226Ra and natural uranium in Bulgarian mineral waters

E Geleva1, D Tonev1, H Protohristov1, N. Goutev1, E. Salkova2, N. Nikolova1

1Institute for Nuclear Research and Nuclear Energy, Bulgarian Academy of Sciences “Tzarigradsko shaussee” 72 Blvd, 1784 Sofia, Bulgaria
2Institute for the State and the Law, Bulgarian Academy of Sciences, “Serdika” Str. 4, 100 Sofia, Bulgaria
elenag@inrne.bas.bg

Abstract. A complex investigation on Bulgarian mineral waters from certain frequently used sources have been carried out. Specific activities of 226Ra and concentration levels of natural uranium in mineral waters samples were analyzed using nuclear and analytical methods. 

226Ra is a naturally occurring radioisotope with a period of half live 1600 years, which specific activity in water was determined through analysis of the daughter 222Rn. The measurements were carried out using a low-level liquid scintillation counting in a Packard Tri-Carb 2770 TR/SL liquid scintillation spectrometer. Uranium concentration was measured in water samples using a luminescent method. In addition to 226Ra and natural uranium, determination of gross alpha and beta activities of waters was made by means of the same liquid scintillation spectrometer. The concentrations values obtained were compared with data reported by other authors in different countries and with reference values accepted for drinking water. The expected annual effective doses for ingestion of natural uranium and 226Ra in the analysed waters were calculated.

1. Introduction.
Waters, one of the most important components of the environment, are part of all food chains and a major route for the entry of radioactive substances into the human body. Therefore, regular and control studies of mineral waters are necessary to guarantee that they have a low level of radioactivity.

Mineral water is one of the most precious natural resources in Bulgaria. There are more than 240 hydrothermal sources having different temperature, mineral composition and radioactivity. Their healing and recreational properties are well known and effectively used since Roman time.

The growing concern about radioactivity in the public sector and the introduction of new regulatory limits for radium activity, gross alpha and beta radioactivity and uranium concentration in water for drinking and domestic purposes [1], lead local authorities in Bulgaria to expressed considerable interest in control and monitoring of certain mineral water sources frequently used by residents and tourists. For this reason, independent investigations of these sources, complementary to the national regulatory control, were performed at INRNE-BAS in order to confirm the recommended low level of radioactivity.

The natural radioactivity of the waters in Bulgaria have been studied since the first decades of the 20th century by Prof. Peter Pencheff, one of European pioneers in radioactivity research [2]. Large scale investigations of water sources, especially in regions with high incidence of Endemic Nephrite,
were performed in the 1950s and 1960s from Prof. E. Karamihailova [3], an eminent Bulgarian and internationally recognized nuclear physicist. Later on radiological studies on mineral waters have been carried out by A. Azmanov, H. Melamed, H. Paparov and others, and in recent years by R. Totseva [4].

Water radioactivity depends on the water origin and its chemical composition. Artificial radionuclides are absorbed into the hydrosphere mainly through radioactive fallout and disposed radioactive liquid waste. The enrichment on natural radionuclides in water is conditioned by emanation processes, leaching and dissolution of mineral substances. Most of the radionuclides originate from minerals dissolved in water (Dissolved Mineral Radioactivity). Radioactive minerals are irregularly deposited in bedrock, similar to other minerals and they could be easily dissolved in water. Bedrock contains various natural radioactive elements including uranium, thorium, radium and potassium. The natural radioactivity in water is therefore resulting from water passage through deposits of naturally occurring radioactive materials [5, 6]. The specific distribution and migration of natural radioactivity in vicinity of large uranium deposits and mining sites, especially in Buhovo [7] and Eleshtnitsa [8], as well as, of artificial radionuclides, like the absorption of the airborne $^{137}$Cs, in soil, plants and wines [9] has been studied previously by precise radioanalytical methods.

The determination of $^{226}$Ra, natural uranium, gross alpha and beta activities in mineral waters is very important from the radiological point of view. The daily consumption of mineral water with high content of natural radionuclides may have a significant contribution to the internal natural radiation exposure of the population. The determination of $^{226}$Ra in water is of primary importance to human health since this isotope is a bone-accumulating radionuclide with a prolonged to life-long residence time and high contribution to the internal dose. Upon entering the human body either by ingestion or inhalation, a fraction of $^{226}$Ra will be translocated to blood, the main site of deposition being the skeleton. As an alpha emitter and bone-seeking radionuclide, $^{226}$Ra has a high potential for causing biological changes in blood forming tissues. It tends to follow the same metabolic pathways as calcium. Once deposited in bone tissue, it continually irradiates the human skeleton for many years, and potentially induces bone sarcoma [10].

