

Trace elements and heavy metals in mineral and bottled drinking waters on the Iranian market

Mohammad Rasoul Hadiani^{a,c}, Shirin Dezfooli-manesh^b, Shahram Shoeibi^c, Parisa Ziarati^b and Amin Mousavi Khaneghah^{d,e,*}

^aHeavy Metals Analysis Laboratory, Food and Drug Laboratory Research Centre, Food and Drug Organization, Tehran, Iran;

^bPharmaceutical Sciences Branch, Islamic Azad University (IAUPS), Tehran, Iran; ^cFood and Drug Reference Laboratories Centre, Food and Drug Organization, Tehran, Iran; ^dDepartment of Food Science and Technology, Islamic Azad University, Science and Research Branch, Tehran, Iran; ^eDepartment of Food Science, Faculty of Food Engineering, University of Campinas (UNICAMP), Campinas, São Paulo, Brazil

(Received 26 June 2014; accepted 19 July 2014)

A survey of Iranian waters, sampled from 2010 to 2013, is presented. A total of 128 water samples from 42 different brands of bottled mineral and drinking water were collected and analysed for contamination levels of lead (Pb), cadmium (Cd), copper (Cu), arsenic (As) and mercury (Hg). Determinations were performed using a graphite furnace atomic absorption spectrophotometer for Pb, Cd and Cu, a hydride vapour generation as well as an Arsenator digital kit (Wagtech WTD, Tyne and Wear, UK) for As and a direct mercury analyser for Hg. Arsenic concentration in six bottled gaseous mineral samples was higher than the related limit. Regardless of these, mean concentrations of Pb, Cd, Cu, As and Hg in all types of water samples were 4.50 ± 0.49 , 1.08 ± 0.09 , 16.11 ± 2.77 , 5.80 ± 1.63 and $0.52 \pm 0.03 \mu\text{g L}^{-1}$, respectively. Values obtained for analysed heavy metals in all samples were permissible according to the limits of national and international standards.

Keywords: graphite furnace atomic absorption spectrophotometer (GF-AAS); mineral water; bottled drinking water; heavy metals

Animal and plant life is highly depended on water. Several functions are vital for life that are influenced directly by consumed waters. A variety of types and sources of water are available for human consumption. Due to recent problems on water resources, the demand and popularity of bottled mineral waters has increased especially after serious concern about safety of Urbana's water resources. Urbanity life in the recent years persuaded many people to use bottled mineral or drinking water for its low price, readily available, fewer impurities and also guaranteed safety properties, so in last decades there has been an increase in consumption of bottled mineral water instead of tap water. Although bottled water is often remarked as more safe than tap water, at some cases water compositions in bottled water violated regulations or guidelines on some toxic natural compounds and heavy metals (Ristic et al. 2011). Since mineral water always contains various minerals and trace elements, there is huge concern about quality and safety of available mineral waters in different societies. Moreover, minerals are essential for human beings for several reasons, such as nutrition, growth, sustaining body functions and well-being, but the types and concentrations of minerals depend highly upon different factors (Baba et al. 2008). Presence and concentrations of trace elements in water depend on soil properties such as pH,

organic matter content, mineralogy and chemical and physical forms in which they are dispersed, which can affect the bioavailability of these elements (Santos et al. 2004). US Food and Drug Administration (2002) defined mineral water as "water that arises from a geologically and physically protected underground source of which its mineral and trace element levels at the source are constant". Between all beverage types, consumption of bottled water has a big proportion at the market. The global bottled water market has grown by 7% in 2006 to reach a value of US\$ 60,938.1 million, whereas with an increase by 41.8% in 2011 its value reached US\$86,421.2 million (Datamonitor 2008). As a result, the quality of drinking water has been noteworthy. Recent surveys showed that levels of some constituents of drinking water, especially toxic trace elements, may be above regulated limits (Misund et al. 1999; Frengstad et al. 2000; Ristić et al. 2011). Thus, water analysis plays an undeniable role in regulations, especially to determine water quality for specific applications, such as for drinking water (Ristic et al. 2011). Hence, due to the important role of bottled drinking and mineral water for human life, and in particular increase of the huge consumption of bottled water during recent years, quality must be controlled at a routine and systematic basis.

