ORIGINAL ARTICLE



### Major and trace elements in some bottled water brands from Khuzestan Province market, SW Iran, and accordance with national and international standards

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**Abstract** In this study, a total of 10 bottled water samples (10 brands) from natural springs and wells packed in 1.5 l plastic bottles were randomly purchased in Khuzestan Province market. The selected bottled water brands were analyzed for 40 parameters using ICP-OES, IC, HGAAS, spectrophotometric, titration and conductometric methods. Major and trace element concentrations differ among analyzed bottled waters, reflecting the different lithologies of the aquifers from which they are extracted. The studied bottled waters are classified as Ca-Mg-HCO<sub>3</sub> type according to Piper diagram, and as "low mineral concentration" type based on Van der Aa's classification. The studied mineral water brands are classified as "very oligohaline", "oligohaline", and "fresh" water types with "very low" to "low mineral concentration" according to Stuyfzand's classification. The amount of nitrate in two and three samples, falling in the range of 20-34 mg/l, exceeds its permitted levels according to Iranian national standard for natural mineral water and USEPA standards, respectively. Since Iranian national standard defines a permissive level for  $\sum$ (nitrate + nitrite), this total amount (>20 mg/l) exceeds its allowed level in three samples. All analyzed samples, however, are in accordance with WHO regulations regarding all parameters for which action levels are defined. The fact that nitrate concentrations in some bottled water brands are above the standard levels has no geologic reason, but it is due to human activities, especially the use of nitrate-bearing chemical fertilizers.

Farhad Ehya ehya@behbahaniau.ac.ir **Keywords** Mineral water · Bottled water · Hydrogeochemistry · Trace elements · Major elements

#### Introduction

The consumption of bottled water has recently increased in Iran, dominantly due to the change of consumption priority from tap water to bottled water. The bottled water is grouped into two classes; natural mineral water, and packed drinking water. According to 80/777/EEC guidance of European Union (EU), natural mineral water is defined as healthy and uncontaminated water from an underground aquifer bottled at the spring site without any refinement, except for eliminating unstable components (iron, sulphur, magnesium and arsenic compounds) and adding some carbon dioxide (Lau and Luk 2002). On the other hand, bottled drinking water is the water, regardless of its origin, being refined using filtering or an appropriate mechanical process, and is packed in bottles for human consumption (Varrica et al. 2013). People know both as mineral water in Iran. The fact that bottled water is known among people as mineral water, on one hand, and on the other hand, as suggested by Naddeo et al. (2008), commercial production of drinking water by some countries may lead the unfair producers toward illegal activities such as packing and selling of drinking water as mineral water.

Groundwater is found as aquifers in underground geologic formations with various lithologies. It flows out naturally as springs, and it can also be pumped from wells. Since water is able to dissolve certain amounts of elements and to transport them for considerable distances, the water that comes to contact with geologic formations is being enriched in chemical elements that are characteristic to those formations. The excess amounts of trace elements

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may also occur in groundwater as a result of human activities (Duffus 1980).

Mineral water is sold annually in billion dollars worldwide (Misund et al. 1999). So, the bottled water is increasingly favoured around the world (Krachler and Shotyk 2009). Italian people are the major producers and consumers of bottled mineral water in the world (Cicchella et al. 2010). The per capita consumption of mineral water is about 12 1 annually in Iran. Compared to Italy, although the consumption of mineral water is very low in Iran, it is specially favoured among people.

There are various brands of mineral water in Khuzestan Province market. These mineral waters are provided from natural springs or from wells. Since the composition of earth's crust differs from place to place, the amount and type of dissolved elements in mineral water brands is also different. Therefore, a better understanding of their chemical composition is a key subject in quality assessment of these waters, especially for those elements which are not under regular control (Dinelli et al. 2010). Since the geologic processes are the most important agent for source controlling and distribution of chemical elements in natural waters, it is desired to be this assessment based on geochemical studies (Cicchella et al. 2010). The aim of current study is to determine the concentration of major and trace elements in some bottled water brands from Khuzestan Province market. The obtained results are compared with national and international standards to clarify whether the concentration of analyzed elements are within the allowed levels or not. Considering the presence of great economic benefits in marketing of this commodity, the geochemical data of mineral water from Khuzestan Province market not only can protect consumers, but also help to define some guidance by regulatory agencies for quality assessment.

