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CONTENT OF HEAVY METALS, URANIUM, RADIUM AND RADON IN DRINKING WATER FROM UNDERGROUND WATER SOURCES IN PROXIMITY TO OLD MINES

Yanakieva T.[1], T. Turnovska[2], P. Nedeva[3], R. Totzeva[4], R. Karaivanova[4], St. Mladenova[1]

[1]Regional Inspectorate of Protection and Control of Public Health - Haskovo, [2]Medical University - Plovdiv, [3]Regional Inspectorate of Protection and Control of Public Health - Plovdiv, [4]National Center of Radiobiology and Radiation Protection -Sofia

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ABSTRACT

In the Haskovo Province polymetal deposit fields have operated for many years. Some of them are the lead-zinc deposits near the villages of Sarnitza, Boyan Botevo, and Spahievo. Besides these, uranium deposits were mined in the past: The 'Fountain' Plot is part of the 'Haskovo' uranium-ore deposit and is situated 6 km to the west of the 'Bolyarovo' District. Taking into consideration that in the past, a number of mines operated on the territory of the city of Haskovo and the Mineral bath Municipality, and also the absence of research into possible contamination of subterranean waters from them, we set a goal to investigate whether there is a Pb, Cd, As, Cu, Zn, U-234, U-235, U-238, Ra-226 and Rn-222 contamination of drinking water from the central water sources located in close proximity to the old mines in the Haskovo and Mineral bath Municipalities. In the month of November 2007 we collected 6 water samples from the above-mentioned water sources to investigate presence of Pb, Cd, Zn, Cu and As and to determining of the radiological indicators and taking and test of drinking water from 9 pumping stations for establishing the level of Rn-222. Content of heavy metals in drinking water from the studied pumping stations are: Pb:of 0 to < 0.004 mg/dm^3,Cd: of 0 to < 0.004 mg/dm^3, Zn: of <0.013 to 0.402 ±0.005 mg/dm^3, Cu: of 0 to <0.018 mg/dm^3, As: of 0.00095 ±0.00002 mg/dm^3 to 0.0130 ± 0.0002 mg/dm^3. Content of uranium, radium-226 and total в-activity in drinking water from studied 6 pumping station are: U-238: of 0.0025 ±20% to <0.0250 mg/l, Ra-226: of 0.0481 ±25% Bq/l to 0.1315 ±25% Bq/l and Rn-222 in 9 central water source in the Haskovo town and Mineral bath Municipality are: of 3.5 ±0.6 Bq/l to 185.5 ±10.4 Bq/l. The total b-activity vary of 0.11 ±10%Bq/l to 1.12 ±10% Bq/l .Conclusion: 1.The content of heavy metals in the studied water sources is within the permissible hygiene standard levels. 2.The studied drinking water is not hazardous to the health of the consumers. The radiation analysis shows that the overall indicative dose is below 0.10 mSv/year), which corresponds to the ordinance documents.3.The established levels of radon in the studied drinking water are probably due to contamination from the exploited uranium fields in the past.

Key words: heavy metals, radiological indexes, drinking waters, health risk, health impact assessment

In the Haskovo Province polymetal deposit fields have operated for many years. Some of them are the lead-zinc deposits near the villages of Sarnitza, Boyan Botevo, and Spahievo (fig.1).
Besides these, uranium deposits were mined in the past: The 'Fountain' Plot is part of the 'Haskovo' uranium-ore deposit and is situated 6 km to the west of the 'Bolyarovo' District. The 'Fountain' exploitation plot borders the villages: Garvanovo, Vaglarovo, and Tatarevo, Mineral Bath Municipality (fig.2). It includes the plots: 'Bolyarovo' and 'Kenana'. The experimental-test work for the extraction of uranium from the 'Fountain' plot began in 1977 - geotechnological plan-drilling method. Its production activities were terminated in 1990.
Of the ore-deposits described above, only the 'Chala' Mine continues to be in operation nowadays, the mine is situated to the southwest of the village of Mineral bath. Gold ore is extracted from the last-mentioned mine.
In the Haskovo Municipality, up until 1992-1993, a uranium-extraction field was in operation between the village of Mineral bath and the 'Bolyarovo' district, city of Haskovo. It is located 2 km to the east of the fork in the road to the village of Tatarevo (fig.2).
Up until 1998-1999 the 'Saje' mine operated near the villages of Sarnitza and Boyan Botevo (fig.1), Mineral bath

Municipality, Haskovo Province which was used to extract lead-zinc ores - raw material for the production of the Lead-Zinc Metallurgical Works in the city of Kardjali. Initially, uranium ore was extracted too.

