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Natural radioactivity of some spring and bottled mineral waters from several central Balkan sites, as a way of their characterization

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Abstract: In this work, a study of the radioactive content of some spring and bottled mineral waters originating from metamorphic rock areas was carried out. A high content of radium isotopes (^{226}Ra, ^{228}Ra), was found by radiometric analysis in the spring waters: Studenica (^{226}Ra: 289 mBq/L), Čibutkovica (^{226}Ra: 92, 4 mBq/L, ^{228}Ra: 610 mBq/L), and Crni Guber (^{226}Ra: 120 mBq/L, ^{228}Ra: 1170 mBq/L). On the other hand, the radiochemical results showed a higher concentration of ^{238}U in the bottled mineral water samples (dissolved uranium concentrations were from 0.21 mBq/L, for "Kopaonik" to 71.5 mBq/L fo "Skadarska") than in the spring water samples (dissolved uranium concentrations were very low ≈ 10 mBq/L). The concentrations of all the present naturally occuring radionuclides: ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{228}Ra and ^{226}Ra were determined by alpha/gamma spectrometric analysis. The activity ratios ^{234}U/^{238}U, ^{226}Ra/^{230}Th and ^{228}Th/^{232}Th, ^{228}Ra/^{228}Th were calculated and are discussed as an indication of the radioactive disequilibrium in bothe the ^{238}U and ^{232}Th radioactive series. The high contents of radium isotopes with respect to the equilibrium values expected from the respective parents ^{232}Th/(^{232}Th series) and ^{230}Th (^{238}U series) found in the spring water samples is the main evidence for the existence of significant radioactive disequilibrium in both the radioactive series.

Keywords: radioactivity: spring waters, mineral bottled waters, spectometry analysis, radioactive equilibirum, activity rations.

INTRODUCTION

Due to the importance of drinking water for human life and the increased consumption of mineral waters, their quality must be carefully and systematically controlled. The recommended control of radioactivity levels in existing or new drinking water includes total alpha/beta activity measurements, as an indication of potentially enhanced radioactivity. In order to guarantee an exposure lower than 0.1

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mSv/y, radioactivity levels for drinking water, recommended by the WHO (World Health Organization), are 0.1 Bq/L for the gross alpha and 1 Bq/L for the gross beta activity. The guideline levels are calculated using a water consumption rate of 2 L daily. For natural mineral waters, the measurement on the naturally occurring radionuclide ^{40}K, which makes up about 0.12 % of natural potassium, is obligatory.[1]

If the gross alpha and/or gross beta activity exceed the recommended values of 0.1 Bq/L and 1 Bq/L, respectively, the contents of specific radionuclides have to be determined by alpha and/or gamma spectrometric measurements.

During routine analysis of water samples mainly from Serbia, only a few samples of spring waters were found to be above the limits of 1Bq/L for beta and 0.1 Bq/L for alpha activity. These are the waters from Serbia (Studenica, Čibutkovica) and one from Bosnia and Herzegovina (Crni Guber). The distribution of naturally occurring radionuclides ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{228}Ra and ^{226}Ra in these waters, obtained by spectrometric analysis, gave evidence of very interesting cases of disequilibrium of radioactive series in the ^{238}U and ^{232}Th decay chains. Since the consumption of spring and mineral waters is continuously growing in most regions in Europe, the monitoring of the radioactivity of drinking water is becoming more important.[2–4] Knowledge of the concentrations of uranium and radium in drinking water is important because an appreciable fraction of the absorbed uranium and radium is deposited in bones, with a corresponding contribution to the internal dose.[5]

The objective of this study was to determine the concentrations of natural radionuclides in some spring and some bottled mineral waters, and to compare them with other studies conducted in the region and to discuss the obtained radioactivity ratios $^{234}U/^{238}U$, $^{226}Ra/^{230}Th$ and $^{228}Th/^{232}Th$, $^{228}Ra/^{228}Th$.

EXPERIMENTAL

Spring water samples were taken at the locations of Studenički izvori and Lazarevac (Serbia) and Srebrenica (Bosnia and Herzegovina). A map of the sampling sites is shown in Fig. 1.

Spring water samples of 10 L were first acidified to pH 2 and then preconcentrated by evaporation under an infrared light to about 450 mL (Table I).[6]

TABLE I. Characteristics of the spring mineral waters

Name	Location	Type of water	Geological setting of aquifer
Studenički izvori	Studenička reka, Studenica	HCO_3–Na	Various schists
Čibutkovica	Reka Grabovica, Lazarevac	HCO_3–Na	Limestone crystalline schiests
Crni Guber	Srebrenica	HCO_3–Na	Bauxite

The studied commercially available bottled natural mineral waters are summarized in Table II, together with some basic data on the aquifers. Water samples$^{(8–12L)}$ are acidified to pH 2 and preconcentrated by evaporation under an infrared light to 450 mL.

