Radon and Radium-226 Content in Some Bulgarian Drinking Waters

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Abstract

Safe drinking water is essential to sustain life. The absence of any unpleasant by the meaning of consumers qualities does not guarantee that water is safe. The radioactivity does not have a taste, odour and color and using water contained radioactivity above the limit can cause cancer or other health problems. Radon and Radium are some of the most important natural radionuclides impacted to public health. In the paper is presented a pilot study of the Radon-222 in Bulgarian drinking waters.
Radon-222 and Radium-226 were determined in 40 Bulgarian drinking waters from South-West and South-East parts of Bulgaria. Sampling points were chosen randomly. For Radon-222 investigation was used ALPHA Guard with Aqua kit equipment and measurement was done on-site. Radium-226 was sampled at the same time as Radon, but radiochemical analysis and measurements was performed in the laboratory.
The obtained results for radon vary between 1,17±0,40 Bq/l and 185,5±10,4 Bq/l. Concentrations of Radium-226 ranged from MDA to 0,15 Bq/l.
We did not find strong relation between radium and radon content in investigated waters.
All results are discussed in view of the EU Drinking Water Directive, WHO Guidelines, Euratom Treaty and Bulgarian rules.

Key words: radon, water, Bulgaria

Introduction

Safe drinking water is essential to sustain life. The absence of any unpleasant by the meaning of consumers qualities does not guarantee that water is safe. The radioactivity does not have a taste, odour and color and using water contained radioactivity above the limit can cause cancer or other health problems. Radon and Radium are some of the most important natural radionuclides impacted to public health. Radon is a radioactive gas and as a member of Group VIII of the periodic table it is fundamentally inert. It occurs as three natural isotopes, commonly named radon, thoron and actinion. Because of the half-life of ^{222}Rn (common name radon) 3.8 days, which is long enough to persist in water and cause a health risk. From the radiation protection point of view the ^{222}Rn is more important and have to be investigated. It is well known that radon has a high solubility in water and solubility decreases with increasing temperature (51 vol. % at 0^0C and 13 vol. % at 60^0C. There are two different sources of radon derivation in water: radioactive decay of dissolved ^{226}Ra and direct release of radon from the mineral matrix from minerals containing members of uranium decay series.
Due to differences in mobilization from rock and water chemistry usually ^{226}Ra and ^{222}Rn are not in radioactive equilibrium with each other in waters. ^{226}Ra is rather insoluble element. Concentrations of radon in water largely depend on six factors (Nelson et al. 1983, Michel 1990, Ball et al. 1991, Albu at al. 1997):
Hydrodynamic factors (e.g. whether groundwater is flowing slowly to approach an equilibrium between mineral and dissolved phases)
Geometric factors. Equilibrium radon concentrations are believed to be inversely proportional to the aperture of groundwater-bearing fracture
The uranium (or strictly speaking, the radium) content of the aquifer host rock (or fracture mineralization)
The mineralogy of the phases containing the radium and uranium
Possibilities for degassing of radium in groundwater
The source of radium, dissolved in the water is the surrounding bedrock, usually geological settings rich of uranium. The half-life of 226Ra is a 1600 years and it is alpha emitter as 222Rn.
Considering the high radiotoxicity of 226Ra, it presence in water require particular attention. It is known that small amounts of radioactive substance may produce a damaging biological effect and that ingested and inhaled radiation can be a serious health risk (Rowland 1993). When radium is taken into the body, its metabolic behavior is similar to that of calcium and an appreciable fraction is deposited in bone, the remaining fraction being distributed almost uniformly in soft tissues (Wrenn et al. 1985). When people are exposed to very high levels of radium for a long period of time, cancer of the bone and nasal cavity may result.
Radon can be lead to exposures by being ingested and also by being inhaled after having been released from the water into indoor air during water usage as washing, cooking and taking shower.

Regulations

The European Commission Drinking Water Directive (98/93/EC) does not give maximum activity concentrations for the individual nuclides excepting tritium. It sets a maximum effective dose of 0,1 mSv/y from ingestion of tap water for the public. The radon and its daughters are excepted from the calculation of this maximum effective dose.

