Cüneyt Güler
Musa Alpaslan

Mersin Üniversitesi, Çiftlikköy Kampüsü, Jeoloji Mühendisligi Bölümü, Mersin, Turkey

Research Article

Chemical Characterization of Carbonated Natural Mineral Waters Produced in Turkey: Compliance with European Water Quality Standards

In this study, a total of 100 samples from 25 brands of carbonated natural mineral waters (CNMWs) produced in Turkey were analyzed for a total of 36 water quality constituents to determine their suitability for human consumption. Parameters examined include pH, electrical conductivity, ammonia, nitrate, nitrite, sulfate, sulfite, orthophosphate, chloride, fluoride, bicarbonate, and 25 major/trace elements analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The presence of these constituents in this type of water was investigated considering recent concerns about their quality and the lack of trace element information on the manufacturer labels. The analytical results obtained in this study were compared to the European Union (EU) norms, labeled values on bottles, as well as values from the literature. Results of this study have shown that Turkish CNMWs may contain high concentrations of sulfite, which is a known allergen, especially for chronic asthmatic population. CNMWs surveyed in this study have also appreciable amounts of fluoride ($>1.5\ mg\ L^{-1}$) that may have detrimental effects on health of children. The EU standards for As, Ba, Mn, and Ni were exceeded in seven CNMWs classified as ''high mineral''. Compared to similar type of bottled waters from Europe and North America, CNMWs from Turkey generally contained higher elemental concentrations.

Keywords: Bottled water; Carbonated natural mineral water; ICP-MS; Trace elements; Water quality

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1 Introduction

Carbonated natural mineral water (CNMW) is consumed for many different reasons; however, there is much debate about its health effects [1, 2]. In Turkey, this type of water is perceived as a commodity having beneficial medicinal and therapeutic effects. It is mainly used or promoted as a curative drink for stomach, intestine, and cardiovascular diseases, osteoporosis and kidney stone [3] and believed to be a strong supporter to diet as it contains zero calories. Apart from the use of CNMW as drinking water, it has also found a wide usage as ingredient in food/drink recipes and skin care/cosmetic products world-wide. However, drinking large volumes of CNMW may have some adverse health effects [4] since they can naturally contain high concentrations of various potentially toxic elements [2]. At elevated concentrations some elements can be harmful to health and can cause morphological abnormalities, mutagenic effects, certain types of cancers, and increased mortality in humans [5]. As far as toxicity is concerned, children are at higher risk due to greater gastrointestinal absorption and a lower threshold for adverse effects [6, 7]. Literature reveals that the levels of some water quality constituents in bottled drinking waters and CNMWs are in violation of standards for various parameters, especially some toxic trace elements [8–12]. Recently, several newspaper articles have also raised doubts about the quality of CNMWs in Turkey and some of the brands are blaimed to contain high concentrations of various toxic constituents (*e.g.*, arsenic and nitrite). Considering these recent concerns and lack of reliable relevant data on manufacturer labels, the main aims of this study are to (1) analyze commonly available 25 CNMW brands produced in Turkey for various water quality constituents and (2) compare the findings of this study to limits specified in EU legislation (Council Directive 80/777/EEC) and to values reported on labels and in the literature.

Turkey is geographically located on the ''Alpine-Himalayan orogenic belt'', which is characterized by a relatively young magmatism/volcanism and continuing tectonic activities. These geological activities have resulted in the formation of numerous cold and hot water springs with varying chemical compositions [13]. There are 224 cold mineral water springs in Turkey with an estimated total yield of 63×10^6 L/day [14]. Many of them contain CO_2 gas naturally. However, at present only 1% of the total resource or 30 of these springs are utilized by the bottled mineral water industry. The springs and production plants are mostly located close to the population centers in the western part of Turkey (Fig. 1). Based on the 2001 and 2007 production data, the mean annual consumption rates for CNMWs were 2.2 and 6.0 L per capita per year, respectively (www.masuder.org.tr). These figures are still very low when compared to the eastern European rates [15], but emphasizes the possibility of higher consumption rates in the future.

Correspondence: Dr. C. Güler, Mersin Üniversitesi, Çiftlikköy Kampüsü, Jeoloji Mühendisliği Bölümü, 33343 Mersin, Turkey
E-mail: cuneytguler@gmail.com

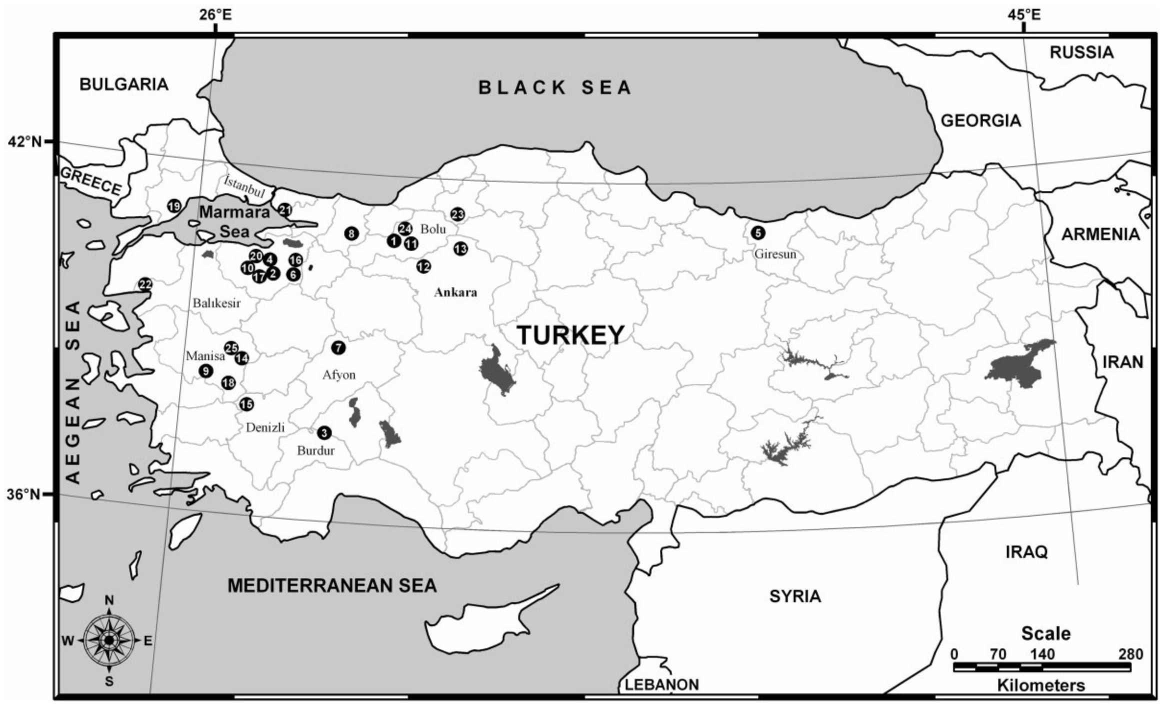

Figure 1. Location of springs and wells used for bottling CNMWs in Turkey.