After preconcentration, all water samples were sealed into Marrineli beakers and left for 28 days to reach the radioactive equilibrium betweeen ^{226}Ra and daughters (^{214}Bi and ^{214}Pb). Gamma-spectrometric measurements were performed using a HPGe Canberra detector with a counting efficiency of 23 %. The activity of ^{228}Ra was determined indirectly from its daughter, the ^{228}Ac iso-

tope (338.4 keV and 911.2 keV energies). The radium isotope ^{226}Ra was determined from its daughters ^{214}Pb (295.1 keV and 351.9 keV) and ^{214}Bi (609.3 keV, 1120.3 keV and 1764.5 keV). The ^{40}K activity was determined from the 1460.8 keV energy line.

TABLE II. Characteristics of the Serbian bottled mineral waters

Trade name	Location	Under-ground depth/m	Type of water	Geological settings of aquifer
"Mivela"	Veluće	90–120	HCO_3–Na,Mg	Various schists
"Karadjordje"	Smederevska Palanka	10–12	HCO_3–Na,Mg,Ca	Limestone crystalline schists
"Kopaonik"	Brus	700	HCO_3–Na	Limestone,vulcanites
"Prolom:	Prolom Spa	200	HCO_3–Na	Vulcanites
"Skadarska"	Skadarlija Brewery	61	HCO_3,SO_4–Ca,Mg	Karstified limes
"Heba"	Bujanovac Spa	200	HCO_3–Na	Crystalline schists

Fig. 1. Map of Serbia and its vicinity; location of the investigated water resources are marked.

The preparation of thin-layer radioactive sources for alpha-spectrometric analysis included the prior radiochemical procedure of separation of uranium and thorium from the sample matrix and purification from each other and finally electroplating onto stainless steel discs.[7] Low-level activity measurements were performed using a Canbera alpha-spectrometry counting system, consisting of a vacuum chamber (20 mbar), PIPS-detector (300 mm^2 surface), with a counting efficiency of 15 % at a distance of 25 mm, a multichannel energy scale of 9.1 keV/ch and a resolution of 24 keV for ^{241}Am.

The water samples were pretreated by evaporating to dryness and ashing with $NaNO_2$, at 550 °C. After precipitation of the hydroxides, the ion-exchange extraction of uranium and thorium from the matrix and separation and fractionation was performed using a DOWEX 1×4 (100–200 mesh) chloride-conditioned resin. A further eluation on the ion-exchange resin was required for the purification of the obtained uranium and thorium fractions. After extraction of iron, thin-layer radioactive sources for alpha-spectrometry measurements were obtained from the uranium fraction by the

Talvities electroplating procedure. The talvities procedure was also employed for the thorium fraction but the obtained sources had to be covered by VINS foil before measurements to prevent detector contamination by recoil.

To obtain the radiochemical yield ^{232}U and ^{229}Th standard tracer solution (Harwell Laboratory, UKAEA, England) were added to each sample.

RESULTS AND DISCUSSION

The gross alpha and beta activaties of the analyzed bottled mineral waters were within the recommended values, except for the "Heba" and "Karadjordje" samples, where the beta activities were enhanced due to the ^{40}K concentration of 1530 and 2800 mBq/L, respectively. The high values of the total alpha and total beta activities found in three of the examined natural spring water originating from the metamorphic rock area, having a similar chemical compositions (carbon-acid), are due to the high content of naturally occuring radionuclides of the ^{238}U and ^{232}Th series. The contect of racionuclides in bottled and spring mineral waters obtained by alpha and gamma spectrometry are summarized in Table III.

It can be seen that the ^{238}U and ^{234}U isotope concentrations in the bottled waters (dissolved uranium concentrations were very low ≈ 10 mBq/L) are higher than in the samples of spring water (dissolved uranium concentrations range from 0.21 mBq/L for "Kopaonik" to 71.5 mBq/L for "Skadarska"). These uranium concentrations are comparable with some others from the region.[3,4] They are even lower than those in