#### Materials and methods

A total of 10 samples from 10 mineral water brands (one sample for each brand) were purchased randomly from supermarkets in Khuzestan Province. All purchased mineral waters are gas-free type and were packed in plastic bottles. The data for selected samples are given in Table 1. The selected mineral water brands were analyzed for 40 parameters. The analyzed parameters and analysis methods are provided in Table 2. All analyses were performed during shelf life of the samples, to avoid possible changes in concentration of chemical components especially those of nitrate and nitrite. Except for U which was determined in Kefa Nano Laboratory (KNL), Tehran, Iran, other parameters were analyzed in the laboratory of Iranian Mineral Processing Research Centre (IMPRC), Karaj, Iran.

#### **Geological considerations**

The studied mineral waters originate from springs and wells located in the Zagros Mountain Ranges (Fig. 1). The Zagros Mountains include numerous mountain ranges that their crests are parallel. These mountains begin from Azerbaijan in northwestern Iran, continuing toward south into Lorestan and Chaharmahal-va-Bakhtyari, and then to Kohgiloye-va-Boyrahmad and Fars Provinces, and finally to Hormoz straight and Minab fault in southeastern Iran.

Table 3 provides geological data for areas from which mineral waters under study are extracted. The well from which mineral water with brand code 1 is extracted locates in Chaharmahal-va-Bakhtyari Province. The majority of the area is covered by Cretaceous sediments including shale, sandstone and limestone. This well is dug in young Ouaternary deposits. The mineral water with brand code 2 is withdrawn from a natural spring in Fars Province. This spring flows out from recent alluviums composed of silt and clay. The dominant lithology in the area is limestone of Oligo-Miocene age. The mineral water with brand code 3 is extracted from a well located in Fars Province. The well is dug in Quaternary alluviums. The prevailing lithologies in the area are Eocene limestone and Quaternary deposits. The mineral water with brand code 4 is withdrawn from a natural spring in Kohgiloye-va-Boyrahmad Province. This spring flows out from a strike-slip fault cutting through rock units composed of shale, marl and argillaceous limestone with Upper Cretaceous to Paleocene ages. The dominant lithologies in the area are limestone and marl of Cretaceous to Tertiary ages. The mineral water with brand code 5 is extracted from another natural spring in Kohgiloye-va-Boyrahmad Province. This spring flows out from a Pliocene conglomeratic unit. The predominant rock units are limestone and marl with Upper Cretaceous to Oligocene ages. The well from which mineral water with brand code 6 is extracted locates in Lorestan Province. The well is dug in Quaternary deposits surrounded by dominant Cretaceous limestones. The well from which mineral water with brand code 7 is extracted locates in Ilam Province. The prevailing rock unit in the area is limestone of Oligo-Miocene age. This mineral water well is located in alluvium deposits. The spring from which mineral water with brand code 8 is withdrawn locates in Lorestan Province. The spring flows out from Quaternary deposits surrounded by vast limestones and evaporites of Cretaceous to Oligo-Miocene ages. The mineral water with brand code 9 is extracted from a natural spring in Esfahan Province. The dominant rock unit in the area is black slates of Jurassic age. The spring flows out from Quaternary alluvium deposits. The mineral water with brand code 10 is withdrawn from a natural spring in East Azerbaijan Province.

Brand code	Mineral water type	Province	Area
1	Well water	Chaharmahal-va-Bakhtyari	Haj Kahva
2	Spring water	Fars	Siyakh Darengoun
3	Well water	Fars	Dehpagah
4	Spring water	Kohgiloye-va-Boyrahmad	Kakan
5	Spring water	Kohgiloye-va-Boyrahmad	Ganjei Kohne
6	Well water	Lorestan	Aleshtar
7	Well water	Ilam	Shabab
8	Spring water	Lorestan	Sarab-e-Robat
9	Spring water	Esfahan	Qudjan
10	Spring water	East Azerbaijan	Kandovan

Table 2 The analyzed parameters and analysis methods for selected mineral water samples