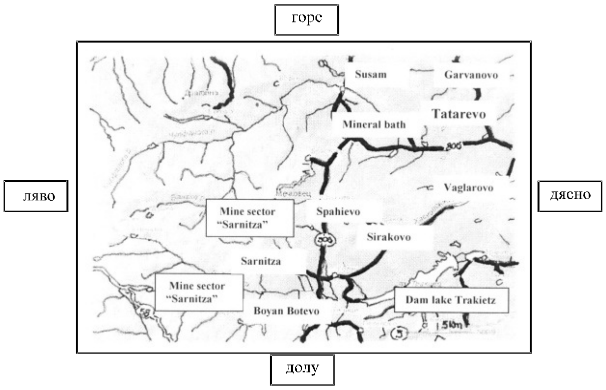

Figure 1

Also, until 1990 uranium ore was extracted from the 'Fountain' exploitation plot, between the 'Bolyarovo' District and the village of Mineral bath. For that reason, a real danger exists of heavy-metal and uranium pollution of drinking water in the neighboring villages. Especially sensitive to environmental pollution with heavy metals, including Pb as well, are children and pregnant women. Lead damages the central and peripheral nervous system, haemopoiesis, the metabolism of vitamin D and calcium, and also the reproductive function (15,11).

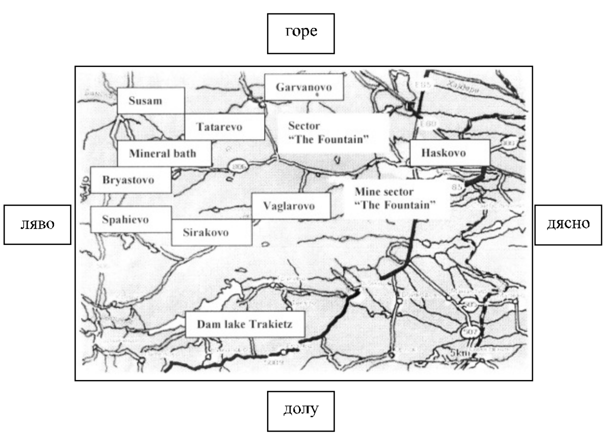

Figure 2

Exposure of people to As is usually caused by the contamination of subterranean water. Use of such water for irrigation raises the possibility of an increase in the arsenic content in crops. (8). Since a great portion of the drinking water in the studied regions is used for irrigation purposes, the pollution may encompass the irrigated fruit and vegetables, and thus, interfere with the food chain. Cadmium also is highly cumulative, it builds up in the soil and bottom sediments along the course of the food chain (2). The content of copper and zinc in drinking water affects organoleptics and induces an astringent-metal taste in the mouth (2). The population consuming drinking water from water sources situated in proximity to the old mines is approximately 19 419, from the Haskovo and Mineral bath municipalities.

Transfer of heavy metals from drinking water to the human organs and their impact on diseases of the liver and kidneys reflects the existing link between ecosystems and human health (11). For instance, heavy metals accumulation in fish is correlated with etiology of many diseases (11).

Another group of pollutants of subterranean drinking water, from the operation of the described mines, are radioactive elements: uranium and radium and their decay product: radon. The content of uranium and Ra-226 in soils depends on the type of the soil, on its physicochemical composition, on the type of rocks which it is made of. Permeation of natural radionuclides from the soil into the water depends on the water spring location, on the route of the water to the point of its intake, as well as on the level of dissolution of uranium and radium, on the physico-mineral composition of the compounds in which they are bonded, on the duration of contact with the water and the soil horizon, on the temperature, pH, on the level of subterranean waters, and on numerous other factors. According to the published specialized literature, of the internal sources of natural radiation, the significance of radon, thoron, 40K и 87Rb is the greatest. They enter an organism mainly through breathing (Rn-222 and Rn-220), or through food and drinking water and cause internal radiation of the organism by building up in some organs. The mentioned Rn-222 and Rn-220 predominantly accumulate in the lungs. Radon is considered the most hazardous because of its quick decay to a-particles. It is the second major cause of lung cancer after smoking (16,18) and it accounts for 21 000 lung cancer deaths per year (18). Naturally-occurring radon gas comprises approximately 55% of the annual background radiation dose (19).

