NATURAL AND ARTIFICIAL (^{90}Sr) RADIONUCLIDES IN SOME CARBONATED MINERAL WATERS USED IN SERBIA

by

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A radiological characterization of 7 different carbonated mineral water samples collected in the local supermarkets in the area of Belgrade (produced in Serbia) was carried out. Analysis included determination of gross alpha and gross beta activities. The obtained results showed that the natural activity concentrations of alpha and beta emitting radionuclides in carbonated mineral water samples were within World Health Organization recommended levels, except for the Heba Strong and Kiseljak samples where the beta activity exceeds 1 Bq/L. For these two water samples gamma spectrometry analysis was performed as well as determination of ^{90}Sr by oxalic method.
The instrumentation used to count the gross alpha and gross beta activities, as well as for ^{90}Sr, was α/β low level proportional counter Thermo Eberline FHT 770 T. Gamma spectrometric measurements were performed using a HPGe Canberra detector with a counting efficiency of 20%. The annual effective dose equivalent due to ingestion of investigated waters was calculated for age group >17, and obtained values are lower than 0.1 mSv recommended reference level. Finally, a comparison of the investigated waters with worldwide data was made.

Key words: carbonated mineral water, radioactivity, ^{90}Sr, annual effective dose

INTRODUCTION

According to the density of occurrences and the diversity of physical and chemical features of mineral waters, the territory of Serbia belongs to one of the most resourceful areas of the European continent, but only a small quantity of these mineral waters is used for bottling. Bottled waters in Serbia are usually HCO_3, with Na or Ca as a dominant cation, and in a large range regarding total dissolved solids [1]. The quality of water is important in environmental studies because of its daily use for human consumption and its ability to transport pollutants. According to a UNSCEAR report [2], drinking water is considered to be an important factor in increasing the natural radiation exposure in humans. Most commonly, natural earth radionuclides have internal effects, *i. e*., they enter the human body through inhalation or ingestion (through drinking water and food of plant or animal origin), and they irradiate human cells internally, which leads to considerable radiation load of human population in certain areas [3].

In general, gross alpha and gross beta analysis which is one of the simplest radio analytical procedures is used as the first step of the radiological characterization of drinking waters as a screening method in the field of radioecology, environmental monitoring and industrial applications as well. Its main advantages are the relatively low costs and simplicity. Nevertheless, the determination of gross alpha and gross beta activities faces some specific problems because a mixed radionuclide composition has to be simultaneously measured. Drinking water samples may contain different natural alpha (^{238}U, ^{234}U, ^{232}Th, ^{226}Ra, and ^{210}Po) and beta emitters (^{40}K, ^{228}Ra, and ^{210}Pb), and artificial radionuclides (^{241}Am, ^{90}Sr) in various concentrations. Most of them are members of a complex decay chain. Naturally occurring alpha or beta emitting radionuclides are frequently dissolved in domestic water supplies and their concentrations vary over an extremely wide range, mainly depending upon the amount of radioelements present in bedrock and soil the water comes in contact with [4]. However, from the viewpoint of radiation hygiene, the result of many worldwide surveys [5-7] indicate that only ^{222}Rn and the long-lived radium isotopes ^{226}Ra and

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^{228}Ra have been found in concentrations that may be of health concern. The contribution of drinking water to the total exposure is very small and is due largely to naturally occurring radionuclides in the uranium and thorium series. World Health Organization recommends for the limits of gross alpha and gross beta radioactivity concentration in drinking water below 0.5 and 1.0 Bq/L, respectively [8]. In Serbia, according to current regulations [9], radioactivity concentrations in drinking water for gross alpha and gross beta should be 0.5 and 1.0 Bq/L, respectively. If one of the guideline values is exceeded, radionuclides have to be identified by alpha and/or gamma spectroscopy, and their individual activity concentrations need to be measured. These guidelines ensure an exposure lower than 0.1 mSv per year assuming a water consumption rate of 2 L/d. If the estimated dose is higher than 0.1 mSv per year the reduction in consumption or radionuclide concentration is necessary.

Radiostrontium is one of the most hazardous fission products that have reached the natural environment in larger quantities after atmospheric nuclear weapon tests and large-scale nuclear accidents like Chernobyl. Once released to either air, soil or freshwater the radionuclide can find their way into the food chain leading to the contamination of human food. As the chemical behavior of Sr is very similar to that of Ca, strontium can be concentrated in bones with a high risk of development of leukemia [10].