Parameter	Unit	Analysis method	Detection limit	Parameter	Unit	Analysis method	Detection limit
Ag	ppm	ICP-OES	0.02	Pb	ppm	ICP-OES	0.05
Al	ppm	ICP-OES	0.05	Sb	ppb	HGAAS	5
As	ppm	HGAAS	5	Se	ppb	HGAAS	5
В	ppm	ICP-OES	0.05	Sr	ppm	ICP-OES	0.02
Ва	ppm	ICP-OES	0.02	Ti	ppm	ICP-OES	0.05
Be	ppm	ICP-OES	0.001	U	ppm	ICP-OES	0.01
Bi	ppm	ICP-OES	0.05	Мо	ppm	ICP-OES	0.05
Ca	ppm	ICP-OES	1	Zn	ppm	ICP-OES	0.05
Cd	ppm	ICP-OES	0.02	NO <sub>3</sub> -	mg/l	IC	5
Co	ppm	ICP-OES	0.02	$Cl^{-}$	mg/l	IC	5
Cr	ppm	ICP-OES	0.02	$PO_4^{3-}$	mg/l	IC	5
Cu	ppm	ICP-OES	0.02	$SO_4^{2-}$	mg/l	IC	5
Fe	ppm	ICP-OES	0.05	CN	mg/l	Spectrophotometry	0.05
Hg	ppb	HGAAS	1	$NO_2-$	mg/l	Spectrophotometry	0.06
Κ	ppm	ICP-OES	0.5	$F^{-}$	mg/l	Spectrophotometry	0.2
La	ppm	ICP-OES	0.05	HCO <sub>3</sub> -	mg/l CaCO3	Titration	10
Li	ppm	ICP-OES	0.05	EC	μS/cm	Electrical conductivity	10
Mg	ppm	ICP-OES	1	TDS	mg/l	Electrical conductivity	10
Na	ppm	ICP-OES	1	pН		pH meter	2
Ni	ppm	ICP-OES	0.05	Mn	ppm	ICP-OES	0.05

This spring flows out from deposits composed of pumicic lahar, tuff and volcanic ash. The predominant deposits in the area are young alluvium sediments.

#### **Results and discussion**

#### Hydrochemistry of mineral waters

The concentrations of major and trace elements, and physical parameters in 10 mineral water brands are given in Table 4. Except for Ba, Li, Sr and Zn, concentrations of other analyzed trace elements (see Table 2) are below detection limits in all studied mineral water brands and, therefore, are not reported in Table 4. The highest amounts of  $HCO_3$ - (bicarbonate) and Ca are found in mineral water with brand code 5 (Table 4), which is extracted from a conglomeratic aquifer. The high amounts of  $SO_4^{2-}$ , Mg and Na in mineral water with brand code 7, and Na and Cl<sup>-</sup> in brand codes 7 and 8 is caused probably by an evaporitic formation, which is especially abundant in the area of brand code 8. The increased amount of K in mineral water with brand code 10 reflects the effect of aquifer lithology on the chemistry of water. Since the pumicic lahars have **Fig. 1** Situation of studied wells and springs in Iran. Well and spring codes as in Table 1



Table 3 Geological data for areas from which studied mineral waters are extracted

Brand code	Dominant lithology in the area	Lithology from which spring/ well flows out	References
1	Cretaceous limestone, shale and sandstone	Quaternary alluvium	Zahedi (1993)
2	Oligo-Miocene limestone	Quaternary silty-clayey flats	Sedaghat and Dabaghian Nezhad (1996)
3	Eocene limestone and Quaternary alluvium	Quaternary alluvium	National Iranian Oil Company (2003)
4	Cretaceous to Tertiary limestone and marl	Upper Cretaceous to Paleocene shale, marl and limestone	Sedaghat and Shaverdi (1975)
5	Upper Cretaceous to Oligocene limestone and marl	Pliocene conglomerate	Sedaghat and Shaverdi (1975)
6	Cretaceous limestone	Quaternary alluvium	National Iranian Oil Company (undated)
7	Oligo-Miocene limestone	Quaternary alluvium	Llewellyn (1974)
8	Cretaceous to Oligo-Miocene limestone and evaporites	Quaternary alluvium	National Iranian Oil Company (undated)
9	Jurassic black slate	Quaternary alluvium	Mohajjel (1992)
10	Quaternary alluvium	Pliocene pumicic lahars, tuff and volcanic ash	Khodabandeh and Amini Fazl (1995)

elevated amount of K, it caused the high level of this element in brand code 10.

