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Trace elements and ions in Italian bottled mineral waters: Identification of anomalous values and human health related effects

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ABSTRACT

Microbiological studies have always had an important role in the evaluation of drinking water quality. However, since geological processes are the most important factors controlling the source and distribution of chemical elements in natural waters, the importance of geochemical data must not be underestimated. This study presents data on pH, conductivity and concentrations of 69 elements and ions (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Br^-, HCO_3^-, Cl^-, F^-, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, SiO_2) from 186 bottled mineral waters of 158 different Italian name brands. Analyses show a large range in concentrations for most of these elements, with variations up to four orders of magnitude. Our data demonstrate that some elements (such as Be), generally considered unlikely to occur, can instead reach surprisingly high levels in drinking water, and also how packaging can release some trace elements to the bottled water. Data analysis shows that the implementation of an international database of bottled water geochemistry and of potential toxicological effects is of paramount importance to provide a robust data set which would be useful to set international action levels and guidelines to secure bottled water quality, whose consumption has steadily increased in the recent years. A new formula to calculate nitrate and nitrite tolerable concentration levels in waters intended for human consumption is proposed, to take into account that about 5% of dietary nitrate in humans is converted to nitrite.

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1. Introduction

This paper presents data on pH, conductivity and concentrations of 69 elements and ions in 186 bottled mineral waters of 158 different brands available on the Italian market (Fig. 1 and Table 1). This work is part of a European project aimed at studying and characterizing the geochemistry of 1785 European mineral bottled waters of different brands carried out by the EuroGeoSurveys Geochemistry Expert Group (Reimann and Birke, 2010).

Italians are the main consumers and producers of bottled mineral waters in the world. In the last few years national mineral water production has grown up to 12 billion liters, with an annual turnover value of almost 3 billion euro. Almost half of the Italian population prefers bottled water to tap water and on average every inhabitant drinks more than half a liter per day (200 l per capita per annum).

More than 300 different brands of mineral water are present on the Italian market (OJEC, 1996, 2000). However, Italy is also a country rich in natural and usually very high quality springs which are connected to aqueducts and used for the distribution of tap water. Various market surveys show that in an age characterized by heavy chemical pollution, consumers still consider bottled water pure, untouched and a symbol of good health. However, even if bottled water quality is good, we should not forget that it can still carry natural contamination since small amounts of potentially harmful elements can be present in the springs.

In Italy mineral waters are classified based on their fixed residue (i.e. amount of mineral salt obtained after drying at 180 °C): 1) mineral water lightly mineralized (<50 mg/l); 2) oligomineral water (50–500 mg/l); 3) medium-mineral water (500–1500 mg/l); 4) water rich in minerals (>1500 mg/l). Waters with a fixed residue up to 1500 mg/L are strongly mineralized waters and their therapeutic properties are widely recognized. Mineral water lightly mineralized makes up about 9% of all the mineral waters on the Italian market, while oligomineral water makes up 65% and medium-mineral 20%. Waters rich in mineral salts (6% of the market share) are defined as medicinal waters.

Usually only major elements concentrations are reported on the labels, while trace elements are ignored. As long as the mineral water is consumed in limited amounts or for short periods of time this may not constitute a problem, but this may not be the case if consumption

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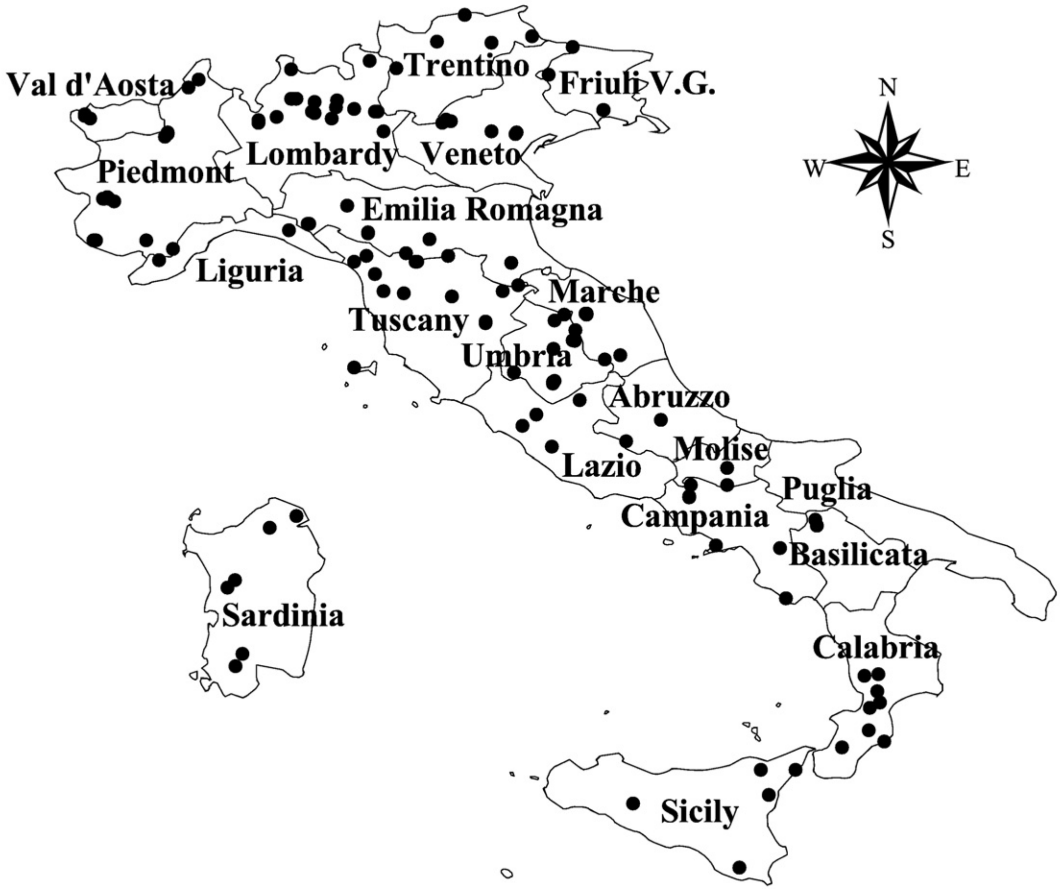


Fig. 1. Water source locations. Because of geographical proximity, some dots represent more than one source.

rates are high. It has long been recognized that trace elements content of drinking water can have either adverse or beneficial effects on human health depending on concentrations (Selinus et al., 2005).

Clinical and pharmacological trials have documented very well the effects on human health. However assessments of drinking water quality are essentially based mainly (if not only) on microbiological studies. Since geology is the most important factor controlling the source and distribution of chemical elements in natural waters, it would be desirable to base these evaluations also on geochemical studies.

Considering the wide public and huge economic interest related to the marketing of this product, geochemical data related to mineral waters available on the Italian market can help to protect the consumers and help regulatory agencies to define guidelines for quality control.

2. Health related guidelines

The World Health Organization (WHO) drinking water guidelines 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.

Standards might be influenced by national priorities and economic considerations and thus the conclusion on whether or not the health benefit of a specific standard justifies the costs involved is left to each individual country.

Legislation in Italy (D.L. 31/2001) and Europe (EU Directive 98/83/EC) provides for drinking water for human consumption an extensive and regular quality control of potentially harmful contaminants, while bottled waters undergo less comprehensive and less frequent testing (D.M. 29/12/2003, EU Directive 2003/40/EC) (Table 2). Increased bottled water consumption over the last few years raises the need to regulate bottled waters similarly to tap water, introducing additional and more detailed labelled information.

Establishing guidelines for drinking water is very difficult since a number of chemical contaminants have been shown to cause adverse health effects in humans only after extended exposure (years rather than months). To make matter worse, the directives of the European Council do not set concentration limits for each element due to the fact that exhaustive information on health effects is not available. Data on the effects on human health are collected through human population and toxicity studies carried out using laboratory animals. However, the results of population studies are limited by scarce information regarding the concentration to which people have been exposed and the possibly undetected simultaneous presence of other toxic agents. Toxicology studies are usually carried out on relatively small numbers of animals using high doses of the element investigated, which adds uncertainty as to the relevance of particular findings on human health.

3. Material and methods

During the spring of 2008, 186 bottles of mineral waters of 158 different brands available on the Italian market were purchased in randomly selected shops all over Italy and shipped for chemical analyses to the German Geological Survey (BGR) in Berlin (Table 1).

Eleven bottles have a natural CO_2 content, 18 are artificially carbonated and 157 are not carbonated. Nineteen bottles are made from glass with a metal cap, while the remaining 167 are made of polyethylene terephthalate (PET) with a polyethylene (PE) cap. Sixty-

Table 1
Geographical coordinates (degrees, decimal minutes) of the bottled mineral water sources.

