Chemosphere 219 (2019) 896–913

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Ultra-trace determination of total mercury in Italian bottled waters

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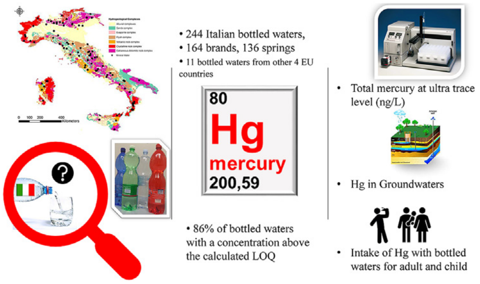
HIGHLIGHTS

- First measurements of mercury at ultratrace levels in a large population of Italian bottled water.
- 244 bottled waters corresponding to 136 Italian springs were analysed.
- 86% of the Italian bottled waters analysed were at concentration above the calculated LOQ.
- Daily and weekly intake of Hg from Italian bottled water were estimated for three population groups.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 May 2018
Received in revised form
23 November 2018
Accepted 2 December 2018
Available online 7 December 2018

Handling Editor:

Keywords:
Natural mineral waters
CV-AFS
Water chemistry

ABSTRACT

Mercury (Hg) is a widespread, highly toxic persistent pollutant with adverse health effects on humans. So far, concentrations below the method detection limit have always been reported by studies on the concentration of mercury in bottled water when determined using instrumental analytical methods. These are often very expensive and are unaffordable for many laboratories. In this work, a less expensive method based on cold vapour atomic fluorescence spectrometry has been employed to determine total mercury (Hg_T) concentrations in bottled natural mineral waters. In all, 255 waters representing 164 different typologies were analysed. They came from 136 springs located in 18 Italian regions. In all samples, Hg_T concentrations were found in the range of sub-nanogram to a few nanograms per litre, well below the National and European regulatory limit ($1\ \mu g\ L^{-1}$). Differences in Hg_T concentrations were related not only to the environmental characteristics of the springs but also to the extent and impact of human activities. Higher concentrations were found in waters coming from regions with former mining and/or natural thermal and volcanic activity. These data allowed us to estimate the mercury intake by

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https://doi.org/10.1016/j.chemosphere.2018.12.020

Daily intake
Risk assessment
Italy

population (adults, children and toddlers) from drinkable mineral waters consumption. The mean mercury daily intake was found to be remarkably lower, not only than the provisional tolerable value ($1\ \mu g\ L^{-1}$ according to European and Italian legislation) but also than the estimated provisional tolerable weekly intake (PTWI) value ($4\ \mu g\ kg^{-1}$ body weight) recommended by the Joint FAO/WHO Expert Committee on Food Additives (JECFA).

1. Introduction

The bottled water industry is growing and is steadily becoming an important economic and public health factor. The estimated global consumption of bottled water in 2005 was around 165 billion litres, which means an annual per capita consumption of 25–26 L (Cicchella et al., 2010; Naddeo et al., 2008). Italy is both one of the largest producers (over 13 billion L per year) and consumers of bottled water in the world, with a consumption of 208 L per capita per year (Beverfood, 2016). Several market surveys show that, in an era characterized by a heavy chemical pollution, consumers still consider bottled water pure, pristine and a symbolic of good health (Allen et al., 1989; D'Ascenzo et al., 1997; Dinelli et al., 2012; Falahee and MacRae, 1995; Saad et al., 1998; Versari et al., 2002). However, only major element concentrations are reported on water labels, whereas trace elements and other potentially harmful substances that can be naturally present in water sources are ignored (2009/54/EC, 2009). Since the severity of adverse health effects are time- and dose-dependent, this may raise concerns due to the high consumption rates of mineral waters (Pokras, 2005). World Health Organization (WHO) guidelines for drinking water derive from internationally agreed procedures for health risk assessment (Graham, 1999; WHO - World Health Organization, 2011). These should in principle be used by national authorities as a basis for establishing their own water quality standards. Both the European and Italian legislations (98/83/EC, 1998) and (D.Lgs. (Legislative Decree) 2/2/2001, 2001) provide detailed quality control criteria for potentially harmful contaminants in water intended for human consumption, but, bottled waters are not subjected to the comprehensive analyses as tap water (2003/40/EC, 2003; Ministerial Decree, D.M. 29/12/2003, 2003). This opens the question of whether bottled waters should be more strictly regulated, with additional and more detailed information on the label (Hussain et al., 1997). Among potential contaminants, heavy metals are highly relevant to water quality. Their concentration depends on many factors, including the source, typology, storage and transportation conditions as well as (possible) release from the packaging bottles. Mercury is one of the more harmful and undesirable contaminants (Eisler, 2004), since in the aquatic environment inorganic mercury may be transformed by biological and chemical and/or abiotic processes to the more toxic, organometallic methylmercury form, making Hg contamination a worldwide concern (Morel et al., 1998). One of the routes of exposure to Hg for humans is drinking water (Clifton, 2007). There is a considerable body of experimental evidence on the toxic effects due to exposure to various types of mercury compounds during short- (acute) or prolonged-term (chronic) incidents (Ratcliffe et al., 1996). Hg has no beneficial biological function, and its presence in living organisms is associated with various degenerative diseases (Bhan and Sarkar, 2005; Valko et al., 2005). Previous studies indicated that Hg induces adverse effects on the central nervous system of foetuses, children and adults (Ask et al., 2002; Snyder, 1971). Moreover, mercury exposure, even at low doses, results in significant renal and liver toxicity (Dieguez-Acuña et al., 2004), fertility decrease (Ernst and Lauritsen, 1991; Harada, 1968), immune system alterations (Soleo et al., 1997) and damage to the cardiovascular system (Sørensen et al., 1999). To ensure the safety of consumers, the European Directive 98/83/EC translated nationally into a legislative decree (D.Lgs. 31/2001 (Legislative Decree), 2001) on the quality of drinking water sets a maximum level of mercury in water of $1\ \mu g\ L^{-1}$ (or 1 ppb). This limit has been also adopted by the Directives 2003/40/EC for mineral water (D.M. 29/12/2003 (Ministerial Decree), 2003). For comparison, a number of national and international standards for mercury in drinking water are listed in Table 1. To satisfy the low detection limit required to quantitatively determine Hg in drinking water, specific methods and suitable instrumentations are required. Different analytical techniques have been used for mercury determination in environmental matrices and other media at low concentrations, including the flow injection mercury system (FIMS) - cold vapour atomic absorption spectrometry (CV-AAS) (Pourreza and Ghanemi, 2009; Rivaro et al., 2007), cold vapour atomic fluorescence spectrometry (CV-AFS) (Bloom and Fitzgerald, 1988; Fitzgerald and Gill, 1979; Geng et al., 2008; Gill and Fitzgerald, 1987; Wu et al., 2006; Yu and Yan, 2004) as well as flow injection analysis systems coupled to atomic fluorescence spectrometry (FIA-AFS) (Leopold et al., 2009). Other common instruments include inductively coupled plasma atomic emission spectrometry (ICP-AES) and electrothermal atomic absorption spectrometry (ET-AAS) (Arpadjan et al., 1997), ICP optical emission spectrometry (OES) and ICP mass spectrometry (MS) (Cairns et al., 2008; de Wuilloud et al., 2002; Minnich et al., 2008; Passariello et al., 1996) and thermal desorption (TD) gas chromatography–mass spectrometry (GC-MS) (Ito et al., 2009). Various pre-treatment, pre-concentration and detection procedures have been applied for mercury speciation analysis in natural waters (Leopold et al., 2010). ICP-MS with isotope dilution (ID) and cold vapour generation has a high sensitivity, high selectivity, and high sample throughput, however, the cost of such instrumentation and the isotopic standards may still be prohibitive to many laboratories (Mann et al., 2003). As an alternative, CV-AFS is less expensive, and it has been used extensively to determine mercury

Table 1
Comparison of the national and international standards for Hg in mineral waters and drinking waters.

Italian Standards for Mineral Waters (I-BW) and Drinking Water (I-DW) $\mu g\ L^{-1}$		
I-BW	1.0	Ministerial Decree D.M. 29/12/2003
I-DW	1.0	Legislative Decree D.Lgs. 31/2001
European Standards for Mineral Waters (EU-BW) and Drinking Water (E-DW)		
EU-MW	1.0	EU Directive 2003/40/EC
EU-DW	1.0	EU Directive 1998/83/EC
International Standards for Mineral Waters (BW) and Drinking Waters		
Chinese BW	1.0	Ministry of Environmental Protection (MEP) GB 2762-2012
Chinese DW	1.0	Ministry of Environmental Protection (MEP) GB 5749-2006
Canadian BW	1.0	Health Canada. Food and Drug Regulations
Canadian DW	1.0	Australian Drinking Water Guidelines
US-EPA BW	2.0	Safe Drinking Water Act (SDWA), 40 CFR 141.62
US-EPA DW	2.0	Food and Drug Administration (FDA). 21 CFR 103.35
WHO	6,0	WHO 2005, WHO/SDE/WSH/05.08/10

due to its low interferences, high sensitivity and relatively low sample consumption (Knox et al., 1995; Zi et al., 2009). In Europe, water brands are recognized by the EU Commission (OJEC, 1996; OJEC, 2010). The list of natural mineral waters is regularly updated and can change year to year. From 2010 to 2014, more than 400 Italian brands were registered by the EU (Ciotoli and Guerra, 2016). Despite the large number of brands on the Italian market, eight companies account for about 71.5% of production (Beverfood, 2016; Bono and Boni, 2001). The remaining fraction of the market is made of small companies with local plants and distribution. The aim of this study is to investigate with very sensitive analytical methods the total mercury (Hg_T) concentrations in Italian bottled waters to understand if a relationships exists between the presence of mercury, the physico-chemical parameters of waters, and the lithology of the aquifer. In addition, these data will be useful in evaluating the potential mercury daily intake from bottled drinking water.