In Turkey, ''natural mineral waters'' are regulated by the Ministry of Health General Directorate of Primary Health Care according to rules laid down in the legislation No. 25657 [16], which became fully enforced in December 2007. As a result, the Turkish legislation became thoroughly harmonized with the European Union (EU) norms in force (*i.e.*, Council Directive 80/777/EEC) concerning the exploitation and marketing of natural mineral waters [17]. According to legislation, natural mineral water is an extremely specific product bound to strict criteria. It is microbiologically wholesome underground water, protected from all risk of pollution and characterized by a constant level of minerals and trace elements [16, 17]. This water cannot be treated, nor added to it any exogenous elements, except for CO_2 gas. The only treatment allowed prior to bottling is the removal of unstable components, such as iron, manganese, sulfides, and arsenic [16, 17]. Both Turkish and EU legislations distinguish three kinds of carbonated mineral water: (1) Naturally CNMW, (2) natural mineral water fortified with gas from the spring, and (3) CNMW. In the present study no such distinction was made and all the surveyed mineral water brands are known to contain CO_2 gas either from natural or other sources.

2 Materials and methods

2.1 Sample collection and preparation

In 2008, four samples from 25 brands (a total of 100 samples) of CNMWs were purchased from supermarkets located in different cities of Turkey (Fig. 1). Sampling of bottled water ''from the shelf'' was preferred because it was our intention to get a realistic estimate of the ingestion amounts of different elements for the consumer. To keep the brand names anonymous, they were given a numerical code from 1 to 25 and an alphabetic code from A to D for the samples of the same brand. Labels on the bottles and production licenses were used as a source of basic information on a particular brand. All CNMWs were in dark green-colored glass bottles (0.2 L) with metal caps, except brand 21, which was in a transparent polyethylene terephthalate (PET) bottle (1.5 L) with plastic screw cap. After the collection of samples, they were transported to the laboratory, where they were stored in their original bottles under refrigeration at 4°C in the dark until analysis. Prior to analysis, bottle caps were opened by the analyst in the laboratory and then a 100-mL aliquot was aseptically removed from each bottle for anion analyses. The aliquots were placed in sterile factory-new high-density polyethene containers, which were carefully rinsed several times with the sample water. For ICP-MS analysis, 1 mL of subsample was directly pipetted from each original bottle into ICP-MS vials and diluted five-fold (with ultrapure water containing 1% v/v Merck Suprapur nitric acid) to reduce the high concentrations of major elements, to avoid clogging of the cones, and to reduce the amount of dissolved CO_2 in the samples. All CNMW samples were allowed to de-gas CO_2 prior to analyses (using sonication), since high concentrations of dissolved inorganic carbon in water may lead to erroneous ICP-MS measurements for certain elements [9, 18, 19]. All analyses were completed within 1 day after opening the bottles.

2.2 Analytical procedures

All analyses were carried out in the Environmental Geochemistry Laboratory at the Mersin University Geological Engineering Department, Mersin, Turkey. Four bottles per brand name were collected and analyzed separately for various physicochemical parameters and mean values were reported. Measurements of pH and electrical conductivity (EC) were made in the laboratory using temperature-compensated WTW Multi 340i/SET (Wissenschaftlich-Technische Werkstätten, Germany) multi-parameter instrument. For the pH measurements the electrode was calibrated against

Table 1. Water quality parameters and analytical methods used during the study.

Parameter or analyte	Unit	Analytical method	Instrument
Electrical conductivity (EC)	$\mu S\,cm^{-1}$	TetraCon 325 graphite probe	WTW Multi 340i/SET
pH	Standard	Sentix 41-3 glass pH probe	WTW Multi 340i/SET
Ammonia (NH_4^+)	$mg\,L^{-1}$	Salicylate method	Spectrophotometer [a]
Nitrate (NO_3^-)	$mg\,L^{-1}$	Cadmium reduction method	Spectrophotometer [a]
Nitrite (NO_2^-)	$mg\,L^{-1}$	Diazotization method	Spectrophotometer [a]
Sulfate (SO_4^{2-})	$mg\,L^{-1}$	Barium sulfate turbidity	Spectrophotometer [a]
Sulfite (SO_3^{2-})	$mg\,L^{-1}$	Colorimetric method	Spectrophotometer [a]
Orthophosphate (PO_4^{3-})	$mg\,L^{-1}$	Ascorbic acid method	Spectrophotometer [a]
Chloride (Cl^-)	$mg\,L^{-1}$	Mercuric thiocyanate method	Spectrophotometer [a]
Fluoride (F^-)	$mg\,L^{-1}$	SPADNS colorimetry	Spectrophotometer [a]
Bicarbonate (HCO_3^-)	$mg\,L^{-1}$	Titrimetric method (EPA 310.1)	Digital burette
Major elements (Ca, Mg, Na, K, Si)	$mg\,L^{-1}$	Mass spectrometry	ICP-MS (Agilent 7500ce)
Trace elements (Al, As, B, Ba, Be, Br, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V, Zn)	$\mu g\,L^{-1}$	Mass spectrometry	ICP-MS (Agilent 7500ce)

[a] Hach Lange DR 2800.

two standard pH buffer solutions of known pH values (pH 4.01 and 7.00). EC electrode was calibrated using 0.01 N KCl conductivity standard solution. The concentrations of ammonia, nitrate, nitrite, sulfate, sulfite, orthophosphate, chloride, and fluoride were determined using Hach Lange DR 2800 spectrophotometer (Hach Lange GmbH, Düsseldorf, Germany) (Tab. 1). Bicarbonate was determined in the laboratory by titration according to EPA 310.1. Analyses for total concentrations of five major and 20 trace elements (Tab. 1) in the samples were carried out (in separate batches) by Agilent 7500ce ICP-MS (Agilent Technologies, Tokyo, Japan) equipped with a collusion/reaction cell in the form of Octopole Reaction System to minimize polyatomic interferences. The external standard calibration method was applied to all determinations, using ^{6}Li, Sc, Ge, Y, In, Tb, and Bi internal standard mix. Five-point calibration curves were constructed by analyzing NIST single-element reference standards prepared by serial dilution of stock solutions. The ultrapure water used throughout the period of experimentation had a resistivity of 18 MΩ cm at room temperature.