Sample	Longitude	Latitude	Sample	Longitude	Latitude	Sample	Longitude	Latitude
ITA001-1	11.07	44.32	ITA045-1	12.53	42.60	ITA102-2	12.93	43.42
ITA001-2	11.07	44.32	ITA046-1	12.67	43.42	ITA103-1	13.15	42.88
ITA002-1	16.23	39.13	ITA047-1	11.22	45.70	ITA103-2	13.15	42.88
ITA003-1	14.75	36.85	ITA048-1	13.82	42.17	ITA104-1	13.33	42.93
ITA004-1	12.77	46.60	ITA048-2	13.82	42.17	ITA104-2	13.33	42.93
ITA004-2	12.77	46.60	ITA049-1	10.52	45.60	ITA105-1	14.60	41.60
ITA004-3	12.77	46.60	ITA049-2	10.52	45.60	ITA106-1	14.60	41.40
ITA004-4	12.77	46.60	ITA050-1	14.47	40.68	ITA107-1	12.53	42.60
ITA004-5	12.77	46.60	ITA051-1	15.23	40.65	ITA108-1	10.33	44.38
ITA005-1	9.97	45.97	ITA052-1	14.15	41.25	ITA109-1	12.03	44.03
ITA006-1	10.35	46.43	ITA053-1	14.17	41.40	ITA110-1	10.78	44.15
ITA007-1	9.67	45.83	ITA054-1	15.30	40.05	ITA111-1	9.70	45.82
ITA007-2	9.67	45.83	ITA055-1	15.67	40.92	ITA112-1	10.42	45.83
ITA007-3	9.67	45.83	ITA056-1	12.77	43.12	ITA113-1	9.95	45.88
ITA008-1	9.03	45.72	ITA057-1	12.53	42.62	ITA114-1	9.70	45.95
ITA009-1	10.52	45.60	ITA058-1	10.52	45.60	ITA115-1	12.92	43.43
ITA010-1	9.42	46.33	ITA059-1	10.17	45.87	ITA116-1	7.18	44.80
ITA011-1	9.42	45.98	ITA059-2	10.17	45.87	ITA117-1	7.10	44.30
ITA012-1	15.42	38.02	ITA060-1	12.08	45.57	ITA118-1	7.20	44.80
ITA013-1	7.95	45.58	ITA060-2	12.08	45.57	ITA119-1	10.17	44.05
ITA013-2	7.95	45.58	ITA061-1	12.85	42.40	ITA120-1	12.07	42.73
ITA014-1	7.70	44.30	ITA062-1	16.28	38.48	ITA121-1	6.97	45.80
ITA015-1	7.95	45.57	ITA063-1	12.17	42.10	ITA122-1	10.17	42.79
ITA016-1	8.02	44.20	ITA064-1	12.33	42.23	ITA123-1	10.76	43.67
ITA017-1	7.07	44.30	ITA065-1	7.85	44.07	ITA124-1	9.42	46.33
ITA018-1	10.42	43.90	ITA066-1	15.23	40.65	ITA125-1	6.97	45.78
ITA019-1	11.28	44.12	ITA067-1	12.52	41.85	ITA125-2	6.97	45.78
ITA019-2	11.28	44.12	ITA068-1	15.67	40.92	ITA126-1	9.39	44.42
ITA020-1	10.52	43.70	ITA069-1	8.66	40.18	ITA127-1	7.92	45.53
ITA021-1	11.80	46.65	ITA070-1	8.66	40.18	ITA128-1	11.15	46.67
ITA021-2	11.80	46.65	ITA071-1	8.75	40.27	ITA128-2	11.15	46.67
ITA021-3	11.80	46.65	ITA072-1	8.75	40.27	ITA129-1	8.20	46.12
ITA022-1	12.55	43.35	ITA073-1	8.75	40.27	ITA130-1	9.03	45.73
ITA023-1	12.80	43.23	ITA074-1	8.75	40.27	ITA131-1	12.12	43.77
ITA024-1	12.55	42.63	ITA075-1	8.76	39.25	ITA132-1	8.32	46.22
ITA024-2	12.55	42.63	ITA076-1	8.76	39.25	ITA133-1	7.32	44.77
ITA025-1	13.48	37.62	ITA077-1	8.76	39.25	ITA134-1	10.67	46.35
ITA026-1	12.10	45.58	ITA078-1	8.76	39.25	ITA135-1	9.90	45.75
ITA027-1	11.27	45.73	ITA079-1	8.76	39.25	ITA136-1	7.32	44.77
ITA028-1	11.80	45.60	ITA080-1	8.76	39.25	ITA137-1	9.03	45.70
ITA029-1	13.40	41.92	ITA081-1	8.84	39.39	ITA138-1	10.45	45.83
ITA029-2	13.40	41.92	ITA082-1	9.17	40.89	ITA139-1	9.63	44.50
ITA030-1	10.33	44.40	ITA083-1	9.48	41.03	ITA140-1	9.43	45.98
ITA031-1	10.08	44.72	ITA084-1	9.48	41.03	ITA141-1	9.62	44.50
ITA032-1	13.13	45.85	ITA085-1	9.48	41.03	ITA142-1	11.93	43.70
ITA033-1	9.48	45.98	ITA086-1	16.38	38.95	ITA143-1	11.26	45.74
ITA034-1	9.25	45.77	ITA087-1	16.28	38.48	ITA144-1	7.23	44.82
ITA034-2	9.25	45.77	ITA088-1	16.38	38.95	ITA145-1	12.28	46.73
ITA035-1	12.93	43.43	ITA089-1	16.40	39.15	ITA146-1	11.48	46.98
ITA036-1	12.93	43.43	ITA090-1	15.10	37.72	ITA147-1	12.28	46.73
ITA036-2	12.93	43.43	ITA091-1	15.97	38.28	ITA148-1	15.67	40.92
ITA037-1	7.08	44.30	ITA092-1	16.30	38.75	ITA149-1	12.54	43.01
ITA038-1	7.25	44.80	ITA093-1	16.42	38.82	ITA150-1	15.30	40.05
ITA039-1	10.90	44.05	ITA094-1	16.47	38.35	ITA151-1	12.48	46.27
ITA039-2	10.90	44.05	ITA095-1	15.00	38.02	ITA151-2	12.48	46.27
ITA040-1	11.33	43.63	ITA096-1	16.38	38.95	ITA152-1	12.54	43.01
ITA040-2	11.33	43.63	ITA097-1	15.65	40.98	ITA153-1	12.79	43.11
ITA041-1	10.32	44.12	ITA098-1	15.67	40.92	ITA154-1	10.45	45.83
ITA042-1	11.73	43.33	ITA099-1	15.67	40.92	ITA155-1	13.13	45.85
ITA042-2	11.73	43.33	ITA100-1	14.17	41.40	ITA156-1	15.67	40.92
ITA043-1	10.92	44.05	ITA101-1	14.15	41.27	ITA157-1	11.32	45.72
ITA044-1	11.73	43.32	ITA102-1	12.93	43.42	ITA158-1	7.03	45.75

seven bottles are coloured, while 119 are clear. In order to compare chemical differences connected to packaging or natural chemistry, five brands were purchased and analyzed both in PET and in glass bottles and four other brands were purchased in both artificially carbonated and non carbonated terms.

Each water sample was analyzed for 69 chemical elements and ions (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Br^-, HCO_3^-, Cl^-, F^-, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, SiO_2). Electrical conductivity (Ec) and pH were also measured on each water sample. Table 3 shows the analytical method and detection limit for each analyzed element in the mineral bottled waters. Analytical methods and the quality controls of analyses are given in Birke et al. (2010-this issue).

4. Results and discussion

Table 4 shows the statistical parameters related to physico-chemical properties and chemical composition of 186 Italian bottled mineral waters. In the analyzed waters the highest median concentrations were

Table 2
Italian and European legal concentration limits of natural mineral waters and drinking waters and US-EPA and WHO guideline values.

	Italian Law DM 29/12/2003 mineral water	Italian Law D.L. 31/2001 drinking water	EU Directive 2003/40/EC mineral water	EU Directive 1998/83/EC drinking water	US-EPA guideline value	WHO guideline value
Ec (μS/cm)	–	2500 (g.v.)	–	2500 (g.v.)	–	–
pH	–	≥6.5–≤9.5 (g.v.)	–	≥6.5–≤9.5 (g.v.)	≥6.5–≤8.5	–
Aluminium (μg/L)	–	200 (g.v.)	–	200 (g.v.)	–	200
Ammonium (mg/L)	–	0.5 (g.v.)	–	0.5 (g.v.)	–	–
Antimony (μg/L)	5	5	5	5	6	20
Arsenic (μg/L)	10	10	10	10	10	10
Barium (μg/L)	1000	–	1000	–	2000	700
Beryllum (μg/L)	–	–	–	–	4	–
Boron (μg/L)	5000	1000	–	1000	–	500
Cadmium (μg/L)	3	5	3	5	5	3
Chloride (mg/L)	–	250 (g.v.)	–	250 (g.v.)	–	250
Chromium (μg/L)	50	50	50	50	100	50
Copper (μg/L)	1000	1000	1000	2000	1300	2000
Fluorides (mg/L)	5 (1,5[a])	1.5	5	1.5	4	1.5
Iron (μg/L)	–	200 (g.v.)	–	200 (g.v.)	200	–
Lead (μg/L)	10	10	10	10	15	10
Manganese (μg/L)	500	50 (g.v.)	500	50 (g.v.)	–	400
Mercury (μg/L)	1	1	1	1	2	6
Molybdenum (μg/L)	–	–	–	–	–	70
Nickel (μg/L)	20	–	20	20	–	70
Nitrates (mg/L)	45 (10*)	50	50	50	10	50
Nitrites (mg/L)	0,02	0.5	0.1	0.5	1	3
Phosphorus (mg/L)	–	–	–	5	–	–
Selenium (μg/L)	10	10	10	10	50	10
Sodium (mg/L)	–	200 (g.v.)	–	200 (g.v.)	–	200
Sulphates (mg/L)	–	250 (g.v.)	–	250 (g.v.)	–	500
Tallium (μg/L)	–	–	–	–	0.5 / 2	–
Uranium (μg/L)	–	–	–	–	30	15
Vanadium (μg/L)	–	50	–	–	–	–
Zinc (μg/L)	–	–	–	–	–	3000

(g.v.) guideline values.
[a] Legal limit for water intended for infants consumption.

observed for Ca, K, Mg, Na, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, and SiO_2, which are all above 1 mg/L. Dinelli et al. (2010-this issue) discuss the major element distribution and chemical composition of the waters as a function of diverse geological terrains.

