Radioactivity of Drinking Waters from Different Regions of Bulgaria in the Period 2017-2019

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Abstract

Radioactivity of drinking waters is determined by trace quantities of natural radionuclides ^{238}U, ^{232}Th, their daughter products and ^{40}K. They are transferred to water by processes of erosion and dissolution of aquifer rocks and minerals. Man-made radionuclides may also occur in water as a result of technological pollution.

Therefore, annual radiological monitoring is a key factor in ensuring water safety.

In the present study, radiological monitoring of drinking waters from different regions in Bulgaria was carried out according to the national regulations in the period 2017-2019. Content of natural uranium, gross alpha and beta activity, radon-222 and tritium in water samples were determined.

Content of radiological indicators under study was not exceeding the reference values in the predominant part of analyzed samples. Relatively higher values of natural uranium and gross alpha activity were observed in insignificant number of samples, probably due to specific hydro-geological characteristics of the aquifers in the respective regions, as well to the presence of closed uranium mining sites near them. Content of radon and tritium in all tested waters were below the parametric values.

As a result of the present survey it can be concluded that drinking waters in the studied regions were not hazardous for human health from radiological point of view.

Keywords: radioactivity of waters, U, gross alpha and gross beta activity, ^{222}Rn, ^{3}H

Introduction

Radioactivity of waters is determined by the normal presence of natural radionuclides ^{238}U, ^{232}Th, their daughter products and ^{40}K. They are transferred to waters by processes of erosion and dissolution of rocks and minerals formed in aquifers. Uranium mining and processing, coal mining and operation of thermal power plants, production and use of mineral fertilizers can lead to man-made intensification of local radiation background and increase in content of natural radionuclides in water (Carvalho et al., 2014, Yordanova et al., 2011, Chalupnik et al. 2001, Azoazi et al., 2001). Man-made radionuclides may also be present in water as a result of technological processes. Therefore, the regular radiological monitoring is a key factor in ensuring drinking water safety.

The aim of the present study was to determine the content of natural uranium, gross alpha and beta activity, ^{222}Rn and ^{3}H in waters from different regions in Bulgaria for the period 2017-2019. Monitoring of the main radiological indicators was carried out in accordance with regulations set in the national legislation (Table 1 and Table 2) (Regulation No. 9, 2001).

Table 1. *Parametric values for radon, tritium and Total Indicative Dose (TID) in water for drinking and household purposes.*

Indicator	Parametric value	Unit
Radon	100	Bq/l
Tritium	100	Bq/l
Total Indicative Dose	0,1	mSv

Table 2. Reference level of gross alpha and beta activity

Indicator	Reference level	Unit
Gross alpha activity	0,1	Bq/l
Gross beta activity	1,0	Bq/l

Materials and Methods

Testing Laboratory of Radioecology and Radioisotope Research at ISSAPP "Nikola Pushkarov" is accredited for determining content of radioactive elements in water, soil, plants, food and food products under BDS EN ISO/IEC 17025:2018.

1040 water samples were analyzed for the period 2017 - 2019.

Content of natural uranium was determined by a method based on formation of tetravalent uranium complex with arsenase III and spectrophotometric measurement of the samples at 655 nm wavelength.

Gross alpha and gross beta activity were determined according to BDS EN ISO 9696/2017 and ISO 9697/2019 respectively. Planchets with dry residue of aliquot part of water samples were prepared and measured by low-background gas proportional alpha/beta counter.

Radon-222 was determined by gamma spectrometry by the line of ^{214}Bi at 609 kV . A DSA 1000 multi-channel analyzer, product of CANBERRA with pure Ge detector, 30% efficiency and 1.8 keV resolution, was used (Naidenov et al.).

Determination of tritium in water samples was carried out according to a method for liquid scintillation counting [Naidenov et al.].

The results are validated by annual participations in interlaboratory comparisons, proficiency test schemes and regular internal quality control.

Results and Discussion

1. Natural uranium, gross alpha and beta activity in water samples

Natural uranium is a mixture of three isotopes - ^{238}U, ^{234}U and ^{235}U. In addition to being radioactive, it is also toxic as chemical element and its ingestion can lead to kidney damage. Maximum permissible concentration of uranium in drinking water under Bulgarian regulations is 0.03 mg/l. The number of water samples with relatively higher uranium content are presented on Fig. 1.

