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Hydrogeochemical analysis on Italian bottled mineral waters: Effects of geology

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ABSTRACT

The use of bottled mineral waters use is increasingly becoming popular and the need for better knowledge of their chemical composition is a key issue for defining their quality, particularly for those elements that are not monitored on a regular basis. The link between geology and water chemistry is well known and can lead to extreme differences in element distribution and is an issue that needs to be addressed. Such an opportunity has been provided by a project of the EuroGeoSurvey Geochemistry Expert Group aimed at the characterization of groundwater geochemistry using bottled mineral waters purchased in supermarkets all over Europe. On these waters pH, conductivity and concentrations of 69 elements and ions were measured at the BGR geochemical laboratories. On a total of 1785 "samples", 158 represent waters bottled in Italy in 126 different sites scattered throughout the country. Most of the purchased mineral water is packaged in PET bottles. In this paper, the dataset concerning Italy has been used to provide an overview on the relationship between natural concentration of the determined chemical elements in groundwater and geo-lithological features. These relationships have been investigated mostly taking into account the surface geology and other information available on water sources. Application of R-Mode factor analysis to the data set allowed the determination of the possible relationship between the distribution of individual elements and lithology or other surface enrichment phenomena. In particular waters draining through volcanic rocks are enriched in elements such as As, B, Br^-, Cl^-, Cs, I, K, Li, Na, NO_3^-, PO_4^{3-}, Rb, Sc, SiO_2, Sr, Te, Ti, and V up to 3 orders of magnitude higher than waters draining through other lithologies. REE and Y show significant difference in median concentration due to interaction of waters with plutonic rocks. Many elements have a large spread of concentrations, which reflects natural variations and interaction with particular lithologies. One of the five R-mode factor analysis associations, recognized as being representative of elements analysed shows high nitrate and V loadings along with As, PO_4^{3-} and Se. The latter association probably reflects a sign of anthropogenic contribution in some aquifers in volcano-sedimentary or silico-clastic deposits and in intensively cultivated areas.

1. Introduction

Consumption of bottled mineral water is increasing significantly worldwide, becoming an important factor both in economic and health issues. This is particularly true for Italy, since the country is one of the largest producers (over 12 billion L/year) and consumers (200 L/per capita/year) of bottled water in the world (Beverfood, 2008). The use of spring water for nutrition and bathing was initiated by the Romans and some well known springs used in ancient times are still exploited today (George, 2001). The production of bottled groundwater in Italy increased by 30% over the last 5 years and remained constant between 2007 and 2008. In Italy, there are 415 official brands according to the European Directive 2009/54/EC (Official Journal L 164 , 26/06/2009 P. 0045 – 0058, 2009) (http://ec.europa.eu/food/food/labellingnutrition/water/index_en.htm,). Despite the large number of brands available on the Italian market, eight companies cover approximately 75% of the whole production with a limited number of brands (Beverfood, 2008). They exploit highly productive sites and have an extensive distribution network (Bono and Boni, 2001; Beverfood, 2008). The remaining fraction of the market is filled by small companies with local plants and distribution (Beverfood, 2008). International holding of some important groups is also the basis for the export of about 1 billion litres per year (Beverfood, 2008).

This study has been conducted in the framework of the EuroGeoSurvey Geochemical Expert Group project, aimed at the geochemical characterization of groundwater by purchasing bottled mineral water in supermarkets all over Europe, whose complete results will be published in an atlas (Reimann and Birke, 2010). On a total of 1785 samples collected in Europe, 158 represent waters

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bottled in Italy in 126 sites. The most important springs for mineral waters analysed are located in central and western Alps, in Tuscany, Umbria, Calabria and Sardinia (Table 1 and Fig. 1). Since the majority of bottled waters in Italy derives from groundwater exploitation, they reflect very well the geochemical features of the aquifers they interact with. In this paper the dataset concerning Italy has been used to provide an overview on the relationships between natural concentration of the determined elements and other parameters (pH, electrical conductivity, EC) in groundwater and geo-lithological features. These relationships have been investigated mostly taking into account the surface geology and other information available on water sources. The discussion has been first based on major chemical composition and then on other minor and trace elements. In addition factor analysis has allowed the determination of the possible relationships between the distribution of individual elements and lithology or other enrichment phenomena. A more detailed discussion of environmental issues is the subject of another paper in this same volume (Cicchella et al., 2010-this volume). This study provides new and important information on bottled mineral waters in Italy. Other published studies on the same issue were mostly based on chemical parameters reported on the labels (Versari et al., 2002; Naddeo et al., 2008) or report analytical results from a very limited number of Italian bottled waters discussed at European or world scale (Misund et al., 1999, Krachler and Shotyk, 2009).

2. Geological and hydrogeological outline

The Italian territory (Fig. 2) is dominated by two important mountain belts, the Alps and the Apennines, originating from the orogenic processes related to the Eurasian and African plate collision and the closing of the Tethyan ocean (Pfiffner, 2005; Carminati and Doglioni, 2005 and references therein). The Pre-Alpine basement crops out in Sardinia, Calabria and locally in the Alps. It is composed of metamorphosed sedimentary successions and Caledonian and Variscan magmatic rocks. Post-Variscan deposits of the Alps and the Apennines consist mainly of sedimentary successions from Permian to Cretaceous age, that record the evolution of the passive margins developed around the Tethyan Ocean, with abundant carbonate deposits in both areas. The first orogenetic phases that led to the formation of the Alps and later of the Apennines are recorded from the Cretaceous age upwards. Thick sequences of silico-clastic sediments, flysch and molasses, accumulated during the Tertiary along the former passive margins of both mountain chains (Carminati et al., 2004).

Table 1
List of bottled water brands discussed in this study. In bold the region name and the corresponding abbreviations used in Fig. 1.

Name
Abruzzo (ABR)
Fonte Primavera
Santa Croce
Basilicata (BAS)
Felicia
Gaudianello
Leggera
Lilia
Sveva
Toka
Vivine
Calabria (CAL)
Calabria
Certosa
Fabrizia
Fontedoro
Fontenoce
Futura
Limpida
Mangiatorella
Serricella
Sorgente dell' Amore
Vita Sana
Campania (CAM)
Acetosella
Don Carlo
Ferrarelle
Fiordaqua
Fonte Ofelia
Lete
Prata
Santagata
Santo Stefano
Emilia-Romagna (EMR)
Cereria
Fonte Chiara
Fonte Lieta — Conad
Fonte Vela
Fonte Ventasso
Fonti San Fermo
Galvanica
Monte Cimone — COOP
Friuli-Venezia Giulia (FVG)
Dolomia
Goccia di Carnia
Paradiso
Pocenia
Latium (LAT)
Acqua di Nepi
Claudia
Cottorella
Egeria
Liguria (LIG)
Fonte Santa Vittoria
Santa Clara
Lombardy (LOM)
Allegra
Balda
Bernina
Boario
Bracca
Coop-sorgente Grigna
Fonte Tavina
Frisia
Gaverina
Leonardo-primaluna alisea
Lievissima
Luna
Maniva
Neve
Pineta-Sorgente Sales
Pureland-Naturale/Primula
San Francesco
San Pellegrino
Santa Corina
Sant'Antonio
Stella Alpina
Vaia
Vitasnella
Marches (MAR)
Casteldelci
Elisa
Frasassi
Gaia
Goccia blue/Frasassi
Nerea
Linnea
Molise (MOL)
Molisia
Sepinia
Piedmont (PIE)
Alpe Guizza
Alpi Cozie
Alte Vette
Cime Bianche
Crodo Lisiel
Fonte delle Alpi
Fonte Gaudenziana
Lauretana
Lurisia
Martina
Monte Rosa
San Bernardo
Sant'Anna di Vinadio
Sparea
Stella del Monviso
Valmora
Sardinia (SAR)
Acqua Light
Boschetta
Candida
Eleonora
Federica
Funte Fria
Levia
Montes
Pura
Quercetta
Rocce Sarde
San Giorgio
San Leonardo
S'Abba
Siete Fuentes
Smeraldina
Tamara
Sicily (SIC)
Cavagrande
Fontalba
Gerasia
Santa Rosalia
Santa Maria
Trentino-Alto Adige (TAA)
Kaiserwasser
Lavaredo
Meraner Mineralwasser
Pejo
Plose
San Zaccaria
Tuscany (TUS)
Acqua Silva
Cintola
Fonte Azzurrina
Fonte de' Medici
Fonte Napoleone
Fonteviva
Goccia Viva
Monteverde
Panna
Santafiora
Sorgente Tesorino
Uliveto
Verna
Umbria (UMB)
Acqua Fabia
Acqua Fabiaviva
Angelica
Conad Acqua Minerale
Fonte Aura
Lieve
Misia
Motette
Orvieto
Rocchetta
Sangemini
Viva
Aosta Valley (VDA)
Courmayeur
Cristalià
Mont Blanc
Veneto (VEN)
Dolomiti
Fontemargherita
Guizza
Recoaro
San Benedetto
Valli del Pasubio–Nuova Acqua Chiara
Vera

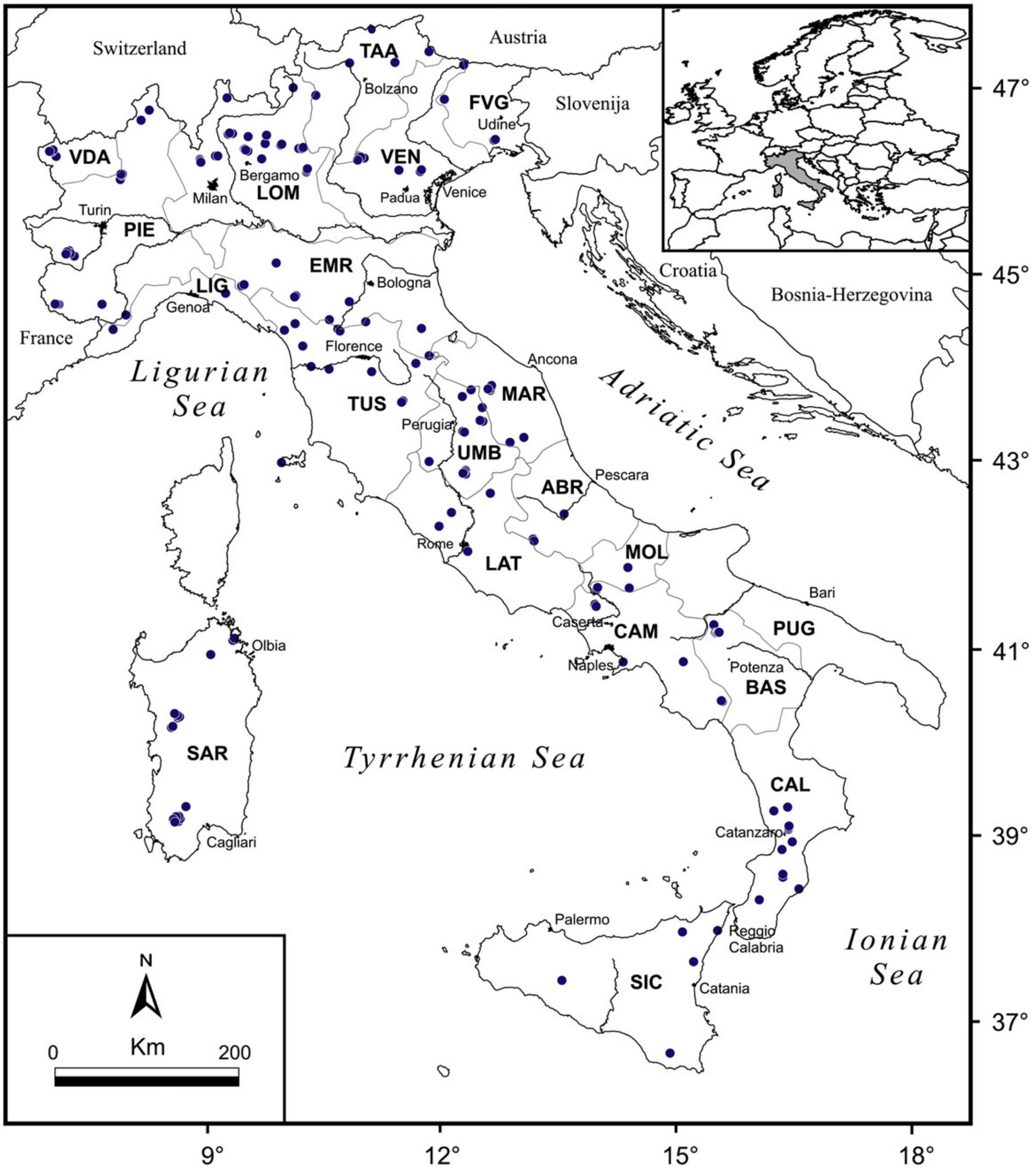


Fig. 1. Location of the springs where purchased waters are bottled with the indication of the Italian region (for abbreviations see Table 2). Some of the points are slightly displaced to limit overlapping.