The median value is below detection limit for Ag, Hf, Hg, Mn, Nb, Ta, NH_4^+ and NO_2^-. Expressed in maximum concentration, 22 elements reach levels of 0.1 mg/L (100 μg/L) or more. The lowest maximum concentrations (all below 0.006 μg/L) are observed for Ta, Th and Bi while the highest (>1000 mg/L) are observed for SO_4^{2-} and HCO_3^-.

Differences in concentration for single elements, expressed as the ratio max/min concentration (column 'spread' in Table 4), range from one to five orders of magnitude. These findings are similar to those of other studies (Misund et al., 1999; Rosborg et al., 2005; Krachler and Shotyk, 2009). Bi, Hf, Ta, Te and Th show the lowest variation, while Ag, Cs and U show the largest. Differences in total variation among elements can be explained by their geochemical behavior. For example the difference between U and Th can be explained by the fact that U has a greater mobility under oxidizing conditions, is present in very varying concentrations in rocks and is redox sensitive. The concentration range observed for the majority of elements covers three to four orders of magnitude (Table 4).

Except for one mineral water, no conductivity values exceed the Italian guideline value of 2500 μS/cm established for drinking water. 20% of all the analyzed waters show pH value<6.5 (see Italian, European and US-EPA guideline value for drinking water) and only 2 water samples have pH value>8.5 (US-EPA guideline).

Hg concentrations (an element potentially very harmful to human health) are below detection limits in all the brands (<5 ng/L). As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, PO_4^{3-}, Sb, Se, Tl and Zn are all below their respective Italian and European maximum admissible concentrations and US-EPA and WHO drinking water standards. Eleven potentially harmful elements (Al, Be, B, Cl^-, F^-, NH_4^+, NO_2^-, NO_3^-, SO_4^{2-}, U and V) are present in several water bottles in amounts exceeding legal limits. These are discussed in more detail in the following paragraphs, along with As.

4.1. Does bottle material influence trace elements concentration?

To investigate the effects of packaging, five of the mineral water brands were analyzed both in PET and in glass bottles. Fig. 2 clearly shows that concentrations of Al, Co, Cr, Cu, Fe, Pb, Sb, Sn, Zr and REE (La, Ce, Pr, Nd, Sm) are strongly influenced by the packaging material.

With the exception of Sb, all elements have higher concentrations in waters packaged in glass bottles. Shotyk et al. (2006) and Shotyk and Krachler (2007a) showed that the higher Sb values in PET bottled waters are caused mainly by leaching of the element from the PET bottles. In fact 90% of PET manufacturers worldwide employ Sb_2O_3 as a catalyst.

The higher contents of all other elements in glass bottles are probably due to leaching from the glass itself rather than from their metal caps, which have a thin PE film that separates water from the metal. Leaching of Pb and other metals from glass bottles into water has been widely documented by Shotyk and Krachler (2007b).

High concentrations of REE (La, Ce, Pr, Nd, Sm) found in waters packaged in glass can be explained by the increasingly more frequent use of these elements as pigments in glass bottles (Kogel et al., 2006).

It should be noticed that the release of these trace metals in the analyzed mineral waters is limited and does not create a hazard for human health since detected concentrations are well below guideline values.

4.2. Potentially harmful elements and ions

Hereafter we focus on the elements and ions for which anomalous concentrations have been found or whose maximum concentrations in bottled waters was found to exceed guideline levels set by Italian (D.L.

Table 3
Analytical methods and detection limits.

Parameter	Unit	Analytical method	Detection limit	Parameter	Unit	Analytical method	Detection limit
pH	–	Potentiometric	–	Nd	μg/L	ICP-QMS	0.0002
EC	μS/cm	Conductometric	–	Ni	μg/L	ICP-QMS	0.01
Ag	μg/L	ICP-QMS	0.001	Pb	μg/L	ICP-QMS	0.002
Al	μg/L	ICP-QMS	0.3	Pr	μg/L	ICP-QMS	0.00005
As	μg/L	ICP-QMS	0.01	Rb	μg/L	ICP-QMS	0.001
B	μg/L	ICP-QMS	0.1	Sb	μg/L	ICP-QMS	0.002
Ba	mg/L	ICP-OES	0.001	Sc	μg/L	ICP-QMS	0.01
Be	μg/L	ICP-QMS	0.001	Se	μg/L	ICP-QMS	0.01
Bi	μg/L	ICP-QMS	0.0005	Sm	μg/L	ICP-QMS	0.0002
Ca	mg/L	ICP-OES	0.01	Sn	μg/L	ICP-QMS	0.001
Cd	μg/L	ICP-QMS	0.001	Sr	mg/L	ICP-OES	0.001
Ce	μg/L	ICP-QMS	0.0005	Ta	μg/L	ICP-QMS	0.001
Co	μg/L	ICP-QMS	0.002	Tb	μg/L	ICP-QMS	0.00005
Cr	μg/L	ICP-QMS	0.03	Te	μg/L	ICP-QMS	0.005
Cs	μg/L	ICP-QMS	0.001	Th	μg/L	ICP-QMS	0.0001
Cu	μg/L	ICP-QMS	0.01	Ti	μg/L	ICP-QMS	0.01
Dy	μg/L	ICP-QMS	0.0001	Tl	μg/L	ICP-QMS	0.0005
Er	μg/L	ICP-QMS	0.0001	Tm	μg/L	ICP-QMS	0.00005
Eu	μg/L	ICP-QMS	0.0001	U	μg/L	ICP-QMS	0.0005
Fe	μg/L	ICP-QMS	0.1	V	μg/L	ICP-QMS	0.01
Ga	μg/L	ICP-QMS	0.0005	W	μg/L	ICP-QMS	0.002
Gd	μg/L	ICP-QMS	0.0002	Y	μg/L	ICP-QMS	0.0005
Ge	μg/L	ICP-QMS	0.005	Yb	μg/L	ICP-QMS	0.0002
Hf	μg/L	ICP-QMS	0.0005	Zn	μg/L	ICP-QMS	0.05
Hg	ng/L	AFS	5.00	Zr	μg/L	ICP-QMS	0.001
Ho	μg/L	ICP-QMS	0.0001	Br^-	mg/L	IC	0.003
I	μg/L	ICP-QMS	0.2	$HCO3^-$	mg/L	titration	2
K	mg/L	ICP-OES	0.1	Cl^-	mg/L	IC	0.01
La	μg/L	ICP-QMS	0.0005	F^-	mg/L	IC	0.003
Li	μg/L	ICP-QMS	0.1	NH_4^+	mg/L	photometric	0.005
Lu	μg/L	ICP-QMS	0.00005	NO_2	mg/L	IC	0.005
Mg	mg/L	ICP-OES	0.01	NO_3	mg/L	IC	0.01
Mn	mg/L	ICP-OES	0.001	PO_4^{3-}	mg/L	ICP-OES	0.02
Mo	μg/L	ICP-QMS	0.001	SO_4^{2-}	mg/L	IC	0.01
Na	mg/L	ICP-OES	0.1	SiO_2	mg/L	ICP-OES	0.05
Nb	μg/L	ICP-QMS	0.001				

[a]ICP-QMS: Inductively Coupled Plasma-Quadrupole Mass Spectrometry.
[b]ICP-OES: Inductively Coupled Plasma-Optical Emission Spectroscopy.
[c]AFS: Atomic Fluorescence Spectrometry.
[d]IC: Ion Chromatography.

31/2001; D.M. 29/12/2003) and European legislations (EU Dir. 98/83/EC and EU Dir. 2003/40/EC) or WHO (1996, 2008) and EPA (2003).

4.2.1. Aluminium

Al concentrations in the investigated bottled waters range from <0.3 to 237 μg/L with a median concentration of 1 μg/L (Table 4).

Several epidemiological studies demonstrate that aluminium exposure is a risk factor in the development or acceleration of onset of Alzheimer's disease in humans (Exley, 2001). WHO sets a guideline value of 200 μg/L even if a population-attributable risk cannot be calculated with precision due to the limitations of the animal data as a model for humans and the uncertainty surrounding the human data.