*Corresponding author. Email: mousavi@fea.unicamp.br

Current Address: Amin Mousavi Khaneghah, Department of Food Science, Faculty of Food Engineering, State University of Campinas (UNICAMP), Campinas, São Paulo, Brazil. Rua Monteiro Lobato, 80. Caixa Postal: 6121. CEP: 13083–862. Campinas. São Paulo. Telephone: +55(19) 3521–0091. Fax: +55(19) 3521–2153. Official Email: mousavi@fea.unicamp.br

As a required condition for marketing mineral water, concentration of constituents should be below the guideline values, which have been determined by authorities considering the toxicity of its constituents and their maximum daily intake. Consumers usually consider bottled water clean, untouched and a symbol of good health. However, attention has to be paid to natural contamination, since small amounts of potentially harmful elements can be present in springs. On the labels, concentrations of major elements are reported, while trace elements are usually ignored. Although some essential elements (e.g. Se, Zn, Ca, Cu, Co, Mg and Mo) are required for human health, some toxic elements, such as lead (Pb), cadmium (Cd), arsenic (As) and sometimes even essential micronutrients when present in excessive levels, could be harmful (Pais & Jones 1997). Almost all trace elements can be accumulated in bones and also in teeth (Berdanier & Failla 1998). It has been recognised that the presence of trace elements in drinking water can have either adverse or beneficial effects on human health, depending on concentrations (Selinus et al. 2005). Some trace elements, such as Pb, Cd, As, mercury (Hg), nickel (Ni), aluminium (Al) and chromium (Cr), may cause variable toxic effects when intake exceeds permissible limits (World Health Organization 1996). For the evaluation of the health risks of trace elements in water, it is necessary to estimate dietary exposure, compared with the provisional tolerable weekly intake (PTWI) as recommended by the Joint Expert Committee on Food Additives of the Food and Agricultural Organization and the World Health Organization. PTWI values for As, Cd, Hg and Pb vary from 0.005 to 0.025 mg kg⁻¹ body weight per week (Institute of Medicine 2001; WHO 2008).

Elemental composition of bottled and mineral water has been studied in some other countries such as Nigeria (Nkono & Asubiojo 1997), Canada (Dabeka et al. 2002), Sweden (Rosborg et al. 2005), Greece (Soupioni et al. 2006; Karamanis et al. 2007), Turkey (Baba et al. 2008) and Serbia (Ristić et al. 2011). Some researchers tested a limited number of water samples consumed in several countries (Misund et al. 1999; Lau & Luk 2002; Krachler & Shotyk 2009), and some others observed compositional information given on bottle labels (Naddeo et al. 2008). Although bottled water is widely consumed in Iran in the last years, there are very few studies about their heavy metal contamination (Nahid & Moslehi 2008). This study is a valid survey of toxic trace elemental contamination in Iranian bottled water. The aims of the present study were to (1) determine five trace elements (Pb, Cd, Cu, As and Hg) in local and imported bottled mineral and drinking water and well water as analysed in the Iranian Food and Drug Organization during 2009 to 2012; (2) compare heavy metal contamination of these three types of water; and (3) determine the legality of them with respect to Iranian legislation and WHO guidelines for the occurrence of toxic elements in mineral and drinking

water. Measurement were performed using graphite furnace atomic absorption spectrophotometer (GF-AAS) for Pb, Cd and Cu, hydride vapour generation (HG-AAS or VGA), an Arsenator digital kit (Wagtech WTD, Tyne and Wear, UK) for As measurements and a direct mercury analyser (DMA-80) for Hg determination.

Materials and methods

Sampling

In this survey, 128 water samples corresponding to 42 different brands and sources were obtained randomly from local markets in Iran, during 2010 to 2013. The samples consisted of 75 bottled mineral waters (22 different brands), 31 bottled drinking waters (9 different brands), 10 bottled gaseous mineral waters (5 different brands) and 12 well waters (6 different brands). All water samples were produced in Iran, except of some bottled gaseous mineral waters, which were imported. All brands were packed in polyethylene terephthalate (PET) containers with plastic screw caps and their volume ranged between 0.5 and 1.5 L, which were denoted with P (PET). Gaseous mineral waters were packed in a glass bottle with a metal screw cap that was denoted G (Glass). The samples were coded with brand and production serial codes and kept at a refrigerator until analysis.

