Hydrogeochemical approach to estimate the quality of bottled waters in Serbia

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Abstract

Bottled waters were analyzed for different chemical parameters and activity concentrations of radionuclides. The hydrocarbonate ion was dominant in all samples, while the major cation composition was a combination of Ca–Mg–Na ions. Physicochemical properties of bottled water samples are influenced by underlying geology. The sum of trace element concentrations varied from 79.7 to 9349.7 µg/l. The dietary reference intake (DRI) system was applied and contributions of some essential elements were calculated according to age group and gender. Hierarchical cluster analysis (HCA) grouped bottled water samples into four clusters based on the similarities of the groundwater quality and essential elements concentrations. The origin of radioactivity is natural and could be traced to minerals in felsic igneous rocks. Two brands exhibited elevated beta activity (1.087±0.134 Bq/l; 1.242±0.146 Bq/l). Effective doses were found to be below the reference level of 0.1 mSv/yr.

Keywords: bottled water, dietary reference intake, essential elements, natural radioactivity, hierarchical cluster analysis, Serbia, water quality.

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According to new data, the production of bottled water in Serbia is threatened by the economic crisis as well as the good quality of the tap water in the country [1]. However, data available from the past years showed that the consumption of bottled water was increasing rapidly [2,3]. Due to the importance of drinking water for human health, their quality must be carefully and systematically controlled [4].

Fourteen mineral elements have been established as essential for good health; these elements in combined form affect bone and membrane structure (Ca, P, Mg and F), water and electrolyte balance (Na, K and Cl), metabolic catalysis (Zn, Cu, Se, Mg, Mn and Mo), oxygen binding (Fe), and hormone functions (I and Cr) [5]. The chemical composition of natural mineral water depends on many factors, including the mineralogy/ /lithology of the aquifer, residence time of the water, amount of solids and trace elements which can be soluble under appropriate pH and redox conditions [6–9].

In the last few years many studies have been focused on the hydrogeochemical properties of bottled waters [2,10–15], on the chemical composition of bottled waters and its health effects [16–18] and also on the radiation dose estimations in various water samples [19–21]. In Serbia, the quality of bottled waters was the subject of only several studies [2,4,14,22,23].

This study covered a wide range of major and trace elements, and also investigated the natural radioactivity of bottled waters. The goal of the research was to examine the potential contribution of bottled waters to essential elements intake and exposure to ionizing radiation.

METHODS

Study area

The study area was the Republic of Serbia which is located in South-eastern Europe, occupying an area of 88.361 km^2. Serbia is consisted of very complex geological units, as part of the Central Balkan Peninsula. The geological framework comprises several geotectonic units [24]: Carpatho–Balkanides composite terrane (CBCT), Serbo–Macedonian composite terrane (SMCT), Vardar zone (VZ), Jadar Block terrane (JBT), Drina–Ivanjica terrane (DIT), Dinaridic ophiolite belt terrane (DOBT) and External Dinarides (ED), Fig. 1.

CBCT extends through eastern Serbia and represents lower Palaeozoic units which are merged before the Upper Permian [25]. Mesozoic limestone and dolomite are the most important aquifer, in this region, with more than 1000 m thickness. SMCT is a crystalline basement which occupies the central part of the territory of Serbia. It is composed of very thick Proterozoic metamorphic rocks: gneiss, micaceous shale, various types of schist, marble, quartzite, granitoid rocks, and igneous rocks. Deep reverse faults constitute the boundary with other geotectonic units [14]. VZ is represented by a composite assemblage of continental and

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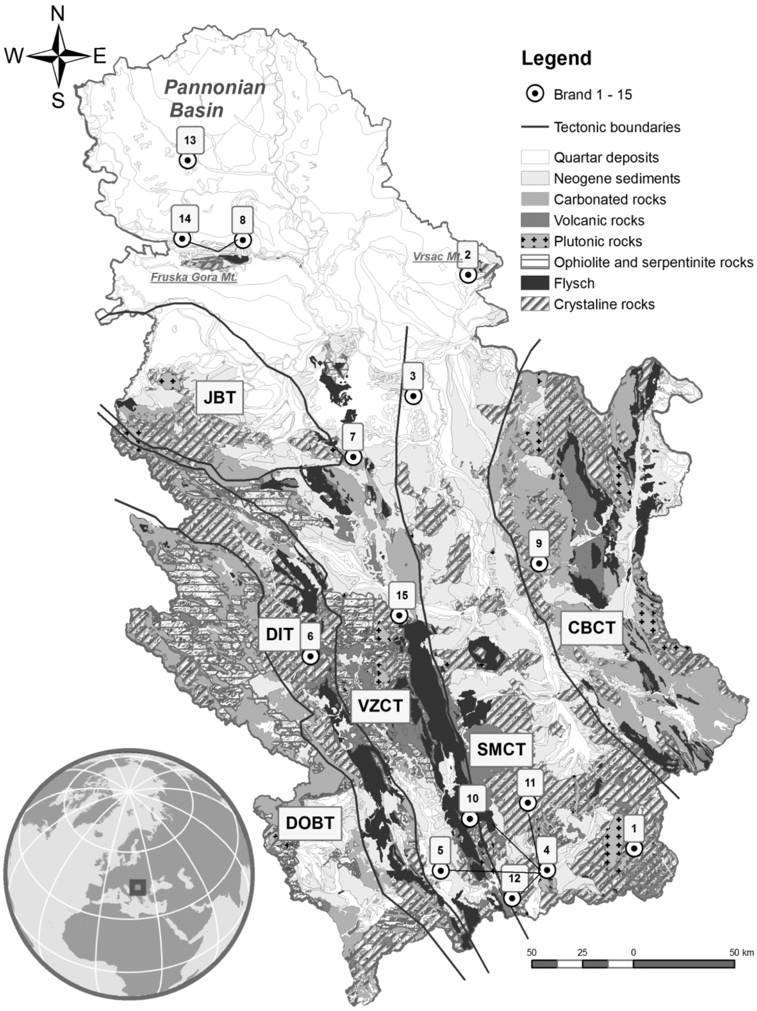

Schematic geotectonic units (Karamata and Krstić, 1996):
JBT – Jadar Block Terrane;VZCT –Vardar Zone Composite Terrane;
DOBT – Dinaride Ophiolite Belt Terrane; DIT – Drina-Ivanjica Terrane;
SMCT– Serbo-Macedonian Composite Terrane;
CBCT – Carpatho-Balkanides Composite Terrane.