2. Geological and hydrogeological setting

The geology of Italy is characterized by the presence of three major orogenic belts: the Alps, the Apennines and the Calabria-Peloritani Arc (CPA). From a geological point of view, there are significant differences among these three belts. A Pre-Alpine basement crops out essentially in Sardinia, Calabria and locally in the Alps. It is composed of metamorphosed sedimentary successions and Caledonian and Variscan magmatic rocks. Post-Variscan deposits consist mainly of sedimentary successions of Permian to Cretaceous age, which record the evolution of the passive margins developed around the Tethyan Ocean, with abundant carbonate deposits in both areas (Sardinia and Calabria). The metamorphic and crystalline Alpine and Hercynian rocks outcropping in Calabria constitute the so called "Calabrian basement Complex". Carbonate mesozoic rocks occur in small tectonic windows below them. Eocene, Oligocene and Lower Miocene terrigenous sequences outcrop as remnants along the over thrust contacts between these basement units, and as tectonic wedges along major high-angle fault zones. Italy is also characterized by four main magmatic episodes, spanning in time from the Permian to recent times, which were related to different geodynamic settings. The most significant are the Permian volcanic episodes, in the Southern Alps, the Eocene–Oligocene rhyolitic–trachitic and basaltic episodes in the Southern Alps; the Tertiary calk-alkaline magmatism (Oligocene–Miocene) in Sardinia and the Plio-Quaternary volcanism in Sardinia, Central and Southern Italy and in Sicily (Beccaluva et al., 2004; Peccerillo, 2005). In this framework, the most important water resources are associated with the alluvial and Mesozoic (limestone and dolomitic limestone) successions characterizing the Alpine, Apennine and CPA areas (Civita, 2008). Volcanic areas mark out isolated groundwater resources, predominantly stored in the pyroclastic deposits. Local water resources are found in siliciclastic and flysch complexes (Civita, 2008). Other important hydrological complexes are associated with the carbonate sedimentary successions of the tertiary age. Although the hydrological complexes related to magmatic (plutonic) or metamorphic rocks outcropping in the Western and Central Alps, in Calabria, in north-eastern Sicily and in Sardinia, are less important from an extensional viewpoint, they can produce several high-quality springs and, as reported by Apollaro (Apollaro et al., 2016) and Vespasiano (Vespasiano, 2015; Vespasiano et al., 2015b, 2015a, 2014) they may be the site of important deep thermal systems.

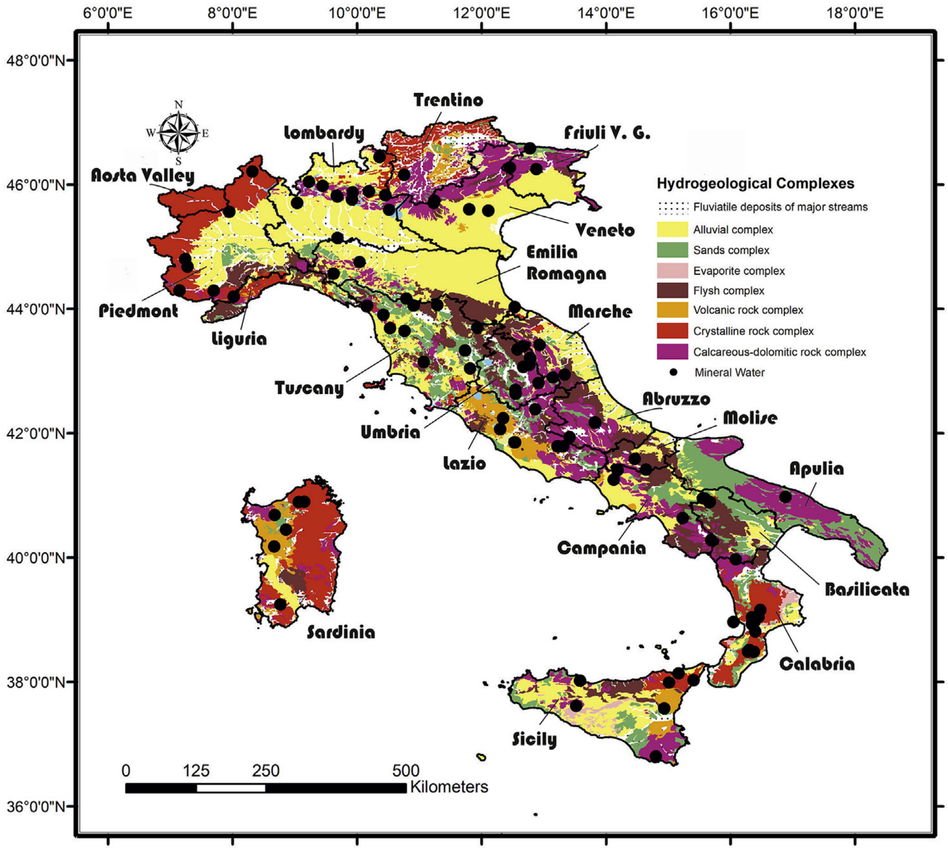

Fig. 1. Schematic hydrogeological map modified after Lithological Map of Italy (1:1.000.000) produced by the Servizio Geologico d'Italia, Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA) where are reported the Italian mineral waters source locations. More sources were represented by the same dot.

Table 2
Summary of Hg concentration and other parameters for Italian bottled mineral waters considered in the study.

Sample ID	Hg (ng L^{-1})	Classification	Mineral content	Zone	Packaging	Bottle colour
ITA001-1	0.32	Non carbonated	Low	Central Italy	PET	Colourless
ITA001-2	0.16	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA001-3	0.42	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA002-3	0.37	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA003-1	0.20	Non carbonated	Low	Central Italy	PET	Colourless
ITA003-3	0.20	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA004-1	0.83	Non carbonated	Low	Central Italy	PET	Coloured (blue)
ITA004-2	0.27	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA004-3	0.27	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA005-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA006-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA007-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA008-1	0.19	Non carbonated	Low	Southern Italy	PET	Colourless
ITA009-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA009-4	0.22	Carbonated	Low	Southern Italy	PET	Coloured (blue)
ITA010-2	0.71	Carbonated	Intermediate	Southern Italy	PET	Coloured (blue)
ITA010-4	0.09	Carbonated	Intermediate	Southern Italy	PET	Coloured (green)
ITA011-1	0.23	Non carbonated	Low	Southern Italy	PET	Colourless
ITA012-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA012-4	0.09	Carbonated	Intermediate	Southern Italy	PET	Coloured (pink)
ITA012-4	0.13	Carbonated	High	Southern Italy	PET	Coloured (green)
ITA013-1	0.30	Non carbonated	Low	Southern Italy	PET	Colourless
ITA014-1	0.28	Non carbonated	Low	Southern Italy	PET	Colourless
ITA014-3	0.30	Carbonated	Low	Southern Italy	PET	Colourless
ITA015-1	0.15	Non carbonated	Low	Southern Italy	PET	Colourless
ITA016-4	<0.09	Carbonated	Intermediate	Southern Italy	PET	Coloured (green)
ITA017-4	<0.09	Carbonated	High	Southern Italy	PET	Coloured (green)
ITA018-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA018-2	<0.09	Carbonated	Low	Southern Italy	PET	Colourless
ITA019-1	0.16	Non carbonated	Low	Southern Italy	PET	Colourless
ITA020-1	0.12	Non carbonated	Low	Southern Italy	PET	Colourless
ITA021-1	0.16	Non carbonated	Low	Southern Italy	PET	Colourless
ITA022-1	<0.09	Non carbonated	Low	Southern Italy	PET	Coloured (blue)
ITA022-2	0.10	Carbonated	Low	Southern Italy	PET	Coloured (blue)
ITA023-1	0.37	Non carbonated	Low	Southern Italy	PET	Colourless
ITA023-2	0.91	Carbonated	Low	Southern Italy	PET	Colourless
ITA024-1	0.14	Non carbonated	Low	Southern Italy	PET	Colourless
ITA025-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA025-2	0.13	Carbonated	Low	Southern Italy	PET	Colourless
ITA026-1	0.14	Non carbonated	Low	Southern Italy	PET	Colourless
ITA027-1	0.10	Non carbonated	Low	Southern Italy	PET	Colourless
ITA027-2	0.11	Carbonated	Low	Southern Italy	PET	Coloured (blue)
ITA028-1	<0.09	Non carbonated	Low	Southern Italy	PET	Coloured (blue)
ITA029-1	0.40	Non carbonated	Very low	Southern Italy	PET	Coloured (blue)
ITA029-2	0.32	Carbonated	Very low	Southern Italy	PET	Coloured (blue)
ITA030-1	0.12	Non carbonated	Low	Southern Italy	PET	Colourless
ITA030-2	0.11	Carbonated	Low	Southern Italy	PET	Colourless
ITA031-1	0.23	Non carbonated	Intermediate	Southern Italy	PET	Colourless
ITA031-2	0.32	Carbonated	Intermediate	Southern Italy	PET	Colourless
ITA032-1	0.36	Non carbonated	Intermediate	Southern Italy	PET	Colourless
ITA032-3	0.30	Carbonated	Intermediate	Southern Italy	PET	Colourless
ITA033-4	1.24	Carbonated	Intermediate	Southern Italy	PET	Coloured (green)
ITA034-1	0.15	Non carbonated	Low	Southern Italy	PET	Colourless
ITA035-3	0.44	Carbonated	Low	Southern Italy	PET	Coloured (green)
ITA036-4	0.21	Carbonated	Intermediate	Southern Italy	PET	Coloured (green)
ITA037-1	0.18	Non carbonated	Low	Southern Italy	PET	Colourless
ITA037-2	0.23	Carbonated	Low	Southern Italy	Glass	Coloured (green)
ITA038-1	0.49	Non carbonated	Low	Southern Italy	PET	Coloured (green)
ITA039-1	0.11	Non carbonated	Low	Southern Italy	Glass	Coloured (green)
ITA040-1	0.44	Non carbonated	Low	Southern Italy	PET	Colourless
ITA040-2	0.43	Carbonated	Intermediate	Southern Italy	PET	Colourless
ITA041-4	0.30	Carbonated	Intermediate	Southern Italy	PET	Coloured (green)
ITA042-1	0.29	Non carbonated	Low	Southern Italy	PET	Colourless
ITA042-2	0.20	Carbonated	Low	Southern Italy	PET	Colourless
ITA043-1	0.36	Non carbonated	Low	Southern Italy	PET	Colourless
ITA043-3	0.36	Carbonated	Low	Southern Italy	PET	Colourless
ITA044-1	0.20	Non carbonated	Low	Northern Italy	PET	Colourless
ITA044-2	0.15	Carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA044-3	0.26	Carbonated	Low	Northern Italy	PET	Colourless
ITA045-1	<0.09	Non carbonated	Low	Northern Italy	PET	Colourless
ITA046-1	0.58	Non carbonated	Intermediate	Northern Italy	Glass	Colourless
ITA046-2	0.35	Carbonated	Intermediate	Northern Italy	Glass	Colourless
ITA047-1	0.30	Non carbonated	Low	Northern Italy	PET	Colourless

(*continued on next page*)

Table 2 (*continued*)

