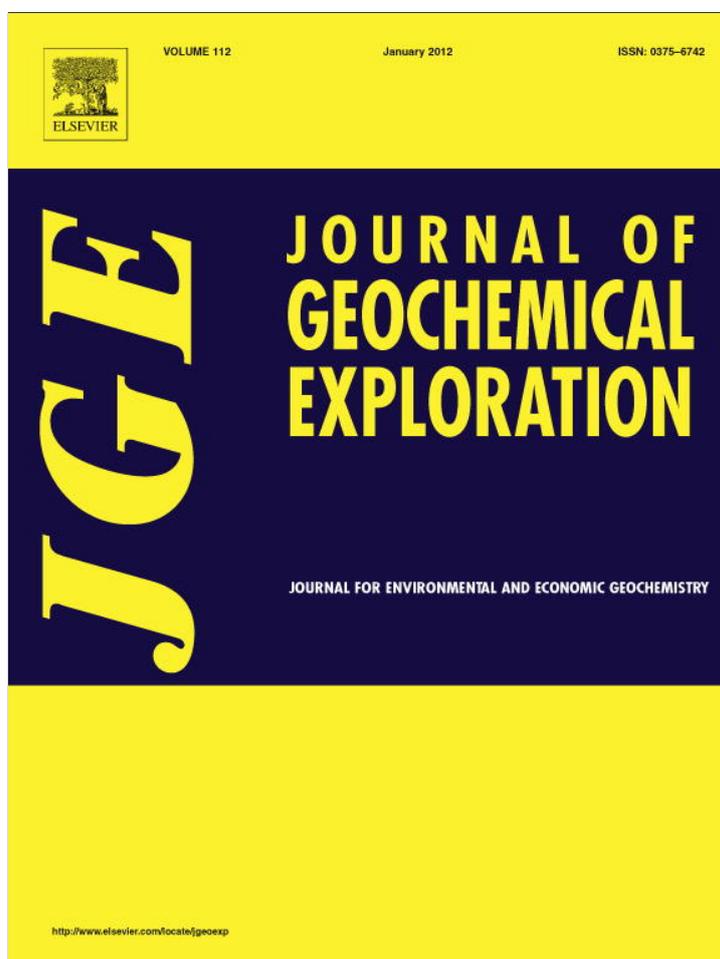


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Major and trace elements in tap water from Italy

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ABSTRACT

Tap water is a fundamental resource for everyday life, it is subjected to several routine controls and needs to fulfill many compliance scheme. Several elements are monitored on a regular basis, but many trace chemical elements are not usually analyzed, so there is the need to have some kind of indication about their concentration and variation ranges in order to better assess the water quality. An opportunity for such investigations 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 which included also the analysis for comparative purpose, of tap water. The initial tap water database of 24 sites has been subsequently increased to the final number of 157 distributed all over Italy and representative of end-user situations (either private houses and public places). In the samples, pH, conductivity and concentrations of 69 elements (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⁻, HCO₃⁻, Cl⁻, F⁻, NH₄⁺, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, SiO₂) were measured at the BGR geochemical laboratories. Some major elements (Ca, HCO₃⁻, Mg), the dominant water type, display limited range of variation whereas for others (Na, Cl⁻) the scattering is wider (3 orders of magnitude). Only one sample for Cl and two samples for NO₃⁻ are above the recommended EU and Italian guidelines. Clear influence of bedrock geology and/aquifer composition is clear for some elements (e.g. As, F, Rb, V, U), other elements are indicator of mixing with deep formation water or sea-spray contribution (e.g. Br, I), others reflect also peculiar geographic area (e.g. B in Tuscany, Se in Emilia-Romagna). Factor analysis enabled the identification of a "corrosion" factor which includes Pb, Zn, Cd, Cu, Mn, Sn and Fe, all elements which are preferentially related to interaction with the distributing system pipelines.

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1. Introduction

Potable or drinking water can be defined as the water delivered to the consumer that can be used for drinking, cooking and washing, a resource that required building of impressive waterworks even in ancient times such as the aqueducts of the Romans. Evidence of concern to water quality dates back to 2000 BC (Agardy et al., 2005). Drinking water quality is continuously monitored by health authorities and distributing companies since it must comply to physical, chemical, bacteriological and radiochemical guidelines before being introduced into the distributing system. Water used for potabilization has various sources: groundwater, spring water; water from rivers, streams, lakes, and artificial reservoirs. Any one of these sources can be present

in a single area, particularly in large urban agglomerates where water can derive from local groundwater sources and/or, is possibly mixed with more distant, and chemically different, sources.

Supply from surface water is prone to air pollution, spillage and other occasional contaminants input in the watershed, change in weather conditions, while groundwater is generally less susceptible to occasional contamination inputs and more likely reflects the nature of the detrital material of the aquifer.

In any case, before being introduced into the distributing system, water needs some kind of treatment, generally stronger if the source is surface water. Treatment include some fundamental steps (De Zuane, 1997; Gray, 2008):

- *Disinfection*, using Cl compounds or ozone and UV treatment, and possibly other compounds such as potassium iodide [KI] or B; disinfection takes place also at the end of the treatment plant and sometimes additional chlorination points are included in the

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distributing system if the distance from the source is high in order to keep the concentration of free reactive Cl high enough up to the end point;

- removal of solid particles by *sedimentation*, generally required for surface water plants;
- *coagulation*: chemicals are added to the raw water to remove colloids and improve physical properties before complete removal of solid particles. Among the coagulants there are Alum $[\text{Al}_2(\text{SO}_4)_3]$, sodium aluminate $[\text{Na}_2\text{Al}_2\text{O}_4]$, activated silica, ferrous sulfate $[\text{FeSO}_4 \cdot 9\text{H}_2\text{O}]$, soda ash $[\text{Na}_2\text{CO}_3]$, quicklime $[\text{CaO}]$; possibly clays or limestone can be added in the treatment;
- *flocculation* is the process of forming larger colloidal aggregate easier to settle and easily removed from water depending on amount of coagulant added, initial characteristics of the water, scale of the plant;
- *filtration*, removal of remaining solid and flocculated particles through mechanical sieving on sand filters, possibly including also anthracite, or diatomaceous earth filters;
- iron and Mn removal, particularly indicated for groundwater that could have high dissolved concentrations of these metals due to the reducing conditions in the aquifer, it is basically obtained by *aeration*, possibly with the addition of other oxidants such as potassium permanganate $[\text{KMnO}_4]$ or Cl. Solid oxy-hydroxides formed by aeration can remove also other elements by co-precipitation or adsorption (e.g., Cu, Zn, Ni, Co, As). Aeration will also remove volatile compounds (H_2S , CH_4 , CO_2 and other odor forming substances) possibly present in water.

The above treatments are meant to improve water quality for its aspect (e.g. turbidity removal), taste (e.g., removing or adding selected elements), odor (e.g., volatile compounds removal) or technical requirements (e.g., pH and hardness control to limit corrosion of the distributing system). These treatments are not designed to remove trace elements, but indirectly some water treatment as aeration, increase in pH, Fe and Mn removal can also affect the concentration of some elements sensitive to pH and Eh, and susceptible to adsorption and/or absorption reaction.

Once the water enters the distributing system it can be subject to losses, deterioration of the microbial quality; it can corrode the pipeline becoming enriched in trace metals and to control this aspect pH and water hardness are key parameters (De Zuane, 1997; Gray, 2008). Acidic waters are much corrosive than neutral or basic waters and a “soft” water is more “corrosive” or “aggressive” than hard water for plumbing systems. In plumbing systems brass, Cu, galvanized Fe, or Pb solders are present and so a soft water could contain higher levels of dissolved elements such as Pb, Cu, Zn, Cd, Ni, Cr and Fe. Key issues are the composition of the material of the distributing system, the age of the distributing system, although the variation trends can vary for the different metals (Veschetti et al., 2010) and basically depend on interaction time.

Italian tap water derives for about 70% by groundwater (11000 million of m^3 per year in 2007) and for the 30% by depurated surface waters (Acquavita et al., 2007). Only in Puglia and Sardinia the amount of depurated surface water exceeds groundwater (Acquavita et al., 2007). Additionally, since Puglia does not have sufficient water supply, receives a large portion of tap water from aqueducts of the neighboring regions of Campania and Basilicata. These waters originate in a geological context very different from the Puglia one. This is the only case of important water interregional distribution occurring in Italy.

This study started in the framework of the EuroGeoSurvey Geochemical Expert Group project aimed at the geochemical characterization of groundwater all over Europe by the analysis of bottled mineral water (Birke et al., 2010a; Reimann and Birke, 2010) which included also analysis of tap water samples for comparison all over Europe (24 from Italy). This first group, collected in 2009, was

integrated in 2010 to reach the total number of 157 sampling sites (Fig. 1, Table 1) covering almost all the Italian territory (only 6 provincial towns out of 111 were not sampled) and analyzed for their inorganic chemical composition. The sampling strategy was directed to the end-consumers, so the data reflect what the people is actually exposed to. We are aware that this introduces some unpredictable factors in the data interpretation, mostly related to interaction with the distributing system. These will be highlighted and discussed, but the main focus of the work will be on the description of the major chemical features of the tap water and to the evaluation of the distribution of some key trace element, focusing basically on the relation with the geological–geochemical features of source areas. Additionally, results will be compared to thresholds set by Italian and EU regulations, and US-EPA, WHO and FAO guideline values, to evaluate their quality. Tap water chemical features will be compared with the Italy bottled mineral waters ones (Cicchella et al., 2010; Dinelli et al., 2010; Lima et al., 2010) in a separate detailed paper in press (Dinelli et al., submitted for publication).

2. Health related guidelines

Italian drinking water supply is generally of excellent quality. However, water in nature is never “pure”. It picks up parts of everything it comes into contact with, including minerals, silt, vegetation, and agricultural run-off. While most of these substances are harmless, some may pose a health risk especially some trace elements. To address the latter risk, the World Health Organization (WHO) has developed guidelines that set out the maximum acceptable concentrations of these substances in drinking water. Table 2 shows WHO guideline values along with U.S. EPA (2009), FAO, the Italian and European ones.

WHO drinking water guidelines (Table 2) are health-based and derived on the basis of internationally agreed procedures for risk assessment (WHO, 1996, 2008). They are not standards per se and should therefore not be considered as mandatory. They are instead intended to be used by national authorities as a basis for setting national standards on water quality. Such guidelines have the scope to guarantee that the drinking water does not represent any significant risk to health over a lifetime of consumption, including different sensitivities that may occur between life stages.

Setting standards for a drinking water contaminant is a very difficult and imperfect process influenced by economic, political and social issues, in addition to scientific considerations. In fact, data relating human health effects to chemicals in drinking water are limited, and scientists have difficulty predicting the effects of drinking small amounts of chemicals for many years. Furthermore, standards do not take into account the presence of multiple chemicals, which may increase or decrease the toxicity of a particular contaminant. For these reasons, it is important to understand that the drinking water standards do not guarantee that water with a contaminant level below the standard is risk-free, nor do they indicate that water with a higher level will cause adverse health effects. Current drinking water standards reflect sound scientific judgment and are based conservatively on all knowledge available at the time the standard was set. They are proposed and revised by the legislators on a regular basis (US EPA, 2003).

Legislation in Italy (D.L. 31/, 2001) and Europe (EU Directive 98/83/EC, 1998) provides for drinking water for human consumption an extensive and regular quality control of potentially harmful contaminants (Table 2). Within this legislative regulations, paradoxically, in some Italian regions is allowed to rise the fixed national limits because of the peculiar lithology of the area, which determines higher background value of some harmful elements. This is the case of Campania for F (limit set at 2.5 mg/L instead of 1.5 mg/L), Latium for As (50 $\mu\text{g}/\text{L}$ instead of 10 $\mu\text{g}/\text{L}$), F (2.5 mg/L instead of 1.5 mg/L), Se (20 $\mu\text{g}/\text{L}$ instead of 10 $\mu\text{g}/\text{L}$), V (160 $\mu\text{g}/\text{L}$ instead of 50 $\mu\text{g}/\text{L}$); Lombardy and Trentino-Alto Adige for As (50 $\mu\text{g}/\text{L}$ instead of 10 $\mu\text{g}/\text{L}$); Piedmont for As (50 $\mu\text{g}/\text{L}$ instead of 10 $\mu\text{g}/\text{L}$) and Ni (50 $\mu\text{g}/\text{L}$ instead of 20 $\mu\text{g}/\text{L}$),



Fig. 1. Location of the tap water samples with indication of the Italian administrative regions (for abbreviations see Table 2).

Sardinia for V (160 $\mu\text{g/L}$ instead of 50 $\mu\text{g/L}$), Tuscany for B (3 mg/L instead of 1 mg/L), As (50 $\mu\text{g/L}$ instead of 10 $\mu\text{g/L}$). This “deregulation” is wrong because such high concentrations of toxic elements, such as As, F, V and Ni, are harmful for human health even if their source is completely geogenic.

3. Geological and hydrogeological outline

The Italian territory (Fig. 2) is dominated by two important mountain belts, the Alps and the Apennines, originating by the orogenic processes related to the Eurasian and African plate collision and the closing of the Tethyan ocean (Carminati and Doglioni, 2005; Pfiffner, 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 orogenic phases that lead 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).

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 calc-alkaline 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 succession widespread on the whole territory (Fig. 2). The latter type of aquifers 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 volcanoclastic deposits, and to the west by limestones. Carbonate hydrological complexes are important as

Table 1

List of the sites where tap water has been sampled. In bold the region name and in parenthesis abbreviations used in Fig. 1.

Abruzzo (ABR)	Towns	Friuli Venezia Giulia (FVG)	Towns	Molise (MOL)	Towns	Trentino-Alto Adige (TAA)	Towns
Chieti	CH	Monfalcone	GO	Campobasso	CB	Bressanone	BZ
Vasto	CH	Pordenone	PN	Isernia	IS	Brunico	BZ
Pescara	PE	Trieste	TS	Piedmont (PIE)		Cardano	BZ
Teramo	TE	Udine	UD	Alessandria	AL	Prato allo Stelvio	BZ
Basilicata (BAS)		Latium (LAT)		Fubine	AL	Ala	TN
Macchia Ferrandina	MT	Gaeta	LT	Asti	AT	Cavalese	TN
Matera	MT	Rieti	RI	Biella	BI	Malè	TN
Matera	MT	Albano Laziale	RM	Cuneo	CN	Trento	TN
Potenza	PZ	Roma	RM	Novara	NO	Tuscany (TUS)	
Rionero in Vulture	PZ	Viterbo	VT	Torino Porta Nuova	TO	Arezzo	AR
Calabria (CAL)		Liguria (LIG)		Torino, Valperga Caluso	TO	S.Giovanni Valdarno	AR
Cosenza	CS	Genova 1	GE	Verbania	VB	Firenze	FI
Catanzaro	CZ	Genova 2	GE	Vercelli	VC	Grosseto	GR
Crotone	KR	Imperia	IM	Puglia (PUG)		Livorno	LI
Campania (CAM)		La Spezia	SP	Alberobello	BA	Lucca	LU
Avellino	AV	Savona	SV	Bari	BA	Massa-Carrara	MS
Benevento	BN	Lombardy (LOM)		Brindisi	BR	Cascina	PI
Caserta	CE	Bergamo	BG	Trani	BT	Pisa	PI
Napoli	NA	Fara Gera d'Adda	BG	Foggia	FG	Volterra	PI
Napoli, Bagnoli	NA	Brescia	BS	Lecce	LE	Prato	PO
Napoli, Chiaiano	NA	Edolo	BS	Ginosa	TA	Cutigliano	PT
Napoli, Gianturco	NA	Como	CO	Taranto	TA	Quarrata	PT
Napoli, Belsito	NA	Cremona	CR	Taranto	TA	Siena	SI
Campagna	SA	Bellano	LC	Sardinia (SAR)		Umbria (UMB)	
Salerno	SA	Lecco	LC	Cagliari	CA	Perugia	PG
Emilia-Romagna (EMR)		Lodi	LO	Carbonia-Iglesias	CI	Terni	TR
Bologna	BO	Monza e della Brianza	MB	Nuoro	NU	Aosta Valley (VDA)	
Imola	BO	Milano	MI	Ogliastro	OG	Aosta	AO
Medicina	BO	Mantova	MN	Oristano	OR	Veneto (VEN)	
Monghidoro	BO	Villa Poma	MN	Olbia-Tempio	OT	Belluno	BL
Porretta Terme	BO	Pavia	PV	Sassari	SS	Sospirolo	BL
Cesena	FC	Sondrio	SO	Medio Campidano	VS	Carmignano di Brenta	PD
Forlì 1	FC	Varese	VA	Sicily (SIC)		Padova	PD
Forlì 2	FC	Marches (MAR)		Favara	AG	Rovigo	RO
Ferrara	FE	Ancona	AN	Catania	CT	Conegliano	TV
Modena	MO	San Benedetto del Tronto	AP	Caronia	ME	Treviso	TV
Piacenza	PC	Fermo	FM	Messina	ME	Mestre	VE
Noceto	PR	Macerata	MC	Patti	ME	Venezia	VE
Bastia	RA	Matelica	MC	Palermo	PA	Lonigo	VI
Faenza	RA	Porto Recanati	MC	Trabia	PA	Vicenza	VI
Ravenna	RA	Tolentino	MC	Ragusa	RG	Verona	VR
Reggio Emilia	RE	Urbino	PS	Siracusa	SR		
Rimini	RN	Urbino	PS	Marsala	TP		
Sant'Agata Feltria	RN	Fano	PU				
		Pesaro	PU				

well 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 the hydrogeological point of view even if often are important sources for bottled mineral waters. These rocks are most common in the Western and Central Alps, in Calabria, in north-eastern Sicily and in 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 hydrological complexes of relative importance and locally to significant manifestations 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 (Roman Comagmatic volcanic province, Washington, 1906; Peccerillo, 2005) or in the Mt. Vulture area (Fig. 2). Productive levels can be related to the overlap of units with different permeability.