Figure 1. Simplified geological map of Serbia showing the distribution of major rock types.

oceanic units, intruded by Oligocene to Pliocene calc--alkaline magmatic rocks [26]. The continental units are characterized by a Paleozoic basement covered by Middle to Late Triassic, mainly carbonate, sequences, whereas the oceanic units are represented by Jurassic ophiolites. In addition, slices of Late Jurassic melange and Late Cretaceous turbidite are also recognized. On the whole, the Vardar zone is regarded as a suture zone developed after the collision between Eurasia and Adria [27]. JBT is an exotic block of the Earth's crust, thought to be derived from further west [28] and is highly correlative with the Dinaride – South Alpine belt. This unit is bounded by deep fault zones and tectonic melanges. DIT occupies the western part of territory of Serbia, where there are large masses of ultrabasic rocks and serpentinites. At the south–east, it has a boundary with the Ophiolite Belt which is mostly covered by Triassic limestone. The north–west part of the terrane is covered by Eocene deposits [24]. DOBT is characterized by ophiolites ranging in age from Triassic to Jurassic, which are regarded as representative of the oceanic basin. This nappe includes a stack of ophiolitic units overlying a sub-ophiolitic melange [29]. Ophiolite includes terrigenous sedimentary rocks, minor cherts and limestones, together with basalts, diabases, various gabbros and ultramafic rocks [24,30,31]. ED is large tectono–stratigraphic unit, composed of Jurassic to Late Cretaceous clastic and carbonate sequences, up to 4000–5000 m thickness [32]. The Pannonian basin (PB) rests on thrust sheets of the Inner Carpathian foldbelt in northern and central areas and, to the south, on those of the Dinarides and Vardar Zone. During the Tertiary period, largely clay and sand sediments were deposited within the basin, whose thickness in the north–east is greater than 2500 m [33]. Neotectonic movements formed the horsts of Fruška Gora Mt. (a part of the VZ) and Vršac Mountains constructed of crystalline schist and granite (part of the SMCT).

Sampling and laboratory methods

During 2012, 15 different bottled water samples were purchased from local markets. The selected brands are the most commonly produced. Locations of groundwater sources are presented in Fig. 1. Major cations (Ca, K, Mg and Na) in the groundwater samples were measured by inductively-coupled plasma optical emission spectrometry (ICP-OES). Major anions were determined by ion chromatography (Dionex ICS–3000 DC). Trace elements were analyzed by HR–ICP/MS high resolution magnetic sector ICP/MS using a Finnegan Mat Element 2 instrument for 57 elements. To test the accuracy and precision of the method, NIST® 1643e "Trace Elements in Water" SRM was analysed and compared to the certificate values.

Gross alpha and beta activities were examined with the procedures recommended by iso 9696 water quality – measurement of gross alpha activity in non--saline water, thick source method, and ISO 9697 water quality – measurement of gross activity in non-saline water [34,35]. Gamma spectrometry analysis was undertaken following the procedure of ISO 10703 water quality – determination of the activity concentration of radionuclides by high resolution gamma-ray spectrometry [36]. Gross alpha/beta activity measurements were made on a low level α,β-proportional counter PIC-WPC-9550 (Protean Instrument Corporation), featuring efficiencies of 31% for alpha radiation and 44% for beta radiation, using the reference materials ^{241}Am and ^{90}Sr. Gamma activity was determined by gamma-spectrometry measurements using a HP Ge detector with relative efficiency of 25% and energy resolution of 1.85 keV (1332.5 keV ^{60}Co). The calibration was made using an AMERSHAM standard in a Marinelli beaker.

Calculation of dietary reference intake

The dietary reference intakes (*DRI*) are a set of reference values for vitamins, minerals, and other nutrients important to human health established by the Institute of Medicine (IOM) of the U.S. National Academy of Sciences. DRI system includes the recommended dietary allowance (RDA), adequate intake (AI) and tolerable upper intake level (UL), and it is used to calculate contributions of the elements essential for human health according to age group and gender [37].

Calculations were done according to the formula:

$$DRI = \frac{100MV}{RDA} \qquad (1)$$

where *M* is element concentration (mg/l); *V* is water consumption according to age group and gender (*L*/*d*) (Table 1); *RDA* – *RDA*/AI/UL (mg/d), Table 1. An *RDA* is an average daily dietary intake level; sufficient to meet the nutrient requirements of nearly all (97–98%) healthy individuals in a group. If sufficient scientific evidence is not available to establish an *RDA*, an *AI* is usually developed. *UL* is the highest level of daily nutrient intake that is likely to pose no risk of adverse health effects to almost all individuals in the general population [37].

Hierarchical cluster analysis (HCA)

Cluster analysis is a multivariate method which aims to classify a sample of objects on the basis of a set of measured variables into a number of different groups such that similar subjects are placed in the same group. Squared Euclidean distances were chosen to measure similarity/dissimilarity among the variables while Ward's linkage method was chosen to link initial clusters resulting from the initial clustering steps. Finally, the result of this statistical method is a graphical representation of individual groups (dendrogram) [38,39].

Estimation of annual effective doses

The annual radiation doses from ^{226}Ra, ^{228}Ra and ^{238}U in the bottled water samples have been calculated using the Recommended Adequate Intakes for water (Table 1) [40], together with the measured radioactivity concentrations and the radiation dose coefficients for ingestion [41].

