{**} = \delta^{18}O^* + 0.00324651 * (Alt - 667) = \delta^{18}O^* + 0.00324651 *Alt - 5.2588$

The structural analysis is performed for the normalized variable. Then, a map of $\delta^{18}O^{**}$ is estimated using ordinary kriging, and the back transform to $\delta^{18}O$ leads to the map $\delta^{18}O$ in precipitation. Figure 2 shows the variograma adjusted to data.



Exponencial model
Nugget: 0.0
Sill: 0.137
Range: 1700 km

Figure 2. Experimental variogramm and exponential model adjusted to $\delta^{18}O^{**}$ data.

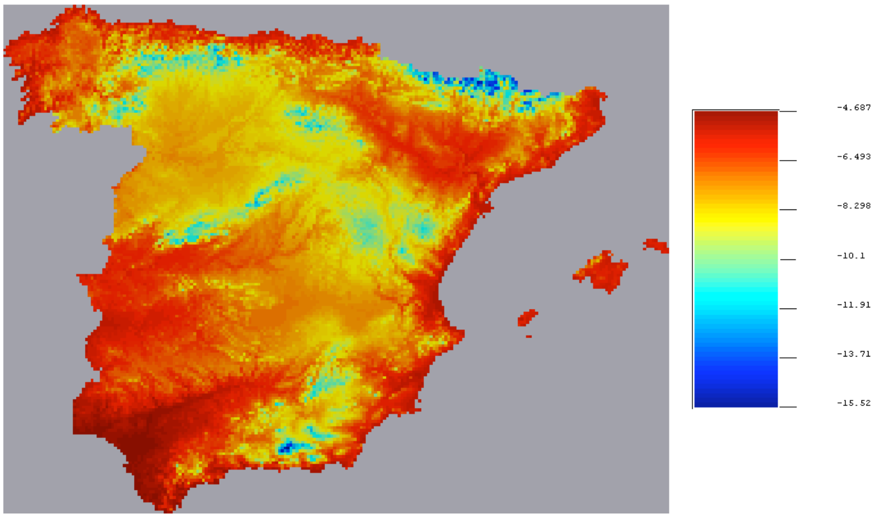


Figure 3. Map of $\delta^{18}O$ obtained by regression-kriging with an exponential variogramme.

Figure 3 shows the final result of the distribution of $\delta^{18}O$. This map has been compared with the map previously obtained (Diaz et al., 2007) using a second order polynomial approach. This polynomial has the form $\delta^{18}O$ = -0.013*Lat^2+0,9507**Lat-0.0037*Alt-22.253. Figure 4 shows the map of differences between the two approaches. While the map obtained by regression was not able to exactly reproduced data at all REVIP stations, yielding some "residuals", the regression-kriging approach is reproducing exactly all data. This means that the latter method is not missing information and, in fact, is extending the data info missed by the second order polynomial to the geographically surrounding areas.

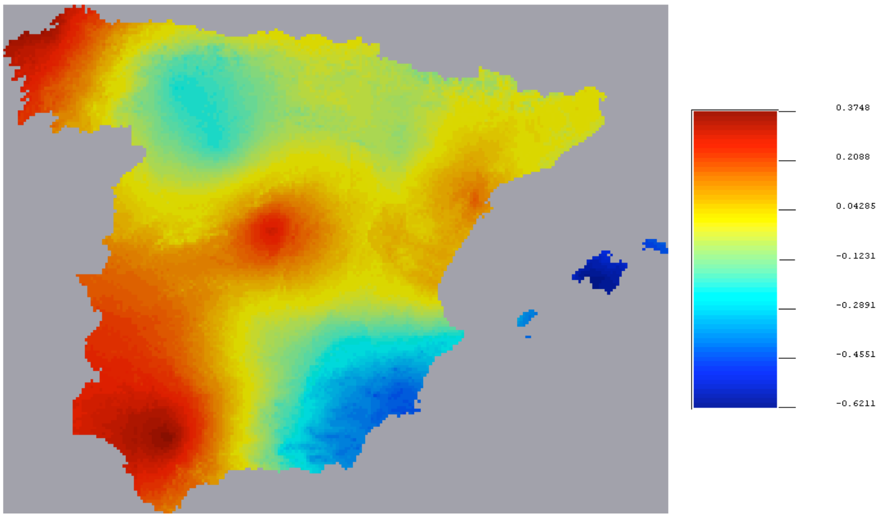


Figure 4. Map of differences between $\delta^{18}O$, obtained by regression-kriging with a exponential variogram, and the map produced by the second order polynomial regression.

Conclusions

This research demonstrates the applicability of a regression-kriging method to obtain accurate maps of δ18O in precipitation using REVIP data. The process requires to identify the trends with Latitude and Altitude and then to obtain a normalized variable where trends due to theses geographical variables are almost inexistent. Other spatial trends – due to climatic conditions - are expected to be captured by ordinary kriging that allows the spatial variation of average values.

We have obtained a good fitting of an exponential variogramme model to REVIP, and the map does reproduce exactly data at REVIP network locations. This is not happening when regression approaches are used.

The "residuals" or errors of the polynomial map are extended by the ordinary kriging yielding a map which reflects more realistically the local climatic conditions (based on frequency and origin of fronts/events that generate precipitations). Thus, in the SE, local data show that precipitation (isotopically lighter) is more of local origen, and there is heavier rainfall in the NW and SW of the peninsula (more influence of precipitations – no snow - from lower Atlantic latitudes).

Acknowledgement

Financial support from the Spanish Ministry of Science and Innovation (Project ISOTOPOSHIDRO, Ref. CGL2009-12977) is gratefully acknowledged.

Bibliography

Bowen, G. J. (2002). Spatial distribution of ^{18}O in meteoric precipitation. Geology, v. 30, no. 4, p. 315–318

Bowen, G. J. and Revenaugh, J. (2003). Interpolating the isotopic composition of modern meteoric precipitation. Water Resources Research, vol. 39, no. 10, doi:10.1029/2003WR002086

Bowen, G. J., Ehleringer, J.R., Chesson, L. A., Stange, E. and Cerling, T.E. (2007). Stable isotope ratios of tap water in the contiguous United States. Water Resources Research, Vol. 43, W03419, doi:10.1029/2006WR005186.

Diaz, M.F., Rodríguez Arevalo, J., Pérez, E., Castaño, S., Araguás-Araguás, L. (2007). Factors controlling the stable isotopic composition of recent precipitation in Spain (IAEA–CN–151/82). Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management (IHS—2007). Proceedings of a Symposium Vienna, 21–25 May 2007, Vol. 1.

Kendall, Carol and Tyler B. Coplen 1. (2001). Distribution of oxygen-18 and deuterium in river waters across the United States Hydrological Processes 15,1363 – 1393. DOI: 10.1002/hyp.217

Lykoudis, S. P. and Argiriou, A. A. (2007). Gridded data set of the stable isotopic composition of precipitation over the eastern and central Mediterranean. Journal of Geophysical Research, vol. 112, D18107, doi:10.1029/2007JD008472