RAD Conference Proceedings, vol. 6, pp. 65-69, 2022
ISSN 2466-4626 (online) | DOI: 10.21175/RadProc.2022.12
www.rad-proceedings.org

RADIOLOGICAL STATUS OF DRINKING WATER FROM THE EASTERN RHODOPES REGION, BULGARIA

Milena Hristozova*, Radoslava Lazarova, Ivanka Yordanova

Institute of Soil Science Agrotechnologies and Plant Protection "N. Poushkarov", Agricultural Academy, Sofia

Abstract. *The quality of drinking water in Bulgaria is controlled by the Ministry of Environment and Water. However, unregulated sources are also often used for drinking purposes. In addition to the impaired chemical, biological and physicochemical parameters, there is a risk of natural radionuclides occurring in concentration above the permissible levels. Higher content of natural uranium in the bedrock can be dissolved by groundwater or surface water and leads to high activity concentrations in drinking waters. The long-term use of water containing high content of uranium can cause kidney problems and poses cancer risks. 35 unregulated water sources from the region of the Eastern Rhodopes were studied. Natural uranium was measured spectrophotometrically. Gross alpha and beta activity were determined by low-background alpha-beta counter. Uranium content was between < 0.002 and 0.020±0.004mg/l, alpha activity: ≤0.001÷0.18±0.04 Bq/l, beta activity: ≤0.02÷0.18±0.04 Bq/l. The study of such unregulated water sources expands the monitoring of drinking waters in the country and makes it possible in case of hazard to inform the relevant authorities and population in order to protect human health.*

Keywords: *radioactivity of waters, gross alpha and beta activity, natural uranium*

1. INTRODUCTION

The Eastern Rhodopes are characterized by a low-mountains and hilly relief, with a low altitude (320 m.) and great fragmentation. This allows the population in the region to build a dense settlement network (14.5 settlements per 100 km^2) [1]. Thus, access and use of natural resources is maximized. A large part of the population in the area does not use the aqueduct system as the main source of drinking water, but unregulated water sources. The waters have a shallow circulation. The water composition is varied, containing mainly hydrocarbonate and sodium-calcium. The dry residue content varies between 0.06 and 0.8 g/l. The significant amount of calcium and magnesium cations determines the greater hardness of the waters in the area. The daily use of these waters for drinking and household needs can lead to the accumulation of a greater amount of salts in living organisms and from there to the development of urolithiasis, risk of atherosclerosis, skin problems, arthritis, polyarthritis. The incorporation of larger amounts of magnesium salts disrupts the functions of the cardiovascular and nervous systems [2].

The soil-forming rocks in the studied area are mainly granites, marbles, gneiss, slates, characterized by increased content of uranium and other natural radionuclides [3]. Weathering processes release uranium and its daughter products into the soil and groundwater. Dissolution of radionuclides in water may lead to concentrations exceeding the permissible health norms. The most important products of uranium decay are radium, polonium, radon-222.

Depending on the content of natural radioisotopes in the bedrock, some radionuclides such as ^{238}U, ^{226}Ra and others dissolve well in surface waters, where their content can be elevated.

Due to increased anthropogenic activity in the area: lead-zinc mines, gold mine, Lead-zinc complex, production of artificial fertilizers, mining of gneiss, marble quarries, etc., the distribution and concentration of natural radioisotopes in the soil increases, resulting in higher level of radioactivity in the water. Besides being a risk to human health, the high amount of radionuclides affects all living organisms. A large part of the studied territory falls within the European ecological network Natura 2000 [4].

2. MATERIALS AND METHODS

35 of the most used, unregulated water sources in the Eastern Rhodopes region were selected as object of the study (see Figure 1). The sources include fountains with natural water, possessing large flow rate and near populated areas. These water sources are used year-round, mainly for drinking needs. The amount of each sample was 3 liters, without conservation. The research was carried out at the Laboratory of Radioecology and Radioisotope Research at the ISSAPP "N. Poushkarov" which is accredited by IA "Bulgarian Accreditation Service" according to BDS EN ISO/IEC 17025:2018 [5] for determining the content of natural and artificial radionuclides in water, soil and food. Gross alpha and gross beta activity in water were determined according to standards: BDS ISO 9696 and BDS ISO 9697 [6], [7]. According to the methodology, 1000 ml of acidified water is concentrated by controlled evaporation to less than 50 ml. 1 ml of sulfuric acid is added and the water is heated until obtaining a dry residue. It is burned in a muffle furnace for 1 hour at a temperature of 350 °C and

* hristozova_m@abv.bg

then cooled in a desiccator. The amount of 0.2000 gr is measured. A planshet is prepared from the absolutely dry residue and measured in an alpha-beta low background apparatus for 600 sec.

