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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 $\delta^{18}O$ 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}O content in precipitation was created using the identified relationship between $\delta^{18}O$/Latitude-Altitude and the spatial distribution of the residuals. The general features of the $\delta^{18}O$ distribution map may be summarised as follows: $\delta^{18}O$ 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.

1. Introduction

In 1961, Craig published his seminal paper in which he showed that $\delta^{18}O$ and δD 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 $\delta D = 8\ \delta^{18}O + 10‰$ 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: $\delta D = 8.20\ (\pm 0.07)\ \delta^{18}O + 11.27\ (\pm 0.07)$ ‰ 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, $\delta^{18}O$ and δD change with the altitude of the terrain and become increasingly depleted in ^{18}O and ^{2}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 ($\delta D = 7.71\ \delta^{18}O + 9.40$), Central ($\delta D = 7.05\ \delta^{18}O + 5.61$) and Southern Italy ($\delta D = 6.97\ \delta^{18}O + 7.32$). 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 $\delta^{18}O$ and δD and their relationships with Italian orography. A high-resolution map of the spatial distribution of ^{18}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^2; there are also many located in the north-east (Friuli

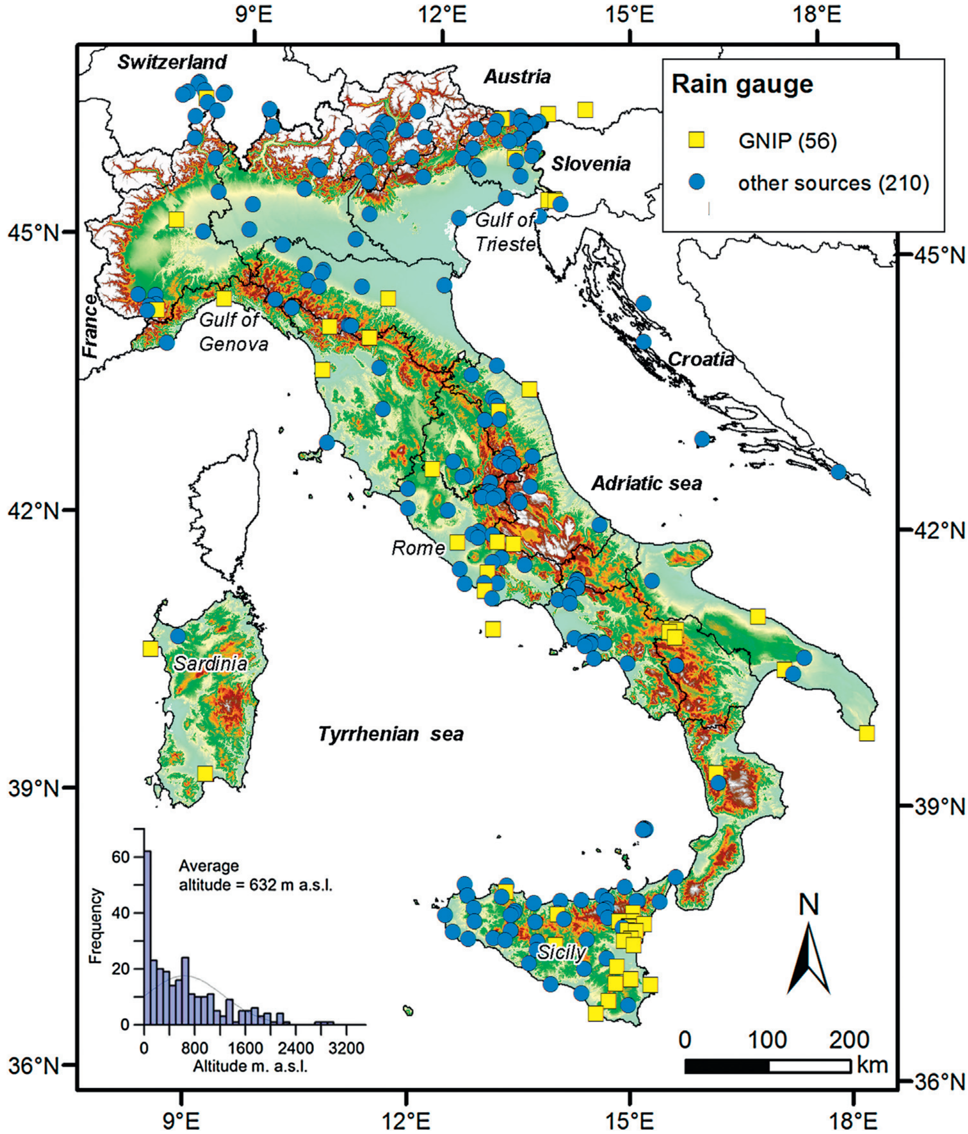

Fig. 1. Map of stations for precipitation monitoring in Italy and adjacent countries, from GNIP database and scientific sources (articles, reports, etc.). In legend, numbers of pluviometers in brackets. Lower left corner: frequency distribution of pluviometer altitudes.

Venezia Giulia and Trentino-Alto Adige, with 23 and 25 rain gauges, respectively) and in central Italy (Latium region, with 29).

Pluviometer elevations differ, from 1 to 2940 m a.s.l., with an average altitude of 632 m. Fig. 1 shows the frequency histogram of elevations. The maximum frequency ranges from 0 to 100 m, above which it falls dramatically and then decreases progressively with altitude. The pluviometers at elevations exceeding 1000 m are mainly located in Alpine regions, although there are several over 1000 m along the Apennine chain and on the flanks of the volcanic edifice of Mt. Etna (which has the highest pluviometer in Italy).

The isotopic data were statistically analysed by multiple regression (Statistica 7.1 software), which provides information on relationships between independent variables (geographical factors: latitude and altitude) and dependent ones (isotopic compositions of oxygen or hydrogen) and can calculate standardised regression coefficients (Beta), the magnitude of which quantifies the relative contribution of each factor in predicting the dependent variable. The coefficients were statistically significant at $p = 0.05$.

The Geographic Information System (GIS) provided the tools to overview the spatial distribution of data, processed by Esri ArcGIS 10^{TM} software. Various interpolation techniques were used to generate spatial representations. The method of Bowen and Wilkinson (2002) was used to map the isotope data across Italy; it consists in: 1) multiple regression model, with elevation and latitude as independent variables; 2) spatial isotopic distribution of the regression by a Digital Elevation

Model (DEM); 3) mapping of the residuals of the calculated and measured isotopes; 4) linear addition of $\delta^{18}O$ and residuals to create a distribution map of $\delta^{18}O$ precipitation. The DEM raster was converted to points to generate a gridded latitude dataset, the latitude for each point was calculated, and the raster was then used to create a new grid with the latitude data. The GTOPO30 (Global 30 arc-second elevation) DEM, from the USGS database (USGS, 2008) with a resolution of $30'' \times 30''$ (about 1 km), was used for the altitude data. This approach partially minimised the irregular distribution of pluviometers across Italy because the gridded datasets of latitude and altitude were built according to an empirical equation for each grid cell by map algebra procedures.

A number of methods have been tested for spatial interpolation, e.g. Inverse Distance Weighted, Natural Neighbour, Spline and Kriging. The method to map the residuals was chosen by examining the results of cross-validation (according to "leaving-one-out" method), evaluating the overall error of each interpolator as the root-mean-square (RMSE) and the average standard error (SE) of the residuals, according to the procedure described by Davis (1987). Ordinary Kriging was the interpolation technique selected to map the spatial distribution of residuals because of the lowest error. Kriging is a geostatistical interpolation method that uses randomly distributed measured data to predict values at any unsampled location within the area of interest, using a weighted average of neighbouring samples; weights are optimized using the semi-variogram model, the location of the samples and all the relevant inter-relationships between known and unknown values. The application of this technique requires to elucidate in advance several aspects of the data (e.g. distribution, trends, directional components), which will influence the selection of the main parameters of the experimental variogram (i.e., sill, range, and nugget). Evaluation of the spatial structure of residuals data was conducted using the Moran's I test; this tool measures the spatial autocorrelation based on both feature locations and feature values simultaneously. The Moran's index of 0.86 with a z-score of 0.99 indicates that the pattern of residuals does not appear to be significantly different from random. Several models, created by setting various parameters, have been tested. Ordinary Kriging, removing a second-order polynomial trend, with a Stable variogram model without anisotropy resulted in the smallest error (RMSE = 0.92; SE = 1.13). The general form of Stable semivariogram is: $\gamma(h) = C_0 + C_1 \left[1 - exp\left(-3\left(\frac{h}{r}\right)^e\right)\right]$ for all h, where $0 < e \leq 2$, C_0 is the nugget effect, C_1 is the sill of the variogram, r is the range parameter, h is the lag distance, i.e. the distance or range of distances between points (Johnston et al., 2001). The experimental model applied to our data results in a nugget value of 0.14, sill value of 1.48, range of 15800 m, power e = 1.9 and lag size of 1800 m. The ratio of the nugget and sill values (0.14 and 1.48, respectively), implying that about 91% of the overall variance in the residual values can be explained in terms of spatial autocorrelation.