Strontium-90 is a man-made radioactive isotope of strontium. It decays with a half-life of 29 years to yttrium-90 and emits a beta particle (an energetic electron) in the decay process. The energy of the beta particles ($E_{\beta,\ max}$ = 546 keV) is sufficient to produce ionizations and excitations of molecules in their path. The average range of these beta particles in water is less than 0.2 cm. Because of the short range of the beta particles, ^{90}Sr outside of the body does not pose much radiation hazard, except in large quantities and in equilibrium with ^{90}Y (half-life 64.4 hours), which produces a stronger beta radiation ($E_{\beta,\ max}$ = 2.283 keV). Due to the pure β-emitting property of ^{90}Sr, determination of this isotope without prior chemical isolation and purification is impossible. Among interference elements such as calcium, barium, magnesium and radium, the most significant interfering element is calcium which is contained in gram amounts in most environmental samples, while Sr is contained in milligram amounts or even less. ^{90}Sr decays according to the scheme [11]

$$^{90}_{38}\mathrm{Sr} \xrightarrow{\beta\ (0.54\ \mathrm{MeV})} {}^{90}_{39}\mathrm{Y} \xrightarrow{\beta\ (2.28\ \mathrm{MeV})} {}^{90}_{40}\mathrm{Zr} \quad (1)$$

Numerous methods for the determination of ^{90}Sr have been developed including: solvent extraction of ^{90}Y with tributyl phosphate (TBP) and beta counting [12], separation of $^{89,\ 90}$Sr, and ^{90}Y and determination by liquid scintillation counting (LSC) [13] and ion-exchange separation of Ca and Sr and measurement of ^{90}Sr by beta counting [14]. In this paper oxalate method for determination ^{90}Sr in water samples was applied.

Determination of natural and artificial radioactivity levels in drinking water has importance because it allows the assessment of population exposure to radiation by the consumption of the water.

The aim of this study was to determine the level of activities in carbonated mineral waters from various manufacturers. The measurement results found in this study can thus be used to determine effective dose rates stemming from ingestion of naturally occurring radionuclides in water. The dose estimates presented here were based on a worst case scenario by considering that gross activities come only from radium isotopes that have the most conversion factors. This assumption provides information on the maximum dose limits that may occur from ingestion of carbonated water.

MATERIALS AND METHODS

Carbonated mineral water samples selected for this study are some of the most commonly produced and consumed carbonated bottled waters in Serbia, and they were all purchased during April 2012 from local supermarkets in the Belgrade area. Before measuring the activity concentration, all samples were first analyzed for pH and conductivity. The pH was measured by Lina pH meter PHS-3BW Microprocessor using combined glass electrodes. Calibration of the instrument was carried out by 4, 7, and 10 pH standard solutions. The conductivity of the samples was measured by Conductometer (HANNA Combo).

Procedure for gross alpha and gross beta activity

Volumes of 3 l of bottled waters were evaporated to a small volume, under infrared lamp. The remaining part was heated to dryness at 450 ºC [15]. The residues were transferred quantitatively to a stainless-steel planchet. Measurements were performed immediately after preparation. The counting time was 3600 s for gross alpha and gross beta activities.

Gross alpha and beta activity in water samples were determined by α β low level proportional counter Thermo Eberline FHT 770 T. Calibration was performed by using standard source of ^{90}Sr (EM145, Prague) with an activity of 189.4 Bq on the day August 1st, 2011, for beta activity and standard source of ^{241}Am (EM445, Prague) with an activity of 224 Bq on the day August 1st, 2011, for alpha activity. The counting gas was a mixture of 90% argon and 10% methane. The counting efficiencies for the system are 23% for alpha radiation and 33% for beta radiation. The background

of each detector was determined by counting an empty planchet for 3600 s.

The accuracy and reproducibility of gas proportional counter were verified on a periodic basis-every week. Total background count rate without a source is monitored to verify that the detector and shield have not been contaminated by radioactive materials. Alpha and beta efficiencies of gas proportional counter were checked with ^{241}Am and ^{90}Sr sources, respectively.

Some of the properties of the detector are influenced by the sample preparation when water is evaporated obtaining the final source in dry residue or precipitate form. Due to energy loss and self absorption of the alpha and beta particles in the sample matrix, their counting efficiency is far less than 100%. It should also be mentioned that no energy resolution is possible with the proportional counters and it is not suitable to determine volatile radionuclides (^{3}H, ^{210}Po). In spite of the disadvantages, proportional counters are very useful for high throughput screening when fast quantitative analyses are required. Gross alpha and gross beta activity can be determined simultaneously which reduces the time of the analysis. Low background can be obtained, which makes proportional counters effective for measuring environmental level radioactivity. The spillover between alpha and beta signals is low, even below statistical significance can be achieved. Several detectors (6) can be installed into one detector housing such that more samples can be measured simultaneously.

Gross alpha and gross beta activity was calculated using the following equation

$$A_{\alpha\beta} \quad \frac{I}{V} \tag{2}$$

where $A_{\alpha\beta}$ [BqL^{-1}] is the activity of the sample, V – the volume of the sample (L) which corresponding to the mass of solid residue, and I is given by the equation

$$I \quad \frac{N \quad B}{ef} \tag{3}$$

where N [s^{-1}] is the count rate for the sample, B [s^{-1}] – the background, and ef – the efficiency of the detectors for alpha and beta measurements.