From Permian to recent, several magmatic episodes with different geodynamic characteristics occurred in Italy: the most significant are the Permian volcanic episodes, in the Southern Alps (Rottura et al., 1998), the Eocene–Oligocene rhyolitic–trachitic and basaltic episodes (both effusive and subvolcanic) in the Southern Alps; the Tertiary calkalkaline magmatism (Oligocene–Miocene) in Sardinia and the Plio-Quaternary volcanism with variable characters in Sardinia, Central and Southern Italy and in Sicily (Beccaluva et al., 2004; Peccerillo, 2005).

From the hydrogeological point of view, the most important water resources are found associated with alluvial aquifers in the alluvial plains and in carbonate aquifers in the mountain areas. Hydrological complexes associated to silico-clastic sediments are widespread along the country: they are of glacial, fluvial or fluvio-lacustrine origin in the internal Po River Plain, along the border between the Alps and of the Apennines. In coastal areas along the Adriatic, Ionian and Tyrrhenian Sea, the aquifers interact more with marine deposits. Other important hydrological complexes are associated with the carbonate successions widespread throughout the whole territory (Fig. 2). The latter type of aquifer is particularly important along the southern border of the Alps characterized to the east, by the occurrence of dolomite, with occasional intercalations of evaporites and volcaniclastic deposits, and to the west by limestones. Carbonate hydrological complexes are also important all over the Apennines, especially in the Umbria–Marche areas (Fig. 2). The hydrological complexes related to flysch deposits, along the Apennines, can be locally important, particularly where sands or conglomerates prevail, but no generalization can be made (Civita, 2008) because the degree of cementation and fracturing affects the productivity of each complex. The hydrological complexes related to magmatic (plutonic) or metamorphic rocks are of limited importance from a hydrogeological point of view even if they are often important sources of bottled mineral waters. These rocks are

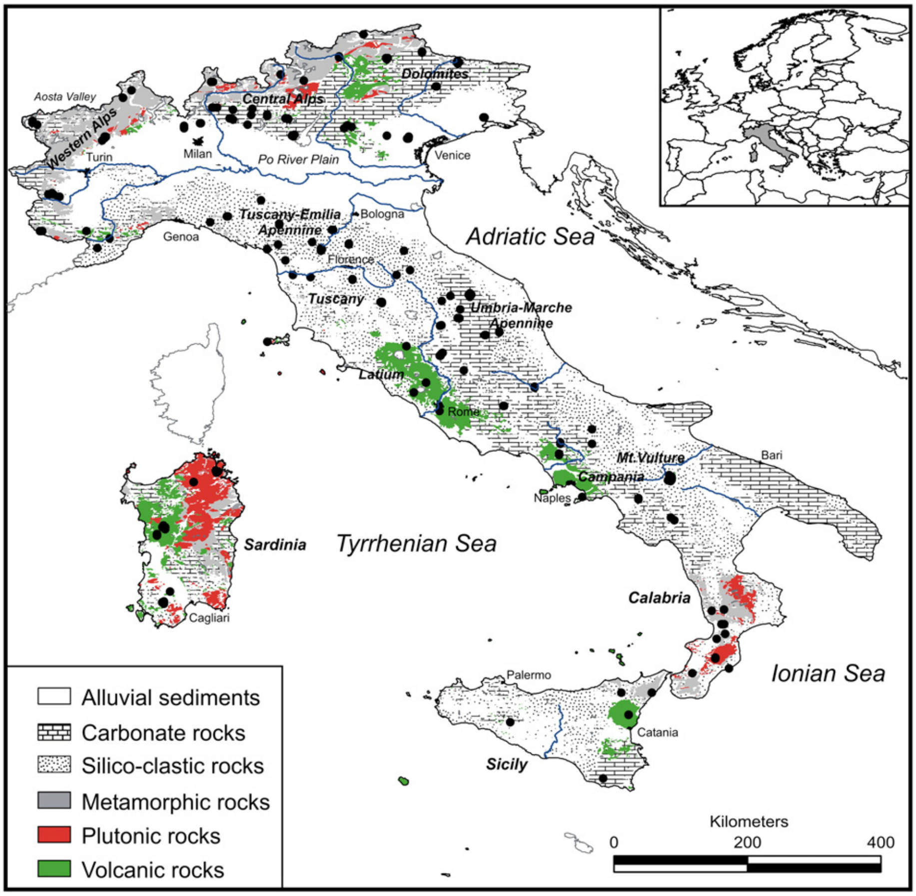


Fig. 2. Water spring locations on a simplified Italian geological map.

most common in the Western and Central Alps, Calabria, north-eastern Sicily and Sardinia (Fig. 2). Magmatic and metamorphic rocks have generally low permeability, although they can locally originate springs; water circulation is generally restricted, not connected and in many cases related to deformation zones (Civita, 2008). Water circulation in volcanic rocks, either unconsolidated or lithified, can lead to relatively important hydrological complexes and locally to significant reservoirs of thermal waters. Where lithified, their productivity is related to fractures, cooling joints or unconformities between lava flows; where unconsolidated pyroclastic rocks are present, as in the case of the Roman and Campanian volcanic areas or in the Mt. Vulture area (Fig. 2), productive levels can be related to the overlap of units with different permeability.

3. Materials and methods

A total of 158 bottled waters representing 126 wells were purchased in supermarkets all over Italy (list in Table 1, location in Fig. 1). Still waters formed the bulk of the database (139 samples), which also included waters containing natural CO_2 (11 samples) and artificially carbonated waters (8 samples). Of the analysed 158 brands, 147 were sold in PET (polyethylene terephthalate) bottles (clear: 97, blue–bluish: 33, green–greenish: 17) and 11in glass bottles (clear: 8, blue–bluish: 1, green–greenish: 2). Cicchella et al. (2010-this volume) discuss the effects of container on water chemistry based on the Italian data set, whereas a general discussion on the overall European database is presented by Reimann et al. (2010).

Waters have been analysed at German Geological Survey (BGR) in Berlin, for 69 elements and ions (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Br^-, HCO_3^-, Cl^-, F^-, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, and SiO_2), in addition, pH and EC have been measured. Detection limits and analytical techniques are reported in Table 2 along with the summary statistics. Details about sample preparation, analytical methods and other technical and operative information can be found in Birke et al. (2010, this same volume).

The statistical analysis has been performed by Excel, whereas maps were produced by ArcGIS software. All the variables were subjected to the Shapiro–Wilk test for normality, and to the non-parametric Kruskal–Wallis test by ranks (Helsel and Hirsch, 1992) to test equality of population medians among groups defined by the dominant bedrock lithologies. The analyses performed by the DAS+S module (Reimann et al., 2008) were also used for exploratory univariate analysis.

For statistical analysis and to perform geochemical maps, elemental concentrations below detection limit were assumed to be equal to 50% of the detection limit.

Factor analysis has been used to investigate the complex multivariate relationships among variables, which are not normally clear by simple correlation analysis. Abundant literature on multivariate statistical methods and on their application to earth sciences is available (e.g. Davis 1984, Morrison 2005).

Before running the factor analysis, a selection of data was obtained with respect to the analytical quality. Elements with a high proportion of data below the detection limit (>25%) were not accepted in the analysis. Of all the REE analysed, only La was included in the analysis as representative of the elemental group.

Table 2
Summary of the whole parameters measured in the Italian bottled waters. Minimum (min), maximum (max) and 25th, 50th 75th percentiles are also shown; n: number of observations above detection limit; An. method: analytical method used; dl: detection limit.

	Min	25	50	75	Max	n	Unit	An. method	dl
pH	4.1	7.1	7.6	7.9	8.8	158		Potentiometric	–
EC	18	205	388	599	3020	158	µS/cm	Conductometric	–
Ca	1.3	19.0	42.9	82.7	473.5	158	mg/L	ICP-OES	0.01
K	0.2	0.6	1.1	2.0	85.2	158	mg/L	ICP-OES	0.1
Mg	0.3	3.9	6.8	16.7	75.7	158	mg/L	ICP-OES	0.01
Na	0.4	2.7	6.7	19.8	428	158	mg/L	ICP-OES	0.1
HCO_3	3.5	74	170	290	1665	158	mg/L	Titration	2
Cl	0.2	2.3	7.6	22.3	323	158	mg/L	IC	0.01
F	0.011	0.061	0.143	0.377	1.75	158	mg/L	IC	0.003
NO_3	<0.01	1.30	3.11	6.37	35.1	152	mg/L	IC	0.01
Br	<0.003	0.005	0.019	0.057	1.21	137	mg/L	IC	0.003
PO_4	<0.02	<0.02	0.03	0.09	0.68	117	mg/L	ICP-OES	0.02
SO_4	1.4	5.8	15.4	34.2	1278	158	mg/L	IC	0.01
SiO_2	0.9	6.4	9.6	17.7	105	158	mg/L	ICP-OES	0.05
Ag	<0.001	<0.001	<0.001	0.001	17.2	43	µg/L	ICP-QMS	0.001
Al	<0.3	0.47	0.95	1.89	237	141	µg/L	ICP-QMS	0.3
As	0.0112	0.11875	0.278	0.77325	8.91	158	µg/L	ICP-QMS	0.01
B	0.41	6.55	16.15	48.65	1170	158	µg/L	ICP-QMS	0.1
Ba	<1	6.3	24	63	440	147	µg/L	ICP-OES	0.001
Be	<0.001	<0.001	0.0013	0.0126	4.69	95	µg/L	ICP-QMS	0.001
Bi	<0.0005	<0.0005	0.00057	0.00100	0.00591	86	µg/L	ICP-QMS	0.0005
Cd	<0.001	0.0019	0.0033	0.0065	0.1610	145	µg/L	ICP-QMS	0.001
Ce	<0.0005	<0.0005	<0.0005	0.0011	0.0862	63	µg/L	ICP-QMS	0.0005
Co	<0.002	0.011	0.016	0.027	0.602	157	µg/L	ICP-QMS	0.002
Cr	<0.03	0.089	0.166	0.309	3.230	157	µg/L	ICP-QMS	0.03
Cs	<0.001	0.0032	0.0159	0.1298	33.3	148	µg/L	ICP-QMS	0.001
Cu	<0.01	0.110	0.185	0.292	5.5	157	µg/L	ICP-QMS	0.01
Dy	<0.0001	0.00054	0.00090	0.00196	0.168	156	µg/L	ICP-QMS	0.0001
Er	<0.0001	0.000263	0.000649	0.001708	0.197	148	µg/L	ICP-QMS	0.0001
Eu	<0.0001	0.00092	0.00199	0.00409	0.0337	155	µg/L	ICP-QMS	0.0001
Fe	<0.1	0.15	0.23	0.49	11.7	146	µg/L	ICP-QMS	0.1
Ga	<0.0005	<0.0005	0.00232	0.00643	0.0277	112	µg/L	ICP-QMS	0.0005
Gd	<0.0002	0.00047	0.00107	0.00243	0.0753	148	µg/L	ICP-QMS	0.0002
Ge	<0.005	0.006563	0.0116	0.0279	0.615	133	µg/L	ICP-QMS	0.005
Hf	<0.0005	<0.0005	<0.0005	0.00055	0.01770	50	µg/L	ICP-QMS	0.0005
Ho	<0.0001	0.00021	0.00032	0.00064	0.05420	147	µg/L	ICP-QMS	0.0001
I	<0.02	1.13	2.35	5.15	160	157	µg/L	ICP-QMS	0.2
La	<0.0005	0.000602	0.00135	0.0046	0.2190	124	µg/L	ICP-QMS	0.0005
Li	<0.1	0.8	3.4	10.5	241	154	µg/L	ICP-QMS	0.1
Lu	<0.00005	0.00007	0.00015	0.00049	0.03440	141	µg/L	ICP-QMS	0.00005
Mn	<0.001	<0.001	<0.001	0.001	0.33	50	mg/L	ICP-OES	0.001
Mo	<0.001	0.14	0.42	0.87	27.7	158	µg/L	ICP-QMS	0.001
Nb	<0.001	<0.001	<0.001	0.00127	0.117	51	µg/L	ICP-QMS	0.001
Nd	<0.0002	0.0006	0.0013	0.0048	0.198	154	µg/L	ICP-QMS	0.0002
Ni	<0.01	0.040	0.114	0.314	6.62	157	µg/L	ICP-QMS	0.01
Pb	<0.002	0.003	0.006	0.012	0.625	150	µg/L	ICP-QMS	0.002
Pr	<0.00005	0.000083	0.000233	0.000954	0.047400	139	µg/L	ICP-QMS	0.00005
Rb	0.04	0.40	0.80	2.73	346	158	µg/L	ICP-QMS	0.001
Sb	0.007	0.208	0.298	0.441	1.720	158	µg/L	ICP-QMS	0.002
Sc	<0.01	0.032	0.055	0.080	1.11	157	µg/L	ICP-QMS	0.01
Se	<0.01	0.071	0.164	0.311	2.030	150	µg/L	ICP-QMS	0.01
Sm	<0.0002	0.0004	0.0008	0.0020	0.0582	150	µg/L	ICP-QMS	0.0002
Sn	<0.001	0.0030	0.0060	0.0102	1.06	153	µg/L	ICP-QMS	0.001
Sr	0.008	0.0633	0.1820	0.6498	14.1	158	mg/L	ICP-OES	0.001
Ta	<0.001	<0.001	<0.001	<0.001	0.00143	5	µg/L	ICP-QMS	0.001
Tb	<0.00005	<0.00005	0.00010	0.00027	0.0148	124	µg/L	ICP-QMS	0.00005
Te	<0.005	<0.005	0.0051	0.0101	0.0801	85	µg/L	ICP-QMS	0.005
Th	<0.0001	0.00020	0.00029	0.00047	0.00506	144	µg/L	ICP-QMS	0.0001
Ti	<0.01	<0.01	0.027	0.054	0.732	98	µg/L	ICP-QMS	0.01
Tl	<0.0005	0.0017	0.0053	0.0107	0.4180	153	µg/L	ICP-QMS	0.0005
Tm	<0.00005	0.00007	0.00012	0.00030	0.0308	137	µg/L	ICP-QMS	0.00005
U	<0.0005	0.11625	0.4745	1.1575	31	157	µg/L	ICP-QMS	0.0005
V	<0.01	0.135	0.309	0.932	48.9	156	µg/L	ICP-QMS	0.01
W	0.0025	0.0100	0.0177	0.0403	1.31	158	µg/L	ICP-QMS	0.002
Y	<0.0005	0.00393	0.00842	0.02255	2.86	156	µg/L	ICP-QMS	0.0005
Yb	<0.0002	0.000377	0.000684	0.002375	0.211	144	µg/L	ICP-QMS	0.0002
Zn	<0.05	0.13	0.31	0.76	46.4	155	µg/L	ICP-QMS	0.05
Zr	<0.001	0.0011	0.0019	0.0067	5.83	126	µg/L	ICP-QMS	0.001

Subsequently, observing the correlation matrix, Cr, Pb and Th were eliminated because they showed no significant correlations (<0.4) with all other elements.

