Rendiconti Lincei. Scienze Fisiche e Naturali (2019) 30:667–680
https://doi.org/10.1007/s12210-019-00847-z

First evaluation of water stable isotopes data for the groundwater bodies in Campania

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Received: 28 August 2018 / Accepted: 7 September 2019 / Published online: 21 September 2019

Abstract

The oxygen ($\delta^{18}O$) and hydrogen (δ^2H) isotope composition of 13 groundwater bodies at 52 monitoring sites was measured in the period 2010–2016 for investigating the recharge areas of the Campania Region Groundwater Bodies as defined by the Southern Italy District Water plan. The results were compared with rainwater reference values from literature taking also marine contamination and elevation effects into account. The groundwater stable istope data matched well with MWL reported in the most recent papers for Southern Italy. The quantitative evaluation of the samples spatial variability was performed with multivariate statistical analysis including cluster analysis. As a first result, mixing processes were detected for sites located near the sea and for hydrothermal springs. The influence of high elevation recharge areas was recognized for some monitoring points in mountain karst aquifers, whereas most of the wells in the alluvial plains showed rather constant values, probably due to the large recharge areas, smoothing local effects. The high correlation of groundwater $\delta^{18}O$ and δ^2H values versus elevation a.s.l. evidenced the prevalence of rainfall recharge for most GWB.

Keywords Stable isotopes · Groundwater · Campania · Statistical analysis

1 Introduction

The stable isotopes of oxygen and hydrogen are useful tracers of the sources of water in aquifers (Epstein and Mayeda 1953; Mazor 2004). Indeed they have been used extensively as environmental tracers in the past decades to investigate water cycles, looking at residence time, recharge areas, climate variability (Kendall and McDonnell 1998; Schiavo et al. 2009; Longinelli and Selmo 2010). Among stable isotopes oxygen-18 ($\delta^{18}O$) and hydrogen-2 (δ^2H) anomalies are useful to assess the recharge areas and water mixing (Nisi et al. 2016 with references). Therefore, it is worthwhile to carry out a oxygen-18 ($\delta^{18}O$) and hydrogen-2 (δ^2H) groundwater study for the sites where the Environment Protection Agency of Campania Region (ARPAC) collects data for the chemical status evaluation of Groundwater Bodies. The aim is to improve the conceptual model of aquifers, according to the EU Water Framework Directive (EC 2000) and the Groundwater Directive (EC 2006). Both regulations require the identification of groundwater bodies (GWB), in order to carry out a long-term monitoring devoted to the classification of the chemical and quantitative status (Onorati et al. 2009). This goal is achieved following a stepwise approach, including geological characterization of aquifers, mapping of GWB, delineation of monitoring network, evaluation of relevant chemical substances, data collection, and classification of GWB (EC CIS for WFD 2009). After classification further research on the pollution sources is often needed. ARPAC in 2002 implemented the GWBs quality monitoring network aiming at the evaluation of the environmental status, measuring chemical substances (Adamo et al. 2007; Onorati et al. 2009). The monitoring started in autumn 2002 and is ongoing; it includes large springs and adduction wells, feeding drinking water aqueducts, as well as wells in

This contribution is the written, peer-reviewed version of a paper presented at the Conference "Foreseeing groundwater resources" held at Accademia Nazionale dei Lincei in Rome on March 22, 2018.

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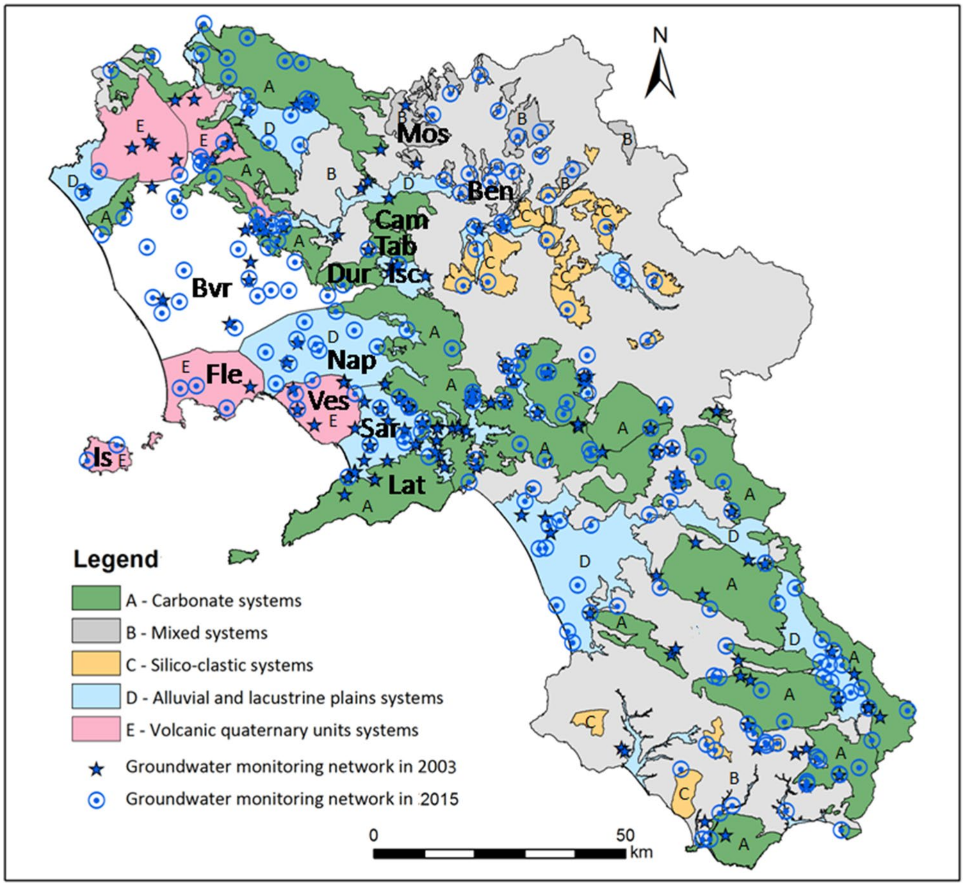

Fig. 1 Groundwater bodies and chemical status monitoring network of Environment Protection Agency of Campania Region (from Ducci et al. 2019). Acronyms refer to the studied areas

alluvial plains (Onorati et al. 2009). The groundwater bodies were mapped according to literature (Celico et al. 2003 published in digital form by De Vita et al. 2018), taking only major aquifers into account (Fig. 1). As a whole the network consisted at the beginning of about 120 monitoring sites for 40 major regional GWBs. In 10 years, the number of the sampling points increased, reaching 183 points for 46 GWBs in 2012. Since 2012 widespread network revision started, aiming at monitoring further 34 GWBs. New sampling points have been added, increasing also the sampling points for GWB in bad chemical status, i.e., with average concentrations for the GWB above thresholds. In 2015, the Campania Region has been partitioned into 80 significant groundwater bodies (PGA 2016): 10% volcanic GWBs, 25% alluvial GWBs, 30% karst GWBs and 35% mixed, at low–moderate permeability. The new monitoring network consists of 320 sampling points, of which 200 active in 2015 (Ducci et al. 2019). However, most of the monitoring sites remained unchanged. Groundwater of these sites are sampled twice a year in order to calculate the annual chemical status classification, (D.lgs. 30/2009; D.M. Env. 6 July 2016). The sampling points guarantee the monitoring of the most important carbonate, volcanic and alluvial aquifers of Campania (Fig. 1), which are the principal drinking water sources, as well as areas affected by high environmental pressures. The carbonate aquifers show hydrogeological features which endanger groundwater resources during drought periods, while the alluvial aquifers represent peculiar pollution risk areas. During the classification of the GWBs and single monitoring point, variations in chemical composition occurred several times, which could not be explained looking only at chemical data. Therefore, a subset of sites for isotope analysis has been defined in order to evaluate recharge and mixing effects (Nisi et al. 2016; Schiavo et al. 2009). The GWB have been chosen also in order to take the geological and geographical variability of Campania Region into account. Since in this research no data on rainfall has been collected, the comparison between groundwater and rain isotope δ^2H–$\delta^{18}O$ is based on datasets and scientific papers. Rain water δs have been extensively studied in the

Table 1 Location of the isotopes monitoring sites in the groundwater bodies of Campania Region