2.3 Determination of precision and accuracy

The precision and accuracy of the analytical technique were evaluated by analyzing a certified standard reference material, CWW-TM-B, Certified Waste Water Trace Metals Solution (B) (High-Purity Standards, Charleston, SC, USA). The relative error (%RE) is less than ±5% for most of the elements (Tab. 2). Precision of the instrument was determined by introducing the same quantity of one sample seven times, then the relative standard deviations (RSD) were calculated for each element (%RSDs are between 0.66 and 2.78). Additionally, after every ten samples, a standard was analyzed as

Table 2. Accuracy and precision of the ICP-MS analysis results for the certified reference material (CWW-TM-B) and detection limit (DL) for the investigated elements (in $\mu g\,L^{-1}$).

Element	Isotope [a]	Measured values ($n = 7$)					%RSD [b]	Certified value	Acquisition mode [c]	DL [d]	%RE [e]
		Min.	Max.	Median	Mean	S.D.					
Al	27	180.30	192.50	182.00	183.86	4.25	2.31	200	No gas	0.069	−8.07
As	75	52.96	55.10	54.64	54.44	0.74	1.36	50	Helium	0.006	8.88
B	11	192.00	204.30	202.55	200.48	5.16	2.58	200	No gas	0.118	0.24
Ba	137	204.50	216.80	210.45	210.30	3.49	1.66	200	No gas	0.027	5.15
Be	9	49.18	51.48	50.56	50.50	0.63	1.24	50	No gas	0.009	1.01
Cd	111	50.80	53.72	52.84	52.56	1.04	1.98	50	No gas	0.021	5.12
Co	59	191.00	201.30	199.80	198.16	3.41	1.72	200	No gas	0.002	−0.92
Cr	52	192.40	208.10	205.80	203.44	5.66	2.78	200	Helium	0.027	1.72
Cu	63	191.80	201.70	199.65	197.86	3.73	1.88	200	Helium	0.082	−1.07
Fe	56	200.40	204.20	202.61	202.48	1.33	0.66	200	Hydrogen	0.415	1.24
Mn	55	192.80	202.60	200.80	199.40	3.17	1.59	200	No gas	0.011	−0.30
Mo	95	197.80	208.30	205.60	204.54	3.38	1.65	200	No gas	0.010	2.27
Ni	60	188.70	200.00	198.15	196.48	3.85	1.96	200	Helium	0.033	−1.76
Pb	208	203.10	215.50	210.85	210.64	3.87	1.84	200	No gas	0.021	5.32
Sb	121	50.44	53.95	52.08	52.02	1.11	2.13	50	No gas	0.004	4.05
Sr	88	192.70	198.80	197.25	196.63	2.28	1.16	200	Helium	0.006	−1.69
V	51	192.90	198.30	196.85	196.25	1.95	0.99	200	Helium	0.005	−1.88
Zn	66	204.10	214.40	212.60	211.08	4.15	1.96	200	No gas	0.073	5.54

[a] Isotopic mass of element measured during analysis.
[b] Relative standard deviation.
[c] Octopole reaction system (ORS) acquisition mode.
[d] Detection limit of the ICP-MS instrument for each isotope.
[e] Percentage relative error.

a sample. If the variation between this sample and standard concentration was more than 10%, the instrument was recalibrated. Additionally, as an independent check of the correctness of the analytical results, the percent charge balance errors (%CBE) were calculated for each CNMW sample as suggested by Freeze and Cherry [20]. Calculated charge balance errors are less than ±4.6%, with a mean value of 2.5%.

3 Results and discussion

3.1 Physical parameters and concentration of major ions

The analysis results of physical parameters and major ionic constituents of 25 CNMWs produced in Turkey are presented in Tab. 3. Results show that CNMWs are very different in character and display a wide range of parameter values. The ranges of values for the physical parameters were: 5.28–7.73 for pH, 513–5080 $\mu S\,cm^{-1}$ for EC, and 410–4835 $mg\,L^{-1}$ for total dissolved solids (TDS). The pH values of the samples were weakly acidic because of the formation of carbonic acid by the addition of CO_2. As it is seen in Tab. 3, there is a great variation in EC and TDS values of the CNMWs. These parameters also show a statistically significant correlation at $p < 0.05$ level ($r = 0.96$). CNMWs examined in this study contain major ions that range in concentrations from traces to more than several thousands of milligrams per liter (Tab. 3). The concentration ranges for the major ions were (in $mg\ L^{-1}$): 43.6–409.7 for Ca^{2+}, 16–483.2 for Mg^{2+}, 7.8–1189 for Na^+, 1.3–56.9 for K^+, 4.9–23.5 for Si, 0.01–1.33 for NH_4^+, 0.89–17.26 for NO_3^-, 0.01–0.12 for NO_2^-, 0.5–600 for SO_4^{2-}, 0.02–12.23 for SO_3^{2-}, 0.05–0.63 for PO_4^{3-}, 2.6–2452 for Cl^-, 0.02–2.34 for F^-, and 285–3150 for HCO_3^-. Table 4 shows the classification of 25 CNMWs in accordance with the EU Council Directive 80/777/EEC [17]. According to EU directive; 76% of the Turkish CNMWs classified as "high mineral" (TDS > 1500 $mg\,L^{-1}$), 20% classified as "intermediate mineral" (TDS = 1500–500 $mg\,L^{-1}$); and 4% classified as "low mineral" (TDS = 500–50 $mg\,L^{-1}$). According to EU norms, Turkish CNMWs can be further classified as containing: Bicarbonate (21 brands), sulfate (3 brands), chloride (3 brands), calcium (16 brands), magnesium (14 brands), fluoride (7 brands), and sodium (10 brands) (Tab. 4). Additionally, only three brands were found suitable for low sodium diet (containing Na $<20\,mg\,L^{-1}$) and none of the brands contained bivalent iron $>1\,mg\,L^{-1}$.