Aluminium is one of the elements for which Italian and European legislations establish a threshold for drinking water (200 μg/L) but not for mineral bottled water (Table 2). Only one sample of mineral bottled water exceeds this limit reaching a concentration of 237 μg/L (Fig. 3). This anomalous value, along with anomalous pH (5.7) and Be (4.69), is detected in a mineral water whose source is located in the alkaline volcanic Roman Province of the Lazio Region (Figs. 4 and 5A). The Al geochemical distribution in the mineral water (Fig. 4) is very similar to that found in the Italian stream waters (De Vivo et al., 2008, 2009; De Vos et al., 2006; Salminen et al., 2005).

4.2.2. Ammonium

Fig. 3 shows that the 95% of samples have NH_4^+ content below detection limit and only 4 water samples have anomalous ammonium concentrations (>0.1 mg/L, Figs. 3 and 5B).

Ammonium has a toxic effect on human health only if the intake becomes higher than the capacity to detoxify. At a dose of about 33.7 mg of ammonium ion per kg of body weight per day ammonium chloride influences metabolism by shifting the acid–base equilibrium, disturbing the glucose tolerance and reducing the tissue sensitivity to insulin. Ammonium is not of direct importance for health in the concentrations observed in the analyzed bottled mineral waters.

4.2.3. Arsenic

The median total As content is 0.25 μg/L entirely in line with the median value (0.24 μg/L) found in European mineral waters (Reimann and Birke, 2010). The concentration range is between 0.01 and 8.91 μg/L (Fig. 3). The As mineral water distribution map (Fig. 5C) shows a pattern very similar to that of stream waters (De Vivo et al., 2008, 2009; De Vos et al., 2006; Lima et al., 2008; Salminen et al., 2005). The highest As value (8.91 μg/L) occurs in a water sample from northern Lazio, which also have anomalous pH (5.8). Other As values between 5 and 6.81 μg/L are also found in Campania and north-western Sardinia due to the presence of alkaline volcanic rocks (Peccerillo, 2005) (Fig. 4).

Numerous epidemiological studies have examined the risk of cancer associated with arsenic ingestion through drinking water. There is overwhelming evidence that consumption of elevated levels of As through drinking water is directly related to the development of several types of cancer (WHO, 2008). The International Programme on Chemical Safety (IPCS, 2001) concluded that long-term exposure to As in drinking water is directly related to increased risk of skin,

Table 4
Summary statistics of trace (μg/L) and major (mg/L) elements and ions data in 186 bottled mineral waters of 158 different Italian brands.

	Min	25%	Median	Mean	75%	Max	Std. dev.	Spread
pH	4.1	6.9	7.6	7.2	7.9	8.8	1.0	2
EC	18	201	388	505	606	3020	484	168
Ag	<0.001	<0.001	<0.001	0.097	0.001	17.2	1.261	17200
Al	<0.3	0.5	1.0	4.4	2.4	237	19.1	790
As	0.01	0.12	0.25	0.89	0.68	8.91	1.54	796
B	0.4	5.9	14.6	61.2	48.4	1170	141.4	2847
Ba	<0.001	0.007	0.024	0.062	0.063	0.44	0.094	440
Be	<0.001	<0.001	0.0013	0.084	0.008	4.69	0.415	4690
Bi	<0.0005	<0.0005	0.0006	0.0008	0.0010	0.0059	0.0008	12
Ca	1.26	19.43	46.05	69.41	84.23	510	83.20	405
Cd	<0.001	0.002	0.003	0.009	0.007	0.161	0.018	161
Ce	<0.0005	0.0003	0.0003	0.0034	0.0016	0.0862	0.0097	172
Co	<0.002	0.011	0.017	0.031	0.028	0.602	0.059	301
Cr	<0.03	0.09	0.17	0.33	0.30	4.72	0.54	157
Cs	<0.001	0.003	0.015	0.653	0.126	33.3	2.953	33300
Cu	<0.01	0.12	0.19	0.35	0.30	5.5	0.59	550
Dy	<0.0001	0.0005	0.0009	0.0051	0.0018	0.168	0.0182	1680
Er	<0.0001	0.0003	0.0006	0.0044	0.0016	0.197	0.0192	1970
Eu	<0.0001	0.0009	0.0021	0.0041	0.0041	0.0337	0.0058	337
Fe	<0.1	0.1	0.2	0.8	0.6	15.9	2.0	159
Ga	<0.0005	<0.0005	0.0022	0.0043	0.0063	0.0277	0.0050	55
Gd	<0.0002	0.0005	0.0011	0.0037	0.0025	0.0753	0.0090	377
Ge	<0.005	0.006	0.011	0.033	0.026	0.615	0.078	123
Hf	<0.0005	<0.0005	<0.0005	0.0007	0.0006	0.0177	0.0016	35
Hg	<5	<5	<5	<5	<5	<5	–	1
Ho	<0.0001	0.0002	0.0003	0.0014	0.0006	0.0542	0.0054	542
I	< 0.2	1.0	2.3	6.6	5.0	160	19.0	800
K	<0.1	0.6	1.0	4.4	1.9	85.2	12.3	852
La	<0.0005	0.0006	0.0015	0.0060	0.0047	0.219	0.0188	438
Li	<0.1	0.8	3.4	15.3	9.3	241	35.4	2410
Lu	<0.00005	0.00007	0.00015	0.00084	0.00040	0.0344	0.00335	688
Mg	0.26	3.91	6.72	13.22	17.20	75.7	14.24	293
Mn	<0.001	0.001	0.001	0.006	0.001	0.33	0.036	330
Mo	0.012	0.140	0.406	1.218	0.869	27.7	3.376	2289
Na	0.4	2.3	5.9	20.0	18.6	428	42.6	1070
Nb	<0.001	0.001	0.001	0.003	0.001	0.117	0.011	117

	Min	25%	Median	Mean	75%	Max	Std. dev.	Spread
Nd	<0.0002	0.0005	0.0013	0.0072	0.0049	0.198	0.0209	990
Ni	<0.01	0.04	0.13	0.41	0.35	6.62	0.91	662
Pb	<0.002	0.003	0.007	0.034	0.013	0.625	0.094	313
Pr	<0.00005	0.00008	0.00024	0.00151	0.00097	0.0474	0.00466	948
Rb	0.044	0.360	0.757	9.292	2.560	346	35.609	7828
Sb	0.007	0.202	0.302	0.349	0.442	1.72	0.249	244
Sc	<0.01	0.03	0.05	0.08	0.08	1.11	0.12	111
Se	<0.01	0.07	0.16	0.26	0.31	2.03	0.29	203
Sm	<0.0002	0.0005	0.0009	0.0026	0.0020	0.0582	0.0062	291
Sn	<0.001	0.003	0.006	0.016	0.011	1.06	0.079	1060
Sr	0.008	0.062	0.191	0.790	0.668	14.1	1.640	1763
Ta	<0.001	<0.001	<0.001	<0.001	<0.001	0.0014	0.0001	1
Tb	<0.00005	0.00005	0.00011	0.00065	0.00024	0.0148	0.00198	296
Te	<0.005	<0.005	0.005	0.009	0.011	0.08	0.011	16
Th	<0.0001	0.0002	0.0003	0.0005	0.0005	0.0058	0.0008	58
Ti	<0.01	<0.01	0.03	0.05	0.05	0.73	0.09	73
Tl	<0.0005	0.0017	0.0053	0.0228	0.0114	0.5	0.0714	1000
Tm	<0.00005	0.00007	0.00012	0.00071	0.00030	0.0308	0.00300	616
U	<0.0005	0.1298	0.4745	1.2878	1.2250	31	2.8848	62000
V	<0.01	0.13	0.30	1.25	0.88	48.9	4.17	4890
W	<0.002	0.01	0.016	0.051	0.034	1.31	0.140	655
Y	<0.0005	0.004	0.0087	0.0624	0.0214	2.86	0.2730	5720
Yb	<0.0002	0.0004	0.0007	0.0048	0.0022	0.211	0.0209	1055
Zn	<0.05	0.14	0.31	1.52	0.76	46.4	5.20	928
Zr	<0.001	0.001	0.002	0.084	0.007	5.83	0.494	5830
Br^-	<0.003	0.004	0.016	0.059	0.053	1.21	0.124	403
$HCO3^-$	3.5	78.8	172.5	236.6	300.3	1665	268.8	476
Cl^-	0.15	1.99	6.64	18.73	21.65	323	34.43	2153
F^-	0.011	0.054	0.143	0.285	0.376	1.75	0.365	159
NH_4^+	<0.005	<0.005	<0.005	0.008	<0.005	0.401	0.036	80
NO_2^-	<0.005	<0.005	<0.005	0.006	<0.005	0.132	0.017	26
NO_3^-	<0.01	1.25	2.76	4.56	5.70	35.1	5.87	3510
PO_4^{3-}	<0.02	<0.02	0.04	0.08	0.11	0.68	0.12	34
SO_4^{2-}	1.38	5.20	14.85	55.62	33.98	1356	158.94	983
SiO_2	0.90	5.98	9.40	16.25	16.88	105	20.16	117

[a]Spread: ratio maximum/minimum concentrations.