4. Materials and methods

A total of 157 tap waters was sampled in private or public distributing system all over Italy (list in Table 1, location in Fig. 1) between 2009 and 2010. Samples represent the present end-user tap water composition, so it is the one we drink every day. Samples were taken at private houses and in public places (bars, restaurants, offices, public fountains), although no systematic recording of the source was carried out. Samples were collected from ordinarily used taps, stored in PET (polyethylene terephthalate) bottles (0.5 L) with PET caps completely filled. Containers were rinsed several times with water flushed from the distributing system for at least 2 min, preferably at the end of the day. This procedure should reduce the effect of interaction between casing system and water, if limited flushing occurs. No filtration were performed during sampling.

Waters have been analyzed 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⁻, HCO₃⁻, Cl⁻, F⁻, NH₄⁺, NO₂⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, SiO₂), in addition pH and EC have been measured. Detection limits and analytical techniques are reported in Table 3

Table 2
US-EPA, WHO and FAO guideline values and Italian and EU normative limits for drinking water.

Parameter	Italian Law D.L. 31/2001	EU Directive 1998/83/EC	U.S. EPA (2003, 2009)	WHO (1996, 2008)	FAO codex 108-1981
	Drinking water	Drinking water	Guideline value	Guideline value	Revision 1997
Ec ($\mu\text{S}/\text{cm}$)	2500 (g.v.)	2500 (g.v.)	–	–	–
pH	≥ 6.5 – ≤ 9.5 (g.v.)	≥ 6.5 – ≤ 9.5 (g.v.)	≥ 6.5 – ≤ 8.5	–	–
Aluminum ($\mu\text{g}/\text{L}$)	200 (g.v.)	200 (g.v.)	–	200	–
Ammonium (mg/L)	0.5 (g.v.)	0.5 (g.v.)	–	–	–
Antimony ($\mu\text{g}/\text{L}$)	5	5	6	20	5
Arsenic ($\mu\text{g}/\text{L}$)	10	10	10	10	10
Barium ($\mu\text{g}/\text{L}$)	–	–	2000	700	100
Beryllium ($\mu\text{g}/\text{L}$)	–	–	4	–	–
Boron ($\mu\text{g}/\text{L}$)	1000	1000	–	500	–
Cadmium ($\mu\text{g}/\text{L}$)	5	5	5	3	3
Chloride (mg/L)	250 (g.v.)	250 (g.v.)	–	250	–
Chromium ($\mu\text{g}/\text{L}$)	50	50	100	50	50
Copper ($\mu\text{g}/\text{L}$)	1000	2000	1300	2000	1000
Fluorides (mg/L)	1.5	1.5	4	1.5	–
Iron ($\mu\text{g}/\text{L}$)	200 (g.v.)	200 (g.v.)	200	–	–
Lead ($\mu\text{g}/\text{L}$)	10	10	15	10	10
Manganese ($\mu\text{g}/\text{L}$)	50 (g.v.)	50 (g.v.)	–	400	500
Mercury ($\mu\text{g}/\text{L}$)	1	1	2	6	1
Molybdenum ($\mu\text{g}/\text{L}$)	–	–	–	70	–
Nickel ($\mu\text{g}/\text{L}$)	–	20	–	70	20
Nitrates (mg/L)	50	50	10	50	50
Nitrites (mg/L)	0.5	0.5	1	3	0.02
Phosphorus (mg/L)	–	5	–	–	–
Selenium ($\mu\text{g}/\text{L}$)	10	10	50	10	10
Sodium (mg/L)	200 (g.v.)	200 (g.v.)	–	200	–
Sulfates (mg/L)	250 (g.v.)	250 (g.v.)	–	500	–
Tallium ($\mu\text{g}/\text{L}$)	–	–	0.5/2	–	–
Uranium ($\mu\text{g}/\text{L}$)	–	–	30	15	–
Vanadium ($\mu\text{g}/\text{L}$)	50	–	–	–	–
Zinc ($\mu\text{g}/\text{L}$)	–	–	–	3000	–

(g.v.) Guideline values.

along with the summary statistics. Sample preparation, analytical methods and other technical and operative information can be found in Birke et al. (2010b).

The statistical analysis have been performed by Excel, whereas maps were produced by ArcGIS software. For statistical analysis and to perform geochemical maps, elemental concentrations below detection limit were assumed to be equal to 50% of the detection limit (Reimann et al., 2008). In the elemental maps displayed, classes are defined according to the values of 50, 75, 95 percentile distribution and the normative guideline value if some observation is above threshold.

Factor analysis (FA) 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 FA, 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. The FA was performed using 37 variables on log transformed data in order to satisfy the optimum normality conditions of the variables. Of all the REE analyzed, only Nd was included in the FA as representative of the elemental group.

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 trials the six model solution has been chosen as the most appropriate one to explain the data variability.

5. Results and discussion

The summary statistic presented in Table 3 and graphical dispersion of the data in Fig. 3 indicate that many elements like Ba, Zn, Mn, Cr, Cu, Pb, U and NO_3^- display wide ranges of concentrations

spanning several orders of magnitude (10^4 – 10^3). Te, Ta, Sc, Hf, Bi and NO_2^- show instead narrow range of variation, of about one order of magnitude, Hg has only one value above detection limit. Chemical elements and compounds, expressed as mg/L, like HCO_3^- , Ca, SO_4^{2-} , Cl^- , Mg, Na, NO_3^- and Si, have the median concentration value that exceeds 1 mg/L (Fig. 3). Peak of concentrations above 1 mg/L is observed in single samples for PO_4^{3-} (16.4), Ba (5 mg/L) and Zn (2.83 mg/L) (Fig. 3). The median value is below detection limit for NH_4^+ , NO_2^- , Te, Ag, Be, Nb, Ta, Bi and Hf because a high percentage of samples has concentrations below the detection limit (Table 3, Fig. 3).

Most of the analyzed tap waters has concentrations that does not exceed the guideline and directive values listed in Table 2. Six samples have pH value exceeding the US EPA pH limit of 8.5, several samples have concentrations of NO_3^- , NH_4^+ , Fe, Al, Mn, As and Pb that exceed EU and Italian threshold (Fig. 3 and Table 2) and one sample has NO_2^- concentration above the WHO (2008) guideline value. Ba concentration, not covered in the European and Italian legislation for drinking water, in one sample is above the WHO, US EPA and FAO guideline values, similarly U concentration, not covered in the European and Italian legislation, in one sample is above FAO guideline value.

5.1. Drinking water classification

Among the compositional parameters used in the classification of drinking water, the amount of dissolved substances is certainly one of the most important. The EC is the parameter that directly reflects the type of water (Hem, 1985). To classify sampled tap water, EC has been utilized, according to the scheme of van der Aa (2003). Table 4 shows the Italian tap water classification. The largest part of samples (138) has low mineral concentration, 17 samples have intermediate mineral concentration, 1 has very low mineral concentration and 1 has high

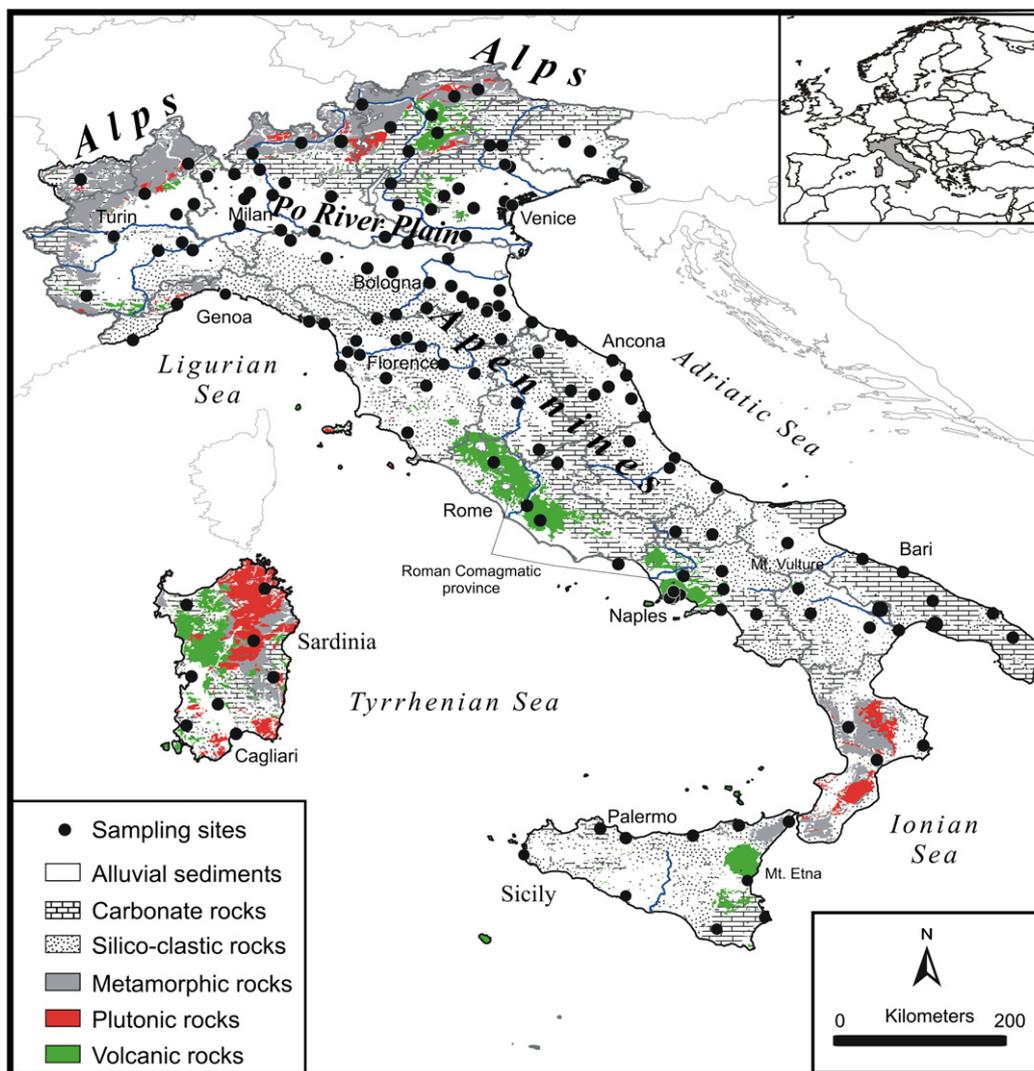


Fig. 2. Tap-water sampling locations on a simplified Italian geological map. For region name see Fig. 1.

mineral concentration. In spite of the different sources of sampled waters, they show great homogeneity.

The Durov diagram (Durov, 1948) is used to classify the waters according to the major cations (Na, K, Mg, Ca) and major anions (Cl^- , SO_4^{2-} and alkalinity or HCO_3^-) plotted as milliequivalent proportions in ternary diagrams; the points are then projected onto a square central field (Fig. 4). On this diagram symbols are proportional to EC so that we can identify different groups of waters based on their major ion chemistry (Fig. 4).

The majority of tap waters are of calcium-bicarbonate type, the more suitable for drinking purposes; generally they are characterized by low to intermediate EC, the latter being almost constant. The Ca–Mg– HCO_3 waters are also abundant and widespread along the entire Italian territory. In addition there are some water samples enriched in Na and Cl, others that have a mixed composition and few samples with a Na–(Ca)– HCO_3 composition.

Ca– HCO_3 water type is common in the samples from the central and southern Apennines away from the coastline (Fig. 5a,b), in close association with extensive outcrops of permeable carbonate rocks, or whose source area includes limestone. Ca–Mg– HCO_3 waters occur extensively in the Po plain area, particularly along the southern border of the Alps and the northern border of Apennines (Fig. 5a, b) which could be related

essentially to dolomite dissolution, extensively outcropping in the southern Alps, but also present in the alluvial deposits of the Po plain exploited for drinking water purposes (Amorosi et al., 2002; Amorosi et al., 2007). Other waters with similar features occur also in the central Adriatic area (Marches and Abruzzi) and in southern Italy between Basilicata and Puglia (Fig. 5a,b).

Water samples rich in Na and Cl occur in Sardinia and Sicily (in these regions the water provided by surface water is larger than the one from groundwater) and in few other coastal locations (Fig. 5a,b). For these waters seawater contribution, in peculiar geologic (abundance of low permeability rocks) and geographic (closeness to the sea) settings can be assumed. Also bottled mineral waters from the same areas show the same Na–Cl contents (Dinelli et al., 2010). Few other samples of such type also occur in Tuscany and in the central Po plain likely related to partial mixing with deep formation water.

Few tap waters of the Na– HCO_3 type are completely Ca depleted likely because of strong aluminosilicate weathering and/or base exchange processes, but could also reflect the presence of devices installed to reduce water hardness.

Water samples with relatively high proportions of SO_4^{2-} occur in the central Alps, along the eastern border of the northern Apennines, in Tuscany and in Sicily (Fig. 5a, b), possibly related to the interaction

Table 3
Summary of the whole parameters measured in the Italian tap waters. Mean, standard deviation (St. dev.), minimum (min), maximum (max), 25th, 50th, 75th and 95th percentiles; n: number of observations above detection limit; dl: detection limit.