Major cation composition of Turkish CNMWs is dominated by $Ca^{2+} > Na^+ > Mg^{2+} > K^+$, whereas predominant anions in waters are $HCO_3^- > Cl^- > SO_4^{2-}$. Calcium, magnesium, sodium, potassium, silica, ammonia, sulfate, orthophosphate, chloride, and bicarbonate were detected in all CNMWs, some of them rather in high concentrations. However, no health-based standards were defined for these parameters [17]. Nevertheless, epidemiological studies suggest that calcium in drinking water may help prevent osteoporosis and magnesium may reduce the frequency of sudden death in humans [21]. Calcium also helps regulate muscle contraction, helps transmit nerve impulses, and regulates ion exchange across cell membranes

Table 3. Analysis results of physical parameters and major ionic constituents of CNMWs produced in Turkey.

Brand code	Physicochemical properties																			
	T a)	pH b)	EC c)	Ca	Mg	Na	K	Si	NH_4^+	NO_3^-	NO_2^-	SO_4^{2-}	SO_3^{2-}	PO_4^{3-}	Cl^-	F^-	HCO_3^-	TDS d)	CBE e)	Yield f)
1	14.2	6.18	3153	269.5	304.2	52.9	5.8	15.8	0.23	15.49	**0.12**	0.5	5.20	0.09	11.8	0.02	2250	2934	4.3	2.0
2	19.0	6.00	1494	173.1	75.9	154.2	26.4	12.8	0.73	1.11	0.03	29.5	2.99	0.18	66.9	1.41	1246	1799	−0.3	0.7
3	19.0	6.12	3603	150.6	483.2	100.7	10.8	22.6	0.06	6.64	0.05	600.0	4.29	0.63	18.5	0.54	2085	3486	4.6	–
4	20.0	5.78	1214	76.3	103.9	56.6	8.3	7.2	0.32	0.89	0.03	30.0	0.05	0.10	22.5	0.73	818	1128	1.7	1.5
5	10.0	5.28	513	73.1	16.0	7.8	1.3	6.4	0.16	6.42	0.01	10.0	0.02	0.09	2.9	0.08	285	410	2.7	1.0
6	18.0	6.25	3738	238.9	146.2	746.4	43.1	9.5	1.33	17.26	0.07	93.3	4.52	0.07	35.2	1.19	3150	4497	2.8	1.0
7	18.5	6.16	3663	49.1	17.8	905.6	29.8	17.4	0.52	5.53	0.02	0.5	0.04	0.09	108.5	2.34	2350	3499	3.9	5.0
8	20.0	6.29	3710	83.0	20.3	712.0	28.0	10.6	0.21	1.80	0.07	0.5	0.04	0.13	314.0	0.61	1720	2914	2.8	–
9	21.0	6.00	1629	257.5	41.2	19.8	4.1	11.0	0.14	0.89	0.02	204.0	4.12	0.06	16.5	0.41	690	1250	3.2	0.8
10	17.5	5.63	1395	131.2	68.0	170.0	17.9	6.6	1.27	3.76	0.02	4.5	6.56	0.08	91.5	1.09	1098	1607	−1.1	1.0
11	19.5	5.90	1933	409.7	37.8	28.5	3.9	5.5	0.12	4.24	0.05	0.5	9.41	0.06	2.6	0.37	1378	1884	4.1	2.0
12	18.0	5.95	2630	231.1	166.2	194.1	38.8	15.1	0.49	7.53	0.07	183.0	7.70	0.09	9.4	0.61	1725	2583	3.2	17.7
13	16.8	5.65	1719	83.1	18.8	346.1	17.7	10.4	0.49	1.55	0.03	95.5	0.08	0.57	334.0	0.81	616	1533	0.5	6.0
14	16.5	6.18	3507	300.0	149.0	471.9	56.9	13.3	0.50	5.33	0.07	0.5	5.25	0.13	134.5	0.37	2550	3694	3.8	0.9
15	17.5	5.98	900	86.8	47.7	14.8	9.5	9.6	0.14	0.89	0.01	37.4	0.08	0.09	7.0	2.25	475	692	1.5	0.6
16	–	6.26	2920	161.6	42.3	421.9	24.7	11.8	0.83	9.52	0.06	32.5	6.38	0.08	25.2	2.08	1810	2557	−0.6	1.0
17	18.5	6.13	2775	225.9	89.4	328.8	35.2	13.8	0.76	15.94	0.06	0.5	7.56	0.07	72.6	0.67	1812	2617	3.5	1.1
18	19.3	5.62	1017	84.0	72.7	57.2	6.0	7.1	0.16	0.90	0.01	102.5	0.05	0.09	14.2	0.26	585	935	4.2	1.5
19	–	6.41	3553	43.6	21.1	839.2	4.2	14.5	0.29	7.08	0.07	0.5	0.04	0.41	43.3	2.16	2245	3226	3.2	0.4
20	–	6.21	2760	206.4	74.0	330.4	37.3	23.1	0.27	2.21	0.07	3.6	1.14	0.08	63.5	0.41	1660	2403	4.2	0.8
21	19.1	7.73	5080	293.7	141.1	1189.0	29.4	6.3	0.45	0.89	0.02	393.2	12.08	0.08	2452.0	0.61	303	4835	−2.5	–
22	–	5.88	2303	347.9	44.8	191.4	20.0	12.5	0.01	4.10	0.06	113.5	10.56	0.07	34.9	0.65	1472	2260	4.2	0.6
23	20.0	6.09	2920	207.5	139.3	119.3	1.6	23.5	0.17	4.65	0.04	45.5	11.09	0.05	33.6	0.14	1473	2067	2.4	1.0
24	19.5	5.90	1939	403.8	38.3	29.5	4.2	4.9	0.13	5.90	0.05	1.0	5.94	0.06	4.2	0.41	1389	1890	3.3	2.0
25	–	5.60	1515	237.3	64.6	46.4	18.6	8.7	0.14	4.25	0.05	104.0	12.23	0.08	7.7	0.49	945	1451	3.7	–
Limits of standard g)	–	–	–	–	–	–	–	–	–	50	0.1	–	–	–	–	5	–	–		

Bold numbers indicate values exceeding limits of standards. All concentrations (except as noted below) are in $mg\,L^{-1}$.
a) Temperature in degrees Celsius (°C) measured at source spring or well.
b) pH measured in the laboratory (standard units).
c) EC measured in the laboratory ($\mu S\,cm^{-1}$).
d) TDS (calculated as sum of all ions) ($mg\,L^{-1}$).
e) Percent charge balance error (%) $= 100 \times (\sum \text{cations} - \sum \text{anions})/(\sum \text{cations} + \sum \text{anions})$.
f) Spring or well discharge ($L\,s^{-1}$).
g) Limits of standard defined in Council Directive 80/777/EEC [17].

Table 4. Classification of Turkish CNMWs in accordance with the Council Directive 80/777/EEC [17].