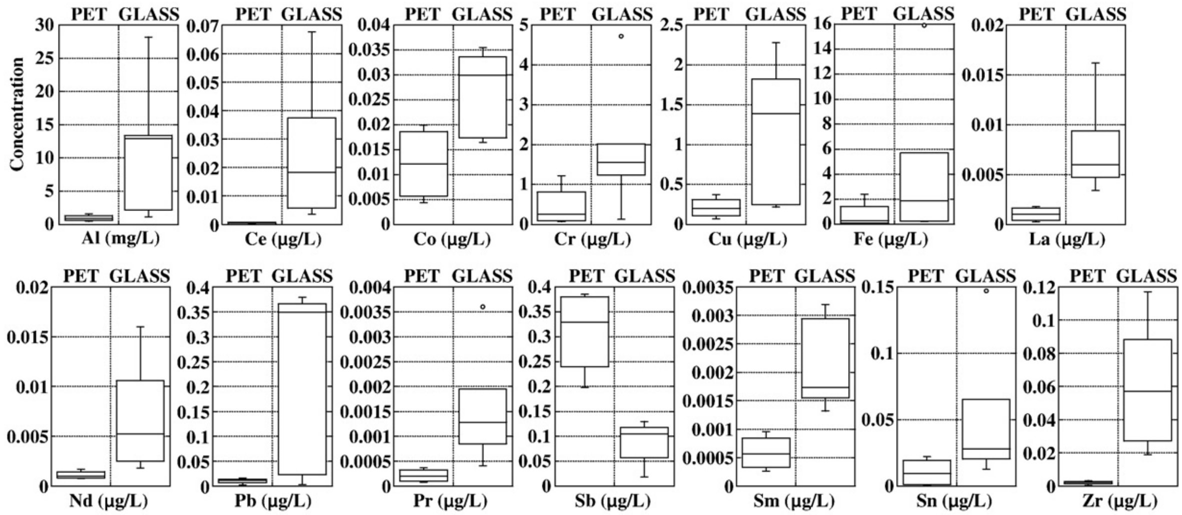


Fig. 2. Boxplot comparison of differences in selected element concentrations in the same mineral water brand as function of the different bottle types (PET or GLASS).

lung, bladder and kidney cancer, as well as other skin ailments such as hyperkeratosis and pigmentation changes.

Inorganic As compounds are classified by the International Agency for Research on Cancer (IARC, 1987) as Group 1 on the basis of sufficient evidence for carcinogenicity in humans and limited evidence for carcinogenicity in animals. Although there is a substantial database on the association between both internal organs and skin cancers and the consumption of As in drinking water, there remains considerable uncertainty over the actual risks at low concentrations.

Although no mineral water samples exceed the threshold values of 10 μg/L, the nine water samples (Fig. 5C) in which the concentration value exceeds 5 μg/L should be constantly monitored.

4.2.4. Boron

Short- and long-term oral exposures to boric acid or borax in laboratory animals have demonstrated that the male reproductive tract is a consistent target of toxicity. Testicular lesions have been observed in rats, mice and dogs given boric acid or borax in food or drinking water (WHO, 2008).

The WHO guideline value for B in drinking water is 500 μg/L, while Italian and European legislations establish a maximum limit of 1000 μg/L. Italian law also establishes a threshold limit of 5000 μg/L for mineral bottled water. The Italian mineral waters are characterized by a mean concentration value for B of 61.2 μg/L, significantly below all guideline values.

The highest concentration value (1170 μg/L), along with anomalous Ec (3020 μS/cm) and pH (6.25), was measured in the sample ITA099-1 whose springs are located in southern Italy in the volcanic area of Mt. Vulture. This value exceeds the WHO and Italian law thresholds for drinking water. Another four samples have B concentrations higher than the WHO guideline value of 500 μg/L (Figs. 3 and 5E).

4.2.5. Beryllium

Italian environmental law (D.L. 152/2006) requires intervention for remediation on an aquifer if Be concentration in the groundwater samples exceeds 4 μg/L, even if such waters are not intended for human consumption. Strangely no limits are set by Italian (or European) laws for Be in drinking water.

The median Be concentration of all analyzed bottled waters (0.001 μg/L) is far below the guideline value (4 μg/L) set by US-EPA (EPA, 2003). Only one bottled water (ITA064-1) from the volcanic area of Lazio (Figs. 3 and 5D) exceeds the US-EPA threshold level of 4 μg/L. Other waters with anomalous Be content originate from sources located in the Roman–Neapolitan Alkaline Province (Peccerillo, 2005) where high contents of Be occur both in stream water and stream sediments, and in topsoil and subsoil samples (De Vivo et al., 2008, 2009; De Vos et al., 2006; Salminen et al., 2005).

Regular consumption of Be rich water might lead to intestinal lesions (EPA, 2003) and Be is listed as a Class A EPA carcinogen and it is one of the most toxic elements in the periodic table (Taylot et al., 2003). Be can mimic Mg chemical behavior (Mg is an essential element for human nutrition) and displace it from certain key enzymes causing their malfunction (Emsley, 2001). For these reasons it appears necessary to introduce a threshold for Be in drinking waters.

4.2.6. Chloride

Chloride values in bottled mineral water range between 0.15 mg/L and 323 mg/L with a median value of 6.64 mg/L (Table 4). Highest Cl^- content (323 mg/L) has been found in ITA050-1 sample from Campania and other high values occur in Tuscany (central Italy) and Sardinia (Figs. 3 and 5F). The 1958 WHO International Standards for Drinking Water suggested that concentrations of chloride greater than 600 mg/L would markedly impair the potability of the water. The 1963 and 1971 International Standards retained this value as a maximum allowable or permissible concentration. In the first edition of the Guidelines for Drinking Water Quality, published in 1984, a guideline value of 250 mg/L was established for chloride, based on taste considerations.

Chloride toxicity has not been observed in humans except in the special case of impaired Na chloride metabolism (e.g., in congestive heart failure). Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a concomitant intake of fresh water. Little is known about the effect of prolonged intake of large amounts of chloride in the diet. As in experimental animals, hypertension associated with Na chloride intake appears to be related to the Na rather than the chloride ion (WHO, 1996). Consumers can, however, become accustomed to concentrations in excess of 250 mg/L.

4.2.7. Fluoride

Fluoride values in mineral waters vary from 0.011 mg/L to 1.75 mg/L, with a median of 0.143 mg/L (Table 4). Lowest F^- contents (<0.3 mg/L) are registered throughout all northern Italy with the exception of two mineral waters in the north-eastern sector of the Alps where dominant lithologies are micaschist, paragneiss and fillades (Fig 4). Other high concentrations are found in central and southern Italy associated with recent volcanic alkaline rocks (Figs. 4 and 6A). The fluoride content