Uranium is naturally occurring, ubiquitous, radioactive heavy metal which originates from several sources, including leaching from natural deposits, release in mill tailings, emissions from nuclear industry and the combustion of coal and other fuels [11]. Drinking water is therefore the major source of uranium to the human body. Many mineral waters have naturally high uranium contents up to 0.1 mg/L. The World Health Organization (WHO) recommended a reference level of the permissible limit of nat. U in drinking water 0.030 mg/L [12].

Natural mineral waters may contain a number of alpha ($^{238}$U, $^{234}$U, $^{232}$Th, $^{226}$Ra and $^{210}$Po) and beta emitters ($^{228}$Ra and $^{210}$Pb) from the natural decay series of uranium and thorium, the primordial isotope, $^{40}$K and artificial isotopes, such as $^{137}$Cs and $^{90}$Sr in various concentrations. The high-energy alpha and beta emitters have significant radiotoxicity.

The lack of any big research facility in Bulgaria like a high-flux nuclear reactor or ion accelerator makes impossible the application of more precise and advanced methods for water quality investigations. Therefore, in the present study we apply the most accurate conventional analytic methods. The National cyclotron centre at INRNE, based on the TR 24 machine, [13] will open a new horizon for such research, as well as for various applications in the field of nuclear physics and radiochemistry.

The present study is aimed to investigate the natural radioactivity in mineral waters originating from certain frequently used sources from different locations in Bulgaria. The expected radiation doses obtained from the consumption of these waters due to their $^{226}$Ra activity and uranium content is calculated.
2. Material and methods

Objects of this research are natural mineral water springs located in the Central and in the South-Western regions of Bulgaria (Figure 1).

The radiological study includes measurements of specific activity of $^{226}$Ra, uranium concentration, gross alpha and beta activities studied mineral waters.

![Geographical distribution of localities, where mineral waters have been investigated](image)

**Figure 1.** Geographical distribution of localities, where mineral waters have been investigated

2.1. $^{226}$Ra activity

$^{226}$Ra specific activity in mineral waters was determined by a combination of solvent extraction and LSC based on a radon extraction by a scintillation cocktail immiscible with water, followed by a measurement with a liquid scintillation counter of the alpha-emission of radon and of its decay products in radioactive equilibrium with the parent. Radon, being a noble gas, is easily and selectively extracted by the organic phase, whereas all the other radionuclides present in ionic form are not extracted [6]. The samples were measured by us using a Liquid Scintillation Counter, Packard TRI-CARB 2770 TR/SL, with pulse shape discrimination (PSD) for separation and acquisition of $\alpha$ and $\beta$ events into different multi-channel analyzers.

2.2. Uranium concentration

Uranium concentration was determined on the basis of the ability of uranium melted with sodium fluoride to produce light under UV illumination. The intensity of induced luminescence is proportional to the concentration of Uranium [4, 14].

2.3. Gross alpha and beta activity

Determination of gross alpha and beta activity in mineral waters was performed by liquid scintillation counting. Acidified water samples to a volume of 1 000 mL were evaporated until dryness (avoiding boiling) and dissolved with 5 mL of 0.1M nitric acid. The solutions were then transferred to a 20 mL polyethylene scintillation vial, and mixed with 15 mL of Packard ULTIMA GOLD AB scintillation cocktail for measurement [15, 16]. The samples were measured in a Liquid Scintillation Counter (PACKARD TRI-CARB 2770 TR/SL). The counting efficiency was evaluated with $^{241}$Am and $^{90}$Sr/$^{90}$Y standards.
3. Results and discussion

3.1. \(^{226}\text{Ra}\) activity

The results of the \(^{226}\text{Ra}\) activity measurements in samples of mineral waters from selected localities in Bulgaria are given in table 1. The specific activity of \(^{226}\text{Ra}\) ranges from 0.025 Bq/L to 0.211 Bq/L. The maximum activity of \(^{226}\text{Ra}\) in the investigated waters is lower than the activity values reported for Slovenia, Croatia, Switzerland and Austria. The obtained \(^{226}\text{Ra}\) activity values do not differ significantly from the data for some mineral waters in Bulgaria [4, 5, 17].

3.2. Natural Uranium concentration

The concentration of natural uranium (nat. U) ranges from values lower than 0.003 to 0.86 mg/L (Table 1). The highest value of nat. U 0.86 mg/L was found in the sample collected at spring “Toplata cheshma” in Strelcha, whereas the lowest \(\leq 0.003\) mg/L at Chiflik. The reason for the high uranium concentration in the mineral water of the spring "Toplata cheshma" (Strelcha) is the relatively high content of carbonate salts in the soil, as well as the high uranium content in granite rocks, which form the local aquifer. The water samples with high carbonate concentration enhances the dissolved uranium of the water, as it has been established that uranium forms complexes with the carbonate ions [5, 18].