Taking into consideration that in the past, a number of mines operated on the territory of the city of Haskovo and the Mineral bath Municipality, and also the absence of research into possible contamination of subterranean waters from them, we set a goal to investigate whether there is a Pb, Cd, As, Cu, Zn, U-234, U-235, U-238, Ra-226 and Rn-222 contamination of drinking water from the central water sources located in close proximity to the old mines in the Haskovo and Mineral bath Municipalities.

MATERIALS AND METHODS

The pumping stations which could be affected by contamination are the following:

1. Bolyarovo (Haskovo 1 - supplies water to the 'Bolyarovo' District and the low part of the city of Haskovo, 'Grancharski' District, 'Bryagovi' (total population - 8 719), Mineral bath Municipality, and 'Kamenitza'Joint- Stock Company - for beer production; The pumping station includes 6 piped wells, it has a capacity of 10 l/s and a water volume of 860 m^3.

2. village of Tatarevo - supplies water to the village of Tatarevo, population of 362, village of Bryastovo - population of 209, and the eastern part of the village of Mineral bath, for the whole municipality - total population of 6 561. The output of the water source is 2.3 l/s, and the water volume is 198m^3 per day.
3. 'Shtarkelite' - used for backup water supply to the village of Mineralni bani, with a total population of 6 561; situated between the villages of Tatarevo and Mineralni bani.
4. village of Sarnitza (0.8 l/s and water volume of 69 m^3 /per day) - supplies water to the village of Sarnitza, population of 699;
5. village of Boyan Botevo supplies water to the villages of Boyan Botevo, Karamantzi, and Angel voivoda, with a total population of 2 295. Its capacity is 2 l/s, and the water volume is 172 m^3 per day.
6. village of Sirakovo is used for water supply of the village of Sirakovo and for backup water supply to the village of Spahievo, with a total population of 574.

In the month of November 2007 we collected 6 water samples from the above-mentioned water sources to investigate presence of Pb, Cd, Zn, Cu and As, complying with all the rules and regulations for sample collecting and transportation. The samples were tested at the accredited by the Executive Environmental Agency test laboratory - regional laboratory for the city of Haskovo. The tests were carried out in accordance with ISO standard 8288(3); BDS EN ISO 11969(1), employing the methods of atomic-absorption spectrophotometry.

The determining of the radiological indicators, included in Ordinance 9/16.03.2001 was carried out at Regional Inspection of Protection and Control-Plovdiv. The sample-collecting was performed in compliance with all regulations for sample taking and transportation of samples for a radiological test.

The sample taking and test of drinking water from 9 pumping stations for establishing the level of Rn-222 was carried on location by experts from the National Center of Radiobiology and Radiation Protection (NCRRP) - city of Sofia.

RESULTS AND DISCUSSION

The results about the content of heavy metals and arsenic in the tested water are presented in table 1.

As it can be seen, the content of Pb, Cd, Cu and Zn in all studied water sources is within the top permissible hygiene standard levels. This presupposes absence of health risk to the population consuming the respective drinking water.

Arsenic at the pumping station - Tatarevo has a borderline level of the indicator, and at pumping station - Shtarkelite it is slightly above the permissible concentration of 0.010mg/dm3. The As level (carcinogen from Group 1) is hazardous to the health, at pumping station - Shtarkelite, and at pumping station - village of Tatarevo. Chronic exposure to As in drinking water is related to the development of nu-

Table 1. Content of heavy metals in drinking water from the studied pumping stations

Pumping station	Pb mg/dm^3	Cd mg/dm^3	Zn mg/dm^3	Cu mg/dm^3	As mg/dm^3
Haskovo-1	<0.004	<0.004	<0.013	<0.018	0.00190 ±0.0002
Tatarevo	<0.004	<0.004	0.120 ±0.007	<0.018	0.0108 ±0.0002
Sharkelite	<0.004	<0.004	0.016 ±0.001	<0.018	0.0130 ±0.0002
Sarnitza	<0.004	<0.004	0.402 ±0.005	<0.018	0.00107 ±0.00002
Boyan Botevo	<0.004	<0.004	0.026 ±0.002	<0.018	0.00095 ±0.00002
Sirakovo	<0.004	<0.004	0.266 ±0.003	<0.018	0.00649 ±0.00009

merous types of cancer, with a life exposure of 6x 10-4, for levels of 10 mg/l there is an established risk of developing skin cancer (2), diabetes, heart diseases, and diseases of the reproductive system, damage to the endocrine system (10).