The concentration of natural uranium was determined by a method developed and validated in the laboratory. The method is based on the formation of colored complex compound of U^{4+} with arsenazo III followed by spectrophotometric measurement of the samples at 655nm wavelength.

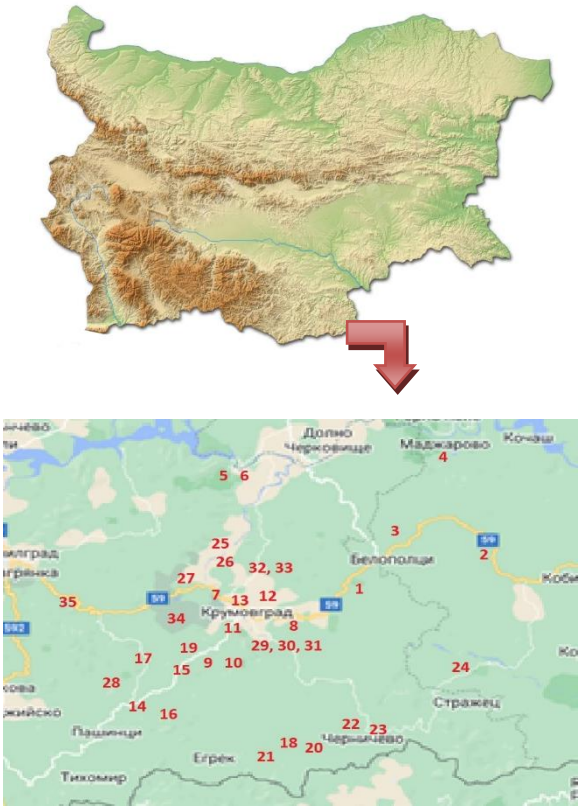

Figure 1. Location of water sources

3. Results and discussion

All living organisms are exposed to the influence of natural radiation, formed both by cosmic radiation and by natural radionuclides in the earth's surface. There are geographical variations, but the average value of the natural background radiation in Bulgaria is 2.3 mSv per year. A small part of it is due to drinking water. Traces of radioactive elements are found in any water. Their composition and concentration depend on the radiochemical composition of the bedrock and soil through which the raw water passes.

The quality of water intended for drinking and household purposes in Bulgaria is controlled by the Ministry of Environment and Water [8]. Ordinance No. 9 of 2001 defines the requirements for the quality and safety of these waters in order to guarantee human health and avoid the adverse effects of drinking polluted water. Constant monitoring of the radiological status of drinking water is carried out. In the Eastern Rhodope region, parallel to the monitored water sources, non-controllable spring waters are used. The preference for spring water is caused by the hardness of the tap drinking water from the region due to the presence of limestone depositing as scale at temperature at about 50°C.

To assess the health risk of drinking water radioactivity, gross alpha and gross beta activity were determined in 35 unregulated water bodies. The amount of natural uranium has been measured. The results are presented in Table 1.

In terms of radiological indicators, acceptable values of gross alpha and beta activity in Bulgaria are less than 0.1 Bq/l and 1.0 Bq/l respectively. The parametric value of the total indicative dose is 0.1 mSv [8]. The use of unregulated sources for drinking and household purposes, may lead to absorption of annual effective dose of all radionuclides exceeding the threshold of 0.1 mSv.

In the studied water bodies, the gross beta activity varied from ≤0.02 to 0.18±0.04 Bq/l. This was below the parametric value for drinking water.