The formula used for this purpose is:

$$D = V\times A^{226}\text{Ra}\times h(g)^{226}\text{Ra} + V\times A^{228}\text{Ra}\times h(g)^{228}\text{Ra} + V\times A^{238}\text{U}\times h(g)^{238}\text{U} \qquad (2)$$

where *V* is water consumption according to age group and gender (Table 1); A^{226}Ra, A^{228}Ra and A^{238}U are activity concentrations of radionuclides (Bq/l); $h(g)^{226}$Ra = $= 4.9\times10^{-7}$ Sv/Bq, $h(g)^{228}$Ra = 6.9×10^{-7} Sv/Bq, $h(g)^{238}$U = $= 4.5\times10^{-8}$ Sv/Bq are dose coefficients for radionuclides.

RESULTS AND DISCUSSION

Water quality: major hydrochemistry, trace elements, compliance with regulations

The major chemical composition of bottled water samples is shown in Table 2. Total dissolved solids (TDS) ranged from 56 to 3400 mg/l with a median of 464 mg/l. pH values ranged from 6.37 to 7.93, while CO_2 concentrations ranged from 7.48 to 1621 mg/l.

The Schoeller diagram was used for a comparative view of bottled water quality (Fig. 2). The hydrocarbonate ion was dominant in all the samples. Low–mineralized water samples (*TDS* < 1000 mg/l) had a preponderance of Ca and Mg ions, while CO_2 rich waters (CO_2 > 250 mg/l) had a preponderance of Na ions. CO_2 rich waters are associated with different regional geological-structural features and related to granite intrusions and volcanic rocks [42]. Bottled water samples 7, 10, 11, 12 and 15 had the highest TDS levels and CO_2 con-

Table 1. Recommended dietary allowances/adequate intakes/tolerable upper intake levels (mg/d) for children, adolescents, adults, pregnant and lactating females (IOM 2004)

Age group		Water obtained from drinks per day (L)	Ca	Cu	Fe	Mg	Mo	Se	Zn	Cr	Mn	K	Na	Cl	B
Children	1–3 y	0.9	700	0.34	7	80	0.017	0.02	3	0.011	1.2	3000	1000	1500	3
Children	4–8 y	1.2	1000	0.44	10	130	0.022	0.03	5	0.015	1.2	3800	1200	1900	6
Boys	9–13 y	1.8	1300	0.7	8	240	0.034	0.04	8	0.025	1.9	4500	1500	2300	11
Girls	9–13 y	1.6	1300	0.7	8	240	0.034	0.04	8	0.021	1.6	4500	1500	2300	11
Boys	14–18	2.6	1300	0.89	11	410	0.043	0.055	11	0.035	2.2	4700	1500	2300	17
Girls	14–18 y	1.8	1300	0.89	15	360	0.043	0.055	9	0.024	1.6	4700	1500	2300	17
Adults	Men > 19 y	3	1000	0.9	8	410	0.045	0.055	11	0.033	2.3	4700	1375	2100	20
	Women >19 y	2.2	1000	0.9	13	320	0.045	0.055	8	0.022	1.8	4700	1375	2100	20
Females	Pregnant 19–50 y	2.3	1000	1	27	355	0.05	0.06	11	0.03	2	4700	1500	2300	20
	Lactating 19–50 y	3.1	1000	1.3	9	315	0.05	0.07	12	0.045	2.6	5100	1500	2300	20

Table 2. Basic chemical composition (mg/l) and aquifer lithology of bottled waters in Serbia

Brand	Aquifer lithology	pH	Ca	Mg	Na	K	HCO_3	SO_4	Cl	*TDS*	CO_2
1	Deluvial deposits	7.93	10	0.91	2.7	1	42.7	5.4	1	56	7.48
2	Crystalline rocks dated Precambrian or Lower Paleozoic	7.65	22.26	8.37	10.91	0.753	109	12	8.2	146	76.56
3	Neogene sediments	7.2	86	50	33.11	1.19	561	9	10	420	36
4	Sandstones and granite sand	7.1	50.46	6	19.32	1.84	189	25	13	221	98
5	Alluvial aquifers comprised of gravels and sands	7.06	37.24	8.75	23	2	165	21	14.9	232	33
6	Serpentinite and limestone/dolomitic limestones	7.4	66.7	42.8	4.1	0.877	398.3	17.9	2.1	319	30.8
7	Dolomitic limestones	7	144	36.4	286	28	1329	14	7.2	1175	1499.52
8	Neogene sediments	7.25	72	28.75	130.7	2.5	578.3	0.35	87.67	603	219
9	Limestones	7.4	70	15	10	1.5	300	20	6	422.5	20
10	Granitoid rocks	6.5	85.4	20.6	1216	52	3290	173	54.1	3400.8	1621
11	Granitoid rocks	6.94	55	11.56	1230	52.8	3100	181	55	3100	1496
12	Granitoid rocks	6.37	84.1	23	930	20.5	3050	174	32	2705	1296
13	Neogene sediments	7.2	26.8	27.63	99.59	0.7	470	5.3	1.2	631	208
14	Neogene sediments	7.85	24.31	22.98	400.3	4.33	774.6	0.35	282.9	1123	203
15	Serpentinite and Paleozoic shales	7.62	72.14	58.36	324.2	3.56	1232	31.6	18.16	1200	599.28

centrations, thus pH values of these brands are slightly acidic to nearly neutral (pH 6.37–6.94). These waters are found in areas of large tectonic faults, in SMCT and VZ units, while low-mineralized waters originated from aquifers present in different geological units (Table 2). Groundwaters enriched in Na and Cl, captured from Neogene sediments in the Pannonian Basin, with a long residence time in aquifer are marked as "mature groundwater" (Fig. 2).

To evaluate the quality of the bottled waters in Serbia, 66 parameters are summarized in Table 3 with the appropriate regulation standards. The sum of trace element concentrations varied from 79.7 to 9349.7 µg/l with few elements significantly below 1 µg/l, namely some of elements of the rare earth group, Th, Ta and Ag. The widest range in trace element concentrations was found for Cs, Ge, Rb, Tl, Cr, B, Mn, Zn, Zr, Nd, La and Ce.