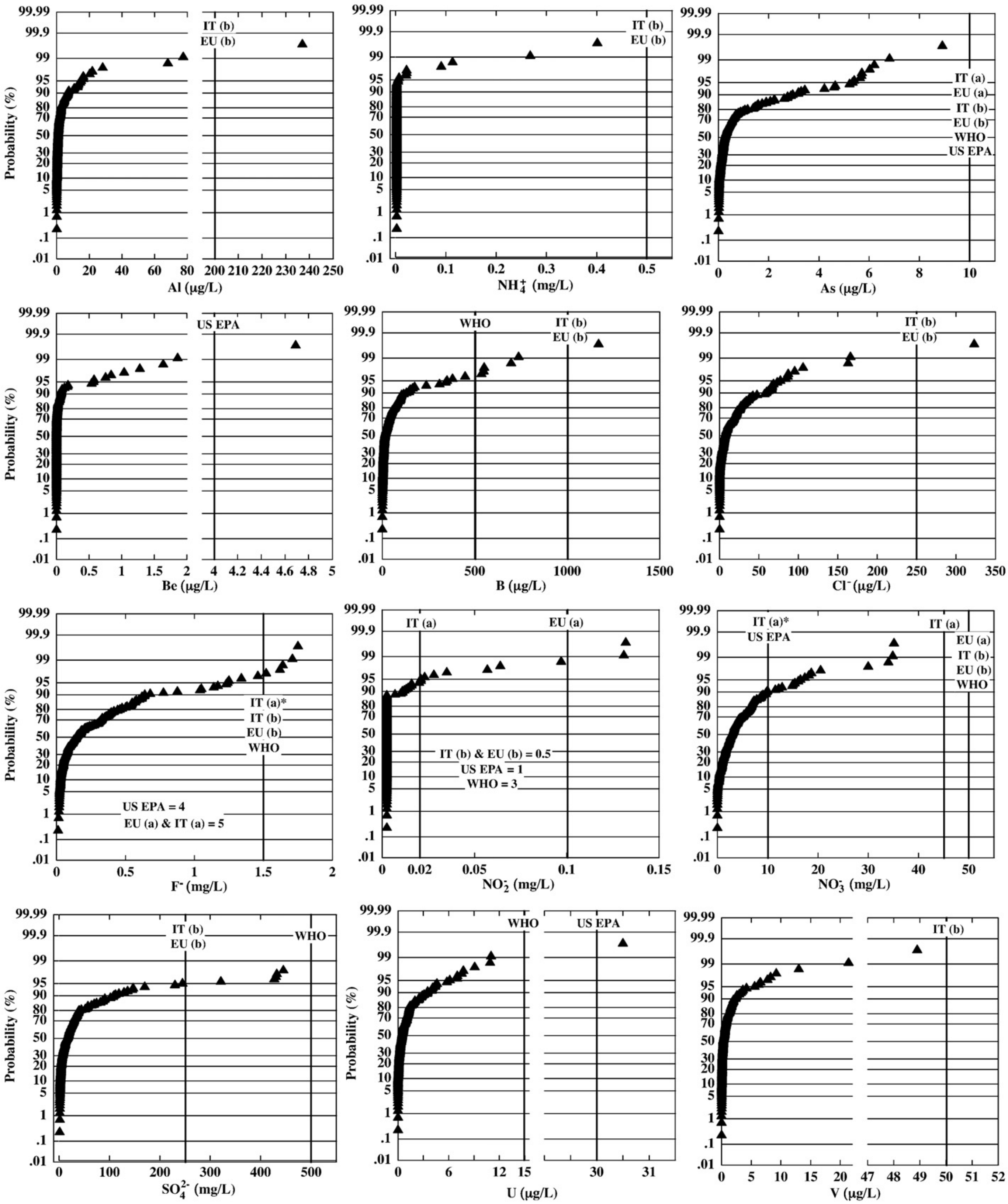


Fig. 3. Cumulative distribution function diagrams for Al, NH_4^+, As, B, Be, Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}, U and V. Also shown are: concentration values limit set by Italian and European directives to water intended for human consumption [IT(a) and EU(a)]; concentration values limit set by Italian and European directives to natural mineral waters and spring waters [IT(b) and EU(b)]; US-EPA guideline values for drinking water quality; WHO guideline values for drinking water quality.

exceeds the guideline value set by WHO, Italian and European legislations on drinking water (1.5 mg/L) in 5 samples (Fig. 3). There is epidemiological evidence that concentrations above this value carry an increasing risk of dental fluorosis and progressively higher concentrations lead to increasing risks of skeletal fluorosis (Fawell et al., 2006).

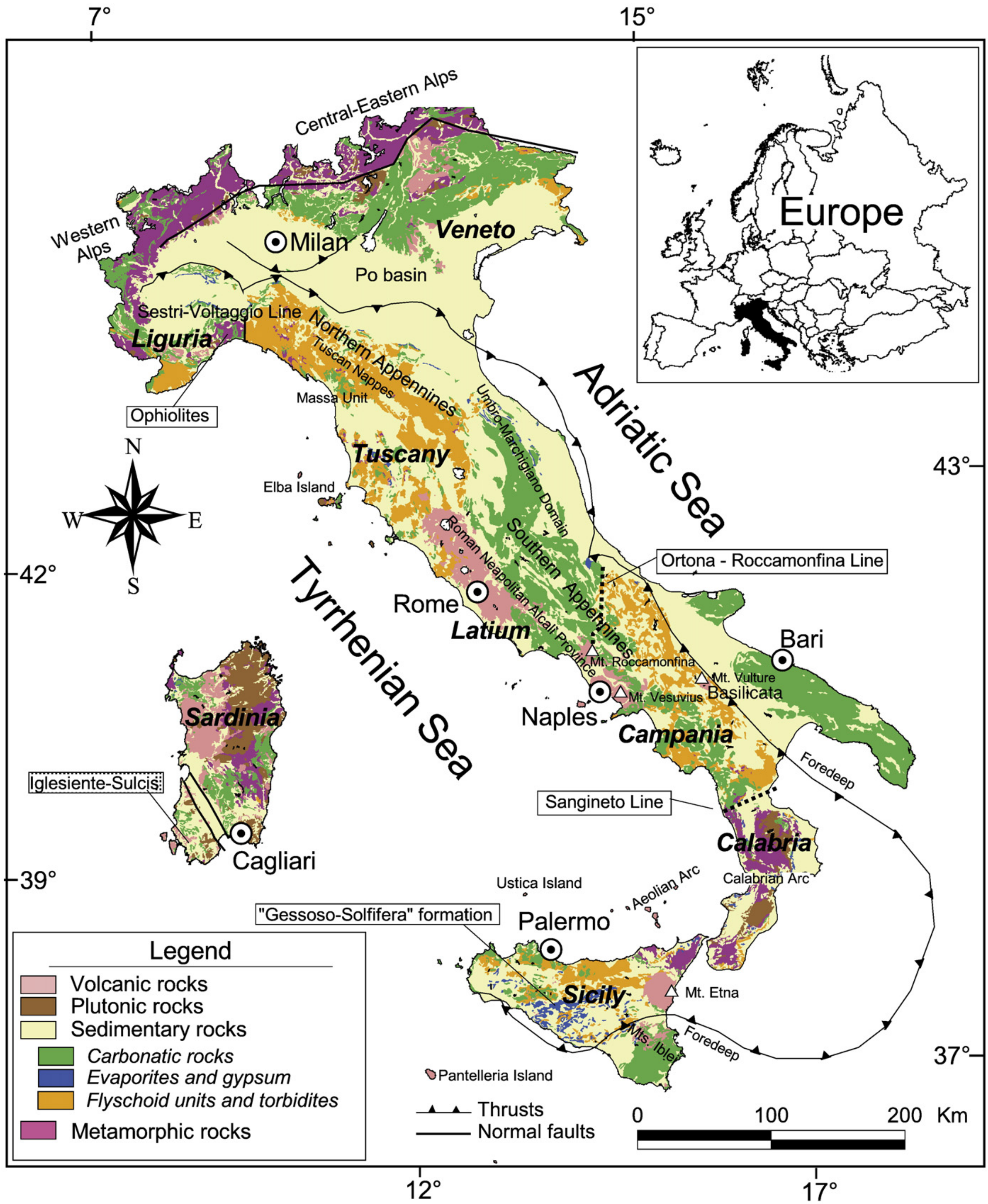
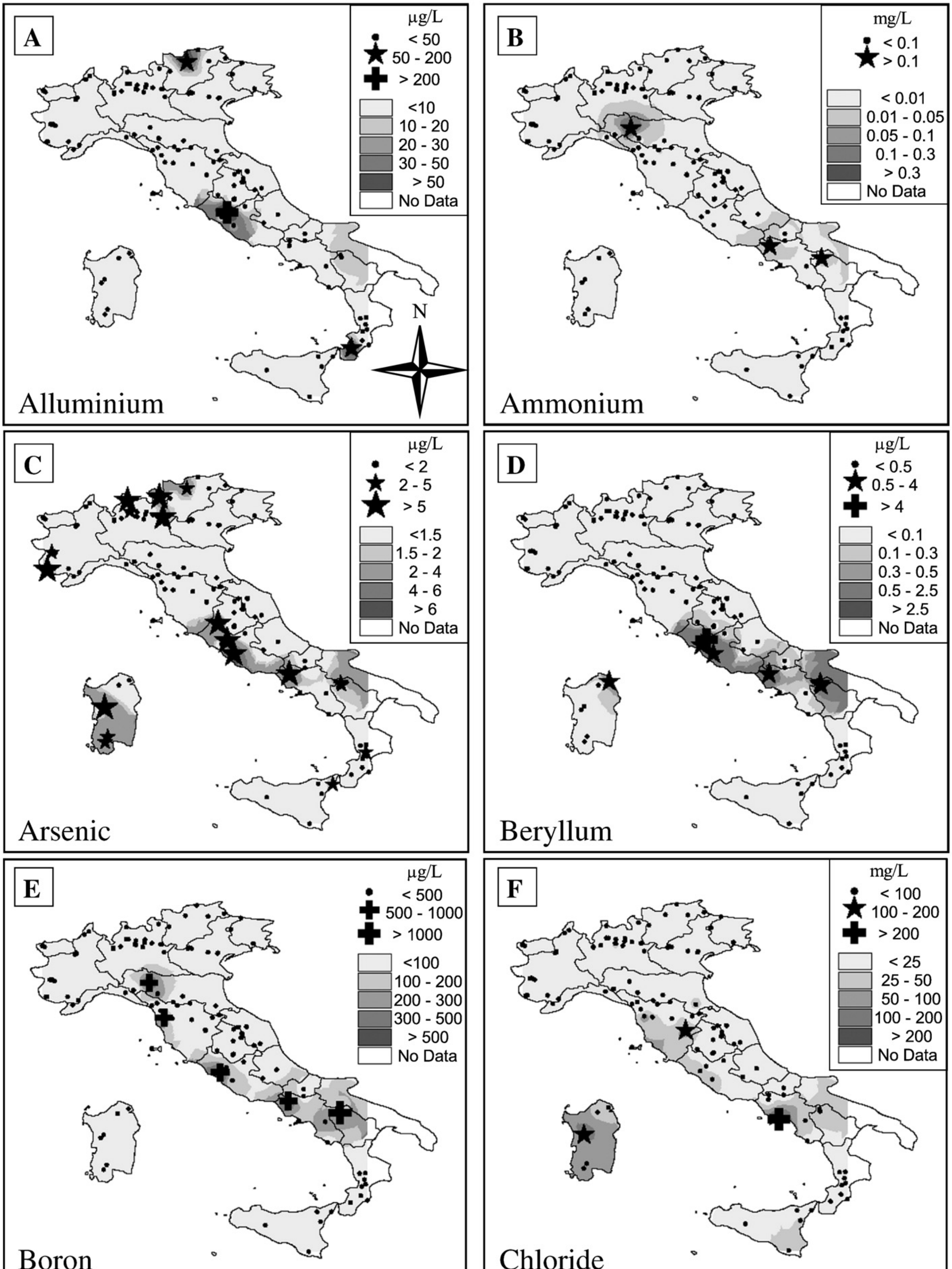


Fig. 4. Geological sketch map of Italy (modified after Doglioni and Flores, 1997).