Single radionuclides reference values are being discussed by EU at present. They shall be reported in the Annex 2 to the EU Council Directive 98/83/EC, not issued yet.

Commission Recommendation 2001/928/Euratom proposes maximum concentration values for radon (100 Bq/l) and its long lived daughters (polonium-210: 0,1 Bq/l and lead-210: 0,2 Bq/l).

The Recommendation of the European Commission K (2001) 4580 concerning radon and its long lived daughters the European countries were asked to define an action level higher than 100 Bq/l ^{222}Rn f or public supplies depending on the national situation. For concentrations higher than 1000 Bq/l remedy actions are justified.

In Bulgarian Regulation, concerning using drinking water for public needs, we have maximum activity concentrations for the respective nuclides and they are: 0,15 Bq/l for ^{226}Ra, 0,06 mg/L for natural uranium, 2 Bq/l for gross beta activity, 1 Bq/l for gross alpha activity and 100 Bq/l for tritium. The maximum effective dose, excluding radon and its daughters is 0,1 mSv/y from ingestion of tap water for the public.

In 2004 in Bulgaria entered into force a new Regulation on basic norms of radiation protection. In them the limit of annual individual effective dose for persons of population is 0,1 mSv/y and a special rights are given to the Minister of Health to take a decisions accordingly concrete example and real social and economic conditions in case of higher values.

The aim of this paper is to show the pilot study of radon determination in some Bulgarian drinking waters, to try to fine if there is any vice-versa between radium and radon concentrations in the investigated waters.

Experimental methods

Sampling and methods

Bulgaria is a very diversity country in point of land structure. The map of Bulgaria is shown on Fig.1. There are mountains with granite rocks, metamorphic rocks, and lignites, uranium-rich minerals of uranite, carnotite, and phosphate deposits. The attitude of mountains and hills varies between 250 m and 2928 m. The origin of the drinking water is mainly from ground water. The surface water used as a drinking purpose is on small scale. Before 1992 in Bulgaria were developed uranium mining activities. Due to the literature it is possible to detect some drinking waters with high content of natural radionuclides including radon.

Fig. 1 Bulgaria map

In the National Center of Radiobiology and Radiation Protection we monitor large numbers of drinking and mineral waters. On the base of received results for uranium and radium content we chose some “interesting” waters to start this pilot study. The meaning of interesting is high concentrations of radium or uranium in tap waters. We started with 12 selected waters and after that made sampling randomly in the same regions. Sampling was done in Haskovo region, Smolian region, Kustendil region, Blagoevgrad region and 3 samples from Sofia region. All these regions are situated in South-West and South-East parts of Bulgaria. ^{222}Rn and ^{226}Ra were determined in 40 Bulgarian drinking waters and 6 mineral waters.

Sampling was done by ourselves and for radium measurements we used five-liter plastic bottles. Before filling the bottles, the water was allowed to flush for some time. To prevent nuclides adsorption on the bottle surfaces 10 ml concentrate nitric acid was added. Once returned to the laboratory, the water samples were treated as soon as practically possible. The time between sampling and analytical procedures ranged from 1 to 7 days.

For radon measurements we collected water in PDF syringes and sampled 100 ml. We tried to fill fully the syringe in order to prevent losses of radon.

Measurement of radon was done by ALPHA Guard with Aqua kit equipment. It was done on-site.

^{226}Ra was determined by its daughter radon-222 after allowing storage of water in gas-tight bottles for 30 days to reach radioactive equilibrium. We used barium chloride as a carrier.

For natural uranium determination the luminescent method was used. It is based on the ability of the hexavalent uranium in a melt with sodium-lithium fluoride to luminescent and there is a straight proportion between the magnitude of the light intensity and the uranium content.

For the Total Indicative Dose determination WHO recommended methodology was used. The annual water ingestion of 730 L/year from one adult was accepted. Critical age group according to the Bulgarian Regulation on Basic Norms of Radiation Protection is the group of individuals between 12 and 17 years.