Reagents and solutions

All chemicals used were reagent grade and purchased from Merck (Darmstadt, Germany). Deionised water used for making standard solutions and reagents was prepared with a resistivity of 18.0 MΩ/cm at room temperature (Elga Labwater, Lane End, UK). Certified standard solutions of Pb, Cd and copper (Cu) were provided by Panreac (Panreac Quimica SA, Barcelona, Spain) as 1000 mg L⁻¹ solutions. Working standard solutions for Pb, Cd and Cu were freshly prepared in 0.1 M HNO₃. For As calibration, a 1000 mg l⁻¹ standard stock solution (Sigma-Aldrich, St. Louis, USA) was used and working standard solutions were prepared in 10% HCl. In addition, Hg calibration standards were provided from a stock solution (Accu Standard, New Haven, USA) in 2% HCl. The T0783 (soft drink)-certified reference material was obtained from the Food Analysis Performance Assessment Scheme program (FAPAS, York, UK). All volumetric containers and pipettes were soaked in 10% (v/v) HNO₃ overnight and rinsed with deionised water prior to analysis.

Apparatus

A Varian Spectra AA-240FS atomic absorption spectrometer (Varian Australia Ltd., Mulgrave, Victoria, Australia) equipped with a GTA-120 graphite furnace atomiser (Varian Australia Ltd.) and deuterium lamp as

background corrector was used in the experiments. For Pb, Cd and Cu, a Varian programmable sample dispenser (PSD120, Varian Australia Ltd.) was employed to inject sample solutions along with orthophosphoric acid solution (1000 mg l^{-1}) as modifier into the furnace. All experiments were performed using pyrolytic-coated partitioned graphite tubes. The signals were measured as peak height. The operating parameters for Pb, Cd and Cu were set as recommended by the manufacturer. For As determination, two analysis methods were used: an Arsenator Wag-WE10500 digital kit (Wagtech, Tyne and Wear, UK) with detection range of $1\text{--}100 \text{ ng ml}^{-1}$ as a preliminary test, as well as a VGA-77 hydride vapours generation system (Varian Australia Ltd.) for the same Varian Spectra AA spectrometer with air/acetylene flame as a confirmatory determination. A DMA-80 tricell direct mercury analyser (Milestone, Sorisole (BG), Italy) was applied to perform Hg determinations. All samples were injected three times (Table 1).

Sample preparation

The bottles were opened for the first time in the laboratory and the content immediately acidified with ultra-pure HNO_3 (1 ml L^{-1}) to $\text{pH} < 2$ and then stored in sealed polyethylene bottles. For Pb, Cd and Cu, the samples were directly injected into the GFAAS along with orthophosphoric acid (1000 mg L^{-1}) as modifier. Arsenic was first measured by an Arsenator digital kit according to its operation manual. Briefly, 50 ml of sample water was poured into the kit flask, and after adding powder and tablet and waiting for 20 min, the colour change of the indicator was measured by a digital scanner in

Table 1. Operating parameters for lead, cadmium, copper, arsenic and mercury measurements in water samples.

Parameters	Lead	Cadmium	Copper	Arsenic	Mercury
Lamp current (mA)	10	6	6	6	–
Wavelength (nm)	283.3	228.8	324.8	193.7	254
Slit width (nm)	0.5	0.5	0.5	0.5	–
Sample volume (μl)	20	15	20	–	200–1000
Modifier volume (μl)	5	5	5	–	–

ng ml^{-1} . As a confirmatory method, As was determined by VGA–AAS according to the method of Mindak and Dolan (1999). Briefly, to 5 ml of each water sample, 4.5 ml of 6 M HCl was added and mixed. Then, 2 ml 50% hydroxylamine hydrochloride and 0.4 ml KI/ascorbic acid solution were added. The solution was diluted to 15 ml by deionised water and As analysis proceeded after waiting at least 1 h to ensure complete reduction of As^{5+} to As^{3+} . Hg analysis was performed by a DMA-80 direct mercury analyser without any sample preparation. The sample is weighed in a sample boat and put in the sampler. An initial drying step (at 300°C) is applied on the sample material, and in the next step the sample decomposed at 850°C after a controlled raise in temperature. The created Hg vapour is carried by a continuous oxygen gas flow to a gold amalgamator, where it is trapped. The amalgamator is then heated and the amalgamated Hg is released as Hg^0 . Finally, the released Hg passes through an atomic absorption spectrophotometer where its absorbance is measured at wavelength 253.65 nm. Three absorption cells embedded inside the instrument measure low to high Hg concentrations.