The factors were extracted as principal components and then rotated according to the Varimax criterion. The "Data Reduction" module of the SPSS software package was applied. After several trial runs, with different numbers of extracted and rotated factors (4, 5, 6 and 8), the five factor solution was accepted.

4. Results and discussion

4.1. Grouping of mineral waters

The analysed waters cover almost the entire Italian territory (Figs. 1 and 2) even if there are areas with a higher density of springs than others. In some cases, extracted from wells of restricted areas (reflecting different aquifers) waters with different compositions are bottled by different brands. Important districts of production (Fig. 2) can be recognized in:

- the Western Alps (with a total of 22 brands) close to Turin and in Valle d'Aosta. These springs are mostly related to the occurrence of metamorphic and plutonic rocks;
- the Central Alps (23 brands), which can be subdivided in a southern sector, where spring sites are located in areas dominated by Permian volcanics and Mesozoic sedimentary (mainly carbonate) series and a northern one where metamorphic rocks are abundant;
- the Dolomitic Alps (11 brands), where the springs, although scattered throughout the area, are generally associated with Mesozoic sedimentary rocks and Permian evaporites;
- the Tuscany–Emilia Apennines (16 brands), where several springs are related to silico-clastic rocks (flysch deposits), with variable amounts of carbonate content (Valloni and Zuffa, 1984; Dinelli et al., 1999) at the contact with less permeable clayey units;
- the Umbria–Marche Apennines (18 brands), with springs mostly related to Mesozoic carbonate series (Boni et al., 1986);
- the Latium (Roman) and Campania area, in central Italy (14 brands), also including the Mount Vulture volcano (east of Naples), characterized by alkaline Pliocene–Pleistocene volcanics (pyroclastics or lava flows) (Peccerillo, 2005). Some springs in this area are influenced by other types of aquifers, mainly located in carbonate rocks;
- central-southern Calabria (11 brands), where springs are associated with plutonic and metamorphic rocks, and with the overlying sedimentary cover;
- Sicily island (5 brands), where scattered springs are associated with metamorphic, volcanic and sedimentary rocks;
- Sardinia island (17 brands), where springs are associated with sedimentary series in the southern sector, with Pliocene volcanic rocks in the central sector, and with plutonic rocks in the north-east sector of the island.

On the basis of the dominating rock types at the aquifer locations, analysed bottled water data were grouped into six categories (Table 3): plutonic, volcanic, metamorphic, sedimentary, volcanic-metamorphic and volcanic-sedimentary. Data associated to sedimentary rocks have been further subdivided in: limestones, dolostones, sandstones and mixed sedimentary (Table 3). Some data could not be attributed to any of the afore-mentioned groups, because of the complex geology of the spring sites.

Table 3
Grouping of analysed bottled waters according to surface geology.

Dominating rock type	Number of waters
Plutonic	8
Volcanic	17
Metamorphic	40
Sedimentary–metamorphic	8
Volcanic–sedimentary	7
Sedimentary	108
Limestones	47
Dolostones	10
Sandstones	9
Mixed sedimentary	35

4.2. General classification of water

Summary statistics for the Italian bottled mineral waters is presented in Table 2. Data show that many elements display wide ranges of concentrations spanning several orders of magnitude (10^6–10^4) as in the case of U, Cs, Ag, Zr, Y; also major constituents generally vary over wide concentration ranges (10^2).

Among the compositional parameters used in the classification of drinking water, the amount of dissolved solids is certainly one of the most important. In the labels of the bottled waters, this information is reflected by two parameters, total solid residue and EC, which are both directly linked to the types of waters (Hem, 1985). We have used EC to classify water types (Table 4) into four categories (van der Aa, 2003): very low, low, intermediate and high mineral concentrations. The low mineral concentration water type dominates over the intermediate and very low water types. Only 2 water samples have high mineral concentration. The prevalence of low mineral concentration waters reflects consumer preference and market demand. Waters characterized by higher concentration of dissolved substances may be preferred by a limited number of persons or used for therapeutic purposes.

Waters are mostly Ca-HCO_3 type (Fig. 3), the most suitable for drinking, which are generally characterized by low to intermediate EC. Higher mineralized waters have different chemical compositions (Fig. 3). In the (Durov, 1948) classificatory diagram (Fig. 3) some well-identified groups (clusters and trends) can be distinguished, related to the geographic distribution of major anions and cations (Fig. 4a and b) and background lithology. In Fig. 4c a classification summary map of the analysed bottled waters based on the Durov plot, is presented which is described in the following section:

1 — Waters with generally low EC of the Ca-HCO_3 group (group 1 in Fig. 3) deriving from interaction with various lithologies, with a prevalence, however, of sedimentary rocks. Waters with such composition are frequent in the central Umbria–Marche Apennine area were carbonate aquifers are common, in the Tuscany–Emilia Apennine in association with sandstones aquifers and also include some waters from the Central (mostly limestones) and Western Alps (metamorphic). Dissolution of calcite is the dominant reaction characterizing these waters, particularly those interacting with sedimentary rocks, while interaction with Ca-bearing silicates likely controls water chemistry in metamorphic rocks.

2 — A group of HCO_3-rich waters (group 2 in Fig. 3), but with a different distribution among the cations (Fig. 4b), particularly with a slightly higher Mg percentage (Ca–Mg–HCO_3 type, Fig. 4c). This group includes basically waters interacting with sedimentary rocks, mainly in the Dolomitic Alps, in the plain area around Venice and in scattered areas of the Central Alps. Interaction with dolomites and Mg-bearing carbonates is the dominant reaction characterizing these waters.

3 — High Na, Ca and carbonate-rich waters (group 3 in Fig. 3), often naturally sparkling with intermediate to high EC. This water type

Table 4
Classification of water types according to EC (van der Aa, 2003).

Water type	EC (μS/cm)	Samples
Very low mineral concentration	<77	12
Low mineral concentration	77–769	120
Intermediate mineral concentration	769–2308	24
High mineral concentration	>2308	2