	Mean	St. dev.	Min	25ile	Median	75ile	95ile	Max	n	Unit	Analytical method	d.l.
pH	8.0	0.3	7.2	7.8	8.1	8.2	8.5	8.6	157	Potentiometric	–	
EC	497	283	76	326	440	616	994.4	2360	157	µS/cm	Conductometric	–
Ag	0.026	0.229	<0.001	<0.001	0.0005	0.0023	0.0328	2.84	75	µg/L	ICP-QMS	0.001
Al	16.6	44.7	<0.3	0.8	1.5	9.0	61.3	454	156	µg/L	ICP-QMS	0.30
As	0.9	2.5	0.02	0.11	0.25	0.73	4.39	27.20	157	µg/L	ICP-QMS	0.01
B	43.9	54.3	0.9	10.8	26.1	59.8	128.0	467	157	µg/L	ICP-QMS	0.1
Ba	75.6	398.9	0.1	14.5	29.7	52.8	145.4	5000	157	µg/L	ICP-OES	0.1
Be	0.004	0.026	<0.001	<0.001	<0.001	0.0015	0.0111	0.3220	62	µg/L	ICP-QMS	0.001
Bi	<0.001	0.0011	<0.0005	<0.0005	<0.0005	<0.0005	0.0015	0.0130	29	µg/L	ICP-QMS	0.0005
Ca	62.3	32.7	0.1	37.9	58.4	79.3	118.6	168.0	157	mg/L	ICP-OES	0.01
Cd	0.039	0.173	<0.001	0.0013	0.0053	0.0146	0.1026	1.75	127	µg/L	ICP-QMS	0.001
Ce	0.010	0.049	<0.0005	0.000513	0.000779	0.00158	0.019	0.391	119	µg/L	ICP-QMS	0.0005
Co	0.039	0.067	<0.002	0.010	0.021	0.044	0.110	0.664	156	µg/L	ICP-QMS	0.002
Cr	0.47	0.83	<0.03	0.12	0.19	0.36	2.30	4.86	150	µg/L	ICP-QMS	0.03
Cs	0.14	0.67	<0.001	0.0028	0.0067	0.0241	0.520	6.780	153	µg/L	ICP-QMS	0.001
Cu	10.8	29.6	0.04	0.91	2.61	6.37	46.94	260	157	µg/L	ICP-QMS	0.01
Dy	0.0016	0.0046	<0.0001	0.00029	0.00047	0.00093	0.00528	0.0353	154	µg/L	ICP-QMS	0.0001
Er	0.0012	0.0027	<0.0001	0.00023	0.00045	0.00077	0.00538	0.0187	149	µg/L	ICP-QMS	0.0001
Eu	0.0013	0.0018	<0.0002	0.00039	0.00070	0.00133	0.00402	0.0123	154	µg/L	ICP-QMS	0.0002
Fe	8.5	24.6	0.22	0.66	1.57	5.39	43.2	235	157	µg/L	ICP-QMS	0.10
Ga	0.1214	0.3458	<0.0005	0.0032	0.0055	0.0117	0.9310	1.82	153	µg/L	ICP-QMS	0.0005
Gd	0.0025	0.0064	<0.0002	0.0006	0.0011	0.0017	0.0059	0.0517	156	µg/L	ICP-QMS	0.0002
Ge	0.0187	0.0555	<0.005	<0.005	0.009	0.017	0.045	0.666	117	µg/L	ICP-QMS	0.005
Hf	0.0007	0.0016	<0.0005	<0.0005	<0.0005	0.0005	0.0020	0.0137	44	µg/L	ICP-QMS	0.0005
Hg	<5	<5	<5	<5	<5	<5	<5	53.6	1	ng/L	AFS	5
Ho	0.00039	0.00091	<0.0001	<0.0001	0.0001	0.0003	0.0015	0.0064	96	µg/L	ICP-QMS	0.0001
I	4.2	4.9	0.34	1.4	2.9	5.1	13.7	27.1	157	µg/L	ICP-QMS	0.20
K	2.6	4.4	0.10	0.80	1.50	2.50	7.92	30.2	157	mg/L	ICP-OES	0.1
La	0.0100	0.0423	<0.0005	0.0011	0.0018	0.0033	0.0279	0.4480	153	µg/L	ICP-QMS	0.0005
Li	5.1	7.1	0.11	1.02	2.86	6.40	16.16	60.8	157	µg/L	ICP-QMS	0.1
Lu	0.00039	0.00055	<0.00005	0.00010	0.00018	0.00037	0.00161	0.00333	150	µg/L	ICP-QMS	0.00005
Mg	14.1	9.0	0.01	7.87	12.70	18.20	29.36	52.60	157	mg/L	ICP-OES	0.01
Mn	2.3	7.6	<0.001	<0.001	0.38	1.34	5.64	59.00	108	mg/L	ICP-OES	0.001
Mo	0.95	2.10	0.04	0.24	0.46	0.88	2.31	20.70	157	µg/L	ICP-QMS	0.01
Na	24.3	36.1	0.3	5.5	12.3	25.5	91.8	256.1	157	mg/L	ICP-OES	0.1
Nb	0.0031	0.0100	<0.001	<0.001	<0.001	0.0014	0.0115	0.0792	47	µg/L	ICP-QMS	0.001
Nd	0.0080	0.0336	<0.002	0.0006	0.0010	0.0020	0.0230	0.2890	154	µg/L	ICP-QMS	0.0002
Ni	0.69	0.95	0.03	0.19	0.40	0.80	2.54	6.94	157	µg/L	ICP-QMS	0.01
Pb	0.48	1.88	0.004	0.026	0.080	0.288	1.818	20.7	157	µg/L	ICP-QMS	0.002
Pr	0.0020	0.0090	<0.00005	0.00014	0.00024	0.00050	0.00627	0.08660	156	µg/L	ICP-QMS	0.00005
Rb	2.8	7.3	0.03	0.4	0.7	1.6	15.4	63.0	157	µg/L	ICP-QMS	0.001
Sb	0.153	0.131	0.007	0.067	0.128	0.205	0.364	1.17	157	µg/L	ICP-QMS	0.002
Sc	0.0318	0.0314	<0.01	0.0143	0.0207	0.0334	0.0994	0.179	142	µg/L	ICP-QMS	0.01
Se	0.34	0.39	<0.01	0.13	0.19	0.37	1.30	2.67	152	µg/L	ICP-QMS	0.01
Sm	0.0027	0.0080	0.0002	0.0006	0.0008	0.0015	0.0070	0.0529	157	µg/L	ICP-QMS	0.0002
Sn	0.006	0.014	<0.001	0.001	0.002	0.005	0.021	0.111	122	µg/L	ICP-QMS	0.001
Sr	0.45	0.46	<0.001	0.159	0.326	0.565	1.120	3.440	156	mg/L	ICP-OES	0.001
Ta	<0.001	0.0015	<0.001	<0.001	<0.001	<0.001	0.0026	0.0149	21	µg/L	ICP-QMS	0.001
Tb	0.00029	0.00086	<0.00005	0.00005	0.00008	0.00015	0.00089	0.00663	120	µg/L	ICP-QMS	0.00005
Te	<0.005	<0.005	<0.005	<0.005	<0.005	0.00593	0.012	0.0222	56	µg/L	ICP-QMS	0.005
Th	0.0019	0.0061	<0.0001	0.00053	0.00070	0.00103	0.00522	0.0551	154	µg/L	ICP-QMS	0.0001
Ti	0.14	0.78	<0.01	<0.01	0.019	0.043	0.223	8.76	117	µg/L	ICP-QMS	0.01
Tl	0.0055	0.0238	<0.0005	0.00084	0.00145	0.00378	0.01506	0.291	136	µg/L	ICP-QMS	0.0005
Tm	<0.00005	0.00039	<0.00005	0.00007	0.00011	0.00020	0.00100	0.00253	141	µg/L	ICP-QMS	0.00005
U	1.1	1.7	0.003	0.3	0.6	1.3	3.1	18.1	157	µg/L	ICP-QMS	0.0005
V	1.03	3.07	0.015	0.16	0.30	0.7	2.9	24.5	157	µg/L	ICP-QMS	0.01
W	0.085	0.274	<0.002	0.00521	0.0112	0.0323	0.4944	1.99	148	µg/L	ICP-QMS	0.002
Y	0.015	0.027	0.0008	0.0041	0.0074	0.0115	0.0677	0.1740	157	µg/L	ICP-QMS	0.0005
Yb	<0.0002	0.0026	<0.0002	0.0004	0.0007	0.0015	0.0071	0.0146	143	µg/L	ICP-QMS	0.0002
Zn	89.7	255.1	0.08	3.49	21.70	60.9	372	2830	157	µg/L	ICP-QMS	0.05
Zr	0.0168	0.0565	<0.001	0.001	0.002	0.008	0.064	0.488	126	µg/L	ICP-QMS	0.001
Br ⁻	0.068	0.196	<0.003	0.01	0.02	0.05	0.27	1.80	145	mg/L	IC	0.003
HCO ₃ ⁻	224.3	106.6	21.1	159.0	217.0	283.0	388.8	612.0	157	mg/L	titration	2.0
Cl ⁻	28.4	51.9	0.3	6.4	16.6	28.1	99.2	536.0	157	mg/L	IC	0.01
F ⁻	0.19	0.19	0.02	0.08	0.13	0.21	0.58	1.43	157	mg/L	IC	0.003
NH ₄ ⁺	0.02	0.14	<0.005	<0.005	<0.005	0.01	0.05	1.64	57	mg/L	photometric	0.005
NO ₂ ⁻	0.004	0.011	<0.003	<0.003	<0.003	0.003	0.012	0.107	43	mg/L	IC	0.003
NO ₃ ⁻	10.1	20.1	0.04	2.44	5.15	11.40	28.20	228.00	157	mg/L	IC	0.01
PO ₄ ³⁻	0.17	1.31	<0.02	<0.02	0.02	0.05	0.25	16.40	101	mg/L	ICP-OES	0.02
SO ₄ ²⁻	34.8	29.1	0.1	13.5	26.8	48.3	93.1	181.0	157	mg/L	IC	0.01
SiO ₂	5.9	5.1	0.6	2.8	4.3	7.9	15.6	35.8	157	mg/L	ICP-OES	0.1
Hardness	213.5	106.6	0.3	139.7	198.3	279.8	400.2	528.8		mg/L CaCO ₃		
ΣREE	42.1	154.8	2.5	6.6	9.7	19.3	118.9	1337.9		ng/L		

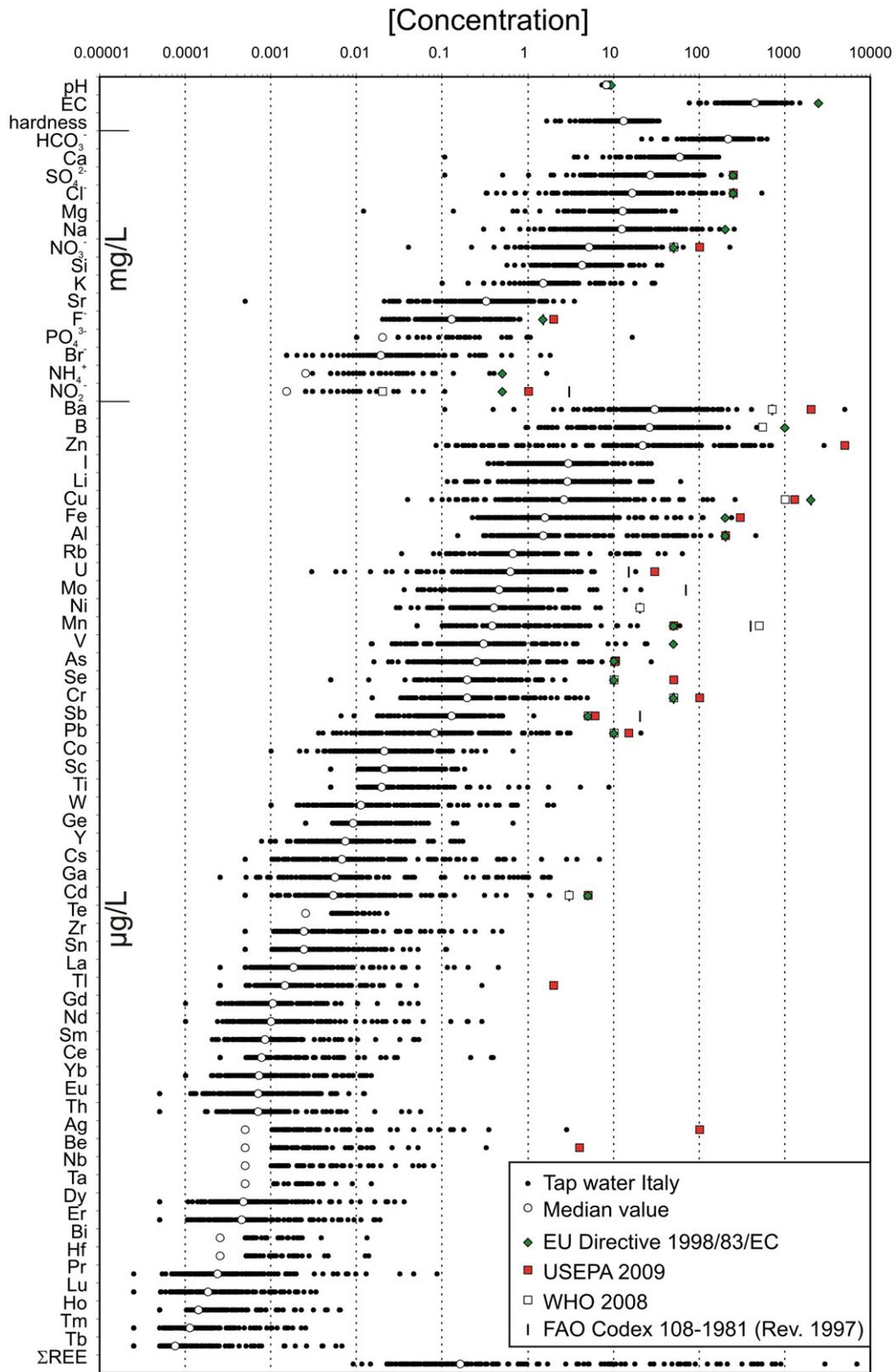


Fig. 3. Variation ranges for the investigated elements and calculated parameters (hardness and ΣREE). Elements are subdivided according to units and in a decreasing median order. The graph include also the normative limits and guideline values reported in Table 2.

with gypsum-bearing evaporitic rocks, Triassic in former case and Messinian in the other cases.

Water hardness, although not issued in any guideline scheme, can have detrimental effects particularly on household electrical appliances.

Several scientific papers suggested that high levels of drinking water hardness have a protective effect against cardiovascular diseases, mainly against ischemic heart disease. Many of these studies found significant evidence of an inverse association between magnesium levels in

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

EC (μS/cm)	Number of samples	Classification
<77	1	Very low mineral concentration
77–769	138	Low mineral concentration
769–2308	17	Intermediate mineral concentration
>2308	1	High mineral concentration

drinking water and coronary heart disease mortality as cerebrovascular mortality; evidence for calcium remains unclear (Catling et al., 2008 and references therein).

Although many ions could contribute to the water hardness, Ca and Mg are the most influencing components, thus it can be directly measured or computed from the analytical data according to Eq. (1):

$$\text{Hardness, mg equivalent/L CaCO}_3 = ([\text{Ca, mg/L}] * 2.497) + ([\text{Mg, mg/L}] * 4.116) \quad (1)$$

Eq. (1) has been applied to calculate tap water hardness. Table 3 shows hardness summary statistics. Median value of 198 mg/L CaCO₃ is rather high and corresponds to a very hard water. The lowest hardness is observed in sites where Na–HCO₃ waters occur; for this reason the presence of softening systems can be assumed. The majority of the tap water is hard and very hard type (Fig. 6), and is found, predominantly, in areas dominated by carbonates. The latter occur frequently in the aquifers of the Po River Plain. Slightly and moderately hard waters characterize the aquifers of sites in the Alps and in Sardinia, likely located in metamorphic and plutonic rocks.

5.2. Distribution of selected elements

It is possible to detect many differences between the sampled sites through the geographic distribution of concentrations of most analyzed elements in the tap waters. As shown in Fig. 7, tap waters grouped on regional basis, display for selected elements significant differences in variation ranges and median values likely related to specific geologic, geographic and/or environmental features. Elements are

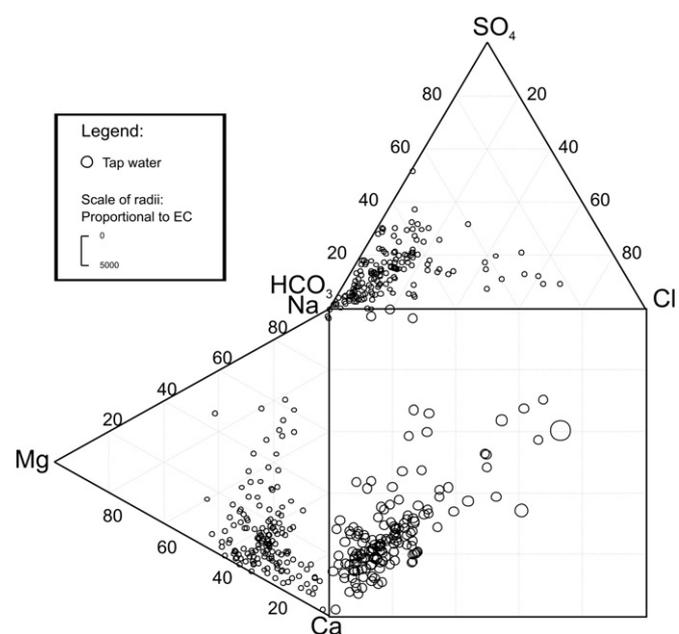


Fig. 4. Durov (1948) classificatory diagram showing the major ionic composition of the analyzed waters. Symbols are proportional to EC and indicate the surface geology where springs are located. Seawater average composition (Chester, 2002) is reported for comparison. Numbers refer to group of samples discussed in the text.

selected according to several criteria that include environmental importance, water source indicator, abundance of observation. It does not include several elements whose distribution is affected extensively by non natural sources, discussed in Section 5.3.

Figs. 8–10 show the spatial distribution of the same elements of Fig. 7, discussed in detail in the next paragraphs. Note that in Figs. 8–10 the concentration values have been classified according to the percentiles shown in Table 3. Since the concentrations below the median value are generally very low the first classification field includes all concentrations below the median. Concentrations that exceed thresholds set by Italian and EU regulations and US-EPA, WHO and FAO guideline values (Table 2) have been highlighted.

5.2.1. Aluminum

Aluminum is the most abundant metal in the lithosphere. It has low mobility under most environmental conditions, its solubility increases at low and high pH values. A significant proportion of Al in stream water is usually transported as colloids or particulates resulting from organic complexation. In groundwater Al content is generally low because of the low solubility of Al-bearing mineral. In any case, the major Al source is the weathering of primary aluminosilicates (feldspar, mica, amphibole) and it is often concentrated in secondary minerals such as clays (e.g. kaolinite, smectite, gibbsite) which may control the Al concentration in soil solution, groundwater and stream water.

The human exposure is primarily from the diet, and the uptake distribution and toxicity of Al are greatly dependent on its physico-chemical form (species). Aluminum speciation has a great impact on its toxicokinetics and toxicodynamics. Complexation increases Al solubility and transport. Drinking water surveys showed a wide range of Al concentrations in tap water (Flaten, 1991; Miller et al., 1984; Nieboer et al., 1995). Water treatment generally increased total Al. The median if Al concentration in drinking water that was not coagulation-treated was 43 μg/L, whereas it was reported to be 112 μg/L in alum-coagulant-treated surface water (Miller et al., 1984). The addition of 1 mg/L fluoride to drinking water produces AlF₃ and AlF₂⁺ in acidic solutions, but Al(OH)₄⁻ predominates at pH 7.5.

The median of Al in terrestrial water has been estimated to be 11 μg/L (Stumm and Morgan, 1996), a value slightly lower than that found in European surface water (median 17.7 μg/L, Saminen et al., 2005) but higher than the one found in Italian surface waters in the framework of the FOREGS project (7.7 μg/L, De Vivo et al., 2008; 2009; 2010). Aluminum concentrations in Italian tap waters range from 0.3 to 454 μg/L, only in one sample is below detection limit; median is 1.6 μg/L, lower than the one found in European tap water (2.5 μg/L, Reimann and Birke, 2010). As shown in Figs. 7 and 8a geographic distribution of Al concentrations is not homogeneous. Sardinia has the largest variation range and the highest median even if the maximum is found in one sample from northern Sicily. The 95% of the samples has Al concentration below 61 μg/L. Relatively high concentrations (>61 μg/L) occurs mostly in Sardinia where the presence of peraluminous granitic lithologies is very diffused. Other scattered high concentrations occur in Matera (Basilicata), Foggia (Puglia) and Arezzo (Tuscany) where abundant terrigenous sediments outcrop. Only one tap water from Messina province (Sicily) has Al concentrations above 200 μg/L (Italian, EU and WHO g.v., see Table 2) (Fig. 8a). The latter can be related to aquifer located in Mt. Peloritani where, as in Sardinia, are present peraluminous granitic lithologies.