Sample ID	Hg (ng L^{-1})	Classification	Mineral content	Zone	Packaging	Bottle colour
ITA048-1	0.41	Non carbonated	Low	Northern Italy	PET	Colourless
ITA048-2	0.39	Carbonated	Low	Northern Italy	PET	Colourless
ITA049-1	0.26	Non carbonated	Low	Northern Italy	PET	Colourless
ITA050-1	0.26	Non carbonated	Low	Northern Italy	PET	Colourless
ITA051-2	0.27	Carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA052-4	0.44	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA053-4	0.89	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA054-2	0.27	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA054-4	0.21	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA055-1	0.44	Non carbonated	Low	Central Italy	PET	Coloured (blue)
ITA055-3	0.38	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA056-1	0.44	Non carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA056-2	0.18	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA056-4	<0.09	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA057-1	0.19	Non carbonated	Low	Central Italy	PET	Colourless
ITA057-3	0.14	Carbonated	Low	Central Italy	PET	Colourless
ITA058-1	<0.09	Non carbonated	Low	Central Italy	Glass	Coloured (green)
ITA058-3	0.21	Carbonated	Low	Central Italy	Glass	Coloured (green)
ITA059-4	0.86	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA060-4	0.27	Carbonated	Intermediate	Central Italy	PET	Colourless
ITA061-4	0.58	Carbonated	Intermediate	Central Italy	PET	Colourless
ITA062-1	0.15	Non carbonated	Low	Northern Italy	PET	Colourless
ITA063-1	0.25	Non carbonated	Intermediate	Northern Italy	Glass	Colourless
ITA064-1	0.23	Non carbonated	Low	Northern Italy	PET	Colourless
ITA064-2	0.26	Carbonated	Low	Northern Italy	PET	Colourless
ITA065-1	0.59	Non carbonated	Low	Northern Italy	Glass	Colourless
ITA065-2	0.40	Carbonated	Low	Northern Italy	Glass	Colourless
ITA066-2	0.18	Carbonated	Low	Northern Italy	PET	Colourless
ITA067-1	0.55	Non carbonated	High	Northern Italy	PET	Colourless
ITA068-1	0.52	Non carbonated	Low	Northern Italy	PET	Colourless
ITA069-1	0.16	Non carbonated	Low	Northern Italy	PET	Colourless
ITA069-2	0.39	Carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA069-3	0.32	Carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA070-1	0.12	Non carbonated	Low	Northern Italy	PET	Colourless
ITA070-2	0.13	Carbonated	Low	Northern Italy	PET	Colourless
ITA070-3	0.19	Carbonated	Low	Northern Italy	PET	Colourless
ITA071-1	0.39	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA072-1	0.22	Non carbonated	Low	Northern Italy	PET	Colourless
ITA072-2	0.13	Carbonated	Low	Northern Italy	PET	Colourless
ITA073-1	0.30	Non carbonated	Low	Northern Italy	PET	Colourless
ITA074-1	0.14	Non carbonated	Low	Northern Italy	Glass	Colourless
ITA074-2	0.13	Carbonated	Low	Northern Italy	Glass	Colourless
ITA075-2	0.23	Carbonated	Intermediate	Northern Italy	PET	Coloured (green)
ITA076-1	0.33	Non carbonated	Low	Northern Italy	PET	Colourless
ITA076-2	0.45	Carbonated	Low	Northern Italy	PET	Colourless
ITA077-1	<0.09	Non carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA078-1	0.24	Non carbonated	Low	Central Italy	PET	Colourless
ITA078-3	0.25	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA079-1	0.35	Non carbonated	Low	Central Italy	PET	Colourless
ITA080-1	0.26	Non carbonated	Low	Central Italy	PET	Colourless
ITA080-3	0.21	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA081-1	0.34	Non carbonated	Low	Central Italy	PET	Colourless
ITA082-3	0.25	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA083-1	0.33	Non carbonated	Low	Central Italy	PET	Colourless
ITA083-3	0.17	Carbonated	Low	Central Italy	PET	Colourless
ITA084-3	0.26	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA085-1	0.21	Non carbonated	Low	Southern Italy	PET	Coloured (blue)
ITA085-2	0.20	Carbonated	Low	Southern Italy	PET	Coloured (green)
ITA086-1	0.21	Non carbonated	Low	Southern Italy	PET	Colourless
ITA087-1	0.15	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA088-1	0.23	Non carbonated	Very low	Northern Italy	Glass	Colourless
ITA088-2	0.25	Carbonated	Very low	Northern Italy	Glass	Colourless
ITA089-1	<0.09	Non carbonated	Low	Northern Italy	PET	Colourless
ITA089-2	0.21	Carbonated	Very low	Northern Italy	PET	Colourless
ITA090-1	0.26	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA090-2	0.27	Carbonated	Very low	Northern Italy	PET	Colourless
ITA091-1	0.37	Non carbonated	Low	Northern Italy	PET	Colourless
ITA092-1	0.14	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA092-2	0.18	Carbonated	Very low	Northern Italy	PET	Colourless
ITA093-1	0.79	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA094-1	0.19	Non carbonated	Very low	Northern Italy	PET	Coloured (blue)
ITA095-1	<0.09	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA096-1	<0.09	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA096-2	<0.09	Carbonated	Very low	Northern Italy	PET	Colourless
ITA097-1	0.36	Non carbonated	Very low	Northern Italy	PET	Colourless

Table 2 (*continued*)

Sample ID	Hg (ng L^{-1})	Classification	Mineral content	Zone	Packaging	Bottle colour
ITA097-2	0.91	Carbonated	Very low	Northern Italy	PET	Colourless
ITA098-1	0.25	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA099-1	0.24	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA099-1	0.11	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA099-2	0.28	Carbonated	Very low	Northern Italy	PET	Colourless
ITA099-3	0.19	Carbonated	Very low	Northern Italy	PET	Colourless
ITA100-1	0.38	Non carbonated	Very low	Northern Italy	PET	Colourless
ITA100-2	0.21	Carbonated	Very low	Northern Italy	PET	Colourless
ITA101-1	0.46	Non carbonated	Low	Southern Italy	PET	Colourless
ITA102-1	0.17	Non carbonated	Low	Southern Italy	PET	Colourless
ITA103-1	0.97	Non carbonated	Low	Southern Italy	PET	Colourless
ITA104-1	0.26	Non carbonated	Low	Southern Italy	PET	Colourless
ITA105-1	0.30	Non carbonated	Low	Southern Italy	PET	Colourless
ITA106-1	0.48	Non carbonated	Low	Southern Italy	PET	Colourless
ITA107-1	0.30	Non carbonated	Low	Southern Italy	PET	Colourless
ITA108-1	0.44	Non carbonated	High	Southern Italy	PET	Coloured (blue)
ITA109-2	0.82	Carbonated	Intermediate	Southern Italy	PET	Coloured (green)
ITA110-1	0.19	Non carbonated	Low	Southern Italy	PET	Colourless
ITA111-1	0.20	Non carbonated	Low	Southern Italy	PET	Coloured (green)
ITA112-1	0.13	Non carbonated	Low	Southern Italy	PET	Colourless
ITA113-1	0.22	Non carbonated	Low	Southern Italy	PET	Colourless
ITA114-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA115-3	<0.09	Carbonated	Intermediate	Southern Italy	PET	Colourless
ITA116-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA117-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA118-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA118-2	<0.09	Carbonated	Low	Southern Italy	PET	Colourless
ITA119-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA120-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA121-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA122-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA123-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA124-1	<0.09	Non carbonated	Low	Southern Italy	PET	Colourless
ITA125-1	0.29	Non carbonated	Very low	Northern Italy	Glass	Colourless
ITA125-2	0.35	Carbonated	Very low	Northern Italy	Glass	Colourless
ITA126-1	0.10	Non carbonated	High	Central Italy	Glass	Colourless
ITA127-1	5.39	Non carbonated	Very low	Central Italy	Glass	Coloured (green)
ITA128-1	0.28	Non carbonated	Low	Central Italy	PET	Colourless
ITA128-2	0.48	Carbonated	Low	Central Italy	PET	Colourless
ITA129-1	0.14	Non carbonated	Low	Central Italy	PET	Colourless
ITA129-2	0.16	Carbonated	Low	Central Italy	PET	Colourless
ITA129-3	0.33	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA130-1	0.37	Non carbonated	Low	Central Italy	PET	Colourless
ITA130-2	0.17	Carbonated	Low	Central Italy	PET	Colourless
ITA131-3	0.30	Carbonated	Low	Central Italy	Glass	Colourless
ITA132-1	0.29	Non carbonated	Low	Central Italy	PET	Colourless
ITA132-2	0.22	Carbonated	Low	Central Italy	PET	Colourless
ITA133-1	0.09	Non carbonated	Low	Central Italy	PET	Colourless
ITA134-1	0.35	Non carbonated	Intermediate	Central Italy	PET	Colourless
ITA134-2	0.32	Carbonated	Intermediate	Central Italy	PET	Colourless
ITA135-1	1.74	Non carbonated	Low	Central Italy	Glass	Coloured (green)
ITA136-1	<0.09	Non carbonated	Low	Central Italy	PET	Colourless
ITA137-1	0.16	Non carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA138-1	0.35	Non carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA139-1	0.24	Non carbonated	Low	Central Italy	PET	Colourless
ITA140-4	0.22	Carbonated	Low	Central Italy	PET	Coloured (green)
ITA141-1	0.20	Non carbonated	Low	Central Italy	PET	Colourless
ITA141-2	0.40	Carbonated	Low	Central Italy	PET	Colourless
ITA142-2	0.15	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA143-2	0.26	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA144-1	0.09	Non carbonated	Low	Central Italy	PET	Colourless
ITA145-1	<0.09	Non carbonated	Low	Central Italy	PET	Colourless
ITA145-2	0.60	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA146-1	0.47	Non carbonated	Low	Central Italy	PET	Colourless
ITA147-1	0.51	Non carbonated	Low	Central Italy	PET	Colourless
ITA147-2	0.19	Carbonated	Low	Central Italy	PET	Colourless
ITA148-1	0.23	Non carbonated	Low	Central Italy	PET	Colourless
ITA148-2	0.20	Carbonated	Low	Central Italy	PET	Colourless
ITA149-1	0.27	Non carbonated	Low	Central Italy	PET	Colourless
ITA149-2	0.45	Carbonated	Low	Central Italy	PET	Colourless
ITA150-4	0.91	Carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA151-1	0.32	Non carbonated	Low	Central Italy	PET	Colourless
ITA152-1	0.24	Non carbonated	Low	Central Italy	PET	Colourless
ITA153-1	0.34	Non carbonated	Low	Central Italy	PET	Coloured (green)
ITA153-2	0.11	Carbonated	Low	Central Italy	PET	Coloured (red)

(*continued on next page*)

Table 2 (*continued*)

Sample ID	Hg (ng L^{-1})	Classification	Mineral content	Zone	Packaging	Bottle colour
ITA153-2	0.38	Carbonated	Low	Central Italy	PET	Coloured (red)
ITA153-3	0.15	Carbonated	Low	Central Italy	PET	Coloured (blue)
ITA154-1	0.27	Non carbonated	Low	Central Italy	PET	Colourless
ITA154-3	0.26	Carbonated	Low	Central Italy	PET	Colourless
ITA155-1	0.38	Non carbonated	Intermediate	Central Italy	PET	Coloured (green)
ITA156-1	0.42	Non carbonated	Low	Central Italy	PET	Colourless
ITA156-3	0.35	Carbonated	Low	Central Italy	PET	Colourless
ITA157-1	0.37	Non carbonated	Low	Central Italy	PET	Colourless
ITA157-2	0.28	Carbonated	Low	Central Italy	PET	Colourless
ITA158-1	0.31	Non carbonated	Low	Central Italy	PET	Colourless
ITA158-3	0.21	Carbonated	Low	Central Italy	PET	Colourless
ITA159-2	0.31	Carbonated	Low	Northern Italy	PET	Colourless
ITA160-2	0.28	Carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA161-1	0.21	Non carbonated	Low	Northern Italy	PET	Colourless
ITA162-1	0.14	Non carbonated	Low	Northern Italy	Glass	Colourless
ITA162-2	<0.09	Carbonated	Low	Northern Italy	PET	Colourless
ITA163-1	0.20	Non carbonated	Low	Northern Italy	PET	Colourless
ITA163-2	0.31	Carbonated	Low	Northern Italy	PET	Coloured (blue)
ITA163-3	0.25	Carbonated	Low	Northern Italy	PET	Coloured (green)
ITA164-1	0.22	Non carbonated	Low	Northern Italy	PET	Colourless
ITA164-2	0.19	Carbonated	Low	Northern Italy	PET	Coloured (green)

National and European regulatory limit of Hg in natural mineral bottled water set at 1 μg L^{-1}

Note: the last no. of the sample code indicates water typology: 1-still. 2-sparkling. 3-lightly sparkling. 4-naturally sparkling.