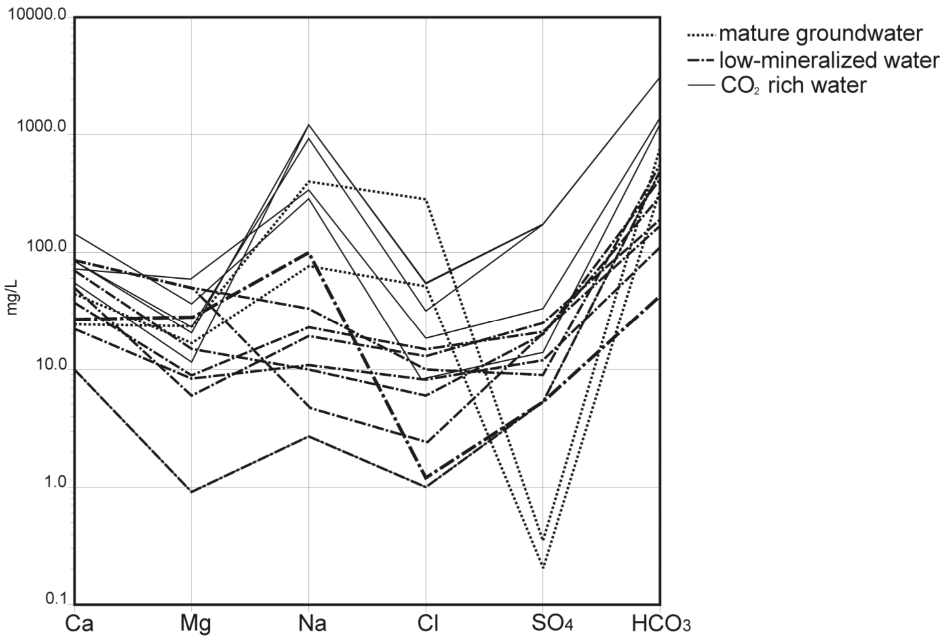

Figure 2. Schoeller diagram of major chemical composition.

Table 3 shows that most samples comply with guidelines. Exceptions include three samples that exceeded national requirements for bottled water. Brand 12 had an elevated concentration of As (10.9 µg/l), Brand 7 an elevated concentration of Fe (238.77 µg/l), and Brand 5 showed an elevated Se concentration (13.97 µg/l).

Toxic elements, such as Cd, Cr, Hg and Pb occur at very low concentrations, mostly below the detection limits in the sampled bottled waters.

Applying the dietary reference intakes

The calculated values of *DRI* for bottled water samples according to age group and gender are presented in Table 4. With regard to mineral intake for children and adults, some waters contribute significantly to the DRIs for Ca (Brand 7: 28.8% for children and 44.64% for adults), Mg (Brand 15: 65.66 and 58.36%), Na (Brand 11: 147 and 254.2 %), B (Brand 12: 142 and 109.9 %), Cr (Brand 3: 99.8 and 106.1 %), Se (Brand 5: 62.8 and 61.87 %), Mo (Brand 7: 21.5 and 22 %) and Cl (Brand 14: 32 and 38.13 %).

Ingestion of Brands 10 and 11 exceeds the maximum recommended daily intake of Na in all groups (up to 246%) and Brand 12 for boys, girls (14–18 years) and adults. Ingestion of Brand 12 exceeds the tolerable upper intake level for B for children (up to 213%), men (106%) and lactating females (109.8%). Cr may have a significant contribution especially in Brand 3 (106.7% of daily intake of Cr for women). Other essential microcomponent elements (Cu, K, Mn, Fe and Zn) have a contribution to *DRI* less than 5.1%, in all considered groups.

Hierarchical cluster analysis (HCA)

HCA was used to identify natural groupings in a dataset according to chemical similarity of the samples. Water quality parameters (pH, CO_2 content, major cations – Ca, Mg, Na and K, major anions – HCO_3, Cl, SO_4 and other essential elements – Cr, Cu, B, Mn, Mo, Fe and Zn) are selected as variables for HCA. Bottled waters are subdivided into four clusters (C1–C4, Fig. 3). Cluster 1 is characterized by low-mineralized water samples (*TDS*: 56–631 mg/l), with pH values greater than 7. Ca and Mg are dominant cations in this group, which make the greatest contribution to DRIs: 2.67% Ca for children (4–8 years) to 21.7% Ca for lactating females and 3% Mg for girls (14–18 years) to 31.08% Mg for children (1–3 years). Other essential elements in C1 have a contribution of less than 5%. Cluster 2 includes Brands 8 and 14, originating from PB, which are enriched with Na and Cl ions. This composition is a consequence of water filtration through sediments formed in marine or lake marine conditions. DRI contribution of Na in C2 is 11.76–82.73% and Cl is 5.2–38.1% (lower value refers to children of 1–3 years, and upper value to lactating females).

In Cluster 3 (Brands 3, 6, 7 and 15) Mg concentrations have a significant contribution to the *DRI*s: 18.2% Mg (in girls 14–18 years group) – 65.66% Mg (in children 1–3 years group). Ca ingestion from these waters is also important: 8% (for children 4–8 years of age) to 46.4% (lactating females). Mg concentrations are related to water circulation through an aquifer formed at the contact of serpentinite and Triassic limestone/dolomitic limestones or Paleozoic shales. Elevated CO_2 concentrations enhance the solubility of Ca and Mg carbo-

