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Levels of natural radioactivity in mineral and thermal waters of Bosnia and Herzegovina

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Abstract. With gamma spectrometric method 23 samples of mineral and thermal waters of Bosnia and Herzegovina were analyzed. Activity concentrations of the investigated radionuclides were in the range 12–346 mBq·L^{-1} for ^{40}K, 1.1–791 mBq·L^{-1} for ^{226}Ra, 0.2–221 mBq·L^{-1} for ^{228}Ra, 13–367 mBq·L^{-1} for ^{238}U, and 0.6–17 mBq·L^{-1} for ^{235}U. For all investigated radionuclides annual effective dose was estimated. The estimated total annual committed effective dose received by population as a result of ingestion of water was in the range 0.11–2.51 μSv·y^{-1} for thermal water and in the range 0.11–38.8 μSv·y^{-1} for mineral water. Measurement of activity concentrations of natural radionuclides in the examined samples was carried out with a gamma-spectrometer with high-purity germanium (HPGe) detector, having a relative efficiency of 70%.

Key words: gamma spectrometry • natural radioactivity • mineral water • thermal water • groundwater • uranium • radium

Introduction

Natural radioactive isotopes exist in water from its creation. Radionuclides in drinking water cause human internal exposure, which is caused by the decay of radionuclides taken into the body through ingestion and inhalation indirectly when they are incorporated as a part of the human food chain [1].

Uranium isotopes (^{238}U, ^{234}U, and ^{235}U) have non-negligible radiotoxicity [2]. The World Health Organisation (WHO) set the uranium limit of 15 μg·L^{-1}, but many countries as, for example, the United States and Canada have higher limits (20 and 30 μg·L^{-1}, respectively) [3, 4]. Recently, Germany set a maximum level of 2 μg·L^{-1} for uranium in mineral water considered to be suitable for infants [4]. Radium is a naturally occurring isotope and has high solubility when compared with uranium causing penetration through fractures into bedrock and can leak out into groundwater [5]. Potassium occurs in various minerals and clays, from which it may dissolve in water through the weathering processes. ^{40}K is released into water bodies, contributing to the presence of radioactive constituents of drinking water [1].

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Screening levels for drinking water, below which no further action is required, are 0.5 $Bq \cdot L^{-1}$ for gross alpha activity and 1 $Bq \cdot L^{-1}$ for gross beta activity. If these values are exceeded, the determination of particular radionuclides dissolved in drinking water needs to be performed. The essence of the evaluation of the gross alpha and gross beta activities is to ensure that the reference dose level of committed effective dose of 0.1 mSv from 1 year's consumption of drinking water is not exceeded [3, 6].

Materials and methods

Study area

Mineral water often originates from very deep aquifers and usually show higher loads of natural radionuclides leached from the surrounding bedrock [4]. Mineral water has more than 1 g of soluble mineral matters in 1 liter, which gives it a specific taste and smell. Thermal water is found at a greater depth, and on its way up it is heated by the warm rocks and the minerals from the rock dissolve in the water. Thermal water and mineral water are valuable natural resources of countries and are popular for medical therapy, tourism, recreation, and rehabilitation [5, 7].

Bosnia and Hercegovina have a large number of registered and unregistered thermal and mineral sources. The water samples were collected in the famous spa centers: Dvorovi Spa, Guber Spa (Mali Guber, Voda Ljepotica), Ilidža Spa, Kulaši Spa, Laktaši Spa, Reumal Spa, Gata Spa, Slatina Spa, and Termalna Rivijera Ilidža. Also, water samples were taken at the following mineral sources: Kiseljak and Voda Miladije from Tuzla, Kiseljak from Kalesija, Kiseljak and Vitinka from Kozluk, Kiseljak in Teslić, Sarajevo Kiseljak, Oraš Planje, Princess and Celvik from Tešanj, Toplice from Živinice, Muška Voda from Kladanj, and Petrak from Lukavac (Fig. 1).