3. Materials and methods

3.1. Sample collection

Between January 2014 and March 2016, 244 bottles of water (mineral, springs and drinking) available on the Italian market were purchased in randomly selected shops from all over Italy. These bottled waters represent 164 brands of water and correspond to 136 springs located in 55 provinces from 18 out of the 20 Italian regions (Fig. 1). In addition, for comparison, 11 bottled waters from 5 brands from other European countries (Denmark, France, Slovenia and Spain) were analysed (see Table S1). For a given brand different water types were analysed; the total number of 255 bottles of water (244 from Italy and 11 from other European Country) consisted of 144 bottled mineral waters (still/not carbonated), 19 with a natural content of carbon dioxide (CO_2) notated as naturally sparkling, and 92 with artificially added CO_2, split between 63 sparkling and 29 lightly sparkling waters.

The bottled water samples collected in this study had two different container types, glass with a metal screw cap with a thin polyethylene (PE) film (21 samples) or polyethylene terephthalate (PET) packaging with a PE screw cap (234 samples). The colour of the bottle containers varied as follows: 78 containers were coloured (32 blue-bluish, 43 green-greenish and 3 red-reddish) and 177 were colourless.

Based on the dry residue content, the samples were classified as very low (28 samples), low (177 samples) and intermediate mineral content (34 samples). Only 5 brands had a concentration of total dissolved solids of up to 1500 mg L^{-1}. A list of samples based on their main chemical compositional parameters (carbonated, mineral content) is reported in Table 2. The geographical coordinates and elevation of springs of all analysed samples are summarized in Table S2.

3.2. Labware, chemicals and reagents

Ultrapure deionized water (Millipore, Milli-Q, 18 MΩ cm, Burlington, MA, USA) was used to rinse all containers, to prepare blank solutions, calibration standards and to dilute concentrated reagents. Laboratory plasticware used (Nalgene, Thermo Scientific, Waltham, (MA), USA) and metal-free tubes (VWR, Radnor, PA, USA) were of either fluorinated polyethylene (FPE) or polypropylene (PP) with high-density polyethylene (HDPE) caps. An alkaline detergent (Micro-90, Sigma-Aldrich Inc., Saint Louis, MO, USA) diluted in deionized water was used to clean the plasticware. Subsequently, all laboratory containers were then filled completely to the neck with a 3.5% (v/v) nitric acid solution (HNO_3, 67-69%, supra-pure quality, SpA, Romil, Cambridge, UK) and were immersed in a hot bath for 6 h at 65 °C. After rinsing a bromine monochloride (BrCl) 1% (v/v) solution was used to completely fill the bottles and tubes for 24 h. Between each step, bottles, tubes and caps were rinsed five times with ultrapure deionized water. Hydrochloric acid (HCl, 33-36%, ultra-pure quality, UpA, Romil, Cambridge, UK) was diluted to 0.5% (v/v) to stabilize samples before analysis. Tin (II) chloride ($SnCl_2 \bullet 2H_2O$), hydroxylammonium chloride ($NH_2OH \bullet HCl$) and BrCl solutions were prepared from high purity quality reagents (ACS, ISO, Reag. Ph Eur grade, Emsure, Merck KGaA, Darmstadt, Germany). Nitrogen (N_2) and argon (Ar) gases at ultra-high purity (UHP) (Grade 5.0, 99.9990%, Rivoira, Milan, Italy) were further purified using a gold-coated sand/bead trap to remove Hg before purging the reagent solutions and use as a carrier gas during sample analysis.

3.3. Analytical methods

Upon arrival in the laboratory, each bottled water was recorded, placed in a plastic zip-lock type bag and stored in a dark environment in the clean laboratory at room temperature (20 °C) to avoid contaminations as well as any temperature or light effects (Rahmanian et al., 2015). Once in the laboratory, water samples were analysed within less than two weeks. Unlike previous authors (Allen et al., 1989) the outer surfaces of the bottled samples were not washed. Mineral waters with carbon dioxide (natural or added) were treated following the same procedure for still waters. To reduce the blank levels, all handling procedures were carried out whilst wearing PP gloves, a clean lab coat and blue PP over shoes (Bertoldi et al., 2011). For each analysis, a 50 g aliquot of water from a newly opened bottle was transferred into a new 50 ml acid precleaned PP tube, and HCl UpA was immediately added to final concentration of 0.5% (v/v) with the aim of minimizing Hg volatilization. All Hg forms were transformed to divalent Hg^{2+} by adding BrCl to a final concentration of 0.5% (v/v), 24-48 h before analysis. To homogenize the sample and allow digestion at room temperature, each PP tube was sealed and agitated, the persistence of the yellow colour of the solution was checked to ensure a BrCl excess. One hour before analysis, $NH_2OH \bullet HCl$, (0.2% v/v solution) was added to reduce any BrCl excess and destroy free halogens. Oxidized divalent mercury (Hg^{2+}) was reduced to elemental mercury (Hg^0) using $SnCl_2 \bullet 2H_2O$ and purged from the sample in a gas-liquid separator with an Hg-free argon streams. From there it was concentrated onto a dual gold-coated bead traps, where Hg^0 was amalgamated in two stages, first onto a "sample" and then onto "analytical" traps (Gill and Fitzgerald, 1987). The elemental mercury was then thermally desorbed from the gold traps and carried to the cell for CV-AFS detection. After each single step, samples were stored in a refrigerator and kept at 4 °C until analysis (Tvermoes et al., 2014). Total mercury concentrations in mineral waters were measured by dual gold amalgamation cold vapour atomic fluorescence spectrometry (CV-AFS) using a Tekran Series 2600 system equipped with pump unit and autosampler (Tekran Corporation Inc., Toronto, (ON), Canada) according to the main procedures outlined in the U.S. EPA Method 1631 version E (US-EPA, 2002) and the European standard (European Committee for Standardization, 2010; ISO 17852, 2006). All water samples were analysed in duplicate, and replicate analysis of each sample was expressed as averaged value.

3.4. *Quality assurance and quality control*

Two different mercury stock standard solutions SRMs, (standard reference material) for ICP and for AAS, 1000 mg L^{-1} Hg in 12% nitric acid (TraceCERT, Sigma-Aldrich Inc., Saint Louis, MO, USA), were diluted to the required concentrations to prepare the standards for the calibration curve and the initial and ongoing recovery solutions (IPR, OPR), matrix spikes and duplicates (MS, MSD) respectively. Standard and reference solutions were analysed following the same procedures used for water samples. The method gave a linear response in the range of 0.1-100 ng Hg L^{-1} with an R^2 value higher than 0.9998, the average recovery ranged between 96 and 117%. Quality assurance and quality control (QA/QC) processes for Hg analyses were performed by using replicates, laboratory reagent blanks, IPR and OPR standards, and MS/MSD solutions. The mean values of the laboratory blanks measured at each analytical run (0.04 ng L^{-1}, RSD < 20% n = 7) were subtracted from the sample values to determine the sample mercury concentration. The method limit of detection (LOD) was calculated as the blank value plus three times the standard deviation of the 7 replicates of the blank solutions as suggested by US-EPA 2003. The method LOD and quantitation limits (LOQ) were estimated to be 0.03 and 0.09 ng Hg L^{-1} respectively. Such analytical performances are in good agreement with those indicated in U.S. EPA Method 1631 E and are comparable to those reported in recent studies (Sprovieri et al., 2017). The IPR and OPR solutions (about 5 ng L^{-1}) analysed prior sample analysis and subsequently after every 12 samples and gave an average recovery of 101% and 89%, respectively. These values were within the quality control acceptance criteria for method performance in the U.S. EPA Method 1631 E (IPR: 79–121% and OPR: 77–123%). Blank and matrix spiked solutions at different concentration levels were analysed. The results are reported in Table 3. Three Certified Reference Materials (CRMs) for Hg in water, BCR- 579 and ERM- CA615, obtained from the Institute for Reference Materials and Measurements of the European Joint Research Centre (IRMM-JRC) and ORMS-5 produced by the National Research Council of Canada (NRCC), were analysed for quality control purposes, to verify the accuracy and precision of method and to detect possible matrix interferences (Ricci et al., 2016, 2012). Recoveries for the CRMs measured during the analytical run ranged between 78 and 115% as can be seen in Table 4. The Relative Standard Deviations (%RSD) calculated from replicates of the lowest calibration standard as well as for the IPR and OPR, and for spiked BCR-579 solutions were within 10% and thus well below 21%, the limit value as indicated in U.S. EPA Method 1631 E (Quality Control Acceptance Criteria for Performance Tests), showing that the method precision was sactisfactory. Fruitful participation in a global inter-laboratory-comparison-exercises (Brooks Rand Inc., Seattle (WA), USA) for Hg in freshwater samples corroborated the high quality of the analytical data presented here (Sprovieri et al., 2017; Vardè et al., 2014).

3.5. *Statistical analysis*

Results for Hg are reported in the text both as median and mean values. Median values were used to compare different samples because they are less affected by outliers. Mean values were used to report replicates of the same sample (see Table 2). Pearson correlation coefficients were calculated to examine the possible relationship between Hg concentration and other parameters present on the labels of the bottled water samples (see Table 5). In calculations, Hg concentrations below LOQ were set equal to 0.09 ng L^{-1}. Pearson's correlation and Principal Component Analysis (PCA) were applied to Hg and another 16 parameters reported on bottle labels (T, pH, EC, TDS, CO_2, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, F^-, SiO_2, spring elevation). One-way ANOVA and Kruskal-Wallis

Table 4
Total mercury concentrations in Certified Reference Materials (CRMs).

CRM	Certified value ± 95% confidence interval [UoM]	Found ± SD
BCR® - 579 (Coastal seawater)	1.9 ± 0.5 [ng kg^{-1}]	[a]1.94 ± 0.20
ORMS - 5 (Elevated mercury in river water)	26.2 ± 1.3 [pg g^{-1}]	[b]27.44 ± 3.81
ERM® - CA615 (Groundwater)	37 ± 4 [μg L^{-1}]	[c]39.10 ± 3.84

Number of replicates [a]n = 62. [b]n = 8. [c]n = 4

Table 3
Total mercury concentrations in Recovery Solutions and Matrix Spikes.

