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Short Communication

Natural Radioactivity in Underground Waters

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Abstract

Nine underground water springs from the Szczawno-Jedlina health resort and one from Zagórze Śląskie were investigated for natural radioactivity content (^{222}Rn, ^{226,228}Ra, ^{238,234}U).

In order to obtain the necessary data, two different nuclear spectrometry techniques were applied: a liquid scintillation counter that enabled us to determine ^{222}Rn and ^{226,228}Ra isotope content, and α spectrometer for measurements of uranium isotopes (^{234,238}U) in investigated samples. The activity concentrations of ^{222}Rn in investigated samples varied from 6 Bq/l to 227 Bq/l. For radium isotopes the concentrations ranged from 13 mBq/l to 808 mBq/l for ^{226}Ra and from below 30 mBq/l to 184 mBq/l for ^{228}Ra. The activity concentrations for uranium isotopes varied from 2.4 mBq/l to 964 mBq/l for ^{234}U, and from 1.0 mBq/l to 725 mBq/l for ^{238}U. The isotopic ratios between uranium and radium isotopes (^{226}Ra/^{228}Ra, ^{226}Ra/^{238}U, ^{234}U/^{238}U) and annual effective doses due to these isotopes' consumption were evaluated. Risk levels due to carcinogenic effects of ^{226,228}Ra and ^{234,238}U radionuclides consumed with water were estimated.

Keywords: Radon, Radium, Uranium, effective doses

Introduction

Natural radionuclides can enter the human body through inhalation and ingestion with water and food. Their presence in water is determined by their concentration in bedrock. A great variety of health resorts can be found in Poland and most of them are situated in the southern part of Poland in the Sudety and the Outher Carpathian Mountains. Among them, the Szczawno-Jedlina health resort has mineral and medicinal waters. Moreover, some of these waters are bottled as medicinal or mineral waters and are distributed all around the country.

The goal of this study was to determine the activity concentration of radon ^{222}Rn, radium isotopes ^{226,228}Ra and uranium isotopes ^{234,238}U in underground waters of Szczawno-Jedlina health resort and Zagórze Śląskie. (The region of interest is presented in Fig. 1.)

The Sudety Mountains (SW Poland) are rich in underground water that often contains higher concentrations of radon, radium and uranium isotopes. This is due to the presence of radium and uranium isotopes in the reservoir rocks [2]. Moreover, the Sudety Mountains are known for uranium exploration that was conducted in the early 1950s.

In Szczawno health resort five out of six underground waters are regarded as mineral or medicinal and are used for balneological purposes. All waters are carbon dioxide-rich and they are HCO_3-Na, HCO_3-Na-Ca types with mineralization up to 3 g/l. In Marta Spring ^{222}Rn concentration is equal to 227±12 Bq/l which classifies this water as medicinal radon waters (>74 Bq/l). Przylibski et al. [3] concluded that ^{222}Rn dissolves in Marta spring water after acidulous water of deep circulation has mixed with poorly

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mineralized shallow water in their outflow zone. This spring is situated close to Szczawnik fault, where brittle deformations (i.e. cracks and fissures) enhance Marta water in ^{222}Rn.

Five waters from Szczawno health resort are available in drinking halls, while two spring waters from Jedlina health resort and one spring water from Zagórze Śląskie are freely available for local inhabitants. Samples from six water intakes from Szczawno Spa and three from Jedlina Spa were collected 3-4 times over a period of 8 years (2000-08). The measurements of radionuclide contents in water sample from Zagórze Śląskie were performed in 2008. Sampling for ^{238,234}U also was performed in 2008.

Experimental Procedures

Water samples were collected in 5 l polyethylene bottles and acidified in order to avoid radionuclide precipitation and adsorption on walls of containers.

The measurements of ^{222}Rn and ^{226,228}Ra content were performed with the use of the WinSpectral α/β 1414 liquid scintillation counter from Wallac, while the determination of ^{234,238}U was performed with the use of an α-spectrometer 7401 VR from Canberra-Packard, USA.

The method for ^{222}Rn determination is based on the ISO norm described by Suomela [4]. A sample of 10 ml of water was drawn by disposable syringe and immediately transferred to a glass vial filled with 10 ml of scintillator Insta-Fluor from Camberra-Packard.

The ^{226,228}Ra activity concentrations in investigated samples were determined based on the chemical procedure described in Polish Norm [5]. The procedure involves preconcentration of radium by co-precipitation with $BaSO_4$ and separation from other radionuclides present in water.

The separation of uranium from other α-radionuclides present in water was performed according to a slightly modified procedure worked out by Suomela [6]. Uranium was separated and purified from other radionuclides on the anion-exchange resin Dowex 1×8 (Cl^-, 200-400 mesh). The thin α-spectrometry source was prepared from uranium fraction by co-precipitation with NdF_3 [7] and filtration on a polypropylene disk (0.1 μm) (Pall Corporation, Gelman Labolatory).

All procedures are described in our previous publication [8]. Minimum Detectable Activity (MDA) was calculated according to Currie's method [9] and was equal to 1 Bq/l, 10 mBq/l, 30 mBq/l, 0.4 mBq/l and 0.6 mBq/l for ^{222}Rn, ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U, respectively.