Station code	Municipality	Type	Monitoring site	LAT WGS84 (°)	LON WGS84 (°)	Surface elevation (m) a.s.l.	Water table elevation (m) a.s.l.
Ben2	Benevento	Well	Pozzo Pezzapiana	41.142595	14.770034	125	110
Ben3	Benevento	Well	Pozzo Rummo	41.149490	14.839160	135	131
Ben5	Benevento	Well	Pozzo Nestlè	41.143685	14.840262	133	130
Bvr16	Acerra	Well	Pozzo n. 4 Ditta NGP ex Montefibre	40.970219	14.368740	23	19
Bvr2	Villa Literno	Well	Pozzi Impianto Depurazione	41.010869	14.010600	4	2
Bvr24	Casal di Principe	Well	Pozzo Campo Sportivo CE1	41.022646	14.138976	14	7
Bvr25	Marcianise	Well	Pozzo Depuratore	41.017179	14.259777	19	13
Bvr26	Marcianise	Well	Pozzo n.1 JABIL C. M. ex DITTA SIEMENS	41.026451	14.290243	25	18
Bvr27	San Marco Evangelista	Well	Pozzo Italiana trasformazione polimeri ex DITTA 3M	41.025509	14.333170	31	22
Bvr28	Villa Literno	Well	Pozzo S. Maria a Pantano	40.983116	14.033018	3	1
Bvr29	Giugliano in Campania	Well	Pozzo Ristorante L'anicrè (ex Zanzara d'Oro)	40.945753	14.030129	0.5	0
Bvr6	Villa Literno	Well	Pozzo Campo Sportivo CE2	41.003925	14.073594	9	1.5
Bvr7	Aversa	Well	Pozzo Ippodromo Cirigliano Aversa	40.958391	14.205393	55	13
Bvr8a	Giugliano in Campania	Well	P.Ditta F.lli Amato	40.944686	14.216808	68	17
Nap10	Nola	Well	Pozzo Ospedale Santa Maria la Pietà	40.925635	14.541594	44	27
Nap15	Acerra	Well	Pozzo Ariston	41.000301	14.411864	31	24
Nap18	Nola	Well	Pozzo n 1 CIS di Nola	40.955433	14.487870	29	24
Nap18a	Nola	Well	Pozzo Masseria Rispoli	40.945778	14.488206	29	23
Nap19a	Volla	Well	Pozzo Località F. Volla	40.893962	14.334611	14	9
Nap20	Pomigliano d'Arco	Well	Pozzo Fiat AUTO exAlfasud	40.932773	14.397497	26	19
Nap21	Castello di Cisterna	Well	Pozzo ROMANA CHIMICI privato	40.916376	14.404071	37	19
Nap22a	Nola	Well	Pozzo Villa Comunale Nola	40.923122	14.526622	37	25
Nap31	Arzano	Well	Pozzo Consorzio TPN o CTP	40.913168	14.275854	70	15
Nap5	Napoli	Well	Pozzo n. 5 KUWAIT ex Mobiloil	40.857501	14.303475	5	3
Nap9	Acerra	Well	Pozzo ARIN Acerra	40.938050	14.352308	24	15
Sar2	Poggiomarino	Well	Pozzo Mariniello Officine	40.814132	14.549287	30	16
Sar7	Santa Maria la Carità	Well	Pozzo stabilimento conserviero Raimo	40.731472	14.512317	8	3
Isc5	Airola	Well	Pozzo stabilimento OLA FIBRO ex SF	41.053071	14.564022	258	230
Cam1	Solopaca	Well	Pozzo campo pozzi (P77 ex 205) Alto Calore	41.193703	14.566227	224	70
Dur4	Maddaloni	Well	Ponte Tavano II	41.017326	14.424427	47	26
Dur5	Sant'Agata dei Goti	Well	Pozzo Razzano già sorgente VIPARELLI	41.100666	14.519992	145	120

Table 1 (continued)

Station code	Municipality	Type	Monitoring site	LAT WGS84 (°)	LON WGS84 (°)	Surface elevation (m) a.s.l.	Water table elevation (m) a.s.l.
Lat1	Castellammare di Stabia	Spring	Sorgente Media Gruppo Vanacore Terme Castel-lam.	40.689796	14.470784	11	11
Lat2	Castellammare di Stabia	Spring	FONTANA GRANDE	40.690650	14.474410	18	18
Lat4	Gragnano	Well	Pozzo Regionale Grag-nano	40.698879	14.508009	80	8
Lat5	Angri	Well	Pozzo n° 5 Regionale Angri	40.722996	14.571978	92	12
Lat9	Castellammare di Stabia	Well	Pozzo Comunale Castel-lammare di Stabia	40.709501	14.495773	23	1.5
Mos1	Morcone	Spring	ACQUA SPASA	41.361142	14.607046	1070	1070
Mos3	Morcone	Well	Pozzo zona pluviometro	41.342274	14.671189	459	370
Tab3	Bucciano	Well	Pozzo Campo Pozzi Fizzo Alto Calore	41.073477	14.591909	275	255
Tab3*	Bucciano	Spring	FIZZO	41.073477	14.591909	275	275
Ves1	Somma Vesuviana	Well	Pozzo Acquedotto Vesuviano Somma Vesuviana	40.866482	14.467291	153	24
Ves10	Ercolano	Well	Pozzo Pugliano	40.811735	14.353906	82	3
Ves2a	S. Giuseppe Vesuviano	Well	Pozzo privato	40.841507	14.490432	138	26
Ves3	Somma Vesuviana	Well	Pozzo rione Trieste	40.869210	14.461205	155	23
Ves4	Torre Annunziata	Well	Pozzo Acquedotto Vesu-viano Napoli	40.756516	14.442652	26	0.5
Ves6	Pollena Trocchia	Well	Pozzo Acquedotto Vesu-viano Pollena Trocchia	40.862968	14.388958	134	18
Ves8	San Giorgio a Cremano	Well	Pozzo Acquedotto Vesu-viano	40.838653	14.349196	78	7
Fle1a	Pozzuoli	Well	Pozzo ditta Urzo floricola	40.850286	14.078727	80	2
Fle7a	Napoli	Well	P.Ditta Russo Autoservizi	40.814009	14.187767	13	1
Fle9b	Pozzuoli	Well	pozzo METRO Cash and Carry	40.853130	14.116308	64	22
Is1	Forio	Well	Pozzo Giardini Poseidon	40.717883	13.861910	9	0.5
Is2	Casamicciola Terme	Well	Pozzi Hotel Terme Le Querce	40.745416	13.931004	65	4

literature (Craig 1961; Rozanski et al. 1993; Gat et al. 1996; Longinelli and Selmo 2003; Dotsika et al. 2010) in order to check the deviations from the MWL (Meteoric Water Line) aiming at the detection of recharge areas. Source areas and seasons of recharge have been detected in Apennine aquifers interpreting δ^2H–$\delta^{18}O$ data of surface water, groundwater and precipitation (Barbieri et al. 2005; Petitta et al. 2010; Mussi et al. 2015). In the last years, many papers faced the variability of δ^2H–$\delta^{18}O$ in precipitation along the Italian Peninsula and in Southern Italy, and defined rain depletion functions and maps (Paternoster et al. 2008; Sappa et al. 2012; Madonia et al. 2014; Giustini et al. 2016 and cited papers).

2 Data and methods

In order to evaluate recharge areas and mixing processes in the GWBs of the Campania Region (Italy), 52 monitoring sites, 48 wells and 4 springs (Table 1), located at elevations ranging from 0 to 1070 m a.s.l., have been measured in the period 2010–2016. On the whole, δ^2H–$\delta^{18}O$ isotopic compositions have been measured for 416 samples in the Benevento Lab of ARPAC using a Thermo Mass Spectrometer. Several instruments are presently used for stable isotopes (Muccio and Jackson 2009). In this research, a GC–IRMS with purge and trap has been used (see also Muccio and Jackson 2009 for description and Session 2006 for analytical methods). A thermo-proprietary software controls all elements of the

Table 2 Key hydrogeological features of the 13 groundwater bodies of Campania Region with isotope measurements

Groundwater body name	Groundwater body code	Groundwater body type	Area (sq km)	Max. elevation (m) a.s.l.	Min. elevation (m) a.s.l.	Average elevation (m) a.s.l.	Annual average infiltration (mm)
Benevento Plain	Ben	Alluvial-porous	49	290	99	152	51
Volturno-Regi Lagni	Bvr	Alluvial-porous	1035	269	0	31	91
Oriente di Napoli Plain	Nap	Alluvial-porous	392	462	0	59	133
Sarno Plain	Sar	Alluvial-porous	194	311	0	35	156
Isclero Plain	Isc	Alluvial-porous	55	516	229	277	214
Camposauro Mountain	Cam	Karst-fractured	69	1387	93	745	317
Durazzano Mountain	Dur	Karst-fractured	63	464	51	384	234
Lattari-Isola di Capri	Lat	Karst-fractured	273	1442	0	291	342
Moschiaturo Mountain	Mos	Karst-fractured	123	1472	0	742	377
Taburno Mountain	Tab	Karst-fractured	49	1392	22	815	336
Somma Vesuvio	Ves	Volcanic porous	157	1275	0	251	179
Campi Flegrei	Fle	Volcanic porous	204	460	0	99	135
Ischia Island	Is	Volcanic porous	46	786	0	190	62