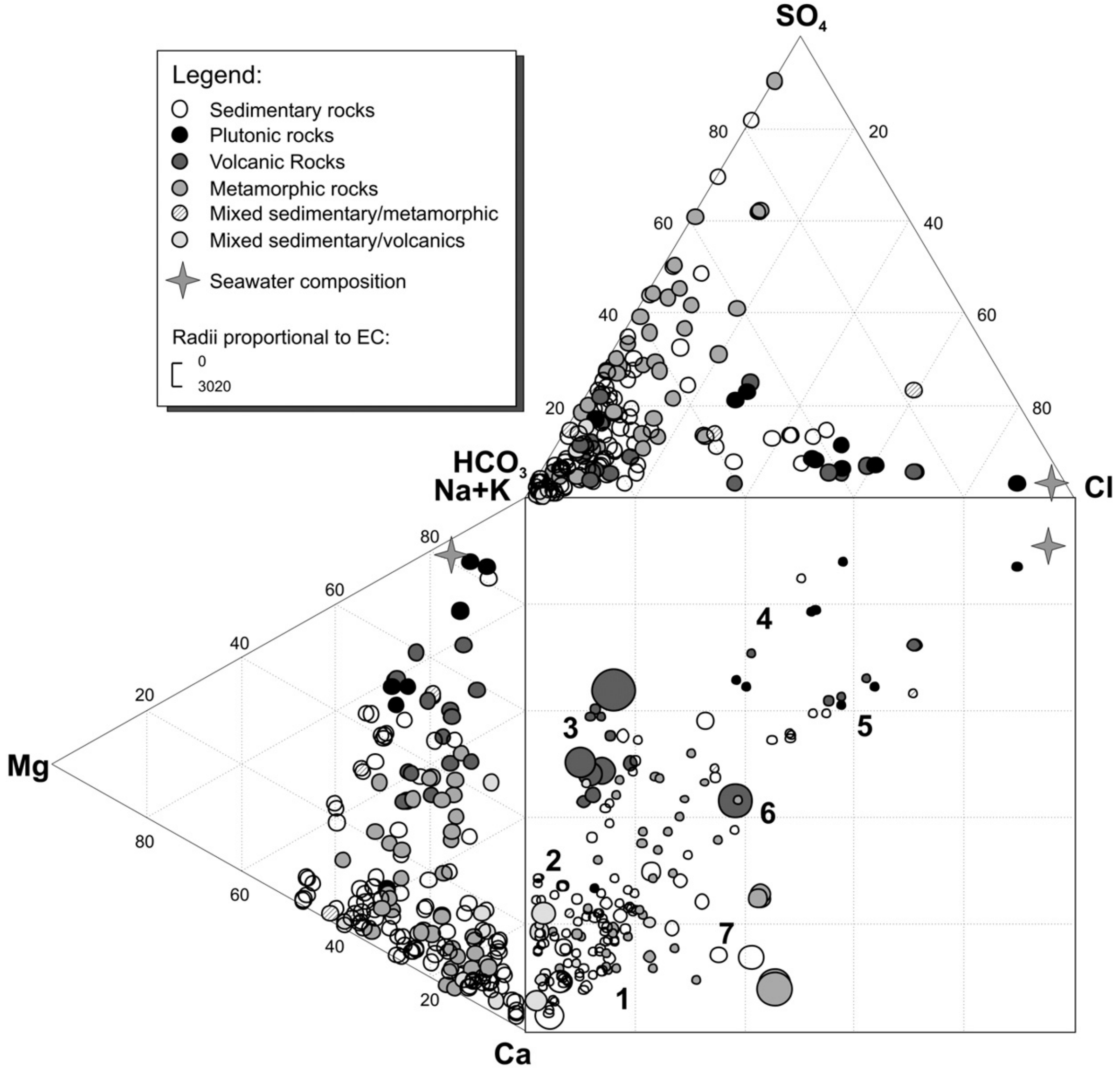


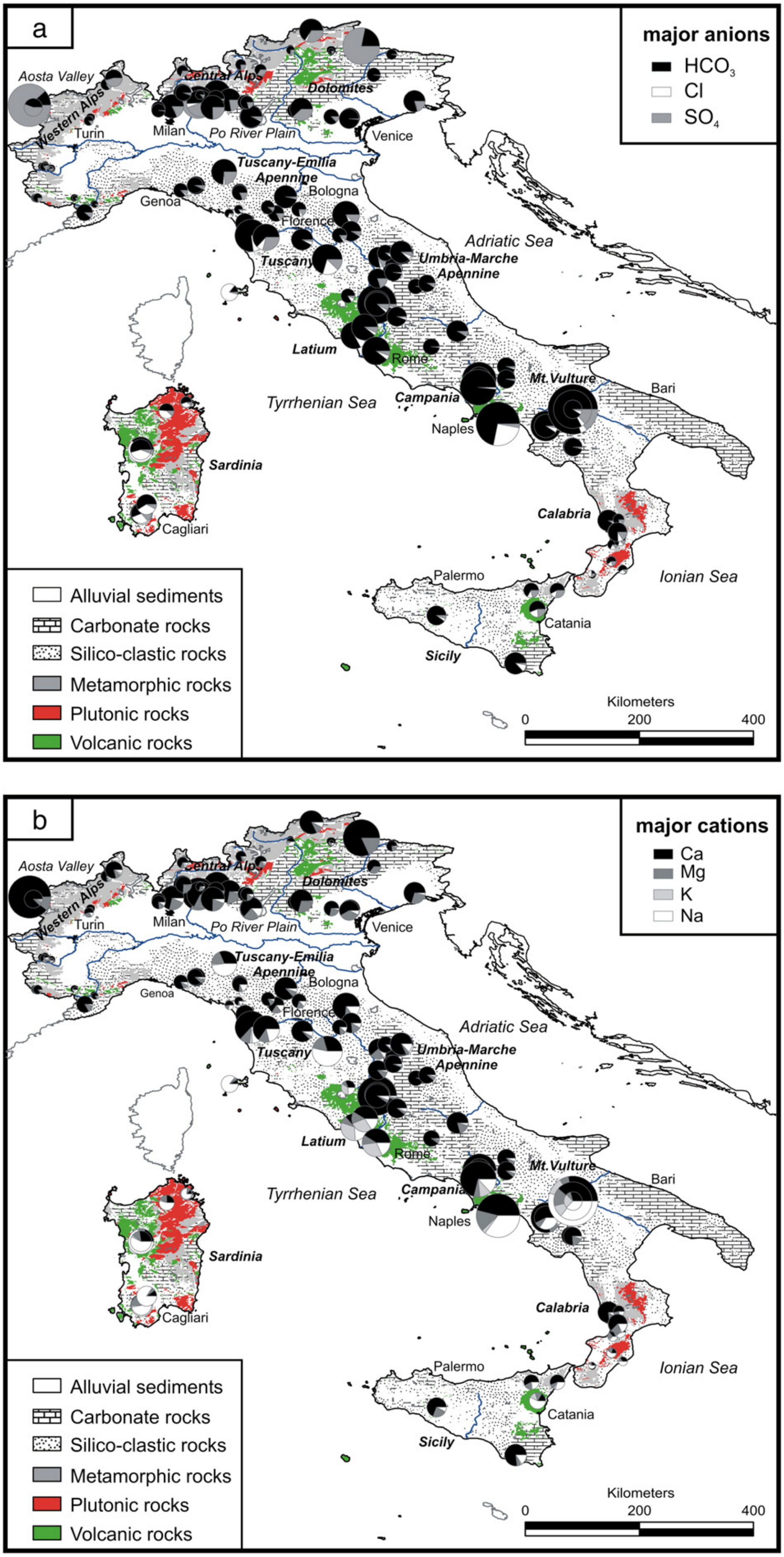
Fig. 3. Durov (1948) classificatory diagram showing the major ionic composition of the analysed waters. Symbols are proportional to EC and indicate the surface geology where springs are located. Seawater average composition (Chester, 2002) is reported for comparison. Numbers refer to group of samples discussed in the text.

includes also Ca–Na–Mg–HCO_3 waters (Fig. 4c), often with high K concentrations. It is correlated to the alkaline Roman Comagmatic volcanic Province (high in K), spanning from southern Tuscany to Mt. Vulture (Washington, 1906; Peccerillo, 2005), also rich in geothermal spring waters. Some distinction can be made among samples deriving from volcanic areas, based on the different proportions of K and Na, as in the case of Mt. Vulture area (Fig. 4a, c). In the latter water type, the dissolution of various K- and Na-bearing silicates (sanidine, plagioclase, leucite, and nepheline) is the main reaction that controls the water composition, but also Mg-bearing minerals are involved in water–rock interaction. Mt. Vulture Na–Mg-rich waters can be related to the presence of carbonatites (Stoppa and Principe, 1998), intrusive or extrusive igneous rocks defined by mineralogic composition, consisting of greater than 50% carbonate minerals.

4 — Low EC waters, with high Na and K (group 4 in Fig. 3) and equivalent Cl and HCO_3, (Na–Cl–HCO_3 water type, Fig. 4c). The latter includes prevalent waters interacting with plutonic rocks whose chemistry is likely controlled by feldspar alteration. Both K and Na may also result from evaporitic deposits and/or from residual seawater salts in sediments. Bottled waters from Tuscany, Sardinia, Calabria and Sicily (Fig. 4c) clearly show this feature and in addition relatively high proportion of Mg which could be related either to involvement of Mg-bearing silicates in water/rock processes or sea water contribution.

5 — Waters directly pointing to a seawater type, albeit with low EC (group 5 in Fig. 3), suggest the importance of marine water contribution (Na–Cl, Na–Ca–HCO_3–Cl types). Several waters from Sardinia and Calabria (Fig. 4a, b, c) belong to this type, with hydrogeological settings not favourable to long water circuits (shallow aquifers in plutonic or metamorphic substrate) and close to the sea. The low EC suggests limited water–rock interaction. In volcanic areas hydrothermal water contribution can also be speculated (De Vivo and Lima, 2008; Albanese et al., 2010)

6 — Ca–Na–Mg–HCO_3–Cl–SO_4 waters, at the centre of the Durov Plot (group 6 in Fig. 3), with a mixed composition, and also characterized by low EC. These include many waters flowing through metamorphic rocks, likely a transition between groups 4


a
major anions
HCO3
Cl
SO4
Aosta Valley
Western Alps
Central Alps
Dolomites
Turin
Milan
Po River Plain
Venice
Tuscany-Emilia Apennine
Bologna
Genoa
Florence
Adriatic Sea
Tuscany
Umbria-Marche Apennine
Latium
Rome
Mt. Vulture
Bari
Tyrrhenian Sea
Campania
Naples
Sardinia
Cagliari
Calabria
Palermo
Ionian Sea
Catania
Sicily
Alluvial sediments
Carbonate rocks
Silico-clastic rocks
Metamorphic rocks
Plutonic rocks
Volcanic rocks
Kilometers
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Ca
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K
Na
Aosta Valley
Western Alps
Central Alps
Dolomites
Turin
Milan
Po River Plain
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Tuscany-Emilia Apennine
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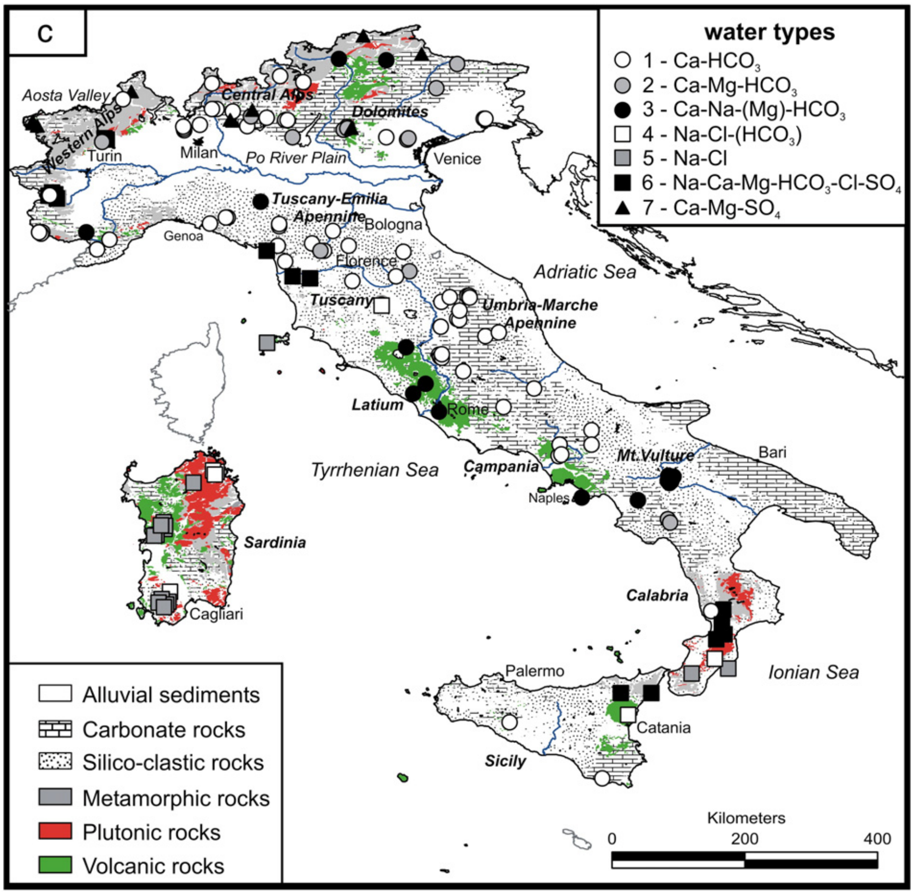


Fig. 4. Geographic distribution of the proportions of major anions (a) and cations (b) of the analysed waters. (c) General distribution of the water types. Symbols in (a) and (b) are proportional to EC. Some points were slightly shifted to reduce the overlaps.

and 5, mostly located in Calabria, Sicily and Tuscany (Fig. 4c). The main elements are present in similar proportions giving to this type of water ill-defined characteristics. In view of the location of the water sources (Fig. 4c), it can be assumed that, in addition to water–metamorphic rock interaction, there is a superimposed marine water contribution.

7 — Ca–(Mg)–SO_4 waters, which record interaction with evaporitic rocks and/or sulphide bearing aquifers (group 7 in Fig. 3). This group includes waters from sedimentary and metamorphic rocks such as the ones from the Valle d'Aosta, in the western sector of the Alps, some waters in the Central Alps and few in the Dolomitic Alps (Fig. 4b, c). Aquifers associated to metamorphic rocks seems to be mostly controlled by sulphide-rich shales, while those associated with Permian sedimentary successions, by sulphate dissolution.

4.3. Differences related to lithology

To verify the occurrence of significant differences between the groups defined by the dominant bedrock lithologies, all the variables were included in a non-parametric statistical test. The Kruskal–Wallis test (Helsel and Hirsch, 1992) is generally applied to variables which do not show normal distribution, as the Shapiro–Wilk test results demonstrated. The null hypothesis for this test is that there is no significant difference between the ranks of the concentrations of a chemical constituent among the lithologic groups. For all hypothesis tests in this study, rejection of the null hypothesis requires that the attained significance level (p), the probability that the observed differences are due to chance rather than the factor tested, is less than 0.001 (99.9% confidence level). The application of the test to the Italian mineral waters as grouped, identified significant differences for some variables, underscored in Table 5.

In general, the most significant differences are related to waters circulating within volcanic rocks, which are characterized by higher median values for many elements (As, B, Br^-, Cl^-, Cs, I, K, Li, Na, NO_3^-, PO_4^{3-}, Rb, Sc, SiO_2, Sr, Te, Ti, and V), with distribution partially overlapping with waters draining through other rock types. This behaviour is shown, for example, by K, Rb and SiO_2, though other elements, such as Li, PO_4^{3-}, Sc, Cl and Br, display rather different distribution (Fig. 5). The spatial distribution clearly shows that the highest values in waters from volcanic areas are displayed by elements such as Rb and Li (Fig. 6a, b).

Rubidium can substitute for K in micas and K-feldspar. Secondary environmental weathering of the common minerals is the main source of Rb, its mobility is strongly controlled by incorporation in clay minerals and adsorption onto clays (Shand and Edmunds, 2008). Geothermal spring waters can also be enriched in Rb. Analysed water concentrations vary from 0.04 (no sample below detection limit) to 346 μg/L with a median of 0.80 μg/L, a value slightly lower than the average world stream water Rb content (1.1 μg/L, Koljonen, 1992) and of the average value of Italian surface water samples (1.15 μg/L, FOREGS project, De Vivo et al., 2009). Data concerning bottled mineral waters, at an European scale (Misund et al., 1999) indicate median value of 4.79 μg/L and 0.87 μg/L, on a global scale (Krachler and Shotyk, 2009). In Italy (Fig. 6a), the highest concentrations are associated to the Roman Comagmatic Province including Mt. Vulture volcanic area. This alkaline volcanic Province is also rich in geothermal spring waters. Rb and K concentrations are anomalous in the latter

Table 5
Results of the Kruskal–Wallis test performed on the Italian bottled waters. The table reports the median for each lithologic group and p-values. Variables in italic and bold have p-values lower than 0.001 (p-values<0.001 are considered significant). MET: metamorphic rocks, PLU: plutonic rocks; SED: sedimentary rocks; SE–M.: sedimentary–metamorphic rocks; SE–V.: sedimentary–volcanic rocks; VOLC: volcanic rocks.