Minimum detectable activity was calculated by eq. (4)

$$MDA \quad \frac{LLD}{V} \tag{4}$$

where LLD [s^{-1}] is the detection limit, and V – the volume of the sample.

Procedure for gamma measurements

All water samples were boiled to reduce their volume from approximately 10000 mL to 200 mL and then poured into 200 mL cylindrical polyethylene vials. The samples were stored for 1 month to reach the radioactive equilibrium. Gamma spectrometric measurements were performed using a HPGe Canberra detector with a counting efficiency of 20%. Geometric efficiency for water matrices in the plastic bottle of 200 mL was determined by a reference water material (Czech Metrological Institute, Praha, 9031-OL-116/8, type ERX) spiked with a series of radionuclides (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{88}Y, ^{113}Sn, ^{85}Sr, ^{137}Cs, and ^{210}Pb) with total activity of 114.9 kBq on the day of March 3, 2008. The spectra were analyzed using the program GENIE 2000. The activity of ^{226}Ra and ^{232}Th was determined by their decay products: ^{214}Bi (609 keV, 1120 keV and also 1764 keV), ^{214}Pb (295 keV and 352 keV), and ^{228}Ac (338 keV and 911 keV), respectively. The activities of ^{40}K were determined from its 1460 keV γ-line. Counting time interval was 60000 s. The background spectrum was recorded regularly after or before the sample counting, with empty 200 mL cylindrical polyethylene vials. The specific activity, A, of the radionuclides in the samples was calculated using the equation

$$A \quad \frac{N}{tP_{\gamma}\, efV} \tag{5}$$

where t [s] is the counting time, and P_{γ} [%] – the probability of gamma decay. Minimum detectable activity was calculated by the equation

$$MDA \quad \frac{LLD}{tP_{\gamma}\, efV} \tag{6}$$

where $LLD \quad 2.71 \quad 4.65\sqrt{B}$. The error of single activity measurement was estimated by standard procedure of additive errors. It is in the range from 8 to 11% due to the level of activity. The major contribution to the total activity come from the errors in geometric efficiency estimation (about 6%) and photo peak counts estimation (about 3-4%), while the errors in all the other parameters of activity evaluation (mass, counting time, interval, probability of gamma disintegration) contribute to less than 1%.

The accuracy and reproducibility of gamma spectrometry systems were verified on a periodic basis – every week. Total background count rate without a source is monitored to verify that the detector and shield have not been contaminated by radioactive materials. Energy calibration is checked in whole region before applying usual QC procedure for gamma spectrometry measurement. The total activity of calibration source will check the efficiency calibration and the general operating parameters of the gamma spectrometry system (source positioning, contamination, library values, and energy calibration). The detector-shield background, detector efficiency, peak shape, and peak drift are measured and verified if they are within the warning and acceptance limits. For that purpose ^{60}Co source was used. All radionuclide sources are bought at Czech Metrological Institute which is traceable to BIPM (Bureau International des Poids et Measures).

Procedure for determination of ^{90}Sr in water samples

A radiochemical procedure was applied to the separation and determination of ^{90}Sr in water samples. Water samples in which ^{90}Sr were determined were boiled to reduce their volume from approximately 10000 mL to 200 mL. The method consists of oxalate departing calcium from strontium [16], firing till oxide, and usage of Al as collector for ^{90}Y. The samples were stored for 18 days to reach the radioactive equilibrium between ^{90}Sr and ^{90}Y. After 18 days ^{90}Y departs on collector $Al(OH)_3$, which is then firing till oxide and after that (half-life period 64.2 hours) on α/β low level proportional counter. The counting time was 3600 s. The specific activity of the ^{90}Sr, A_{Sr} in Bq/L, in the water samples was calculated using the equation

$$A_{Sr} \quad \frac{(N \quad B)e^{\frac{\ln 2}{T_{1/2}}t}}{ef\,p_{Al}\,pV} \tag{7}$$

where $T_{1/2}$ [h] is the half-life of ^{90}Y, t [h] – the time since separation of ^{90}Y, p_{Al} – the yield of Al, and p – the yield of method. Minimum detectable activity was calculated by