Solutions	n. of replicates	Quantity of Hg added	Quantity of Hg found		Recovery (%)[a]
IPR (Initial Precision Recovery)	[n = 10]	5.00	5.05	ng L^{-1}	101.0
OPR (Ongoing Precision Recovery)	[n = 20]	5.48	4.89	ng L^{-1}	89.2
Matrix Spike					
Ultra Pure Water	[n = 6]	1.05	1.04	ng L^{-1}	99.0
Natural Mineral Water[b]	[n = 6]	1.12	1.09	ng L^{-1}	97.3
Rainwater[b]	[n = 6]	2.90	2.79	ng L^{-1}	96.2
Seawater[b]	[n = 6]	3.40	3.41	ng L^{-1}	100.3

[a] 100 x [(Found-base)/added].

[b] Base value of real samples has been not reported but subtracted from found value.

Table 5
Summary of Pearson correlation matrix for mercury and parameters considered in this study.

	Hg (ng L^{-1})	T (°C)	pH (20 °C)	EC (20 °C)	TDS (mg L^{-1})	CO_2 (mg L^{-1})	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	HCO_3^- (mg L^{-1})	Cl^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	NO_3^- (mg L^{-1})	F^- (mg L^{-1})	SiO_2 (mg L^{-1})	Altitude a.s.l. (m)
Hg (ng L^{-1})	**1.00**																
T (°C)	−0.06	**1.00**															
pH (20°C)	−0.34	−0.48	**1.00**														
EC (20 °C)	0.02	0.66	−0.48	**1.00**													
TDS (mg L^{-1})	−0.01	0.64	−0.46	0.98	**1.00**												
CO_2 (mg L^{-1})	0.04	0.47	−0.72	0.71	0.64	**1.00**											
Na^+ (mg L^{-1})	0.19	0.32	−0.24	0.71	0.65	0.52	**1.00**										
K^+ (mg L^{-1})	0.07	0.41	−0.53	0.59	0.51	0.86	0.72	**1.00**									
Ca^{2+} (mg L^{-1})	−0.11	0.53	−0.45	0.79	0.83	0.53	0.16	0.16	**1.00**								
Mg^{2+} (mg L^{-1})	−0.18	0.68	−0.34	0.81	0.87	0.41	0.25	0.18	0.89	**1.00**							
HCO_3^- (mg L^{-1})	0.11	0.37	−0.41	0.88	0.83	0.74	0.83	0.66	0.58	0.49	**1.00**						
Cl^- (mg L^{-1})	0.18	0.51	−0.26	0.69	0.60	0.48	0.93	0.67	0.12	0.26	0.73	**1.00**					
SO_4^{2-} (mg L^{-1})	−0.17	0.60	−0.36	0.71	0.80	0.34	0.10	0.08	0.91	0.97	0.37	0.08	**1.00**				
NO_3^- (mg L^{-1})	0.15	−0.02	−0.16	−0.08	−0.12	0.04	−0.02	0.10	−0.17	−0.04	−0.12	0.09	−0.11	**1.00**			
F^- (mg L^{-1})	−0.12	0.72	−0.61	0.79	0.83	0.67	0.26	0.46	0.85	0.90	0.49	0.26	0.90	−0.01	**1.00**		
SiO_2 (mg L^{-1})	0.04	0.39	−0.72	0.25	0.20	0.78	0.05	0.67	0.23	0.17	0.19	0.09	0.16	0.35	0.52	**1.00**	
Altitude a.s.l. (m)	0.00	−0.66	0.29	−0.34	−0.27	−0.36	−0.24	−0.34	−0.19	−0.21	−0.30	−0.40	−0.11	−0.13	−0.26	−0.32	**1.00**

ANOVA were used to investigate possible differences in Hg concentration between bottled water samples based on their origin, mineral content, and typology, as well as any differences from due to container type (material and colour). A p value < 0.05 was considered as being statistically significant. Graphical and statistical analyses were performed using Statistica 8 software (2008).

4. Results and discussion

4.1. Physico-chemical parameters

Mineral waters showed different physico-chemical characteristics and composition in terms of major and trace elements. In general, the chemical content of bottled water is determined by the lithological composition of the reservoir rocks. Similar types of rock, however, may lead to different types of mineral water. Indeed, the chemical content depends on the amount of mineralizing agents, such as CO_2, redox conditions and complexants (Anke et al., 2009; Birke et al., 2010; Merkel and Planer-Friedrich, 2005; Siegel, 2002; Voigt, 1972). Physico-chemical features were obtained from the bottled water labels. In general, the examined mineral waters showed a mean temperature of 13.04 °C (min 3.20 °C, max 33.30 °C, median 12.35 °C), a mean pH of 7.18 (min 5.28, max 8.40, median 7.31) and a mean electrical conductivity (EC) of 497.67 $\mu S\ cm^{-1}$ (min 15.20, max 3630.00, median 399.00).

4.2. Water classification

The water chemistry of bottled waters was initially examined by means of: (a) triangular plots involving major cations and anions expressed as in equivalent units (Fig. 2), as suggested by Zaporozec (1972); (b) correlation graphs of Ca^{2+}+Mg^{2+} vs. Na^++K^+, where iso-salinity lines have been drawn for reference (see Fig. 3); and, finally, (c) chloride plots (Fig. 4). Some samples were not reported on these graphs due absence of data on their labels. Fig. 2 shows that: (i) roughly 130 mineral water samples belong to the Ca–HCO_3 chemical type. The exceptions are: 5 samples showing Na–Cl composition, 14 samples with Na–HCO_3 composition and 3 samples with Ca–SO_4 composition. Mineral waters showed Total Ionic Salinity (TIS) within the range of 0.28-105 meq L^{-1}, as indicated by the correlation plot Ca^{2+}+Mg^{2+} vs. Na^++K^+ (Fig. 3). Most of samples (132) fell below the iso-salinity line of 20 meq L^{-1} and only 4 samples were characterized by TIS values higher than 40 meq L^{-1}, probably due to deep thermal conditions and a long residence time of the water in the reservoirs. Chloride plots (Fig. 4) were useful for appraising mixing and other processes occurring in the aquifers, such as calcite precipitation and water-rock interactions. Each diagram was characterized by the presence of the hypothetical dilution line created by starting from the composition of sea water (Nordstrom et al., 1979). The Cl^- vs. Na^+ plot (Fig. 4a) shows that most of samples fell in proximity to, or slightly above, the sea water dilution line, indicating a negligible water-rock interaction. In particular, Na–Cl waters are on the seawater dilution line, and their low salinity, allows them to be considered as immature waters and representative of the rainwater component. Some samples (6) fell slightly above the dilution line suggesting minor water rock interactions with Na-enriched phases, like Albite. Likewise, a Cl^- vs. K^+ plot (Fig. 4b) underlined that most of waters fell close to the sea water dilution line reinforcing the predominance of the rainwater component. In some cases, there were samples above the dilution line suggesting a prolonged water-rock interaction with K-enriched phases, like K-Feldspar, volcanic and evaporitic deposits, etc. Furthermore, all samples showed Ca^{2+}, Mg^{2+} and SO_4^{2-} enrichment (Fig. 4c, d and 4e) probably from water-rock interactions with calcite, dolomite and/or Mg-enriched minerals as biotite and olivine. The SO_4^{2-} probably derives from the dissolution of minerals

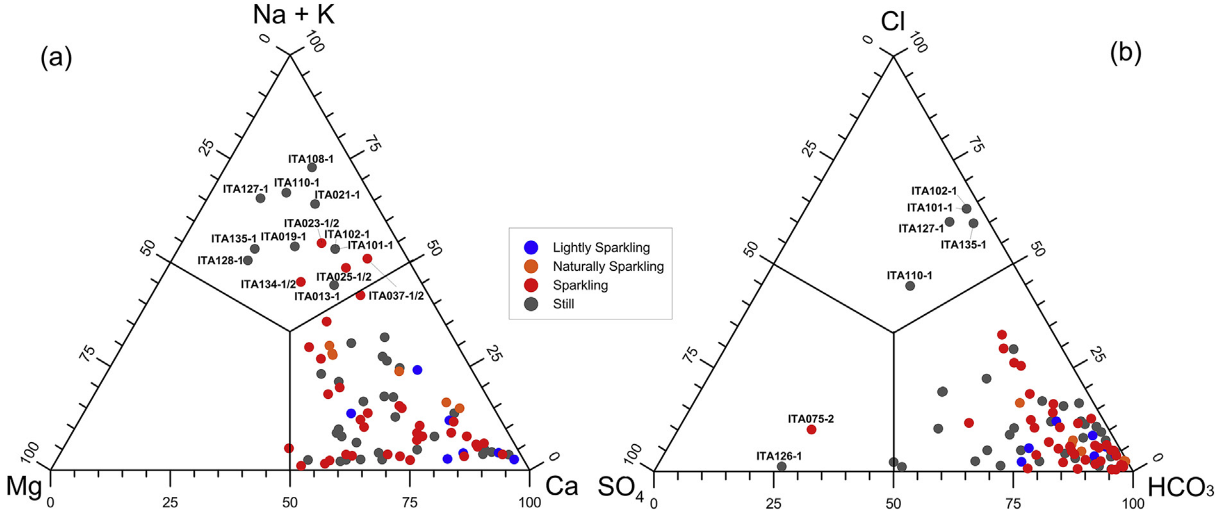

Fig. 2. Triangular plots of (a) major cations and (b) major anions (concentrations in equivalent units).