Thermal water from the Ilidža Spa has a constant temperature of 28.5°C and by its chemical content is grouped into sodium-calcium-magnesium-sulfate water. Thermal water of Slatina Spa is hydrocarbonate-sulfate-calcium-magnesium. Water in Reumal Spa and Laktaši Spa is hydrocarbonate-calcium. Thermal water of Dvorovi Spa has therapeutic value because of the fluorine content. By its chemical content, the water of Gata Spa is classified as sodium-calcium-sulfate-hydrocarbonated water. The main feature of the Mali Guber, Vode Ljepotice is the presence of bivalent iron [8]. Tešanj and Teslić mineral waters (Oraš Planje, Celvik, Princess, and Kiseljak) are classified as cold mineral waters (temperature of 14–18°C) [8–10]. Mineral water from Voda Miladije, Petrak, Muška Voda, Toplice, Kiseljak from Husino and Vitinka is classified as a soft mineral type of water. Mineral water from Kiseljak from Kalesija, Kiseljak from Kozluk and Sarajevski Kiseljak has a temperature of 12°C and contains a significant amount of magnesium [8, 11].

Experimental procedure

Gamma spectrometric analysis of the samples of thermal and mineral waters was carried out to test the samples of mineral or thermal water collected. For each sample we took 100 L of water; afterward we started the laboratory preparation of samples for gamma spectrometric analysis. After sampling, the samples of water were evaporated on a gas stove to a dry residue, at a temperature of 70°C. The average

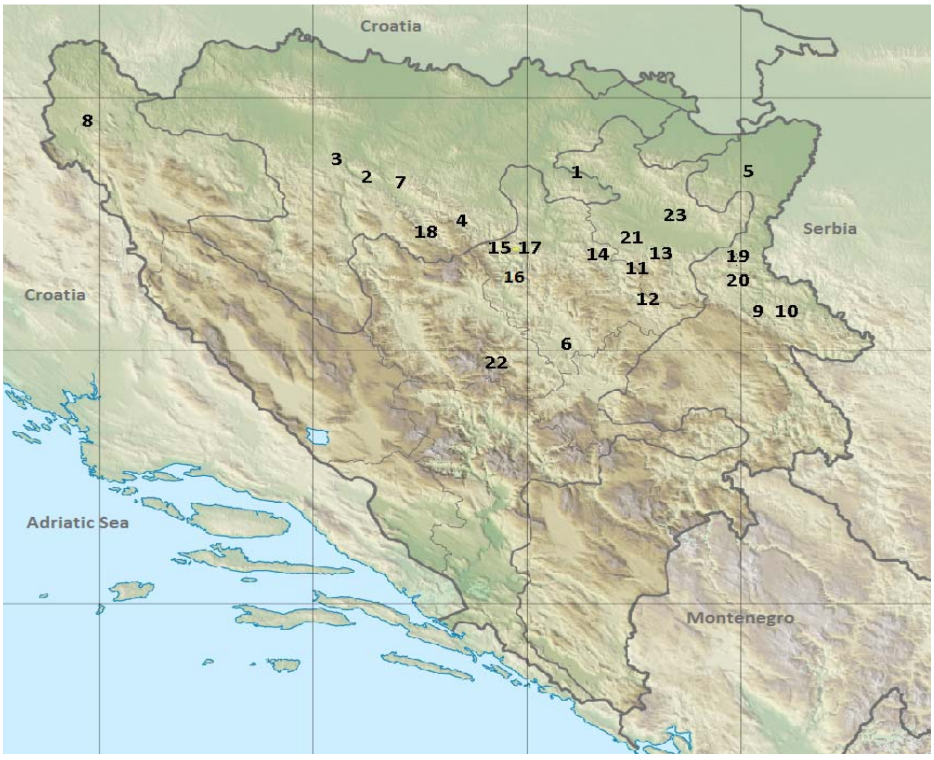

Fig. 1. Map of the investigated locations of thermal and mineral waters in Bosnia and Herzegovina.

time of evaporation per sample of water amounted up to 21 days. After cooling the dry residue to room temperature, the dry residue was soaked with 100 ml of 37% hydrochloric acid and distilled water.