Analytical quality assurance

For method validation, related parameters were determined, including limit of detection (LOD), limit of quantification (LOQ), linearity range and accuracy (recovery level). The results are summarised in Table 2. According to the definition, LOD is the concentration of each element corresponding to three times the standard deviation of 10 reagent blanks or as $3 \sigma \text{ s}^{-1}$ and the LOQ is the concentration of each element corresponding to 10 times the standard deviation of 10 reagent blanks or as $10 \sigma \text{ s}^{-1}$, σ is the standard deviation of the blank signal ($n = 20$) and s is the slope of the calibration curve (Miller & Miller 2000). To determine method accuracy, recovery tests were performed by adding increasing amounts of each analyte to blank samples at three spiking levels within 3 days, which were then passing the analysis procedures. The results are reported in Table 3. Mean recoveries for Pb, Cd,

Table 2. Linear calibration range and limits of detection and quantification (ng ml^{-1}) for the elements analysed.

Parameters	Pb	Cd	Cu	As	Hg (ng)
Linear range	3–20	0.6–10	5–50	3–20	0.5–20
Limit of detection	1	0.2	1	1	0.1
Limit of quantification	3	0.6	3	3	0.3

Table 3. Average recovery of lead, cadmium, copper, arsenic and mercury from water samples within 3 days.

Element/Concentration	Pb			Cd			Cu			As			Hg		
Spike level (ng g^{-1})	5	10	15	1.5	3	4.5	10	20	40	5	10	15	0.5	1	2
Mean result (ng g^{-1})	5.2	9.6	14.5	1.3	2.5	4.2	11	23	37.1	5.3	10.4	14.5	0.51	0.99	1.9
Mean recovery (%)	104	96	97	90	85	94	110	115	92.7	106	104	97	103	99	96

Table 4. Measured elements in certified reference material T0783 (FAPAS).

Reference material	Element	Certified (ng ml ⁻¹)	Found* (ng ml ⁻¹)
Soft drink	Cd	70.9 (39.7–102.1)	67 ± 4
	As	196 (116–276)	203 ± 6
	Cu	405 (257–553)	411 ± 4

Note: * (± SD, *n* = 3).

Cu, As and Hg were 99%, 89.6%, 105.9%, 102.3% and 99.3%, respectively. Also, for further validation, a certified reference sample (FAPAS soft drink T0783) was analysed, which confirmed the validity of all determinations (Table 4).

Results and discussion

The concentrations of Pb, Cd, Cu, As and Hg in bottled mineral, drinking and well water are presented in Table 5. Each measurement was measured three times for each element. Results are explained and compared with other related studies in Table 6.

Lead

Traditionally, the environmental contamination and toxicity of Pb is well described before. Entry of Pb in the human food chain can cause various health problems worldwide. Cicchella et al. (2010) showed that levels of some elements such as Pb, Cu, Al, Co and Cr are significantly higher in packed water stored in glass bottles. Pb was detectable (above LOQ) in 48% of mineral, 60 % of gaseous mineral, 61% of drinking and 67% of well water samples, with means of 4.2 ± 1.1 , 4.7 ± 0.5 , 4 ± 0.5 and $5.1 \pm 0.6 \mu\text{g L}^{-1}$, respectively. The maximum level for Pb in both drinking and mineral water is $10 \mu\text{g L}^{-1}$ according to the national limit of Iran (ISIRI 2011, 2012) and according to WHO standards (WHO 1996, 2008). Pb contents in all water samples analysed were lower than the permitted limits. The range of Pb contamination found in different types of water in the present study ($3\text{--}7.6 \mu\text{g L}^{-1}$) is higher than reported in Italy (Cicchella et al. 2010), European countries (Barroso et al. 2009; Bertoldi et al. 2011), USA (Ikem et al. 2002) and Egypt (Saleh et al. 2001).

Cadmium

Cd as a major contaminant has a wide distribution in soil, plants, water, air and food supplies. Generally, the Cd levels in most foods are very low. In this survey, obtained Cd mean concentrations were 1 ± 0.2 , 1.1 ± 0.2 , 1 ± 0.3 and $1.2 \pm 0.2 \mu\text{g L}^{-1}$ in the mineral (51%), gaseous mineral (70%), drinking (71%) and well water (83%) samples, respectively. The presence of Cd as an impurity

Table 5. Occurrence of trace elements ($\mu\text{g L}^{-1}$) in different types of water samples examined during 2010–2013.