In the prevailing number mineral water samples, the results for the \(^{226}\text{Ra}\) activity are higher than those calculated for nat. U (figure 2). Different chemical properties of radium and uranium are the reason for their different behaviour in the environment of underground water which is manifested as the lack of correlation between their measured specific activities [19]. Radium always appears in second valence and it can be easily leached from the solid matrix, while natural uranium appears in the compounds which have low dissolution coefficient.

Table 1. Specific activities of \(^{226}\text{Ra}\), nat. U concentrations, gross alpha and beta activities in certain Bulgarian mineral waters

| No | Name of mineral source         | \(^{226}\text{Ra}\) [Bq/L] | nat. U [mg/L] | Gross alpha activity [Bq/L] | Gross beta activity [Bq/L] |
|----|--------------------------------|-----------------|---------------|-----------------------------|---------------------------|
| 1  | Strelcha, spring Banski        | 0.084 ± 0.013   | 0.003 ± 0.001 | \(\leq 0.003\)               | 0.110 ± 0.017             |
| 2  | Strelcha, spring Toplata cheshma | 0.10 ± 0.01   | 0.86 ± 0.02   | 3.82 ± 0.57                 | 4.29 ± 0.51               |
| 3  | Strelcha, spring Bancheto      | 0.08 ± 0.01     | 0.003 ± 0.001 | \(\leq 0.003\)               | 0.135 ± 0.019             |
| 4  | Hissar, spring Momina Banya    | 0.086 ± 0.013   | 0.004 ± 0.001 | 0.482 ± 0.072               | 0.256 ± 0.038             |
| 5  | Hissar, spring Momina Salza    | 0.111 ± 0.017   | 0.090 ± 0.002 | 2.43 ± 0.26                 | 0.994 ± 0.12              |
| 6  | Krasnovo                       | 0.078 ± 0.012   | 0.003 ± 0.001 | \(\leq 0.003\)               | 0.117 ± 0.015             |
| 7  | Staro Zhelezare                 | 0.025 ± 0.012   | 0.023 ± 0.002 | 0.349 ± 0.042               | 0.165 ± 0.021             |
| 8  | Banya                           | 0.091 ± 0.014   | 0.003 ± 0.001 | 0.072 ± 0.009               | 0.091 ± 0.012             |
| 9  | Chiflik                         | 0.18 ± 0.01     | \(\leq 0.003\) | 0.099 ± 0.013               | 0.176 ± 0.023             |
| 10 | Shipkovo, natural spring       | 0.211 ± 0.032   | 0.003 ± 0.001 | 0.416 ± 0.049               | 0.242 ± 0.029             |
| 11 | Shipkovo, well number L-28     | 0.124 ± 0.019   | 0.003 ± 0.001 | 0.234 ± 0.035               | 0.221 ± 0.028             |
| 12 | Dolna banya                     | 0.097 ± 0.015   | 0.004 ± 0.001 | 0.139 ± 0.021               | 0.305 ± 0.046             |
| 13 | Kostenets                       | 0.083 ± 0.012   | 0.003 ± 0.001 | 0.038 ± 0.005               | 0.089 ± 0.012             |
| 14 | Momin prohod                   | 0.166 ± 0.025   | 0.039 ± 0.002 | 8.50 ± 0.72                 | 3.25 ± 0.46               |
3.3. Gross alpha and beta activities

The results of gross alpha and gross beta activities are shown in Table 1. The gross alpha activity ranges from values lower than 0.003 Bq/L (minimum detectable activity) to 8.50 ± 0.72 Bq/L. We established that, for 57 % of mineral water studied the gross alpha activities are over the recommended level (0.1 Bq/L). These higher values are related with the geologic characteristics of the rocks which form the aquifer.

The gross beta activities range from 0.089 ± 0.012 Bq/L to 4.29 ± 0.51 Bq/L. In general, the beta activity is lower than the recommended level (1 Bq/L) with the exception for the samples, collected at spring “Toplata cheshma” in Strelcha and Momin prohod, which exceeded this value. The water samples originated from regions where the bedrock is mainly granite, rich on natural radioactive elements.

3.4. Expected annual effective dose

Based on the results for the $^{226}$Ra specific activity and for the concentration of nat. U (the latter one converted also in activity) in mineral waters, presented in Table 1, the expected annual effective doses for adult individual were calculated. The effective doses were calculated for 730 L/year water consumption which corresponds to 2 L of water consumed daily. The dose reference level of 0.1 mSv/y, suggested by WHO was used for comparison with our results [12]. The total effective dose was calculated separately from radium and uranium content.