Table 3. Summary of the 66 parameters measured in the bottled waters in Serbia

Parameter	Unit	Detection limit	Min	Max	Median	Official Gazette of Serbia and Montenegro 53/05	EU Directive 2003/40/EC	Brand above national standards
Ca	mg/l	0.05	10	144	66.7			
Mg	mg/l	0.05	0.91	58.36	22.98			
Na	mg/l	0.05	2.7	1230	99.59			
K	mg/l	0.05	0.7	52.8	2.5			
HCO_3	mg/l	0.05	42.7	3290	561			
SO_4	mg/l	0.05	0.35	181	14.4			
Cl	mg/l	0.05	1	282.9	13			
pH		–	6.37	7.93	7.2			
TDS	mg/l	–	56	3400	420			
Ag	μg/l	0.002	<0.002	0.0038	0.0038			
Al	μg/l	0.5	<0.5	8.47	3.69	200		
As	μg/l	0.02	<0.1	10.91	0.75	10	10	Brand 12
B	μg/l	0.1	3.32	7087.75	149.45			
Ba	μg/l	0.01	0.86	191.25	55.66		1000	
Be	μg/l	0.001	<0.001	0.013	0.0038			
Bi	μg/l	0.001	<0.001	0.031	0.0075			
Cd	μg/l	0.001	<0.005	0.26	0.029	3	3	
Ce	μg/l	0.001	<0.001	0.59	0.015			
Co	μg/l	0.001	<0.001	0.081	0.02			
Cr	μg/l	0.01	<0.01	12.05	0.075	50	50	
Cs	μg/l	0.001	<0.001	118.04	0.27			
Cu	μg/l	0.05	<0.05	12.06	0.86	2000	1000	
Dy	μg/l	0.0005	0.0005	0.017	0.002			
Er	μg/l	0.00005	0.00032	0.011	0.00096			
Eu	μg/l	0.00005	0.00253	0.079	0.023			
Fe	μg/l	1	<1	238.77	7.47	200		Brand 7
Ga	μg/l	0.001	<0.001	0.012	0.0025			
Gd	μg/l	0.00005	<0.00005	0.016	0.0002			
Ge	μg/l	0.001	<0.001	16.2	0.21			
Hf	μg/l	0.00005	<0.00005	0.007	0.0002			
Hg	μg/l	0.05	<0.05	<3	–	1	1	
Ho	μg/l	0.00001	0.00001	0.002	0.0003			
In	μg/l	0.0001	0.0034	<0.0185	–			
La	μg/l	0.001	<0.001	0.66	0.012			
Li	μg/l	0.05	1.51	985	13.82			
Lu	μg/l	0.00005	<0.0005	0.003	0.001			
Mn	μg/l	0.05	<0.05	39.5	1.5	50	500	
Mo	μg/l	0.005	<0.005	3.55	0.26			
Nb	μg/l	0.0001	<0.0001	0.005	0.00034			
Nd	μg/l	0.0001	<0.0001	0.086	0.003			
Ni	μg/l	0.05	< 0.05	1.49	0.23	20	20	
Pb	μg/l	0.005	<0.005	0.78	0.19	10	10	
Pr	μg/l	0.00005	<0.00005	0.025	0.00087			
Rb	μg/l	0.005	<0.005	253.98	1.22			
Re	μg/l	0.0001	0.0004	0.16	0.026			
Sb	μg/l	0.001	0.029	2.2	0.59	5	5	
Sc	μg/l	0.01	<0.01	0.35	0.038			
Se	μg/l	5	<5	13.97	9.6	10	10	Brand 5

Table 3. Continued

Parameter	Unit	Detection limit	Min	Max	Median	Official Gazette of Serbia and Montenegro 53/05	EU Directive 2003/40/EC	Brand above national standards
Si	mg/l	0.03	0.3	41.5	13			
Sm	μg/l	0.0005	<0.0005	0.017	0.002			
Sn	μg/l	0.01	<0.01	0.35	0.14			
Sr	μg/l	0.01	20.45	1490	475.03			
Ta	μg/l	0.0005	<0.0005	0.0025	0.0023			
Tb	μg/l	0.00002	<0.00002	0.0045	0.00075			
Te	μg/l	0.001	<0.001	0.23	0.0075			
Th	μg/l	0.00002	<0.00002	0.0014	0.000075			
Ti	μg/l	0.01	<0.01	0.64	0.038			
Tl	μg/l	0.0001	<0.0001	0.31	0.0008			
Tm	μg/l	0.0001	<0.0001	0.0014	0.00038			
U	μg/l	0.0001	0.0072	3.45	0.1			
V	μg/l	0.001	0.0065	4.45	0.20			
W	μg/l	0.001	<0.001	0.49	0.1			
Y	μg/l	0.0005	<0.0005	0.093	0.013			
Yb	μg/l	0.00005	<0.00005	0.009	0.00075			
Zn	μg/l	0.5	<0.5	360.8	15.2			
Zr	μg/l	0.001	<0.001	1.11	0.0375			

Table 4. Dietary reference intakes (DRI): essential elements from bottled water samples