Water types	Number of Brands	Pb		Cd		Cu		As		Hg	
		N	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD	n	Mean ± SD
Bottled mineral water	22	39	<LOQ	37	<LOQ	30	<LOQ	39	<LOQ	35	<LOQ
		36	4.2 ± 1.1	38	1 ± 0.2	45	16.5 ± 5.4	36	4.5 ± 1.3	40	0.47 ± 0.1
Bottled gaseous mineral water	5	4	<LOQ	3	<LOQ	2	<LOQ	0	<LOQ	0	<LOQ
		6	4.7 ± 0.5	7	1.1 ± 0.2	8	15 ± 2.2	10	$7.9 \pm 0.4^*$	10	0.5 ± 0.1
Bottled drinking water	9	12	<LOQ	9	<LOQ	10	<LOQ	12	<LOQ	7	<LOQ
		19	4 ± 0.5	22	1 ± 0.3	21	13.2 ± 4.6	19	4.5 ± 0.8	24	0.5 ± 0.1
Well water	6	4	<LOQ	2	<LOQ	3	<LOQ	5	<LOQ	1	<LOQ
		8	5.1 ± 0.6	10	1.2 ± 0.2	9	19.7 ± 2.6	7	6.3 ± 1	11	0.6 ± 0.1

Notes: * Mean concentration of 4 samples < $10 \mu\text{g L}^{-1}$. Arsenic contents found in six other bottled gaseous mineral water samples are explained in the text.

Table 6. Comparison with other studies. Levels expressed in $\mu\text{g L}^{-1}$.

Country/Element	Pb	Cd	Cu	As	Hg	Reference
EU	<LOD – 0.44	<LOD – 0.69	<LOD – 112	–	–	Bertoldi et al. (2011)
Italy	<0.002–0.625	0.161–<0.001	<0.01–5.5	0.01–8.91	<5	Cicchella et al. (2010)
USA	<LOD – 3	<0.2–5	<0.2–2	<LOD – 12	<LOD – 79	Ikem et al. (2002)
Egypt	0.02–0.21	0.01–0.06	0.74–10.5	<LOD – 0.71	0.01–0.15	Saleh et al. (2001)
Portugal	0.55–2.22	0.1	–	<LOD	0.06–0.8	Barroso et al. (2009)
Taiwan	–	–	–	13.8–881	–	Kar et al. (2013)
Poland	–	–	–	1–1.9	–	Niedzielski et al. (1999)
Pakistan	1.6–372	0.15–20.4	0.88–270	–	–	Khan et al. (2013)

in the zinc of galvanised pipes or Cd-containing solders in fittings, taps, water coolers and water heaters may import this contaminant in drinking water. The WHO guideline as well as Iranian limit for Cd in drinking and mineral water is $3 \mu\text{g L}^{-1}$ (WHO 1996, 2008, 2012; ISIRI 2011). Cd content in all water samples analysed was lower than these limits. The range of Cd contamination found in different types of water in the present study ($0.6\text{--}1.5 \mu\text{g L}^{-1}$) was lower than found in the USA (Ikem et al. 2002) and higher than reported in Portugal (Barroso et al. 2009), Italy (Cicchella et al. 2010), the European countries (Bertoldi et al. 2011) and Egypt (Saleh et al. 2001). Entry of Cd to human organs above permissible limits can cause salivation, nausea, sensory disturbances, vomiting, liver injury and renal failure in the short term. It may also cause damage to kidney, bone, liver and blood at long-term exposure (US EPA 1998).

Copper

Cu was detectable in 60% of mineral ($16.5 \pm 5.4 \mu\text{g L}^{-1}$), 80% of gaseous mineral ($15 \pm 2.2 \mu\text{g L}^{-1}$), 68% of drinking ($13.2 \pm 4.6 \mu\text{g L}^{-1}$) and 75% of well water ($19.7 \pm 2.6 \mu\text{g L}^{-1}$) samples. However, in one bottled mineral, four bottled drinking and two well water samples, Cu was detected around 100, 60 and $30 \mu\text{g L}^{-1}$, respectively. These findings were far below the Iranian limit of $1000 \mu\text{g L}^{-1}$ and the WHO guideline value of $2000 \mu\text{g L}^{-1}$ in mineral and drinking water. The range of Cu contamination found in different types of water in the present study ($6.3\text{--}26.8 \mu\text{g L}^{-1}$) was higher than found in Egypt (Saleh et al. 2001), Italy (Cicchella et al. 2010) and the USA (Ikem et al. 2002) and very lower than reported in European countries (Bertoldi et al. 2011) and Pakistan (Khan et al. 2013).

Arsenic

In soil and many kinds of rocks, especially in minerals that contain Cu and Pb, As is naturally detectable (Selene et al. 2003). Also, this element is a natural constituent of water. As was not detected in 52%, 39% and 42% of bottled mineral, bottled drinking and well water, respectively.