Results for gross alpha activity ranged from ≤0.01 to 0.18±0.04 Bq/l. In 33 of the sites, no additional radiological examination was necessary, since gross alpha-activity and gross beta-activity were lower than the thresholds, and the indicative dose was assumed to be lower than 0.1 mSv. In two of the sources, activities above the control levels were found (respectively 0.1±0.02 in source 33 and 0.18±0.04 Bq/l in source 7). In such cases an analysis to identify specific radionuclides is required, according to Ordinance 9 of 2001 [8]. The amount of natural uranium in these samples explained the higher results.

Further analysis carried out found that gross alpha activity was due to the contribution of uranium in samples 7 and 33 and was 0.06 and 0.05 Bq/L, respectively. In both cases, this value was lower than 0.1 Bq/l, which is the derived concentration of Po-210 under Ordinance 9. Polonium exhibits the highest radiotoxicity and poses the greatest risk to human health. Based on these results the two waters were assumed as not being hazardous for human health from radiological point of view. Sampling of both waters was also repeated during the summer hydrological minimum, characteristic of the Eastern Rhodope region. The results were comparable. Although in these two cases the calculated indicative dose was below 0.1 mSv, the long-term cumulative exposure of absorbed radionuclides must be taken into account, because of the health problems they might cause [9]. Radionuclides absorbed into the blood accumulate in certain tissues, for which they become toxic. More than half of the uranium is rapidly eliminated in the urine, and the remainder is stored in the kidneys, bones, and soft tissues. Radium is mainly deposited in the bones [10].

Alpha-emitting radionuclides with high energies (with high linear energy transfer), such as radium-226, polonium-210, uranium, Radium-228 and its decay products, have the largest contribution to gross alpha activity. These radioactive elements and their decay products are included in the earth's surface to varying degrees, according to the chemical composition of the main rock. Metamorphic rocks, gneisses, marbles and amphibolites predominate in the geological

composition of the Eastern Rhodopes. These rocks contain high concentrations of natural uranium [11].

Table 1. Investigated radiological indicators in unregulated water sources in the Eastern Rhodopes region

No.	Location	Natural uranium mg/l	Gross alpha activity Bq/l	Gross beta activity Bq/l	Indicative dose mSv
1	"Stanka cheshma"	≤0.002	≤0.01	0.03±0.01	<0.1
2	"Ilieva niva"	0.006±0.001	≤0.01	≤0.02	<0.1
3	v. Kolibary	0.006±0.001	0.02±0.01	≤0.02	<0.1
4	Madjarovo	≤0.002	≤0.01	0.06±0.01	<0.1
5	"Studen kladenets"	0.002±0.0004	0.02±0.01	0.09±0.02	<0.1
6	v. Studen kladenets	0.003±0.001	≤0.01	0.07±0.02	<0.1
7	"Mirchova cheshma"	0.012±0.003	0.18±0.04	0.06±0.02	<0.1
8	mountain hut Svejest	0.005±0.001	≤0.01	≤0.02	<0.1
9	"Suflar dere" 1	0.003±0.001	≤0.01	≤0.02	<0.1
10	"Suflar dere" 2	0.004±0.001	≤0.01	≤0.02	<0.1
11	"Drujba", Krumovgrad	0.004±0.001	0.02±0.01	0.18±0.04	<0.1
12	Krumovgrad 1	0.004±0.001	≤0.01	0.05±0.01	<0.1
13	Krumovgr–draw well	0.008±0.002	0.05±0.01	≤0.02	<0.1
14	v. Tokachka	0.003±0.001	≤0.01	≤0.02	<0.1
15	v. Kandilka 1	0.004±0.001	≤0.01	≤0.02	<0.1
16	v. Leshtarka	≤0.002	≤0.01	≤0.02	<0.1
17	v. Metlika	0.003±0.001	0.02±0.01	≤0.02	<0.1
18	v. Avren - v. Bashtino	≤0.002	0.02±0.01	≤0.02	<0.1
19	v. Kandilka - fossils	0.005±0.001	≤0.01	≤0.02	<0.1
20	v. Avren 1	0.005±0.001	≤0.01	0.04±0.01	<0.1
21	v. Avren 2	≤0.002	≤0.01	≤0.02	<0.1
22	v. Chernichevo 1	0.003±0.001	≤0.01	≤0.02	<0.1
23	v. Chernichevo 1	0.003±0.001	≤0.01	≤0.02	<0.1
24	v. Kazak	0.003±0.001	≤0.01	≤0.02	<0.1
25	v. Dolna kula 1	0.004±0.001	≤0.01	≤0.02	<0.1
26	v. Dolna kula 2	0.004±0.001	0.03±0.01	≤0.02	<0.1
27	v. Gorna kula	0.008±0.002	0.08±0.02	0.03±0.01	<0.1
28	v. Malka chinka	0.004±0.001	≤0.01	≤0.02	<0.1
29	"Adatepe" 1	0.003±0.001	≤0.01	≤0.02	<0.1
30	"Adatepe"-draw well	0.004±0.001	≤0.01	≤0.02	<0.1
31	"Adatepe" 2	0.003±0.001	≤0.01	0.1±0.02	<0.1
32	v. Kovil - rock well 1	0.004±0.001	0.02±0.01	0.03±0.01	<0.1
33	v. Kovil - rock well 2	0.005±0.001	0.1±0.02	0.09±0.02	<0.1
34	v. Lulichka	0.020±0.004	≤0.01	0.08±0.02	<0.1
35	Momchilgrad	0.003±0.001	≤0.01	0.15±0.03	<0.1