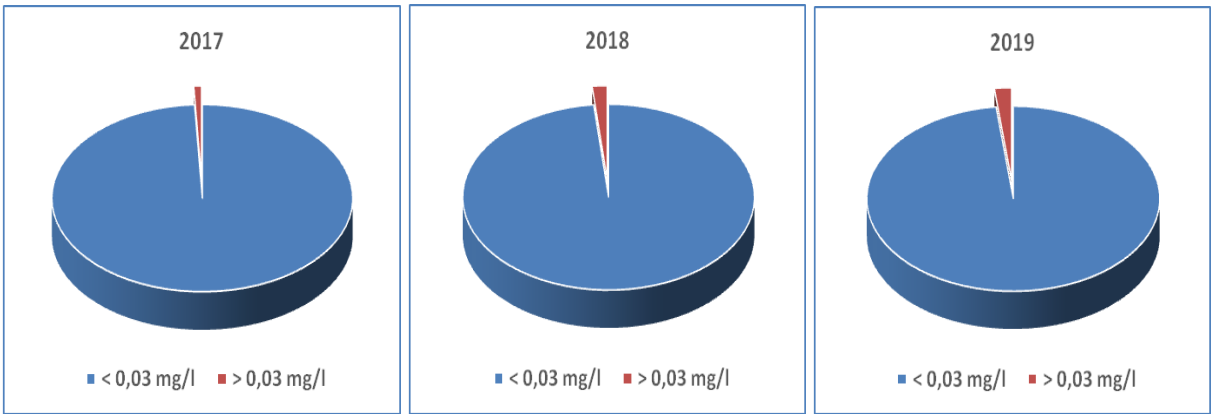

Fig. 1. *Number of the samples with increased content of natural uranium per year.*

The percentage of waters with increased content of natural uranium for the three years period was 1%.

Gross alpha activity in water is mainly due to uranium isotopes (^{238}U, ^{234}U, ^{235}U) and ^{226}Ra. Beta activity is usually due to a large extent to ^{40}K and short-lived beta emitters of the ^{238}U family. Determination of gross alpha and beta activity is a relatively fast and effective method for preliminary screening of water. The reference levels specified in Regulation 9 for gross alpha and beta activity are 0.1 Bq/l and 1 Bq/l, respectively. If they are not exceeded it is assumed that the Total Indicative Dose (TID) is under the reference level of 0,1 mSv/year set in the regulations.

Results of gross alpha activity measurements in water samples are presented in Fig. 2.

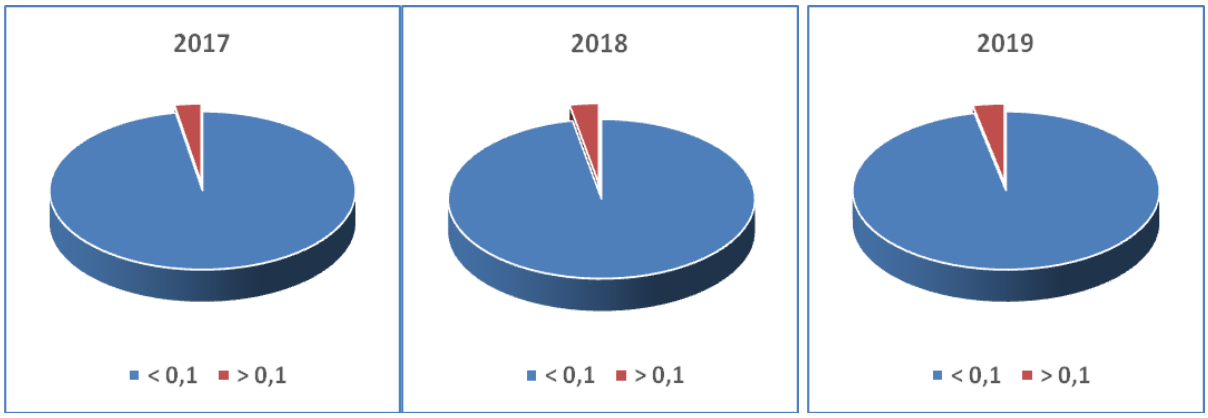

Fig. 2. *Number of the samples with increased content of gross alpha activity from the total number of tested samples per year.*

Increased gross alpha activity was found in 3 % of all waters tested in the period 2017 - 2019. The data for gross beta activity in all samples were below the reference level of 1 Bq/l.