The concentration of nitrate  $(NO_3-)$  in mineral water with brand code 8 is below detection limit (Table 4; Fig. 2). The mineral water brands whose nitrate amounts are higher than others include brand codes 1, 6 and 7

(Fig. 2). The other mineral water brands have nearly similar concentrations of nitrate. Considering geology of the corresponding areas for brand codes 1, 6 and 7, no relation can be drawn between the high amounts of nitrate and geological factors. Alternatively, the excess nitrate levels are produced possibly by human activities, especially the

Table 4 Con	centratio	ons of mi	ajor and	trace e.	lements, ai	nd physic	cal para	meters in	analyzed 1	mineral wa	tter brand	s (units of	measure	d paramet	ters as in	Table 2)			
Brand code	Hq	TDS	EC	Ca	K	Mg	Na	$HCO_3^-$	$\mathrm{F}^{-}$	$NO_2^-$	$NO_3^-$	CN	$CI^{-}$	$\mathrm{PO}_4^{3-}$	$\mathrm{SO}_4^{2-}$	Ba	Li	Sr	Zn
1	7.8	204	384	63	<0.5	22	10	165	0.2	<0.06	20	<0.05	9	9	$\Diamond$	0.02	0.57	1.11	0.26
2	7.9	169	323	46	<0.5	14	$\overline{\vee}$	150	<0.2	<0.06	9	<0.05	$\Diamond$	7	Ŷ	<0.02	0.07	0.52	<0.05
3	7.8	184	349	33	<0.5	22	$\overline{\vee}$	165	<0.2	<0.06	8	<0.05	$\Diamond$	9	Ŷ	<0.02	0.06	0.71	<0.05
4	8	123	232	37	<0.5	8	$\overline{\vee}$	110	<0.2	<0.06	9	<0.05	$\Diamond$	9	Ŷ	<0.02	<0.05	0.10	<0.05
5	7.5	269	519	71	0.53	20	4	240	<0.2	<0.06	9	<0.05	15	9	40	0.03	<0.05	0.41	<0.05
6	7.7	182	341	52	<0.5	13	б	145	<0.2	<0.06	22	<0.05	$\Diamond$	9	9	0.03	<0.05	0.60	<0.05
7	7.8	266	501	53	0.82	32	22	170	0.2	<0.06	34	<0.05	11	8	40	0.06	0.13	0.75	0.08
8	7.3	178	334	35	0.65	10	20	100	0.2	<0.06	$\Im$	<0.05	31	9	14	0.06	<0.05	0.44	<0.05
9	8.1	133	241	41	<0.5	S	б	105	<0.2	<0.06	8	<0.05	9	$\Diamond$	28	<0.02	<0.05	0.30	<0.05
10	7.2	103	197	27	2.27	4	4	80	<0.2	<0.06	10	<0.05	Ŷ	$\Diamond$	$\langle$	0.04	<0.05	0.16	0.10



Fig. 2 Concentration of nitrate in analyzed mineral water brands

use of nitrate-bearing fertilizers. While rain and irrigation waters leach the soil extra-treated by nitrate-bearing fertilizers, the natural waters are contaminated by nitrate (Mesa et al. 2003).

Figure 3 shows variations of Ca, Mg and bicarbonate ions concentrations and total dissolved solids (TDS) in studied mineral waters. The extent of variations for Ca and Mg is more restricted than that of bicarbonate ion. So, another source must be considered for bicarbonate generation in aquifers of mineral waters under study, in addition to carbonate dissolution. The variation patterns of Ca, Mg and bicarbonate ions are in accordance with that of TDS. This suggests that the most important agent for increasing TDS in groundwater from which mineral waters are produced is carbonate dissolution. The amounts of electrical conductivity (EC) for all mineral water brands are less than 520 µS/cm, which is in line with that of common groundwater (30-2000 µS/cm; Sedaghat 2008).