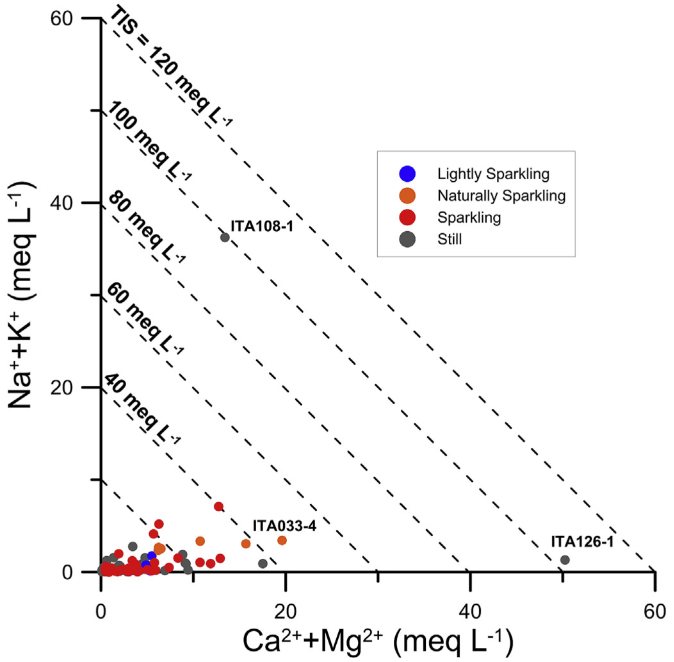

Fig. 3. Correlation diagram of Na^++K^+ vs. $Ca^{2+}+Mg^{2+}$ showing mineral water samples. Iso-salinity lines are drawn for reference.

like pyrite (oxidative dissolution) and gypsum (Fig. 5). In addition, the set of results summarized in the Pearson correlation table (Table 5) were graphically highlighted by a principal component analysis (PCA) reported in Fig. 6. The first two principal components account for 65.40% of the total data variability. There are very high correlations between groups of system variables (eg $Ca^{2+}+Mg^{2+}$, Na^++K^+, Cl^-, $CO_2+HCO_3^-$, EC+TDS). The variables of the second quadrant (K^+, Na^+, Cl^-, CO_2, HCO_3^-, SiO_2) are positively correlated to the two variables (Hg, NO_3^-) that characterize the second axis. The variables of the third quadrant ($Ca^{2+}+Mg^{2+}$, Na^++K^+, Cl^-, $CO_2+HCO_3^-$, EC+TDS) are positively linked to each other and show a slightly negative correlation with those of the second axis (Hg, NO_3^-). The SiO_2 variable is not related to the parameters of the second quadrant, while Fluoride (F^-) is positively tied to the third quadrant variables (excluding temperature) while having a negative relationship with second quadrant variables (excluding silica). In the 4th quadrant, pH and altitude have a weak positive relationship. In conclusion, by considering both the Pearson correlation table and PCA there are not any statistically significant relationships between total mercury concentration and the other considered parameters. However, a weakly positive correlation between Hg and NO_3^-, and (at least qualitatively) an inverse relationship between Hg and pH is suggested (Mann et al., 2003). The increasing Hg concentration with decreasing pH could be due to a prolonged interaction with Hg-bearing metal-sulfides that can induce pH decreases (Fig. 6), as suggested in previous studies (Boszke et al., 2002; Mann et al., 2003).

4.3. Mercury concentration in bottled waters

4.3.1. Sampling size

A total of 244 different bottled waters from Italy and 11 from other EU Countries were analysed to determine their Hg concentration. Three (or more) bottled waters were analysed for each water typology to check inter- and intra-sample variability, these were found to be lower than 5% and 1%, respectively. Hg_T was found at concentration above the LOD in 209 of 244 Italian bottled waters (86% of total). Results on mercury concentrations are summarized in Fig. 7 (Boxplot comparison of Hg concentrations), while all parameters reported on the bottle label (i.e. pH, EC, TDS etc.) are reported in Table S3. Total mercury was found at ultra trace levels in Italian bottled waters. Concentrations indeed ranged from <0.09 to 5.39 ng L^{-1}, with a mean of 0.33 ± 0.41 ng L^{-1}; the median was 0.26 ng L^{-1}. Preliminary results on Hg_T in Italian mineral natural waters were presented for bottled waters from Calabria and Campania (Vardè et al., 2015; Vardè et al., 2017). For 11 bottled waters from other EU countries, mercury was in the concentration range of 0.12-0.36 ng L^{-1}, with a mean of 0.22 ± 0.07 ng L^{-1}; and median of 0.22 ng L^{-1} (Fig. 7a). Thirty-eight bottle waters out of 255 (corresponding to 15%) had mercury concentrations below the LOQ; in 152 samples, mercury was in the range between < 0.09-0.26 ng L^{-1} (59.61%), while 100 bottle samples had Hg_T between 0.27 and 0.97 ng L^{-1} (39%). Only for three different italian brands (1.8%), had Hg_T values as high as 1.0 ng L^{-1}. Of these, two were from Tuscany, and the other from Campania. To evaluate differences in mercury concentrations in bottled waters considered in this study, samples were subdivided on the basis of (in parenthesis number of samples): i) national origin either Italy (244) or EU (11); ii) typology:

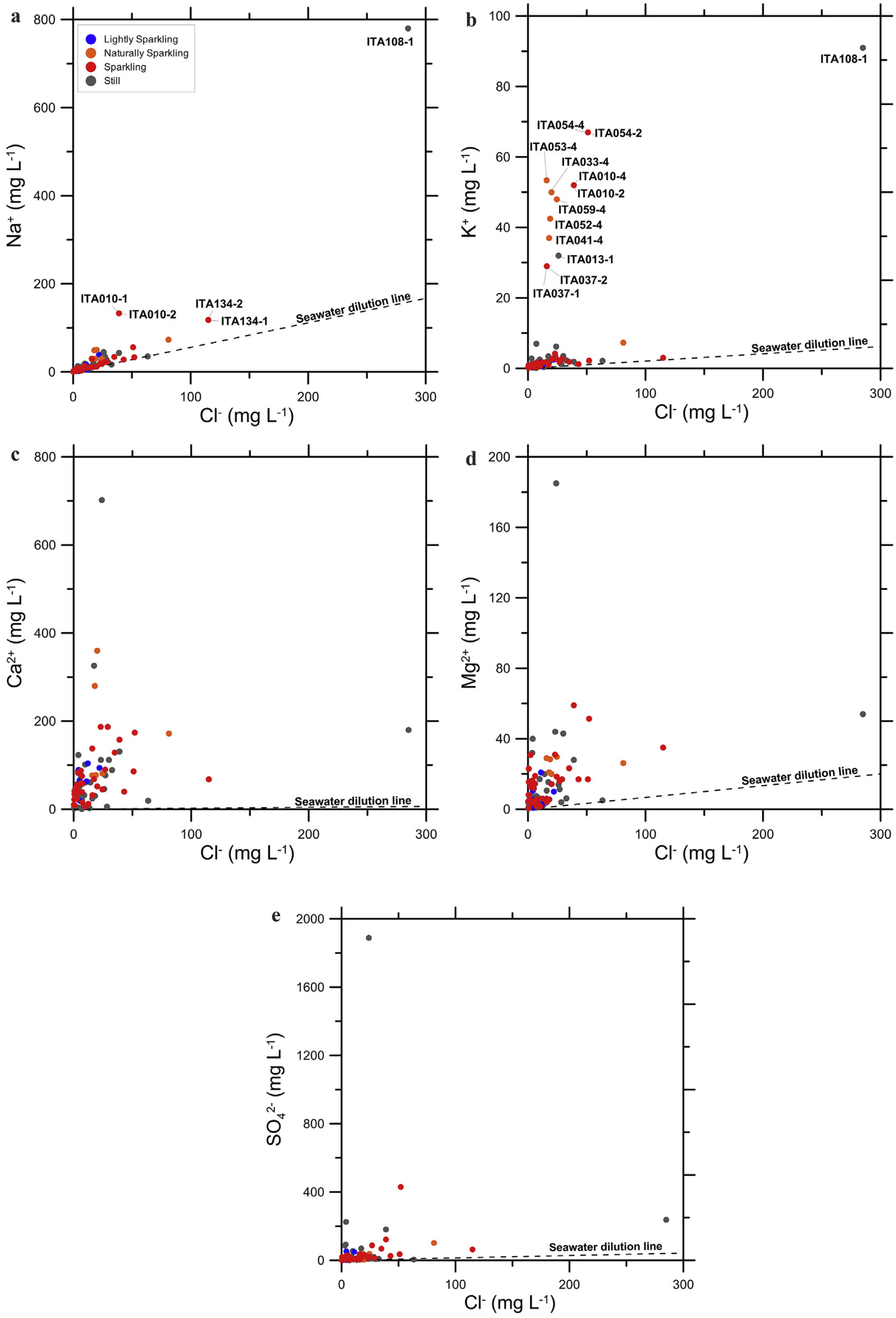

Fig. 4. Correlation diagram of Na^+ vs. Cl^- (a).K^+ vs. Cl^- (b).Ca^{2+} vs. Cl^- (c).Mg^{2+} vs. Cl^- and SO_4^{2-} vs. Cl^- (d) showing Italian mineral water samples.

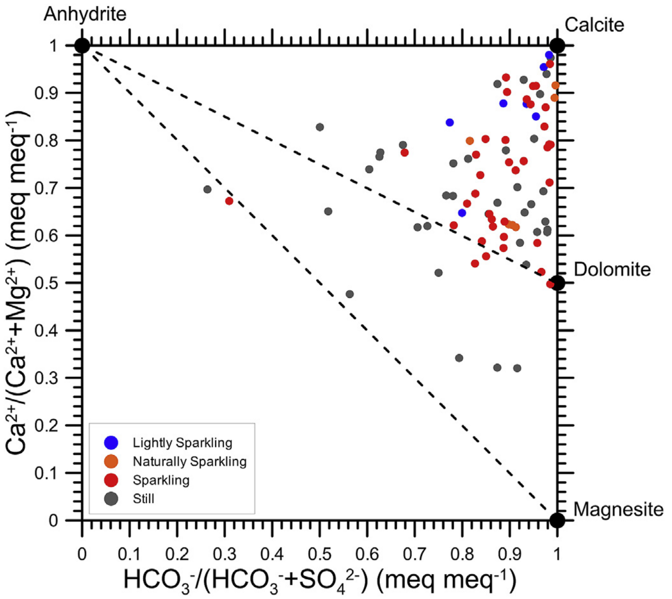

Fig. 5. Modified Langelier-Ludwig diagram where $HCO_3^-/(HCO_3^-/SO_4^{2-})$ (meq meq^{-1}) are plotted against $Ca^{2+}/(Ca^{2+}+Mg^{2+})$ (meq meq^{-1}).