GC–IRMS system, allowing for a coherent management of the GC and the IRMS components, with the processing of chromatographic and isotopic data. The analysis in the GC uses a purge-and-trap injection method. For water environmental samples, where crowded chromatograms are common, separation of chromatographic peaks is the most important factor limiting the acquisition of accurate isotopic data; anyway an adequate length of capillary column is useful to minimize this problem. Another crucial point is the interface between GC and IRMS which has several important functions: it must convert substances to the molecular form needed for measurement, it removes undesirable reaction products, and it hinders large pressure fluctuations. The IRMS unit includes electron-impact ionization sources, a magnetic-sector analyzer, multiple Faraday detectors affording a highly stable detection of ion beam currents. Standardization has been performed using standards developed in the laboratory. The method used by ARPAC for groundwater sample collection is described in the guidance for planning and undertaking groundwater sampling to survey the quality of groundwater, provided by the International Standard ISO 5667-11 (ISO 2009). The stable isotope ratios are expressed in δ units in parts per mile representing the deviations of the ratio between heavy and light isotopes of a sample with respect to the same ratio in a reference material, which for waters is the Vienna-Standard Mean Ocean Water (V-SMOW) international standard (Craig 1961; Rozanski et al. 1993). The maximum analytical uncertainty for $\delta^{18}O$ is ± 0.62‰, with an average of 0.45‰, while for $\delta^{2}H$ the maximum is ± 1.35‰, with an average of 0.90‰. These values have been taken into account in the dataset evaluation. The collected data concern 13

Table 3 Descriptive statistics of the $\delta^{2}H$ and $\delta^{18}O$ values of the samples measured in the GWBs of Campania Region (416 analytical determinations, 52 points, 13 GWB) reported in ‰ against the V-SMOW standard

Statistical parameter	$\delta^{2}H$‰	$\delta^{18}O$‰
Mean	− 39.28	− 6.70
Mode	− 40.65	− 6.77
Median	− 39.98	− 6.87
Maximum	− 6.30	− 1.32
Minimum	− 58.52	− 9.32
Stand. dev	7.86	1.26
Skewness	1.59	2.39
Kurtosis	4.77	7.53

GWB (Fig. 1, Table 2), monitored at 52 sites (Table 1) of which 5 are karst aquifers (Lattari Mts., Durazzano Mts., Taburno Mt., Moschiaturo Mt., Camposauro Mt.) 5 alluvial plains (Benevento Plain, Volturno Regi Lagni Plain, Eastern Naples Plain, Sarno Plain, Isclero Plain) 3 volcanic apparatus (Ischia, Campi Flegrei, Vesuvius). The average elevations range between 31 m (Volturno Regi Lagni Plain) and 815 m (Taburno Mt.), average infiltration ranges between 51 and 377 mm. Rain stable isotopes reference data on $\delta^{18}O$ and $\delta^{2}H$ have been downloaded and processed from the Global Network of Isotopes in Precipitation (GNIP) (Terzer et al. 2013; IAEA/WMO 2018) created following a geostatistical approach (Bowen and Revenaugh 2003; Van der Veer et al. 2009; West et al. 2014). From the global gridded values dataset, the values of the $\delta^{18}O$ and $\delta^{2}H$ of the five geographical coordinates centered on Campania have been extracted, mapped and plotted (Fig. 3), they show very similar pattern. Moreover,

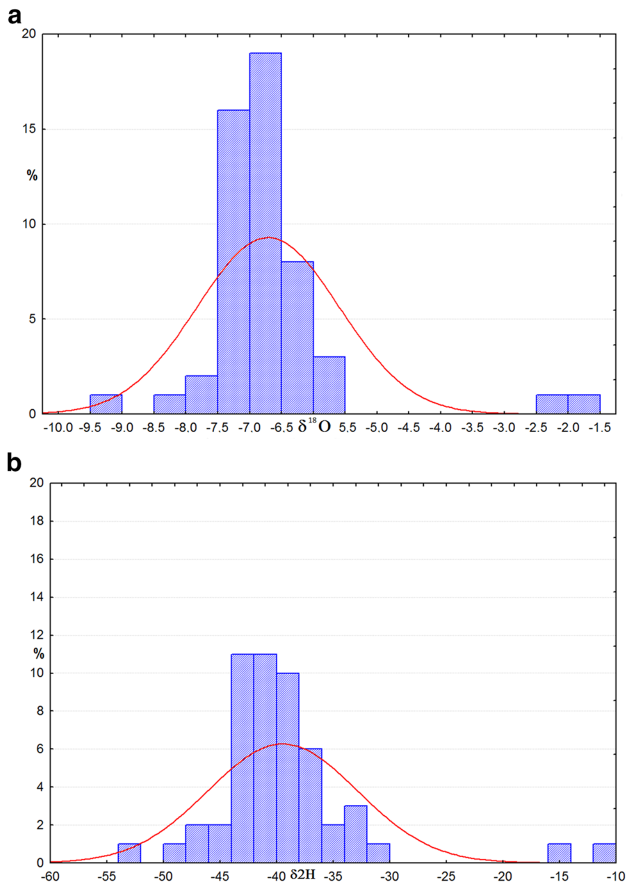

Fig. 2 **a**, **b** Frequency distribution of the 416 samples of δ^{18}O‰ (**a**) and δ^2H‰ (acronyms) (**b**) (concentrations vs. V-SMOW). The diagrams show the presence of outliers with higher values

looking at the GNIP dataset with the aid of wiser software (IAEA/WMO 2018) the availability of rain data for Campania Region has been checked. The only data available are those from sites in neighboring regions: Zannone, Fogliano, Subiaco in Latium, Vulture in Basilicata, Bari in Apulia, Cosenza in Calabria. These datasets, collected in 1998–2003 have been analyzed. For Campania the dataset by Madonia et al. (2014) concerning Mt. Vesuvius has been taken into account. The δ^{18}O map by Giustini et al. (2016) shows for Campania values ranging between − 6‰ along the coast and − 10‰ in mountain areas near Apulia.

3 Statistical analysis

In order to evaluate the influence of spatial position and time for many measured δ, statistical analysis is a useful tool. Data processing has been performed using the STATISTICA software ver. 7.1. The values measured in groundwater (Table 3) range between − 58.52 and − 6.30‰ for δ^2H and between − 9.32 and – 1.32‰ for δ^{18}O with a huge variability. The frequency distribution of data is on the whole normal with mean, mode and median with similar values and a low skewness, however the kurtosis shows the effect of outliers. The differences between δ^{18}O and δ^2H distributions (Fig. 2a, b) is clear looking at the frequency diagrams: the first is less dispersed, however both show a secondary group with high values. The secondary groups concern less than 5% of the global populations. The normalized standard deviation is the largest for Is1 and Bvr 29 and very low for many Volturno plain wells (Table 4). The dataset evidences the larger variability for δ^2H with respect to δ^{18}O as known in the literature (Craig 1961). Two sites: Is1 (Forio thermal well) and Bvr29 (near a coastal marsh) show peculiar values and pattern, with δ^2H larger than − 20‰ and δ^{18}O of about − 2‰. Therefore, these values have been further investigated in detail. The lowest values are those of Mt. Moschiaturo spring (mean 53.4‰ δ^2H and 9.1‰ δ^{18}O). For the other sites the δs are very stable. The groundwater data set has been compared with up-to-date rain data. The most relevant statistics concerns the correlation between δ^2H and δ^{18}O values and MWL curves (Figs. 4, 5, 6). In the graphs the MWL lines GMWL (Rozanski et al. 1993) EMWL (Gat et al. 1996) SIMWL (Giustini et al. 2016) Vesuvius MWL (Madonia et al. 2014) Pontina Plain MWL (Sappa et al. 2012) are plotted against Campania GWB monitoring sites data. The groundwater data taken into account are both the whole samples data set (Figs. 4, 5) and the averages for each site (Fig. 6, Table 4). The relationships between GWB elevations and δ^2H–δ^{18}O have been also investigated looking at the surface mean elevation of the GWB (Fig. 7a, b). For the sites with more than 10 samples the temporal variability has been checked, since time-dependent variations have been observed, average yearly δ have been also calculated (Fig. 8a, b). Furthermore for the GWB Monti Lattari, with many monitoring points a comparison among sites has been plotted showing local trends (Fig. 9). In order to compare the characterizing parameters of the sample points (Table 4), the cluster analysis is a useful tool for grouping the sites (Kendall 1975). Hence a dendrogram has been built-up (Fig. 10) choosing the Ward method (Ward 1963) with Euclidean distances, and the results have been mapped (Fig. 11).

4 Discussion

The most important factors influencing ^{18}oxygen (δ^{18}O) and ^{2}hydrogen (δ^2H) compositions are altitude and continental effect (Longinelli and Selmo 2003; Giustini et al. 2016). The latter, however, seems to be negligible for coastal regions like Campania, and significant only for GWBs located eastward of the Apennine axis. Moreover, temperature has also an effect on isotopes enrichment, as well as rainfall regime.