$$MDA \quad \frac{LLD}{V}e^{\frac{\ln 2}{T_{1/2}}t} \tag{8}$$

RESULTS AND DISCUSSION

Table 1 reports on pH, conductivity, dry residue, and main dissolved ions concentrations. Total dissolved solids as a dry residue at 180 ºC ranged between 323 and 3200 mg/L. Six investigated waters belong to the medium-mineral class (residue >500 mg/L) except for a Golijska Bistrica water, which belong to the low-mineral class (residue 50-500 mg/L). Difference in the conductivity value is related to the mineral salts and the origin of the source. High conductivity value for water Minaqua confirms its natural mineralization. The value for conductivity was in a range from 81 to 1755 S/cm. According to Regulation on Quality and other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water [17], recommended value for conductivity should be up to 2500 S/cm. Also, the pH value for Minaqua water is the lowest compared to other investigated sample. All water samples have pH values which are weakly acid, because of the formation of carbonic acid by the addition of CO_2. All waters are bicarbonate (HCO_3), except Golijska Bistrica. Content of cation is in a large range, in some waters Na and K ions prevail, in some Ca ions, and Mg is the cation that prevails only in one sample (Mivela). Magnesium water is very rare which makes this water very special.

Table 2 shows the results for gross alpha and gross beta activity concentrations from all the analyzed samples. Gross alpha activity in three water samples was lower than the minimum detectable activity. The activity values of the rest water samples were higher than MDA and below than recommended level of 0.5 Bq/L [9] for gross alpha activity. A good correlation is found between gross alpha activity and dry residue ($r = 0.77$) (fig. 1). Gross beta activities ranged between 0.317 to 2.219 Bq/L. Table 2 shows that the gross beta activity is always higher than the gross alpha activity. The highest gross beta activities, 2.219 and 2.080 Bq/L, was observed in the most mineralized waters (Karadjordje and Heba Strong). A good correlation was found between gross beta activity and dry residue ($r = 0.78$) (fig. 2). These results show that gross alpha and gross beta activity concentrations are related to the dry residue of the samples, *i. e.* to the content of salts in the analyzed waters.

Due to the fact that the gross beta activity in samples Karadjordje and Heba Strong is higher than the

Table 1. Chemicl parameters of six brands of carbonated mineral water samples [mgL^{-1}]

Brand	Knjaz Miloš	Minaqua	Mivla	Premia	Heba Strong	Karađorđe	Golijska Bistrica
pH	5.63	5.17	5.94	5.47	6.05	6.10	5.44
Dry residue	1037	1184	1622	848.5	3200	1710	323
Conductivity/μScm^{-1}	108	1755	103	84	140	150	81
Ca^{2+}	106	31.8	25.2	232.4	65	104	57.7
K^+	16.7	4	9.5	5.6	56	53	0.897
Mg^{2+}	60	20.7	333.2	18.2	14	63	37
Na^+	247	397.7	123.4	56	1059	250	4.76
Cl^-	10	306.4	14	14.4	57	54	4.2
$Fe^{2+/3+}$	<0.05	–	–	–	–	–	–
F^-	1.3	–	0.4	–	1.45	–	–
Selen						<0.001	
I^-	–	0.94	–	–	–	–	
SO_4^{2-}	12.2	–	2.1	11.3	198	61	19.1
HCO_3	1183	757	2002.8	988	3110	1260	–
Content of CO_2 [min]	3000	3000	3000	3000	3000	2200	3000

Table 2. Gross alpha and gross beta activity concentrations in all analyzed waters

Brand	Gross alpha activity concentration [BqL^{-1}]	Gross beta activity concentration [BqL^{-1}]
Knjaz Miloš	0.178 0.069	0.921 0.122
Minaqua	<0.156	0.407 0.082
Mivela	<0.131	0.649 0.095
Premia	<0.082	0.449 0.074
Heba Strong	0.460 0.184	2.080 0.440
Karadjordje	0.372 0.087	2.219 0.161
Golijska Bistrica	0.099 0.032	0.317 0.044