Age group			*RDA* / %							*AI* / %		*UL* / %			
			Ca	Mg	Cu	Fe	Mo	Se	Zn	Cr	Mn	Na	K	Cl	B
Children	1–3 y	Min	1.29	1.02	0.08	0.00	0.07	23.54	0.01	1.44	0.12	0.24	0.02	0.06	0.10
		Max	18.51	65.66	3.19	0.16	18.80	62.87	0.36	98.62	2.91	110.70	1.58	16.97	212.63
		Median	7.07	21.36	0.32	0.02	2.02	43.20	0.04	4.17	0.50	6.64	0.06	0.69	4.03
	4–8 y	Min	1.2	0.84	0.08	0.00	0.07	20.92	0.01	1.40	0.13	0.27	0.02	0.06	0.07
		Max	17.28	53.87	3.29	0.14	19.37	55.89	0.29	96.43	3.10	123.00	1.67	17.87	141.76
		Median	6.60	17.53	0.33	0.01	2.09	38.40	0.03	4.08	0.53	7.38	0.06	0.73	2.69
	Boys 9–13 y	Min	1.38	0.68	0.07	0.01	0.07	23.54	0.01	1.26	0.16	0.32	0.02	0.08	0.05
		Max	19.94	43.77	3.10	0.27	18.80	62.87	0.27	86.79	3.67	147.60	2.11	22.14	115.98
		Median	7.62	14.24	0.31	0.03	2.02	43.20	0.03	3.67	0.63	8.86	0.08	0.90	2.20
	Girls 9–13 y	Min	1.23	0.61	0.07	0.01	0.06	20.92	0.01	1.34	0.16	0.29	0.02	0.07	0.05
		Max	17.72	38.91	2.76	0.24	16.71	55.89	0.24	91.84	3.88	131.20	1.88	19.68	115.98
		Median	6.77	12.66	0.27	0.02	1.80	38.40	0.02	3.89	0.66	7.87	0.07	0.80	2.20
	Boys 14–18 y	Min	2.00	0.58	0.08	0.01	0.08	24.72	0.01	1.45	0.22	0.47	0.03	0.11	0.05
		Max	28.80	37.01	3.52	0.29	21.47	66.05	0.29	99.88	5.11	213.20	2.92	31.98	108.40
		Median	11.00	12.04	0.35	0.03	2.31	45.39	0.03	4.23	0.87	8.32	0.11	1.30	2.05
	Girls 14–18 y	Min	1.38	0.46	0.06	0.00	0.05	17.12	0.01	1.32	0.19	0.32	0.02	0.08	0.05
		Max	19.94	29.18	2.44	0.14	14.87	45.73	0.24	90.40	4.36	147.60	2.02	22.14	108.40
		Median	7.62	9.50	0.24	0.01	1.60	31.42	0.02	3.83	0.74	8.86	0.07	0.90	2.05
Adults	Men	Min	3.00	0.65	0.10	0.01	0.08	28.53	0.01	1.50	0.22	0.54	0.03	0.13	0.05
		Max	43.20	41.69	4.02	0.45	23.68	76.21	0.33	103.32	5.06	246.00	3.37	36.90	106.32
		Median	16.50	13.56	0.40	0.05	2.55	52.37	0.03	4.37	0.86	14.76	0.12	1.50	2.01
	Women	Min	2.20	0.63	0.07	0.00	0.06	20.92	0.01	1.54	0.20	0.40	0.02	0.10	0.04
		Max	31.68	40.12	2.95	0.15	17.36	55.89	0.33	106.07	4.74	180.40	2.47	27.06	77.97
		Median	12.10	13.06	0.29	0.01	1.87	38.40	0.03	4.49	0.81	10.82	0.09	1.10	1.48
	Pregnant	Min	2.30	0.60	0.07	0.00	0.06	20.05	0.01	1.34	0.19	0.41	0.02	0.10	0.04
		Max	33.12	38.35	2.77	0.10	16.34	53.56	0.25	92.41	4.46	188.60	2.58	28.29	81.51

Table 4. Continued

Age group			*RDA* / %							*AI* / %		*UL* / %			
			Ca	Mg	Cu	Fe	Mo	Se	Zn	Cr	Mn	Na	K	Cl	B
Adults	Pregnant	Median	12.65	12.48	0.28	0.01	1.76	36.80	0.03	3.91	0.76	11.32	0.09	1.15	1.54
	Lactating	Min	3.10	0.91	0.07	0.01	0.08	23.16	0.01	1.21	0.20	0.56	0.03	0.13	0.05
		Max	44.64	58.36	2.88	0.42	22.02	61.87	0.31	83.04	4.62	254.20	3.21	38.13	109.86
		Median	17.05	18.99	0.29	0.04	2.37	42.52	0.03	3.51	0.79	15.25	0.12	1.55	2.08

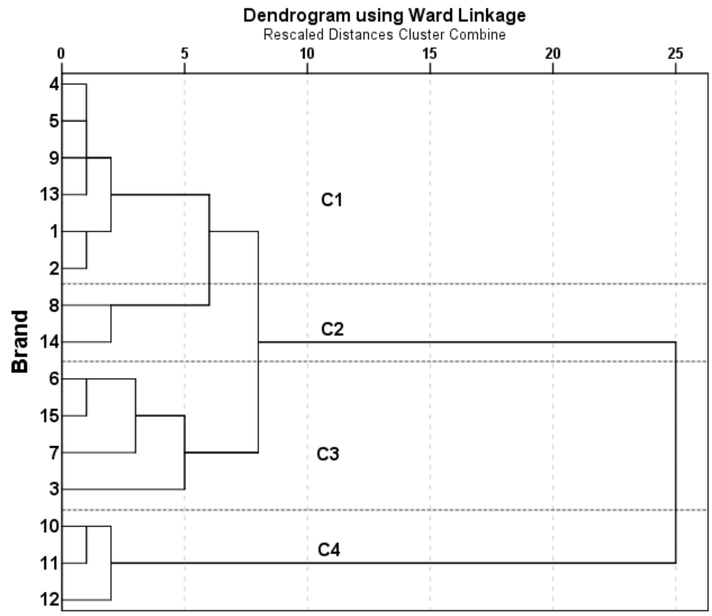

Figure 3. HCA dendrogram of bottled waters.

nates, and consequently, increase Ca/Mg concentrations in the groundwater, in the case of Brands 7 and 15. Brand 3 is specific by a high contribution to the Cr intake (83% in lactating females – 106% for women) and Mg concentrations (25% for girls 14–18 years of age to 56.26% for children 1–3 years of age). Cluster 4 included Brands 10, 11 and 12, which belong to $NaHCO_3$-water type and which originated from aquifers in granitoid rocks. They are characterized by elevated concentrations of dissolved solids and CO_2 concentrations. The contribution of Na in C4 is 83.7% for children (1–3 years) to 192.2% in lactating females, while the contribution of B is 78% for women to 212.6% for children (1–3 years of age).

Radioactivity of bottled waters and annual effective doses

Exposure to ionizing radiation is expressed by the effective dose which is estimated for human beings to be, on average, 2.5 mSv/year from natural radiation [41,43]. In general, water consumption is a minor source of radionuclide intake compared to food [44]. The guideline value for drinking water requires that the total estimated dose per year from all radionuclides, excluding the dose from ^{40}K should not exceed 0.1 mSv (K is an essential element, absorbed mainly from ingested food and ^{40}K does not accumulate in the body) [43,45].