Table 4 Statistical parameters of δ^2H and r δ^{18}O reported in ‰ against the V-SMOW standard for each sampling point (lacking data for single values)

GW station code	No. of samples	δ^2H Mean	δ^2H Max	δ^2H Min	δ^2H Norm st dev	δ^2H Skewness	δ^2H Kurtosis	δ^{18}O Mean	δ^{18}O Max	δ^{18}O Min	δ^{18}O Norm st dev	δ^{18}O Skewness	δ^{18}O Kurtosis
Ben2	4	− 47.1	− 40.1	− 52.3	− 0.11	0.8	− 0.1	− 7.3	− 6.6	− 7.9	− 0.07	0.9	1.8
Ben3	5	− 42.7	− 37.2	− 47.9	− 0.10	0.2	− 1.9	− 6.7	− 6.0	− 7.2	− 0.07	0.5	− 1.7
Ben5	5	− 44.1	− 37.3	− 54.8	− 0.15	− 1.2	2.1	− 6.9	− 6.0	− 7.8	− 0.10	0.0	0.4
Bvr16	11	− 40.1	− 36.0	− 45.2	− 0.08	− 0.2	− 1.3	− 6.8	− 6.4	− 7.2	− 0.04	0.2	− 1.6
Bvr2	4	− 39.0	− 36.7	− 42.0	− 0.06	− 0.3	− 3.6	− 7.0	− 6.9	− 7.0	− 0.01	0.0	− 3.4
Bvr24	2	− 34.6	− 31.4	− 37.9	− 0.13			− 6.0	− 5.5	− 6.5	− 0.12		
Bvr25	4	− 37.8	− 33.3	− 43.8	− 0.14	− 0.4	− 3.9	− 6.4	− 5.6	− 7.1	− 0.11	0.1	− 4.6
Bvr26	4	− 42.8	− 38.2	− 45.6	− 0.08	1.3	1.2	− 7.2	− 6.6	− 7.6	− 0.06	0.6	− 2.6
Bvr27	4	− 37.8	− 34.4	− 41.0	− 0.09	0.0	− 5.4	− 6.4	− 5.7	− 6.9	− 0.09	0.3	− 3.5
Bvr28	4	− 37.5	− 34.6	− 39.1	− 0.05	1.5	2.3	− 6.4	− 6.3	− 6.7	− 0.03	− 2.0	3.9
Bvr29	7	− 14.3	− 11.3	− 19.9	− 0.21	− 1.1	1.6	− 2.2	− 1.6	− 2.9	− 0.18	0.1	1.6
Bvr6	4	− 38.5	− 35.6	− 40.5	− 0.05	1.0	0.6	− 6.5	− 6.3	− 6.9	− 0.04	− 0.4	− 3.5
Bvr7	4	− 39.4	− 36.2	− 41.0	− 0.06	1.8	3.5	− 6.7	− 6.5	− 7.0	− 0.03	0.0	− 2.9
Bvr8a	3	− 37.4	− 36.4	− 38.9	− 0.04	− 1.4		− 6.3	− 5.8	− 6.8	− 0.08	1.1	
Nap10	11	− 41.9	− 36.4	− 53.8	− 0.14	− 1.4	0.7	− 7.1	− 6.6	− 8.2	− 0.08	− 1.1	0.1
Nap15	1	− 37.3						− 6.9					
Nap18	1	− 33.0						− 5.8					
Nap18a	6	− 35.9	− 31.8	− 40.4	− 0.10	− 0.1	− 2.3	− 6.1	− 5.9	− 6.2	− 0.02	0.9	− 1.6
Nap19a	5	− 38.9	− 34.3	− 44.0	− 0.09	− 0.3	1.1	− 6.5	− 6.1	− 6.9	− 0.04	0.1	− 0.6
Nap20	11	− 39.2	− 34.6	− 45.0	− 0.08	0.0	− 0.4	− 6.6	− 6.1	− 7.0	− 0.04	0.2	− 0.1
Nap21	12	− 40.7	− 33.8	− 46.1	− 0.11	0.7	− 0.9	− 7.0	− 6.2	− 8.3	− 0.08	− 0.8	1.7
Nap22a	6	− 42.3	− 37.2	− 48.8	− 0.11	− 0.4	− 1.6	− 7.3	− 6.7	− 8.1	− 0.07	− 0.5	− 0.5
Nap31	9	− 39.0	− 33.8	− 42.7	− 0.08	0.4	− 1.4	− 6.7	− 6.3	− 7.2	− 0.05	0.0	− 1.0
Nap5	11	− 41.8	− 38.3	− 52.8	− 0.09	− 2.4	6.8	− 7.2	− 6.6	− 9.3	− 0.12	− 2.0	3.8
Nap9	10	− 37.4	− 33.0	− 41.1	− 0.08	0.4	− 1.9	− 6.4	− 5.3	− 6.9	− 0.07	1.2	1.8
Sar2	6	− 39.8	− 36.3	− 45.0	− 0.08	− 0.6	0.3	− 6.7	− 6.4	− 7.1	− 0.04	− 0.8	1.4
Sar7	2	− 40.8	− 37.2	− 44.5	− 0.13			− 6.9	− 6.2	− 7.5	− 0.13		
Isc5	5	− 42.2	− 32.9	− 54.2	− 0.19	− 0.7	0.7	− 7.0	− 5.8	− 8.1	− 0.14	0.1	− 1.7
Cam1	5	− 47.1	− 42.6	− 54.8	− 0.10	− 1.6	3.2	− 8.0	− 7.4	− 8.8	− 0.07	− 1.2	2.6
Dur4	4	− 41.7	− 36.6	− 45.1	− 0.09	− 0.8		− 7.2	− 6.7	− 7.4	− 0.04	1.5	
Dur5	5	− 43.5	− 39.5	− 52.9	− 0.12	− 1.9	3.5	− 72	− 6.8	− 8.0	− 0.07	− 2.0	4.3
Lat1	9	− 33.8	− 27.8	− 39.2	− 0.12	0.1	− 1.6	− 5.9	− 4.9	− 6.6	− 0.11	0.6	− 0.8
Lat2	17	− 41.8	− 34.7	− 48.6	− 0.11	− 0.2	− 1.2	− 7.2	− 6.0	− 8.2	− 0.09	0.4	− 0.6
Lat4	20	− 39.9	− 28.9	− 48.9	− 0.14	0.2	− 0.9	− 7.0	− 5.4	− 8.4	− 0.10	0.4	0.2

Table 4 (continued)

GW station code	No. of samples	δ^2H Mean	δ^2H Max	δ^2H Min	δ^2H Norm st dev	δ^2H Skewness	δ^2H Kurtosis	$\delta^{18}O$ Mean	$\delta^{18}O$ Max	$\delta^{18}O$ Min	$\delta^{18}O$ Norm st dev	$\delta^{18}O$ Skewness	$\delta^{18}O$ Kurtosis
Lat5	7	− 38.8	− 32.1	− 43.0	− 0.10	0.9	− 0.6	− 6.8	− 5.6	− 7.5	− 0.10	1.0	0.3
Lat9	19	− 41.7	− 35.9	− 48.2	− 0.10	0.3	− 1.3	− 7.4	− 6.2	− 8.2	− 0.07	− 0.4	− 0.8
Mos1	4	− 53.4	− 51.8	− 55.3	− 0.03	− 0.2	− 4.8	− 9.1	− 8.7	− 9.3	− 0.03	0.3	− 4.1
Mos3	4	− 42.0	− 32.2	− 52.6	− 0.20	− 0.3	1.5	− 6.9	− 5.6	− 8.2	− 0.16	0.0	1.5
Tab3	2	− 44.0	− 41.7	− 46.3	− 0.07			− 8.0	− 7.7	− 8.2	− 0.05		
Tab3*	3	− 49.0	− 46.3	− 53.6	− 0.08	− 1.7		− 8.0	− 7.7	− 8.3	− 0.04	1.4	
Ves1	14	− 42.5	− 37.4	− 54.9	− 0.10	− 2.0	6.0	− 7.4	− 6.4	− 8.7	− 0.07	− 1.1	4.6
Ves10	18	− 40.8	− 34.5	− 55.0	− 0.13	− 0.9	1.6	− 6.8	− 6.1	− 8.1	− 0.08	− 0.7	0.1
Ves2a	19	− 40.7	− 34.4	− 45.9	− 0.10	0.2	− 1.8	− 7.0	− 6.5	− 7.5	− 0.05	0.2	− 1.2
Ves3	8	− 44.1	− 42.3	− 47.0	− 0.04	− 0.8	0.0	− 7.4	− 7.2	− 7.8	− 0.02	− 1.2	1.5
Ves4	8	− 43.2	− 38.4	− 45.1	− 0.07	1.4	0.0	− 7.3	− 6.8	− 7.6	− 0.03	1.2	1.5
Ves6	18	− 40.5	− 35.0	− 44.3	− 0.08	0.6	− 1.3	− 6.9	− 6.4	− 7.4	− 0.05	0.0	− 1.4
Ves8	10	− 39.6	− 34.4	− 46.5	− 0.11	− 0.5	− 1.3	− 6.8	− 6.1	− 7.3	− 0.06	0.4	− 0.7
Fle1a	16	− 41.1	− 32.3	− 58.5	− 0.19	− 1.4	1.4	− 7.0	− 6.1	− 9.0	− 0.12	− 1.5	1.4
Fle7a	15	− 42.8	− 35.3	− 48.4	− 0.10	0.4	− 0.9	− 7.2	− 6.5	− 7.8	− 0.07	0.2	− 1.6
Fle9b	4	− 33.3	− 31.8	− 35.9	− 0.06	− 1.3	1.3	− 6.4	− 5.9	− 7.1	− 0.09	− 0.8	− 0.9
Is1	13	− 12.3	− 6.3	− 19.0	− 0.37	− 0.4	− 0.9	− 1.8	− 1.3	− 2.5	− 0.21	− 0.4	− 0.2
Is2	13	− 33.3	− 26.2	− 43.1	− 0.15	− 0.2	− 0.3	− 5.9	− 5.2	− 7.3	− 0.09	− 1.2	2.4