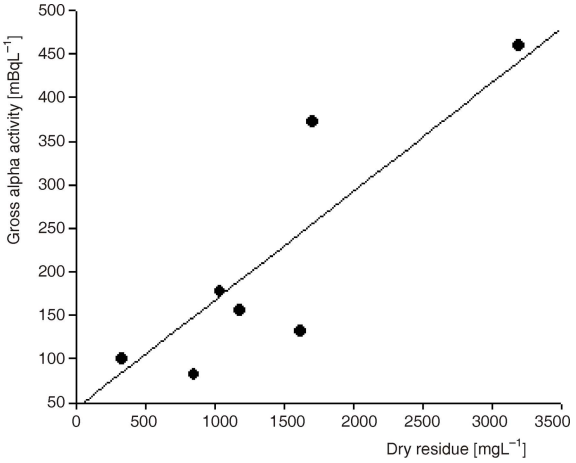

Figure 1. Correlation between the dry residue and gross alpha activity

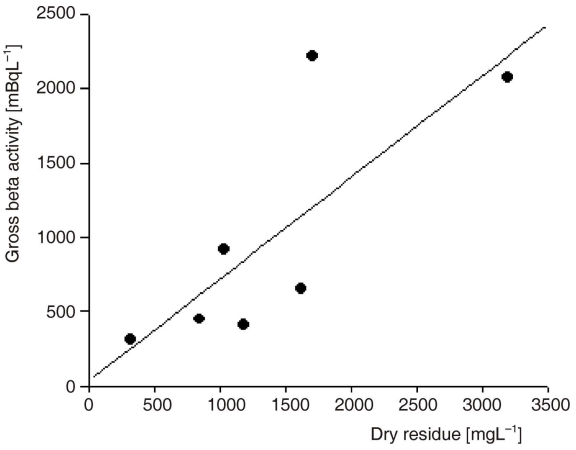

Figure 2. Correlation between the dry residue and gross beta activity

recommended level of 1 Bq/L, it is necessary to performed gamma spectroscopy. The specific activities of natural radionuclides ^{226}Ra, ^{232}Th, ^{235}U, and ^{238}U and artificial radionuclide ^{137}Cs in these samples were below the detection limits of our measuring system. Serbian law recommends that activity concentration in drinking water should not exceed 490 mBq/L for ^{226}Ra and 590 mBq/L for ^{232}Th [9].

Radionuclide ^{40}K is detected in both samples and its concentration was 1.63 0.33 Bq/L for Heba Strong and 1.93 0.41 Bq/L for Karadjordje sample. Since the ^{40}K participate in total beta activity with 89%, we may conclude that the gross beta activity of 2.219 (Karadjordje) and 2.080 Bq/L (Heba Strong) originates mainly from ^{40}K. However, it is evident that in addition to ^{40}K in these samples there are also some other beta emitters present. Because of that in these two samples ^{90}Sr was also determined. Concentration of ^{90}Sr in Heba Strong sample was 0.014 0.003 Bq/L, while concentration for Karadjordje was 0.016 0.005 Bq/L. ^{90}Sr is found at a concentration far below that the one allowed by regulations for drinking water (4.6 Bq/L) [9]. Values for ^{90}Sr obtained in this paper are slightly higher than the values of ^{90}Sr obtained in tap water in Switzerland (<0.005 Bq/L) [18]. In Pakistan concentration of ^{90}Sr in drinking water is 0.03 Bq/L [19].

The similar results for gross alpha and gross beta activities have been found by Joksić *et al*. [20] for mineral waters in Serbia that were analyzed during 2007, where Heba water had gross beta activity >1 Bq/L due to the high ^{40}K contribution of 1530 mBq/L. Table 3 compares our results for gross alpha and gross beta activities with the corresponding values in different countries. In tab. 3 the results for bottled mineral waters from Serbia [21] which are not carbonated, show lower gross alpha and gross beta activities than the carbonated bottled waters investigated in this paper.

Table 4 presents the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in waters of different origin. The concentrations of ^{226}Ra in mineral waters obtained in different countries are of wide range, from 0.14 mBq/L in Slovenia to 4000 mBq/L in Spain. On the other hand, ^{232}Th was detected in a small number of analyzed water and its concentration varied within the range from 7.1 mBq/L in Hong Kong to 190 mBq/L in Bangladesh. The content of ^{40}K was from 15.7 to 10064 mBq/L in Poland (tab. 4).

In order to evaluate the annual effective dose for age group >17 years, it was assumed that for 5 investigated waters (Knjaz Miloš, Minaqua, Mivela, Premia and Golijska Bistrica), where the gross alpha and gross beta activity does not exceed 0.5 and 1 Bq/L, respectively, the gross alpha and gross beta activities originates from ^{226}Ra and ^{228}Ra concentrations [4]. According to WHO guidelines, the daily drinking water consumption is in average about 2 liters. Data concerning the average daily bottled carbonated mineral

Table 3. Gross alpha and gross beta activity concentrations comparison with literature values

Origin	Gross alpha activity concentration [BqL^{-1}]	Gross beta activity concentration [BgL^{-1}]	References
Serbia (bottled mineral water)	0.001-0.013	0.041-0.173	[21]
Turkey (tap water)	0.0002-0.0150	0.0252-0.2644	[22]
Mexico (bottled mineral water)	<0.011-0.415	<0.026-0.695	[7]
Spain (bottled mineral water)	0.03-0.86	0.04-2.28	[23]
Hungary (bottled mineral water)	0.008-1.15	0.035-0.97	[24]
Greece (bottled mineral water)	0.008-0.094	0.071-0.35	[25]
Poland (bottled mineral water)	0.002-0.592	0.053-1.784	[26]
Republic of Srpska (bottled mineral water)	<0.016-0.025	<0.02-0.7	[27]

Table 4. The activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in waters from different origin