Kriging interpolation method extrapolates values outside the extent of the sample points (i.e. the rectangular area defined by the minimum and maximum x-y pairs of coordinates), consequently this allows not to have blank areas (i.e. areas without data predictions).

The maps of this study have the same cell resolution as the DEM, i.e., $30'' \times 30''$. The GTOPO30 DEM constrains map resolution; a DEM with better resolution could not be applied because of hardware limitations in dealing with a huge number of cells.

Only $\delta^{18}O$ maps were built, since many pluviometric data reviewed from the literature cited here do not include δD analysis.

3. Previous isotope studies on precipitation in Italy

Table 1 lists the parameters of the LMWLs (slope, δD intercept, number of samples, R^2), sampling characteristics (period, frequency), methods used to calculate regression equations (monthly or yearly data, arithmetic or weighted averages by amount of precipitation) and vertical isotopic gradients, from the literature.

The slopes of the LMWLs show a large variability, ranging from 4.9 to 9.2 with a mean value of 7.3. Considering that the GMWL of Rozanski et al. (1993) is 8.20, it is possible to confirm that the GMWL equation is generally inadequate to describe precipitation over the Mediterranean area. In northern and central Italy, the LMWL slope values are on average higher than those in southern Italy. Generally, slopes under 8.0 would indicate secondary evaporation, which occurs after condensation as raindrops fall through a column of dry air, imparting kinetic fractionation on the drops themselves (Dansgaard, 1964). This effect is best observed in arid regions like those of southern Italy because, as mathematically demonstrated by Gonfiantini (1986), when humidity is low, kinetic evaporation is maximised and the slope will also be low. When the slope exceeds that of the GMWL, the high values may be due to an artefact of the dataset used (e.g., a dataset which includes two summer seasons and only one winter season, or vice versa) or to anomalous climatic seasons with temperatures higher than the long-term calculated average, as in the case reported by Elmi et al. (2013). In the same way, evaporation and other local processes (annual average temperature, amount of precipitation, elevation, distance from the sea, sea surface temperature, air humidity, wind speed) all influence the values of the δD intercept, which ranges between −9.70 and +21.47, averaging +8.7. In particular, δD intercept values over 10 may indicate primary evaporation controlled by the humidity in the vapour source, as in the case of the eastern Mediterranean meteoric water line, $\delta D = 8\ \delta^{18}O + 22$ (Gat and Carmi, 1970). Cases of negative intercept are often associated with pluviometers located on high, steep slopes in mountain areas (Liotta et al., 2006a; Paternoster et al., 2008; Johnston et al., 2013; Madonia et al., 2013), where the coefficients of the regression lines are influenced by evaporative enrichment of ^{18}O and ^{2}H in raindrops as they fall beneath the cloud base, which is greater at low altitudes where the cloud base is typically high above ground level (the "pseudo-altitude effect"; Moser and Stichler,

Table 1
Local meteoric water lines and altitude isotopic gradients measured in Italy and adjacent countries, from literature. Data type: R = pluviometer; P = well; S = spring; C = cave, drip water; numbers in brackets = number of pluviometers or springs. N = number of samples; D = daily sampling; M = monthly sampling; BM = bimonthly sampling; RA = random sampling; A = annual average; AA = annual arithmetic average; W = weighted average; CA = calculated. Period: Dis = discontinuous.

Data	Region	Area/name of rain gauge	Altitude (m)	Note	Period	N	$\delta^2H = a\ \delta^{18}O + b$		R^2	$\delta^{18}O$‰/100m	Reference
							a	b			
R (77)	Italy		2–2263	W	at least one year		7.61	9.21			Longinelli and Selmo, 2003
R (14)	Western Mediterranean region					146	8.00	13.70			Celle, 2000; Celle-Jeanton et al., 2001
R (9)	Eastern Mediterranean region						7.09	9.40	0.98		Gat et al., 1996
Northern Italy											
R (36)		Northern Italy					7.09	9.40	0.98		Longinelli and Selmo, 2003
R (8)	Valle d'Aosta	Southern Alps	350–3500		1993–1994					−0.23	Novel, 1995
R (7)	Piemonte-Liguria	Maritime Alps	400–2000		1974; 1976		8/7.9	12.8/13.4	0.99	−0.31	Bortolami et al., 1978
R (5)	Trentino	Riva del Garda		M, W	02/2007–01/2008	12	8.23	7.06	0.98		Longinelli et al., 2008
R (12)	Trentino	Eastern Alps	91–2730	M	11/2010–10/2012	143	6.11	7.84	0.94	−0.16	Flaim et al., 2013
R (1)	Trentino	N-E Italy	1176–2731	M [a]	06/2011–10/2012	34	7.6/8	2.7/7.8	0.94	−0.12	Chiogna et al., 2014
C (4)	Trentino	Valsugana Adige/Valley	225–1880		09/2010	21	6.10/6.17	−4.85/−7.20	0.96	−0.08/−0.15	Johnston et al., 2013
R (2)	Trentino	Trento area	312–2125		10/1997–09/1999					0.30/−1.46	Longinelli and Selmo, 2010
R (8)	Veneto-Trentino	Venice region, Venetian Alps	2–2000	W	1970–1974					−0.03/−0.27	Zuppi and Bortolami, 1982
R (1)	Friuli Venezia Giulia (FVG)	Trieste	365	M	09/2001–12/2003	23	7.39	6.5	0.98		Bono et al., 2005
R (13)	FVG	Overall FVG		M						−0.29	Arpa, 2006
R (20)	FVG	Overall FVG	10–1760	M, W, AA	Dis. 2004–2012		7.38/7.98	5.93/10.6	0.97	−0.17	Michelini, 2013
R (1), S	FVG	Basin of Natisone river								−0.29	Pezdič et al., 1996
R (2)	Lombardia-Swiss	Val Chiavenna	330–2150		1998					−0.15/−0.23	Minissale and Vaselli, 2011
R (1)	Lombardia	Pavia			03/2006–09/2007	17	8.8	14.5	0.96		Elmi et al., 2013
R (1)	Lombardia	Milano	122		01/2002–12/2004	9	7.06	2.48	0.98		Longinelli et al., 2006
R (1)	Emilia Romagna	Parma	55		01/2002–12/2004	9	7.73	8.94	0.98		Longinelli et al., 2006
R (1)	Emilia Romagna	Bologna	35	[b]	03/1996–03/2000	48	6.68/7.33	−1.76/4.22	0.92		Cortecci et al., 2008
R (4), S	Emilia Romagna	Parma area	58–495		Dis. (1995–2005)	406	7.56	8.59	0.98	−0.36	Iacumin et al., 2009
	Toscana	Pisa					8.2	11.6			La Ruffa and Panichi, 2000
C (1)	Toscana	Apuan Alps	1637	RA, C	06/2003–02/2007	28	8.95	21.47	0.81		Piccini et al., 2008
	Toscana	Apuan Alps					7.14	6.77	0.98		Mussi et al., 1998

Central Italy											
R (26)	Central Italy	Central Italy, Tyrrhenian side	2–2263	W	at least one year		7.05	5.61	0.95	−0.15	Longinelli and Selmo, 2003
S	Marche	Central Apennine			1987–1990					−0.24	Ciancetti et al., 1991
S (10)	Umbria-Marche	Mts. Sibillini	1310–1836		2003					−0.22	Tarragoni, 2006
R (3), S	Umbria-Marche	Central Apennine	170–1700		2006–2009		7.69	9.38		−0.23	Tazioli et al., 2007
R (9)	Umbria-Marche	Central Apennine	170–1700	M, W [a]	2006–2009	90	7.61	8.35	0.98	−0.17	Nanni et al., 2013
S (18)	Umbria	Eastern Umbria			03/1990–04/1991					−0.24	Conversini and Tazioli, 1993
R (2)	Abruzzo	Gran Sasso massif	685–1024		2000–2001	2	7.76	9.95		−0.24	Barbieri et al., 2005
S (39)	Abruzzo	Central Apennines	400–2200		03,06,11/2002		7.70	9.4	0.98	−0.13	Desiderio et al., 2005
S (20)	Abruzzo	Gran Sasso – Mt. Sirente system	250–1350		1979–1982					−0.14	Celico et al., 1983
S, P (96)	Lazio-Abruzzo	Tyrrhenian side	1–1520		1979–1981		7.62	12.5		−0.13	Celico et al., 1983
R (2)	Lazio	Marcellina Guidonia	67–380		03/2008–09/2009	16	6.7/9.2	2.59/19.63		−0.28	Carucci, 2010
R (5)	Lazio	Tyrrhenian side	5–1750	M, W	09/1998–04/2003	106	7.5	8.8	0.97	−0.24	d'Antona, 2004; Bono et al., 2005
R (7)	Lazio	Rieti plain – Mt. Terminillo	387–1693	W	04/2005–03/2007	110	6.92	0.99	0.78	−0.19	Spadoni et al., 2010
R (11)	Lazio-Umbria-Marche	Tyrrhenian side	4–1452		1971–1972					−0.17/−0.54	Zuppi et al., 1974
R (5)	Lazio-Umbria-Marche	Adriatic side	4–1452		1971–1972					−0.11/−0.33	Zuppi et al., 1974
R (4)	Lazio-Campania	Pontina plain	17–620	M, W			7.07	7.97	0.88	−0.22	Sappa et al., 2012
R (10)	Campania	Mt. Vesuvius	50–1200	M, W	06/2002–05/2004	18	7.2	13	0.98		Madonia et al., 2014
Southern Italy											
R (26)		Southern Italy					6.97	7.32	0.95		Longinelli and Selmo, 2003
R (5)	Basilicata	Mt. Vulture	320–1285	M	04/2002–03/2004	110	6.56	4.12	0.94	−0.17	Paternoster et al., 2008
R (5)	Basilicata	Mt. Vulture	320–1285	M, W	04/2002–03/2004	110	4.92	−9.7	0.94		Paternoster et al., 2008
R (3)	Molise	Isernia area; southern Italy	635–1150	CA	11/2007–10/2008					−0.16	Petrella et al., 2009
R (2)	Molise	Acqua dei Faggi. Longano	1014–1150	M	05/2008–08/2009	15	7.7	12.7	0.96		Petrella and Celico, 2013