	Unit	MET	PLU	SED	SE–M.	SE–V.	VOLC	p-value
Ag	μg/L	0.0005	0.0005	0.0005	0.0005	0.00185	0.0005	0.0221
Al	μg/L	1.25	0.6905	0.7725	1.02	1.41	1.26	0.09295
As	μg/L	0.652	0.03495	0.221	0.0543	0.759	2.23	6.03E−07
B	μg/L	5.68	12.925	19	7.4	15.1	99.5	1.17E−06
Ba	mg/L	0.005	0.0005	0.048	0.009	0.019	0.021	9.33E−09
Be	μg/L	0.00107	0.09425	0.00107	0.00187	0.0376	0.0221	9.35E−08
Bi	μg/L	0.00025	0.0006625	0.0005795	0.000572	0.000733	0.00025	0.9868
Br	mg/L	0.003	0.0655	0.017	0.0065	0.013	0.1	1.55E−09
Ca	mg/L	19.2	4.435	58.45	22.1	135	35.7	1.14E−07
Cd	μg/L	0.00375	0.00565	0.002655	0.00321	0.0113	0.00353	0.002074
Ce	μg/L	0.00025	0.00649	0.00025	0.00025	0.00207	0.00025	0.0006559
Cl	mg/L	1.09	23.35	7.24	2.715	5.99	37	1.00E−09
Co	μg/L	0.0132	0.0129	0.016875	0.0129	0.0354	0.0149	0.3718
Cr	μg/L	0.149	0.07745	0.182	0.224	0.489	0.183	0.1128
Cs	μg/L	0.00717	0.1105	0.006735	0.0296	0.0875	0.224	5.80E−05
Cu	μg/L	0.167	0.2585	0.18825	0.201	0.149	0.154	0.8181
Dy	μg/L	0.00128	0.0131	0.0006155	0.000741	0.00361	0.000895	2.01E−06
EC	μS/cm	157	153.5	456	196	701	781	9.61E−09
Er	μg/L	0.00101	0.009415	0.0004775	0.000369	0.00309	0.00053	3.99E−05
Eu	μg/L	0.00057	0.0002725	0.0007225	0.00111	0.000849	0.000393	0.4088
F	mg/L	0.126	0.2305	0.136	0.101	0.144	0.511	0.06226
Fe	μg/L	0.155	0.4375	0.228	0.2105	0.495	0.354	0.002402
Ga	μg/L	0.00338	0.00025	0.00223	0.00445	0.00025	0.00223	0.1424
Gd	μg/L	0.001	0.013	0.000941	0.000383	0.0045	0.000905	0.001885
Ge	μg/L	0.00674	0.01105	0.013475	0.00775	0.00887	0.0189	0.002297
HCO_3	mg/L	56	33.85	226.5	85.5	469	279	6.93E−10
Hf	μg/L	0.00025	0.0004575	0.00025	0.00025	0.0015	0.00025	0.01176
Ho	μg/L	0.00038	0.003075	0.000311	0.000228	0.00119	0.000321	0.0002836
I	μg/L	0.647	2.885	2.705	1.18	3.84	4.93	6.31E−07
K	mg/L	1.2	0.65	0.9	0.6	1.2	29.6	1.99E−07
La	μg/L	0.00158	0.00379	0.001165	0.000632	0.00741	0.000904	0.008803
Li	μg/L	1.35	3.66	3.84	1.3	1.69	17.1	0.001407
Lu	μg/L	0.00015	0.001795	0.0001265	0.0000726	0.000651	0.000176	0.00092
Mg	mg/L	4.79	2.955	9.705	8.06	13.2	11.9	9.67E−06
Mn	mg/L	0.5	1	0.5	0.5	2	0.5	0.006704
Mo	μg/L	0.482	0.367	0.4505	0.418	0.317	0.0455	0.04642
Na	mg/L	1.8	22	6.3	2.85	4.4	50.2	1.54E−10
Nb	μg/L	0.0005	0.0005	0.0005	0.0005	0.00429	0.00161	0.0003254
Nd	μg/L	0.00251	0.007535	0.001021	0.00074	0.00554	0.00101	0.0003122
Ni	μg/L	0.0412	0.07215	0.1535	0.2005	0.115	0.264	0.004552
NO_3	mg/L	2.92	1.73	2.4875	3.2	4.77	8.69	0.0008221
Pb	μg/L	0.0067	0.009805	0.005615	0.0121	0.0104	0.00418	0.359
pH		7.5	7.025	7.7	7.4	7.2	6.9	6.39E−06
PO_4	mg/L	0.02	0.01	0.03	0.02	0.17	0.36	8.46E−10
Pr	μg/L	0.00032	.001014	0.000157	0.000115	0.000196	0.000122	0.002301
Rb	μg/L	0.718	0.6985	0.6235	0.98	3.11	33.8	1.82E−08
Sb	μg/L	0.33	0.268	0.2865	0.391	0.408	0.304	0.5893
Sc	μg/L	0.0329	0.0536	0.054	0.0444	0.0562	0.246	2.24E−07
Se	μg/L	0.152	0.148	0.196	0.198	0.0673	0.165	0.1279
SiO_2	mg/L	7.4	11.55	9.15	8	12.7	72.7	4.83E−08
Sm	μg/L	0.00084	0.00746	0.000801	0.000373	0.00291	0.00068	0.0018
Sn	μg/L	0.00448	0.008855	0.00565	0.00552	0.00989	0.00651	0.3082
SO_4	mg/L	11.7	6.975	20.75	20	4.33	19.6	0.02344
Sr	mg/L	0.066	0.038	0.2885	0.079	0.18	0.445	2.95E−06
Ta	μg/L	5.00E−04	5.00E−04	5.00E−04	5.00E−04	5.00E−04	5.00E−04	0.9553
Tb	μg/L	1.65E−04	2.18E−03	7.53E−05	6.03E−05	6.78E−04	1.09E−04	9.07E−05
Te	μg/L	0.0025	0.0025	0.005875	0.0025	0.0025	0.0118	0.001994
Th	μg/L	0.00029	0.0002545	0.000277	0.000214	0.000666	0.000421	0.1615
Ti	μg/L	0.005	0.0339	0.0265	0.0224	0.005	0.0767	0.0001338
Tl	μg/L	0.00519	0.00097	0.005485	0.00567	0.0203	0.00145	0.06922
Tm	μg/L	0.00014	0.001325	0.0000895	0.0000832	0.000481	0.000144	4.80E−05
U	μg/L	0.6	1.495	0.3815	0.267	0.785	0.105	0.1399
V	μg/L	0.197	0.3055	0.3015	0.299	0.819	2.5	0.0006449
W	μg/L	0.0416	0.0289	0.01515	0.0109	0.0263	0.0118	0.0008285
Y	μg/L	0.01318	0.11505	0.006155	0.00629	0.0369	0.0104	0.0001086
Yb	μg/L	0.00081	0.009635	0.00051125	0.000534	0.00286	0.000977	0.0001269
Zn	μg/L	0.263	0.464	0.273	0.318	0.83	0.25	0.1372
Zr	μg/L	0.0005	0.00169	0.00293	0.00183	0.102	0.00251	0.0003452
Σ REE	μg/L	13.1088	177.92	9.7505	5.1686	34.832	7.3421	0.000233

areas, in agreement with the results of the FOREGS project (Salminen, 2005; De Vos et al., 2006; De Vivo et al., 2008; 2009). The differences among mean parameters in bottled mineral waters, compared to the European waters (Misund et al., 1999), likely reflect the European water database, the presence and the weight of Rb-rich waters from Eastern Europe.

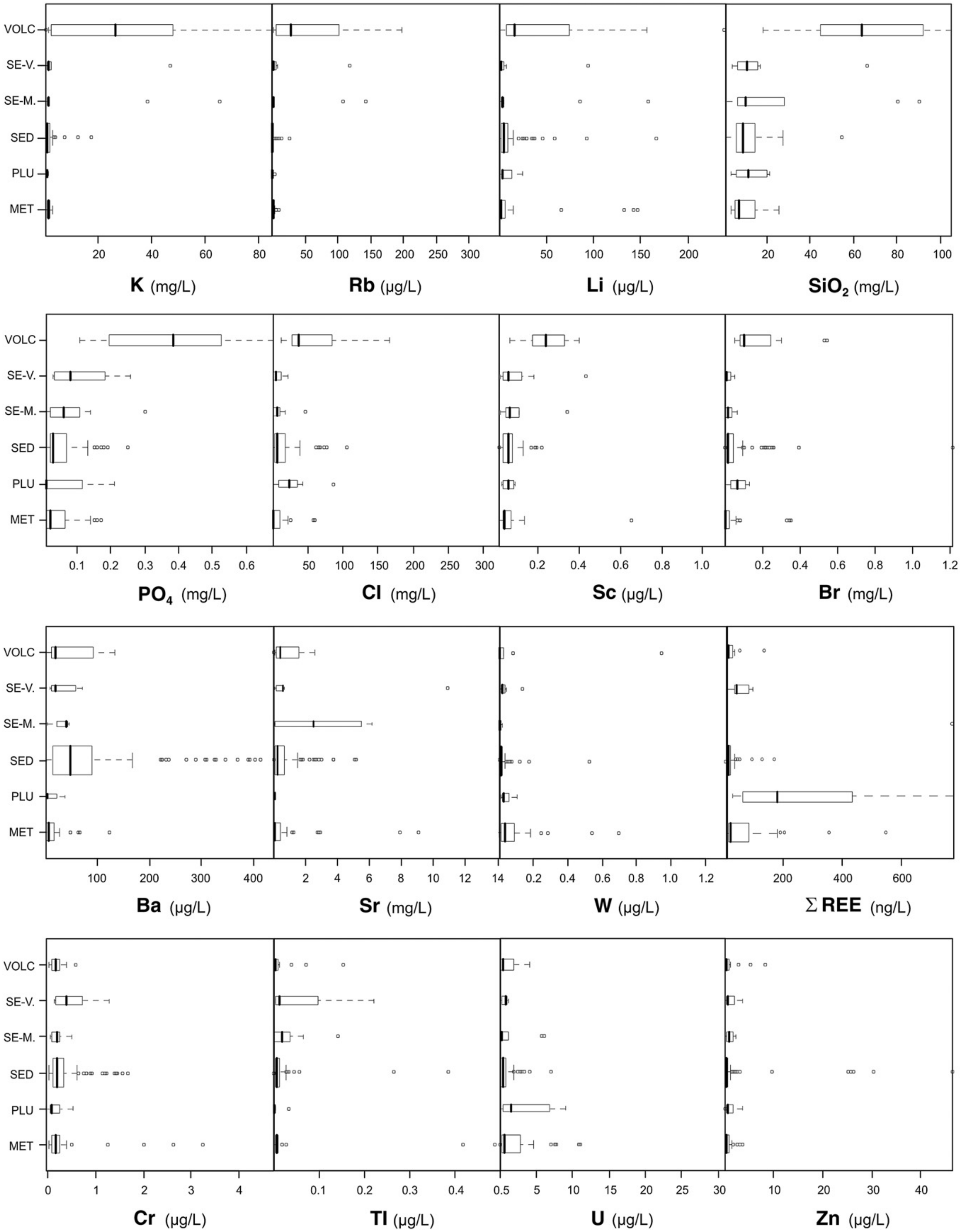


Fig. 5. Boxplot of selected elements to highlight differences between lithological groups (for abbreviations see Table 5).

Lithium is generally enriched in acidic rocks, commonly in minerals crystallised from late-stage melts, and in many sedimentary rocks. From geochemical point of view micas, K-feldspars, amphiboles and clay minerals have the most important contents of Li. Brines associated to granitoids intrusions are strongly enriched in Li and it can also be concentrated in formation waters by exchange reaction

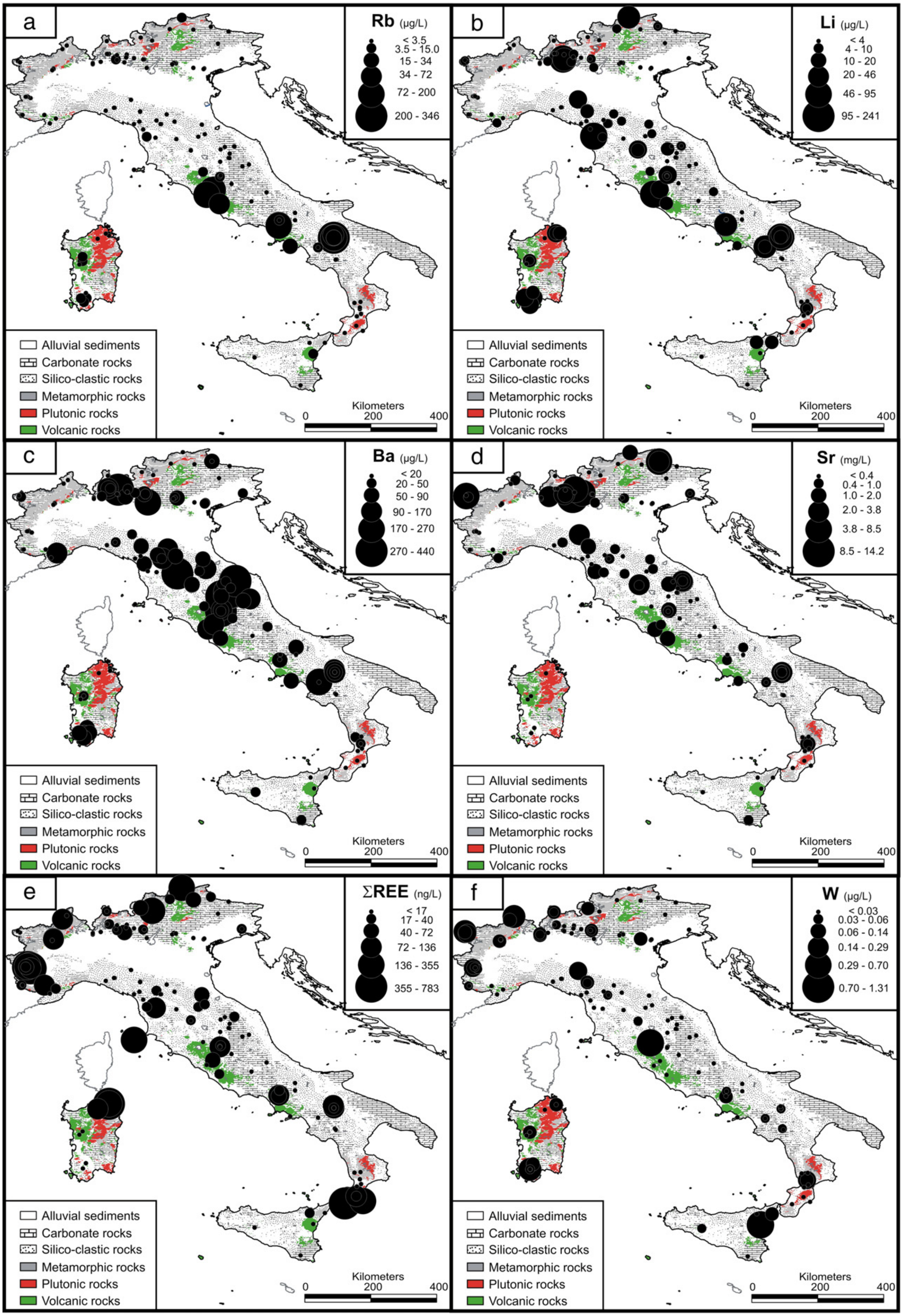


Fig. 6. Italian bottled waters dot maps of Rb (a), Li (b), Ba (c), Sr (d), ΣREE (e) and W(f).