Origin	Activity concentrations of radionuclides [mBqL^{-1}]			Reference
	^{226}Ra	^{232}Th	^{40}K	
Poland	0.8-437		15.7-10064	[26]
Croatia	300-600			[28]
Slovenia	0.14-32			[29]
Serbia	10-530		200-1130	[30]
Greece	0.6-22.1			[25]
Hungary	4.3-910			[24]
Germany	0.8-350			[31]
Italy	0.2-1200			[31]
Spain	20-4000			[31]
France	7-700			[32]
USA	0.4-1.8			[32]
Turkey	11-36		80-169	[32]
Pakistan			31-140	[32]
Algeria	26	30	1000	[33]
Hong Kong		7.1	110	[33]
Bangladesh		190	4160	[33]

water consumption in the particular age group are not available. Therefore, it has been assumed here that the daily carbonated mineral water consumption for age group >17 is 200 mL per day, N in eq. (9). The annual effective dose rate to an individual, D, caused by absorption of natural radioactive elements in water can be calculated using the following equation [8]

$$D(\mathrm{Sv}) \quad N\eta W \tag{9}$$

where W [BqL^{-1}] is the concentration of the radioisotope and η [SvBq^{-1}] – the age dependent dose conversion factor . The dose conversion factors are defined for age group >17 years) (tab. 5).

Table 5 contains the calculated annual effective dose equivalents coming from the ^{226}Ra and ^{228}Ra for age group >17 years. The annual effective dose values due to the ingestion of ^{226}Ra in the water varied from 1.68 to 9.40 Sv per year (for all investigated waters) and 15.97 to 46.39 Sv per year for ^{228}Ra. The annual effective doses are below the WHO recommended reference level of 0.1 mSv per year [8].

For water samples Heba Strong and Karadjordje, where the gross beta activity exceeds recommended level of 1 Bq/L, it was necessary to performed gamma spectroscopy and identified radionuclides. Beside the gamma spectrometry, determination of ^{90}Sr in these two samples was performed. Based on the obtained activity concentrations for ^{40}K and ^{90}Sr, annual effective dose equivalents coming from the ^{40}K and ^{90}Sr for age group >17 years, using appropriate dose conversion factors (tab. 5) was calculated. Since the ^{40}K contribution to gross beta activity is 89%, the residue belongs to other beta emitters, such as ^{90}Sr, ^{3}H, ^{228}Ra *etc*. We did not determined ^{3}H, so we assume that in addition to ^{40}K and ^{90}Sr, other beta activity originates from ^{228}Ra. Calculated values for effective dose equivalents coming from the ^{40}K, ^{90}Sr, and ^{228}Ra, for waters Heba Strong and Karadjordje are presented in tab. 5. Based on the calculated values for annual effective dose for these two samples), these values were below the WHO recommended reference level of 0.1 mSv per year [8].

CONCLUSIONS

Seven different brands of bottled carbonated mineral water on sale in Serbia have been examined for their radiochemical content. The gross alpha activ-

Table 5. Dose conversion factor [34], water consumption for age class >17 and annual effective dose from ^{226}Ra, ^{228}Ra, ^{40}K, and ^{90}Sr

Brand	Radionuclide and dose conversion factor [SvBq^{-1}] for annual water consumption of 73 L	Annual effective dose [μSv]
Knjaz Miloš	^{226}Ra (2.8 10^{-7})	3.63
Minaqua		3.19
Mivela		2.68
Premia		1.68
Heba Strong		9.40
Karadjordje		7.60
Golijska Bistrica		2.02
Knjaz Miloš	^{226}Ra (6.9 10^{-7})	46.39
Minaqua		20.50
Mivela		32.69
Premia		22.62
Golijska Bistrica		15.97
Heba strong		31.03*
Karadjordje		24.83*
Heba strong	^{40}K (5.0 10^{-9})	0.59
Karadjordje		0.70
Heba strong	^{90}Sr (2.8 10^{-8})	0.029
Karadjordje		0.033

*The annual effective dose originates from ^{228}Ra after subtracting ^{40}K and ^{90}Sr from gross beta activity

ity in analyzed waters are below the level allowed by Serbian regulations. The gross beta activity for five samples are below the recommended reference level of 1 Bq/L, except for the Heba Strong and Karadjordje water, where gross beta activity exceeds the recommended limits. For this water it is necessary to perform gamma spectroscopy. In these two waters ^{40}K was detected in concentration of 1.63 0.33 Bq/L for Heba Strong and 1.93 0.41 Bq/L for Karadjordje water, while the concentrations of ^{226}Ra, ^{232}Th, ^{235}U, and ^{238}U were below the detection limits. ^{90}Sr was determined also for these waters, and specific activity was 0.014 0.003 Bq/L for Heba Strong and 0.016 0.005 Bq/L for Karadjordje. The concentration of ^{90}Sr is below the reference values for ^{90}Sr in drinking water (4.6 Bq/L). Since the ^{40}K is included in total beta activity with 89%, we can conclude that the gross beta activity of 2.219 (Karadjordje) and 2.080 Bq/L (Heba Strong) originates mainly from ^{40}K and from ^{90}Sr.