Table 1 (*Continued*)

Data	Region	Area/name of rain gauge	Altitude (m)	Note	Period	N	$\delta^2H = a\,\delta^{18}O + b$		R^2	$\delta^{18}O$‰/100m	Reference
							a	b			
R, S (6)	Calabria	Terme Sibarite,	200–300			14	6.7	5.2	0.97		Apollaro et al., 2012
R (2)	Sardegna	Sardegna	1–200			16				−0.29	Nuti et al., 1977
R (3)	Sicilia	North-western Sicily	0–1600		06/1976–03/1979	53				−0.20	Hauser et al., 1980
R (11)	Sicilia	Mt. Etna	0–3000		10/1997–10/2000	270				−0.06/−0.27	D'Alessandro et al., 2004
	Sicilia	Mt. Etna (SE flank)								−0.30	Anzà et al., 1989
R (6)	Sicilia	Mt. Iblei (SE Sicily)	5–980	M	02/1999–01/2001	108	6.5	9.87		−0.20	Grassa et al., 2006
R (1)	Sicilia	Palermo		D/D [c]	10/2005–09/2006	48	6.49/6.81	5.28/6.18	0.90		Liotta et al., 2008
R (2)	Sicilia	Central-western Sicily	530–800	M	12/2000–11/2001	21	6.4	5.5		−0.26	Fontana et al., 2009
R (11)	Sicilia	Northwestern Sicily	12–1100	M, W	02/2002–03/2003	149	4.7	−8.2	0.96	−0.18	Liotta et al., 2006a
R (7)	Sicilia	Northwestern Sicily	12–400	M, W	02/2002–03/2003		7.0	6.0	0.78		Liotta et al., 2006a
R (6)	Sicilia	Stromboli- Aeolian Islands	5–900	BM	10/2003–10/2005	73	6.5	6.7	0.95	−0.22	Liotta et al., 2006b
R (50)	Sicilia	Overall Sicily	5–2490	M, W	05/2004–06/2006	1033	6.75	8.2	0.96	−0.12	Liotta et al., 2013
C (19)	Sicilia	Western Sicily	22–1125		05–12/2010	33	5.20	−3.3	0.77	−0.20	Madonia et al., 2013
Average values (only rainfall data)							**7.3**	**8.6**			
Neighbouring states											
R (5)	Slovenia	Slovenia, on the border with Italy	50–1070	M, W	1993–1995					−0.24	Stichler et al., 1997
R (2)	Slovenia	North Adriatic	2–497	M	2001–2003	36	7.7	7.3/9.6		−0.30	Vreča et al., 2006
R (4)	Croatia	South Adriatic	5–1594	M	2001–2003	35	7.6/6.9	5.1/10.5		−0.24	Vreča et al., 2006
C (1)	Croatia	Zadar (Modrič Cave)	32	BM	05/1999–09/1999	7	7.5	7.1	0.48		Miko et al., 2002
C (1)	Croatia	Zadar (Modrič Cave)	32		07/2007–05/2008	6	7.5	8.5	0.45		Surić et al., 2010
R (6)	Swiss	Northern central Swiss Alps	500–2000							−0.21	Pearson et al., 1991
R (8)	Swiss	Central Alps, Swiss	600–2300		1970–1999		7.65	4.7		−0.23	Ofterdinger et al., 2004
R (2)	France/Swiss	Northern Alps	385–1980							−0.27	Maréchal and Etcheverry, 2003
R (8)	Austria	Eastern Alps								−0.21	Kralik et al., 2003

[a] Rain + snow.
[b] Samples with negative *d* excess not included.
[c] Daily sampling, LMWL calculated as weighted monthly.

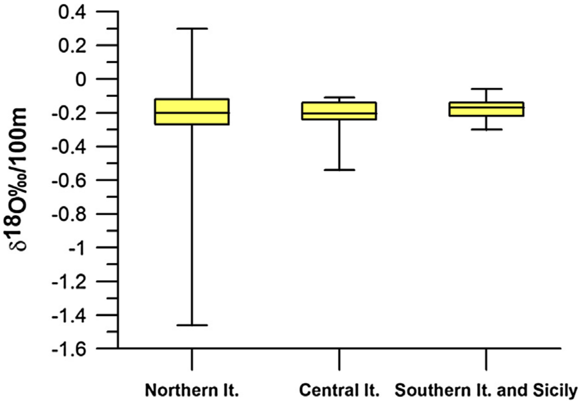

Fig. 2. Box-and-whisker plot of vertical isotopic gradients ($\delta^{18}O$‰/100 m) from literature, in northern (N = 23), central (N = 24) and southern Italy/Sicily (N = 17). See Table 1 for data References.

1974). LMWLs have sometimes been calculated by integrating precipitation data with data from springs (Tazioli et al., 2007; Apollaro et al., 2012), or using spring data alone (Celico et al., 1983; Desiderio et al., 2005). Using groundwater data to determine the isotopic composition of precipitation is generally effective, because the weighted mean annual composition of precipitation over a given region is typically reflected in the isotopic composition of shallow groundwaters in that region (Clark and Fritz, 1997). However, many local factors can substantially change the stable isotope composition of those waters, e.g., a regional water budget dominated by winter snowmelt at high elevation, insufficient infiltration of precipitation during warmer months when evapotranspiration is high, massive evaporation before and/or during infiltration, or interactions with deep fluids enriched in CO_2, H_2S and CH_4, species which characterise the natural gas emissions widespread in Italy (Friedman et al., 1992; Simpkins, 1995; Grassa et al., 2006; Cinti et al., 2011; Liotta et al., 2013). For this reason, LMWLs calculated from groundwater data should be used with caution and, although they are listed in Table 1, they were not included in our database and were not used for further processing of our data.

Lastly, Table 1 also lists the LMWLs calculated in Croatia and Slovenia (Vreča et al., 2006), to compensate for the scarcity of data from pluviometric stations in the Adriatic region. The extrapolation seems to be reasonable, because the values obtained clearly match the meteoric water line of northern Italy reported by Longinelli and Selmo (2003).

The isotope compositions of drip waters in cave systems (Table 1) have been published by many authors (Miko et al., 2002; Piccini et al., 2008; Surić et al., 2010; Johnston et al., 2013; Madonia et al., 2013). The LMWLs reported in these studies are often comparable with data on meteoric lines in the same areas. However, the results are often conflicting, because the isotope signatures of drip waters may sometimes be affected by fractionation due to evaporation: it was for this same reason that such data were excluded from our database and from our later processing.

One of the most useful isotope applications in hydrology is identification of the mean elevation of the recharge area, accomplished by comparing the isotope composition of waters from springs and wells with those of precipitation. This is possible because there is an inverse correlation between $\delta^{18}O$ or δD and elevation: adiabatic cooling due to the rise of a moist air mass causes condensation and loss of moisture, in which water enriched in ^{18}O will condense and precipitate more readily than water enriched in the lighter isotope, ^{16}O, in a temperature-dependent distillation process. Isotopic gradients are described by local-specific regression lines (usually estimated by $\delta^{18}O = a + b^{*}altitude$) obtained by best-fitting data available for a certain area; these gradients show significant variations from one area to another.

The literature data of the vertical isotopic gradients of Italy and adjacent countries, expressed as $\delta^{18}O$‰/100m, are listed in Table 1; the gradient values are also plotted in the box-and-whisker plot of Fig. 2. For northern Italy, the altitude gradient has a mean value of −0.22‰/100 m (N = 23) and ranges from −1.46‰/100 m to +0.30‰/100 m. This large range may be due to the varying positions of the pluviometers in question with respect to the prevailing wind direction and the "shadow effect" of mountain reliefs. This effect is the consequence of an air mass moving over a topographic barrier and the isotopic "altitude effect": the relatively dry air masses on the lee side of mountain ranges have water which is enriched in ^{16}O with respect to wetter air masses on the windward side (Smith et al., 1979; Dray et al., 1997). The higher the range, the more pronounced the isotopic rain shadow. Fig. 2 shows that, apart from extreme values, the largest group of isotopic gradient data fall within the lower and upper quartiles of the dataset (range −0.15 to −0.25‰/100 m).