Figure 2 shows a comparative overview of values of the annual effective dose of $^{226}$Ra and nat. U in mineral water samples. The annual effective doses for $^{226}$Ra and nat. U were in the range 0.0051–0.0431 mSv/y and 0.0000986–0.0283 mSv/y, respectively. It can be noted that the annual effective dose originating from $^{226}$Ra is several orders of magnitude higher than that from uranium. Based on the results obtained, we can conclude that the main contribution to the formation of the total annual effective dose is due to $^{226}$Ra.
Figure 3. Annual effective dose obtained from $^{226}$Ra and nat. U in mineral water samples

Similar measurements of water samples from different areas of Bulgaria were reported in reference [20].

4. Conclusions
A complex investigation of mineral water samples from certain frequently used sources in different locations in Bulgaria, by means of radiological and microanalytical methods were carried out.

The results show that the concentration of $^{226}$Ra ranges from 0.025 Bq/L to 0.211 Bq/L.

The concentration of nat. U in all samples, excluding the spring "Toplata cheshma" in Strelcha, is below the recommendation level of 0.03 mg/L.

The results show that the specific activity ranges from $< 0.03$ Bq/L to $8.50 \pm 0.72$ Bq/L and from $0.089 \pm 0.012$ Bq/L to $4.29 \pm 0.51$ Bq/L for gross alpha and gross beta activity respectively. This wide distribution of values is related in complex way with the water temperature, the dissolved inorganic salts, pH, the geological substructure and other characteristic features of the locations of interest.

The expected total annual effective doses for adults (730 L/y water consumption) were calculated from the measured $^{226}$Ra activity and the nat. U concentrations, converted in activity. For all selected sources the expected total annual effective doses do not exceed the limit of 0.1 mSv/y.

The obtained new results are used to assess the temporary radiation status of the investigated waters. They will support timely and adequate measures to reduce the harmful impact of ionizing radiation on the population in future cases of increased radioactivity.

Acknowledgements
This research has been supported by Bulgarian Science Fund under Contract No. DN08/6 and National programme "Post-doctoral students" funded by the Bulgarian Ministry of Education and Science.

References
[1] Ordinance No 9 on the quality of water intended for drinking and domestic purposes, SG 30 of 2001, 2001 and Amendments, Ministry of Environment and Waters (in Bulgarian).
[2] Pentcheff P 1914 *Journal of the Bulgarian Academy of Sciences*, 9(1) 1
[3] Karamichailova E, Nikolov E, Dojchinova K, Michailova V, 1960 *Endemic Nephrite in Bulgaria* 1952

[4] Kamenova-Totzeva R, Kotova R, Tenev J, Ivanova G, Badulina V 2013 *Rad. Prot. Journal*, 35

[5] Botezatu E, Iacob O, Aflorie A, Elisei G, Capitanu O 2001 *J. Prevent. Medicine* 9(3) 3

[6] Geleva E. 2017 *Journal of Balkan Ecology*, 20 (3) 312

[7] Kostov L K, Chankova-Bunzarova N, Kostova L G, Mladenov Ml, Nankov N, Ch. Procochristov Ch and Stoyanov Ch 2005 *BgNS Transactions* 10(1) 84

[8] Kobilarov R, Kostov L, Procochristov Ch 2016 *Ecology & Safety* 10 166

[9] Tonev D et al. 2016 *Comptes rendus de l’Academie bulgare des Sciences*, 69 (6) 707

[10] Marovic, G, Sencar J, Franic Z 1997 $^{226}$Ra *Environmental Monitoring and Assessment*, 46 233

[11] Alirezazadeh N, Garshasbi H 2003 *Iran. J. Radiation Res.*, 1(3) 139

[12] WHO 2011 *Guidelines for drinking-water quality* (4th ed.), Geneva, Switzerland: World Health Organization

[13] Tonev D, Goutev N and Georgieva L 2016 *J. Phys: Conf. Ser.* 724 012049

[14] Cho H, Jung E, Cha W, Song K 2013 *Analytical Chemistry* 85(9) 4279

[15] Dias F, Taddei M H, Pontedeiro E, Jacomingo V 2009 *International Nuclear Atlantic Conference - INAC 2009*, Rio de Janeiro, RJ, Brazil

[16] Palomo M, Villa M, Casacuberta N, Penalver A, Borull F, Aguilar C 2011 *Appl. Radiat. Isot.*, 69 1274

[17] Kralik C, Friedrich M, Vojir F 2003 *J. Environ. Radioact.* 65 233

[18] Virk H 2016 *Global Journal of HUMAN-SOCIAL SCIENCE: B Geography, Geo-Sciences, Environmental Science & Disaster Management* 16(5) 31

[19] Kozlowska B, Walencik A, Dorda J, Przylibski T A 2007 *Radiation Measurements* 42(8) 1380

[20] Geleva E, Tonev D, Goutev N, Nikolova N, Procochristov H, Bashev V, Salkova E 2019 *Comptes rendus de l’Academie bulgare des Sciences*, 72 (12) 1641