Then soaked dry residue was transfered in Marinelli vessels of 1 L volume. One liter of distilled water was added and the vessels were filled up completely. Marinelli vessels are additionally sealed with wax and wrapped with tape. The samples were stored for 4 weeks to reach radioactive equilibrium between ^{226}Ra and its daughters ^{214}Bi and ^{214}Pb. Measurement of activity concentrations of natural radionuclides in investigated samples was carried out with a gamma-spectrometer (HPGe detector) of relative efficiency 70% and with the resolution of 2.3 keV at 1.33 MeV, and 1.20 keV at 122 keV. The counting time was 172 800 s. For recording the background radiation spectrum, Marinelli vessel having the same geometry and filled with distilled water was used.

Energy and efficiency calibration was performed using reference sample MIX-CBSS2 (Czech Metrology Institute-IIR, Prague). It is a silicon matrix of 0.985 ± 0.01 g·cm^{-3} density and the corrections for self-absorption are negligible. For gathering and analysis of the spectrum from multichannel analyzer the full version of Gamma Acquisition and Analysis Software package Genie 2000 (Canberra) was used [12]. With Genie 2000 Gamma Analysis Software, each spectrum was analyzed for interferences and coincidence summing correction.

Activity concentration of ^{226}Ra was determined by their products: ^{214}Bi (609.3 keV) and ^{214}Pb (351.9 keV). ^{238}U was determined by ^{234m}Pa (1001.0 keV). Activity concentrations of ^{40}K were determined from its 1460.8 keV γ-line. ^{228}Ra was calculated from ^{228}Ac (968.9 keV). The activity concentration of ^{238}U was determined after 4 months (about 120 days), after reaching the radioactive equilibrium between ^{238}U and ^{234}Th and ^{234m}Pa.

Activity concentration of ^{235}U was determined from the concentration ^{238}U, using the fact that the natural ^{235}U/^{238}U activity ratio has a constant value 0.04604 [13].

The activity concentration of the radionuclide was obtained from the following equation

$$A = \frac{N(E_\gamma)}{I_\gamma(E_\gamma) \cdot \varepsilon\left(E_\gamma\right) \cdot t \cdot V} \tag{1}$$

where: $N(E_\gamma)$ is the full-energy peak, $I_\gamma(E_\gamma)$ is the emission probability of the measuring γ-rays with the given energy; $\varepsilon(E_\gamma)$ is the full-energy peak efficiency; V is the volume of water sample [L]; t is the counting time [s] [13]. When the activity concentration was determined on the basis of a few lines, the weighted average was calculated.

Assessment of annual committed effective dose rate received by population as a result of ingestion of water for natural radionuclides ^{40}K, ^{226}Ra, ^{228}Ra, ^{238}U, and ^{235}U was carried out on the basis of the following equation

$$H_i = C_i \cdot D_i \cdot V \tag{2}$$

where: H_i is the annual committed effective dose obtained by the ingestion of tested thermal and mineral samples [μSv·y^{-1}]; C_i is the activity concentration of i-isotope of a natural radionuclide [mBq·L^{-1}]; D_i is the ingestion dose conversion factor for individual radionuclides [Sv·Bq^{-1}]; V is the water consumption [L] per year [14].

According to the International Commission of Radiological Protection (ICRP-30) [15], the treatment by drinking thermal water usually takes 1–4 weeks, during which the patient consumes one liter of water per day. Thermal water for treatments by ingestion was used for 4 weeks in investigated spa centers, with consumption amounting to one liter per day. Based on the above mentioned points, the annual committed effective dose received by the population as a result of ingesting thermal water was calculated.