The gradients obtained for central and southern Italy are less scattered than those for the north (Fig. 2). For central Italy, gradients range from −0.54‰/100 m to −0.11‰/100 m. Despite such extreme values, due to peculiar climatic and geographic situations, the overall mean value for central Italy is −0.22‰/100 m (N = 24), very close to that for northern Italy, and the range between quartiles is similar and slightly narrower.

The values of vertical gradients in southern Italy are even less scattered than those for the rest of the country, but the number of cases is also lower and calculated almost exclusively for Sicily (14 out of 17) (Fig. 2). The average value is −0.19‰/100 m (N = 17). A very low vertical gradient is reported for pluviometric stations from the active volcanic massif of Mt. Etna, where mixing with ^{18}O-rich volcanic vapour affects the isotope composition of precipitation (D'Alessandro et al.,

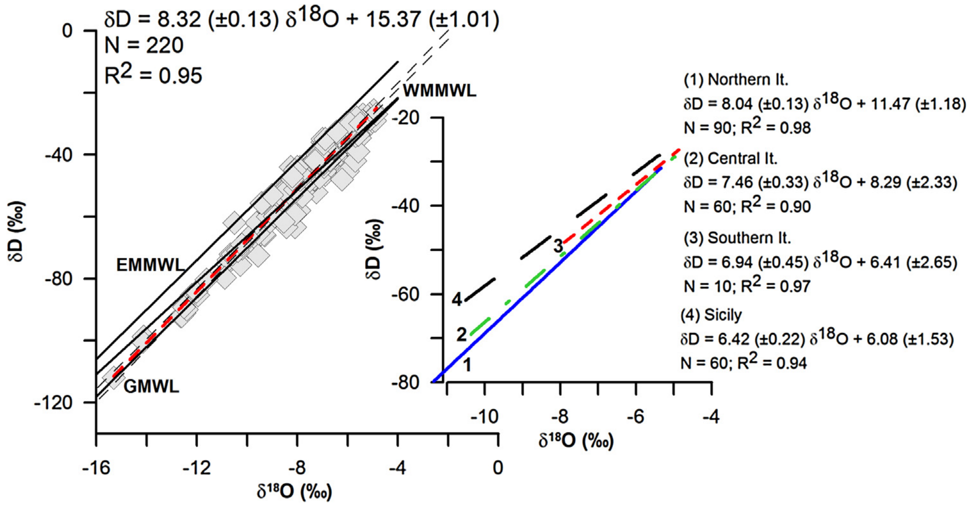

Fig. 3. δD vs. $\delta^{18}O$ diagram of precipitation in Italy. Also shown: Eastern Mediterranean meteoric water line (EMMWL; Gat and Carmi, 1970), Western Mediterranean meteoric water line (WMMWL; Celle, 2000) and global meteoric water line (GMWL; Craig, 1961). The black dashed lines indicate 95% confidence intervals. Right: meteoric water lines calculated for northern, central, southern Italy and Sicily.

2004).The vertical gradients calculated by several authors using data from springs and wells also fall between the upper and lower quartiles (−0.15 and −0.25‰/100 m; Fig. 2) (Celico et al., 1983; Ciancetti et al., 1991; Conversini and Tazioli, 1993; Desiderio et al., 2005; Tarragoni, 2006; Tazioli et al., 2007). Some authors (e.g., Tarragoni, 2006; Spadoni et al., 2010; Minissale and Vaselli, 2011) have evaluated the possibility of using perched, high-mountain springs or karst springs with high flow rates as natural pluviometers. Both approaches seem to be effective, although the same limitations reported for LMWLs calculated from groundwater data remain.

The magnitude of the altitude effect is generally constant, and can be described by linear regression lines, although in some cases the gradient decreases with increasing altitude. This is generally observed in inter-mountain valleys and on the lee side of mountain ranges, and may be due to the "pseudo-altitude effect" (Moser and Stichler, 1974). Examples of non-linear isotopic vertical gradients and/or orographic control on $\delta^{18}O$ have been reported for the Alps (Johnston et al., 2013) and Vesuvius (Madonia et al., 2014), and, in Sicily, for Etna (D'Alessandro et al., 2004) and the western mountain chains (Liotta et al., 2006a; Madonia et al., 2013).

4. Results and discussion

4.1. Isotope composition of precipitation

The relationship between the oxygen and hydrogen isotope composition of precipitation according to the database created for this study is shown in Fig. 3 (for data [yearly average of $\delta^{18}O$ and δD, and related *d*-excess values] and their sources, see online Supplementary material). The isotopic data show a large range of values ($\delta^{18}O$ from −15.30 to −4.11‰, N = 266; δD from −112 to −20‰, N = 221). The most depleted ^{18}O and deuterium values correspond to samples collected at Alpine stations, and the most ^{18}O and D-enriched values to the maritime station of Cagliari-Elmas (Sardinia).

The $\delta^{18}O$ vs. δD plot shows that almost all the precipitation data fall between the GMWL of Craig (1961) and the eastern Mediterranean meteoric water line (EMMWL) of Gat and Carmi (1970). The best-fit regression line, representing the Italian Meteoric Water Line (IMWL), is:

$$\delta D = 8.32(\pm 0.13)\delta^{18}O + 15.37(\pm 1.01)(N = 220; R^2 = 0.95) \quad (1)$$

which, considering the uncertainties reported as the standard error of the slope and intercept, is very close to the GMWL. The IMWL is also very close to the western Mediterranean meteoric water line (WMMWL) (δD = 7.43 $\delta^{18}O$ + 8.06; calculated using the data reported in Celle, 2000), as expected because Italy is open to the influence of air masses coming from Atlantic ocean and Africa. The GMWL and WMMWL partly fall within the 95% confidence limits of the IMWL. Statistical differences between Celle's WMMWL and IMWL, and Rozanski et al.'s GMWL and IMWL are summarized in Table 2. The IMWL has a slope statistically different from the slope of the regression line of WMMWL at p level <0.01, and it has not from that of the GMWL of Rozanski et al. Setting an identical value of the IMWL-GMWL slopes, it is possible to calculate the new intercept values that give the offset of the two lines: they have a difference of 3.26‰ with a statistical significance at $p < 0.0001$ level.

Examining separately the values from northern (above lat. 43.5° N), central (between 43.5° and 40.4° N), southern Italy (between 40.4° and 39.0° N) and Sicily (less than 39.0° N), four different equations can be formulated (Fig. 3). The northern meteoric water line (slope 8.04, intercept 11.47) is the value most similar to the GMWL, whereas the lines for central and

Table 2
Report of the analysis of variance between GMWL, WMMWL and IMWL.

ANOVA	Degrees of freedom	Sum of squares	Mean square	F	p-value
Comparison Coefficient between WMMWL and IMWL	1	269.01	269.01	12.83	0.0004
Intercept	1	180.12	180.12	19.17	<0.0001
Comparison Coefficient between GMWL and IWML	1	12.693	12.693	0.80	0.3705
Intercept	1	1125.26	1125.26	71.24	<0.0001

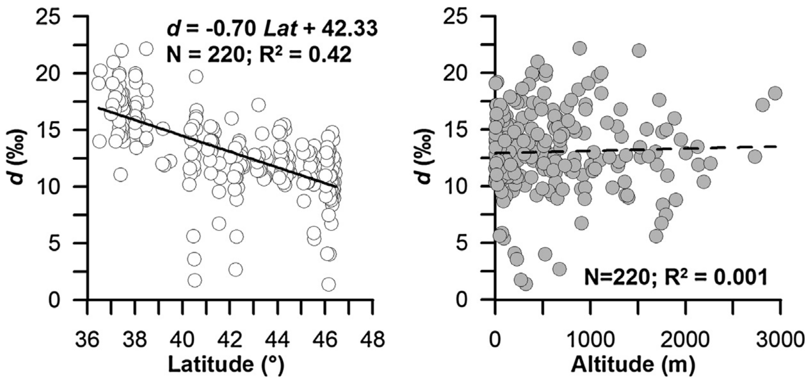

Fig. 4. Deuterium excess in precipitation, plotted versus latitude and altitude.