and prolonged water–rock interaction (Shand et al., 2007). The Li^+ ion is generally stable and soluble in the groundwater environment, its mobility is controlled by sorption onto clay minerals and zeolites. The lithium concentrations in the Italian mineral waters vary from <0.1 (4 samples below the detection limit of 0.1 μg/L) to 241 μg/L with a median value of 3.4 μg/L which is comparable to the average world river composition (3 μg/L, Koljonen, 1992) and slightly lower than the average composition of Italian surface water (4.25 μg/L, De Vivo et al., 2009). Data concerning bottled mineral waters, at European scale (Misund et al., 1999) indicate median value of 15.7 μg/L and 4.80 μg/L on a global scale (Krachler and Shotyk, 2009). Lithium shows high concentrations in association with alkalic volcanics of central-southern Italy (De Vivo et al., 2008; 2009) (Fig. 6b). Other areas with high concentrations can be interpreted as the mixing with formation waters, particularly those located in Tuscany and in the Emilia–Tuscany Apennine. Another important source of Li could be represented by interaction of aquifers with evaporites, which are known to be enriched in this element (Hounslow, 1995). Italian bottled mineral waters show a mean Li content lower than the European ones (Misund et al., 1999), likely reflecting the contribution of Li-rich waters from other European countries.

Waters draining sedimentary rocks do not display any prevalent feature (Table 5), probably because of extreme heterogeneity. Only Ba, among all the investigated elements is characterized by the highest median value in these lithologies (Table 5), showing an overlap with other rock types (Fig. 5), and several outliers. The latter is a feature common to other elements (e.g., Li, Cl, Br, and Sr, in Fig. 5) in waters draining sedimentary rocks.

The principal Ba mineral is barite but it often occurs in the lattices of some common silicates like feldspars and mica. In the secondary environment, Ba is not very mobile but it can be mobilized by acidic waters. Barium concentrations in water are usually relatively low because it is easily precipitated as sulphate or carbonate and can be also strongly adsorbed to clays, to Fe and Mn oxides and hydroxides. However, Ba solubility in water is controlled by saturation with respect to barite and accordingly Ba concentration should be low in high sulphate waters (Shand and Edmunds, 2008). Italian mineral water Ba concentrations range from <1 (11 samples below the detection limit of 1 μg/L) to 440 μg/L, with a median value of 24 comparable to the average world river composition (20 μg/L, Koljonen, 1992), to the average composition of Italian surface water (20 μg/L, De Vivo et al., 2009), to bottled mineral waters, at European scale (26.25 μg/L, Misund et al., 1999) and, on a global scale (21 μg/L, Krachler and Shotyk, 2009). Lanciotti et al. (1989) report different Ba concentrations for Italian mineral bottled waters (range 7–660 μg/L, median 80 μg/L), but they refer to a lower number of samples (60) and brands different from the ones analysed in this study. Many of the analysed waters are oversaturated with respect to barite (Fig. 7, according to Ander et al., 2006) and include low sulphate water sources located in Umbria–Marche Apennine which is the area with highest frequency of high-Ba concentrations (compare Fig. 5 and 6c). In this area, dominated by carbonate rocks, Ba geogenic concentrations, in different media, are intermediate to high (De Vivo et al., 2008, 2009). Other oversaturation situations linked to different conditions and where waters drain volcanic and other sedimentary lithologies, are characterized by intermediate to high sulphate content related to sulphide or sulphate dissolution according to the geological setting. Supersaturation can be explained by aqueous complexation increasing the apparent solubility of barite in solution (Appelo and Postma 1994).

Another element which shows relatively high concentrations in sedimentary rocks is Sr, even if the highest median value is associated with potassic volcanic lithologies. Sr^{2+} ion can substitute Ca^{2+} and K^+ in the crystal lattices of many rock forming minerals: K-feldspar, plagioclase, gypsum and, especially, calcite and dolomite. In the secondary environment, the weathering of these minerals brings Sr naturally into the water. The observed Sr concentration in Italian bottled mineral waters range from 0.008 (no sample below detection limit) to 14.1 mg/L with a median of 0.18 mg/L which is higher than the average stream water composition (0.07 mg/L, Koljonen, 1992) but much lower than the median for Italian surface water (0.34 mg/L, De Vivo et al., 2009). At European scale (Misund et al., 1999) bottled mineral waters indicate median value of 0.448 mg/L and 0.17 mg/L on a global scale (Krachler and Shotyk, 2009). Strontium highest concentrations are displayed by Roman Comagmatic Province, in central and southern Italy matching those observed within the FOREGS database (De Vivo et al., 2008, 2009). High concentrations are shown by waters draining through the carbonate succession of Umbria–Marche Apennine as well as other areas where limestones are common (e.g., the Southern Alps) (Fig. 6d). For some waters, particularly those sulphate-rich, an origin related to evaporite (gypsum and/or anhydrite) dissolution is probable.

The mineral water associated to the mixed volcanic-sedimentary group is characterized by the highest median values for some elements (Ca, HCO_3^-, Nb, and Zr, Table 5) although for other elements, which are typically enriched in volcanic lithologies, both median values and distribution are very different (e.g., Rb, Li, and SiO_2, Fig. 5). This would suggest that the contribution from sedimentary lithologies is more important than from the volcanics (Fig. 5). In any case, few of these waters are naturally sparkling, HCO_3-rich, and with low pH (maximum 6.2). They are located in the area north of Naples, where volcanic rocks are superimposed on sedimentary rocks, particularly limestones. Natural presence of CO_2 and relatively low pH suggests strong water–rock interaction with dissolution of limestone rocks (Bono and Boni, 2001) mixing with other waters, characterized by elements more directly indicative of interaction with volcanic rocks (e.g., high SiO_2, Zr, Rb, K, Li, and Mg).

Bottled mineral waters draining areas of plutonic rocks are characterized by relatively high median values of many elements belonging to the REE group (Ce, Dy, Gd, Er, Ho, Lu, Pr, Tb, Tm, and Yb) as well as the ΣREE. Yttrium, classified as a heavy REE, displays statistically significant difference when compared to other rock types. Berillium (see Cicchella et al., 2010-this volume) is also enriched in this group. Values of ΣREE in mineral waters in Italy range from 2.1 ng/L to 783 ng/L with a median value of 10 ng/L. In this case, a direct comparison with average stream water composition is not possible, whereas FOREGS data on surface water from Italy (De Vivo et al., 2009) record much higher values (ΣREE range: 17–4424 ng/L, median value: 64 ng/L). The maxima are located all along the country, in the Western Alps, Calabria and Sardinia, all areas where there is widespread outcrop of crystalline rocks (Fig. 6e). In general, REE show high concentrations in granites (Turekian and Wedephol, 1961); in Italy the highest values are found in mineral waters draining through granites in Sardinia (ΣREE >700 ng/l). Other high values are also found in waters draining through other lithologies such as metamorphic rocks in Calabria and in the western Alps. Increased REE concentrations have been observed in glass containers (Cicchella et al., 2010-this volume; Reimann et al., 2010) but their number is limited, so the effects on the results are negligible.

Worth noting are the high median values of Cl, Na and Cs (Table 5), which, in plutonic rocks show concentrations in the same order of magnitude of waters draining through volcanics. Considering that the mineral waters with such high values occur particularly in Sardinia, it is likely that they might reflect an influence of seawater. Tungsten, shown in Figs. 5 and 6, displays the highest median value in metamorphic rocks (Table 5) even if the highest concentration (1.31 μg/L) is found in a water sample associated with volcanics. The W concentrations range from 0.0025 (no sample below detection limit) to 1.31 μg/L, with median value of 0.0177 μg/L which is lower than the mean composition of stream waters (0.03 μg/L, Koljonen, 1992) and comparable with the median value of Italian surface water (0.012 μg/L, De Vivo et al., 2008, 2009). Bottled mineral waters at

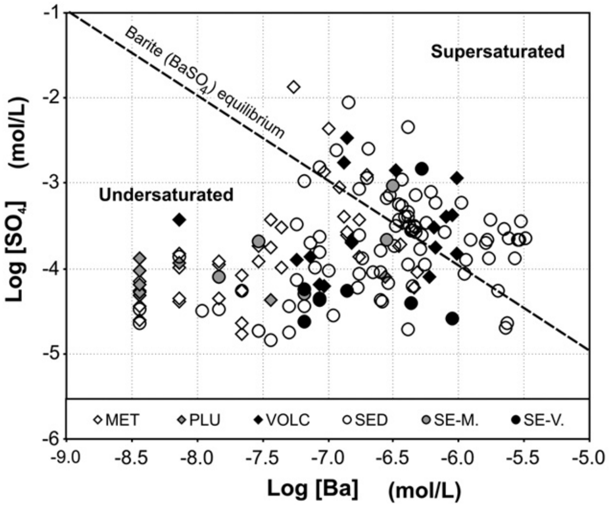


Fig. 7. Ba vs. SO_4 diagram for Italian bottled waters. Quite a few samples fall in the supersaturated field. Symbols according to rock type groups (Table 4).

European scale (Misund et al., 1999) indicate median value of 0.775 μg/L. Tungsten has low mobility in surface water, but it seems to be dependent on pH, being higher at pH near 8 (Fig. 8). Geochemical data available from the FOREGS database indicate, anomalous distribution in soils from volcanic areas in central Italy and in the Central-Western Alps (De Vivo et al., 2009) although possible relationships with mineralization cannot be excluded in Sicily (Omenetto et al., 1988) or in the Alps (Brigo and Omenetto, 1983).

4.4. Differences not systematically related to lithology

In this section we discuss the distribution of few elements, such as Cr, Tl, U and Zn, that are not systematically related to specific lithologies (Table 5) but have important environmental significance. Their distribution among the different lithologic groups does not show any clear-cut discrimination (Fig. 5), even if some outliers are frequent in metamorphic and sedimentary rocks.

Chromium is generally enriched in mafic and ultramafic rocks, and has low mobility in moderately oxidizing and reducing conditions and at neutral pH. In sedimentary rocks it tends to be enriched in shales and clastic sediments. The measured concentrations range from <0.03 (only one sample below detection limits) to 3.23 μg/L, with a median value of 0.165 μg/L which is much lower than the world river composition (0.7 μg/L, Koljonen, 1992) and the average composition of Italian surface water (1.8 μg/L, De Vivo et al., 2008, 2009). Data concerning bottled mineral waters, at European scale, indicate median value of 2.915 μg/L (Misund et al., 1999) and 0.82 μg/L, on a global scale (Krachler and Shotyk, 2009). The Cr anomalous waters in the Western Alps and in Calabria are associated with outcrops of basic metamorphic rocks and ophiolites (Fig. 9a); the latter effect is not systematic, since other waters from the same sites do not show the same Cr content. The high frequency of intermediate to high Cr concentration in waters in the northern Apennines can be related to a regionals enhanced background concentration related to the significant quantities of ultramafic detritus present in the clastic formations of the area (Van de Kamp and Leake, 1995; Dinelli et al., 1999). The element is also sensible to the type of container (Chicchella et al., this same volume); this is particularly evident for some bottled waters of few sites, where only glass bottles were available for the scope of our study.