To calculate the annual committed effective dose received by the population as a result of ingesting mineral water for selected natural radionuclides, it was taken that the average water consumption per year was 100 L [16].

Dose conversion factors used for the calculation were taken from the WHO publication (2004) and were equal to 6.2×10^{-9} Sv·Bq^{-1}, 2.8×10^{-7} Sv·Bq^{-1}, 6.9×10^{-7} Sv·Bq^{-1}, 4.5×10^{-8} Sv·Bq^{-1} and 4.7×10^{-11} Sv·Bq^{-1} for ^{40}K, ^{226}Ra, ^{228}Ra, ^{238}U, and ^{235}U, respectively [3, 17].

Results and discussion

The measurement of natural radioactivity in samples of mineral and thermal waters was carried out throughout Bosnia and Herzegovina. The results of the measured activity concentrations of ^{40}K, ^{226}Ra, ^{228}Ra, ^{235}U, and ^{238}U isotopes in samples of mineral and thermal waters of Bosnia and Herzegovina are presented in Table 1.

The activity concentrations for ^{40}K vary from 12 to 346 mBq·L^{-1}. The lowest activity concentration of ^{40}K was 12 mBq·L^{-1} in Laktaši Spa and the highest was 346 mBq·L^{-1} at the site of Kiseljak in Kozluk. The highest value of ^{40}K activity concentration is lower than the concentrations of ^{40}K observed in Jordan (23.2–34.8 Bq·L^{-1}) [18].

The activity concentration of radium isotopes was in the range from below 1.1 mBq·L^{-1} to 791 mBq·L^{-1} for ^{226}Ra and from below 0.2 mBq·L^{-1} to 221 mBq·L^{-1} for ^{228}Ra. At the Reumal Spa, activity concentrations of ^{226}Ra were up to 4.5 times higher than those of ^{228}Ra. The obtained values for ^{226}Ra and ^{228}Ra do not differ significantly from the results for some thermal and mineral waters in Croatia [19]. The activity concentration of ^{226}Ra at the Kiseljak in Kozluk was higher than 0.5 Bq·L^{-1}. According to the WHO Guidelines for Drinking Water Quality the concentration should not exceed 0.5 Bq·L^{-1} for gross alpha activity and 1 Bq·L^{-1} for gross beta activity [3, 6].

The activity concentration of ^{238}U was in the range 13–367 mBq·L^{-1}. The highest value of ^{238}U 367 mBq·L^{-1} was found in the sample collected at

Table 1. Activity concentration and total annual committed effective dose of the investigated radionuclides in samples of mineral and thermal waters of Bosnia and Herzegovina