As it was mentioned above, except for Ba, Li, Sr and Zn, concentrations of other trace elements are below detection limits. The higher amounts of these four elements in some mineral water brands compared to others can be explained by geology of the respecting areas. The highest amount of Ba (0.06 mg/l) belongs to mineral waters with brand codes 7 and 8 (Table 4). The higher concentration of



Fig. 3 Variations of Ca, Mg and bicarbonate ions concentrations and TDS in studied mineral waters

**Fig. 4** Piper diagram for analyzed mineral water brands (Bc is the abbreviation for Brand code)



Table 5Classification of watertypes based on EC and TDS(Van der Aa 2003)

Dissolved compounds	TDS (mg/l)	EC (µS/cm)	Brand code
Very low mineral concentration	<50	<77	
Low mineral concentration	50-500	77–769	1, 2, 3, 4, 5, 6, 7, 8, 9, 10
Intermediate mineral concentration	500-1500	769–2308	
High mineral concentration	>1500	>2308	

 Table 6
 Classification of water based on chloride concentration (Stuyfzand 1986, 1993)

Fresh-salt classes	Code	Chloride (mg/l)	Brand code
Very oligohaline	G	<5	2, 3, 4, 6, 10
Oligohaline	g	5-30	1, 5, 7, 9
Fresh	F	30-150	8
Fresh-brackish	f	150-300	
Brackish	В	300-1000	
Brackish-salt	b	1000-10,000	

Ba in these two brands is possibly related to an evaporitic formation prevailing in the respecting areas (Table 3). Dissolution of sulfatic evaporites causes the increase of Ba concentration in mentioned brands. The high amount of Li and Sr in mineral water with brand code 1 can be considered as a result of dominant presence of Cretaceous limestones in the area. Partial dissolution of carbonate rocks might produce excess amounts of Li and Sr in this mineral water. The highest concentration of Zn (0.26 mg/l) also belongs to brand code 1, which could be caused by abundant shale beds in the area (Table 3).

#### **Classification of mineral waters**

The differences in chemical composition of waters are shown on Piper diagram. This diagram discriminates clearly between different types of waters (Peh et al. 2010), classifies and compares them based on ion compositions

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Fresh-salt classes	Brand code
(Very) oligohaline	1, 2, 3, 4, 5, 6, 7, 9, 10
(Very) oligohaline-fresh	1, 2, 3, 4, 5, 6, 7, 8, 9, 10
B (Very) oligohaline-Brackish	
b Oligohaline-brackish/salt	
	Fresh-salt classes         (Very) oligohaline         (Very) oligohaline-fresh         B       (Very) oligohaline-Brackish         b       Oligohaline-brackish/salt

Table 7 Classification of water based on dissolved compounds (Stuyfzand 1986, 1993)

(Baba et al. 2008). The Piper diagram is a graphical presentation of chemical content of water samples. Cations and anions are presented on separate triangular diagrams, then, their compositional position appears inside a diamond-shaped diagram (Brike et al. 2010). The concentrations of cations and anions are nearly the same in all studied mineral water samples; this similarity is more outstanding among anions than cations. In overall, by evaluating the concentrations of major anions and cations, and based on Piper diagram all mineral water brands are classified as Ca–Mg–HCO<sub>3</sub> type (Fig. 4).

Electrical conductivity (EC) and TDS are two important parameters frequently used to clarify prominent differences between mineral waters (Van der Aa 2003). So, to gain a correct insight about the natural variations in mineral concentrations of mineral water samples under study, they are classified according to EC and TDS (Table 5). As reported in Table 4, the TDS values of all mineral water brands fall in the range of 50–500 mg/l. These low values may suggest that groundwater has gone through a relatively short distance, before being bottled as mineral water. The EC values for all mineral water samples fall in the range of 77–769  $\mu$ S/cm. Therefore, according to Van der Aa (2003) classification, all mineral water brands are classified as "low mineral concentration" type (Table 5).

In Stuyfzand (1986, 1993) classification, water types are classified into 6 classes based on chloride concentration, and into 4 classes based on the amount of dissolved compounds (Tables 6, 7). Considering the chloride values reported for mineral water brands (Table 4), codes 2, 3,4,6 and 10 are classified as "very oligohaline", codes 1, 5, 7 and 9 as "oligohaline", and code 8 as "fresh" types based on Stuyfzand (1986, 1993) classification. In this classification, "very oligohaline", "oligohaline", and "fresh" water types have "very low" to "low mineral concentration" (Table 7).