Radionuclides, produced by the decay of uranium-238 and thorium-232, are widely distributed in the earth's crust. Most of them are alpha emitters and include isotopes of polonium, radon and radium [12]. Therefore, an increased amount of dissolved uranium decay products transported from the bedrock and soil into the aquifer is expected. Uranium concentrations in drinking waters studied was from ≤0.002 to 0.020±0.004 mg/l. The results obtained were lower the permissible concentrations for drinking water (0.03 mg/l). Five of them were below the limit of detection ≤0.002 mg/l.

In the studied area, there is an increased anthropogenic activity due to the presence of ore and non-ore deposits (lead-zinc and polymetallic ores), exploitation of gneiss and marble deposits, gold mining, etc. These activities may cause an increased content of radioactive elements such as ^{40}K, ^{210}Pb, ^{235}U, ^{238}U, ^{232}Th and ^{226}Ra in soils [13]. In addition, the Rhodopes are the territory of Bulgaria with the highest contamination by man-made cesium (^{137}Cs), as a result of the Chernobyl accident [14], [15], [16]. This presents an additional risk for anthropogenic radionuclides entering the aquatic environment. Soil studies were performed around all studied water bodies. The results obtained do not show significant deviations from the average values for the soils of Europe and for other territories of Bulgaria [17].

4. Conclusions

The gross α and β activity of 35 unregulated sources of drinking water in the Eastern Rhodope region were investigated in order to ensure the safety of drinking water and public health.

The levels of α and β activity in 33 of the investigated unregulated water sources in the Eastern Rhodopes were lower than the parametric values for drinking water in Bulgaria, ensuring the water was safe for human consumption.

The content of the heaviest element in nature - uranium in the studied reservoirs was within the normal background level.

There were no changes in the values of gross alpha and beta activity in the waters sampled during the summer hydrologic minimum and during spring-autumn sampling.

The present study is important as it shows the radiological status of non-monitored water sources. Values above the norm can be established and informing the population or corrective actions such as closing the relevant water source could be undertaken.