Mineral content	Mineral water classification	Brand code
TDS [a)] > 1500	High mineral	1, 2, 3, 6, 7, 8, 10, 11, 12, 13, 14, 16, 17, 19, 20, 21, 22, 23, 24
TDS [a)] = 1500–500	Intermediate mineral	4, 9, 15, 18, 25
TDS [a)] = 500–50	Low mineral	5
TDS [a)] < 50	Very low mineral	–
Bicarbonate >600	Containing bicarbonate	1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 16, 17, 19, 20, 22, 23, 24, 25
Sulfate >200	Containing sulfate	3, 9, 21
Chloride >200	Containing chloride	8, 13, 21
Calcium >150	Containing calcium	1, 2, 3, 6, 9, 11, 12, 14, 16, 17, 20, 21, 22, 23, 24, 25
Magnesium >50	Containing magnesium	1, 2, 3, 4, 6, 10, 12, 14, 17, 18, 20, 21, 23, 25
Bivalent iron >1	Containing iron	–
Fluoride >1	Containing fluoride	2, 6, 7, 10, 15, 16, 19
Sodium >200	Containing sodium	6, 7, 8, 13, 14, 16, 17, 19, 20, 21
Sodium <20	Suitable for low sodium diet	5, 9, 15

[a)] TDS = total dissolved solids. All concentrations are in $mg\,L^{-1}$.

[21]. Most of the CNMWs surveyed in this study contain very high concentrations of sodium (Tab. 3). Previous studies have shown that excess sodium in the diet may increase the risk of high blood pressure (hypertension) and cardiovascular disease [22]. Several CNMWs (brands 1, 7, 8, 10, 11, 14, 17, 19, 20, and 24) are distinguished from others by their low sulfate (SO_4^{2-}) concentrations (<5 $mg\,L^{-1}$). Labeled sulfate values of these brands range between 5.35 and 31.90 $mg\,L^{-1}$, which are significantly higher than the measured values. The difference between measured and labeled values may be attributable to bacterial reduction of sulfate during storage. Sulfate is generally regarded as a harmless constituent, except for its effect on taste above 250 $mg\,L^{-1}$. Among the analyzed samples in this study, brand 3 CNMW has the highest sulfate concentration (600 $mg\,L^{-1}$). The major physiological effects resulting from drinking high sulfate water are catharsis, dehydration, and gastrointestinal irritation [23]. Additionally, results of this study have shown that CNMWs contain sulfite (SO_3^{2-}) with values ranging from 0.02 to 12.23 $mg\,L^{-1}$ (Tab. 3). A high concentration of sulfite is not a common occurrence in natural waters [24]. Sulfites are often used in a wide range of foods, beverages, and pharmaceuticals as preservatives and bacterial inhibitors [25]. Sulfites are counted among the top nine food allergens in Canada (www.inspection.gc.ca/english/fssa/labeti/allerg/sulphe.pdf) and hypersensitivity to sulfites is usually found within the chronic asthmatic population [25]. The source of high sulfite concentrations in Turkish CNMWs is currently unknown and should be investigated further since Council Directive 80/777/EEC strictly prohibits the addition of any exogenous elements to these products. The maximum concentrations of NO_3^- and NO_2^- were well below their respective standards, except for brand 1, for which the standard value for NO_2^- (0.1 $mg\,L^{-1}$) was slightly exceeded (Tab. 3). CNMWs surveyed in this study have also appreciable amounts of fluoride, but none of them is above the standard value set by the EU directive (5 $mg\,L^{-1}$) (Tab. 3). Fluoride is an essential element and it plays a major role in the development of strong teeth and bones. Optimal fluoride range for human health is considered to be between 0.7 and 1.2 $mg\,L^{-1}$ [26]. However, excessive amounts of fluoride in drinking water may cause certain type of diseases including dental and skeletal fluorosis [27]. According to EU legislation, CNMWs with a fluoride concentration exceeding 1.5 $mg\,L^{-1}$ shall bear on the label the words "contains more than 1.5 $mg\,L^{-1}$ of fluoride: not suitable for regular consumption by infants and children under 7 years of age". In our study, four brands exceeded 1.5 $mg\,L^{-1}$ fluoride limit, but only one of them (brand 19) had such a warning on its label. Therefore, parents should be aware of this fact to protect the health of their children and to avoid lethal consequences. Results of this study have shown that CNMWs from Turkey generally contained much higher levels of Ca^{2+}, Mg^{2+}, Na^+, K^+, and F^- than most of the North American and European mineral waters [2, 9, 12, 28, 29]. This can be explained by the geothermal origins of the CNMWs produced in Turkey.

3.2 Concentration of trace elements

Total trace element composition of 25 CNMWs is presented in Tab. 5. The concentration range for the 20 trace elements were (in $\mu g\,L^{-1}$): 3.26–174.15 for Al, 0.03–16.93 for As, 32.1–19 000 for B, 10.14–1428.67 for Ba, trace–1.64 for Be, 12.14–10 240 for Br, trace–0.58 for Cd, trace–22.54 for Co, 0.74–17.05 for Cr, trace–18.04 for Cu, trace–31.75 for Fe, 0.38–1664 for Mn, trace–23.14 for Mo, trace–435.28 for Ni, trace–5.54 for Pb, 0.03–3.04 for Sb, 180.9–4331 for Sr, 1.93–12.22 for Ti, trace–4.21 for V, and trace–29.7 for Zn. All elements presented different variations among the minimum and maximum values. Lowest concentration ranges were observed for elements Al, Cd, Cr, Cu, Fe, Sr, Ti, and Zn. For several elements a concentration range of only a few hundred-fold (*i.e.*, As, B, Ba, Be, Br, Co, Mo, Ni, Pb, Sb, and V) to a few thousand-fold (*i.e.*, Mn) was established.

The analysis results have shown that the maximum concentrations of Al, Cd, Cr, Cu, Pb, and Sb were all well below their respective standard values (Tab. 5). Maximum Al concentrations were observed for brands 15 and 20 (174.15 and 135 $\mu g\,L^{-1}$, respectively), which are lower than the EU standard value defined (200 $\mu g\,L^{-1}$) [17]. However, recent studies suggest that a concentration of Al in drinking water above 100 $\mu g\,L^{-1}$ may be a risk factor of Alzheimer's disease [30]. Cadmium concentrations, in 21 out of 25 brands analyzed, were found to be non detectable (n.d.) and in the rest of the samples it was significantly lower than the standard value set in accordance with EU legislation (3 $\mu g\,L^{-1}$) (Tab. 5). Measured Pb and Sb concentrations in CNMWs deserve further attention because recent studies have shown that substantial amounts of both Pb and Sb can be released from commercially available glass and PET containers used for drinking waters [18, 31, 32]. PET plastic is usually made with antimony-based catalysts. Therefore, Sb concentrations in PET bottles increase over time during storage, especially when they are exposed to high temperatures [32]. Some researchers [33] have

Table 5. Trace element concentrations of Turkish CNMWs determined by ICP-MS (concentrations are in $\mu g L^{-1}$).