5.2.2. Arsenic

Arsenic is a trace element occurring in three main oxidation states (–3, +3, +5). It forms in nature arsenopyrite (FeAsS), but can be present as trace element in other sulfides (galena, pyrite, sphalerite) and phosphates. In contrast to other toxic metals arsenic is generally mobile under neutral to alkaline pH conditions (Smedley and Kinniburgh, 2002) but its mobility in the secondary environment is limited because of its strong tendency to be sorbed by secondary hydroxides (especially

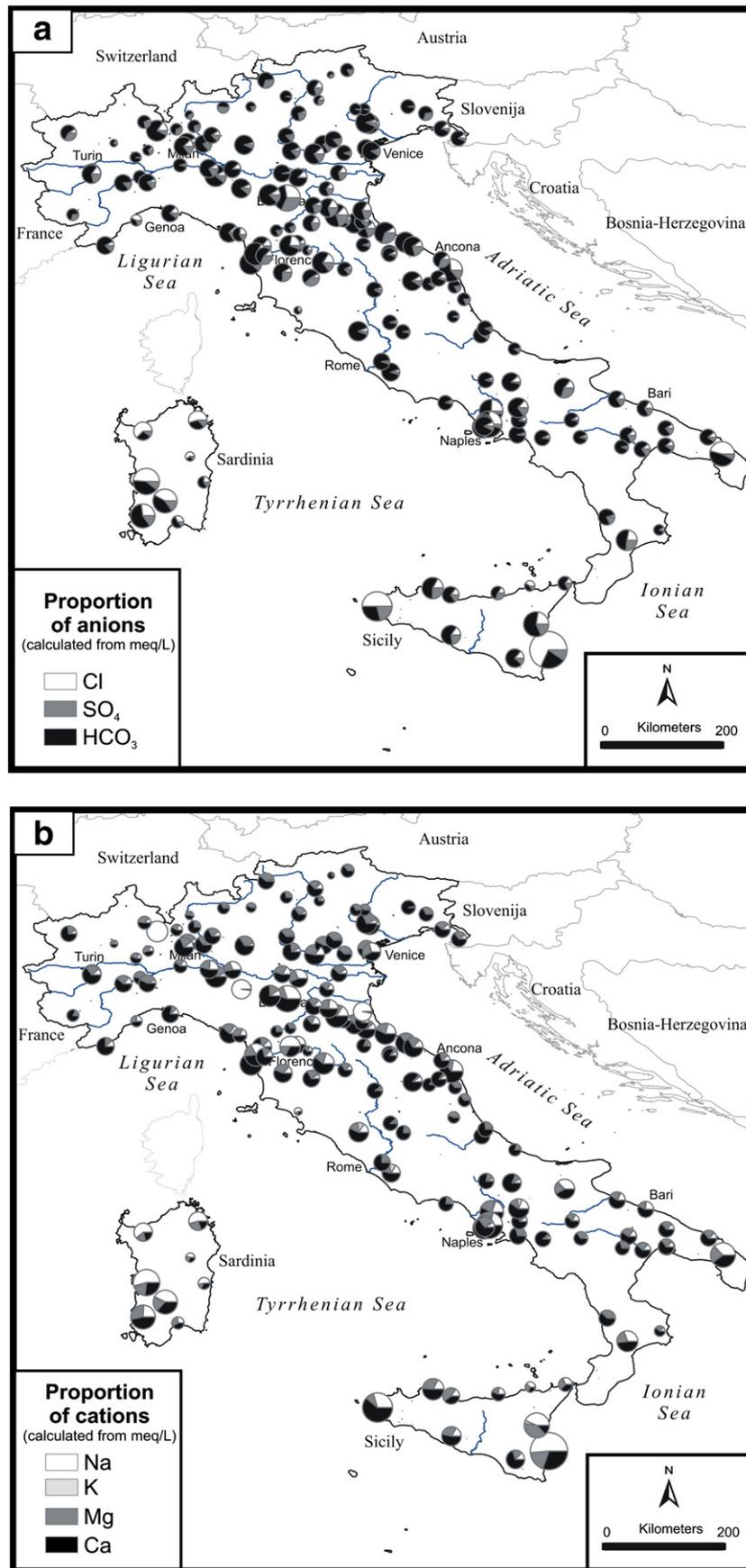


Fig. 5. Geographic distribution of the proportions of major anions (a) and cations (b) of the analyzed waters. Symbols in (a) and (b) are proportional to EC. Some points were slightly shifted to reduce the overlaps.

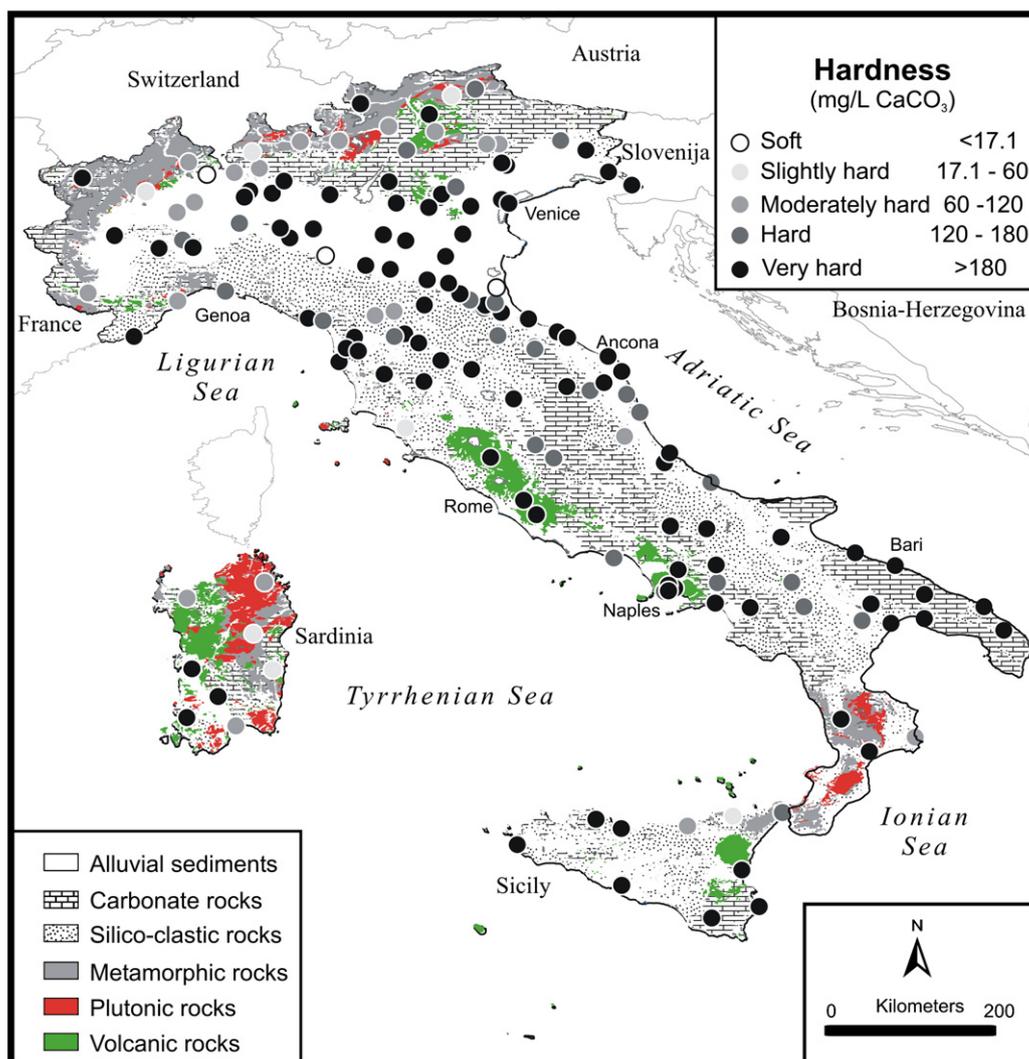


Fig. 6. Map of water hardness of Italian tap water. Classification is presented in the legend.

ferric oxyhydroxides) and organic matter. It is a typical element enriched in hydrothermal waters and an indicator of hydrothermal alteration zones (Banks et al., 2004). The retention of As in solution is constrained by co-precipitation with Fe along with other elements like Ba, Co, Ni, Pb and Zn (Fordyce et al., 1995).

The median concentration of As in surface water has been estimated to be 2 µg/L (Ivanov, 1996), a value too high compared with the median for European surface water (0.63 µg/L, Saminen et al., 2005), for Italian surface waters from FOREGS database (0.47 µg/L, De Vivo et al., 2008; 2009) and for European tap water (0.19 µg/L, Reimann and Birke, 2010). Italian tap waters range from 0.016 to 27.2 µg/L with no value below detection limit, the median is 0.25 µg/L. Fig. 7 shows that the geographic distribution of As concentrations, at regional scale, is not homogeneous with the highest medians in Lombardy and Campania. The 95% of the samples has As concentrations below 4.4 µg/L. High concentrations (>4.4 µg/L) occur in Lombardy (4 samples), in Latium (2 samples), in Calabria (1 sample) and in Tuscany (1 sample). Latium, Campania and southern Tuscany belong to the Roman Comagmatic volcanic Province which is well known for its high As background values, recorded in soils and stream waters (De Vivo et al., 2008; 2009; 2010) related to the alkaline volcanic products (Achene et al., 2010; Dall'Aglio et al., 2001; Giuliano et al., 2005; Vivona et al., 2006) and to the hydrothermal activity (Mantelli et al., 2005). Accordingly As concentrations in samples collected in the Neapolitan area (Fig. 8b) can be due to the water interaction with volcanic rocks enriched in As (Cicchella et al., 2005;

Cocoziello et al., 2005). The latter samples, even if collected in the same area, show different As concentrations indicating different sources for the tap water supplied. Other areas where high As concentrations are known in groundwater are Lombardy (Castelli et al., 2005) and the central Po River Plain (Boscolo et al., 2005; Castelli et al., 2005; Farina et al., 2005) where relatively high As concentrations in tap waters have also been found. In Trentino-Alto Adige As rich waters are likely associated to deep circulating thermal waters (<http://www.provincia.bz.it/acque-energia/acqua/arsenico.asp>).

The highest value (27.2 µg/L) has been registered in a tap water from Viterbo (Latium) exceeding the EU and Italian drinking water limit of 10 µg/L (Table 2). For Latium, because of its elevated As background values, registered in different environmental media (De Vivo et al., 2009), as already pointed out, the threshold has been increased to 50 µg/L by regional authorities. This poses some questions because chronic exposure to As increases the risk of cancer and skin pigmentation (WHO, 1996).

5.2.3. Boron

Boron is a trace element occurring in groundwater in the form of the amphoteric boric acid (H₃BO₃) or one of its complex ions (e.g. metaborate B(OH)₄⁻ at high pH). Borax and tourmaline are two typical B minerals, the first easily soluble, the latter almost insoluble.

Fresh water in lakes and rivers has a range from <10 µg B/L to 1500 µg B/L, with most lower than 300 µg B/L (Nielsen, 2001). For the

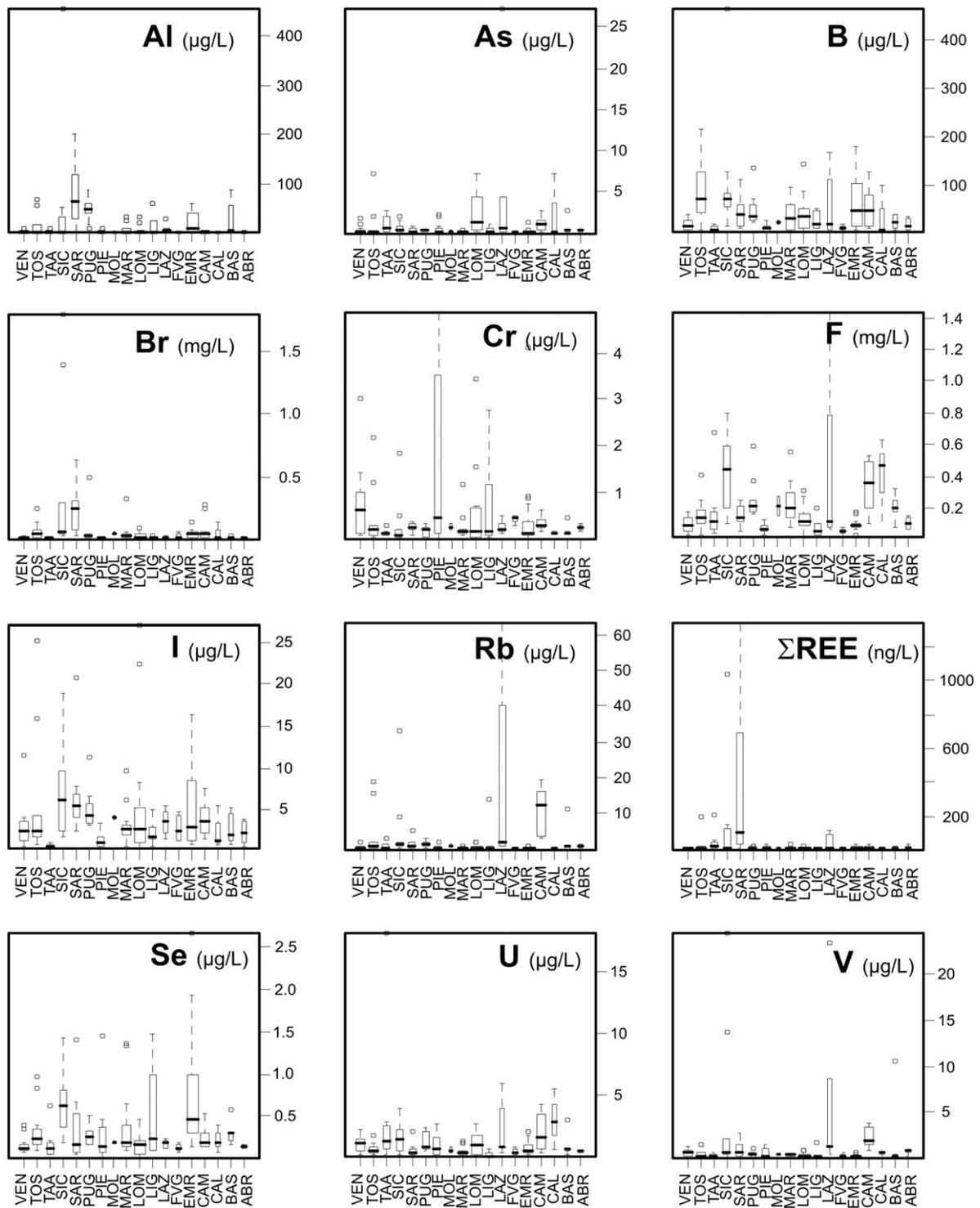


Fig. 7. Differences related to geographic provenance for selected elements. For abbreviations of region names see Table 1.

general population, the greatest exposure to boron comes from food (e.g. vegetables, pulses, nuts, fruits, wine and beer). Several studies since late 1980s showed that boron was a beneficial nutrient for humans.

Hydrothermal processes lead to B enrichment that can be strongly enriched in thermal springs (Hem, 1985) and water interacting with volcanic rocks. Boron minerals are common in many evaporitic deposits. The average B concentration in seawater is 4.5 mg/L (Shand et al., 2007).

The median of B in world surface water has been estimated to be 20 μg/l (Ivanov, 1996), a value comparable with median of European

surface water (15.6 μg/L, Saminen et al., 2005) and of European tap water (16 μg/L) (Reimann and Birke, 2010) but lower than the median of the Italian surface water (34.3 μg/L, De Vivo et al., 2009).