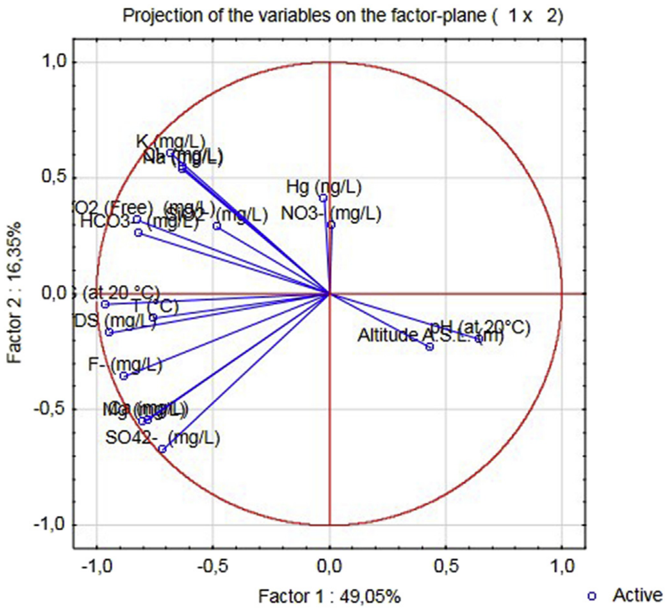

Fig. 6. Correlation circle graph for all variables of this study.

still (144), sparkling (63), lightly sparkling (29) and naturally sparkling (19); iii) mineral content: very low (28), low (184), intermediate (35) and high (7); iv) geographical zone: southern, central, northern and, finally, (v) region by region (see Table 2 and S1). Mean values of Hg_T were not statistically different between the different categories in which the samples were divided. Indeed, for non carbonated and carbonated waters (Fig. 7b) values of 0.31 ± 0.21 ng L^{-1} and 0.35 ± 0.53 ng L^{-1} were obtained, respectively; for still, sparkling, naturally sparkling and lightly sparkling waters, the following values were found: 0.35 ± 0.53 ng L^{-1}, 0.30 ± 0.19 ng L^{-1}, 0.44 ± 0.36 ng L^{-1} and 0.27 ± 0.08 ng L^{-1} (see Fig. 7c); for waters with different mineral content, Hg_T was 0.51 ± 1.03 ng L^{-1}, 0.28 ± 0.19 ng L^{-1}, 0.42 ± 0.28 ng L^{-1} and 0.31 ± 0.22 ng L^{-1} (see Fig. 7d). Analogous conclusions can be drawn for waters coming from different geographical zones such as southern, central, northern Italy (see Fig. 7e and f). A possible explanation for such low Hg_T concentrations in Italian mineral water can be found in light of the geological structure of the aquifers, the occurrence and amount of organic matter and clay fractions (Sposito, 1989), and the texture and pH of the soil, which altogether contribute to a low mobility for Hg, so it stays strongly adsorbed onto particle surfaces (Różański et al., 2016). To conclude this paragraph, in Fig. 8a, the elevation (m) vs. Hg_T (ng L^{-1}) plot is reported. Mean and median concentrations of Hg were reported for each altitude class. Four altitude classes have been grouped at around 500 m altitude intervals. Although, the correlation is not statistically significant, the qualitative decrease of Hg_T with increasing altitude could be due to evaporative effects and/or prolonged water rock interaction, which for low-altitude areas is evidenced by the higher concentration of mobile elements such as chloride (see Fig. 8b) (Boszke et al., 2002).

4.3.2. *Tuscany and Campania anomalies*

The highest Hg_T values were found for ITA127-1 and ITA135-1 samples (5.39 ng L^{-1} and 1.74 ng L^{-1} respectively). In both cases, they were still waters from springs located in the North-West of Tuscany (see Fig. 7c and f). A possible explanation can be found in past Tuscan mining activities (Levigliani, Tuscany). Mercury has been extracted in the past from the metamorphic basement (Hercynian basement) outcropping in the area and made up by phyllites, quartzites, calcschists, metalimestones, dolostones, graphitic shales and metavolcanic rocks. Local lithology and former mining activities for extraction and processing of Cinnabar (HgS) influenced Hg concentrations in groundwater system located in a large area of southern Tuscany close to Mt. Amiata as confirmed by recent studies (Vaselli et al., 2015). In a previous paper, bottled water samples from Tuscany had shown several different elements and ions above the Italian law thresholds which was explained by the authors as due to the presence of thermal sources (Naddeo et al., 2008). In addition, the water sample (naturally sparkling) from Roccamonfina, a volcanic aquifer in the province of Caserta, Campania, had a concentration of 1.24 ng L^{-1} (see Fig. 7e and f). This result is in agreement with that reported by (Bagnato et al., 2009).

4.3.3. *Packaging material and preservation influence on Hg measurements in environmental samples*

The use, preparation and storage of appropriate material containers for sampling environmental matrices for mercury has been evaluated in previous works. Contamination and losses of mercury have been reported for seawater samples, stored in PE bottles, due to the passage of gaseous Hg from ambient air to the sample or vice versa through the walls of the container (Bothner and Robertson, 1975). Hg contamination of water samples treated and preserved in different containers (of both glass and polymeric materials) has been verified even with different laboratory handling techniques using different oxidizing reagents (Cragin, 1979). In one study, the influence of containers materials (HDPE, PP, FEP and PFA) and acid treatment on the concentrations of 62 elements in water was investigated. Among all the metals considered, mercury (II) was recognized as having the characteristic of adsorbing on the bottle surface. Between the different types of polymeric materials used, and whether a pre and after washing-treatment had been carried out, the Hg concentration measured did not show any noticeable discrepancies (Reimann et al., 1999). To preserve the samples, and avoid blank problems we have used pre acid-cleaned on FEP containers with acidification of the samples with low Hg HCl (0.5% v/v) and the subsequent treatment with BrCl (Parker and Bloom, 2005). Under these conditions both Teflon and glass containers have been demonstrated to preserve aqueous samples containing Hg at ppt

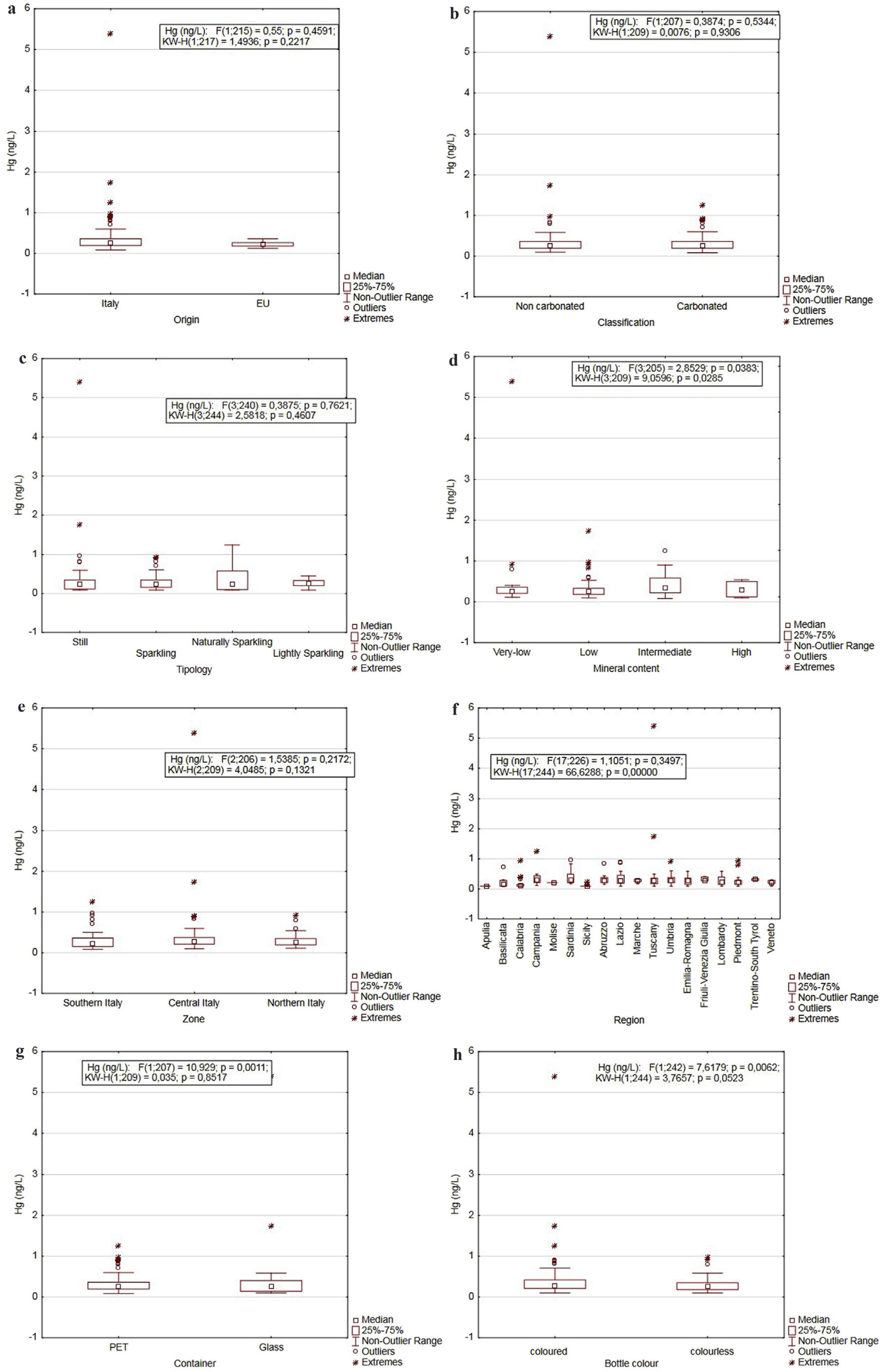

Fig. 7. a-h. Boxplot comparison of Hg concentration in (a) different bottle waters from Italy (n = 244) and EU (n = 11); (b) carbonated and non-carbonated bottled water samples from Italy; (c) different tipologies of bottled water samples from Italy; (d) bottled water samples with different mineral content from Italy; (e) different macro area of Italy; (f) Italian bottled waters region by region; (g) in different container; (h) different colour of bottled waters.

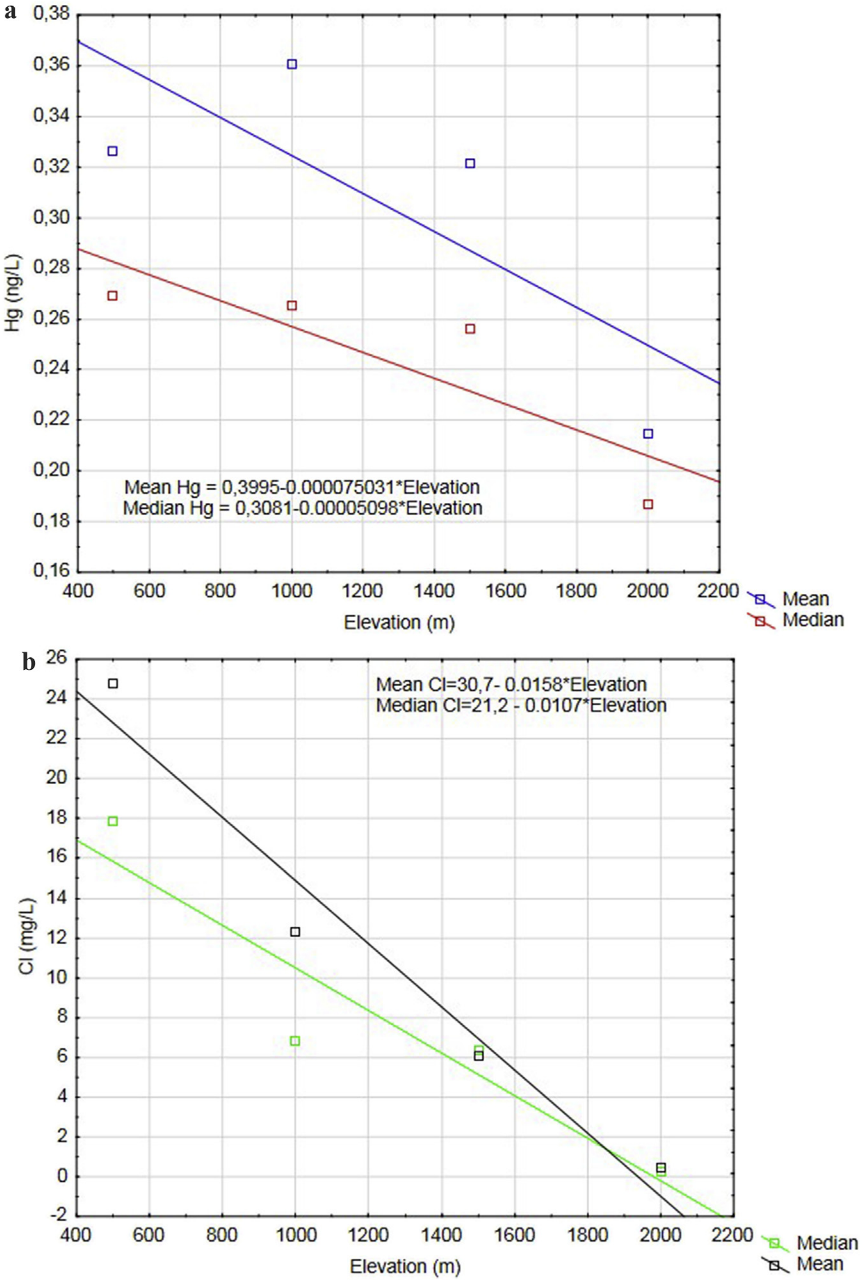

Fig. 8. Elevation spring (m) vs Hg (mean and median) concentration (ng L^{-1}) (a); vs Cl^- (mean and median) concentration (mg L^{-1}) (b).