Brand code	Trace elements																			
	Al	As	B	Ba	Be	Br	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	Sr	Ti	V	Zn
1	3.58	0.65	474.87	692.75	0.21	20.60	0.58	22.54	16.03	1.30	21.85	264.10	n.d.	**322.70**	4.94	1.11	1078.85	9.71	2.07	19.43
2	11.23	0.88	6792.50	273.60	0.28	174.25	0.34	0.70	2.05	n.d.	17.50	114.66	1.93	5.95	1.29	0.42	697.90	6.98	0.99	9.55
3	3.26	0.29	786.00	25.79	0.01	86.24	n.d.	0.68	3.05	1.24	13.44	206.07	1.73	7.89	1.37	0.24	1495.00	12.10	1.13	13.12
4	27.82	1.69	1976.00	156.43	0.05	67.29	n.d.	0.74	3.97	n.d.	9.08	107.13	7.37	10.32	1.08	0.17	408.77	4.25	0.44	5.88
5	22.72	0.03	32.11	10.14	n.d.	12.14	n.d.	0.25	1.55	n.d.	n.d.	32.33	0.20	1.88	0.65	0.09	180.93	3.38	0.44	8.58
6	22.49	2.49	6152.25	94.68	0.47	152.00	n.d.	2.03	2.16	n.d.	n.d.	364.03	0.26	11.86	2.14	0.07	3181.00	6.44	0.35	17.53
7	12.02	8.66	11910.00	37.98	0.91	242.57	n.d.	0.11	1.29	n.d.	n.d.	60.56	0.09	n.d.	0.76	0.10	440.93	10.02	3.01	4.74
8	21.45	1.24	19000.00	**1281.00**	1.64	568.40	n.d.	n.d.	3.76	18.04	11.49	29.59	4.01	1.58	3.31	2.52	2369.00	5.33	3.46	29.70
9	19.63	3.46	82.20	63.20	n.d.	18.40	n.d.	0.50	14.27	n.d.	n.d.	3.57	3.50	1.99	2.89	0.19	807.50	1.93	0.42	8.77
10	13.98	0.71	4748.50	343.23	0.44	136.15	n.d.	0.51	4.42	n.d.	4.97	54.06	0.43	5.65	0.87	0.20	1697.33	5.15	0.92	6.22
11	25.95	2.99	489.60	623.60	n.d.	29.97	n.d.	1.12	4.16	n.d.	5.20	0.38	n.d.	9.51	0.87	0.09	1600.25	3.75	0.03	5.43
12	10.03	2.78	1664.67	83.72	0.18	77.12	n.d.	0.60	3.34	1.35	22.02	**540.75**	6.05	3.77	0.62	0.04	1568.25	7.97	0.54	1.68
13	22.18	**16.93**	6181.33	20.20	n.d.	230.07	n.d.	0.11	2.84	0.70	31.75	1.52	3.08	1.28	0.76	0.34	1328.67	5.55	1.43	12.27
14	45.62	0.90	2891.33	397.60	0.39	395.47	n.d.	0.85	10.05	n.d.	11.92	186.63	2.01	**435.28**	0.04	0.10	1707.00	8.84	1.60	n.d.
15	174.15	1.37	118.35	76.99	1.46	63.23	n.d.	n.d.	17.00	13.26	8.02	6.20	13.41	2.25	2.51	2.61	494.30	4.30	n.d.	6.93
16	14.02	0.85	5758.00	170.83	0.07	143.47	0.16	0.35	0.74	14.06	1.70	34.22	n.d.	3.42	1.24	0.10	1943.00	5.07	0.48	11.63
17	10.08	0.93	7736.33	**1428.67**	n.d.	244.87	n.d.	0.64	2.66	3.40	n.d.	67.42	n.d.	5.42	0.82	0.05	4331.00	5.61	0.45	4.06
18	15.44	0.42	4219.50	99.18	0.02	74.95	n.d.	0.44	13.99	0.31	8.90	79.01	n.d.	5.05	0.67	0.13	306.30	4.27	0.27	2.41
19	23.45	0.39	2628.67	267.40	n.d.	223.00	n.d.	0.21	1.81	0.59	1.31	234.03	0.22	1.08	0.37	0.09	808.00	7.17	1.18	n.d.
20	135.00	1.37	102.40	83.73	1.45	60.33	n.d.	n.d.	17.05	12.80	8.83	3.02	23.14	2.04	2.39	2.54	521.30	4.40	n.d.	5.80
21	8.63	1.70	532.90	47.74	1.39	10240.00	n.d.	0.06	13.60	n.d.	5.15	0.69	3.75	11.42	2.41	3.04	3178.00	3.64	4.21	1.91
22	19.72	0.20	4256.00	64.63	0.08	241.90	n.d.	5.19	2.56	1.02	3.41	**1664.00**	n.d.	12.97	0.95	0.03	959.73	7.28	0.78	10.42
23	10.64	0.37	6658.33	20.19	n.d.	209.53	0.47	0.85	1.91	4.68	1.23	228.97	n.d.	4.19	4.57	0.04	773.83	12.22	0.34	17.76
24	27.38	1.41	500.60	585.77	n.d.	32.50	n.d.	1.08	2.16	1.12	n.d.	1.09	n.d.	9.21	n.d.	0.09	1630.67	3.24	0.03	11.66
25	14.23	0.09	302.85	107.33	n.d.	48.99	n.d.	0.56	2.25	0.24	n.d.	2.86	n.d.	8.99	5.54	0.13	1355.33	5.56	0.04	11.94
Limits of Standard [a]	200	10	–	1000	–	–	3	–	50	1000	–	500	–	20	10	5	–	–	–	–

Bold numbers indicate values exceeding limits of standards.
[a] Limits of standard defined in Council Directive 80/777/EEC [17].
n.d. = not detected or values below ICP-MS detection limits.

also demonstrated that in glass containers significant concentrations of Co, Fe, Sb, and Zn can be found. Sb concentrations measured in Turkish CNMWs range between 0.03–3.04 $\mu g L^{-1}$ (Tab. 5). Highest Sb and V concentrations were observed for the only PET sample in this study (brand 21). High concentration of Sb in brand 21 may be attributable to leaching of Sb from the container material (PET), but this result needs further testing. However, very low concentrations of Co (0.06 $\mu g L^{-1}$) and Zn (1.91 $\mu g L^{-1}$) in brand 21 (PET container) and higher concentrations of these elements in other brands (glass containers) (Tab. 5) may be accepted as an evidence for leaching of Sb from PET container and Co plus Zn from glass container types. Although the measured concentrations of Pb and Sb are generally well below the standard values set by the EU directive, the data from the literature suggest that concentrations may increase with increased storage time and temperatures [32]. Both Pb and Sb are particularly well known because of their acute toxicity for human health.