No.	Location	Type of water	^{40}K [mBq·L^{-1}]	^{226}Ra [mBq·L^{-1}]	^{228}Ra [mBq·L^{-1}]	^{238}U [mBq·L^{-1}]	^{235}U [mBq·L^{-1}]	H_{total} [μSv·y^{-1}]
1.	Ilidža Spa	Thermal	157 ± 6	61.2 ± 1.3	20.4 ± 0.4	30 ± 8	1.3 ± 0.3	0.90 ± 0.1
2.	Slatina Spa	Thermal	328 ± 7	187 ± 3	45 ± 4	55 ± 10	2.5 ± 0.4	2.31 ± 0.02
3.	Laktaši Spa	Thermal	12 ± 5	5.7 ± 0.6	6.1 ± 0.7	32 ± 8	1.4 ± 0.4	0.18 ± 0.03
4.	Reumal Spa	Thermal	23 ± 5	182 ± 2	40 ± 3	33 ± 10	1.5 ± 0.5	2.21 ± 0.03
5.	Dvorovi Spa	Thermal	92 ± 5	116 ± 2	43 ± 2	52 ± 22	2.4 ± 1.0	1.81 ± 0.04
6.	Termalna Rivijera Ilidža	Thermal	79 ± 5	120 ± 2	79 ± 4	86 ± 12	3.9 ± 0.6	2.51 ± 0.08
7.	Kulaši Spa	Thermal	45 ± 5	1.4 ± 0.7	0.3 ± 0.1	73 ± 54	3.3 ± 2.3	0.11 ± 0.07
8.	Gata Spa	Thermal	91 ± 5	50.3 ± 1.1	11 ± 3	17 ± 5	0.7 ± 0.2	0.61 ± 0.01
9.	Mali Guber	Thermal	126 ± 5	10.5 ± 0.4	15 ± 0.3	68 ± 7	3.1 ± 0.2	0.41 ± 0.05
10.	Voda Ljepotica	Thermal	79 ± 9	22 ± 13	24 ± 1	81 ± 17	3.7 ± 0.8	0.60 ± 0.1
11.	Toplice	Mineral	33 ± 4	10 ± 4	4 ± 1	250 ± 61	11.5 ± 2.8	1.70 ± 0.5
12.	Muška Voda	Mineral	18 ± 4	1.9 ± 0.4	0.4 ± 0.2	124 ± 71	5.7 ± 3.3	0.60 ± 0.3
13.	Voda Miladije	Mineral	40 ± 5	2.5 ± 0.4	0.9 ± 0.7	13 ± 9	0.6 ± 0.2	0.20 ± 0.1
14.	Petrak	Mineral	65 ± 5	17 ± 9	0.9 ± 0.2	24 ± 11	1.1 ± 0.5	0.70 ± 0.3
15	Oraš Planje	Mineral	60 ± 5	1.5 ± 0.4	0.9 ± 0.3	20 ± 8	0.9 ± 0.4	0.20 ± 0.1
16	Princess	Mineral	14 ± 5	1.1 ± 0.5	0.2 ± 0.1	15 ± 8	0.6 ± 0.3	0.11 ± 0.05
17.	Celvik	Mineral	190 ± 6	80 ± 1.3	95 ± 4	136 ± 10	6.3 ± 0.4	8.40 ± 0.4
18.	Kiseljak, Teslić	Mineral	257 ± 10	97 ± 2	81 ± 4	189 ± 17	8.7 ± 0.8	8.80 ± 0.4
19.	Kiseljak, Kozluk	Mineral	346 ± 8	791 ± 9	221 ± 40	304 ± 13	14.0 ± 0.6	38.80 ± 3.6
20.	Vitinka	Mineral	148 ± 6	161 ± 1.2	73 ± 4	83 ± 12	3.8 ± 0.5	9.80 ± 0.4
21.	Kiseljak, Husino	Mineral	52 ± 5	16 ± 6	2.0 ± 1.2	106 ± 64	4.8 ± 2.9	1.10 ± 0.6
22.	Sarajevski Kiseljak	Mineral	86 ± 5	19 ± 1	10 ± 1	19 ± 4	0.8 ± 0.1	1.20 ± 0.1
23.	Kiseljak, Kalesija	Mineral	219 ± 6	219 ± 2	137 ± 4	367 ± 16	17.0 ± 0.7	16.70 ± 0.4
	Mean value		111	94	39	95	4.3	4.3

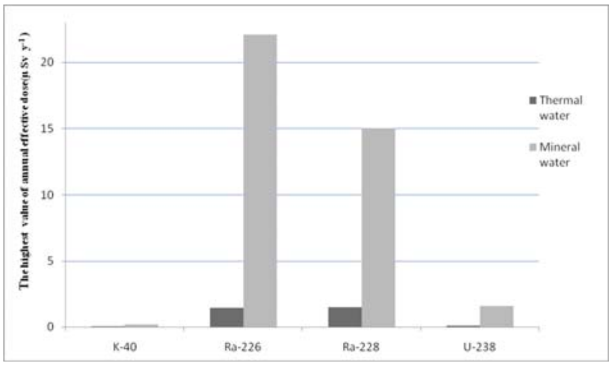

Fig. 2. The comparative overview of the highest value of annual committed effective dose of ^{40}K, ^{226}Ra, ^{228}Ra, and ^{238}U in thermal and mineral water samples.