southern Italy and Sicily have progressively smaller slopes (7.46, 6.94, 6.42, respectively) and the intercepts consequently have the same tendency (8.29, 6.41, 6.08). Similar features of oxygen and hydrogen isotope data have been observed and documented at various locations worldwide, and are attributed to factors such as condensation temperature (Dansgaard, 1964; Hartley, 1981), origin of air mass vapour (Gat and Dansgaard, 1972), and evaporation and isotopic exchange between falling rain and atmospheric water vapour (Stewart, 1975). As noted by Longinelli and Selmo (2003), this north-south trend is due to air masses of various provenances which interact in the central Mediterranean basin, as also confirmed by the variability in the deuterium excess values. The deuterium excess is the difference $d = \delta D - 8\,\delta^{18}O$, a parameter first introduced by Dansgaard (1964) and still regarded as the most useful factor for characterising the origin of water vapour (Gat and Carmi, 1970). In general, high *d* values reflect fast evaporation, due to lower relative humidity and more pronounced kinetic isotope effects during evaporation; conversely, low *d* values reflect slow evaporation due to high humidity (Clark and Fritz, 1997). Therefore, air masses deriving from the Mediterranean Sea have higher deuterium excess values (d = +22‰; Gat and Carmi, 1970) than those of Atlantic provenance (d = +10‰; Craig, 1961). Deuterium excess in Italian precipitation varies between 1‰ and 22‰ and is correlated with latitude, not with elevation (Fig. 4.). The relatively low correlation ($R^2 = 0.42$) between *d* and latitude suggests more complex relationships between these variables, which probably require monthly or daily data before a more definite conclusion can be reached. In low-latitude regions (i.e., southern Italy, especially Sicily), *d* values of up to 22‰ indicate that the moisture prevalently originates from the Mediterranean Sea; increasing latitude, *d* values are around 10‰, indicating the greater influence of air mass vapour originating from the Atlantic. The lack of correlation between deuterium excess and altitude may depend on the different provenance and evolution of the moisture. Some relatively low-altitude stations in central-northern Italy have *d* values of less than 10‰; such values are frequent in Europe (Rank and Papesch, 2005; Carreira et al., 2005; Vreča et al., 2006; Stumpp et al., 2014) and are attributed to fractionation processes such as snow formation, partial evaporation of raindrops in a warm, dry atmosphere, and/or the peculiar morphology of the area in question (Araguás-Araguás et al., 2000; Rank and Papesch, 2005).

4.2. Isotope effects due to latitude vs. altitude

The differing locations of rain gauges imply that geographical factors – latitude and altitude – influence the oxygen and hydrogen isotope composition of precipitation. Italian pluviometric stations are distributed between 36°N and 47°N in latitude, whereas station altitudes range from sea level (both Tyrrhenian and Adriatic coastal stations) to 2940 m (on Etna).

The regression coefficients in a multiple regression analysis were calculated, to evaluate the relative contribution of each geographical factor on oxygen and hydrogen isotope compositions. Correlation coefficients for latitude and altitude versus oxygen isotopes were −0.390 ($p \le 0.05$) and −0.602 ($p \le 0.05$), respectively, indicating that both factors are correlated with the $\delta^{18}O$ of precipitation, although the altitude effect contributes most. For hydrogen, the correlation coefficients are −0.533 ($p \le 0.05$) for latitude and −0.519 ($p \le 0.05$) for altitude variable; according to these results, the regression indicates that both factors are important geographic controls. In principle, variations in $\delta^{18}O$ and δD are coupled, so that any difference in the results of the two regressions may be caused either by the different dataset used or different kinetic fractionation processes of hydrogen and oxygen during evaporation. In order to eliminate the possibility that the different results of the

Table 3
Beta coefficients of multiple regression analysis. Coefficient significance: $p < 0.05$.

Variable	N	Beta	Std. Err. of Beta	B	Std. Err. of B	t	p-value
$\delta^{18}O$ (Italy, including Sicily)	265					t (262)	
Latitude		−0.390	0.040	−0.227	0.023	−9.818	0.000
Altitude		−0.602	0.040	−0.002	0.000	−15.148	0.000
$\delta^{18}O$ (Italy, excluding Sicily)	198					t (195)	
Latitude		−0.362	0.041	−0.340	0.039	−8.775	0.000
Altitude		−0.648	0.041	−0.002	0.000	−15.708	0.000
δD (Italy)	220					t (217)	
Latitude		−0.533	0.041	−2.536	0.193	−13.141	0.000
Altitude		−0.519	0.041	−0.013	0.001	−12.801	0.000
$\delta^{18}O$ [a] (Italy)	220					t (217)	
Latitude		−0.403	0.044	−0.226	0.025	−9.184	0.000
Altitude		−0.589	0.044	−0.002	0.000	−13.441	0.000

[a] Coefficient calculated with same dataset used for δD.

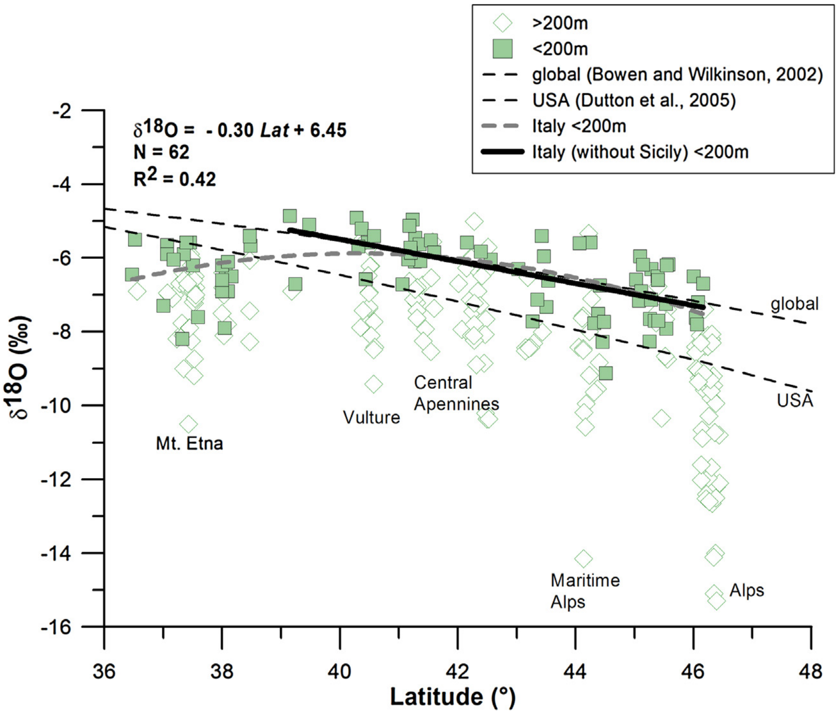

Fig. 5. $\delta^{18}O$ values of precipitation plotted versus latitude. Stations over elevation of 200 m not considered in calculation of regression lines. Also shown: main mountain reliefs. Best-fit line describing dependency of latitude and $\delta^{18}O$ for Italian precipitation (excluding data from Sicily) is shown (solid line) and equation is that reported in figure. Dashed grey line: approximation line including Sicily (see Eq. (2) in text). For comparison, second-order polynomial best-fit lines from global and USA precipitations (dashed black lines) (Bowen and Wilkinson, 2002; Dutton et al., 2005), both calculated for stations lower than 200 m.

regression were due to the different dataset used for oxygen and hydrogen, a new regression was performed on the oxygen isotope compositions for the same stations which were used in the hydrogen regression. The new coefficients for latitude and altitude turned out to be −0.403 ($p \leq 0.05$) and −0.589 ($p \leq 0.05$), respectively, confirming the results obtained with the larger dataset, i.e., the coefficients for latitude and altitude differ by about the same amount, and that altitude contributes more than latitude to the geographic control of $\delta^{18}O$ distribution (Table 3).

To better explore the latitude effect and separate it from that of altitude, which may interfere because most of the high-latitude stations are in mountainous regions, $\delta^{18}O$ values versus latitude were plotted, distinguishing stations lower than 200 m from higher ones (Fig. 5). This elevation limit was selected because there is no significant relation between $\delta^{18}O$ and elevation below 200 m (Bowen and Wilkinson, 2002; Dutton et al., 2005; Dotsika et al., 2010). The mean values of $\delta^{18}O$ from stations at <200 m ($\delta^{18}O$ = −6.43‰, N = 85) and >200 m ($\delta^{18}O$ = −8.33‰, N = 181) are statistically different at the 99% significance level (Student's *t*-test). The relationship between $\delta^{18}O$ and latitude showed in Fig. 5 is evidently not linear, because isotope data concentrated at low latitudes, especially in Sicily, tend to be more depleted in ^{18}O than expected at such latitudes (see the grey dashed line). In order to quantify the latitudinal gradient alone, we calculated a second-order

Table 4
Report of the analysis of variance of the linear and quadratic regressions.

Linear		Std. Err.	Stat t		p-value
R	0.65				
R^2	0.42				
Std. Err.	0.74				
coeff.1	−0.30	1.95	3.30		1.1E−08
coeff.2	–				
Intercept	6.45	0.05	−6.62		1.62E−03
ANOVA	Degrees of freedom	Sum of squares	Mean square	F	p-value
Regression	1	24.194	24.194	43.840	1.1E−08
Residual	60	33.112	0.5519		
Tot.	61	57.306			
Quadratic		Std. Err.	Stat t		p-value
R	0.65				
R^2	0.42				
Std. Err.	0.75				
coeff.1	−0.62	51.85	0.26		0.89
coeff.2	0.0037	2.42	−0.26		0.80
Intercept	13.33	0.03	0.13		0.80
ANOVA	Degrees of freedom	Sum of squares	Mean square	F	p-value
Regression	2	24.204	12.102	21.570	9.31E−08
Residual	59	33.102	0.5611		
Tot.	61	57.306			

Table 5
Vertical isotope gradient, independent of latitude effect, calculated by difference between $\delta^{18}O$ measured and predicted by latitude model of Eq. (3) (see text).