References

1. Д. Симеонов, Д. Симеонова, *География на България - стопански, социални и регионални особености,* В. Търново, България: Унив. изд. "Св. св. Кирил и Методий", 2021.
   (D. Simeonov, D. Simeonova, *Geography of Bulgaria – economic, social and regional features*, Veliko Tarnovo, Bulgaria: Univ. ed. "St. St. Cyril and Methodius", 2021).
2. P. Sengupta, "Potential health impacts of hard water," *Int. J. Prev. Med.*, vol. 4, no. 8, pp. 866–875 Aug. 2013. PMID: 24049611 PMCID: PMC3775162 Retrieved from: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3775162/ Retrieved on: June 15, 2022
3. Л. Райков, *Радиоактивни елементи в почвата и усвояването им от растенията*, София, България: Земиздат, 1978.
   (L Raykov, *Radioactive elements in the soil and their absorption by plants*, Sofia, Bulgaria: Zemizdat, 1978).
4. *Fifth National Report on the Implementation of the Convention on Biological Diversity*, Ministry of Environment and Water, Sofia, Bulgaria, 2013. Retrieved from: https://www.cbd.int/doc/world/bg/bg-nr-05-en.pdf Retrieved on: June 15, 2022
5. *Общи изисквания за компетентността на лаборатории за изпитване и калибриране*, Стандартен но. ISO/IEC 17025:2017, 15 януари 2018.
   (*General requirements for the competence of testing and calibration laboratories*, Standard no. ISO/IEC 17025:2017, Jan. 15, 2018).
6. *Качество на водата. Обща алфа-активност. Метод за изпитване с концентриран източник*, Стандартен но. ISO 9696:2017, 14 декември 2017.
   (*Water quality - Gross alpha activity - Test method using thick source*, Standard no. ISO 9696:2017, Dec. 14, 2017).
7. *Качество на водата. Обща бета активност. Метод за изпитване с използване на концентриран източник*, Стандартен но. ISO 9697:2018, 2 ноември 2018.
   (*Water quality - Gross beta activity - Test method using thick source*, Standard no. ISO 9697:2018, Nov. 2, 2018).
8. Правителство на Република България. (28 март 2001 г.). *Наредба № 9 за качеството на водата, предназначена за питейно-битови цели.*
   (Government of the Republic of Bulgaria. (March 28, 2001). *Regulation No. 9 on water quality intended for drinking and household purposes.)*
   Retrieved from: https://eea.government.bg/bg/legislation/water/naredba9_21.pdf
   Retrieved on: Jun. 15, 2022
9. The Council of European Union. (Oct. 22, 2013). *Council Directive 2013/51/EURATOM laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption*.
   Retrieved from: http://extwprlegs1.fao.org/docs/pdf/eur128382.pdf
   Retrieved on: Jun. 15, 2022
10. M.E. Wrenn et al. "Metabolism of ingested U and Ra," *Health Physics*, vol. 48, no. 5, pp. 601–633, May, 1985. https://doi.org/10.1097/00004032-198505000-00004
11. K. Ivanova, Z. Stojanovska, V. Badulin, B. Kunovska, M. Yovcheva, "Radiological impact of surface water and sediment near uranium mining sites," *Journal of Radiological Protection,* vol. 35, no. 4, pp. 819–834, 2015. https://doi.org/10.1088/0952-4746/35/4/819
12. *Ionizing Radiation, Levels and Effects, United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) 1972 Report,* Report to the General Assembly with Scientific Annexes, UNSCEAR, New York (NY), USA, 1972. https://doi.org/10.18356/5513731d-en
13. Б. Христов, М. Христова, "Възстановяване на нарушени от уранодобива земи," *Минно Дело и Геология*, кн. 54 но. 4, стр. 32–36, 1999.
   (B. Hristov, M. Hristova, "Land reclamation of disturbed by uranium mining territory," *Minno Delo i Geologiya*, vol. 54, no. 4, pp. 32–36, 1999.)

14. I. Yordanova, D. Staneva, Tz. Bineva, N. Stoeva, "Dynamics of the radioactive pollution in the surface layer of soils in Bulgaria twenty years after the Chernobyl nuclear power plant accident," *Journal of Central European Agriculture*, vol. 8, no. 4, pp. 407–412, 2007. https://doi.org/10.5513/JCEA.V8I4.478
15. I. Yordanova, D. Staneva, L. Misheva, Ts. Bineva, M. Banov, "Technogenic radionuclides in undisturbed Bulgarian soils," *Journal of Geochemical Exploration*, vol. 142, pp. 69–74, Jul. 2014. https://doi.org/10.1016/j.gexplo.2014.01.011
16. I. Yordanova, M. Banov, L Misheva, D. Staneva, T. Bineva, "Natural radioactivity in virgin soils and soils from some areas with closed uranium mining facilities in Bulgaria," *Open Chemistry*, vol. 13, pp. 600–605, 2015. https://doi.org/10.1515/chem-2015-0065
17. M. Hristozova, R. Lazarova, "Radiation status of soils from the region of the Eastern Rhodopes (Southern Bulgaria)," *BioRisk*, vol. 17, pp. 45–57, Apr. 2022. https://doi.org/10.3897/biorisk.17.77432