For the calculations we used the formula:

$$IDnuclide = Cmeasured*Gdose*L,$$

where:

IDnuclide – indicative dose of water ingestion of some nuclide in (mSv/year);

Cmeasured – measured activity of some nuclide in 1 L water (Bq/l);

Gdose – Dose coefficient - depend on the nuclide and on the age(mSv/Bq);

L – the volume of water intake from one individual per one year – depend on the age(L/year)

The conversion dose factor for ^{226}Ra is $2,8.10^{-4}$ mSv/Bq

The conversion dose factor for ^{222}Rn is $0.1.10^{-4}$ mSv/Bq

Results and discussion

Results on the analyzed drinking waters are reported in Table 1 and Fig.2. The Graff is on a logarithmic scale to see the dependence better. On the (x) axis are given the number of the samples. The numbers between 1 and 8 are from Haskovo region; between 9 and 20 are from Kustendil region; between 21 and 23 are from Blagoevgrad region; between 24 and 36 are from Smolian region, between 37 and 40 are from Sofia region and between 41 and 46 are mineral waters

Radon-222

Only two samples drinking water showed values higher than 100 Bq/l ^{222}Rn: village Tatarevo 138 Bq/l and pump station Boliarevo 185 Bq/l, Haskovo region, both situated in the Rodopi Mountain. Activity concentrations of 12 samples drinking water were between 10 and 99 Bq/l. The corresponding sampling sites were in the Rodopi Mountain. 26 samples showed radon values smaller than 10 Bq/l.

We investigated 6 mineral waters and we received result for^{222}Rn content as follow: 1 mineral water with value higher than 100 Bq/l, 2 mineral waters between 10 and 99 Bq/l and 3 mineral waters with values smaller than 10 Bq/l.

We expect to find more tap waters with ^{222}Rn activity concentration of about 60 Bq/l and more because of the relieve and rocs structure, but this is a pilot study and it is not representative enough. We did not find strong relation between radium and radon content in investigated waters.

Concentrations of Rn-222 and Ra-226 in water samples					
№	Object	Rn-222		Ra-226	
		A [Bq/l]	SD [Bq/l]	A [Bq/l]	SD [Bq/l]
1	pump station Starkelovo, obl. Haskovo	3.52	0.58		
2	Tatarevo - obl. Haskovo	138.31	8.00		
3	pump station Boliarevo, obl. Haskovo	185.43	10.37		
4	Botevo - obl. Haskovo	16.85	1.81		
5	Sirakovo - obl. Haskovo	35.32	2.84		
6	Surnitsa - obl. Haskovo	47.34	3.09		
7	Susam - obl. Haskovo	34.16	2.52		
8	Garvanovo - obl. Haskovo	16.31	1.61		
9	Kladnitsa - obl. Pernik	0.28	0.09	0.06	0.03
10	Uglyartsi - obl. Pernik	20.52	1.60	0.10	0.03
11	Tsurvenyano - obl. Kyustendil	4.71	0.78	0.108	0.034
12	Bunovo - obl. Kyustendil	3.01	0.61	0.031	
13	Gyueshevo - obl. Kyustendil	5.01	0.74	0.106	0.032
14	Gyueshevo - obl. Kyustendil , border	7.33	0.50		
15	Dragovishtitsa - obl. Kyustendil	11.89	1.17	0.076	0.026
16	Rajdavitsa - obl. Kyustendil	9.89	0.93	0.031	
17	Kyustendil	1.19	0.50	0.068	0.031
18	Nevestino - obl. Kyustendil	10.60	1.05	0.083	0.029
19	Dupnitsa - obl. Kyustendil	1.21	0.68	0.076	0.031
20	Monastery of Saint Ivan of Rila - obl. Kyustendil	1.60	0.54	0.039	
21	Bansko - obl. Blagoevgrad	5.34	0.45	0.03	
22	Banya - obl. Blagoevgrad	6.47	0.98	0.078	0.033
23	Blagoevgrad	0.70	0.29	0.041	0.019
24	Asenovgrad - obl. Plovdiv	6.56	0.80		
25	Narechenski bani - obl. Plovdiv	1.22	0.40		
26	Chepelare - obl. Smolyan	2.04	0.53		
27	Smolyan, s. Braloto	3.85	0.57	0.045	
28	Smolyan, s. St. Ivan	3.28	0.55	0.046	0.027
29	Smolyan, s. Ezerataq distr. Kaptaja	34.74	2.56		
30	Smolyan, s. Sredorek	38.52	2.70	0.041	
31	Smolyan, s. Balieva voda	31.15	2.36		
32	Smolyan, s. Ezerata	2.67	0.89		
33	Kiselichevo - obl. Smolyan	10.57	1.25	0.036	
34	Mogilitsa - obl. Smolyan	7.45	0.88	0.036	
35	Smilyan - obl. Smolyan	7.21	1.37		
36	Smolyan, prison	2.53	0.69	0.046	0.027
37	Kostinbrod - obl. Sofia	0.90	0.12	0.093	0.035
38	"Полкомерс", МВ	2.12	0.19	0.069	0.032
39	Jeleznitza - obl. Sofia	2.10	0.47	0.036	
40	Bistritza - obl. Sofia	0.38	0.11	0.062	0.031
41	Sofia - mineral water, central bath	144.29	8.43	0.036	
42	Nevestino - obl. Kyustendil - mineral water	51.75	3.40	0.192	0.046
43	Narechenski bani - obl. Plovdiv, mineral water	80.60	4.92		
44	Sofia, mineral water Gorna Bania s. No 3	4.65	0.90		
45	Sofia, mineral water Gorna Bania s. No 4	4.11	0.59	0.062	0.029
46	Sofia, mineral water Bankia	3.71	0.62	0.054	0.028