# Comparison with national and international standards

Severe regulations have been innovated for maximum allowed concentration of certain parameters in mineral water during last two decades. In different countries, different government officials are responsible for maintaining the health of the people through determining allowed concentrations for given parameters in tap and mineral waters (Birke et al. 2010). Iranian government has also executed some standards to protect consumers, to maintain individual and public health and safety, to attain confidence regarding the quality of products, and to observe the environmental and economic considerations. Among these standards is the natural mineral water standard (Institute of standards and industrial research of Iran 2011) which was prepared in 1985. Moreover, to prevent potential risks regarding high concentration of trace elements in mineral water and to protect public health, international standards were innovated by World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) (Birke et al. 2010). The allowed levels according to national and international standards for major and trace elements, and physical parameters in mineral water are given in Table 8. Since the organic contaminants have not been tested in this study, they are not considered in Table 8.

The permitted levels are defined for elements that are essential and nontoxic, but there is no allowed level for elements whose biological role is unknown or are very toxic (e.g., Ag, Mo, Br and V) (Brike et al. 2010). The reason suggested by WHO for the fact that allowed levels have not been published for such elements is that their concentration is extremely low in drinking water and it is not anxious for health. For example, the concentration of Mo in drinking water is commonly less than 0.01 mg/l. Molybdenum is considered as an essential element and it has been estimated that adults need 0.1–0.3 mg Mo daily, while it occurs in very low concentrations in drinking water in levels that is harmful for health (WHO 2011).

As it can be seen in Table 8, there are usually obvious differences in permitted levels between national and international standards (e.g., Ba,  $F^-$ , NO<sub>2</sub>- and NO<sub>3</sub>-). In national standard for natural mineral water, and in WHO standard for drinking water no permitted levels are specified for Cl-, SO<sub>4</sub><sup>2-</sup>, Fe, Al, pH and Zn, but USEPA defines allowed levels for these elements. The values of these parameters in studied mineral water brands are in accordance with USEPA standard. The concentrations of F<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, As, B, Ba, Cr, Hg, Sb, Se and Cu in analyzed

Table 8 Concen	trations of 1	major ai	nd tra	ice eleme	nts, an	d physic	al para	neters	ın natı	ional a	nd interr	lational	standar	ds tor m	ineral wa	ter (units	of param	eters as 11	n Table	(7		
Standards	Al	$\mathbf{As}$	В	Cd	$CI^-$	CN	Cr	Cu	$\mathbf{F}^{-}$	Fe	Hg	Mn	Ni	$NO_2^-$	$NO_3^-$	Pb	Hd	Sb	Se	$\mathrm{SO}_4^{2-}$	Zn	U
Iranian standard		0.01	5	0.003		0.07	0.05	1	4		0.001	0.4	0.02	0.1	20	0.01		0.005	0.01			
WHO (2011)		0.01		0.003			0.05	7	1.5		0.006		0.07	3	50	0.01		0.02	0.04			0.03
USEPA (2003)	0.05-0.2	0.01		0.005	250		0.1	1.3	4	0.3	0.002	0.05		1	10	0.015	6.5-8.5	0.006	0.05	250	5	0.03

samples are in acceptable ranges of national and international standards. The amount of Ni is <0.05 mg/l in all studied brands, so it cannot be compared with Iranian standard (0.02 mg/l), but it is in accordance with WHO. In USEPA standard, no allowed level is defined for this element. The amounts of Mn in mineral waters are in accordance with Iranian standard, while international standards do not consider a level for it. The U values in samples agree with WHO and USEPA standards, but the Iranian standard does not report a permitted level for this element. The amounts of CN in studied samples are in agreement with Iranian standard. The international standards do not define an allowed level for CN. Since the values of Pb and Cd are below detection limits, they cannot be compared with national and international standards.

All analyzed mineral water samples were packed in plastic bottles. Shotyk et al. (2006) showed that the higher amounts of Sb in plastic bottles are caused dominantly by leaching of elements from plastic bottles. In spite of plastic packing for the analyzed samples, the amounts of Sb in mineral waters do not exceed the allowed levels specified by national and international standards.