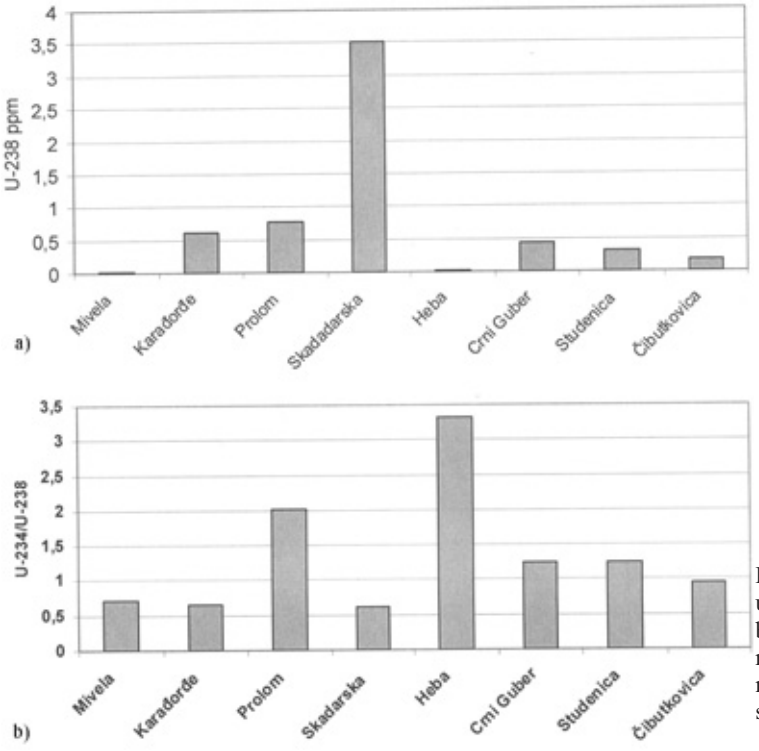

Fig. 2. a) Total uranium content (ppm) and b) $^{234}U/^{238}U$ activity ratio in the measured mineral bottled and spring waters.

TABLE III. Activities (mBq/L) of uranium, thorium and potassium isotopes in the investigated water samples

Water Sample	U-238	U-234	U-235	Th-232	Th-230	Th-228	Ra-228	Ra-226	K-40
"Mivela"	0.29±0.06	0.21±0.07	< 0.02	< 0.86	< 0.86	14±5	< 3	< 26	155±26
"Karadjordje"	7.61±1.00	5.05±0.75	0.22±0.11	< 0.2	< 0.2	4.75±0.53	< 3	26	280±400
"Kopaonik"	0.21±0.18	< 0.16	< 0.02	< 0.2	< 0.2	4.75±0.53	18±5	29±7	300±31
"Prolom"	9.38±1.10	18.9±2.1	0.34±0.1	< 0.4	< 0.2	10.4±1.9	M3	< 26	< 70
"Skadarska"	43.4±4.6	26.3±2.8	1.8±0.4	< 0.06	< 0.06	6.91±0.85	< 3	34±5	230±8
"Heba"	0.22±0.05	0.73±0.11	< 0.05	< 0.05	< 0.05	15.04±1.62	100±15	60±6	1530±30
Crni Guber	5.36±1.0	6.6±1.3	< 0.37	1.20±0.4	< 0.24	152±18	1170±110	120±16	750±12
Studenica	3.80±0.46	4.7±0.6	0.17±0.04	0.44±0.10	0.350±0.08	6.00±0.77	< 20	2280±254	1700±260
Čibutkovica	2.20±0.2	2.1±0.2	< 0.2	0.90±0.3	2.4±0.5	48.9±4.0	610±200	92.4±30.5	1670±120

some bottled waters from Northen Italy.[8] The $^{234}U/^{238}U$ activity ratio values in the bottled samples were within the range from 0.6–3.3, which is in accordance with the reported results.[8,9] However, the low content of ^{238}U in the "Heba" (0.22 mBq/L) and "Prolom" (9.38 mBq/L) samples corresponds to a $^{234}U/^{238}U$ ratio greater than 1 (2 and 3.3, respectively), Fig. 2. The ^{234}U excess compared to the ^{238}U content in waters may be explained by *in situ* leaching through alpha-recoil tracks.[10] The same correlation in well waters was attributed to the changes in the oxidizing/reducing conditions of the aquifer environment,[11] being characteristic in oxidizing zones.[12] Elevated temperatures and strong reducing conditions usually result in the opposite relations, due to the acceleration of isotope exchange processes.[13]

The $^{234}U/^{238}U$ ratios obtained for the spring waters Crni Guber, Studenica and Čibutkovica were 1.22, 0.95 and 1.24, respectively, indicating the ^{238}U series radioactive equilibrium.

The content of ^{226}Ra and ^{228}Ra isotopes, originating from the ^{238}U and ^{232}Th decay series, was quite low in the analyzed bottled mineral waters, compared to the values obtained for other bottled mineral waters[3,4] and the investigated spring waters (Crni Guber, Studenica and Čibutkovica).

The spring water samples were poor in uranium and rich in radium. The highest concentrations of the Ra isotopes were found in the limestone regions, where Ra is more soluble in HCO_3^- waters.[9] The values obtained show that a large a amount of ^{226}Ra does not necessarily indicate a high ^{238}U content, since the radium may migrate and be deposited randomly from the surrounding rock areas.[14] In geothermal sources, where the temperature is high and the concentration of chlorine elevated and the reducing potential is very weak, the $^{226}Ra/^{238}U$ ratios are often high,[15] even in the order of 10^3–10^4.[16] In a reducing medium, with uranium less mobile than radium, the disappearance of sulphates allows high radium concentrations in solution.[17]

The high content of radium isotopes with rescept to the equilibrium values, expected from the parent isotopes ^{232}Th(^{232}Th series) and ^{230}Th(^{238}U series), found in the spring water samples, are evidence of the existence of a significant radioactive disequililbrium in both radioactive series.