Kiseljak in Kalesija, whereas the lowest 13 mBq·L^{-1} at Voda Miladije. The obtained values for activity concetration of ^{238}U are significantly lower than the activity concentration for ^{238}U in Jordan (2.1–5.9 Bq·L^{-1}) [18].

The activity concentration of ^{235}U was calculated from ^{235}U/^{238}U ratio. The activity concentration was in the range 0.6–17 mBq·L^{-1}. The highest value of 17 mBq·L^{-1} was found in the sample collected at Kiseljak in Kalesija, and the lowest 0.6 mBq·L^{-1} at Princess in Tešanj. These results are lower than the activity concentration of ^{235}U in some mineral waters in Tunisia (60 mBq·L^{-1}) [20].

Based on the results found for activity concentration of five radionuclides in mineral and thermal waters presented in Table 1, the annual committed effective dose was estimated. Further, the dose reference level of 0.1 mSv·y^{-1} suggested by WHO has been used for comparison with our results [3, 6]. Some of the results obtained in this study were compared with the results from earlier studies for other countries.

Figure 2 shows a comparative overview of the highest value of the annual committed effective dose of ^{40}K, ^{226}Ra, ^{228}Ra, and ^{238}U in thermal and mineral water samples.

The annual committed effective dose of ^{40}K was in the range 0.002–0.056 μSv·y^{-1} and 0.01–0.2 μSv·y^{-1}, for thermal and mineral waters, respectively. The annual committed effective dose for ^{226}Ra and ^{228}Ra was in the range 0.01–1.43 μSv·y^{-1} and 0.004–1.5 μSv·y^{-1}, respectively, when considering thermal waters. The annual committed effective dose for ^{226}Ra and ^{228}Ra were in the range 0.04–22.1 μSv·y^{-1} and 0.01–15.0 μSv·y^{-1}, respectively, when considering mineral waters. The annual committed effective dose of ^{238}U was in the range 0.021–0.1 μSv·y^{-1} and 0.05–1.6 μSv·y^{-1}, for thermal and mineral waters, respectively. The maximum value of annual committed effective dose received by population as a result of ingestion of investigated mineral and thermal waters of Bosnia and Herzegovina for the ^{235}U, was 0.005 nSv·y^{-1} for thermal waters and 0.07 nSv·y^{-1} for mineral waters. These values do not exceed the limit of 0.1 mSv·y^{-1} [3, 6].

The total committed effective dose for investigated thermal and mineral water samples was estimated (Table 1). According to the WHO publication ^{40}K does not accumulate in the human body so it was not added to the total dose [3, 6]. The estimated total annual committed effective dose received by the population as a result of ingestion of water was in the range 0.11–2.51 μSv·y^{-1} for thermal water and in the range 0.11–38.8 μSv·y^{-1} for mineral water. These values do not exceed the limit of 0.1 mSv·y^{-1} [3, 6].

Conclusions

These measurements present the first measurements of activity concentrations and annual committed effective dose of ^{40}K, ^{226}Ra, ^{228}Ra, ^{238}U, and ^{235}U, in the investigated samples of mineral and thermal waters of Bosnia and Herzegovina. The activity concentrations of ^{226}Ra in all samples, excluding the location of Kiseljak in Kozluk, are below the recommendation level of 0.5 Bq·L^{-1} [3, 6]. The activity concentrations of ^{238}U and ^{235}U in all investigated samples are below the recommendation level of 0.5 Bq·L^{-1} [3, 6]. The estimated value of total annual committed effective dose for investigated samples of mineral and thermal waters do not exceed the limit of 0.1 mSv·y^{-1} [3, 6]. The results show that thermal and mineral waters from investigated locations of Bosnia and Herzegovina vary considerably in radionuclide activity concentrations and thus the annual committed effective doses.

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