Assuming that every adult drinks 200 mL of carbonated mineral water per day, the calculated annual effective dose caused by intake of the radium isotopes as well as ^{40}K and ^{90}Sr is lower than 0.1 mSv for all investigated waters.

This study has shown that the mineral waters that found on the territory of Serbia are in accordance with current international and domestic regulations and can be used as drinking water.

Monitoring of bottled waters radioactivity should be strongly recommended; special regulations should be enforced to protect the most exposed class of age.

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AUTHOR CONTRIBUTIONS

The manuscript was written by M. Janković. Experiments were carried out by M. Janković, N. Sarap, and D. Todorović, and results were analyzed and discussed by all authors. Tables and figures were prepared by M. Janković.

REFERENCES

[1] Petrović, T., *et al*., Hydrogeological Conditions for the Forming and Quality of Mineral Waters in Serbia, *Journal of Geochemical Exploration, 107* (2010), 3, pp. 373-381
[2] ***, UNSCEAR Sources and Effects of Ionising Radiation, Report of the United Nations Scientific Committee on the Effects of Atomic Radiation to the General Assembly, United Nations, New York, USA, 2000
[3] Obradović-Arsić, D. R., *et al.*, Natural Ionizing Radiation and Human Health in Serbia, *Nucl Technol Radiat, 25* (2010), 3, pp. 192-197
[4] Malanca, A., Repetti, M., Macedo, H. R., Gross Alpha and Beta Activities in Surface and Ground Water of Rio Grando do Norte, Brazil, *Appl. Radiat. Isot., 49* (1998), 7, pp. 893- 898
[5] Duenas, C., *et al.*, ^{226}Ra and ^{222}Rn Concentrations and Doses in Bottled Waters in Spain, *J. Environ. Radioact., 45* (1999), 3, pp. 283-290