	N	$\delta^{18}O_{RES}$‰/100m	R^2
Italy	198	−0.22	0.60
Northern Italy	104	−0.23	0.58
Central Italy	83	−0.20	0.58
Southern Italy	11	−0.22	0.52

polynomial regression $\delta^{18}O/Lat$, without the stations higher than 200 m, following the examples for global scale precipitation (Bowen and Wilkinson, 2002) and for precipitation in the USA (Dutton et al., 2005) and in Greece (Dotsika et al., 2010):

$$\delta^{18}O_{<200m} = -0.052Lat^2 + 4.15Lat - 89.4 (N = 85; R^2 = 0.30) \quad (2)$$

where *Lat* is latitude expressed in decimals. The correlation is low ($R^2 = 0.30$), probably because Italy has a limited range of latitudes, and substantial local effects and mixed moisture provenance from the Atlantic Ocean and the Mediterranean Sea may occur. Such different sources of water vapour make the isotopic compositions of Italian precipitations more positive than those of North America at comparable latitudes (Fig. 5): mixed moisture from Africa and the Atlantic Ocean, which is influenced by the warm Gulf Stream waters, imparts an ^{18}O-enriched character to precipitation. The trend of Italian precipitation matches the global model between lat. 40°N and 47°N, corresponding to the range of latitude of peninsular Italy; here, the relationship between latitude and precipitation $\delta^{18}O$ is approximately linear, with a decreasing gradient of −0.30‰/°*Lat*. This value is lower than those observed for coastal and continental stations in Europe and the USA (i.e. −0.6‰/°; Gat et al., 2001), but comparable with that from China (i.e. −0.22‰/°; Liu et al., 2014). Clearly, the discrepancy between the behaviour of the $\delta^{18}O/Lat$ relationship of Italian and worldwide precipitation is due to data concentrated at low latitudes, i.e. in Sicily, where it may reasonably be assumed that isotopes in precipitation are influenced by local conditions because of its insular nature. If the data for Sicily are excluded, the $\delta^{18}O/Lat$ relationship produces a different covariation which can be better approximated by a linear equation:

$$\delta^{18}O_{<200m} = -0.30Lat + 6.45 (N = 62; R^2 = 0.42) \quad (3)$$

represented in Fig. 5 by the solid black line, running parallel to the USA and Global lines and even showing an improved correlation. The statistical comparison between linear and quadratic (that is commonly used in literature) approximations using data without Sicily is summarized in Table 4. It mainly indicates that the curvature of the second order approximation is scarcely significant and the linear regression is statistically the best choice.

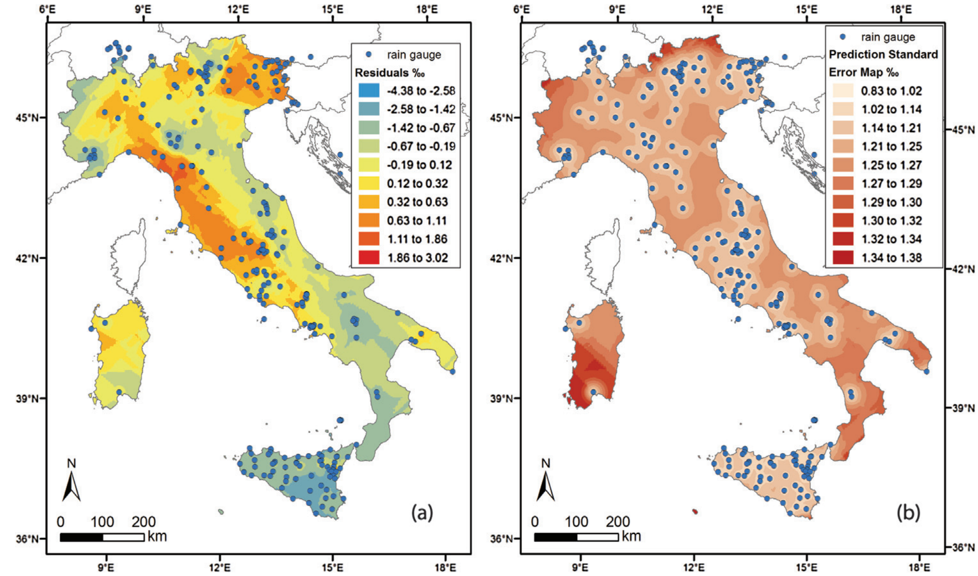

Fig. 6. (a) Spatial distribution of differences between measured and predicted $\delta^{18}O$ produced with Kriging interpolation method; (b) prediction standard error map of the Kriging model.

$\delta^{18}O$ values become depleted with increasing altitude, as expected by the Rayleigh distillation process of water vapour as air masses orographically rise and cool. The isotope/elevation correlation was quantified (Table 5) as:

$$\delta^{18}O_{RES} = -0.0022h(N = 198; R^2 = 0.60) \quad (4)$$

where $\delta^{18}O_{RES}$ is the difference between measured $\delta^{18}O$ and that predicted by Eq. (3) and h is station elevation in metres, with zero intercept. This approach allows us to examine the latitude-independent effect of altitude on oxygen isotope composition (Bowen and Wilkinson, 2002; Dutton et al., 2005). The slope of Eq. (4), which can also be expressed as −0.22‰/100 m, is very close to the mean value of the vertical gradients measured in the Italian literature, in which $\delta^{18}O$ (measured) vs. altitude were simply calculated by linear regression (Fig. 2, Table 1). Eq. (4) can be used to calculate the gradient value of −0.23‰/100 m (N = 104) for northern Italy, −0.20‰/100 m (N = 83) for the centre, and −0.22‰/100 m (N = 11) for the south (excluding Sicily) (Table 5). All these gradients are comparable with those reported in the literature (Fig. 2; Table 1).

On the scale of the whole of Italy, the oxygen isotope composition of precipitation may be represented by the sum of latitude and altitude effects by linear addition of Eqs. (3) and (4):

$$\delta^{18}O = -0.30Lat + 6.45 - 0.0022h \quad (5)$$

The differences between measured and $\delta^{18}O$ values calculated by Eq. (5) range from −4.3 to +3.3‰, standard deviation σ 1.24‰ and mean −0.183‰. These differences, greater in the more depleted samples, may reflect factors influencing $\delta^{18}O$, such as the amount effect, relative humidity and the "shadow effect" of mountain reliefs. The differences between measured and predicted $\delta^{18}O$ were mapped using the Ordinary Kriging interpolation method described in Section 2 (Fig. 6a). Cross validation was applied (i.e. leaving one point out and use the rest to predict the value at that location). The results of that validation show that the predicted values match those measured: the mean prediction error (ME = 0.014) and the mean standardized error (MSE = 0.009) are close to zero, indicating that the interpolation method is unbiased (centred on the true values) and the model is accurate; the average standard error (SE = 1.13) is greater than the root mean squared prediction error (RMSE = 0.92), and this shows that the interpolation method slightly overestimates the variability in the predictions. Fig. 6b shows the standard error map (in ‰); the values of the contour map give the width of one standard deviation. Near rain gauges, the uncertainty about residuals is very low; at a great distance from the nearest rain gauges, such as in the south Sardinia, over the Alps and partly in south of the peninsula, the uncertainty is relatively large and the standard error can exceeds 1‰, up to 1.38‰.

The map of the residuals (Fig. 6a) highlights the areas where local factors (i.e., independent of altitude and latitude) play a role in determining the isotopic composition of precipitation, taking also into account that remarkable residuals may be generated in those areas where the interpolation uncertainty is high. The map shows that the residuals are strongly affected by the orography: predicted values are more negative than those measured mainly in north-east Italy and along the Tyrrhenian coast and, to a lesser extent, in a few random points along the peninsula. In these areas, one or more local processes tend to enrich the ^{18}O content of precipitation: relative humidity, temperature, amount of precipitation, wind direction, large bodies of surface water and orography. In particular, because Italy has a complicated terrain, some parameters such as the distance from the nearest coast, the slope and aspect of the terrain, the presence of narrow valleys or isolated reliefs, can influence the isotope composition of precipitation. To investigate such relationships, the analysis of correlation (F-test)

Table 6
Report of the analysis of variance between $\delta^{18}O$ and the distance from the nearest coast, slope, sine and cosine values of the aspect of the terrain.