However, all bottled gaseous mineral water samples had As levels above LOQ, distinguishable in three significant different groups. Four had levels below Iranian and WHO limits of $10 \mu\text{g L}^{-1}$ in mineral water ($7.9 \pm 0.4 \mu\text{g L}^{-1}$), whereas six samples exceeded these limits. All these were imported gaseous mineral waters from Armenia and Azerbaijan countries. The maximum As concentration of $525.6 \mu\text{g L}^{-1}$ was found in an Armenian sample. As content in two of these six samples was $49.9 \pm 3.8 \mu\text{g L}^{-1}$. The other four samples showed arsenic over $400 \mu\text{g L}^{-1}$ with a mean of $467.3 \pm 55.1 \mu\text{g L}^{-1}$. The range of $3.1\text{--}525.6 \mu\text{g L}^{-1}$ is similar to a report by Kar et al. (2013) in Taiwan who found As content in water samples at a range of $13.8\text{--}881 \mu\text{g L}^{-1}$. Drinking water is one of the most important sources of As exposure. As is listed among the European main pollutants (EU 2000) for its highly toxic nature, so its occurrence in water must be evaluated. Many studies on chronic As effects resulting from drinking water reported high levels of As in endemic areas worldwide (Selene et al. 2003). Recently, it was shown that there are positive relationships between low-dose As exposures and cumulative incidence ratios of lung-, bladder- and urinary-related cancers (Liao et al. 2009). Contamination of drinking water and food at too high levels of As may cause spontaneous abortion and stillbirths, black foot disease, hyper pigmentation, skin cancer and cardiovascular diseases (US EPA 1998; Jain & Ali 2000; WHO 2001).

As previously mentioned, As content in water samples was determined by two different methods. At first, water samples were analysed for As by the Arsenator digital kit. Because of probable false-positive results, confirmation was obtained by hydride the VGA–AAS method. There was a good correlation between obtained results from both methods, since the concentration ranges from VGA and Arsenator kit were 3–8.1 and 4–10, respectively, excluding the gaseous mineral water samples.

Mercury

Hg is one of the most dangerous contaminants in the human food chain, because of its presence in a variety of foods,

bioaccumulation, persistence in the environment and transport in the aquatic chain. It is widely distributed by natural processes such as volcanic activity. Moreover, it is used in various human activities among electrical appliances, laboratory apparatus, industrial and control instruments and as a raw material for some synthetic compounds such as fungicides, dental amalgams, preservatives, antiseptics, pharmaceuticals, reagents and electrodes. However, use of Hg is decreasing because of environmental legislation in many countries (IPCS 2003). In this survey, all water samples had Hg levels below the LOQ. Mean Hg levels had a mean of $0.5 \pm 0.1 \mu\text{g L}^{-1}$ in the mineral, gaseous mineral and drinking water and $0.6 \pm 0.1 \mu\text{g L}^{-1}$ in well water samples. These data are similar to the reports in Italy (Cicchella et al. 2010) and Portugal (Barroso et al. 2009). Comparing with our results, Ikem et al. (2002) measured much higher Hg concentrations in USA water samples, of up to $79 \mu\text{g L}^{-1}$.

Conclusions

This study was conducted to assess the safety of consumed bottled water in Iran in terms of trace elements. A combination of GF-AAS (for Pb, Cd and Cu), hydride vapour generation (VGA-AAS, for As), Arsenator digital kit (for As) and direct mercury analyser (DMA, for Hg) techniques was used. Obtained data revealed that internal bottled mineral and drinking water was safe according to Iranian and WHO limits for their Pb, Cd, As, Hg and Cu content during a 4-year period. However, some of the imported bottled gaseous mineral waters showed significantly higher As concentrations, which exceeded the limits. Although As is a natural constituent of water, presence of high quantities in gaseous mineral waters may be due to As pollution of the riverbed soil or spring in producing countries. Such waters may not be suitable for human consumption. This study, like other studies, showed that natural spring waters may not be completely free of contaminants. Also, the Arsenator digital kit showed to be an adequate instrument for rapid measurements of As in water samples with accurate results.

Funding

This study was supported by the Food and Drug Reference Laboratories Center, Food and Drug Organization, Tehran, Iran.