In small, non-toxic doses As usually alters the gene expression of RAR-response element-luciferase construct and the endogenous TR-regulated type I of deiodinase (D101), gene in a similar manner in GH3 cells. 'RAR' and 'TR' mediators of gene regulation in these examined steroid receptors are critical for the normal development and growth function, and disruption of their regulation is related to the development of numerous diseases (10).

Table 2. Content of uranium, radium-226 and general β-activity in drinking water from the studied pumping

Pumping Station	**Natural Uranium (U-234,U-235, U-238) (mg/l)**	**Ra -226 (Bq/l)**	**Total β-activity (Bq/l)**
Haskovo-1	0.0100 ±20%	0.1315 ±25%	0.97 ±10%
Tatarevo	0.0075 ±20%	0.1130 ±25%	0.22 ±10%
"Shtarkelite"	<0.0250	0.1278 ±25%	1.12 ±10%
Sarnitza	0.0025 ±20%	0.0518 ±25%	0.11 ±10%
Boyan Botevo	0.0025 ±20%	0.0481 ±25%	0.13 ±10%
Sirakovo	0.0075 ±20%	0.0888 ±25%	0.36 ±10%

With lower As concentrations in drinking water, a harmful respiratory effect is observed (12). The established borderline value of As in this case cannot be accepted as hazardous, but further investigation of contamination in order to explain its dynamics is required. Although the Shtarkelite -

pumping station is used only for backup water supply to the village of Mineral bath, it should comply with health regulations. In the other pumping stations the As concentration is within the permissible limits, and it does not constitute a health risk to the consumers of this drinking water.

The results from the tests on radioactive elements in drinking water are presented in table 2.

The presented results show that all studied pollutants are within the permissible hygiene standard levels (Appendix 1 Table D - Radiological indicators) (5). The common indicative dose is below 0.10 mSv/year, which means that there is no health risk to the consumers of this drinking water.

Table 3. Content of uranium, radium-226 and total в-activity in drinking water from the investigated pumping stations from previous years

Pumping Station	Natural Uranium (U-234,U-235, U-238) (mg/l)	Ra-226 (Bq/l)	Total-β-activity (Bq/l)
Haskovo-1	<0.0025	0.0555	0.40
Tatarevo	0.00025	0.0444	0.25
Shtarkelite	0.001	0.0296 ±25%	0.14 ±10%
Sarnitza	0.001	0.0296	0.12
Boyan Botevo	<0.001	0.0259	0.07
Sirakovo	0.0001	0.0370	0.34

If the obtained results for U-234, U-235, U-238, Ra-226 and total в-activity are compared with the study of drinking water for these indicators from previous years, it can be established that there is a slight increase in the values of natural uranium and radium-226 in 2007, while the general в-activity maintains stable values for the last years of the study. A more considerable increase in the level of Ra-226 in 2007, in comparison with previous studies, was found in the Tatarevo pumping station and Shtarkelite pumping station, but - within the permissible hygiene standard levels.

In the past, extraction of uranium from rocks was performed by using sulfates which afterwards drain away into the subterranean horizons and into subterranean waters, and from there - into wells used for drinking and household needs. This fact can significantly increase the content of sulfates in drinking water. That is why we traced their values for the studied 6 pumping stations (table 4).

No regularity in the values of sulfates in the studied water sources was found through the course of investigation. They maintain comparatively stable values, with small increases in some of the examined years which is probably due to negligible drainage of fertilizers into subterranean waters when using fertilizers on agricultural crops. Despite this fact, sulfates in all studied pumping stations are within the permissible hygiene standard levels, while their values are more significant in the drinking water from “Shtarkelite” and “ Tatarevo” but theycorrespond to the regulations of the operative ordinance on the quality of drinking water (5). The pH levels in the studied 9 water

Table 4. Content of sulfates in the studied 6 pumping stations over the course of the last 3 years

Pumping Station	2005 year	2006 year	2007 year
Haskovo-1	No data	No data	No data
Tatarevo	119.3 mg/l	140 mg/l	127.55 mg/l
"Shtarkelite"		234.0 mg/l	
Sarnitza	9.24 mg/l	8.0 mg/l	7.1 mg/l
Boyan Botevo	38.94 mg/l	34.0 mg/l	28.79 mg/l
Sirakovo	44.55 mg/l	41.0 mg/l	72.6 mg/l

sources vary between 6.9 - 7.8, i.e. in the neutral zone, or corresponding to the permissible ones.