According to the regulations, if gross alpha activity exceeds the screening level of 0.1 Bq/l, content of individual radionuclides should be determined and Total Indicative Dose calculated. Further analysis of data found the increased gross alpha activity in the samples was entirely due to the contribution of uranium. In general uranium chemical toxicity is much more marked than its radiotoxicity (Rump et al., 2019). Radium, which is much more radiotoxic, has a relatively low solubility in water and does not form soluble complexes. Uranium isotopes (^{234}U and ^{238}U) are generally the most common radionuclides in water. Uranium forms soluble stable complexes (e.g. carbonates) under oxidative conditions and can

migrate on long distances (Nuccetelli et al., 2012). Total Indicative dose (TID) was calculated with the respective uranium concentrations and uranium dose coefficient (Eckerman et al., 2012). It was below the parametric value in all cases and the waters were considered safe for human health.

Comparison of results of radiological indicators in waters from different regions in Bulgaria obtained in the years, showed the number of samples with increased content of uranium and gross alpha activity raised upon entry into force of more conservative reference values for natural uranium (twice lower) and gross alpha activity (five times lower) in Bulgarian legislation.

Waters with relatively high uranium concentrations were from the regions around Plovdiv, Rakovski, Haskovo and Burgas and those with increased gross alpha activity from regions around Burgas, Plovdiv, Rakovski, Haskovo, Petrich, Dobrich, Vratsa and Tran.

Higher concentration of uranium in waters from these regions may be explained with the specific hydro-geological characteristics of the aquifers and the presence of rocks like granites, gneisses and schists containing higher quantities of natural uranium. Another reason could be the former uranium mining and processing carried out on sites in the regions in the past.

2. ^{222}Rn activity concentration in water samples

The world average annual effective dose obtained from external and internal exposure to the natural radiation background is 2.4 mSv/y. 50% of it is due to the inhalation of radon and its short-lived daughter products contained in atmosphere (Brenner, 1994). 98% of human internal exposure is result of the inhalation of radon daughter products retaining in the body and affecting bronchial epithelium in lungs, and only 2% are due to radon (radon-222) itself.

Although radiation risk of radon exposure through water consumption is much lower than the caused by indoor radon inhalation, European legislation and the relevant Regulation 9 have set a parametric value of 100 Bq/l for the radionuclide in drinking water. Corrective action shall be taken in all cases where radon activity concentration exceeds 1000 Bq/l to provide radiation protection.

Radon-222 content was measured in 300 drinking water samples. All results were under the parametric value, the predominant part of them being below the minimum detectable activity (MDA) of the measurement (10 Bq/l). Activity concentration over MDA was determined in 63 samples (Table. 1).

Table 3. *^{222}Rn activity concentration in water samples [Bq/l]*

	Sampling site	^{222}Rn, Bq/kg
1	Burgas District, Vratitsa	25±5
2	Burgas District, Detelina	25±5
3	Burgas District, Dimchevo	15±10
4	Burgas District, Dobrinovo	30±10
5	Burgas District, Zhytosvyat	50±5
6	Burgas District, Krumovo gradishte	25±3
7	Burgas District, Lesnovo	20±5
8	Burgas District, Livada	16±5
9	Burgas District, Pirene	20±5
10	Burgas District, Pchelin-1	40±4
11	Burgas District, Pchelin-2	75±7