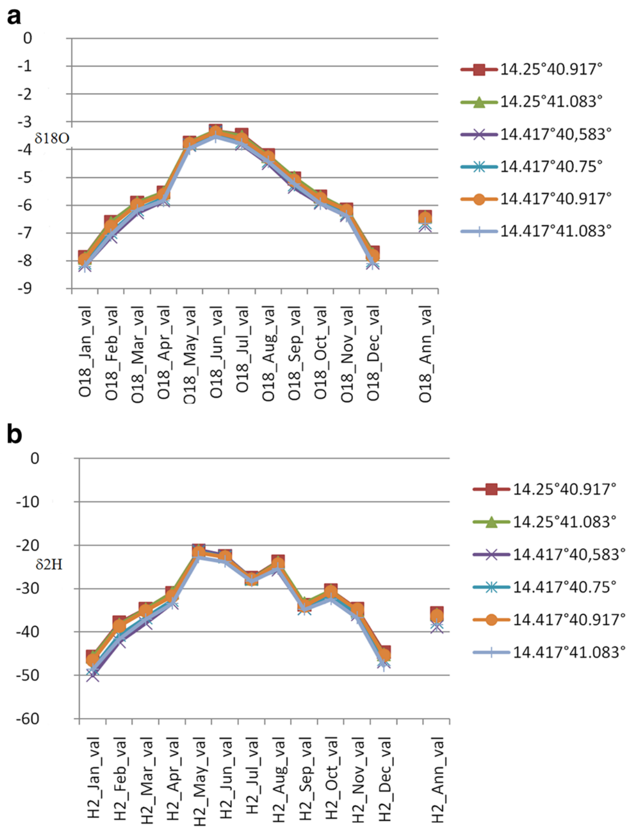

Fig. 3 **a**, **b** Model estimation of monthly and yearly δ^{18}O‰ (**a**) and δ^{2}H‰ (acronyms) (**b**) (concentrations vs. V-SMOW) for the grid points of reported Lat and Long coordinates (values in geographical degrees) extracted from IAEA site (IEAEA/WMO 2013)

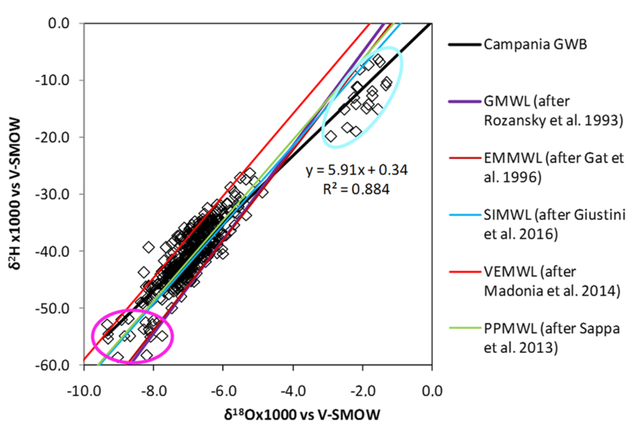

Fig. 4 Relationships between δ^{2}H‰ and δ^{18}O‰ (concentrations vs. V-SMOW) (52 sites, 416 samples) with ellipses are outlined the samples with marine water contamination (upper left corner of graph), and the sites at higher elevation and those with relevant winter recharge (lower right corner of graph). The 5 MWL lines have been redrawn from cited datasets

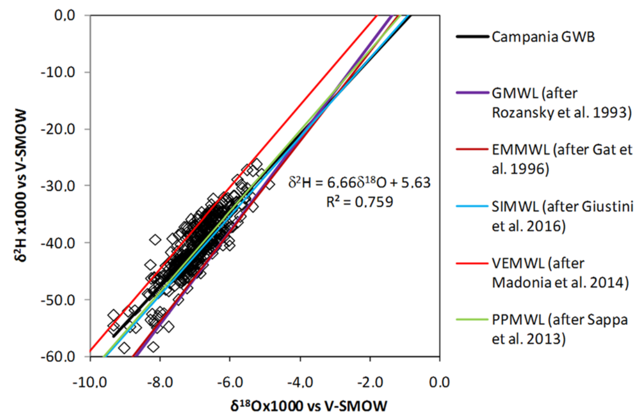

Fig. 5 Relationships between δ^{2}H‰ and δ^{18}O‰ (concentrations vs. V-SMOW) for samples without relevant marine contamination (50 sites 396 samples) with regression equation and R^2 for the Campania GWB line. The 5 MWL lines have been redrawn from cited datasets

Indeed seasonal variations of rainfall stable isotopes are large (Fig. 3a, b, and GNIP dataset extracted with wiser software IAEA/WMO 2018) and must be taken into account for detailed annual recharge studies. The comparison between groundwater samples and MWL lines (Figs. 4, 5) shows that the Campania line drawn from GWB data is crosscutting all the MWL lines, due to a group of samples with higher δ^{2}H–δ^{18}O. Indeed two sites show peculiar characteristics, with δ near to V-SMOW (Fig. 5, Table 4). For these sites, a contamination of sea water probably occurs since the sites are located at Ischia (Is1) and near Patria Lake (Bvr29) less than 1 km from the Tyrrhenian Sea. In order to check for sea water influence versus rain stable isotope fingerprint, reference rain values have been taken into account together with seawater of Mediterranean Sea (Bigg and Rohling 2000; Cox et al. 2011) (Table 5). The rainfall patterns suitable for this check are those of Vesuvius (Madonia et al. 2014), Zannone Island and the IAEA model (IAEA/WMO 2018) which are the datasets at the lowest distance from the Ischia and Patria lake sites and show also coherent rainfall δ. A simple mass balance evaluation has been performed with coherent results for δ^{2}H–δ^{18}O (Table 5), therefore the groundwater stable isotopes measured values of Is1 and Bvr29 should be due to water mixing, the proportion is in the order of 50% seawater and 50% rainfall, the best estimates seem those from IAEA Model and Zannone Island weighted averages. In the comparison of groundwater stable isotopes with rainfall and altitude, Is1 and Bv29 data have been hence discarded. After the withdrawal of samples from Is1 and Bvr29 outliers, the Campania groundwater line falls within the rainfall MWLs (Fig. 5), almost overlapping the SIMWL (Giustini et al. 2016) and the correlation, for a dataset encompassing several GWB with different elevation and geology, is high, with R^2 above 0.75. This result shows that rainfall infiltration is

Table 5 Mass balance for Is1 and Bvr29 groundwater

	Elevation (m) a.s.l.	Period	Source	$\delta^{18}O$	δ^2H	*Is1* Mass balance % sea water estimated from $\delta^{18}O$	*Is1* Mass balance % sea water estimated from δ^2H	*Bvr29* Mass balance % sea water estimated from $\delta^{18}O$	*Bvr29* Mass balance % sea water estimated from δ^2H
Rainfall									
Zannone simple average rainfall	118	1998–2003	IAEA/WMO	− 4.8	− 23.5	38.3%	37.9%	43.3%	31.1%
Zannone monthly averaged rainfall	118	1998–2003	IAEA/WMO	− 5.3	− 28.2	42.9%	46.5%	47.5%	40.6%
Lon 14.25° lat 40.917° model rainfall	100	2000–2010	IAEA/WMO	− 6.4	− 35.7	51.4%	56.1%	55.3%	51.3%
S. Sebastiano al Vesuvio	230	2002–2004	Madonia et al. (2014)	− 6.1	− 42.0	49.3%	61.9%	53.4%	57.7%
Torre Annunziata	50	2002–2004	Madonia et al. (2014)	− 6.0	− 38.5	48.6%	58.9%	52.8%	54.4%
Groundwater									
Is1	9	2010–2016	This study	− 2.5	− 12.3				
Bvr29	0.5	2010–2016	This study	− 2.2	− 14.3				
Sea water									
Mediterranean sea water	− 2	2000–2010	Cox et al. (2011)	1.2	6.0				