The ^{226}Ra concentration in the spring mineral waters, exceeding the equilibrium value corresponding to the ^{230}Th content, with $^{226}Ra/^{230}Th$ ratios of 38.5 and 6514 (Table IV), for the Čibutkovica and Studenica samples, respectively, show a significant of disequilibrium level of the ^{238}U series.

TABLE IV. Radioactivity ratios of radionuclides from the ^{238}U and ^{232}Th series in the spring water samples

Mineral water	$^{234}U/^{238}U$	$^{226}Ra/^{230}Th$	$^{228}Th/^{232}Th$	$^{228}Ra/^{228}Th$
Crni Guber	1.24	/	126.7	7.7
Studenica	1.24	6514	13.6	/
Čibutkovica	0.95	38.5	54.3	12.4

Considering the ^{232}Th series, the ^{228}Ra/^{228}Th and ^{228}Th/^{232}Th ratios obtained for the spring waters were much higher than expected from the amounts determined for the parent isotopes (Table IV). The ^{228}Ra excess in the waters may be attributed to the different solubility of thorium and radium and a partly upward diffusion from the surrounding sediments.[9] In the decay process from ^{232}Th to ^{228}Th, the ^{228}Ra radionuclide ($t_{1/2}$ = 5.75 y) is in the middle. Since the chemical properties of radium and thorium are different, the high ^{228}Th content derives from ^{228}Ra.

CONCLUSION

Radiochemical analyses of some natural mineral bottled waters from several locations in the central Balkan area showed the presence of naturally occurring radionuclides from both the ^{238}U and ^{232}Th series. The relevant activity ratios ^{234}U/^{238}U, ^{226}Ra/^{230}Th, ^{228}Th/^{232}Th, ^{228}Ra/^{228}Th were indicative of radioactive disequilibrium, especially in the spring water samples.

Higher ^{238}U activities in some bottled, when compared with the examined spring waters, show the reverse trend in the ^{238}U activity *versus* the ^{234}U/^{238}U activity ratio. The ^{238}U and ^{234}U isotope concentrations in the bottled waters were found to be up to 71.5 mBq/L.The contents of ^{226}Ra and ^{228}Ra isotopes were quite low and, in some cases below the detection limit.

The very high ^{226}Ra and ^{228}Ra activities in the spring waters do not necessarily indicate high concentrations of their parents in the ^{238}U and ^{232}Th series.

The analyzed water samples are selected for analysis due to their enhanced gross alpha/beta activity. The study gives a contribution to the radionuclides mapping of natural mineral waters in metamorphic petrology areas.

ИЗВОД

ПРИРОДНА РАДИОАКТИВНОСТ НЕКИХ ИЗВОРСКИХ И ФЛАШИРАНИХ МИНЕРАЛНИХ ВОДА СА НЕКОЛИКО ЛОКАЦИЈА НА ЦЕНТРАЛНОМ БАЛКАНУ, КАО НАЧИН ЊИХОВЕ КАРАКТЕРИЗАЦИЈЕ

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У овом раду су приказани резултати испитивања садржаја радионуклида у неким изворским и флашираним минералним водама који потичу из метамофрних области. У изворским минералним водама је измерен висок садржај радијумових изотопа (^{226}Ra, ^{228}Ra): Студеница (^{226}Ra: 2280 mBq/L), Чибутковица (^{226}Ra: 92,4 mBq/L, ^{228}Ra: 610 mBq/L) и Црни Губер: (^{226}Ra: 120 mBq/L, ^{228}Ra: 1170 mBq/L). Са друге стране, већа концентрација ^{238}U је детектована у флашираним минералним водама (концентрације уранијума се крећу од 0,21 mBq/L за "Копаоник" до 71,5 mBq/L за "Скадарску") него у изворским (концентрације уранијума су реда величине ≈ 10 mBq/L). Концентрације присутних радионуклида, ^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th, ^{228}Ra и ^{226}Ra, су одређена алфа и гама спектрометријски. Као индикација радиоактивне неравнотеже у оба низа (^{238}U, ^{232}Th) изра-

чунати су и дискутовани следећи односи: $^{234}U/^{238}U$, $^{226}Ra/^{230}Th$, $^{228}Th/^{232}Th$, $^{228}Ra/^{228}Th$. У узорцима изворских вода садржај радијумових изотопа је изнад равнотежне вредности која се очекује на основу садржаја родитељских нуклида.

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