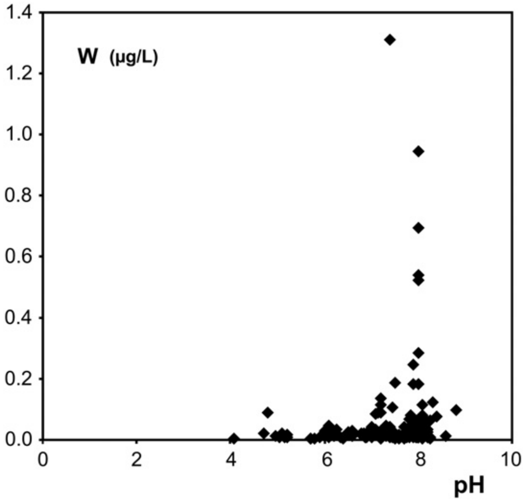


Fig. 8. W vs. pH diagram of the analysed Italian bottled waters.

Thallium is a very toxic, although rare, element that shares a common geochemical behaviour with K and Rb, so it is expected to be enriched in acidic igneous rocks and other K-rich rocks; it is reported to be enriched also in metal ores. In aqueous systems it is quite soluble, its concentrations being basically controlled by adsorption onto clay minerals (Shand et al., 1998). The measured concentrations range from <0.0005 μg/L (5 samples below detection limits) to 0.418 μg/L, with a median value of 0.0053 μg/L, which is much lower than the estimated world river concentration (0.04 μg/L, Koljonen, 1992), but comparable to the average composition of Italian surface water (0.0055 μg/L, De Vivo et al., 2008, 2009). Data concerning bottled mineral waters indicate comparable median values of 0.007 μg/L at European scale (Misund et al., 1999) and of 0.002 μg/L at world scale (Krachler and Shotyk, 2009), with both general datasets displaying wider ranges of variations. The element is not systematically discriminated among different lithologies (Fig. 5). Its distribution (Fig. 9b) shows intermediate to high concentrations in waters associated with volcanic rocks from central-southern Italy; the latter behaviour is also evident in the different geomedia reported by De Vivo et al. (2009). The maximum values are localized in the Central Alps in waters also characterized by high concentrations of other elements (e.g., B, Cs, Mo, U, Br, and SO_4^{2-}) which agree well with the complex geology of the area, characterized by occurrence of evaporites, black shales in the sedimentary succession and interbedded volcanics.

Uranium is an incompatible element enriched in late-stage igneous products, as well as in hydrothermal fluids, but it is also enriched in black shales. In aqueous systems it has relative high mobility in oxidizing alkaline conditions and tends to form various oxyanionic forms. The measured concentrations range from <0.0005 μg/L (only one sample below detection limits) to 31 μg/L, with a median value of 0.4745 μg/L, which is much higher than the estimated world river concentration (0.04 μg/L, Koljonen, 1992) but lower than the average composition of Italian surface water (1 μg/L, De Vivo et al., 2008, 2009). Data concerning bottled mineral waters indicate lower median values of 0.104 μg/L at European scale (Misund et al., 1999) and of 0.23 μg/L on a global scale (Krachler and Shotyk, 2009). Uranium is not distinctly discriminated between different lithologic groups (Fig. 5), even if a slightly higher median value is observed in plutonic rocks (Table 5). The geographic distribution (Fig. 9c) shows maxima associated with different geological context: in Sardinia the absolute maximum is observed in association to Hercynian granites; several high values are observed in relation to alkaline volcanic rocks of central-southern Italy (De Vivo et al., 2008; 2009); other high values are observed in the central Alps, in association with U-ore occurrences (Castaldo and Stampanoni, 1975), and in the western Alps related to waters interacting with black shales.

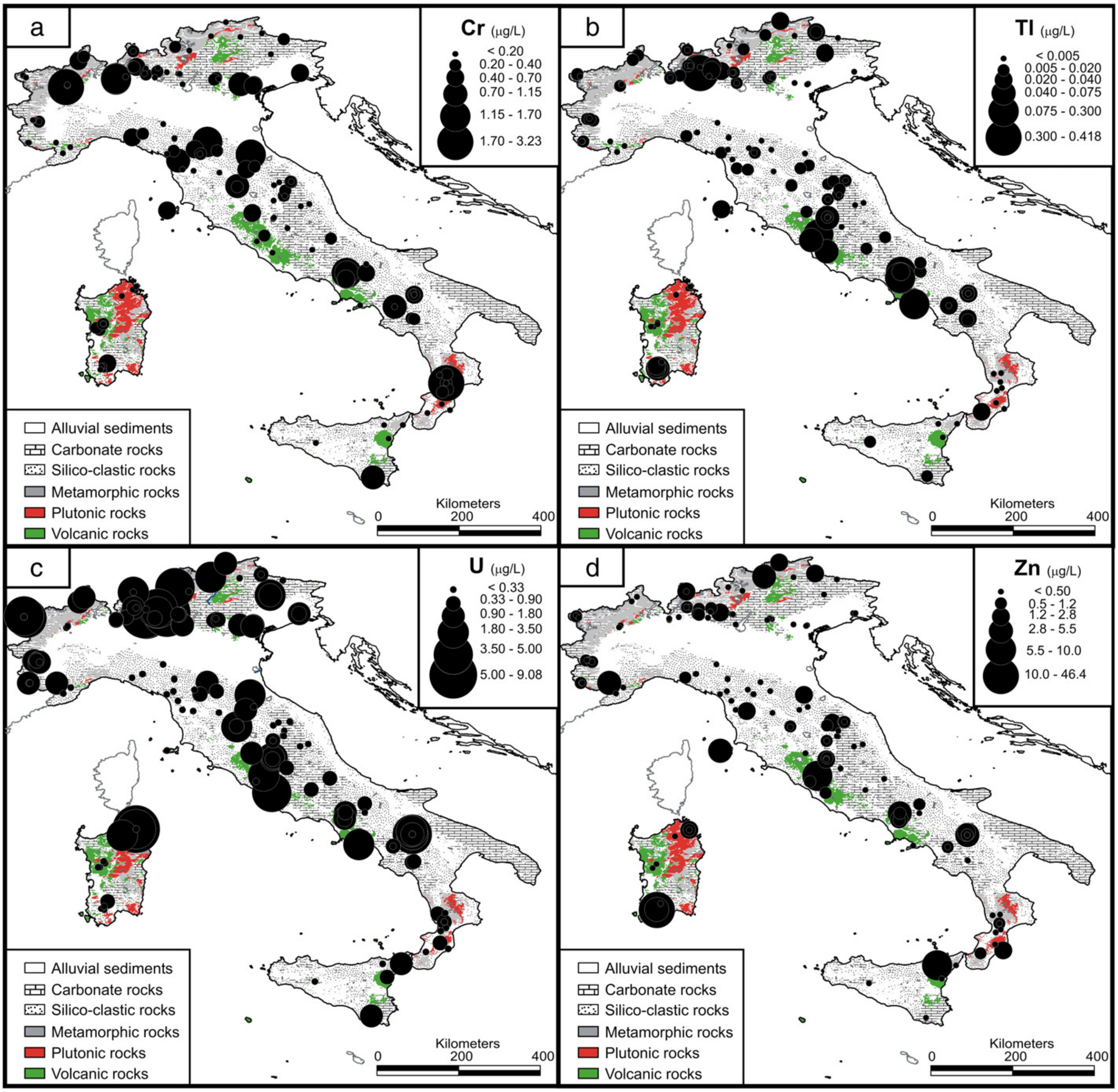


Fig. 9. Cr (a), Tl (b), U (c), and Zn (d) dot maps of Italian bottled waters.

Zinc is an essential elements for all living organisms. It is generally found in ores as sulphide, but it is rather widespread in all the most important rock types. Its mobility in aqueous environments is relatively high, its solubility being controlled by reaction with carbonate and by hydroxide formation (Shand et al., 2007). Adsorption with clays and oxyhydroxide is the main limiting reaction controlling dissolved Zn concentrations. The measured concentrations range from <0.05 µg/L (3 samples below detection limits) to 46.4 µg/L, with a median value of 0.3705 µg/L which is much lower than both the estimated world river concentration (15 µg/L, Koljonen, 1992) and the average composition of Italian surface water (3.2 µg/L, De Vivo et al., 2008, 2009). Data concerning bottled mineral waters indicate higher median values of 2.965 µg/L at European scale (Misund et al., 1999) and of 0.64 µg/L on a global scale (Krachler and Shotyk, 2009). Its geographic distribution is patchy, with maxima observed in south-western Sardinia, where a well known Pb–Zn mining district occurs (De Vivo et al., 1997), in Latium and in eastern Sicily, where polymetallic mineralizations are also present (De Vivo et al., 1993).

4.5. Factor analysis

R-mode factor analysis has been performed to determine the possible relationship existing between the distribution of individual elements (and other parameters) and lithology or surface enrichment phenomena related to ore deposits, the weathering and environmental conditions, or to anthropogenic sources.

Table 6 lists the five factor solutions accepted along with rotated factors' loadings. This solution accounts for 67.4% of the total variance. Table 6 shows the rotated factors' loadings with variables in alphabetical order, communalities, eigenvalues and percentages of

Table 6
Five factor solution by R-mode factor analysis. Rotated factors' loadings in bold and underlined indicate very strong factor loadings (>0.70); in bold strong ones (between 0.70 and 0.50) and in italic the moderate factor loadings (between 0.50 and 0.40). Negative correlations are in rectangle.

	Factors					
Element	1	2	3	4	5	Communalities
Al	−0.11	−0.05	**0.66**	0.21	0.08	0.51
As	−0.06	0.25	0.10	**0.52**	**0.50**	0.60
B	**0.53**	**0.66**	0.12	0.06	0.04	0.73
Ba	**0.68**	0.12	−0.07	0.09	−0.24	0.54
Be	−0.22	**0.58**	**0.62**	−0.11	0.02	0.78
Br–	0.28	**0.85**	−0.08	−0.04	−0.10	0.82
Ca	**0.91**	0.08	0.03	0.14	0.03	0.86
Cd	0.04	−0.03	**0.74**	−0.01	0.18	0.58
Cl–	0.31	**0.83**	−0.12	−0.02	−0.13	0.81
Co	0.40	0.03	**0.53**	0.11	−0.19	0.48
EC	**0.86**	0.40	0.03	0.07	0.06	0.91
F–	0.28	**0.62**	0.34	−0.12	0.32	0.69
Fe	0.29	0.24	**0.62**	−0.01	−0.07	0.54
HCO_3^-	**0.87**	0.27	−0.05	0.17	0.01	0.86
I	*0.46*	**0.59**	−0.05	0.06	−0.11	0.57
K	0.31	**0.67**	0.31	0.35	0.13	0.78
La	−0.13	−0.05	**0.72**	−0.02	−0.08	0.54
Li	*0.47*	**0.66**	0.20	−0.18	0.23	0.77
Mg	**0.78**	0.33	−0.02	−0.01	0.14	0.73
Mo	0.39	−0.16	0.00	−0.16	**0.71**	0.71
Na	0.26	**0.91**	0.03	0.02	0.01	0.91
NO_3^-	0.13	−0.10	0.01	**0.83**	−0.12	0.73
pH	0.08	−0.26	**−0.69**	0.05	0.13	0.57
PO_4^{3-}	0.02	**0.54**	0.23	**0.52**	−0.11	0.63
Se	0.33	−0.31	−0.10	**0.50**	0.08	0.47
SiO_2	0.05	**0.81**	0.15	0.35	0.00	0.80
SO_4^{2-}	**0.69**	0.16	0.14	−0.21	0.29	0.65
Sr	**0.88**	0.17	0.03	0.04	0.10	0.81
Te	**0.60**	0.22	0.14	0.11	0.08	0.45
Tl	0.36	0.02	**0.56**	−0.06	0.10	0.46
U	0.30	−0.24	0.20	0.23	**0.61**	0.61
W	−0.22	0.17	−0.26	0.03	**0.71**	0.66
V	0.02	0.32	−0.02	**0.74**	0.13	0.66
Eigenvalue	17.00	15.54	3.68	3.55	3.42	
Cumulative eigenvalue	17.00	32.55	36.23	39.77	43.19	
% variance explained	21.20	19.80	11.80	7.90	6.70	
Cumulative % variance	21.20	41.10	52.80	60.70	67.40	

variance accounted for the five factors associations. Very strong factor loadings (>0.70) are indicated with bold and underlined characters, the strong ones (between 0.70 and 0.50) in bold and the moderate factor loadings (between 0.50 and 0.40) in italic characters. Negative correlations are highlighted by a rectangle. Fig. 10 shows the distribution maps of factor scores and a summary table of loaded determinants. Here only the general distribution patterns of individual factors will be discussed. It is to be pointed out that if the element has an high loading in a strong factor, closer is the similarity to the element map (e.g., Sr map in Fig. 6d and factor scores F1 map, Fig. 10a). The chemical elements loaded in different factors associations show a spatial distribution which is only partially similar to that of the factors associations. In this case, each factor pattern corresponds to a specific mode of occurrence of the element in the territory (e.g., As presents in Factor 4 and 5, Table 6).