For Italian tap water B concentrations range from 0.9 to 467 μg/L, with no value below detection limit. The median is 26 μg/L, slightly lower than Italian surface water. The geographic distribution is not homogeneous and Sicily and Tuscany have the highest median values, followed by Emilia-Romagna and Campania (Fig. 7 and 8c). The 95% of samples has B concentrations below 128 μg/L. In Tuscany (Fig. 8c) sampled tap waters have B concentrations > 128 μg/L in areas where

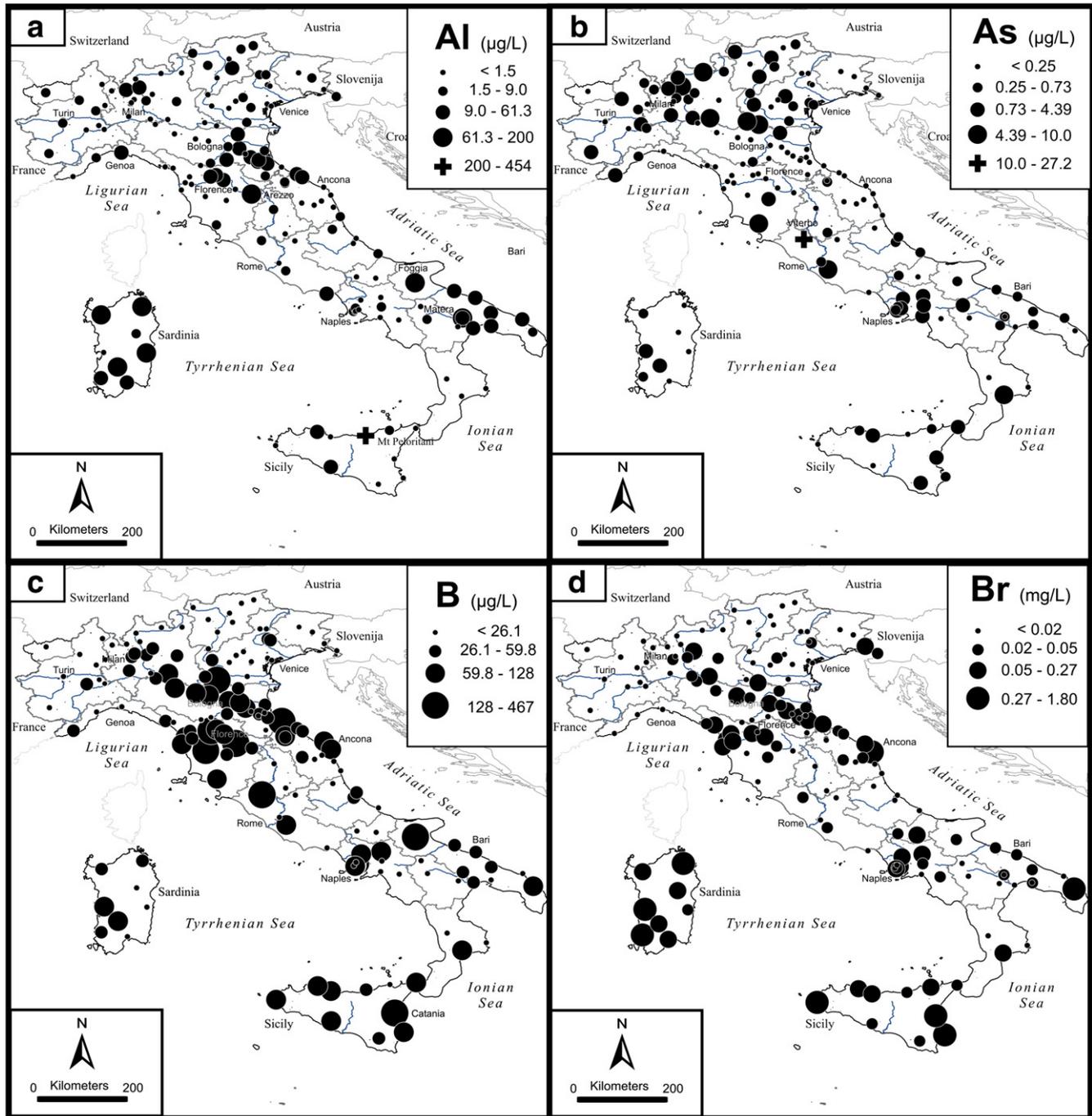


Fig. 8. Hydrogeochemical maps for Al (a); As (b); B (c); Br (d).

boric acid fumaroles occur (e.g. Bianchini et al., 2005) and close to evaporitic rock outcrops (Cortecci et al., 2009). Similarly the relatively high values observed along the eastern Emilia-Romagna apenninic margin could be related to the water interaction with evaporitic rocks and/or to the contribution of deep formation waters enriched in B (Boschetti et al., 2011; Conti et al., 2000). The maximum value (467 µg/L) is from Catania (eastern Sicily), located at the border of the Mt. Etna volcano for which an origin related to water/volcanic rock interaction and hydrothermal water circulation has been invoked (Giammanco et al., 1998), even if a possible contribution by deep sedimentary waters has also been suggested (Aiuppa et al., 2003).

No sample exceeded the threshold of the Italian and EU drinking water directive but the B concentration in Catania tap water is very close to the FAO guideline value (Table 2 and Fig. 3).

5.2.4. Bromide

Bromine is a trace element of some rock forming minerals such as biotite, amphiboles, apatite, eudialyte and sodalite, mostly as a replacement for Cl. Coal and organic matter accumulate Br and some sedimentary rocks that can show elevated Br concentrations.

Bromide (Br⁻) is the most common (and highly mobile) form of bromine in the aqueous environment and is highly enriched in the marine environment, ocean waters have a mean concentration of

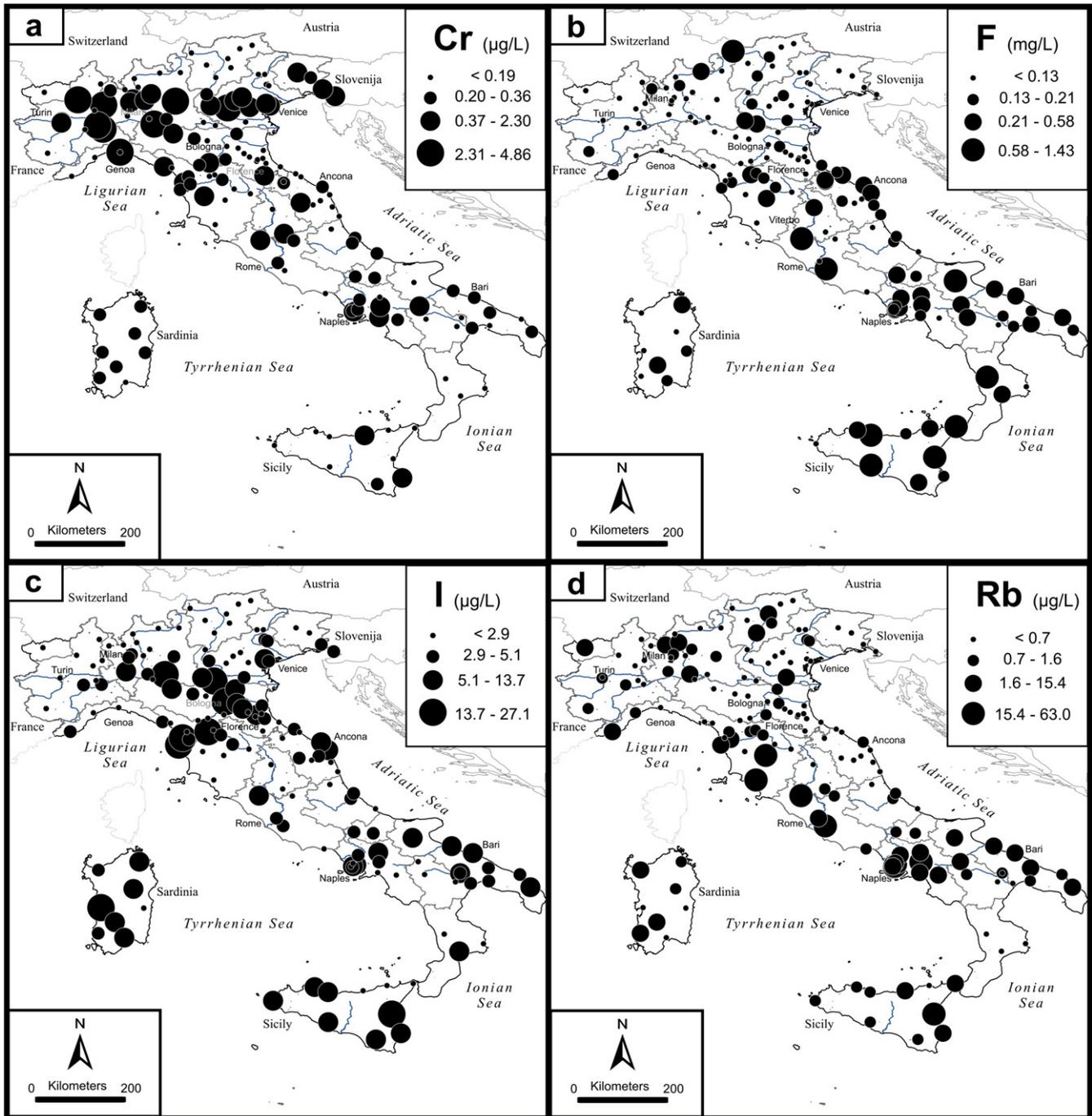


Fig. 9. Hydrogeochemical maps for Cr (a); F (b); I (c); Rb (d).

67,000 µg/L. It has a geochemistry very similar to chloride (Edmunds, 1996). High bromide concentrations can also be expected in natural brines and thermal waters.

Median of Br⁻ in world surface water has been estimated to be 20 µg/L (Ivanov, 1996) a value comparable with median observed for European surface water (<30 µg/L, Saminen et al., 2005) and Italian tap water, whereas European tap waters have a median slightly lower (10 µg/L, Reimann and Birke, 2010). The general population will mainly be exposed to bromide via their food. The role of bromide as a residue in food and water necessitated its broad toxicological evaluation (Pavelka, 2004). In Italian tap water Br⁻ concentrations range from 2 to 1800 µg/L, 15 samples are below the detection limits. The 95% of samples has Br⁻ concentrations below 270 µg/L (Table 3). At regional scale the highest median is recorded in Sardinia (Fig. 7, Fig. 8d), followed by Tuscany,

Emilia-Romagna and Campania. The relatively high concentrations (>270 µg/L) are located mostly in Sardinia and Sicily associated to alkaline volcanic and evaporitic lithologies but a seawater contribution to the groundwater supply systems can also be argued, particularly important in Sardinia where drinking water is dominantly supplied by artificial reservoirs. Bromine is positively correlated to Cl (r=0.92 with 145 couples of data) supporting seawater contribution and shallow circulation in the groundwater system mostly in the islands and in coastal sites. Where water supply system utilizes deep connate waters by deep wells, like in the areas located in alluvial plains (Boschetti et al., 2011; Toscani et al., 2007) Br⁻ should be associated with B. This is the case of the sites in the inner Po river plain and Emilia Romagna (Conti et al., 2000) with Br⁻ concentrations between 51 and 270 µg/L (Fig. 8d). The latter range has also been registered in many samples

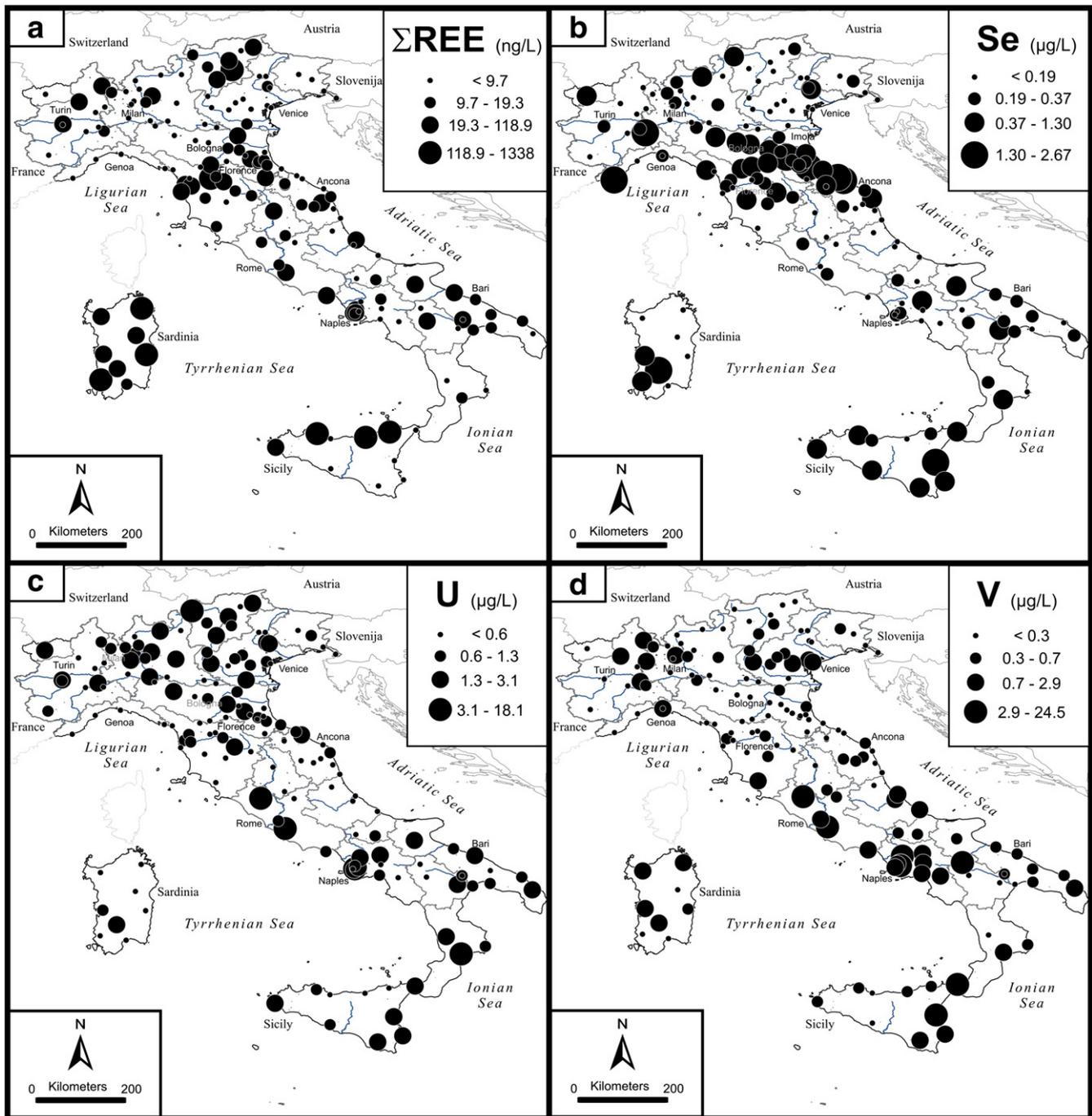


Fig. 10. Hydrogeochemical maps for SREE (a); Se (b); U (c); V (d).

from Tuscany where high Br concentrations were already known in surface waters (Nisi et al., 2008) and in coastal areas groundwater (Grassi and Cortecchi, 2005).

5.2.5. Chromium

Chromium occurs in a variety of oxidation states of which +3 and +6 are the most important under the common Eh–pH range found in nature (Richard and Bourg, 1991). It forms several minerals, including chromite (FeCr_2O_4) that is the most common, and is present in traces in several rock forming minerals, such as spinel, pyroxenes, amphiboles, micas and garnets. It is strongly enriched in mafic and ultramafic rocks. Chromium mobility is generally low, unless under strongly oxidizing conditions, so its dissolved concentrations are usually low.

The median concentration of Cr in uncontaminated surface water has been estimated to be $0.7 \mu\text{g/L}$ (see Koljonen, 1992) higher than median value of European surface water ($0.38 \mu\text{g/L}$) as presented by Saminen et al. (2005), and than Italian surface water data of the FOREGS project ($0.29 \mu\text{g/L}$, De Vivo et al., 2009). The Cr median for European tap water is low ($<0.2 \mu\text{g/L}$) and similar to the Italian tap water one of $0.2 \mu\text{g/L}$, ranging from 0.032 to $4.86 \mu\text{g/L}$ with 7 samples below detection limit. Veschetti et al. (2010) in their extensive study on Italian tap water report a Cr median $<1 \mu\text{g/L}$ and the highest concentration of $36 \mu\text{g/L}$.

At regional scale, Veneto and Piedmont show the highest dispersion (Fig. 7) and the highest Cr median. The 95% of samples has Cr concentrations below $2.3 \mu\text{g/L}$ (Fig. 9a). The relatively high concentrations ($>2.3 \mu\text{g/L}$) are mostly located in north western regions (Piedmont,

Lombardy and Liguria) where metamorphosed ophiolitic rocks extensively outcrop (Anselmi et al., 1978; Dinelli and Lucchini, 1999). Tap water derived from groundwater exploitation in the northwestern part of Italy could also be influenced by interaction with detrital grains in porous aquifers derived from alpine sources areas (Vezzoli et al., 2010; Vezzoli and Garzanti, 2009). Similarly, in the Veneto region the sample with high Cr concentration (Fig. 9) is related to the Paleocene–Eocene mafic rocks. Ophiolitic rocks occur in Tuscany as well and clearly affect the dissolved concentration of Cr in the surface water (Cortecci et al., 2008; 2009). Chromium in tap water can also originate by interaction with parts of the distributing system and by the tap itself. Sampling procedures should have limited this effect, and could however originate spot anomaly and not related to particular lithologies as previously discussed. Chromium could be introduced in the groundwater by anthropogenic activities since it is widely used in the steel, tanning and wood industry. There is evidence of alteration of its geochemical cycles by extensive industrial impact such as the case of certain areas in Veneto (Bini et al., 2008 and reference therein), Tuscany (Cortecci et al., 2008; Dinelli et al., 2005) and Liguria (Bonaria and Cipolli, 2003). Concentrations in tap waters are far below any guideline value (Fig. 3) and are mainly controlled by natural water–rock interactions.

5.2.6. Fluoride

Fluorine is an element present in solution as fluoride anion. Fluorite (CaF_2) is the most important F mineral, although F also occurs in other minerals, such as micas, amphiboles, tourmaline and apatite, and it is abundant also in seawater (about 1 mg/l F^-).

Fluorine in water tends to complex strongly with certain specific cations (Fe, Al and Be). Its concentration in solution is controlled by the solubility of fluorite and its mobility should be limited in Ca-rich waters. It also sorbs to mineral surfaces like gibbsite, kaolinite and halloysite. Fluoride is particularly enriched in waters from volcanic areas (Shand et al., 2007) and in waters from acidic igneous and metamorphic rocks although atmospheric deposition can be enhanced by sources of industrial pollution.

Fluorine-bearing groundwater is often the formation water in structure made up of sedimentary rocks and fracture-vein sodium-bicarbonate and sodium-sulfate types of water in the zones of tectonic activity in magmatic and metamorphic rock massifs. In these types of water, fluorine levels can reach several hundreds of milligrams per liter.