References

- Baba A, Ereeş FS, Hıçsönmez Ü, Çam S, Özdilek HG. 2008. An assessment of the quality of various bottled mineral water marketed in Turkey. *Environ Monit Assess.* 139:277–285. doi:10.1007/s10661-007-9833-9
- Barroso MF, Ramosc S, Oliva-Telesa MT, Delerue-Matosa C, Salesa MGF, Oliveirab MBPP. 2009. Survey of trace elements (Al, As, Cd, Cr, Co, Hg, Mn, Ni, Pb, Se, and Si) in retail samples of flavoured and bottled waters. *Food Addit Contam Part B Surveill.* 2:121–130. doi:10.1080/02652030903081945
- Berdanier CD, Failla ML. 1998. *Advanced nutrition: micronutrients*. Boca Raton (FL): CRC Press.
- Bertoldi D, Bontempo L, Larcher R, Nicolini G, Voerkelius S, Lorenz GD, Ueckermann H, Froeschl H, Baxter MJ, Hoogewerff J, Brereton, P. 2011. Survey of the chemical composition of 571 European bottled mineral waters. *J Food Compos Anal.* 24:376–385. doi:10.1016/j.jfca.2010.07.005
- Cicchella D, Albanese S, De Vivo B, Dinelli E, Giaccio L, Lima A, Valera P. 2010. Trace elements and ions in Italian bottled mineral waters: identification of anomalous values and human health related effects. *J Geochem Explor.* 107:336–349. doi:10.1016/j.gexplo.2010.04.004
- Commission of the European Communities. 2000. Directive 2000/60/EC of 23 October 2000 establishing a framework for Community action in the field of water policy. *Off J Eur Commun (Luxemburg).* 43:1–73.
- Dabeka RW, Conacher HB, Lawrence JF, Newsome WH, McKenzie A, Wagner HP, Chadha RK, Pepper K. 2002. Survey of bottled drinking waters sold in Canada for chlorate, bromide, bromate, lead, cadmium and other trace elements. *Food Addit Contam.* 19:721–732. doi:10.1080/02652030210140905
- Datamonitor: BottledWater – Global Industry Guide [Internet]. 28 February 2008. London (UK): Datamonitor Research Store; [cited 2010 Jun 14]. Available from: <http://www.companiesandmarkets.com/Summary-Market/>.
- Frengstad B, Skrede AK, Banks D, Krog JR, Siewers U. 2000. The chemistry of Norwegian groundwaters: III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP-MS techniques. *Sci Total Environ.* 246:21–40. doi:10.1016/S0048-9697(99)00413-1
- Ikem A, Oduyungbo S, Egiebor NO, Nyavor K. 2002. Chemical quality of bottled waters from three cities in eastern Alabama. *Sci Total Environ.* 285:165–175. doi:10.1016/S0048-9697(01)00915-9
- [IOM] Institute of Medicine. 2001 of National Academies: Dietary reference intakes for vitamin A, vitamin K, arsenic, boron, chromium, copper, iodine, iron, manganese, molybdenum, nickel, silicon, vanadium and zinc [Internet]. [cited 2008 Aug 27]. Available from: <http://www.iom.edu/object.file/>
- [IPCS] International Programme on Chemical Safety. 2003. *Elemental mercury and inorganic mercury compounds: human health aspects*. Geneva: World Health Organization.
- ISIRI. 2011. Packaged (bottled) drinking water-specifications. No. 6694, 1st revision. Tehran: ISIRI.
- ISIRI. 2012. Natural mineral water-specifications and test methods. No. 2441, 2nd revision. Tehran: ISIRI.
- Jain CK, Ali I. 2000. Arsenic: occurrence, toxicity and speciation techniques. *Water Res.* 34:4304–4312. doi:10.1016/S0043-1354(00)00182-2
- Kar S, Das S, Jean J, Chakraborty S, Liu C. 2013. Arsenic in the water–soil–plant system and the potential health risks in the coastal part of Chianan Plain, Southwestern Taiwan. *J Asian Earth Sciences.* 77:295–302.
- Karamanis D, Stamoulis K, Ioannides KG. 2007. Natural radionuclides and heavy metals in bottled water in Greece. *Desalination.* 213:90–97. doi:10.1016/j.desal.2006.03.604
- Khan S, Shahnaz M, Jehan N, Rehman S., Shah MT, Din I. 2013. Drinking water quality and human health risk in Charsadda district, Pakistan. *J Clean Prod.* 60:93–101. doi:10.1016/j.jclepro.2012.02.016