Regression statistics		ANOVA	Degrees of freedom	Sum of squares	Mean square	F	p-value
$\delta^{18}O$ – distance from the nearest coast							
R	0.73	Regression	1	502.210	502.210	299.159	2.78E–45
R^2	0.53	Residual	263	441.508	1.679		
Std. Err.	1.30	Tot.	264	943.718			
$\delta^{18}O$ – slope							
R	0.26	Regression	1	37.365	37.365	17.360	4.34E–05
R^2	0.07	Residual	237	510.106	2.152		
Std. Err.	1.47	Tot.	238	547.471			
$\delta^{18}O$ – aspect (cosine)							
R	0.06	Regression	1	2.063	2.063	0.896	0.344696
R^2	0.00	Residual	237	545.394	2.301		
Std. Err.	1.52	Tot.	238	547.457			
$\delta^{18}O$ – aspect (sine)							
R	0.03	Regression	1	0.527	0.527	0.228	0.633213
R^2	0.00	Residual	237	546.930	2.308		
Std. Err.	1.52	Tot.	238	547.457			

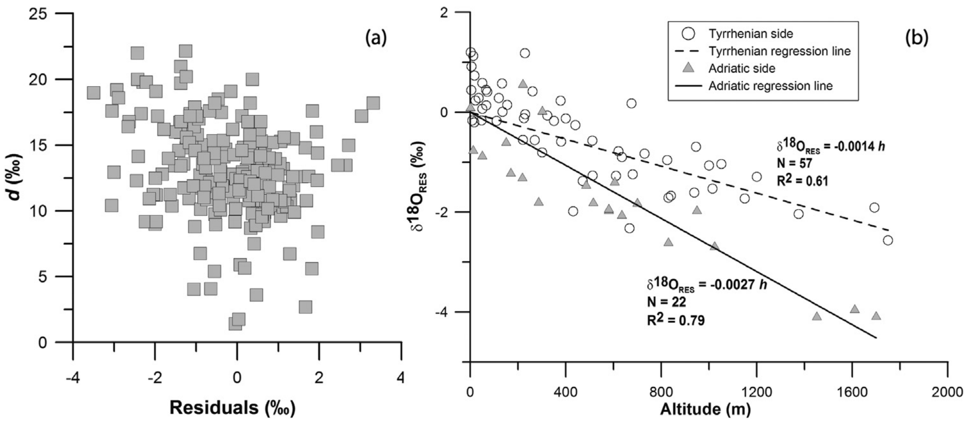

Fig. 7. (a) Precipitation deuterium excess plotted versus residuals calculated from Eq. (5); (b) $\delta^{18}O_{RES}$ versus elevation for Adriatic and Tyrrhenian coasts.

between $\delta^{18}O$ and the distance from the nearest coast, the slope and aspect (converted to sine and cosine values to capture the west-east and the north-south gradient, respectively) of the terrain (calculated from DEM) were explored; isotope data show high correlation with the distance from the coast, as expected; the slope and aspect of the terrain do not evidence any significant correlation (Table 6).

As a general consideration, relative humidity does not seem to be the main factor enriching oxygen isotope composition, because of the low correlation between deuterium excess and $\delta^{18}O$ residuals (Fig. 7a). The other factors cannot be evaluated on this scale, and detailed regional studies may help to explain these positive anomalies and quantify the relative importance of each factor.

The predicted values are higher than those measured in some alpine regions, in a north-south band in the southern Apennines and in some points along the eastern flank of the Apennines. In particular, it should be noted that the Adriatic side of the peninsula has oxygen isotopic values which are about 2‰ lower than those on the Tyrrhenian side at the same latitude. This is due to the rain shadow of the Apennine barrier which Eq. (5) evidently cannot fully represent; this effect is also visible when $\delta^{18}O_{RES}$ is plotted vs. rainfall elevation on the Adriatic and Tyrrhenian sides of the peninsula, as the Apennine watershed is the dividing line between the two sectors (Fig. 7b). The $\delta^{18}O$/altitude gradient in linear regression turns out to be highly variable across the peninsula from west to east, from −0.14‰/100 m to −0.27‰/100 m.

4.3. Mapping ^{18}O content in Italian precipitation

As water-stable isotopes are one of the most frequently used natural tracers in hydrogeological and climatological studies, many maps of isotopic compositions of precipitation have recently been produced, on several scales and according to various approaches: from global (Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003; van der Veer et al., 2008; Terzer et al., 2013) to regional or national (Araguás-Araguás and Díaz Teijeiro, 2005; Dutton et al., 2005; Millot et al., 2010; Dotsika et al., 2010; Lykoudis et al., 2010; Delavau et al., 2011; Lechler and Niemi, 2011; Holko et al., 2012). Although Bowen and Wilkinson method has been firstly conducted on global scale, however it was successfully applied in a number of subsequent regional

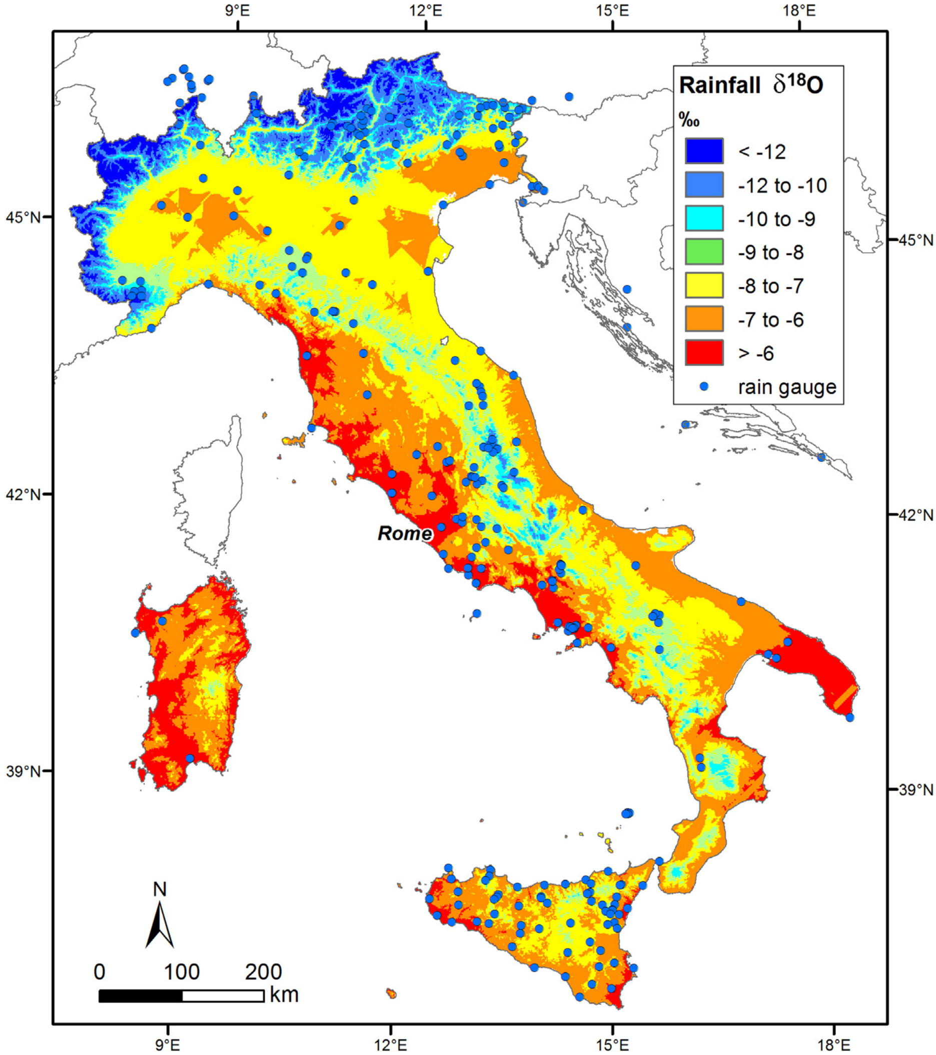

Fig. 8. Map of spatial distribution of $\delta^{18}O$ (‰) of precipitations in Italy.

contexts (Dutton et al., 2005; Dotsika et al., 2010). In the present paper we have preferred the Bowen and Wilkinson method to others because it allows to model and emphasize the altitude and latitude parameters, which are statistically important factors. In addition, using the empirical relation we would emphasize the role of the residuals, that allows to highlight the areas where local factors influence the ^{18}O content.

Although many papers and data exist about the oxygen isotope compositions of precipitation in Italy, only two contour maps of $\delta^{18}O$ on a national scale are available. The first was developed by IAEA from GNIP data (IAEA, 2001), as part of the worldwide mapping project. Obviously, it is on a very small scale, on which only regional trends can be identified: northern-central Italy is characterised by an undistinguished range of precipitation with $\delta^{18}O$ between −8‰ and −11‰, whereas southern Italy, including the islands of Sicily and Sardinia, fall between −5‰ to −8‰. The map by Longinelli and Selmo (2003) was the first to be produced on a national scale and was based on a large number of isotopic data (77 stations). It gives the overall variability of the mean oxygen isotope composition of precipitation in Italy using contour lines, although the authors do not explain which interpolation method they applied to make it. This map shows that, despite its wide latitudinal extension, the depletion in $\delta^{18}O$ with increasing latitude may be considered negligible in most of the peninsula, although a slight latitude effect can be found in the south-easternmost section (Apulia), partly favoured by local morphology. Instead, with few exceptions, isotope variations are greatly affected by orography and by the marked "rain shadow effect" due to the Apennine range.

In the present work, a new map of $\delta^{18}O$ distribution of precipitation in Italian territory (Fig. 8) was generated with a considerable number of data (N = 266) from the literature reviewed here, and from Bowen and Wilkinson's (2002) method for spatial interpolation. Isotopic data from stations in France, Switzerland, Austria, Slovenia and Croatia were also used to constrain interpolations at Italian borders.