Median of F^- in surface water has been estimated to be 0.1 mg/L (Ivanov, 1996) similar to the one observed for European surface and tap waters (respectively 0.1 mg/L , Saminen et al., 2005 and 0.087 mg/L , Reimann and Birke, 2010), and the median of the Italian surface and tap waters (respectively 0.09 mg/L , De Vivo et al., 2009 and 0.127 mg/L). Fluorine is an essential micronutrient for mammals and levels below 0.5 mg/L may lower dental health, while concentrations much above 1.5 may induce skeletal and dental disorders, and cause harm to kidneys, nerves and muscles. Fluorine concentrations in Italian tap water range from 0.02 to 1.43 mg/L with no sample below detection limit. The 95% of the samples has concentrations below 0.58 mg/L .

Geographic distribution at regional scale displays highest median in Sicily, Campania and Calabria although the maximum is found in Latium (Fig. 7). The relatively high concentrations ($>0.58 \text{ mg/L}$) are mostly found in southern Italy controlled by climatic and geographical conditions and by lithology as well (Fig. 9b). In Latium are clearly related to water interaction with alkaline volcanic rocks (Fig. 9b) as also mentioned for surface waters (De Vivo et al., 2009), groundwater (Preziosi et al., 2010) and for bottled mineral waters (Cicchella et al., 2010).

Although not exceeding the threshold value of the Italian legislation, the highest F^- concentration (1.43 mg/L) occurs in Latium (Viterbo Province), a region where the permitted has been raised because of high F^- background values in surface waters.

5.2.7. Iodine

Iodine is a trace element that occurs in several oxidation states, the main are: -1 , $+1$, $+3$, $+5$ and $+7$, although -1 is the most common in the surface environment. It forms rare minerals and is present in trace amounts in several minerals, apatite is the most important. The element shows the highest concentrations in phosphatic evaporitic rocks. Marine water is an important reservoir for I cycle with its high concentrations ($60 \text{ } \mu\text{g/L}$, Hem, 1985).

Iodine is very mobile in the secondary environment, and is a typical element of brines. It is an essential trace element for humans because it provides a substrate for the synthesis of thyroxide hormones and is essential to normal growth and development.

The median of I in surface water has been estimated to be $2 \text{ } \mu\text{g/L}$ (Ivanov, 1996). This value is much higher than the median observed for European surface water ($0.33 \text{ } \mu\text{g/L}$, Saminen et al., 2005), but lower than the tap water one ($3.2 \text{ } \mu\text{g/L}$, Reimann and Birke, 2010). Italian tap waters I concentrations range from 0.34 to $27.1 \text{ } \mu\text{g/L}$, with no sample below detection limits and with a median of $2.92 \text{ } \mu\text{g/L}$.

At regional scale the highest median values are observed in Sicily, Sardinia and Puglia, although the maximum value is recorded in Lombardy (Fig. 7). The 95% of samples has concentrations below $13.7 \text{ } \mu\text{g/L}$. Relatively high I concentrations ($>13.7 \text{ } \mu\text{g/L}$) are mostly located in the Po river Plain and in Tuscany; high concentrations occur as well in Sardinia and in Sicily. For coastal areas the explanation could be the marine influence. At the same time for locations in alluvial plains, such as the Po river Plain, contribution from formation waters locally enriched in I (Boschetti et al., 2011; Conti et al., 2000) can be argued.

5.2.8. Rubidium

Rubidium occurs in nature in oxidation state $+1$, it does not form its own minerals but substitutes K in micas, K-feldspar, leucite and in other K-bearing minerals. Despite its high solubility in aqueous solutions Rb mobility in the secondary environment is generally very low, due to its strong sorption by clay minerals such as illite (Shand et al., 2007). Geothermal spring waters can also be enriched in Rb. Average Rb concentration in ocean waters is about two orders of magnitude higher than in fresh water.

In surface water median of Rb has been estimated to be $2 \text{ } \mu\text{g/L}$ (Ivanov, 1996), comparable with the median of European surface waters ($1.32 \text{ } \mu\text{g/L}$, Saminen et al., 2005), with Italian surface water ($1.15 \text{ } \mu\text{g/L}$, De Vivo et al., 2009) and with European tap water ($0.91 \text{ } \mu\text{g/L}$, Reimann and Birke, 2010). Italian tap waters have a median slightly lower, $0.67 \text{ } \mu\text{g/L}$, and range from 0.03 to $63 \text{ } \mu\text{g/L}$, no sample has Rb concentration below the detection limit. At regional scale Latium has the largest variation range and Campania the highest median, the tap waters from the other regions have very low Rb concentrations with occasional outliers (Fig. 7). The 95% of samples has concentration $<15 \text{ } \mu\text{g/L}$. Similarly to the bottled mineral waters (Dinelli et al., 2010), relatively high concentration ($>15 \text{ } \mu\text{g/L}$) are concentrated in central-southern Italy, in correspondence of the Roman Comagmatic volcanic Province characterized by the occurrence of alkaline volcanic rocks, and also rich in geothermal spring waters (Fig. 9d). In Sicily a tap water with relatively high Rb concentration is located as well in Mt. Etna area where volcanic rocks and hydrothermal springs are known.

5.2.9. ΣREE (Rare Earth Elements summation)

We describe the entire group of REE using the sum of the single element concentrations as the key parameter. REE is a composite group of elements (La, Ce, Dy, Gd, Er, Ho, Lu, Pr, Tb, Tm, Yb), with generally similar geochemical behavior apart from Ce and Eu which are affected by changes in redox conditions. They can be concentrated in several rock forming minerals, such as monazite [(Ce,La,Nd,Dy,Th,Nd)PO₄], xenotime [(Y,Ce)PO₄], apatite, allanite, zircon and garnet (particularly the Heavy REE). Their mobility is, generally very low, so their concentrations are in the order of ng/L .

Table 5
Six 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).

Parameter	Factors						Communality
	F1	F2	F3	F4	F5	F6	
Al	−0.031	0.303	−0.058	−0.081	0.281	0.619	0.57
As	−0.027	−0.003	0.774	−0.065	−0.131	−0.040	0.62
B	0.844	−0.033	0.198	0.300	0.144	0.036	0.86
Ba	<u>0.237</u>	−0.092	−0.156	0.733	0.033	0.181	0.66
Br [−]	0.811	0.105	0.114	<u>0.185</u>	0.082	0.071	0.73
Ca	0.105	0.012	0.068	0.906	0.081	−0.117	0.86
Cd	−0.089	0.795	0.030	<u>0.009</u>	−0.088	0.031	0.65
Cl [−]	0.884	0.120	0.028	0.168	0.197	0.052	0.87
Co	0.549	0.382	−0.170	−0.096	0.377	0.076	0.63
Cr	0.044	0.192	−0.041	−0.072	0.048	− 0.554	0.35
Cs	0.138	0.069	0.763	−0.085	−0.051	0.194	0.65
Cu	0.163	0.697	−0.022	−0.005	0.028	0.047	0.52
F	0.342	−0.171	0.599	0.167	0.148	0.243	0.61
Fe	0.276	0.492	0.155	−0.143	0.017	0.541	0.65
HCO ₃ [−]	0.466	−0.031	0.066	0.494	0.182	− 0.425	0.68
I	0.785	0.060	0.110	0.246	−0.121	−0.076	0.71
K	0.604	0.015	0.549	0.297	0.238	0.088	0.82
Li	0.577	−0.146	0.227	0.287	0.289	0.364	0.70
Mg	0.144	0.042	0.139	0.806	0.058	−0.079	0.70
Mn	0.388	0.601	0.101	−0.004	−0.037	0.315	0.62
Mo	−0.104	−0.104	0.572	0.276	0.343	0.018	0.54
Na	0.940	0.048	0.082	0.021	0.125	0.077	0.91
Nd	<u>0.074</u>	0.329	0.133	−0.153	−0.016	0.629	0.62
Ni	0.374	0.385	−0.044	0.042	0.440	−0.172	0.52
Pb	0.003	0.818	−0.078	−0.013	−0.039	0.024	0.68
Rb	0.215	<u>0.075</u>	0.836	0.122	0.056	0.110	0.78
Sb	−0.082	0.095	0.138	−0.134	0.579	0.234	0.44
Se	0.275	−0.101	−0.027	0.170	0.754	−0.031	0.68
Si	0.573	−0.036	0.397	−0.016	−0.268	−0.173	0.59
Sn	−0.035	0.536	0.172	−0.040	0.170	0.135	0.37
SO ₄ ^{2−}	0.357	−0.081	−0.086	0.253	0.687	0.081	0.68
Sr	0.274	−0.094	0.022	0.850	0.147	0.098	0.84
Tl	0.074	0.407	0.481	0.019	0.243	0.125	0.48
U	0.000	−0.050	0.343	0.236	0.718	−0.183	0.72
V	0.188	0.147	0.662	−0.128	0.113	− 0.353	0.65
Y	0.194	0.391	0.075	0.182	0.013	0.610	0.60
Zn	−0.054	0.810	−0.028	−0.062	−0.108	−0.020	0.68
% Variance explained	24.6	13.8	9.1	6.8	5.8	5.5	
Cumulative % variance	24.6	38.4	47.5	54.3	60.1	65.6	

About Σ REE concentration in surface waters there is no reference data with the exception of the ones from FOREGS that indicate a median for European surface water of 192 ng/L (Saminen et al., 2005), higher than the Italian one (64 ng/L, De Vivo et al., 2009). Σ REE concentrations in Italian tap waters range from 2.5 to 1338 ng/L with a median of 9.7 ng/L, much lower than European and Italian surface water medians. Literature have shown significant difference in REE concentration if filters <0.45 μ m are used (Cidu and Frau, 2009) for the presence of colloids adsorbing the elements. This could explain the observed difference in median values between surface and tap water.

Fig. 7 shows that Sardinia unlike other regions has the largest variation range and the highest median. The 95% of samples has Σ REE concentration <119 ng/L. Relatively high Σ REE concentrations (>119 ng/L) are found in Sardinia, Trentino-Alto Adige, Sicily and Latium. They are associated to acidic plutonic and volcanic rocks in Sardinia and Trentino-Alto Adige (Fig. 10a), to alkaline volcanic rocks in Central Italy and to metamorphic rocks in Sicily and Sardinia.

5.2.10. Selenium

Selenium occurs in nature with oxidation states -2 , $+2$, $+4$ and $+6$ and its chemistry is very similar to that of S and frequently substitutes this element in sulfides. Selenium is highly mobile under oxidizing, acidic, neutral and alkaline conditions and its mobility decrease with decreasing pH. It is immobile under reducing conditions and is

adsorbed by clay and ferric oxides. Selenite and selenate (corresponding to sulphite and sulfate) are the main forms in aqueous solution.

The median of Se in surface water has been estimated to be 0.2 μ g/L (Ivanov, 1996), a value comparable with European surface water (median 0.34 μ g/L, Saminen et al., 2005), slightly lower than the median of Italian surface water of the FOREGS project (0.54 μ g/L, De Vivo et al., 2009). The median for European for tap water (0.12 μ g/L, Reimann and Birke, 2010), is slightly lower than the median value for Italian tap water (0.20 μ g/L). The latter ranges from 0.014 to 2.67 μ g/L and five samples are below detection limit. At regional scale, Fig. 7 shows that the highest medians are observed in Sicily and Emilia-Romagna. The 95% of samples has Se concentrations <1.3 μ g/L. Relatively high concentrations (>1.3 μ g/L) are scattered: one sample respectively in Sardinia, in Sicily, in Liguria, and in Piedmont. In Emilia Romagna there are three samples located in the south eastern Po river plain, along the coast and close to the border of the northern Apennines (Fig. 10b), close to areas where Se anomaly are known (up to 9 μ g/L Se, Vinceti et al., 2000).

The highest value (2.67 μ g/L), found in a tap water from Imola (Emilia Romagna), is well below the threshold value reported by various organizations (Table 2 and Fig. 3). Selenium is an essential element in the diet of many organisms, it is needed for growth and fertility in animals, while deficiency in humans leads to hearth and bone diseases (Mertz, 1987). For adult humans 30–40 μ g/L day^{−1} is needed (WHO, 1996) and this amount is provided through grains, cereal and meat that usually contain

enough Se. The optimal dietary requirement for Se lies in a narrow range and it is toxic at higher levels.

5.2.11. Uranium

Uranium occurs in five main oxidation states (+2, +3, +4, +5, +6), of which +4 and +6 are most common in nature. It is mobile under oxidizing conditions (+6) and immobile under reducing conditions. It forms own minerals (Uraninite/pitchblende [UO₂]) but it is also present as an accessory element in zircon, monazite, apatite and allanite.

The median of U concentrations in surface water has been estimated to be 0.5 µg/L (Ivanov, 1996). The median reported for European surface water is 0.32 µg/L (Saminen et al., 2005) whereas the median for Italian

surface water is slightly higher (0.98 µg/L, De Vivo et al., 2009). U concentrations in Italian tap water range from 0.003 to 18.1 µg/L and no sample below detection limit. The median is 0.62 µg/L double compared with European tap water (0.31 µg/L, Reimann and Birke, 2010).

Fig. 7 shows that Calabria and Campania have slightly higher median values compared with other regions, although the maximum value is observed in Trentino-Alto Adige in a mineralized area (Dall'Aglio, 1971). The 95% of samples have U concentrations below 3.1 µg/L, relatively high concentrations (>3.09 µg/L) are mostly located in central Italy in regions belonging to the Roman Comagmatic Province (4 samples) already well known for U anomaly in soils and stream waters associated to alkaline volcanic rocks (De Vivo et al., 2008; 2009; Lima et al., 2005). Other relatively high values are located: in Siracusa

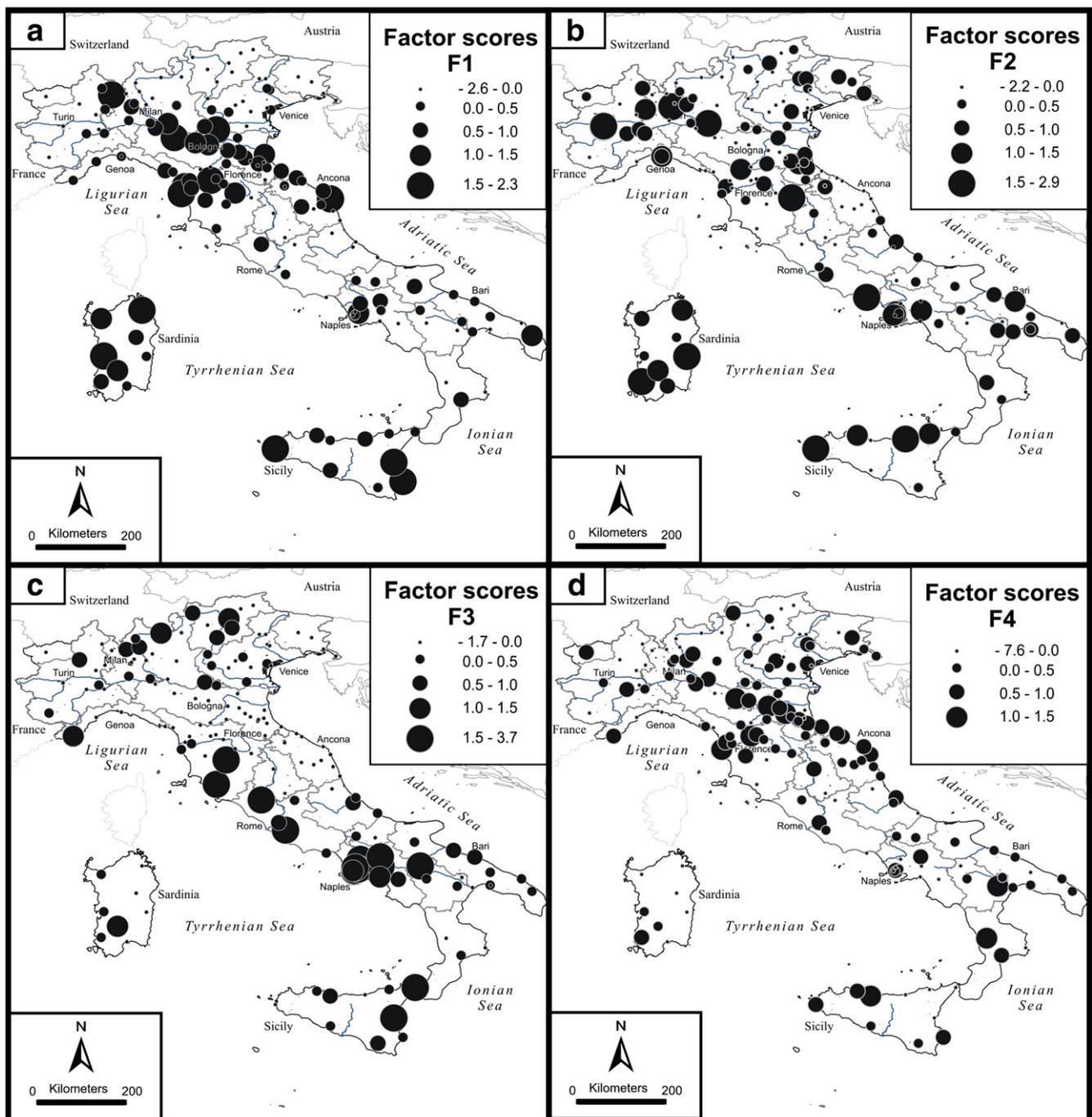
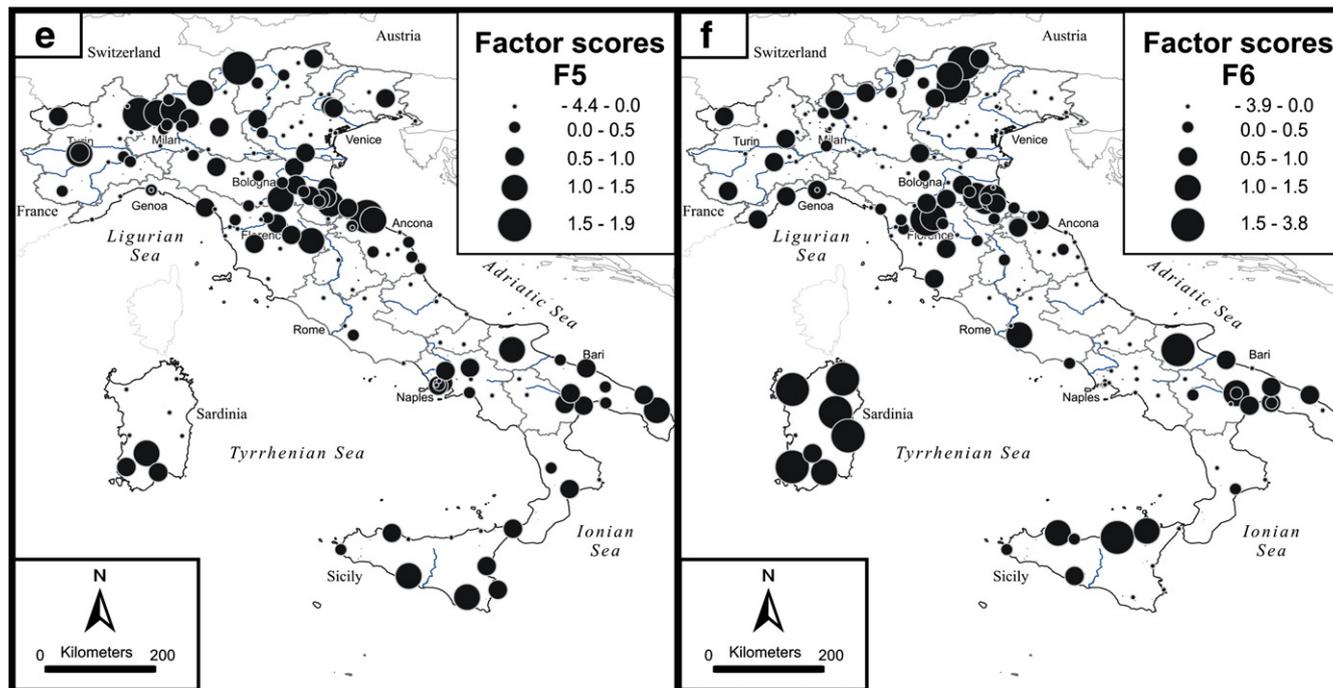