Calculations have been carried out using both δ^2H and $\delta^{18}O$ reported as ‰ concentrations vs. V-SMOW as tracers, rain and seawater data have been reanalysed from cited papers

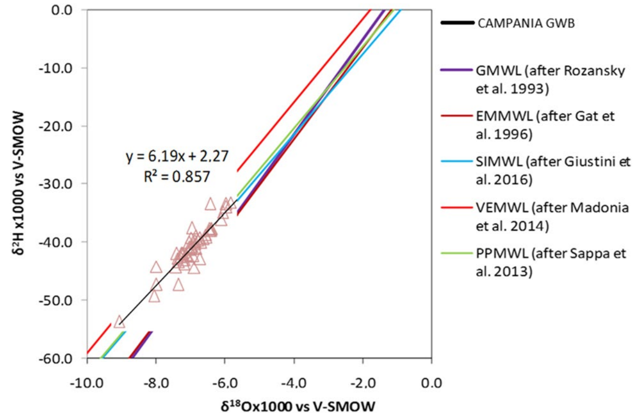

Fig. 6 Relationships between the mean of δ^2H‰ and $\delta^{18}O$‰ (concentrations vs. V-SMOW) (50 relevant sites) not included the samples with marine water contamination, with regression equation and R^2 for the Campania GWB line. The 5 MWL lines have been redrawn from cited datasets

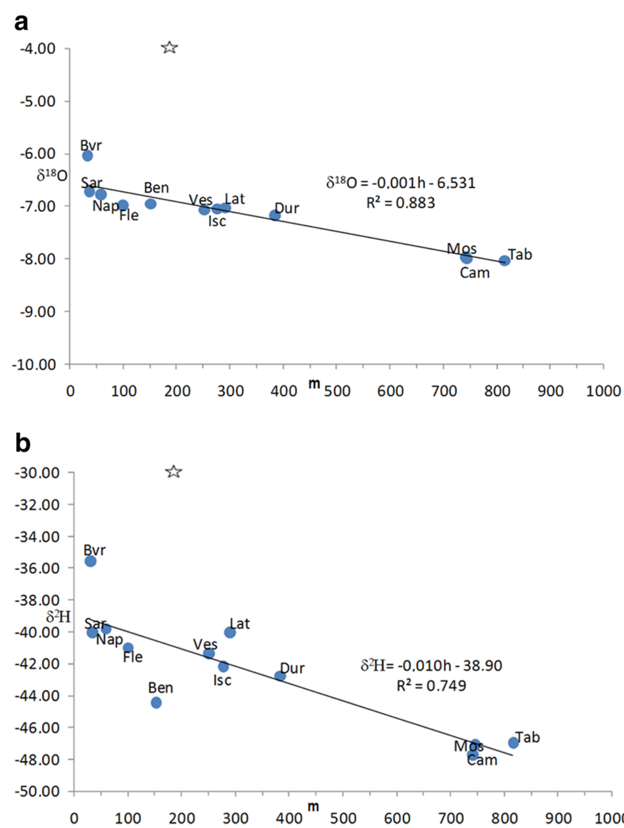

Fig. 7 **a**, **b** Comparison between mean δ^2H‰ and $\delta^{18}O$‰ (concentrations vs. V-SMOW) and mean elevation of the groundwater bodies (13 GWBs). Ischia outlier (star) has not been included in the statistics, while Bvr has been taken into account although including a site with marine ingression

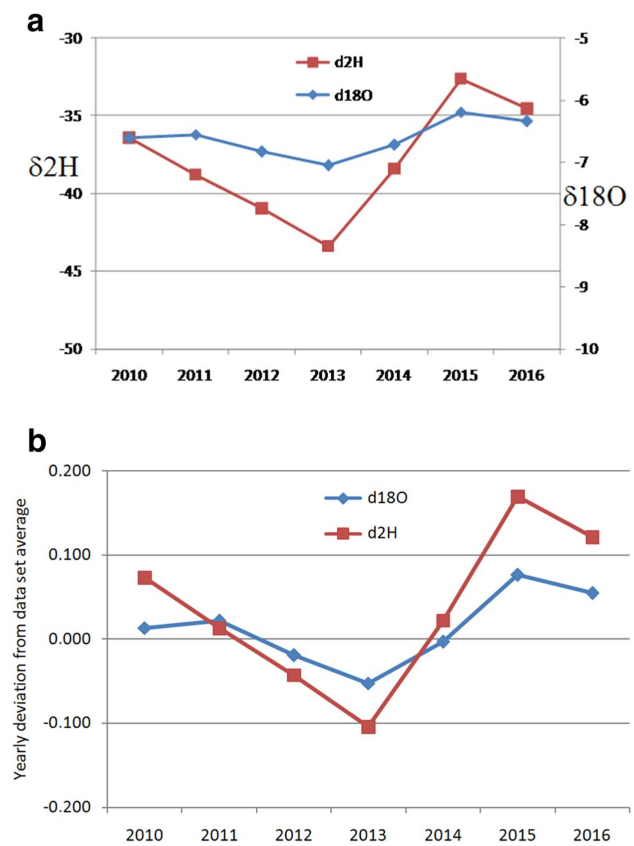

Fig. 8 **a**, **b** Comparison between mean δ^2H‰ and $\delta^{18}O$‰ (concentrations vs. V-SMOW) yearly mean values: **a** mean values showing a negative anomaly in 2013, **b** normalized values with a marked 2013 negative anomaly for both δ^2H‰ and $\delta^{18}O$‰

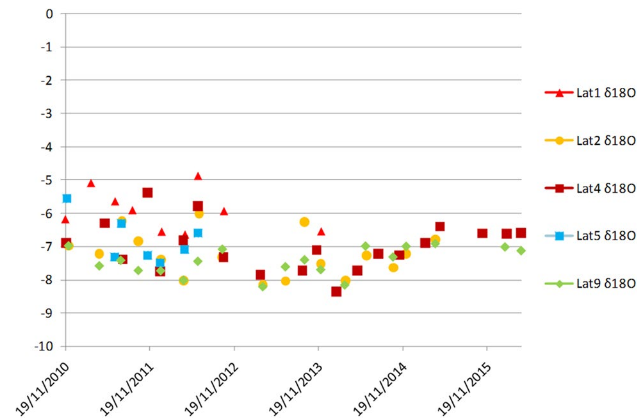

Fig. 9 $\delta^{18}O$‰ (concentrations vs. V-SMOW) 2010–2016 time series in the 5 sites of Lattari Mts. The lowest values are those of winter 2013

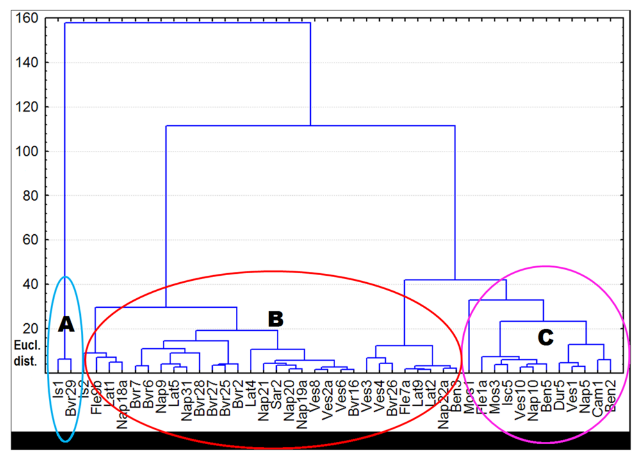

Fig. 10 Dendrogram created according the Ward method with Euclidean distances, data set is reported on Table 4. Missing cases have been discarded, 44 samples have been classified. With ellipses are outlined three groups: the samples with marine water contamination (**a**), those in alluvial plains and volcanic edifices (**b**), the sites at higher elevation or with relevant winter recharge (**c**)