B, Be, Br, Co, Fe, Mo, Sr, Ti, V, and Zn were also detected in most of the CNMWs, some of them being in rather high concentrations (Tab. 5). Remarkably high concentrations were found for B (in brand 8:19 000 $\mu g L^{-1}$), Br (in brand 21:10 240 $\mu g L^{-1}$), Co (in brand 1:22.54 $\mu g L^{-1}$), Mo (in brand 20:23.14 $\mu g L^{-1}$), and Sr (in brand 17:4331 $\mu g L^{-1}$). Analytical results for these trace elements cannot be evaluated, since no health-based standard values were available for those elements in the EU directive [17]. The reason for that is there are no suitable oral data on which a toxicologically supportable guideline value could be based. However, Mo is considered to be an essential element, with an estimated daily requirement of 0.1–0.3 mg for adults [34].

During the bottling process, CNMWs are generally subjected to ozonation processes in order to remove unstable components, such as iron, manganese, sulfides, and arsenic. Conditions for using ozone-enriched air for the treatment of CNMWs are laid down in EU directive 2003/40/EC [35]. However, if the source water contains high concentrations of halides (*e.g.*, Cl and Br), during the ozonation, several by-products such as bromate and haloacetic acids (HAAs) may be produced. Bromate has been judged by both WHO and EPA [www.who.int/water_sanitation_health/dwq/guidelines3rd/en; www.epa.gov/safewater/mcl.html] as a potential carcinogen even at sub microgram levels. HAAs, especially dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were also found to be animal carcinogenic at low concentration [36, 37]. Turkish CNMWs contain substantial amounts of Cl and Br, but ozonation by-products are never reported on the product labels.

The standard values for four trace elements (As, Ba, Mn, and Ni) were exceeded at least once in seven CNMWs (brands 1, 8, 12, 13, 14, 17, and 22) classified as "high mineral" (TDS values range between 1533 and 3694 $mg L^{-1}$) (Tab. 5). Special attention should be paid to As, since measured arsenic concentration in one CNMW (brand 13: 16.93 $\mu g L^{-1}$) was almost twice the standard value set by EU directive [17]. In addition, in brand 7, measured As concentration was 8.66 $\mu g L^{-1}$, very close to standard value for As (10 $\mu g L^{-1}$) [17]. Arsenic is naturally introduced into water by dissolution of minerals and by the percolation of groundwater through arsenic-enriched rocks. High concentrations of arsenic in water could pose a risk to individuals who consume those CNMWs on a regular basis. Arsenic is a highly toxic element and epidemiological studies had shown that chronic arsenic consumption is generally associated with increased risk of various forms of cancer in humans [38, 39]. CNMWs analyzed in this study also contain substantial amounts of Ba (Tab. 5). The highest Ba concentrations were measured in brands 8 and 17 (1281 and 1429 $\mu g L^{-1}$, respectively), exceeding the standard value defined in the EU directive (1000 $\mu g\,L^{-1}$) [17]. The greatest concern for high Ba concentrations in water appears to be its potential to cause hypertension [40]. Mn concentration in two CNMWs (brands 12 and 22:540.75 and 1664 $\mu g\,L^{-1}$, respectively) exceeded the standard value established by EU directive (500 $\mu g\,L^{-1}$) (Tab. 5). Mn is an essential element for humans and adverse effects can result from both deficiency and overexposure. Available information on its effects on health is limited but epidemiological studies suggest that adverse neurological problems may occur following long-term exposure to very high Mn levels in drinking water [23, 41, 42]. Two CNMWs surveyed in this study (brands 1 and 14) showed extremely high Ni concentrations (322.70 and 435.28 $\mu g\,L^{-1}$, respectively), greatly exceeding (16–21 times) the standard value defined (20 $\mu g\,L^{-1}$) (Tab. 5). Even though, inhaled Ni compounds are known to be carcinogenic to humans, there is lack of evidence of a carcinogenic risk from oral exposure to nickel [43]. Results of this study have shown that CNMWs from Turkey generally contained higher levels of trace elements (*e.g.*, Al, As, B, Ba, Cr, Mn, Ni, Pb, Sb, Sr, Ti, and V) than the great majority of the European and North American mineral waters analyzed in recent studies [9, 12, 44, 45].

3.3 Comparison of measured vs. labeled values

Comparison of the study results with the reported label values for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Si, NH_4^+, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, Cl^-, F^-, HCO_3^-, Al, and Fe were made in Fig. 2. For the purposes of constructing Box and Whisker plots and calculating median concentration values, data below analytical detection limits were set to a value of half the detection limit [46]. In this figure, median values are indicated with a line inside the box, lower and upper quartiles (25 and 75%) with lower and upper borders of the box, minimum and maximum values, marked as the end of the whiskers, outliers are plotted as circles. As can be seen in Fig. 2, no analytical results were reported on the bottle labels for the parameters SO_3^{2-}, As, B, Ba, Be, Br, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V, and Zn. Hence, for these parameters no comparison can be made. The label on each brand contained different information. The number and type of parameters reported on the labels of Turkish bottled water showed a lack of homogeneity. For instance, only 16 brands displayed PO_4^{3-} concentrations, but Ca and Mg concentrations were consistently reported for all 25 brands (Fig. 2). Comparison of the values indicated on the bottle labels for 15 elements with our analytical results has shown that labeled and analyzed values are surprisingly well comparable for most of the parameters. For instance, correlation analysis results have shown that statistically significant (at $p < 0.05$ level) correlations (r) exist between the labeled and analytical values of Ca^{2+} (0.69), Na^+ (0.79), K^+ (0.80), Cl^- (0.86), SO_4^{2-} (0.98), HCO_3^- (0.85), NO_3^- (0.81), and NH_4^+ (0.82). For the rest of the parameters, especially for Al and Fe, no significant correlations were present. Median concentrations of labeled and measured values are relatively close for the major species, but they are generally higher than the values reported on the bottle labels (Fig. 2). Nevertheless, a similar trend was not observed for Si and PO_4^{3-}, where comparison of labeled and analytical values revealed no relationship between the two. In brand 1, the magnesium content was found to be about six times the value stated on the bottle and while sodium content of brand 15 was almost seven times the measured value. In general, the amount of anions (*e.g.*, Cl^-, SO_4^{2-}, HCO_3^-, and PO_4^{3-}) was slightly lower than the concentration values claimed by the manufacturers, whereas for F^-, NO_3^-, NO_2^-, and NH_4^+ the same cannot be said.