Table 1. Concentrations of radium and radon in water from Bulgaria

Radium-226

Radium activity concentrations higher than 0.15 Bq/l (the Bulgarian maximum permitted value) were not found in investigated for this study drinking waters. Values of ^{226}Rn vary between MDA and 0.11 Bq/l. For the village Tzervianino, Kustendil region we received in a previous study 0.19 Bq/l ^{226}Rn, but it was investigated at different season and some effect of water table is possible.

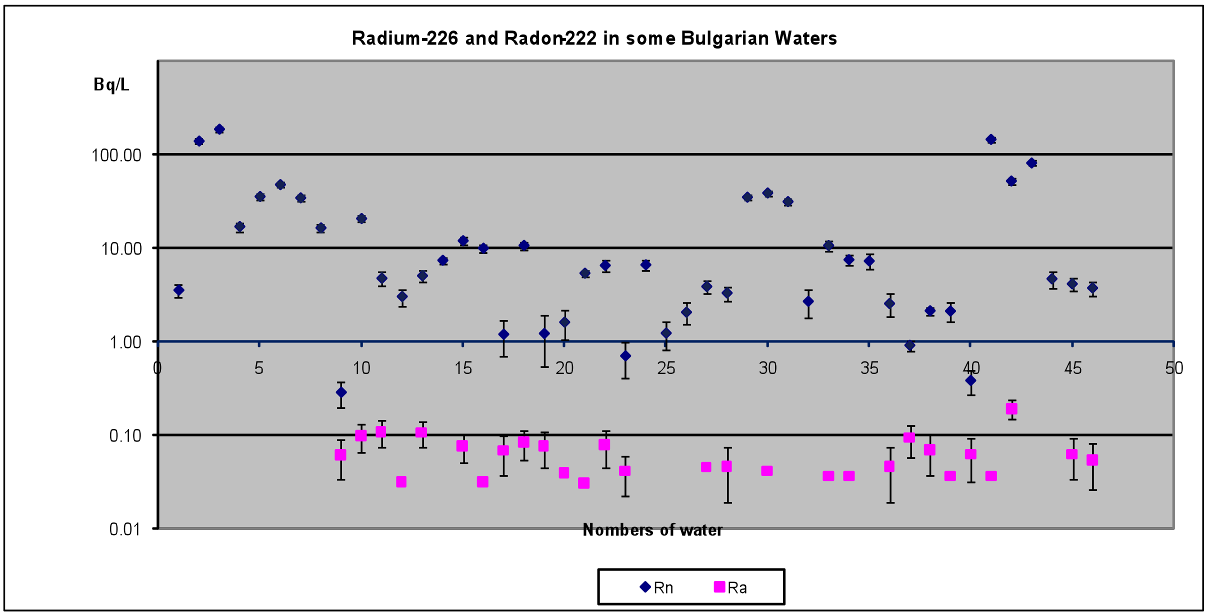

Fig.2 Radium and Radon content in some Bulgarian waters

Dose calculation

The effective dose arising from the ingestion of a radioisotope in a particular chemical form was estimated using a dose coefficient. Data for age-related dose coefficients for ingestion of radionuclides have been published by the ICRP and the International Atomic Energy Agency. The higher age-dependent dose coefficients calculated for children (accounting for the higher uptake and/or metabolic rates) do not lead to significantly higher doses due to the lower mean volume of drinking-water consumed by infants and children. Consequently, the recommended RDL of committed effective dose of 0.1mSv/y from 1 year's consumption of drinking-water applies independently of age. No deleterious radiological health effects are expected from consumption of drinking-water if the concentrations of radionuclides are below the guidance levels (equivalent to a committed effective dose below 0.1mSv/year). Only samples with higher than 0.6 Bq/l ^{226}Ra activity concentrations and higher than 10 Bq/l ^{222}Rn levels were listed.

The Indicative Dose was calculated with the intake of individual radionuclides and ingestion dose coefficients (mSv/Bq) reported in Bulgarian Regulation on basic norms of radiation protection.

The estimation was made on the base of:

Ingestion dose coefficient for radium-226 - 2,8.10^{-4} mSv /Bq;

Ingestion dose coefficient for radon-222 – 0,1.10^{-4} mSv/Bq;

Annual intake of water – 730 l;

The results are shown in Table 2.

Effective dose from ingestion [mSv/y]			
No	Sample	Ra-226	Rn-222