Factor 1 (Ca, Sr, HCO_3^-, EC, Mg, SO_4^{2-}, Ba, Te, Li, and I) is the strongest of the five factors, accounting for 21.2% of the total variance within the data. It is characterized by very high major ion content (Ca, HCO_3^-, Mg, and SO_4^{2-}) and Sr as lithophile trace element. High EC loading (0.86) indicates high mineralisation of waters where positive high factor scores occur (Fig. 10a). Among the limited number of minor components present in this association (Ba, Te, Li and I), only Ba and Te have a loading >0.5.

The factor scores pattern of F1 association (Fig. 10a) is similar to the Ca distribution map (not showed in this paper), and to the Sr and EC distribution maps (Figs. 4a–b and 6d). Fig. 4c also shows that the Ca–HCO_3 water-type distribution, whose compositions are characteristic of this factor, is almost coincident with the positive factor score distribution of this association.

The F1 higher factor scores (Fig. 10a) appear to be clearly dependent on geological composition of the substrate, being located mostly in correspondence to carbonate rocks. Waters in limestone acquifers have Ca and HCO_3^- as the major dissolved species. Mg is also present, deriving from either magnesian calcite or dolomite; other species are generally subordinate.

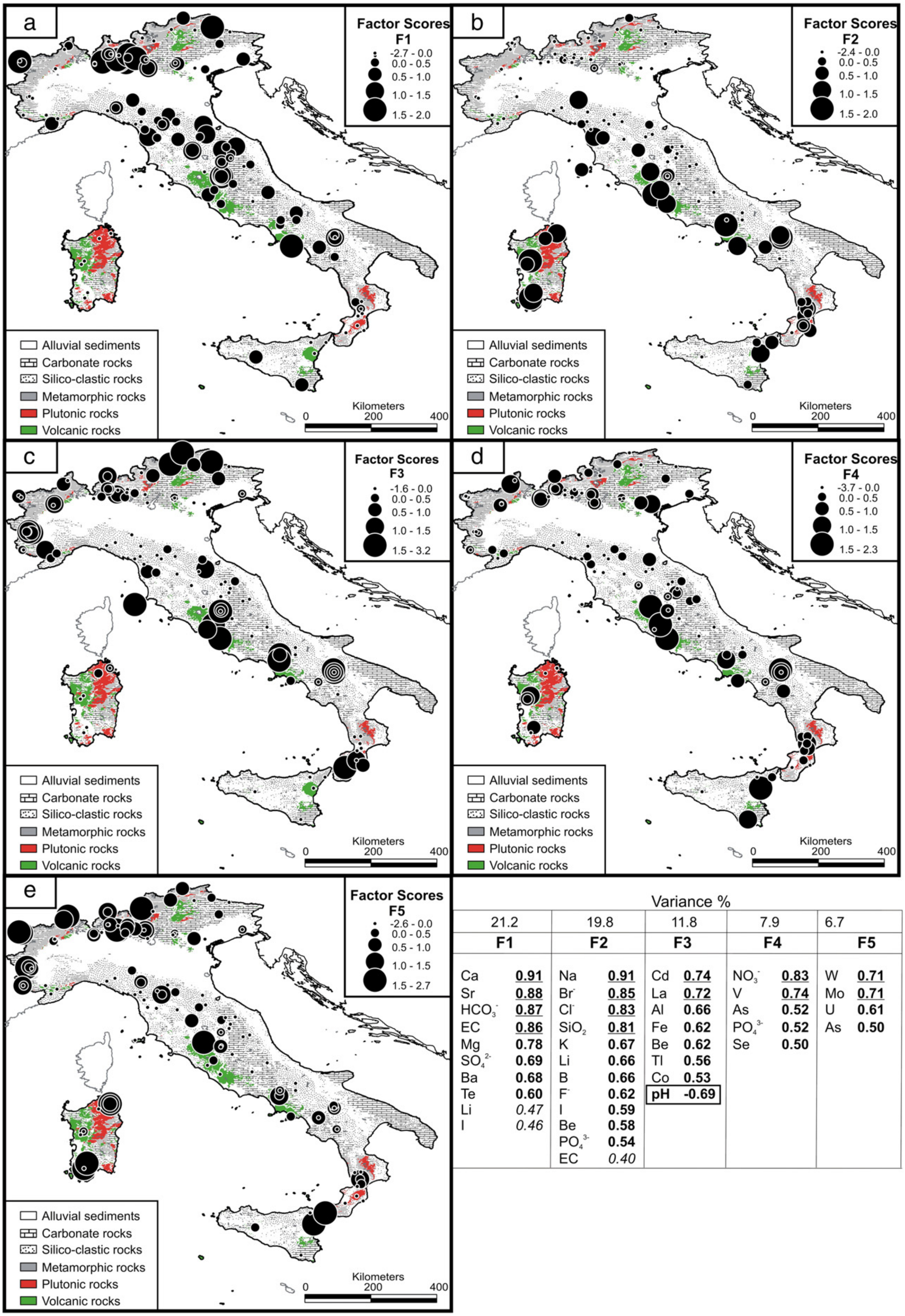
The lowermost values (negative) occur in the Western Alps, Sardinia, northern Sicily and Calabria, indicating low mineralized waters interacting with different lithotypes.

Factor 2 (Na, Br^-, Cl^-, SiO_2, K, Li, B, F^-, I, Be, PO_4^{3-}, and EC) accounts for 19.80% of the total variance within the data. This association may be interpreted as reflecting mostly lithological control due to the interaction of acquifers with volcanic rocks (Fig. 10b). In volcanic area (e.g. Roman Province, Etna area) where very high factor scores occur, a contribution from hydrothermal fluids can also be assumed. Such hydrothermal fluids reflecting a contribution from deep magmatic sources, have enriched elements grouped in this association. In coastal areas (e.g., in Calabria) with factor scores in the range 0–0.5 (Fig. 10b), mixing with seawater or with formation waters can also be assumed. Aquifers located in Tuscany and in the Tuscany–Emilia Apeninnes likely reflect mixing with deep formation waters, as confirmed by studies on thermal waters (Minissale, 1991) and formation waters (Conti et al., 2000).

Factor 3 (Cd, La, Al, Fe, Be, Tl, Co, and −[pH]) accounts for 11.80% of the total variance. The behaviour of these metals in the environment under oxidizing conditions at low pH (inverse pH loading) is soluble and mobile. As pH rises their concentrations tend to decrease, first because of adsorption and then because of limited solubility of carbonates and oxides or hydroxides. The highest factor scores of F3 association occur in the eastern sector of Alps and in the southern part of Calabria in correspondence with metamorphic rocks and with the Roman Comagmatic Volcanic Province. This association includes potentially harmful elements (e.g., Cd, Al, Pb, Be, and Tl), but their concentrations in bottled waters rarely exceed legislative thresholds (Cicchella et al., 2010-this volume).

Factor 4 (NO_3^-, V, As, PO_4^{3-}, and Se) accounts for 7.90% of the total variance. The determinands of this factor might reflect both geogenic and anthropogenic contribution to the aquifers (Fig. 10d). The strikingly high nitrate and V loadings, along with moderate As, PO_4^{3-} and Se factor loadings, could be an indication of contamination by fertilizers, agricultural wastes or sewage, or reflect interaction with volcano-sedimentary lithologies (Latium, Vulture and Etna areas). Nitrate also occurs in rainfall, derived from the release of ammonia to the atmosphere by industrial processes. Moderately high factor scores also occur in silico-clastic deposits mostly in Lombardy, Veneto, Calabria and Sicily. In particular the areas where highest factor scores occur are affected by intensive agricultural activities.

Factor 5 (W, Mo, U, and As) weakly accounts for 6.70% of the total variance. This factor reflects mostly the control of certain lithologies and mineralisation. High factor scores (Fig. 10e) are located along the central-western Alps and in northern Sicily, associated with metamorphic rocks; in Sardinia in correspondence with alkali granites (north-east) and of Pb–Zn mining district (south-west); and in central-southern Italy in correspondence with the alkaline volcanic rocks (De Vivo et al., 2009). A factor association more or less similar to this one is reported in surface waters of Italy by Pirc et al. (2006) in central-western Alps and central Italy.



Variance %	21.2		19.8		11.8		7.9		6.7
F1		**F2**		**F3**		**F4**		**F5**	
Ca	**0.91**	Na	**0.91**	Cd	**0.74**	NO_3^-	**0.83**	W	**0.71**
Sr	**0.88**	Br^-	**0.85**	La	**0.72**	V	**0.74**	Mo	**0.71**
HCO_3^-	**0.87**	Cl^-	**0.83**	Al	**0.66**	As	**0.52**	U	**0.61**
EC	**0.86**	SiO_2	**0.81**	Fe	**0.62**	PO_4^{3-}	**0.52**	As	**0.50**
Mg	**0.78**	K	**0.67**	Be	**0.62**	Se	**0.50**		
SO_4^{2-}	**0.69**	Li	**0.66**	Tl	**0.56**				
Ba	**0.68**	B	**0.66**	Co	**0.53**				
Te	**0.60**	F^-	**0.62**	**pH**	**-0.69**				
Li	*0.47*	I	**0.59**						
I	*0.46*	Be	**0.58**						
		PO_4^{3-}	**0.54**						
		EC	*0.40*						

Fig. 10. Factor score distributions of the five factor solution by R-mode factor analysis.

5. Concluding remarks

This study, stressing the importance of bedrock lithology on the composition of bottled mineral water in Italy, has permitted the following main conclusions:

- A total of 158 brands, 147 in PET containers and 11 bottled in glass were considered in the study. Waters have been grouped mostly on the base of surface geology and, where available, of information from literature or directly from the companies.
- About 76% of the investigated waters are classified as “low mineral content waters” which reflects the taste preference of the market. Only 2 samples are classified as high mineral concentration waters. Waters are spread all over the country, even if in some areas (Western Alps, Central Alps, Dolomite Alps, Tuscany–Emilia Apennine, Umbria–Marche Apennine, volcanic territories of central Italy, Calabria, and Sardinia) there is a remarkable concentration of spring sites representing important districts of production.
- The majority of waters are generally of the $\mathrm{Ca{-}HCO_3}$ type although also other water chemistry can be recognized, reflecting local or regional features. $\mathrm{Ca{-}Mg{-}HCO_3}$ waters reflect dissolution of dolomite and are frequent in the Central and in the Dolomite Alps; $\mathrm{Ca{-}Na{-}HCO_3}$ and $\mathrm{Ca{-}Na{-}Mg{-}HCO_3}$ waters, often K-rich, are associated with the volcanic rocks of central-southern Italy and Sardinia; $\mathrm{Na{-}Cl{-}HCO_3}$ and Na–Cl, $\mathrm{Na{-}Ca{-}HCO_3{-}Cl}$, often Mg bearing, originate from areas where predominate metamorphic and plutonic rocks, or from areas close to coastal settings or in islands (Calabria, Sicily, and Sardinia) reflecting variable degree of sea water contribution; $\mathrm{Ca{-}Na{-}Mg{-}HCO_3{-}Cl{-}SO_4}$ waters with a mixed major chemical composition, likely reflect a transition between more extreme water types; $\mathrm{Ca{-}(Mg){-}SO_4}$ waters deriving from interaction with evaporites or sulphide dissolution in the aquifer.
- The occurrence of many elements can be directly related to aquifer lithology. In particular volcanic lithologies provide a clear and distinct hydrogeochemical signal in the groundwaters. As, B, $\mathrm{Br^-}$, $\mathrm{Cl^-}$, Cs, I, K, Li, Na, $\mathrm{NO_3^-}$, $\mathrm{PO_4^{3-}}$, Rb, Sc, $\mathrm{SiO_2}$, Sr, Te, Ti, and V are enriched (up to 3 orders of magnitude) in waters draining through volcanic rocks compared to waters draining through other lithologies, in many cases with limited overlap among groups. Waters draining through sedimentary rocks do not display any distinct behaviour and only show high median values for Ba. Waters draining through plutonic rocks display highest median values for many REE (Ce, Dy, Gd, Er, Ho, Lu, Pr, Tb, Tm, and Yb) and Y. Tungsten is the only element showing highest median concentration values in waters draining through metamorphic rocks, likely being related to occurrence of mineralization in the aquifer system.
- Other environmentally important elements such as Cr, Tl, U and Zn, show distributions likely of a geogenic nature, but not in a systematic way. Their presence in waters reflects the influence of mineralizations, geochemical provinces, and the occurrence of particular lithologies.
- The physico-chemical conditions of the waters are likely to favour the presence in solution of those elements forming soluble oxy-complexes in solution such as $\mathrm{NO_3^-}$, V, Cr, Se, W, Mo, U, and As.
- Many elements, even the major ones, show very large natural variations; this is important information regarding the behaviour of many elements for which few data are available so far. Their concentrations are independent from measured EC and likely reflect local settings.
- The five factor associations by R-mode factor analysis confirm that the distribution of certain groups of elements mainly reflects the geological patterns. In addition it emphasizes that in intensively cultivated areas and where there is a large use of fertilizers, a likely sign of anthropogenic contribution is present.

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