Fig. 11. Factor score distributions of the five factor solution by R-mode factor analysis.



	F1	F2	F3	F4	F5	F6
Na	0.940	Pb 0.818	Rb 0.836	Ca 0.906	Se 0.754	Nd 0.629
Cl ⁻	0.884	Zn 0.810	As 0.774	Sr 0.850	U 0.718	Al 0.619
B	0.844	Cd 0.795	Cs 0.763	Mg 0.806	SO ₄ ²⁻ 0.687	Y 0.610
Br ⁻	0.811	Cu 0.697	V 0.662	Ba 0.733	Sb 0.579	Fe 0.541
I	0.785	Mn 0.601	F 0.599	HCO ₃ ⁻ 0.494	Ni 0.440	V -0.353
K	0.604	Sn 0.536	Mo 0.572		Si -0.268	HCO ₃ ⁻ -0.425
Li	0.577	Fe 0.492	K 0.549			Cr -0.554
Si	0.573	Nd 0.419	Tl 0.481			
Co	0.549	Tl 0.407				
HCO ₃ ⁻	0.466					
% variance	24.6	13.8	9.1	6.8	5.8	5.5

Fig. 11 (continued).

(Sicily), also affected by alkaline volcanism; in Catanzaro (Calabria) due to leaching from alkaline granitic rocks that outcrop in the area; and in the central Alps (one sample), in Bolzano (Trentino Alto Adige) where U-ore deposits occur (Castaldo and Stampanoni, 1975). The latter has the highest U concentration (18.1 µg/L) that exceeds the FAO guideline value (15 µg/L). Uranium is a non-essential element and the overall risk arising from the biochemical toxicity of U as a heavy metal in drinking water is considered to be about six orders of magnitude higher than those deriving from its radioactivity (Milvy and Cothorn, 1990).

5.2.12. Vanadium

Vanadium occurs mainly as trace constituent in pyroxenes, amphiboles, micas and apatite even if can originate from some own-minerals. It has three main oxidation states: +3, +4 and +5.

Vanadium is a highly mobile element, whose solubility is strongly controlled by its oxidation state. It displays the highest solubility in oxic environments, where vanadate ions (e.g. H₂VO₄⁻) typically dominate the water chemistry (oxycations can occur at lower pH, e.g. vanadyl VO²⁺). Under more reducing conditions the less soluble V³⁺ state dominates: the presence of U and phosphates can further restrict the solubility of V³⁺ complexes. In the secondary environment, V is sorbed by Fe and Mn oxides, clay and organic matter.

The median V concentration in surface water has been estimated to be 1 µg/L (Ivanov, 1996), almost double compared with European surface water (0.46 µg/L in Saminen et al., 2005) and the Italian surface water (0.58 µg/L, De Vivo et al., 2009). The European tap water median is lower (0.17 µg/L, Reimann and Birke, 2010) than Italian tap water one of 0.30 µg/L. V concentrations in Italian tap water range from 0.01 to 24.5 µg/L and no value is below the detection limit. Campania and Latium are the two regions with highest medians (Fig. 7) even if Latium displays the highest variation range. The 95% of samples has concentrations below 2.9 µg/L. The distribution map (Fig. 10d) clearly indicates that the occurrence of relatively high V concentrations (>2.9 µg/L) are due to the leaching of volcanic rocks belonging to the Roman Comagmatic volcanic province (Preziosi et al., 2010), to the Mt. Vulture, and to the Mt. Etna (Aiuppa et al., 2003).

No samples exceed the maximum threshold set for V by Italian law for drinking water (50 µg/L).

As shown in Table 2 no guideline values exist for V likely because available evidence does not indicate that V in drinking water poses health problems.

5.3. Factor analysis

R-mode factor analysis has been performed to determine the possible relationship existing between the distribution of individual elements and

other parameters such as lithology, weathering processes environmental condition, geographic position and other factors including possible anthropogenic contamination and corrosion from distributing systems

Six factor solution has been chosen as the appropriate one to explain data variability. This solution accounts for 65.6% of the total variance. Table 5 shows the rotated factors' loadings with variables in alphabetical order, communalities, eigenvalues and percentages of variance accounted for the six factor 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, and also the strongest negative correlation are highlighted. Fig. 11 shows the distribution maps of factor scores.

Factor 1 (Na, Cl⁻, B, Br⁻, I, K, Li, Si, Co, HCO₃⁻) is the strongest of the six factors, accounting for 24.6% of the total data variance. It is characterized by high factor loadings of elements generally enriched in seawater such as Na, Cl, B, Br, I, and also K, Li and Si present mostly in acidic, alkaline and pegmatitic rocks. This association can be considered representative of the contribution of this two end-member. High factor scores are located: in Sardinia were the two end member coexists. There is occurrence of alkaline granitic rocks and closeness to the sea. In Sicily, again in coastal areas and in alkaline volcanic rocks; in Tuscany and in the Po River Plain where a contribution of deep formation waters can be argued.

Factor 2 (Pb, Zn, Cd, Cu, Mn, Sn, Fe) accounts for 13.8% of the total data variance. The elements are listed in decreasing order of importance (Table 5) and just below the 0.4 threshold there are also Co and Ni. These are all elements that are widely used in the different material that can be in contact with water in the distributing systems, either the central ones, for which information about composition should be available from the companies managing the distribution system, but also in the "last mile", that is when the water leaves the main line and enters the "in house" distributing system. That is the most critical point because monitoring is limited, controls on materials used not available and historic intervention very likely. Some critical factors are:

- type and quality of the material used in the tube system, in the solders, in the tap that affect the element release;
- age of the entire system, which can have contrasting effect on element release (Veschetti et al., 2010);
- modality of use, which affects basically the reaction time between water and the hosting system;
- properties of the water, among the most important pH, alkalinity, water hardness, in general low pH increase corrosion, alkalinity has a buffer effect on pH and stabilize the system, hard water are more prone to form a "protective coating" (De Zuane, 1997).

We have direct control on this last one and in general the conditions observed for pH, alkalinity and hardness and generally all these parameters are not favorable to the presence of high metal concentration in solution. High factor scores are scattered all over the Italian territory (Fig. 11b). Despite these consideration, effects of geological setting could partially affect some of the elements important in this factor; this is the south western Sardinia where the high factor scores could be related as well to the interaction of the groundwater with Pb–Zn mineralization (De Vivo et al., 1997).

Factor 3 (Rb, As, Cs, V, F⁻, Mo, K, Tl) accounts for 9.1% of the total data variance. The elements with the highest factor loadings are generally enriched in volcanic rocks and in particular in alkaline volcanic rocks as outlined by the low density sampling results of the FOREGS project (De Vivo et al., 2009). Fig. 11c clearly shows that high factor scores are located in volcanic areas belonging to the Roman Comagmatic Province, and includes as well the Mt. Vulture area, and in Sicily the Mt. Etna area.

Factor 4 (Ca, Sr, Mg, Ba, HCO₃⁻) accounts for 6.8% of the total data variance. It includes elements that can be associated to carbonate

dissolution and in fact the highest factor scores are found in waters in the northern and central Apennines (Fig. 11d), whose contribution have to be connected to interaction with limestone rocks and in areas of the Po River Plain where carbonate material is present in the sandy aquifers. High values characterize also the tap-water samples of central Tuscany near Florence.

Factor 5 (Se, U, SO₄²⁻, Sb, Ni, -Si) accounts for 5.8% of the total data variance. It includes one major element (sulfate) and other elements present as oxyanion as dominant form in water. The geographic distribution of the high factor scores identify cluster in the Tuscany-Emilia Romagna Apennine (Fig. 11e), where SO₄²⁻ and Se concentrations in tap waters are generally high. Similarly, high positive factor scores in the central Alps are associated to elevated U and relatively high Se, Sb and SO₄²⁻ concentrations. It is difficult to explain why this association includes elements with similar geochemical behavior (e.g. SO₄²⁻ and Se), and similar speciation in water (as oxyanion), although with different mobility under varying redox condition. Water interaction with mineralized veins could be a local valid explanation for some high values. Noteworthy is that Ni, is included, with relatively high loadings at least in three factors (F1, F2 and F5) probably attributable to multiple sources (natural and related to infrastructure) governing the distribution of the element.

Factor 6 (Nd, Al, Y, Fe, -V, -HCO₃⁻, -Cr) accounts for 5.5% of the total data variance. It includes Nd, representative of REE, Y, an element considered similar to HREE, and two important and key elements such as Al and Fe. High positive factor scores of this association (Fig. 11f) are located in Sardinia, northern Sicily and the Central Alps, comparable to the geographic distribution of ΣREE (Fig. 10a). Al and Fe are likely present in solution as colloidal particles, given the pH values measured. These particles likely affect also the occurrence of the other elements in solution via adsorption reaction. REE and Y are strongly affected by Fe- and Al-colloidal particles (Cidu and Frau, 2009; Ingri et al., 2000; Pokrovsky et al., 2006). Low values identify waters at the northern border of the Po river Plain, enriched in Cr with negative Factor loading, and waters from central Italy, with relatively high content in HCO₃⁻.

6. Concluding remarks

The large tap water database available enabled us the definition of the following main conclusions:

- The analysis of 69 chemical parameters on 157 samples of tap water from domestic and public points shows a very homogeneous composition as concerns EC (88% of the samples of low mineral concentration). The dominating water type is Ca–Mg–HCO₃⁻, which has a nationwide distribution. Na–Cl waters are frequent in Sardinia and Sicily, where the weight of supply from treated artificial reservoir water is the dominant source, reflecting contribution from marine spray; in areas far from the sea, such as Tuscany and central Po River Plain this signal is related to the exploitation of marine carbonate waters. High sulfate concentrations are related to gypsum dissolution either in the Alps and along the northern apenninic border.
- As trace metals are concerned, it is worth to note the variability observed for some of the investigated elements such as Ba, Zn, Mn, Cr, Cu, Pb and U, whose results span over several orders of magnitude (10⁴–10³).
- Compared to existing directive (Italian and EU) and health guidelines (WHO and FAO) the results are satisfactory. Few waters have trace element concentrations above thresholds. These include six samples with pH value exceeding the US EPA pH limit of 8.5, different samples have NO₃⁻, NH₄⁺ and Fe, Al, Mn, As, Pb concentrations exceeding EU and Italian thresholds, even if some regional government authorities issued enhanced threshold for several elements because of high geological background. One sample has NO₂⁻ concentration above the WHO guideline value. Ba concentration, not

covered in the European and Italian legislation for drinking water, in one sample exceeds the WHO, US EPA and FAO guideline values, similarly U concentration, not covered in the European and Italian legislation, in one sample exceeds FAO guideline value.

- Some elements clearly identify well defined relation with local geological context such as As, Rb, U, V, F, related to interaction with alkaline volcanic rocks.
- The six R-mode factor analysis associations confirm that the distribution of certain groups of elements mainly reflects the geological patterns (e.g. contribution from carbonate dissolution, interaction with volcanic rocks, mixing with connate water) and geographic influence (e.g., contribution from seawater). In addition it emphasizes the possible effects of corrosion from the distributing tap water pipeline systems.