2	Tatarevo - obl. Haskovo		1.010
3	pump station Boliarevo, obl. Haskovo		1.354
4	Botevo - obl. Haskovo		0.123
5	Sirakovo - obl. Haskovo		0.258
6	Surnitsa - obl. Haskovo		0.346
7	Susam - obl. Haskovo		0.249

Effective dose from ingestion [mSv/y]			
No	Sample	Ra-226	Rn-222
8	Garvanovo - obl. Haskovo		0.119
9	Kladnitsa - obl. Pernik	0.012	0.002
10	Uglyartsi - obl. Pernik	0.020	0.150
11	Tsurvenyano - obl. Kyustendil	0.022	0.034
13	Gyueshevo - obl. Kyustendil	0.022	0.037
15	Dragovishtitsa - obl. Kyustendil	0.016	0.087
17	Kyustendil	0.014	0.009
18	Nevestino - obl. Kyustendil	0.017	0.077
19	Dupnitsa - obl. Kyustendil	0.016	0.009
22	Banya - obl. Blagoevgrad	0.016	0.047
29	Smolyan, s. Ezerataq distr. Kaptaja		0.254
30	Smolyan, s. Sredorek	0.008	0.281
31	Smolyan, s. Balieva voda		0.227
33	Kiselichevo - obl. Smolyan	0.007	0.077
37	Kostinbrod - obl. Sofia	0.019	0.007
38	Sofia	0.014	0.015
40	Bistritza - obl. Sofia	0.013	0.003
41	Sofia - mineral water, central bath	0.007	1.053
42	Nevestino - obl. Kyustendil - mineral water	0.039	0.378
43	Narechenski bani - obl. Plovdiv, mineral water		0.588
45	Sofia, mineral water Gorna Bania s. No 4	0.013	0.030

Table 2. Effective dose from ingection in mSv/y

No sample with radium doses near or higher than the dose limit of 0.1 mSv/y was found. The highest values were 0.04 mSv/y (mineral water) and 0.02 mSv/y (drinking water).
The highest values for effective dose of radon are 1.4 mSv/y (drinking water) and 1.05 mSv/y (mineral water).

Conclusions

The estimated Indicative Doses from radium-226 are many times below than recommended level of 0.1mSv/year.
Consequently, the health hazards related to radium-226 in drinking water are expected to be negligible in the areas studied.

In this pilot study of tap water samples taken randomly from South-West and South-East parts of Bulgaria, maximum effective dose from ingestion of radon-222 was 1.4 mSv/y.
We did not find strong relation between radium and radon content in invest tigated waters.
This pilot study has to be expanded in order to establish radon action level for Bulgaria.

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