



## Mapping oxygen stable isotopes of precipitation in Italy



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### ABSTRACT

*Study region:* Italy.

*Study focus:* The oxygen isotope composition from 266 pluviometers was used to study the spatial variability of  $\delta^{18}\text{O}$  and its relationship with Italian orography. The local meteoric water lines (LMWLs) of northern, southern and central Italy and Sicily are reformulated and a new definition of isotopic variations with elevation is provided.

*New hydrological insights for the region:* Altitude and, to a lesser extent, latitude are the main geographical factors affecting the isotopic signature of precipitation in Italy. A high-resolution map of the spatial distribution of  $^{18}\text{O}$  content in precipitation was created using the identified relationship between  $\delta^{18}\text{O}$ /Latitude-Altitude and the spatial distribution of the residuals. The general features of the  $\delta^{18}\text{O}$  distribution map may be summarised as follows:  $\delta^{18}\text{O}$  distribution over the Alps clearly depends on latitude and altitude, whereas over the Apennines, which run down the whole peninsula from north-west to south-east, it is more affected by altitude, the contour lines roughly following the axis of the chain. The isotope compositions on the western side of the peninsula are generally higher than those of the east at the same elevation and latitude; they are more or less uniform in the northern plain of Italy.

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### 1. Introduction

In 1961, Craig published his seminal paper in which he showed that  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in precipitation on a global scale are linearly related, and was the first to define the Global Meteoric Water Line (GMWL), represented by the equation  $\delta\text{D} = 8\delta^{18}\text{O} + 10\text{‰ SMOW}$ . Subsequent monitoring of the stable isotope composition of precipitation worldwide, carried out through the Global Network for Isotopes in Precipitation (GNIP), jointly operated by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO), allowed this relationship to be refined. In the first comprehensive review of isotopic data gathered by the GNIP network, Dansgaard (1964) formulated a number of empirical relationships between the observed isotopic composition of monthly precipitation and environmental parameters, such as surface air temperature, amount of precipitation, latitude, altitude, and distance from the coast. Subsequent reviews of the GNIP database (Yurtsever and Gat 1981; Rozanski et al., 1993) largely confirmed the early findings of Dansgaard and indicated that the GMWL equation should be updated, as follows:  $\delta\text{D} = 8.20 (\pm 0.07) \delta^{18}\text{O} + 11.27 (\pm 0.07) \text{‰ VSMOW}$  (Rozanski et al., 1993). Craig's line and later revisions are only global in application, and there are currently many regional or "Local Meteoric Water Lines" (LMWLs) which differ from the global line in both slope and deuterium intercept, as a result of varying climatic and geographic parameters.

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Italy lies in the centre of the Mediterranean and comprises the boot-shaped peninsula and the two largest islands in the area (Sicily and Sardinia). Four factors (both climatic and geographic) affect Italian meteoric precipitation isotopes, which consequently vary widely (Minissale and Vaselli, 2011). These factors are: i) the differing contributions of precipitation coming from either northern Europe and the Atlantic Ocean and/or Africa and the Mediterranean Sea; ii) latitudinal extension (Italy lies between latitudes 35° and 47° N); iii) the very narrow shape of the central part of the peninsula; iv) the mostly mountainous internal conformation of the country (with several mountain peaks and massifs exceeding 4000 m in the Alps and 2000 m in the Apennines). The last factor is of particular importance for the isotopic composition of precipitation because, as a rule,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  change with the altitude of the terrain and become increasingly depleted in  $^{18}\text{O}$  and  $^2\text{H}$  at higher elevations. This *altitude effect* is particularly intense in Italy, due to the rugged topography which influences the isotopic composition of precipitation much more than latitudinal extension (Longinelli and Selmo, 2003). This effect has facilitated one of the most useful applications in isotope hydrology and hydrogeology, because it can distinguish groundwaters recharged at high altitudes from those recharged at low altitudes (Clark and Fritz, 1997).

Longinelli and Selmo (2003) studied the isotopic composition of precipitation in Italy, drew the first nation-wide contour map of the oxygen isotope composition, and defined three Local Meteoric Water Lines, for Northern ( $\delta\text{D} = 7.71 \delta^{18}\text{O} + 9.40$ ), Central ( $\delta\text{D} = 7.05 \delta^{18}\text{O} + 5.61$ ) and Southern Italy ( $\delta\text{D} = 6.97 \delta^{18}\text{O} + 7.32$ ). The above authors noted the marked variations among the Italian regions in the isotopic composition of precipitation. Many precipitation isotope datasets have been produced in Italy since the 1970s, when such studies developed rapidly. Their data mainly refer to hydrology/hydrogeology and, to a lesser extent, to other disciplines (e.g., climatology, speleology). However, some of these data were published in Italian, and the results have not been easily available to the international scientific community.