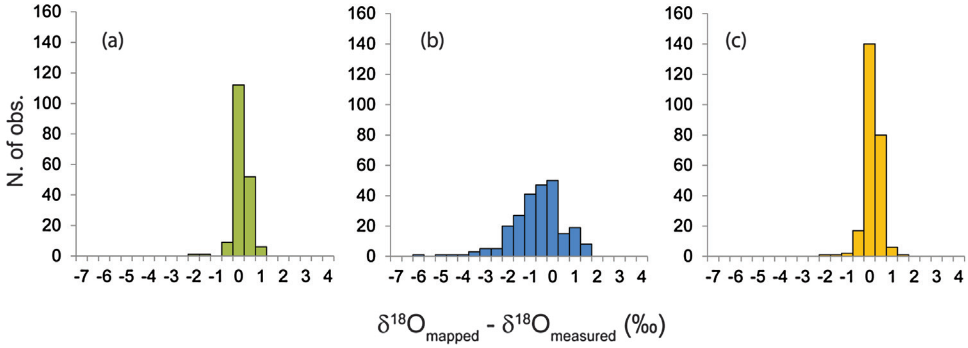

Fig. 9. Histograms of deviations mapped from measured data. (a) $\delta^{18}O$ deviations mapped in Fig. 8 from $\delta^{18}O$ measured; (b) deviations of $\delta^{18}O$ of a map made according to Eq. (2), including data from Sicily, from $\delta^{18}O$ measured; (c) deviations of $\delta^{18}O$ mapped in Fig. 8 from $\delta^{18}O$ measured, including deviations of data from Sicily.

This map is the result of the linear addition of the residual map (Fig. 6a) and the raster grid of $\delta^{18}O$ values obtained from Eq. (5); in this way, the influence of latitude and altitude variables was combined with local factors highlighted by the residual map. The resulting values are in remarkably good agreement with the values measured, as can clearly be seen from the histogram illustrating the mapped − measured oxygen isotopic compositions (Fig. 9a). Maximum deviations of 2‰ are reported only for a few cases; those of the data from Sicily are not represented. The histogram of these differences was also created using isotopes calculated by Eq. (2), which also includes data from Sicily, and the consequent residuals (Fig. 9b); the much larger distribution of deviations (from −6‰ to 2‰) is evident, demonstrating that the quantity and value of the Sicilian data deteriorate the representation of the isotopes in Italian peninsula precipitation and that the map of Fig. 8 is the best possible one. The last histogram of Fig. 9c shows the distributions of deviations from measured data, including those predicted from Sicily, although the Sicilian measured data were not used to formulate Eq. (5).

The map suffers from some limitations reported previously in similar studies: (i) it is not based on consistent time-interval data (yearly averages of $\delta^{18}O$ refer to different periods of time for different recording stations, and all stations selected had been active for one year at least, but not all of them were operating during the same time-interval); (ii) unverified local "bulls-eye" anomalies were occasionally observed, probably as a consequence of the interpolation routine, although regional trends are still clearly visible beyond the anomalies.

The map is very sensitive to variations in latitude and altitude. The $\delta^{18}O$ distribution over the Alps clearly depends on latitude and altitude, while 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 follow the axis of the chain, tracing the orography in detail and in a clear-cut pattern. The isotope compositions on the western side of the Italian peninsula are generally higher than those on the eastern side at the same elevation and latitude, and isotope compositions are generally uniform in the northern plain. In southern Italy and on Sardinia, where the density of pluviometers is minimum, Bowen and Wilkinson's (2002) method allows intense extrapolation, assuming that the algorithm used for building the map is valid throughout the peninsula. Precipitation in Sicily, although not represented in Eq. (5) to model the isotope distribution of Italian precipitation, is nevertheless well represented in the map (Fig. 8) with the negative isotopic peak of Mt. Etna and the isotopic distribution over the main island elevations. In any case, representing Sicilian isotope precipitation can be more effectively performed by treating Sicily separately.

Longinelli and Selmo's (2003) map, at first sight, looks similar to the map created in this study, but it does differ in several respects. Apart from the different level of detail, that the number of recording stations we used and the method used to draw the map obviously imply, the two maps differ in some macroscopic contexts. The former does not represent the positive inflection of isotope values to the north from the gulfs of Genova and Trieste, and overestimates the positive excursion of contour lines into the Po Plain and northern Adriatic coast. In addition, the isotope values of the reliefs are generally less negative than those of our map, which profits by the large number of stations at high elevations in both the Alps and the Apennines. Lastly, the behaviour of precipitation in southern Italy could not be predicted in detail on Longinelli and Selmo's map because of the limited number of pluviometric stations and the weaker extrapolation power of the interpolator used.

5. Conclusions

This paper reviews all the available data of local meteoric water lines and vertical isotopic gradients of Italian precipitation in the literature. Using published $\delta^{18}O$ data, we studied the spatial distribution of this parameter in order to provide basic information and identify locally significant parameters which affect isotopic distributions of precipitation in Italy.

Our new Italian meteoric water line is $\delta D = 8.32\ (\pm 0.13)\ \delta^{18}O + 15.37\ (\pm 1.01)$ ($N = 220$; $R^2 = 0.95$). Four local meteoric water lines, for northern ($\delta D = 8.04\ (\pm 0.13)\ \delta^{18}O + 11.47\ (\pm 1.18)$), central ($\delta D = 7.46\ (\pm 0.32)\ \delta^{18}O + 8.29\ (\pm 2.33)$) and southern Italy ($\delta D = 6.94\ (\pm 0.45)\ \delta^{18}O + 6.41\ (\pm 2.65)$) and Sicily ($\delta D = 6.42\ (\pm 0.22)\ \delta^{18}O + 6.08\ (\pm 1.53)$) were also formulated. Deuterium excess values confirm the provenance of moisture in southern Italy mainly from Mediterranean Sea, while in central and northern Italy it appears to be the product of mixing of Mediterranean and Atlantic waters.

Geographic controls on the oxygen isotope composition of precipitation were examined by multiple regression analysis: both altitude and latitude are correlated with $\delta^{18}O$, but the altitude effect is statistically the most significant factor. On the scale of the whole country, $\delta^{18}O$ can be described by the equation $\delta^{18}O = -0.30\ Lat + 6.45 - 0.0022\ h$, to formulate which only data from pluviometers at altitudes under 200 m were used. This was done to isolate the effect of latitude from that of altitude. The isotope data from Sicily were not considered, as they seemed to be affected by local effects, showing an anomalous decrease when compared with data for the peninsula. Vertical isotopic gradients, calculated as the difference between $\delta^{18}O$ measured and predicted by the equation $\delta^{18}O/Lat$, are quite stable from north to south, at a value of about −0.22‰/100 m, but they vary considerably from west to east (−0.14‰/100 m to −0.27‰/100 m).

A map of the spatial distribution of $\delta^{18}O$ was drawn according to the above equation and the interpolation method, as described by Bowen and Wilkinson (2002). Data for adjacent countries were taken into account to better constrain contour lines along borders. The map differs from the only previously published map of isotopes of meteoric water specific to Italian territory by Longinelli and Selmo (2003), primarily because of the greatly increased spatial density of recording stations across the interior of Italy, with a remarkable contribution from high-altitude stations. The main features of the new map are: 1) the isotopic signatures of Italian precipitations vary with latitude and altitude over the northern Alpine regions, but generally follow elevations along the Apennines in the peninsula; 2) the "rain shadow effect" of the Apennines with respect to the Adriatic side of the peninsula is clear-cut, since the isotopic signatures are about 2‰ depleted with respect to those of the Tyrrhenian coast at the same latitude; 3) in the northern Italian plain, isotope compositions are more or less uniform between −7 and −8‰. Despite the small number of pluviometers in the southernmost parts of Italy and on Sardinia, the method of making the map does reliably represent the distribution of $\delta^{18}O$ in precipitation in every part of the peninsula. Sicily is also represented on our map, with good results, although previous studies focussed on $\delta^{18}O$ distribution devoted exclusively to the island might have generated an even better representation (Liotta et al., 2013).

Unlike the $\delta^{18}O$ map of Longinelli and Selmo (2003), the new map is much more detailed in the isotope patterns of $\delta^{18}O$ distribution, and also highlights two areas in the north-east and north-west (the gulfs of Trieste and Genova, respectively) characterised by relatively high isotopic values, perhaps due to the geography of the areas and the origin of air masses; the isotope values of the Alpine and Apennine reliefs are generally more negative.

The map of the residuals (Fig. 6a), between the $\delta^{18}O$ values predicted by Eq. (5) and measured ones, highlights the areas where local factors play an important role in determining the isotopic composition of precipitation. In these areas, detailed regional studies can help to clarify what processes generate these anomalies and to quantify their relative importance.

The map of the spatial distribution of $\delta^{18}O$ in Italy could be used as a reference for studies concerning hydrology and hydrogeology, paleoclimatology and archaeology, wherever water sources have to be assumed. The online Supplementary material provides a GIS map giving the isotopic compositions of every point on Italian territory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ejrh.2016.04.001.

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