Fig. 5. Interpolated and dot maps of Al, NH_4^+, As, B, Be and Cl. The star symbol shows high concentration values while the cross symbol indicates the samples that exceed concentration values limit set by WHO and/or US-EPA and/or Italian and/or European directives to water intended for human consumption.


A
µg/L
< 50
50 - 200
> 200
<10
10 - 20
20 - 30
30 - 50
> 50
No Data
N
Alluminium
B
mg/L
< 0.1
> 0.1
< 0.01
0.01 - 0.05
0.05 - 0.1
0.1 - 0.3
> 0.3
No Data
Ammonium
C
µg/L
< 2
2 - 5
> 5
<1.5
1.5 - 2
2 - 4
4 - 6
> 6
No Data
Arsenic
D
µg/L
< 0.5
0.5 - 4
> 4
< 0.1
0.1 - 0.3
0.3 - 0.5
0.5 - 2.5
> 2.5
No Data
Beryllum
E
µg/L
< 500
500 - 1000
> 1000
<100
100 - 200
200 - 300
300 - 500
> 500
No Data
Boron
F
mg/L
< 100
100 - 200
> 200
< 25
25 - 50
50 - 100
100 - 200
> 200
No Data
Chloride

4.2.8. Nitrites and nitrates

Fig. 3 shows that more than 5% of bottled waters have a NO_2^- concentrations above 0.02 mg/L (limit set by Italian Law for NO_2^- in mineral water). These anomalous values are found in northern Italy (Fig. 6B). About 90% of the all analyzed mineral waters (Fig. 3) show a NO_2^- content below detection limit (0.005 mg/L).

All analyzed samples have a NO_3^- content below 45 mg/L (the Italian regulation limit, Fig. 3), however 10% of analyzed waters exceeds the threshold limit of 10 mg/L established for consumption by children (Table 2). Highest NO_3^- values (>10 mg/L) occur mostly in water sample of northern Lazio, northern Sardinia, southern Sicily and north-eastern Italy (Fig. 6C). These high NO_3^- concentrations are probably a consequence of the use of fertilizers and the spread of manure over agricultural land.

The main public health concern on nitrates relates to adverse effects in bottle-fed infants. It is well known that nitrate being reduced in the body to nitrite causes oxidation of hemoglobin to methemoglobin and thus reduces the oxygen-binding capacity of this protein (WHO, 2008). This might lead to the so-called "blue-baby syndrome". At the moment there is insufficient epidemiological evidence for an association between nitrate–nitrite intake and cancer (WHO, 2008).

In vitro and in vivo studies have shown that nitrate can be reduced to nitrite by bacterial and mammalian metabolic pathways. The amount of nitrites formed is dependent on the nitrate reductase activity of the microbial population and the availability of nitrate. In humans about 5% of dietary nitrate is converted to nitrite (Gangolli et al., 1994 and references therein).

Because nitrate and nitrite might simultaneously occur in drinking water, and since they have the same effect on human health, when assessing the risk the correct procedure is to consider the sum of the two substances. Through the Council Directive 98/83/EC the European Commission establishes that "Member States must ensure that the condition that $[NO_3^-]/50+[NO_2^-]/3\leq 1$ is met and that the value of 0.1 mg/L for nitrites is complied with ex water treatment works".

Most Italian mineral bottled water meet this requirement (Fig. 7) and only 5% of the brands exceed the legal value of 0.02 mg/L for nitrites. Since nitrate when ingested is reduced to nitrite in amount equal to 5%, the authors suggest that a more realistic condition to be met for human health purpose is: $[NO_3^-]/20+[NO_2^-]\leq GV_{NO2}^-$.

On the basis of the new suggested condition, plotting all analyzed mineral waters on the CDF-diagrams (cumulative distribution function in Fig. 7), we can see that more than 60% of them have the potential content of nitrites above the legal limit set by European directives for mineral water; 10% is above the legal limit set by Italian and European directives for drinking water; 5 samples exceed the US-EPA guideline value and all are below WHO guideline value (Table 2).

4.2.9. Sulphates

No health-based guideline is proposed for sulphate by WHO. However, because of the gastrointestinal effects resulting from ingestion of drinking water containing high sulphate levels, Italian and European directives set a limit threshold at 250 mg/L for drinking water. 5% of the analyzed bottled mineral water exceeds this threshold (Fig. 3); most of these waters originate from sources in Northern Italy and only one from southern Italy (Fig. 6D). Specifically, the highest value of 1278 mg/L is found in a bottled water from Valle d'Aosta in north-western Italy.

4.2.10. Uranium

For U, WHO Guidelines (2008) establish a provisional health-based guideline value of 15 µg/L. US-EPA sets a guideline value of 30 µg/L, although sets a target of zero for U concentration (ATSDR, 1999) since the majority of U intake for humans can occur through drinking water.

The anomalous U concentration value (31 µg/L) found in the Sardinian mineral water sample ITA084-1 (Fig. 6E), exceeds both WHO and US-EPA guideline values. In Sardinia, U concentrations in the water may be elevated due to leaching from granitic rocks (Fig. 4). Very high values found in the north-western Italian water samples (10.9 and 11 µg/L) are probably linked to the weathering of graphitic shale characterized by an abundance of U-bearing minerals, leading to elevated U concentrations in groundwater. Other high values (around 6–7 µg/L) are found in Lombard water bottles (North Italy) sourced from metamorphic reservoirs. However, 3.5% of samples have U contents greater than 5 µg/L.

The overall risks arising from the biochemical toxicity of U as a heavy metal are considered to be about six orders of magnitude higher than those derived from its radioactivity (Milvy and Cothern, 1990). Nephritis is the primary chemically induced effect of U in humans. Little information is available on the chronic health effects of exposure to environmental uranium in humans. A number of epidemiological studies of populations exposed to U in drinking water have shown a correlation with alkaline phosphatase and β-microglobulin in urine along with modest alterations in proximal tubular function (WHO, 2008). Raymond-Whish et al. (2007) state that U is an endocrine-disrupting chemical and populations exposed to environmental U (also through drinking water with U below the EPA guideline limit) should be followed for increased risk related to fertility problems and reproductive cancers. Considering that the overall risks arising from the biochemical toxicity of U as a heavy metal are considered to be about six orders of magnitude higher than those deriving from its radioactivity (Milvy and Cothern, 1990), it is necessary to fix a very low (at least <5 µg/L) mandatory threshold for all drinking water, including the bottled ones.