concentrations for up to at least 1 year. Comparison of Hg_T levels in Italian bottled waters packaged either in glass (21) or in PET (234) are shown on box plot in Fig. 7g. As it can be seen, Hg_T median values between different containers (glass 0.62 ± 1.21 ng L^{-1}, PET 0.30 ± 0.18 ng L^{-1}) were not statistically significant. As previously mentioned, differences in a few outlier values are probably not attributable to different container materials. In addition, the colour of both type of containers, glass and PET, was evaluated. The bottle colour (coloured and not coloured) had no influence on the concentration of Hg_T in the two groups (Fig. 7h), such as reported in a previous study where authors described results on leaching of sixty chemicals, included Hg, for both coloured/non-coloured in both glass and PET bottles used as containers of natural mineral waters (Reimann et al., 2012).

5. Estimation of risk of human exposure to Hg from bottled waters

The major source of human exposure to mercury is through food, such as in fish and shellfish, as methyl mercury. Inorganic mercury Hg^{2+} is considered the main form of Hg in drinking water, in the absence of anthropogenic contamination. Only under particular conditions can it be transformed into more toxic organic compounds (Baldi, 1997; Ullrich et al., 2001). In 2005, the WHO estimated an average daily intake of 1 μg Hg from water, assuming a concentration of 0.5 μg L^{-1} in drinking water. This resulted in a guideline value of 6 μg L^{-1} of Hg in water, to keep the TDI (total daily intake) for a 60 kg adult, drinking 2 L of water a day, below 10% of the total TDI from food (2 μg kg^{-1}) (WHO - World Health Organization, 2005). Considering that the average intake of total

Table 6
Daily (D_T) and estimated weekly intake (EWI) and hazard quotient (HQ) for Hg_T calculated from bottled water concentrations for adults, children and toddlers.

	Calculated from bottled water concentrations (this work)			From literature values for fish[a], or fish and shellfish[b]		
Group of population	D_T	EWI	HQ [e]	EWI [a]	EWI [b, c]	EWI [b, d]
Adults	1.10E-05	7.70E-05	3.66E-05	0.45–1.35	0.8–3.2	n.d. – 4.6
Children	4.80E-05	3.36E-04	1.60E-04	n.a.	1.3–5.5	n.d. – 8.0
Toddlers	7.30E-05	5.11E-04	2.43E-04	n.a.	n.a.	n.a.

D_T and EWI were expressed as μg kg^{-1} (Bw) d^{-1}; μg kg^{-1} (Bw) w^{-1} respectively.
n.d. = not detected; n.a. = not available.
[a] Jinadasa et al. (2014).
[b] Spada et al. (2012).
[c] Hg_T from fish.
[d] Hg_T from shellfish.
[e] HQ < 1 suggests no health risk effect for a healthy exposed population; HQ > 1 indicates an increasing probability for the occurrence of harmful effects in the exposed population; HQ = 1 is the safe level limit value.

mercury assumed through food is in the range 2-20 μg d^{-1} with only 10% of the TDI allocated to drinking water, in 2011 the Committee has decided to set a provisional tolerable weekly intake (PTWI) for inorganic mercury of 4 μg kg^{-1} of body weight (Bw) lowering the previous value (5 μg kg^{-1} d^{-1}) fixed in 1972 by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). Assuming that we only have inorganic mercury in drinking water, as per the indications by WHO (FAO et al., 2011; WHO - World Health Organization, 2011, 2008, 2005) and total mercury data obtained in this study, can be used to estimate the mercury intake from the consumption of bottled water in Italy. Following the approach proposed by previous authors (Ayedun et al., 2015; Batayneh, 2010), the Hg dose was calculated as follows using equation (1).

$$D_T = \frac{D_W \text{ x } C_{Hg}}{Bw} \tag{1}$$

where:

D_T is the calculated dose taken, from water (μg kg^{-1} d^{-1}), Dw represents the average volume of bottled water consumed every day (L d^{-1}), C_{Hg} is the average concentration of mercury (μg L^{-1}) and Bw represents the average body weight (kg). Considering that an adult has an average weight of 60 kg and 2 L daily water consumption, one gets a value of:

D_T (adults) = 1.10E-05 μg kg^{-1} (Bw) d^{-1}

However, children take 70–75% of their total liquid consumption from water and products prepared from drinking water, but mercury has the same limit values for adults and children/infants in agreement with the WHO (WHO, 2011), making them the subpopulation most sensitive to chemical contaminants (Balbus and Lang, 2001). On the Italian market 38 out of the 244 samples were sold as bottled water intended for consumption by infants. The mean Hg value in these was found to be 0.48 ng L^{-1}, so the Hg dose taken by children and toddlers was estimated by considering only these samples. Using equation (1), the following data were obtained for a child with an average weight of 10 kg with 1 L of daily water consumption, and for toddlers (infants) with an average weight of 5 kg with a water consumption of 0.75 L:

D_T (children) = 4.80E-05 μg kg $^{-1}$ (Bw) d^{-1}

D_T (toddlers) = 7.3 E-05 μg kg $^{-1}$ (Bw) d^{-1}

So, despite drinking waters suggested for consumption by infants and children, and in lower quantities than adults, the daily mean consumption of Hg from bottled water follows the trend: toddlers (infants) > children > adults.

For comparison, these values can be converted into an EWI (Estimated Weekly Intake) by multiplying by 7 the D_T values. The calculated results are reported in Table 6. In addition, a risk assessment can be performed by a comparative analysis between a reference dose (RfD) and the mean daily exposure to mercury (D_T) by calculating a hazard quotient (HQ) for the three age groups according to the following formula (equation (2)):

$$HQ = \frac{D_T}{RfD} \tag{2}$$

where RfD is the reference dose for $HgCl_2$, which has an established value of 3.00E-04 mg kg^{-1} d^{-1} (US-EPA, 1995). The HQ values obtained for adults, children and toddlers (infants) are reported in Table 6. The values found are several orders of magnitude under the value obtained if the reference dose is consumed, resulting in an HQ value of 1 and is indicative of the maximum concentration with an acceptable risk. The quantification of these HQs related to the average intake of mercury from bottled water should be useful when evaluating the total mercury exposure from food, so a mercury hazard index (HI) can be calculated for the entire population of Italy. These findings highlight the fact that the assumption of Hg from natural mineral water bottled in Italy is orders of magnitude lower than the Hg_T consumed from fish and seafood (Jinadasa et al., 2014; Spada et al., 2012), reported for comparison in Table 6. Our results obtained for both Hg concentrations in bottled waters on a national (Italian) scale and and the calculated daily dose of Hg taken by different groups of the Italian population confirmed that the mean mercury daily intake was widely lower than the provisional tolerable daily intake suggested by the JEFCA. Along with the EWI data and HQ data, this suggest that there is little or no risk for mercury consumption from Italian bottled waters at the present time.

6. Overview and conclusions

Hg is one of the more toxic hazardous trace elements and it is ubiquitous in the environment. Therefore, measuring Hg levels on a national scale in environmental matrices is very relevant. This is confirmed by the priorities established in the Minamata Convention which proposed controls on it's use in artisanal mining and industry, with the aim of reducing Hg release into the environment. This should protect human health as well as the environment. To date, for Hg, there are no systematic or comprehensive studies on its occurrence in natural mineral waters. Therefore, it was not possible to estimate mercury intake with drinking water (see Studies on bottled mineral waters in literature in Supplemenary Information). The bottled waters considered in our study showed quantities of mercury at ultra-trace levels from 0.09 to 5.39 ng L^{-1}. Despite considerable variability in the water sources, a low variability of the Hg amount between water typologies (mineral content, carbonated and not carbonated samples), regional origins and packaging materials, suggests that the aquifers from which groundwater is drawn and bottled are not in general affected by anthropogenic contamination. However, we found a few brands from Tuscany and Campania with higher concentration of Hg compared to the mean and median values of all the other water samples. We ascribe this to the geological structure of the aquifer and thermal and volcanic activity as well as former metal extraction activities from mines. The data collected in this work on Hg concentrations in Italian bottled waters provides information missing from previous studies and confirms what was already known about Hg in bottled water, and generally in aquifers exploited for the potable water supply in Italy (ARPAV - Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto, 2013). This hopefully will improve our understanding of the processes and mechanisms related to mobilisation of toxic elements. Our analytical results demonstrate a natural (geogenic) presence of this potentially harmful element at a very low level, which implies good water quality and a safe geological environment with respect to Hg contamination. Being one thousand times below the maximum allowable concentration (MAC) of EU and Italian legislation ($1\ \mu g\ L^{-1}$), mercury concentrations in Italian natural mineral waters should not cause for any adverse health effects as evidenced by the daily and weekly intake values found in this study resulting in very low HQ (hazard quotient) results.

Acknowledgements

This work was funded by the authors themselves. The mention of commercial products does not constitute approval or recommendation by the authors. We are very grateful to Dr. Mario Gensini and Mr. Valentino Mannarino that respectively helped us to collect samples and log bottled waters in the laboratory. We thank the Institute for Atmospheric Pollution Research of the Italian National Research Council (CNR-IIA) that allowed us to perform all the analytical steps and instrumental analysis in their laboratories at the unit in Calabria. Our thanks are due to Dr. Riccardo Ferrante, Department of Medicine, Epidemiology, Hygiene and Environment (DiMEILA), INAIL Research Centre, Monte Porzio Catone (Rome), Italy, for giving support in searching and selecting public health publications of our interest in this topic. The manuscript was reviewed, and helpful suggestions and language editing were provided by Dr. Maddalena Parafati, and Prof. Alessandro Scarso to whom that are acknowledged with gratitude.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.12.020.

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