Table 3. *^{222}Rn activity concentration in water samples [Bq/l] (continue)*

12	Burgas District, Raklinovo	20±5
13	Burgas District, Raklitsa	25±5
14	Burgas District, Sinyo Kamene - 1	30±3
15	Burgas District, Sinyo Kamene - 2	25±3
16	Burgas District, Sinyo Kamene village -3	45±10
17	Burgas District, Sinyo Kamene -4	25±10
18	Burgas District, Sinyo Kamene village-5	25±10
19	Burgas District, Sadievo	35±10
20	Burgas District, Troyanovo	80±8
21	Burgas District, Trastikovo	25±5
22	Burgas District, Chukarka , zone 1	50±10
23	Burgas District, Chukarka, zone 2	20±5
24	Burgas District, Zheleznik	30±3
25	Veliko Tarnovo District, Elena	25±3
26	Veliko Tarnovo District, Pavlikeni	30±3
27	Veliko Tarnovo District, Suhindol	30±3
28	Veliko Tarnovo District, Byala Cherkva,	15±3
29	Veliko Tarnovo District, Visovgrad	20±5
30	Veliko Tarnovo District, Delyanovtsi	20±5
31	Veliko Tarnovo District, Karaisen	30±3
32	Veliko Tarnovo District, Koevtsi	30±3
33	Veliko Tarnovo District, Krumchevtsi	30±3
34	Veliko Tarnovo District, Mihaltsi	30±3
35	Veliko Tarnovo District, Novachkini	30±3
36	Veliko Tarnovo District, Ovcha Mogila	30±3
37	Veliko Tarnovo District, Ovcha Mogila	70±6
38	Veliko Tarnovo District, Rusalya	25±5
39	Veliko Tarnovo District, Stefan Stambolovo	25±5
40	Veliko Tarnovo District, Hotnitsa	40±4
41	Veliko Tarnovo District, Hanevtsi	70±7
42	Veliko Tarnovo District, Chervena	20±3
43	Dobrich District, Dobrich, catchment	30±3
44	Dobrich District, Dobrich	70±7
45	Montana District, Montana	30±10
46	Montana District, Boychinovtsi	30±10
47	Montana District, Vladimirovo	25±8
48	Pernik District, Trun Municipality, Brul	70±15
49	Pernik District, Trun Municipality, Glogovitsa	50±10
50	Pleven District, Kneja	30±10
51	Plovdiv District, Katunitsa	50±10
52	Plovdiv District, Kosovo	50±5
53	Plovdiv District, Markovo	20±8
54	Razgrad District, Ezerche	25±3

Table 3. *^{222}Rn activity concentration in water samples [Bq/l] (continue)*

55	Razgrad District, Kamenar	20±3
56	Razgrad District, Kostandenets	25±3
57	Razgrad District, Malak Porovets,	30±5
58	Razgrad District, Staro Selishte	25±5
59	Silistra District, Vodno Dulovo	65±6
60	Silistra District, Staro Selo	45±9
61	Sofia District, Dolna Banya	40±10
62	Sofia District, Kremikovtsi	40±10
63	Stara Zagora District, Kazanlak	25±5

Radon content in drinking waters may vary widely. For comparison, in some European countries the following ^{222}Rn activity concentrations were determined in Bq/l: Austria - 1.46-644 (Wallner and Steininger, 2007), Germany - <1.3-1800 (Beyerman et al., 2010), Portugal - 1.12-112.77 (Lopes et al., 2005), Greece - 0.23-24 (Nikolopoulos et al., 2008).

3. Tritium content in waters from different regions of the country

Tritium is a cosmogenic radionuclide that forms in the upper atmosphere. It occurs in rainwater in the form of treated water (HTO) with activity concentration of about 5 Bq/l. Tritium has low radiotoxicity. Its dose coefficient is three to four orders of magnitude lower than the coefficients of natural chain radionuclides.

Natural levels of ^{3}H in environment increased in result of nuclear weapon tests carried out from 1945 to 1963. Another source of tritium are nuclear power plants (NPPs), as ^{3}H is produced as a by-product of uranium fission. Tritium contamination around NPPs is mainly found in nearby surface waters (Querfeld et al., 2019).

The parametric value set for tritium in Regulation 9 is 100 Bq/l. Elevated levels of tritium may by indicative for the presence of other artificial radionuclides and if ^{3}H activity concentration exceeds the parametric value, an analysis for other artificial radionuclides is required.

^{3}H content was determined in 423 water samples in the three years period. Tritium activity concentration in all samples was lower than the parametric value within the range <3 ÷ <20 Bq/l. in 80% of the samples the values were below the minimum detectable activity of 3 Bq/l. No technological contamination with tritium was found.

Conclusion

In the predominant part of analysed samples radiological indicators under under monitoring did not exceed the values set in the regulations.

Relatively higher values of natural uranium and gross alpha activity were observed in minimal number of samples. They could be probably explained both by the specific hydro-geological characteristics of aquifers in the observed regions and by sites of closed uranium mining and processing near them.

Increased gross alpha activity in the samples was found to be due to the contribution of natural uranium. Total Indicative dose (TID) was calculated with the respective uranium concentrations and uranium dose coefficient. It was below the parametric value in all cases and the waters were considered safe for human consumption.

The measurements of ^{3}H content in waters did not indicate any technological contamination in result of uncontrolled leakage of the radionuclide in studied waters.

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