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References

- Achene, L., Ferretti, E., Lucentini, L., Pettine, P., Veschetti, E., Ottaviani, M., 2010. Arsenic content in drinking water supplies of an important volcanic aquifer in central Italy. *Toxicological and Environmental Chemistry* 92, 509–520.
- Acquavita, A., Barbano, A., Barisiello, O., Braca, G., Bussettini, M., Carrer, S., Cordella, M., Dacquino, C., De Angelis, R., De Gironimo, G., De Vincenzi, S., Donati, A., Fava, A., Ferla, M., Ferrari, G., Iaccarino, S., Lastoria, B., Licopodio, E., Marcaccio, M., Mattassi, G., Nardone, G., Negri, P., Paleari, M., Predonzani, S., Salvati, S., Silvestri, C., Sinapi, L., Spada, E., Tromellini, E., Venturoli, S., Vicini, C., 2007. L'idrosfera. Annuario 2007 dati ambientali. APAT, pp. 742–934.
- Agardy, F.J., Sullivan, P., Clark, J.J., 2005. *The Environmental Science of Drinking Water*. Elsevier Science & Technology Books.
- Aiuppa, A., Bellomo, S., Brusca, L., D'Alessandro, W., Federico, C., 2003. Natural and anthropogenic factors affecting groundwater quality of an active volcano (Mt. Etna, Italy). *Applied Geochemistry* 18, 863–882.
- Amorosi, A., Centineo, M.C., Dinelli, E., Lucchini, F., Tateo, F., 2002. Geochemical and mineralogical variations as indicators of provenance changes in Late Quaternary deposits of SE Po Plain. *Sedimentary Geology* 151, 273–292.
- Amorosi, A., Colalongo, M.L., Dinelli, E., Lucchini, F., Vaiani, S.C., 2007. Cyclic variations in sediment provenance from Late Pleistocene deposits of Eastern Po Plain, Italy. In: José, A., Salvatore, C., Johnsson, M.J. (Eds.), *Sedimentary Provenance and Petrogenesis: Perspectives from Petrography and Geochemistry*. Geological Society of America Special Paper, 420, pp. 13–24.
- Anselmi, B., Brondi, A., Falchi, G., Ferretti, O., 1978. Lineamenti granulometrici e mineralogici generali dei sedimenti fluviali costieri del territorio italiano. Studio di supporto a ricerche sulla dinamica costiera e sulla contaminazione. Memorie della Società Geologica italiana 19, 307–314 (in Italian).
- Banks, D., Markland, H., Smith, P.V., Mendez, C., Rodriguez, J., Huerta, A., Sæther, O.M., 2004. Distribution, salinity and pH-dependence of elements in surface waters of the catchment areas of the Salars of Coipasa and Uyuni, Bolivian Altiplano. *Journal of Geochemical Exploration* 84, 141–166.
- Beccaluva, L., Bianchini, G., Siena, F., 2004. Tertiary-Quaternary volcanism and tectono-magmatic evolution in Italy. Special Volume of the Italian Geological Society for the IGC 32 Florence-2004, pp. 153–160.
- Bianchini, G., Pennisi, M., Cioni, R., Muti, A., Cerbai, N., Kloppmann, W., 2005. Hydro-chemistry of the high-boron groundwaters of the Cornia aquifer (Tuscany, Italy). *Geothermics* 34, 297–319.
- Bini, C., Maleci, L., Romanin, A., 2008. The chromium issue in soils of the leather tannery district in Italy. *Journal of Geochemical Exploration* 96, 194–202.
- Birke, M., Demetriades, A., De Vivo, B., 2010a. Mineral waters of Europe, Special Issue of *Journal of Geochemical Exploration*, 107, pp. 217–422.
- Birke, M., Reimann, C., Demetriades, A., Rauch, U., Lorenz, H., Harazim, B., 2010b. Determination of main and trace elements in European bottled mineral water – analytical methods. *Journal of Geochemical Exploration* 107, 217–226.
- Bonaria, V., Cipolli, F., 2003. The Genoa sheet of the geochemical map of Italy: explanatory notes. In: Ottonello, G., Serva, L. (Eds.), *Geochemical Baselines of Italy*. Pacini editore, Pisa, pp. 207–226.
- Boschetti, T., Toscani, L., Shouakar-Stash, O., Iacumin, P., Venturelli, G., Mucchino, C., Frape, S.K., 2011. Salt waters of the Northern Apennine Foredeep Basin (Italy): origin and evolution. *Aquatic Geochemistry* 17, 71–108.
- Boscolo, C., Ferronato, A., Mion, F., Vazzoler, P., 2005. presenza e monitoraggio dell'arsenico nelle acque sotterranee del Veneto. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilitazione*. I quaderni di ARPA, Bologna, pp. 51–66.
- Carminati, E., Doglioni, C., 2005. Mediterranean tectonics. In: Selley, R.C., Robin, L., Cocks, M., Plimer, I.R. (Eds.), *Encyclopedia of Geology*, vol. 1. Elsevier, Amsterdam, pp. 135–146.
- Carminati, E., Doglioni, C., Scrocca, D., 2004. Alps vs Apennines. Special Volume of the Italian Geological Society for the IGC 32 Florence-2004, pp. 141–151.
- Castaldo, G., Stampanoni, G., 1975. Memoria illustrativa della carta mineraria d'Italia scala 1:1.000.000. Servizio Geologico d'Italia, Roma. Italian.
- Castelli, A., Chiesa, S., Deriu, G., Pezzerà, G., Vescovi, E., Zanotti, M., Zonca, B., 2005. Note sulla presenza di arsenico nel sottosuolo e nelle acque sotterranee della Lombardia. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilitazione*. I quaderni di ARPA, Bologna, pp. 39–50 (in Italian).
- Catling, L.A., Abubakar, I., Lake, I.R., Swift, L., Hunter, P.R., 2008. A systematic review of analytical observational studies investigating the association between cardiovascular disease and drinking water hardness. *Journal Water Health* 6 (4), 433–442.
- Chester, R., 2002. *Marine Geochemistry*, 2 Edition. John Wiley & Sons, p. 520.
- Cicchella, D., De Vivo, B., Lima, A., 2005. Background and baseline concentration values of elements harmful to human health in the volcanic soils of the metropolitan and provincial area of Napoli (Italy). *Geochemistry: Exploration, Environment, Analysis* 5, 1–12.
- Cicchella, D., Albanese, S., De Vivo, B., Dinelli, E., Giaccio, L., Lima, A., Valera, P., 2010. Trace elements and ions in Italian bottled mineral waters: identification of anomalous values and human health related effects. *Journal of Geochemical Exploration* 107, 336–349.
- Cidu, R., Frau, F., 2009. Distribution of trace elements in filtered and non filtered aqueous fractions: insights from rivers and streams of Sardinia (Italy). *Applied Geochemistry* 24, 611.
- Civita, M., 2008. L'assetto idrogeologico del territorio italiano: risorse e problematiche. *Quaderni della Società Geologica Italiana* 3, 1–34 (Italian).
- Cocozziello, B., Di Donna, A., Di Meo, T., Imperatrice, M.L., Mainolfi, P., Onorati, G., Romano, V., 2005. L'arsenico nelle acque sotterranee della Campania. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilitazione*. I quaderni di ARPA, Bologna, pp. 107–126.
- Conti, A., Sacchi, E., Chiarle, M., Martinelli, G., Zuppi, G.M., 2000. Geochemistry of the formation waters in the Po plain (Northern Italy): an overview. *Applied Geochemistry* 15, 51–65.
- Cortecci, G., Dinelli, E., Boschetti, T., Arbizzani, P., Pompilio, L., 2008. The Serchio River catchment, Northern Tuscany: geochemistry of stream waters and sediments and isotopic composition of dissolved sulphate. *Applied Geochemistry* 23, 1513–1543.
- Cortecci, G., Boschetti, T., Dinelli, E., Cidu, R., Podda, F., Doveri, M., 2009. Trace element geochemistry in running waters from the Arno River catchment, northern Tuscany, Italy. *Applied Geochemistry* 24, 1005–1022.
- D.L. 31/2001. Decreto legislativo 2 febbraio 2001, n. 31, attuazione della direttiva 98/83/CE relativa alla qualità delle acque destinate al consumo umano. *Gazzetta Ufficiale* n. 52 del 03-03-2001.
- Dall'Aglio, M., 1971. A study of the circulation of uranium in the supergene environment in the Italian Alpine Range. *Geochimica et Cosmochimica Acta* 35, 47–59.
- Dall'Aglio, M., Giuliano, G., Amicizia, D., Andrenelli, M.C., Cicioni, G.B., Mastroianni, D., Sepicacchi, L., Tersigni, S., 2001. Assessing drinking water quality in northern Latium by trace element analysis. In: Cidu, R. (Ed.), *Proceedings of the 10th International symposium on Water-Rock Interaction, WRI-10*, pp. 1063–1066.
- Davis, J.C., 1984. *Statistical Data Analysis in Geology*. John Wiley & Sons, New York.
- De Vivo, B., Boni, M., Marcello, A., Di Bonito, M., Russo, A., 1997. Baseline geochemical mapping of Sardinia (Italy). *Journal of Geochemical Exploration* 60, 77–90.
- De Vivo, B., Lima, A., Bove, M.A., Albanese, S., Cicchella, D., Sabatini, G., Di Lella, L.A., Protano, G., Riccobono, F., Frizzo, P., Raccagni, L., 2008. Environmental geochemical maps of Italy from the FOREGS database. In: Reimann, C. (Ed.), *A Darnley Special issue: Geochemistry: Exploration, Environment, Analysis*, 8, pp. 267–277.
- De Vivo, B., Bove, M., Lima, A., Albanese, S., Cicchella, D., Grezzi, G., Frizzo, P., Sabatini, G., Di Lella, A., Protano, G., Raccagni, L., Riccobono, F., 2009. Atlante geochimico ambientale d'Italia. *Geochemical environmental atlas of Italy*. Aracne Editrice, Roma, p. 514.
- De Vivo, B., Birke, M., Cicchella, D., Giaccio, L., Dinelli, E., Lima, A., Albanese, S., Valera, P., 2010. *Acqua di casa nostra*. *Le Scienze* 506, 76–85 (Italian).
- De Zuane, J., 1997. *Handbook of Drinking Water Quality*, Second Edition. John Wiley & Sons, Inc.
- Dinelli, E., Lucchini, F., 1999. Sediment supply to the Adriatic sea basin from the Italian rivers, geochemical features and environmental constraints. *Giornale di Geologia* 61, 121–132.
- Dinelli, E., Cortecci, G., Lucchini, F., Zantedeschi, E., 2005. Sources of major and trace elements in the stream sediments of the Arno river catchment (northern Tuscany, Italy). *Geochemical Journal* 39, 531–545.
- Dinelli, E., Lima, A., De Vivo, B., Albanese, S., Cicchella, D., Valera, P., 2010. Hydrogeochemical analysis on Italian bottled mineral waters: effects of geology. *Journal of Geochemical Exploration* 107, 317–335.
- Dinelli, E., Lima, A., Albanese, S., Birke, M., Cicchella, D., Giaccio, L., Valera, P., De Vivo, B., submitted for publication. Comparative study between bottled mineral and tap water in Italy. *Journal of Geochemical Exploration*. 18 May 2011.
- Durov, S.A., 1948. Natural waters and graphic representation of their composition. *Doklady Akad Nauk USSR* 59, 87–90.
- Edmunds, W.M., 1996. Bromine geochemistry of British groundwaters. *Mineralogical Magazine* 60, 275–284.

- EU Directive 98/83/EC, 1998. Council Directive of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Union L 330, 32 (5.12.1998.).
- Farina, M., Marcaccio, M., Martinelli, G., 2005. La presenza di arsenico nelle acque sotterranee dell'Emilia-Romagna. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilitazione*. I quaderni di ARPA, Bologna, pp. 67–78.
- Flaten, T.P., 1991. A nation-wide survey of the chemical composition of drinking water in Norway. *Science of the Total Environment* 201, 35–73.
- Fordyce, F.M., Williams, T.M., Pajitpapapon, A., Charoenchaisei, P., 1995. Hydrogeochemistry of arsenic in an area of chronic mining-related arsenism, Ron Phibun District. British Geological Survey Technical Report series No. WC/94/79R, Keyworth, Nottingham, U. K. 73 pp.
- Giammanco, S., Ottaviani, M., Valenza, M., Veschetti, E., Principio, E., Giammanco, G., Pignato, S., 1998. Major and trace elements geochemistry in the ground waters of a volcanic area: mount Etna (Sicily, Italy). *Water Research* 32, 19–30.
- Giuliano, G., Preziosi, E., Vivona, E., 2005. Valutazione della qualità delle acque sotterranee a scopi idropotabili: il caso del Lazio settentrionale. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilitazione*. I quaderni di ARPA, Bologna, pp. 97–106.
- Grassi, S., Cortecchi, G., 2005. Hydrogeology and geochemistry of the multilayered confined aquifer of the Pisa plain (Tuscany – central Italy). *Applied Geochemistry* 20, 41–54.
- Gray, N.F., 2008. *Drinking Water Quality*, Second Edition. Cambridge University Press.
- Hem, J.D., 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*, U.S. Geological Survey, Water-Supply Paper 2254, 3rd ed. .
- Deroga per l'arsenico nell'acqua potabile <http://www.provincia.bz.it/acque-energia/acqua/arsenico.asp>. Lastly accessed 01/11/2010.
- Ingrì, J., Widerlund, A., Land, M., Gustafsson, Ö., Andersson, P., Öhlander, B., 2000. Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles. *Chemical Geology* 166, 23–45.
- Ivanov, V.V., 1996. *Ekologicheskaya geokhimiya elementov* (in Russian). Ekologia 1–6 Moskva (Environmental Geochemistry of Elements. Ecology, 1–6, Moscow).
- Koljonen, T., 1992. Suomen geokemian atlas, osa 2: moreeni. The Geochemical Atlas of Finland, Part 2: Till. Geological Survey of Finland, Espoo.
- Lima, A., Albanese, S., Cicchella, D., 2005. Geochemical baselines for the radioelements K, U, and Th in the Campania region, Italy: a comparison of stream-sediment geochemistry and gamma-ray surveys. *Applied Geochemistry* 20, 611–625.
- Lima, A., Cicchella, D., Giaccio, L., Dinelli, E., Albanese, S., Valera, P., De Vivo, B., 2010. Che acqua beviamo. *Le Scienze* 503, 68–77 (in italian).
- Mantelli, F., Cavalieri, S., Palmieri, R., 2005. L'arsenico nelle acque della Toscana. In: Scialoja, M.G. (Ed.), *Presenza e diffusione dell'arsenico nel sottosuolo e nelle risorse idriche italiane, nuovi strumenti di valutazione delle dinamiche di mobilitazione*. I quaderni di ARPA, Bologna, pp. 79–95.
- Mertz, W. (Ed.), 1987. *Trace Elements in Human and Animal Nutrition*. Academic Press, New York. 480 pp.
- Miller, R.G., Koppler, F.C., Kelty, K.C., Stober, J.A., Ulmer, N.S., 1984. The occurrence of aluminum in drinking water. *Journal of American Water Works Association* 76, 84–91.
- Milvy, P., Cothorn, R., 1990. Scientific background for the development of regulations for radionuclides in drinking water. In: Cothorn, R., Rebers, P. (Eds.), *Radon, Radium, and Uranium in Drinking Water*, pp. 1–16.
- Morrison, D.F., 2005. *Multivariate Statistical Methods*, 4th Ed. Thomson Brooks/Cole, Belmont, CA, USA. 469 pp.
- Nieboer, E., Gibson, B.L., Oxman, A.D., Kramer, J.R., 1995. Health effects of aluminum: a critical review with emphasis on aluminium in drinking water. *Environmental Review* 3, 29–81.
- Nielsen, F.H., 2001. Boron, manganese, molybdenum, and other trace elements. In: Bowman, B.A., Russell, R.M. (Eds.), *Present Knowledge In Nutrition*. : Eight edition. ILSI Press, Washington DC, pp. 384–400.
- Nisi, B., Buccianti, A., Vaselli, O., Perini, G., Tassi, F., Minissale, A., Montegrossi, G., 2008. Hydrogeochemistry and strontium isotopes in the Arno River Basin (Tuscany, Italy): constraints on natural controls by statistical modeling. *Journal of Hydrology* 360, 166–183.
- Pavelka, S., 2004. Bromine. In: Anke, M., Ihmat, M., Stoepler, M. (Eds.), *Elements and their Compounds in the Environment*. Wiley-VCH Verlag GmbH & Co.KGAA, Weinheim, pp. 1445–1455.
- Peccerillo, A., 2005. Plio-Quaternary volcanism in Italy. *Petrology, Geochemistry, Geodynamics*. Springer, Heidelberg. 365 pp.
- Piffner, A., 2005. The Alps. In: Selley, R.C., Robin, L., Cocks, M., Plimer, I.R. (Eds.), *Encyclopedia of Geology*. : Elsevier. Amsterdam, Vol I, pp. 125–135.
- Pokrovsky, O.S., Schott, J., Dupré, B., 2006. Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basaltic terrain in Central Siberia. *Geochimica Cosmochimica Acta* 70, 3239–3260.
- Preziosi, E., Giuliano, G., Vivona, R., 2010. Natural background levels and threshold values derivation for naturally As, V and F rich groundwater bodies: a methodological case study in Central Italy. *Environmental Earth Sciences* 61, 885–897.
- Reimann, C., Birke, M. (Eds.), 2010. *Geochemistry of European Bottled Water*. Borntraeger Science Publishers, Stuttgart. 268 pp.
- Reimann, C., Filzmoser, P., Garrett, R., Dutter, R., 2008. *Statistical Data Analysis Explained. Applied Environmental Statistics with R*, Wiley, Chichester.
- Richard, F.C., Bourg, A.C.M., 1991. Aqueous geochemistry of chromium: a review. *Water Resources Research* 25, 807–816.
- Rottura, A., Bargossi, G.M., Caggianelli, A., Del Moro, A., Visonà, D., Tranne, C.A., 1998. Origin and significance of the Permian high-K calc-alkaline magmatism in the central-eastern Southern Alps, Italy. *Lithos* 45, 329–348.
- Salminen, R. (Chief-editor), Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S., Ottesen, R.T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. *Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps*. Geological Survey of Finland, Espoo.
- Shand, P., Edmunds, W.M., Lawrence, A.R., Smedley, P.L., Burke, S., 2007. The natural (baseline) quality of groundwater in England and Wales. *British Geological Survey Groundwater Programme Research Report RR/07/06*.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17, 517–568.
- Stumm, W., Morgan, W., 1996. *Aquatic Chemistry: Chemical Equilibria and Rates In Natural Waters*. John Wiley & Sons, New York. 1022 pp.
- Toscani, L., Boschetti, T., Maffini, M., Barbieri, M., Mucchino, C., 2007. The groundwaters of Fontevivo (Parma Province, Italy): redox processes and mixing with brine waters. *Geochemistry: Exploration, Environment, Analysis* 7, 23–40.
- U.S. EPA, 2009. <http://www.epa.gov/safewater/contaminants/index.html#inorganic> 2009 (last accessed March 1, 2010).
- US E.P.A., 2003. *Drinking water standards*. Office of Drinking Water. US Environmental Protection Agency, Washington, DC.
- van der Aa, M., 2003. Classification of mineral water types and comparison with drinking water standards. *Environmental Geology* 44, 554–563.
- Veschetti, E., Achene, L., Ferretti, E., Lucentini, L., Citti, G., Ottaviani, M., 2010. Migration of trace metals in Italian drinking waters from distribution networks. *Toxicological and Environmental Chemistry* 92, 521–535.
- Vezzoli, G., Garzanti, E., 2009. Tracking paleodrainage in pleistocene foreland basins. *Journal of Geology* 117, 445–454.
- Vezzoli, G., Forno, M.G., Ando, S., Hron, K., Cadoppi, P., Rossello, E., Tranchero, V., 2010. Tracing the drainage change in the Po basin from provenance of Quaternary sediments (Collina di Torino, Italy). *Quaternary International* 222, 64–71.
- Vinceti, M., Cann, C.I., Calzolari, E., Vivoli, R., Garavelli, L., Bergomi, M., 2000. Reproductive outcomes in a population exposed long-term to inorganic selenium via drinking water. *The Science of the Total Environment* 250, 1–7.
- Vivona, R., Preziosi, E., Madé, B., Giuliano, G., 2006. Occurrence of minor toxic elements in volcanic-sedimentary aquifers: a case study in central Italy. *Hydrogeology Journal* 15, 1183–1196.
- Washington, H.S., 1906. *The Roman Comagmatic Region*. Carnegie Institute Publication no 57, pp. 1–99.
- WHO, 1996. *Guidelines for drinking-water quality*, 2nd ed. Health Criteria and Other Supporting Information, vol. 2. World Health Organization, Geneva.
- WHO, 2008. *Guidelines for drinking-water quality*, 3rd ed. Recommendations. Incorporating 1st and 2nd Addenda, vol. 1. World Health Organization, Geneva.