- Krachler M, Shotyk W. 2009. Trace and ultratrace metals in bottled waters: survey of sources worldwide and comparison with refillable metal bottles. *Sci Total Environ.* 407:1089–1096. doi:10.1016/j.scitotenv.2008.10.014
- Lau OW, Luk SF. 2002. A survey on the composition of mineral water and identification of natural mineral water. *Int J Food Sci Technol.* 37:309–317. doi:10.1046/j.1365-2621.2002.00571.x
- Liao CM, Shen HH, Chen CL, Hsu LI, Lin TL, Chen SC, Chen CJ. 2009. Risk assessment of arsenic-induced internal cancer at long-term low dose exposure. *J Hazard Mater.* 165:652–663. doi:10.1016/j.jhazmat.2008.10.095
- Miller JN, Miller JC. 2000. *Statistics and chemometrics for analytical chemistry*. London: Pearson Education.
- Mindak WR, Dolan SP. 1999. Determination of arsenic and selenium in food using a microwave digestion-dry ash preparation and flow injection hydride generation atomic absorption spectrometry. *J Food Compos Anal.* 12:111–122. doi:10.1006/jfca.1999.0814
- Misund A, Frengstad B, Siewers U, Reimann C. 1999. Variation of 66 elements in European bottled mineral waters. *Sci Total Environ.* 243–244:21–41.
- Naddeo V, Zarra T, Belgiorno V. 2008. A comparative approach to the variation of natural elements in Italian bottled waters according to the national and international standard limits. *J Food Compos Anal.* 21:505–514. doi:10.1016/j.jfca.2008.02.010
- Nahid P, Moslehi P. 2008. Heavy metal concentrations on drinking water in different areas of Tehran as ppb and methods of remal them. *Iran J Food Sci Technol.* 5:29–35.
- Niedzielski P, Siepak J, Kowalczyk Z. 1999. Speciation analysis of arsenic, antimony and selenium in the surface waters of Poznari. *Pol J Environ Stud.* 8:183–187.
- Nkono NA, Asubiojo OI. 1997. Trace elements in bottled and soft drinks in Nigeria – a preliminary study. *Sci Total Environ.* 208:161–163. doi:10.1016/S0048-9697(97)00289-1
- Pais I, Jones JB. 1997. *The handbook of trace elements*. Boca Raton (FL): St Lucie Press.
- Ristić M, Popović I, Pocajt V, Antanasijević D, Perić-Grujić A. 2011. Concentrations of selected trace elements in mineral and spring bottled waters on the Serbian market. *Food Addit Contam Part B Surveill.* 4:6–14. doi:10.1080/19440049.2010.535216
- Rosborg I, Nihlgård B, Gerhardsson L, Gernersson ML, Ohlin R, Olsson T. 2005. Concentrations of inorganic elements in bottled waters on the Swedish market. *Environ Geochem Health.* 27:217–227. doi:10.1007/s10653-004-1612-8
- Saleh MA, Ewane E, Jones J, Wilson BL. 2001. Chemical evaluation of commercial bottled drinking water from Egypt. *J Food Compos Anal.* 14:127–152. doi:10.1006/jfca.2000.0858
- Santos EE, Lauria DC, Silveira CLP. 2004. Assessment of daily intake of trace elements due to consumption of foodstuffs by adult inhabitants of Rio de Janeiro city. *Sci Total Environ.* 327:69–79. doi:10.1016/j.scitotenv.2004.01.016
- Selene CHSJ, Chou J, De Rosa, CT. 2003. Case studies-Arsenic. *Int J Hyg Environ Health.* 206:381–386. doi:10.1078/1438-4639-00234
- Selinus O, Alloway B, Centeno JA, Finkelman RB, Fuge R, Lindh U, Smedley P, editors. 2005. *Essentials of medical geology: impacts of the natural environment on public health*. Amsterdam: Elsevier.
- Soupioni MJ, Symeopoulos BD, Papaefthymiou HV. 2006. Determination of trace elements in bottled water in Greece by instrumental and radiochemical neutron activation analyses. *JRNC.* 268:441–444.
- [EPA] United States Environmental Protection Agency. 1998. Small system compliance technology list for the non-microbial contaminants regulated before 1996. Washington, DC: Office of Water. EPA 815-R-98-002.
- [USFDA] US Food Drug and Administration. 2002. *Bottled water regulation*, Center for Food Safety and Applied Nutrition. Washington (DC): USFDA.
- [WHO] World Health Organization. 1996. *Trace elements in human nutrition and health*. Geneva: WHO.
- [WHO] World Health Organization. 2001. *Environmental health criteria 224*. In: *Arsenic and Arsenic Compounds*. 2nd ed. Geneva: WHO; p. 1–166.
- [WHO] World Health Organization [Internet]. 2008. Homepage website. Available from: <http://www.inchem.org/>