The levels of nitrate and NO<sub>2</sub><sup>-</sup> (nitrite) are important criteria in quality assessment of water. Comparing the results (Table 4) with standards (Table 8), it is found that two brand codes 6 and 7 have higher nitrate concentrations than Iranian standard. On the other hand, three brand codes 1, 6 and 7 have high nitrate concentrations compared to USEPA standard. Nevertheless, the amounts of nitrate in all samples agree with WHO standard. Nitrite values in all brands are in accordance with national and international standards. Since the  $\sum$ (nitrate + nitrite) value should not exceed 20 mg/l according to Iranian national standard for natural mineral water, the  $\sum$ (nitrate + nitrite) values in brand codes 1, 6 and 7 is greater than this permitted level. The nitrate ions are not directly toxic, but they are converted by nitrate reductase bacteria to harmful nitrite ions (Bories and Bories 1995). Methaemoglobinaemia in human is the result of reaction between nitrite and hemoglobin in red globules in the form of methaemoglobin that sticks to oxygen, preventing oxygen transport in blood. Moreover, nitrate is converted to nitrite, reacting with amines to produce nitrosamine that is a carcinogenic agent (WHO 2011).

## Comparison between analyzed results and values on bottle's label

According to Iranian national standard for packed natural mineral water, the data which have to be labeled on each bottle include name, product type (gas-containing or gasfree), name and geographic location of natural mineral water spring, name, complete address and trade mark of



Fig. 5 Comparison between analyzed chemical composition and values on bottle's label for mineral water brands

producer, and a table giving the values of chemical compounds present in the natural mineral water. Furthermore, volume of bottle, number of manufacture permit, permanent duration, and keeping conditions (temperature and light) also should be cited on bottle. The least chemical compounds whose values should be indicated on bottle include calcium, magnesium, fluoride, chloride, nitrate and nitrite in mg/l, total hardness (TH) in mg/l CaCO3, TDS and pH.

The amounts of calcium, magnesium, chloride and nitrate were cited on all mineral water brands. Except for brand codes 5 and 10, the amounts of pH and fluoride were indicated on other brands. The values of nitrite are not cited on brand codes 5, 6, 8 and 10. The mineral water codes 2, 3, 6 and 8, and 2, 3, 8 and 9 have not labeled amounts of TH and TDS, respectively. Because the values for chloride and fluoride in some brands are below detection limits, they cannot be compared with labeled amounts on bottles. So, only the amounts of calcium, magnesium, nitrate and pH are compared with labeled values (Fig. 5). As Fig. 5 shows, the analyzed values for these parameters differ considerably from those on bottle's label. The difference is more outstanding for nitrate, which a permitted level is defined for it in national and international standards.

#### Conclusions

The analyzed mineral water brands represent differences in their chemical compositions. These differences reflect the effect of aquifer lithology on the chemistry of water. The most important agent for increasing TDS in groundwater from which mineral waters are produced is carbonate dissolution. The low values of TDS in studied mineral waters may suggest that groundwater has gone through a relatively short distance, before being bottled as mineral water. No relation was found between the high amount of nitrate in some brands and geological factors. The excess levels of nitrate are produced possibly by human activities, especially the use of nitrate-bearing fertilizers.

Based on Piper diagram, all mineral water brands are classified as  $Ca-Mg-HCO_3$  type. According to Van der Aa's classification, all mineral water brands are classified as "low mineral concentration" type. The studied mineral water brands are classified based on Stuyfzand's classification as "very oligohaline", "oligohaline", and "fresh" water types with "very low" to "low mineral concentration".

Comparison between chemical composition of studied mineral water brands with national and international

standards show that two brand codes 6 and 7 have higher nitrate concentrations than Iranian standard. Three brand codes 1, 6 and 7 have nitrate concentrations in excess of USEPA standard. The amounts of nitrate in all samples agree with WHO standard. Nitrite values in all brands are in accordance with national and international standards. The  $\sum$ (nitrate + nitrite) values in brand codes 1, 6 and 7 is greater than the allowed level according to Iranian national standard. The analyzed values in mineral water brands differ considerably from those on bottle's label.

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