4.2.11. Vanadium

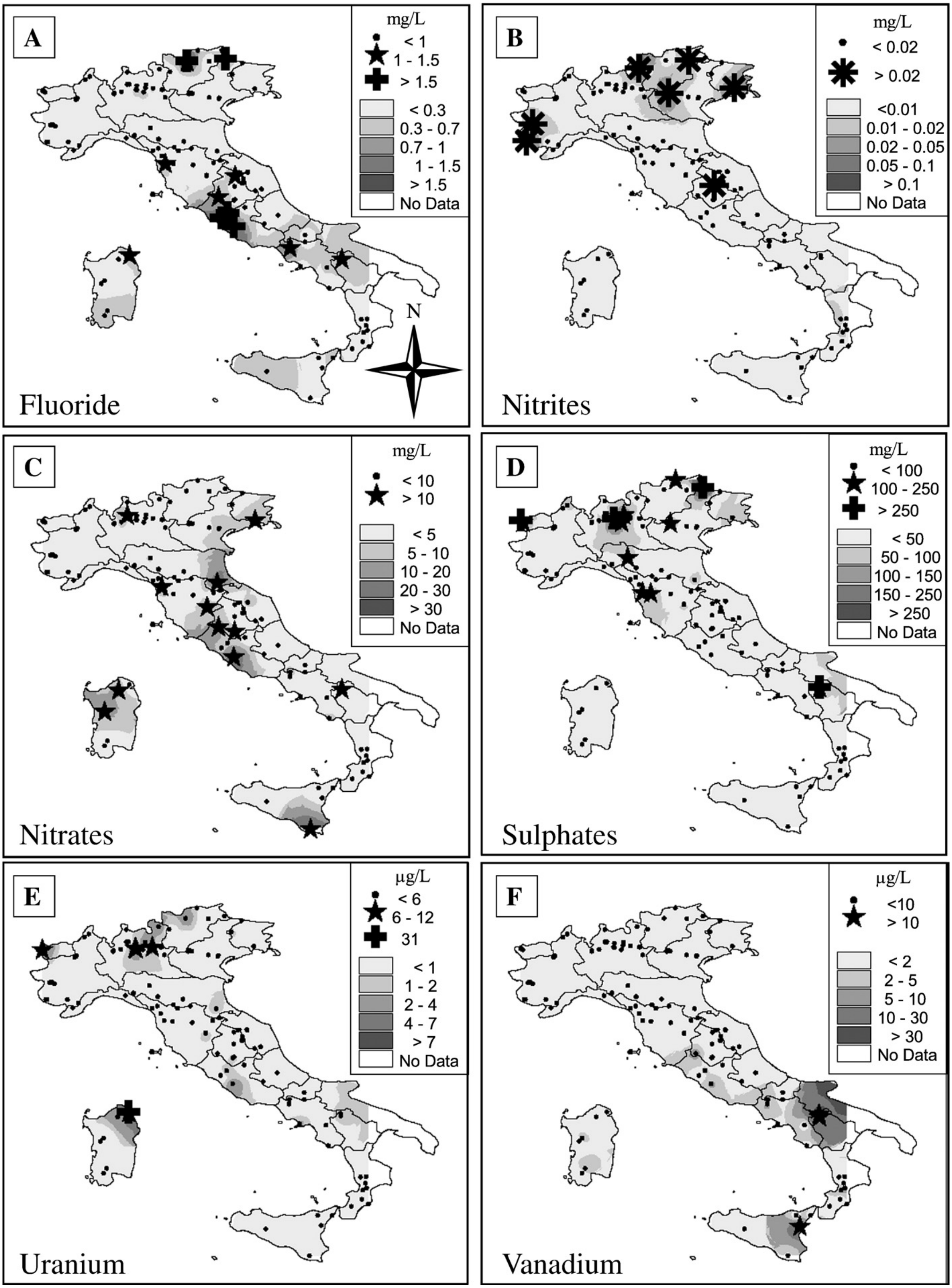
Vanadium content in all analyzed bottled mineral waters is below the maximum threshold set by Italian law for drinking water (50 µg/L). Vanadium concentrations vary between 0.01 µg/L and 48.9 µg/L and the median value is 0.3 µg/L (Table 4). High concentrations (>10 µg/L) occur in water samples from southern Italy corresponding to the volcanic areas of Basilicata and eastern Sicily (Fig. 6F).

There are no data on V oral toxicity. Some epidemiological data have shown positive correlations between the V content of urban air and mortality from bronchitis, pneumonia, nephritis, cancer (other than lung cancer in males) (Stocks, 1960) and "heart disease" (Hickey et al., 1967). However these analyses did not take into account important factors such as exposure to other chemicals, smoking habits, etc. (Vouk, 1979). The lack of data on acute or chronic oral toxicity is not surprising because of the extremely low absorption of V from the gastrointestinal tract. Inhaled V can produce adverse health effects, but the available evidence does not indicate that V in drinking water is a problem.

5. Concluding remarks

- Analyses of 186 bottled mineral waters from Italy for 69 elements show a wide spread in composition for most of these elements. The difference between lowest and highest measured concentrations is up to five orders of magnitude. It is very important that lawmakers realize that in mineral waters most of the elements have a natural source (geogenic), with no anthropogenic contribution at all.
- Packaging of the bottled waters appears to have a certain influence on concentrations of some trace elements in water. The data presented in this paper do not leave any doubt that bottled waters

Fig. 6. Interpolated and dot maps of F, NO_2^-, NO_3^-, SO_4^{2-}, U and V. Symbols like in Fig. 5. The asterisk symbol on the nitrites map shows the samples that exceed concentration values limit set by Italian and European directives for bottled mineral water.


A
mg/L
< 1
1 - 1.5
> 1.5
< 0.3
0.3 - 0.7
0.7 - 1
1 - 1.5
> 1.5
No Data
N
Fluoride
B
mg/L
< 0.02
> 0.02
<0.01
0.01 - 0.02
0.02 - 0.05
0.05 - 0.1
> 0.1
No Data
Nitrites
C
mg/L
< 10
> 10
< 5
5 - 10
10 - 20
20 - 30
> 30
No Data
Nitrates
D
mg/L
< 100
100 - 250
> 250
< 50
50 - 100
100 - 150
150 - 250
> 250
No Data
Sulphates
E
μg/L
< 6
6 - 12
31
< 1
1 - 2
2 - 4
4 - 7
> 7
No Data
Uranium
F
μg/L
<10
> 10
< 2
2 - 5
5 - 10
10 - 30
> 30
No Data
Vanadium

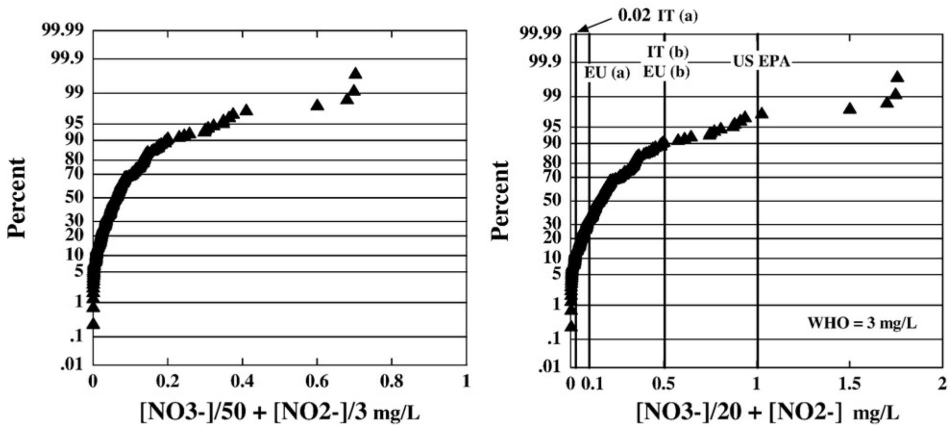


Fig. 7. Cumulative distribution function diagrams for nitrites taking into account the European Commission condition (EU 98/83/EC) that $[NO_3^-]/50+[NO_2^-]/3\leq 1$ and the condition suggested by authors $[NO_3^-]/20+[NO_2^-]\leq GV_{NO2}$.

stored in PET are contaminated with Sb from their containers, while the samples from glass bottles show significantly higher levels of elements like Al, Co, Cr, Cu, Fe, Pb, Sn, Zr and REEs. However, the release of these elements from containers occurs at rates which can be considered negligible for the customers.

- Of the waters examined in this study, 5% have one parameter (NO_2^-) that is not in compliance with the mineral water standards in Italy and 10% exceed the Italian legal limit set for NO_3^- (10 mg/L) if the mineral water is intended for infants consumption. These waters should report on the label the statement: not suitable for infants consumption.
- Considering that in humans about 5% of dietary nitrate is converted to nitrite, the authors calculate that the relationship $[NO_3^-]/20+[NO_2^-]\leq GV_{NO2}$ is more appropriate to establish nitrate and nitrite tolerable concentration levels in the waters intended for human consumption. Based on this new and more effective relationship, when compared to the guideline value set by the European directives for mineral waters, more than 60% of brands have nitrite content potentially harmful to consumers' health. However, all analyzed bottled mineral waters have nitrite values well below the WHO guideline for drinking water quality.
- Five brands have fluoride content higher than Italian legal limit (1.5 mg/L) established for infants' consumption and one bottled mineral water in North-East Sardinia exceeds the WHO and US-EPA guideline values set for U.
- Other trace elements (such as Be for instance) are not yet regulated by legal limits. Possible regulation of this element should be considered because some bottled waters have considerable Be concentrations. It is noticeable that the Italian environmental law requires site remediation where Be content in ground water exceeds 4 µg/L, while allowing citizens to drink water with Be content higher than 4 µg/L. In our opinion this contradiction should be resolved. While WHO excludes Be from the guideline value derivation because it is "unlikely to occur in drinking water" (WHO, 2008), our work clearly demonstrates that this is definitely not the case for Italian mineral waters.
- The results point to the need to implement an international database that provides a robust data set of element concentration ranges, aiming to supply useful information to producers, consumers and regulatory agencies. Such a database would help authorities to set meaningful action levels based on a toxicological evaluation on a limited number of elements that are really critical for public health.
- There is a considerable variation in the quality of source water for bottled water production within each geographical area and wider differences exist from place to place and for the different aquifer types. The popular notion that natural spring water is "clean" is misleading since many toxic elements are naturally present in mineral waters. Natural concentrations of potentially harmful elements can be surprisingly high. For many of them, maximum allowable concentration levels for drinking water have not been set.
- This study shows that elements like Be, Co, Li, Mo, REEs, Th, Sn, and U can reach surprisingly high concentrations in the mineral waters. It is hence of paramount importance once to conduct toxicological studies on their effects on human health and subsequently set action levels. While the selection of standards might be influenced by national priorities, technical limits and economic considerations, this should not be done at the expenses of public health.

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