the prevailing recharge process. Looking in further detail at average values of each site (Fig. 6), the δ^2H–$\delta^{18}O$ data show an even better correlation ($R^2=0.857$), with the most negative values for Moschiaturo Mt. For this site values below − 50‰ δ^2H and − 8.5‰ $\delta^{18}O$ are the witness of an important influence of precipitation in higher recharge areas, with $\delta^{18}O$ of − 8 to − 9 (Giustini et al. 2016). In Italy typically the altitude effect for precipitation ranges from − 0.1 to − 0.4‰ of $\delta^{18}O$/100 m (Giustini et al. 2016). For Southern Italy the effect is approximately of − 0.2‰ $\delta^{18}O$/100 m, Campania literature data are in the range of − 0.11‰ to − 0.27‰ near Molise (Longinelli and Selmo 2003, 2010), in Petitta et al. (2010) the reported gradient for an area lying 40 km N of Campania is − 0.19‰ $\delta^{18}O$/100 m, in Giustini et al. (2016) a review of gradients is reported, with altitude effect for precipitation ranging from − 0.1 to − 0.6‰ of $\delta^{18}O$/100 m. For Campania groundwater samples, the relationships of elevations versus δ^2H and $\delta^{18}O$ show, with respect to the cited rainfall data, lower gradients for $\delta^{18}O$: − 0.1‰/100 m (Fig. 7a), while for δ^2H of − 1.0‰/100 m (Fig. 7b) the literature is poor due to weaker elevation/δ^2H correlations. The low Campania groundwater $\delta^{18}O$ versus elevation gradients should be due to the fact that most of the cited research on rainfall/elevation deal with the Apennine chain, while the GWBs of this study lie nearby the coast. The high correlations between δs and GWB average elevations is related to the prevailing recharge of aquifers from rainfall, while the Ischia outlier and the Bvr (Regi Lagni Volturno Basin) anomalous value testify the mixing of different waters: rainfall recharge water and sea water, as discussed above. For Campania the groundwater δ^2H and $\delta^{18}O$ data set is based on 2 to 4 samples each year, not sufficient for robust seasonal studies, so annual averages are considered; however, part of the variability of data is certainly related to seasonality, and the monthly variations are much larger than uncertainty (Figs. 3, 8a, b). Only a part of the monitoring sites (Table 2)

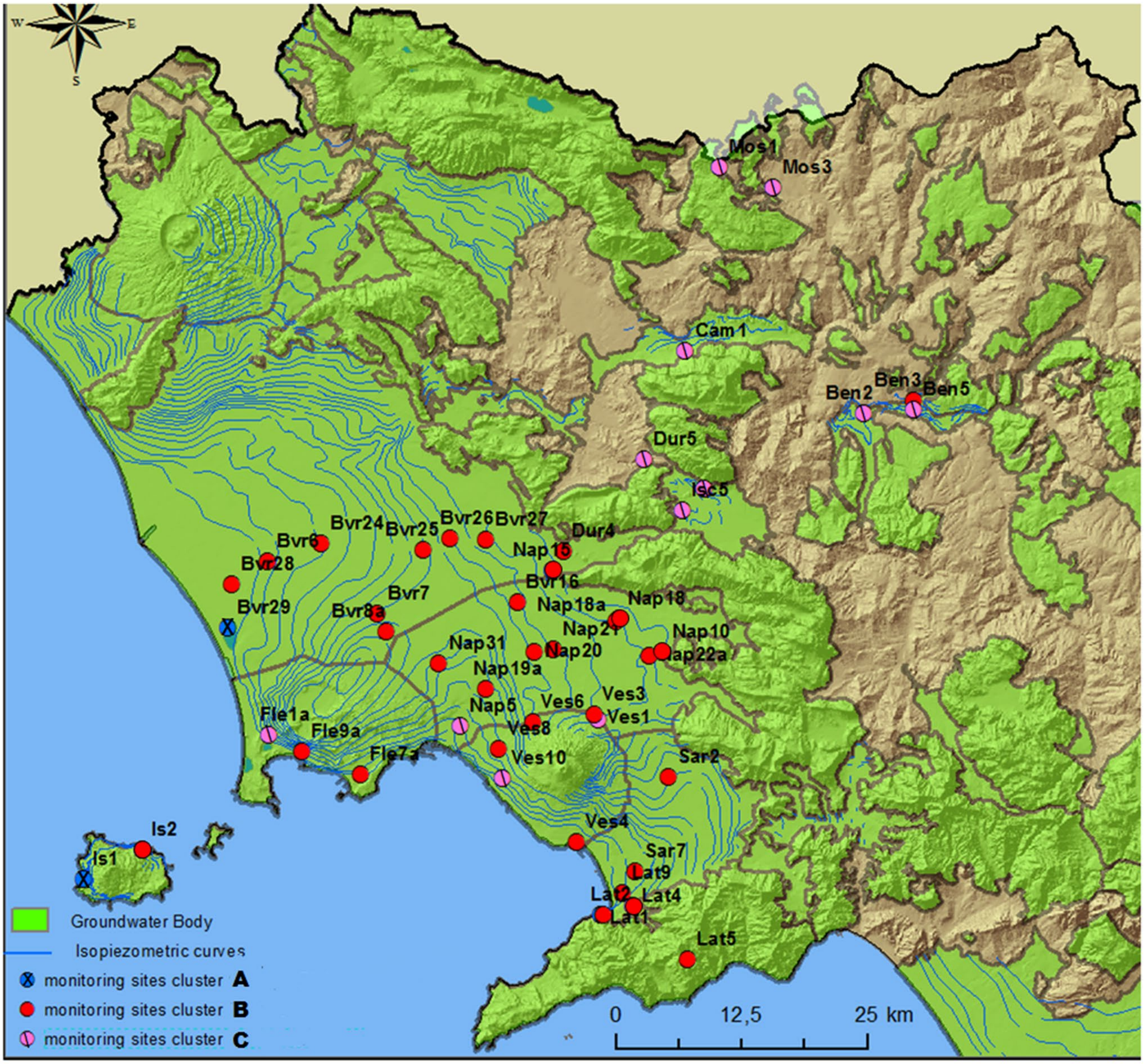

Fig. 11 Geographic location of the classes of the dendrogram created according the Ward method with Euclidean distances. The blue dots with a × correspond to the samples with marine water contamination (Class A), in magenta with a\ are the sites at higher elevation and those with relevant winter recharge (Class C), the red dots refer to the other points, mostly in alluvial plains and volcanic edifices (Class B)

has been measured for the whole period 2010–2016 and the results for Mt. Lattari GWB sites with long series are shown in Fig. 9. Indeed the "short" time series 2010–2016 are not adequate for trend analysis, however they show a coherent pattern, with low δ^2H and δ^{18}O values measured in 2013 and high values in 2015 (Fig. 8a); this pattern is even more evident looking at the data normalized with respect to average values (Fig. 8b). The annual pattern is also apparent looking at single time series (Fig. 9). Indeed rainfall in winter was above average in the Campania region in 2013, with lower δs as typical for this season as shown in Fig. 3.

However, to explain the yearly variations of isotope values, further comparison between groundwater and climatologic data is needed. In order to check for spatial variations of isotope values, with cluster analysis three major groups of monitoring sites have been detected (Fig. 10): the groundwater influenced by seawater intrusion, the GWBs located in the alluvial plains and volcanic edifices (in red), including most of the wells which show rather constant values, probably due to the large recharge areas, smoothing local effects. The third group encompasses the points at higher elevation, as well as some sites which should be further investigated (in magenta) in order to check for contamination with less depleted waters. The spatial distribution of the classes is shown in a map (Fig. 11). The detection of outliers by means of cluster analysis and mapping proved to be a useful tool for the identification of sites with anomalous δ^2H and $\delta^{18}O$, which needs further local investigations.

5 Conclusions

The ARPAC δ^2H–$\delta^{18}O$ archive is a robust data set (416 samples, 52 sites, 13 GWB, period 2010–2016) filling a gap in reference knowledge of Campania Region stable isotopes hydrogeochemistry. In the first evaluation of the data set performed in this study, the pattern of δ^2H and $\delta^{18}O$ data set has been described, with the aid of statistics. Some peculiar sites with marine intrusion have been detected, whereas for the other coastal monitoring point no major saltwater intrusion has been observed. Springs and wells with recharge areas at high elevation (above 700 m a.s.l.) show a more "cold and continental" stable isotope finger tip. For most of the sites in the alluvial plains local variability is low. The comparison between groundwater δ^2H–$\delta^{18}O$ (excluding Is1 and Bvr29 seawater contaminated samples) and MWL redrawn from literature show that the samples, the sites and the GWB of Campania fall within de SIMWL (Giustini et al. 2016) with a very slight deviation toward $\delta^{18}O$ (Fig. 6), hence direct rainfall recharge of aquifers is the prevailing mechanism. The vertical gradients for groundwater samples of δ^2H–$\delta^{18}O$, fall within the values reported in literature for rainfall, however the 0.1‰/100 m $\delta^{18}O$ gradient is low, anyway in most of the papers on this topic (see Giustini et al. 2016 for citations) the gradients are evaluated for small watersheds, whereas in this study the GWBs area stretches for about 100 × 100 km creating a smoothing effect. The cluster analysis proved to be a useful tool in detecting groups of sites with similar characteristics, associated with analogous groundwater recharge sources. This approach can be further applied to each GWB in detailed studies concerning single hydrostructures. A detailed comparison of the stable isotope measurements with meteorological and water quality data as well as geostatistics of data (Van der Veer et al. 2009) is the next step to improve the interpretation of GWB recharge in the Campania Region.