The radioactivity in groundwater comes mainly from radionuclides of the natural decay chains ^{238}U and ^{232}Th, and ^{40}K in soil and bedrock. Some radionuclides can dissolve easily in water, depending on the mineralogical and geochemical composition of rock, redox conditions and the residence time of ground water in bedrock, as a result of the reaction of the ground water with soil and bedrock [46]. To gain insight into the radioactive properties of bottled waters of Serbia, radionuclide activity concentrations of ^{238}U, ^{228}Ra, ^{226}Ra and ^{40}K were examined.

Summary statistics for gross alpha and beta activities and activity concentrations of ^{238}U, ^{226}Ra, ^{228}Ra and ^{40}K are presented in Table 5. With respect to water quality standards [43,47] bottled waters showed that no brand exceeded the guidance level for alpha activity. Two brands exhibited elevated beta activity (Brand 10: 1.087±0.134 Bq/l; Brand 11: 1.242±0.146 Bq/l), measured in samples whose composition was formed in contact with granitoid rocks or circulation through the granites.

Table 5. Gross alpha and beta activities and gamma spectrometry findings in 15 bottled water samples (Bq/l)

Value	α	β	^{40}K	^{228}Ra	^{238}U	^{226}Ra
Min	0.018±0.01	0.018±0.003	0.025±0.001	<0.01	<0.05	<0.01
Max	0.3±0.037	1.242±0.146	1.27±0.07	<0.1	<0.8	0.12
Median	0.04	0.103	0.15	0.04	0.1	0.02
Guidance level (Official Gazette of RS, 2011.)	0.5	1	–	0.2	3	0.49
Guidance level (WHO, 2011.)	0.5	1	–	1	10	1

Alpha and beta activities correlated very well with the *TDS* (R^2 = 0.945 and 0.629, respectively), significant at P < 0.01. ^{40}K was also significantly correlated with gross beta activity (R^2 = 0.982, Fig. 4), which may indicate that β-radioactivity originates from ^{40}K which is present in felsic igneous rocks.

Calculations of the effective doses based on Eq. (2) for the 15 bottled water samples showed that all effective doses were below the recommended limit of 0.1 mSv/yr (Fig. 5).

Consequently, all samples of bottled water complied with quality standards for bottled water, such that these waters may be consumed on a daily basis. The largest doses are observed in CO_2 rich waters, especially for lactating females and men, groups that have the highest water intake.

CONCLUSION

The results obtained in this study show that Serbian bottled waters are rich in various trace and ultra-trace elements. All samples comply with European standards for bottled waters, while three samples exceeded national requirements (Fe, As and Se). The majority of bottled waters have a preponderance of a combination of Ca–Mg–Na–HCO_3, while more mature mineral waters of the Na–Cl–HCO_3 type are found in sediments formed in marine or lake marine conditions. A wide range of TDS values (56–3400 mg/l) were found in bottled water samples.

Several conclusions can be made from the methods applied:

– Ca, Mg, Na, B, Cr, Se, Mo and Cl intake from selected commercially available bottled waters may be appreciably high, while other essential elements intake (Cu, K, Mn, Fe, Zn) contributes less than 5.1% to DRIs in all considered groups.

– The highest potential contributions of low-mineralized bottled waters to RDA is for Ca (up to 21.7%) and Mg (up to 31.08%) ingestion, which are major components of the given bottled waters (TDS: 56–631 mg/l, pH > 7).

– Mature groundwaters enriched with Na and Cl concentrations, have a DRI contribution of Na 11.76––82.73% and Cl 5.2–38.1% (the lower value refers to children 1–3 years of age, while the upper value refers to lactating females).

– Mg intake from waters related to serpentinite rocks or limestone/dolomitic limestones amounts 18.2% Mg for girls (14–18 years of age) to 65.66% Ca for children (1–3 years of age).

– CO_2 rich waters from granitic rock aquifers (Brands 10–12) were particularly enriched with Na and B ions. Consumption of such water (according to recommended adequate water intake) exceeds the maximum RDA or UL of these elements.

– Alpha and beta activities correlated very well with the TDS. Brands 10 and 11 (from granitoid rocks) with elevated concentrations of dissolved solids, registered the highest beta activity.

– The calculated effective doses were below the recommended limit of 0.1 mSv/yr, therefore these waters may be consumed on a daily basis.

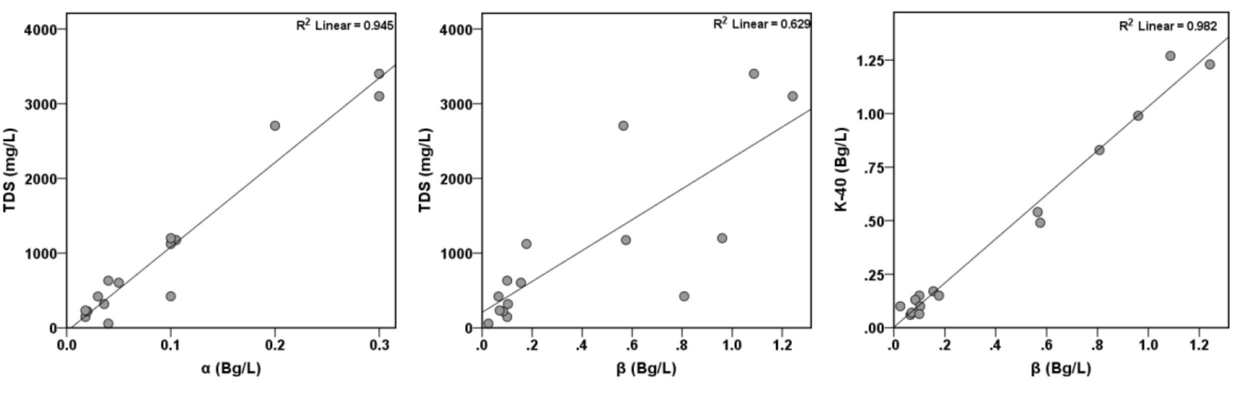

Figure 4. Correlation diagrams of the alpha activity vs. TDS, beta activity vs. TDS, and beta activity vs. ^{40}K.