The variations in chemical composition of bottled waters may be due to seasonal variation in source water quality or may be due to the fact that the waters are subjected to several processes before bottling (*e.g.*, ozonation and removal and addition of certain elements). These processes are not indicated on the bottle labels. Additional changes to water chemistries can occur during the storage of the bottles such as (co)precipitation and transformation of constituents or leaching of some constituents from the bottle material itself. Another reason for the observed changes may be due to accuracy, precision, or detection limits of the employed analytical methods/instruments used. Furthermore, information reported on the bottle labels is simply based on analysis results obtained several years (even decades) ago, during which significant changes may have occurred in the source water chemical compo-

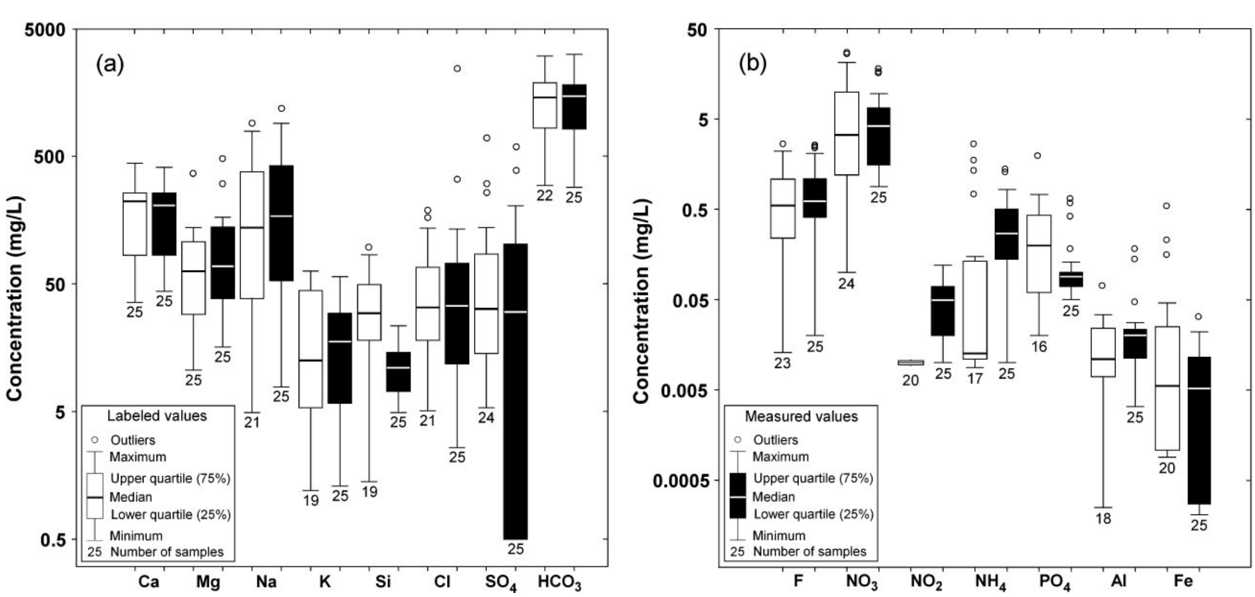

Figure 2. Box and Whisker plot comparison of the major and trace element data observed in the 25 CNMW brands from Turkey.

sition. The abnormal differences between measured and labeled values can be due to simply a typographic error on labels (*e.g.*, wrong decimal places or reporting units). Whatever the reason for the change, the results have shown that there can be a significant difference between labeled and measured values, which is even more pronounced for the trace element data.

4 Conclusions

In Turkey, CNMW consumption is still very low, especially when compared to European countries (*e.g.*, Italy and Germany). But its consumption shows an upward trend owing to successful advertising campaigns, urban people's attitude toward a healthy life style and fitness, and introduction of fruit flavored varieties in 2002. In Turkey, mineral water sources used for bottling are mostly located close to geothermal regions. Because of that they contain rather high concentrations of major and trace elements. This type of water is traditionally believed to have some beneficial medicinal and therapeutic effects for a wide range of ailments. This study demonstrates that there is a great variability in major and trace element concentrations of 25 Turkish CNMW brands, some of these surpassing the values reported in the literature for similar water types from the Europe and North America. While the majority of inorganic chemicals are below standard limits set by EU mineral water directive, measured As, Ba, Mn, and Ni concentrations were exceeded in seven CNMW brands. Especially, in two CNMW brands, Ni concentrations greatly exceeded (16 and 21 times) the standard value defined in the EU directive and therefore they should be strictly monitored in the future due to high toxicity of Ni in the environment. Additionally, 22 out of 25 brands analyzed had Na concentrations higher than $20\,mg\,L^{-1}$, therefore not suitable for people having hypertension and sodium-restricted diets. Moreover, four surveyed brands exceeded $1.5\,mg\,L^{-1}$ fluoride limit, but only one of them had a warning on its label cautioning children under 7 years of age for the high fluoride content. Consumption of water having high concentrations of these elements may have serious health consequences, even for healthy population. In some Turkish CNMWs high sulfite concentrations were detected, which may cause mild to severe allergy-like symptoms, especially for the people with chronic asthma. More importantly, for most of the major and trace elements surveyed in this study, no health-based standard limits exist to protect humans from possible adverse effects. It is suggested that bottled water consumers, especially those who consume this type of water regularly and in large amounts should be aware of these facts when choosing their favorite brands. The results of this study suggest that there is a need for a stricter monitoring of the quality of the bottled CNMWs by the government authorities in order to prevent health hazards for the consumer. Future studies about commercially available Turkish CNMWs should focus on testing other hazardous substances not tested in this study (*e.g.*, organic compounds, radioactive elements, and ozonation by-products) and as well as their microbiologic quality.

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