The obtained results are within the permissible values, according to a Decision of the European Commission, article 35/Rapport La Hague F-05/6, which gives the boundary values for all radionuclides to be 200 Bq/l (13). We compared the data with the approved recommended values of

Table 5. Content of radon in drinking water from subterranean water sources in the municipalities of Haskovo and Mineral bath

Pumping Station/or Central Drinking Water source	Contents of Rn-222 (Bq/l)
Haskovo-1	185.5 ±10.4
Tatarevo	138.3 ±8.0
Shtarkelite	3.5 ±0.6
Sarnitza	47.4 ±3.1
Boyan Botevo	16.9 ± 1.9
Sirakovo	35.4 ±2.9
Mineral bath village, Central Water Sourse	6.0 ±1.0
Susam village, Mineral bath Municipality, Central Water Sourse Str."Saedinenie" N32	34.2 ±2,5
Fountain in the City Park of Haskovo	144.3 ±8.5

radon in public water sources in the Republic of Slovakia which vary between 50 to 500 Bq/l. The annual boundary dose for drinking water is 1 mSv/year (14). For Ireland the referential level of radon in drinking water is 500 Bq/l. In conformity with a recommendation by the EC on radon in drinking water 2001/928 (17), for levels below 100 Bq/l no measures need to be taken, and for concentrations over 1000 Bq/l - taking particular measures is justified, in point of view of radiation protection since such water is not fit for use, while concentrations over 100 Bq/l are needed for the development of public water plants (20). Nevertheless, the European Commission recommends discussing activities and particular programs for human health protection at radon levels over 100 Bq/l. For concentrations of radon in water at the level of 1000 Bq/l the annual effective dose varies between 0.2 mSv and 1.8 mSv, depending on the annual water consumption (17).

According to the operative standard orders in Bulgaria, Ordinance 1 /15.11.1999, the general б-activity in the surface and subterranean waters should not exceed 500 Bq/m3 (4). We determined that in the drinking water from 3 central water sources: Bolyarovo district-pumping station - Haskovo 1 and Tatarevo pumping station and a fountain faucet in the City Park of Haskovo, the concentrations of radon are higher than 100 Bq/l. This, we believe, can be explained with contamination from the existing uranium-extracting field, part of the exploitation plot 'Fountain', located near the villages of Garvanovo, Vaglarovo, and Tatarevo (fig.1). A similar finding was determined in the town of Aldama, Chihuahua - Mexico. The high activity of U-238 in soils was due to the processing or uranium 20 years before that, in these regions (9).

Radon in drinking water is not a significant factor for the radiation of humans, with small exceptions. People take in a large amount of the needed water through food and hot drinks, and cooking and heating of water eliminate radon. So that, the more substantial intake of radon in the organism comes from drinking water. Furthermore, the main part of the received radon in this manner, is quickly taken away by the lungs, while the highest radiation received is that of the stomach. The annual boundary of the average radiation on a world level, due to drinking water, containing radon is estimated at 0.002 mSv/y (7). In general, the radiation of humans, when drinking water containing radon, is smaller than the radiation from the inhalation of radon which is released from water when it flows down the tap (7).

In order to draw conclusions on the overall radioactivity in the studied region we should take into consideration the level of radioactivity of soils as well. We cannot bypass the fact that as a result of the Chernobyl Atomic Power Station failure in 1986 the pollution of the soils in Southern Bulgaria with technogenic radionuclides is higher than the pollution in Northern Bulgaria. From a performed study in Bulgaria it was established that for Southern Bulgaria the content of Cs137, including that for Haskovo, Harmanli, Slavyanovo, Ivanovo, Yabalkovo, Varbitsa, is below 60 Bq/kg (6). In comparison with the year 1986 the content of Cs137 and Sr 90 has considerably decreased.

CONCLUSION

1. The content of heavy metals in the studied water sources is within the permissible hygiene standard levels.
2. The studied drinking water is not hazardous to the health of the consumers. The radiation analysis shows that the overall indicative dose is below 0.10 mSv/year), which corresponds to the ordinance documents.
3. The established levels of radon in the studied drinking water are probably due to contamination from the exploited uranium fields in the past.

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