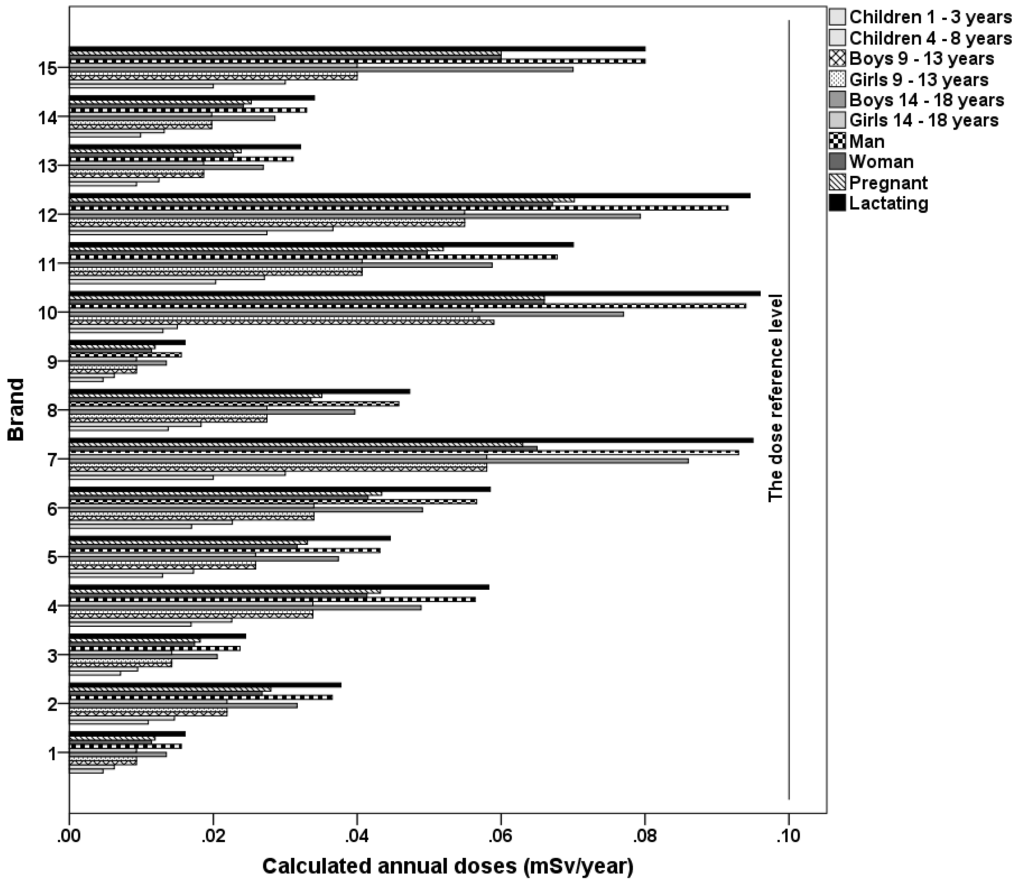

Figure 5. Sum of calculated annual effective doses (mSv/year) by age and gender groups.

Taking all these facts into consideration, mineral waters can be a significant source of essential elements for human health. In the case of waters with high TDS levels, reduced amounts of water intake are preferred because daily intake of certain elements can be above the recommended levels.

Acknowledgement

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IZVOD

HIDROGEOHEMIJSKI PRISTUP PROCENE KVALITETA ODABRANIH FLAŠIRANIH VODA U SRBIJI

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(Naučni rad)

Za potrebe izrade ovog rada odabrano je 15 uzoraka flaširanih voda sa domaćeg tržišta u kojima su određene koncentracije makro i mikro elemenata i aktivne koncentracije radionuklida. Cilj rada je bio da se ispita kvalitet voda i da se izračuna potencijalni unos esencijalnih elemenata konzumiranjem flaširanih voda. Hidrokarbonantni jon je dominantan u svim uzorcima, dok katjonski sastav čini kombinacija Ca–Mg–Na jona. Analizirane vode pripadaju slabo kiselim do blago alkalnim vodama (vrednost pH indeksa 6,37–7,93). Suma koncentracija mikroelementa u uzorcima varira od 79,7 do 9349,7 µg/l. Korišćenjem dijetetskog referentnog unosa (*DRI*) izračunat je doprinos određenih esencijalnih elemenata prema starosnim grupama, na osnovu konzumiranja preporučenog dnevnog unosa flaširanih voda. Unos Ca, Mg, Na, B, Cr, Se, Mo i Cl iz flaširanih voda može da bude značajno visok, dok ostali elementi (Cu, K, Mn, Fe and Zn) imaju niske dijetetske unose u svim razmatranim grupama. Kao statistička metoda korišćena je hijerarhijska klaster analiza (HCA) kako bi se izvršilo grupisanje većeg broja podataka u manje grupe prema hemijskoj sličnosti uzoraka. Korišćeni su parametri kvaliteta vode (pH, sadržaj CO_2, glavni katjoni – Ca, Mg, Na, K, glavni anjoni – HCO_3, Cl, SO_4 i drugi esencijalni elementi – Cr, Cu, B, Mn, Mo, Fe, Zn) kao varijable za ovu analizu. HCA je grupisala uzorke flaširanih voda u četiri klastera na osnovu čega je razmatrana veza esencijalnih elemenata sa geološkim uslovima. Dva uzorka flaširanih voda su pokazala povišenu beta aktivnost (1.087±0.134 Bq/l i 1.242±0.146 Bq/l), međutim utvrđeno je da su sve efektivne doze ispod referentnog nivoa od 0,1 mSv/god.

Ključne reči: Flaširane vode • Dijetetski referentni unos • Esencijalni elementi • Hijerarhijska klaster analiza • Prirodna radioaktivnost • Srbija • Kvalitet voda