This paper presents an extensive review of the literature from international and Italian sources, in order to gather all available local meteoric water isotope data produced in Italy and some bordering regions. A large dataset was created, consisting of the yearly average data of oxygen and hydrogen isotopes of precipitation from a total of 266 locations. These data were processed to evaluate the spatial variability of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  and their relationships with Italian orography. A high-resolution map of the spatial distribution of  $^{18}\text{O}$  contents in precipitation in Italy was created. New vertical isotopic lapse rates were also calculated for various Italian latitudes.

These new findings will enable researchers to have access to correctly constrained pluviometric isotope data, which can be applied to all studies in which the exact location of a given example of precipitation must be determined as precisely as possible.

## 2. Data and methods

Rain gauges and/or pluviometric stations, many of them still operating, are widespread in Italy and adjacent countries. For this work, a database was created to include most of the isotope data produced from them (see online Supplementary material). Data are reported in the form of yearly means of monthly measurements, referred to here as “measured” as opposed to “calculated” isotope data. Fifty-six examples of data from pluviometric stations were extracted from the database of the Global Network for Isotopes in Precipitation (GNIP) (IAEA/WMO, 2004), and 210 more were reviewed from international and Italian sources, including ISI articles, technical reports, proceedings of conferences and theses (Oeschger and Siegenthaler, 1972; Zuppi et al., 1974; Nuti et al., 1977; Bortolami et al., 1978; Hauser et al., 1980; Siegenthaler and Oeschger, 1980; Schotterer et al., 1982; Zuppi and Bortolami, 1982; Pearson et al., 1991; D’Amelio et al., 1994; Pezdič et al., 1996; La Ruffa and Panichi, 2000; Longinelli and Selmo, 2003; Maréchal and Etcheverry, 2003; D’Alessandro et al., 2004; d’Antona, 2004; Ofterdinger et al., 2004; Barbieri et al., 2005; Bono et al., 2005; Arpa, 2006; Grassa et al., 2006; Liotta et al., 2006a,b, 2008, 2013; Longinelli et al., 2006, 2008; Vreča et al., 2006; Grillo, 2007; Cortecci et al., 2008; Paternoster et al., 2008; Fontana et al., 2009; Iacumin et al., 2009; Petrella et al., 2009; Spadoni et al., 2010; Surić et al., 2010; Minissale and Vaselli, 2011; Carucci et al., 2012; Elmi et al., 2013; Flaim et al., 2013; Michelini, 2013; Nanni et al., 2013; Madonia et al., 2014). Only data produced from stations which had been active for at least one year were selected. When more than one source had published data for the same station, the yearly averages were used (the differences between the yearly averages of one station reported by other authors may be up to 2%). In some cases, the geographic coordinates of the pluviometers were not precisely reported but only approximately positioned in a given area, and were assumed to be located at the coordinates of the nearest municipality. When it was not possible to identify even an approximate location, the relative data were excluded from our database.

The geographic distribution of the stations examined in this work is shown in Fig. 1; oxygen and hydrogen isotope composition, *d*-excess values, altitude and the geographic coordinates of the gauges are provided in the online Supplementary data. The pluviometers were divided into two groups according to the source of the data: I) those registered in the GNIP database, and II) the larger group of those reported in ISI articles, technical reports, proceedings of conferences and theses. Overall, Italy clearly has an extensive precipitation monitoring network, although there are some regions in which pluviometers are not uniformly distributed: in particular, they are sparse in southern Italy (excluding Sicily), along the Adriatic coast, in the north-western Alps and in Sardinia. In order to compensate for the low density of stations in these areas, the pluviometers located in adjacent countries turned out to be particularly useful, e.g., pluviometric stations in Croatia and Slovenia were of great importance in representing isotopes in precipitation over the Adriatic, and those in Switzerland and Austria for those of the Alpine region. Sicily, instead, is the Italian administrative region with the highest number of pluviometers (67), regularly distributed over a relatively small area of about 25,700 km<sup>2</sup>; there are also many located in the north-east (Friuli

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