Acknowledgements We wish to thank the two referees, whose comments and suggestions stimulated a strong improvement of the discussion on the isotope monitoring data set.

Data set The data set is available at the internet ARPAC site: (2018) Isotopic analysis groundwater data http://www.arpacampania.it/web/guest/365.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Adamo N, Imperatrice ML, Mainolfi P, Onorati G, Scala F (2007) Acqua—Il monitoraggio in Campania 2002–2006. ARPAC, Napoli, pp 1–257

Barbieri M, Boschetti T, Petitta M, Tallini M (2005) Stable isotopes (2H, 18O e 87Sr/86Sr) and hydrochemistry monitoring for groundwater hydrodynamics analysis in a karst aquifer (Gran Sasso, Central Italy). Appl Geochem 20:2063–2081

Bigg GR, Rohling EJ (2000) An oxygen isotope data set for marine water. J Geophys Res 105:8527–8535

Bowen GJ, Revenaugh J (2003) Interpolating the isotopic composition of modern meteoric precipitation. Water Resour Res 39(10):78. https://doi.org/10.1029/2003wr002086

Celico PB, De Vita P, Monacelli G, Scalise AR, Tranfaglia G (2003) Carta Idrogeologica dell'Italia Meridionale. Istituto Poligrafico e Zecca dello Stato, Rome

Cox KA, Rohling EJ, Schmidt GA, Schiebel R, Bacon S, Winter DA, Bolshaw M, Spero HJ (2011) New constraints on the Eastern Mediterranean 18O: D relationship. Ocean Sci. https://doi.org/10.5194/osd-8-39-2011

Craig H (1961) Standard for reporting concentrations of hydrogen and oxygen-18 in natural waters. Science 3467:1833–1834. https://doi.org/10.1126/science.133.3467.1833

De Vita P, Allocca V, Celico F, Fabbrocino S, Mattia C, Monacelli G, Musilli I, Piscopo V, Scalise AR, Summa G, Tranfaglia G, Celico P (2018) Hydrogeology of continental southern Italy. J Maps 14(2):230–241

D.lgs. 30/2009 (2009) Italy: Transposition of Directive 2006/118/EC, of the European Parliament and of the council on the protection of groundwater against pollution and deterioration. GU 2009

D.M. Env. 6 July 2016 Italy (2016) Transposition of Directive 2014/80/EC, modifying the annex II of the Directive 2006/118/EC

Dotsika E, Lykoudis S, Poutoukis D (2010) Spatial distribution of the isotopic composition of precipitation and spring water in Greece. Glob Planet Change 71(3):141–149. https://doi.org/10.1016/j.gloplacha.2009.10.007

Ducci D, Della Morte R, Mottola A, Onorati G, Pugliano G (2019) Nitrate trends in groundwater of the Campania region (southern Italy). Environ Sci Pollut Res 26:2120–2131

EC (2000) Directive 2000/60/EC 23 October 2000 framework for Community action in the field of water policy. Off J Eur Community L 327:1–72

EC (2006) Directive 2006/118/EC 12 December 2006 protection of groundwater against pollution and deterioration. Off J Eur Union L 372:19–31

EC (2009) Common Implementation Strategy for the WFD guidance on groundwater status and trend assessment. Guidance 18:1–81. https://doi.org/10.2779/77587

Epstein S, Mayeda T (1953) Variation of O18 content of waters from natural sources. Geochim Cosmochim Acta 4(5):213–224. https://doi.org/10.1016/0016-7037(53)90051-9

Gat JR, Shemesh A, Tziperman E, Hecht E, Georgopoulos D, Basturk O (1996) The stable isotope composition of waters of the Eastern Mediterranean Sea. J Geophys Res 101:6441–6451

Giustini F, Brillia M, Patera A (2016) Mapping oxygen stable isotopes of precipitation in Italy. J Hydrol Reg Stud 8(2016):162–181. https://doi.org/10.1016/j.ejrh.2016.04.001

IAEA/WMO (2018) Global Network of Isotopes in Precipitation (GNIP). The IAEA's Water Resources Programme and the World Meteorological Organization (WMO). http://www-naweb.iaea.org/napc/ih/IHS_resources_gnip.html. Accessed 2018–2019

ISO 5667-11 (2009) Water quality—sampling—Part 11: Guidance on sampling of groundwater. https://www.iso.org/standard/42990.html

Kendall M (1975) Multivariate analysis. Charles Griffin Co. LTD, London, p 210

Kendall C, McDonnell JJ (1998) Isotope tracers in catchment hydrology. Elsevier, Amsterdam

Longinelli A, Selmo E (2003) Isotopic composition of precipitation in Italy: a first overall map. J Hydrol 270:75–88

Longinelli A, Selmo E (2010) Isotope geochemistry and the water cycle: a short review with special emphasis on Italy. Mem Descr Carta Geol Ital 90:153–164

Madonia P, Federico C, Favara R (2014) Isotopic composition of rain- and groundwater at Mt. Vesuvius: environmental and volcanological implications. Environ Earth Sci 72:2009–2018. https://doi.org/10.1007/s12665-014-3110-3

Mazor E (2004) Applied chemical and isotopic groundwater hydrology, 3rd edn. Marcel Dekker, New York, p 453

Muccio Z, Jackson G (2009) Isotope ratio mass spectrometry. Analyst 134:213–222. https://doi.org/10.1039/b808232d

Mussi M, Nanni T, Tazioli A, Vivalda PM (2015) The Mt Conero limestone ridge: the contribution of stable isotopes to the identification of the recharge area of aquifers. Ital J Geosci 136(2):186–197. https://doi.org/10.3301/IJG.2016.15

Nisi B, Raco B, Dotsika E (2016) Groundwater contamination studies by environmental isotopes: a review. In: Jiménez E et al (eds) Environment, energy and climate change I: environmental chemistry of pollutants and wastes. Springer, Berlin. https://doi.org/10.1007/698_2014_281

Onorati G et al (2009) II Relazione sullo Stato dell'Ambiente in Campania. Capitolo Acque sotterranee. ARPAC, Napoli

Paternoster M, Liotta M, Favara R (2008) Stable isotope ratios in meteoric recharge and groundwater at Mt. Vulture volcano, southern Italy. J Hydrol 348:87–97

Petitta M, Scarascia Mugnozza G, Barbieri M, Bianchi Fasani G, Esposito C (2010) Hydrodynamic and isotopic investigations for evaluating the mechanisms and amount of groundwater seepage through a rockslide dam. Hydrol Process 24:3510–3520. https://doi.org/10.1002/hyp.7773

PGA (2016) Distretto idrografico dell'Appennino meridionale—Piano di gestione delle acque ciclo 2015–2021. p 459

Rozanski K, Araguas Araguas L, Gonfiantini R (1993) Isotopic patterns in modern global precipitation. In: Swart PK et al (eds) Climate change in continental isotopic records, vol 78. Geophysical monograph series. AGU, Washington, DC, pp 1–36

Sappa G, Barbieri M, Ergul S, Ferranti F (2012) Hydrogeological conceptual model of groundwater from carbonate aquifers using environmental isotopes (18O, 2H) and chemical tracers: a case study in Southern Latium Region, Central Italy. J Water Resour Prot 4(9):695–716. https://doi.org/10.4236/jwarp.2012.49080

Schiavo MA, Hauser S, Povinec PP (2009) Stable isotopes of water as a tool to study groundwater–sea water interactions in coastal south-eastern Sicily. J Hydrol 364(1):40–49. https://doi.org/10.1016/j.jhydrol.2008.10.005

Session AL (2006) Isotope-ratio detection for gas chromatography. J Sep Sci 29:1946–1961. https://doi.org/10.1002/jssc.200600002

Terzer S, Wassenaar LI, Araguás-Araguás LJ, Aggarwal PK (2013) Global isoscapes for $\delta^{18}O$ and $\delta^{2}H$ in precipitation: improved prediction using regionalized climatic regression models. Hydrol Earth Syst Sci 17(11):4713–4728. https://doi.org/10.5194/hess-17-4713-2013

Van der Veer G, Voerkelius S, Lorentz G, Heiss G, Hoogewerff JA (2009) Spatial interpolation of the hydrogen and oxygen-18 composition of global precipitation using temperature as ancillary variable. J Geochem Explor 101(2):175–184. https://doi.org/10.1016/j.gexplo.2008.06.008

Ward JH (1963) Hierarchical grouping to optimize an objective function. J Am Stat Assoc 58:236–244

West AG, February EC, Bowen GJ (2014) Spatial analysis of hydrogen and oxygen stable isotopes ("isoscapes") in groundwater and tap water across South Africa. J Geochem Explor 145:213–222. https://doi.org/10.1016/j.gexplo.2014.06.009