[6] Otwoma, D., Mustapha, A. O., Measurements of ^{222}Rn Concentration in Kenyan Groundwater, *Health. Phys., 74* (1998), 1, pp. 91-95
[7] Rangel Davila, J. I., *et al*., Radioactivity in Bottled Waters Sold in Mexico, *Applied Radiation and Isotopes, 56* (2002), 6, pp. 931-936
[8] ***, *Guidelines for Drinking Water Quality: Radiological Aspects*, 3rd ed., World Health Organization 1, 2004
[9] ***, Regulation on Limits of Radionuclide Content in Drinking Water, Foodstuffs, Feeding Stuffs, Drugs, Items of General Use, Building Materials and Other Goods to be Placed on the Market, Official Gazette of the Republic of Serbia, 86/11, 2011
[10] Zhu, S., *et al*., Interference of ^{91}Y with the Rapid Determination of ^{90}Sr Originating from the Chernobyl Fallout Debris, *Radiochima Acta, 51* (1990), 6, pp. 195-198
[11] Petrović, Dj., *et al*., Electrochemical Separation of 90-ytrium in the Electrochemical ^{90}Sr/^{90}Y Generator and Its Use for Radiolabelling of Dota-Conjugated Somatostatin Analog [dota^{o}, Tyr^{3}] Octreotate, *Nucl Technol Radiat, 27* (2012), 3, pp. 260-268
[12] Petrow, H. G., Rapid Determination of ^{90}Sr in Bone Ash Via Solvent Extraction of ^{90}Y, *Analytical Chemistry, 37* (1965), 4, pp. 584-586
[13] Randolph, R. B., Determination of ^{90}Sr and ^{89}Sr by Cerenkov and Liquid Scintillation Counting, *Applied Radiation and Isotopes, 26* (1971), 1, pp. 9-16
[14] Juznic, K., Fedsina, S., Radiochemical Determination of ^{90}Sr and ^{89}Sr in Soil, *Fresenius' Journal of Analytical Chemistry, 323* (1986), 1, pp. 61-63
[15] ***, EPA Prescribed Procedures for Measurement of Radioactivity in Drinking Water. EPA-600/4-80-032. Method 900.0., 1980
[16] Brnović, R., Strontium 90 in the Human Environment, M. Sc. thesis, Faculty of Science, Belgrade, 1972
[17] ***, Regulation on Quality and Other Requirements for Natural Mineral Water, Spring Water and Bottled Drinking Water, Official Gazette of Serbia and Montenegro, 53/05, 2005
[18] Froidevaux, P., Friedrich-Benet, K., Valley, J. F., Simple Determination of ^{90}Sr in Water in Environmental Radioactivity Survey, *Journal of Radioanalytical and Nuclear Chemistry, 261* (2004), 2, pp. 295-299
[19] Jabbar, T., *et al*., Determination of ^{90}Sr in Environment of District Swat, Pakistan, *Journal of Radioanalytical and Nuclear Chemistry, 279* (2009), 2, pp. 377-384
[20] Joksić, J., Radenković, M., Miljanić, Š., Natural Radioactivity of Some Spring and Bottled Mineral Waters from Several Central Balkan Sites, as a Way of their Characterization, *J. Serb. Chem. Soc., 72* (2007), 6, pp. 621-628
[21] Janković, M. M., *et al*., Natural Radionuclides in Drinking Waters in Serbia, *Applied Radiation and Isotopes, 70* (2012), 12, pp. 2703-2710
[22] Damla, N., *et al*., Gross α and β Activities in Tap Waters in Eastern Black Sea Region of Turkey, *Chemosphere, 62* (2006), 6, pp. 957-960
[23] Palomo, M., *et al*., Measurement of Radioactivity in Bottled Drinking Water in Spain, *Applied Radiation and Isotopes, 65* (2007), 10, pp. 1165-1172
[24] Kovacs, T., *et al*., ^{238}U, ^{226}Ra, ^{210}Po Concentrations of Bottled Mineral Waters in Hungary and their Committed Effective Dose, *Radiation Protection Dosimetry, 108* (2004), 2, pp. 175-181
[25] Karamanis, D., Stamoulis, K., Ioannides, K. G., Natural Radionuclides and Heavy Metals in Bottled Water in Greece, *Desalination, 213* (2007), 1-3, pp. 90-97
[26] Dinh Chau, N., Michalec, B., Natural Radioactivity in Bottled Natural Spring, Mineral and Therapeutic Waters in Poland, *Journal of Radioanalytical and Nuclear Chemistry, 279* (2009), 1, pp. 121-129
[27] Todorović, D., Janković, M. M., Cvrkalj, D., Measurement of Radioactivity in the Mineral Waters of the Republic of Srpska, Second International Congress on "Environment, Health, Work, Sport", Banja Luka, Book of Abstracts, June 25-26 , Banja Luka, Republic of Srpska, 2008, pp. 341-342
[28] Bituh, T., *et al*., Natural Radio-Activity of ^{226}Ra and ^{228}Ra in Thermal and Mineral Waters in Croatia, *Radiat. Prot. Dosim., 133* (2009), 2, pp. 119-123
[29] Benedik, L., Jeran, Z., Radiological of Natural and Mineral Drinking Waters in Slovenia, *Radiat. Prot. Dosim. 151* (2012), 2, pp. 306-313
[30] Tanasković, I., Erenić-Savković, M., Javorina, L. J., Radioactivity of Spa Water in Serbia, *Proceedings*, 26 Symposium of Society for Radiation Protection of Serbia and Montenegro, October 12-14, Tara, Belgrade, Serbia, 2011, pp. 137-140
[31] Beyermann, M., *et al*., Occurrence of Natural Radioactivity in Public Water Supplies in Germany: ^{238}U, ^{234}U, ^{235}U, ^{228}Ra, ^{226}Ra, ^{222}Rn, ^{210}Pb, ^{210}Po, and Gross Activity Concentrations, *Radiat. Prot. Dosim., 141* (2010), 1, pp. 72-81
[32] Ajayi, O. S., Owolabi, T. P., Determination of Natural Radioactivity in Drinking Water in Private Dug Wells in Akure, *Southwestern Nigeria, Radiat. Prot. Dosim., 128* (2008), 4, pp. 477-484
[33] Amrani, D., Natural Radioactivity in Algerian Bottled Mineral Waters, *J. Radioanal. Nucl. Chem., 252* (2002), 3, pp. 597-600
[34] ***, International Basic Safety Standards no. 115, IAEA, Vienna, 1995

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ПРИРОДНИ И ПРОИЗВЕДЕНИ (^{90}Sr) РАДИОНУКЛИДИ У ГАЗИРАНИМ МИНЕРАЛНИМ ВОДАМА КОЈЕ СЕ КОРИСТЕ У СРБИЈИ

У раду су приказани резултати испитивања садржаја природних и произведених радионуклида у газираним минералним водама које се производе и флаширају у Србији. Укупна алфа активност је унутар дозвољених вредности, док укупна бета активност превазилази дозвољене вредности од 1 Bq/L за узорке Хеба Стронг и Карађорђе. За ова два узорка активност радионуклида одређена је спектрометријом гама емитера, и нађено је да укупна бета активност у великој мери потиче од ^{40}K. Такође, у узорцима Хеба Стронг и Карађорђе одређен је садржај произведеног радионуклида ^{90}Sr. На основу свих добијених резултата израчуната је годишња ефективна доза, за старосну групу преко 17 година, услед ингестије испитиваних вода. Добијене вредности су ниже од 0.1 mSv, максимално дозвољене дозе за становништво.

Кључне речи: газирана минерална вода, радиоактивност, ^{90}Sr, годишња ефективна доза