Results

Activity concentrations of ^{222}Rn, ^{226,228}Ra and ^{238,234}U isotopes in investigated waters are presented in Table 1a. The activity concentrations for radon varied from 6±0.8 Bq/l to 227±12 Bq/l, for ^{226}Ra from 13±1 mBq/l to 808±80 mBq/l, and for ^{228}Ra were in a range from below 30 mBq/l to 184±24 mBq/l. For uranium isotopes the concentration ranged from 2.4±0.4 mBq/l to 964±48 mBq/l for ^{234}U and

Fig. 1. Localization of the studied region on the map of Poland; a) the Sudety Mountains, b) the investigated region located in the Sudety Mountains; A – Szczawno spa, B – Jedlina spa, C – Zagórze Śląskie, 1 – The region of low-mineralized water i.e. up to 1 g/l, at depths of 300-800 m b.g.l., 2 – Acidulous water (1 g CO_2/l), 3 – Radon water (above 74 Bq/l), 4 – Thermal water (20ºC) (based on [1]).

Table 1. Mineral and medicinal waters from Sudety Mountains: (a) their characteristics and activity concentrations, (b) isotopic ratios, annual doses and risk assessment.

a)

Location	Spring	Water description	TDS [mg/l]	^{222}Rn [Bq/l]	^{226}Ra [mBq/l]	^{228}Ra [mBq/l]	^{234}U [mBq/l]	^{238}U [mBq/l]
Szczawno Spa	Mieszko-14	HCO_3-Na-Ca, bottled as "Anka", drinking hall	701	11.0±1.5 (3)	79±26 (3)	49±1 (2)	48.3±3.2 (1)	12.0±1.0 (1)
	Dąbrówka	HCO_3-Na-Ca, bottled as "Dąbrówka" medicinal water	2122	24.4±0.5 (3)	67±10 (3)	65±9 (2)	12.1±1.1 (1)	4.0±0.5 (1)
	Odwiert 14	currently not used	461	31±11 (3)	14±2 (3)	<30	23.9±1.8 (1)	6.0±0.7 (1)
	Młynarz	HCO_3-Na-Ca, drinking hall	2291	32±3 (3)	92±26 (3)	58±4 (2)	36.2±2.6 (1)	17±1 (1)
	Mieszko	HCO_3-Na, bottled as "Mieszko" medicinal water, drinking hall	3025	31±2 (4)	110±14 (4)	45±13 (4)	31.8±2.5 (1)	7.9±0.9 (1)
	Marta	HCO_3-Na-Ca, Rn, drinking hall	2319	227±12 (4)	808±80 (4)	140±40 (1)	964±48 (1)	725±36 (1)
Jedlina Spa	J-300	HCO_3-Na-Ca, bore hole, currently not used	447	NA	109±25 (1)	184±24 (3)	366±20 (1)	54±3 (1)
	No. 1	free access	NA	15±2 (3)	13±1 (1)	<30	2.8±0.7 (1)	1.1±0.4 (1)
	No. 2	free access	NA	8±4 (2)	142±7 (1)	<30	2.4±0.4 (1)	1.0±0.3 (1)
Zagórze Śląskie		bore hole, free access	NA	6.0±0.8 (1)	15±2 (1)	<30	3.6±0.3 (1)	2.7±0.3 (1)

(n) - denotes the number of analysis.

b)

Spring	U[µg/l]	^{226}Ra/^{228}Ra	^{226}Ra/^{238}U	^{234}U/^{238}U	Effective dose from ^{222}Rn [µSv/year]	Summed effective dose* [µSv/year]	Assumptions for TR calculations			TR	Confidence interval	
							[l/day]	[day/yr]	[yr]		2.5 perc	97.5 perc
Mieszko-14	1.0±0.1	1.6±0.5	6.6±2.3	4.0±0.4	7.0	10.7	Min 0.13 Max 0.25	Min 150 Max 365	Min 1 Max 30	$1.7\cdot10^{-6}$	$1.7\cdot10^{-7}$	$4.6\cdot10^{-6}$
Dąbrówka	0.3±0.04	1.0±0.2	17.0±3.4	3.0±0.5	15.6	11.7				$1.9\cdot10^{-6}$	$1.9\cdot10^{-7}$	$4.9\cdot10^{-6}$
Odwiert 14	0.5±0.1	-	2.3±0.4	4.0±0.5	-	-				$2.8\cdot10^{-7}$	$2.9\cdot10^{-8}$	$7.1\cdot10^{-7}$
Młynarz	1.3±0.1	1.6±0.5	5.5±1.7	2.2±0.2	20.7	12.4				$2.0\cdot10^{-6}$	$2.0\cdot10^{-7}$	$5.1\cdot10^{-6}$
Mieszko	0.6±0.1	2.5±0.8	14.0±2.4	4.0±0.5	20	11.6				$1.9\cdot10^{-6}$	$1.8\cdot10^{-7}$	$4.9\cdot10^{-6}$
Marta	58.4±2.9	5.8±1.7	1.1±0.1	1.3±0.1	145	73				$1.2\cdot10^{-5}$	$1.2\cdot10^{-6}$	$3.0\cdot10^{-5}$
J-300	4.3±0.3	0.6±0.2	2.0±0.5	6.8±0.5	-	-	Min 0.5 Max 1.5	Min 150 Max 365	Min 1 Max 60	$1.6\cdot10^{-5}$	$1.2\cdot10^{-6}$	$4.6\cdot10^{-5}$
No. 1	0.09±0.03	-	12.0±4.6	2.6±1.1	9.3	2.8				$1.1\cdot10^{-6}$	$7.8\cdot10^{-8}$	$3.1\cdot10^{-6}$
No. 2	0.08±0.02	-	144±41	2.4±0.8	4.8	29.1				$1.1\cdot10^{-5}$	$8.3\cdot10^{-7}$	$3.2\cdot10^{-5}$
Zagórze Śląskie	0.21±0.02	-	5.6±0.8	1.3±0.2	3.9	3.3				$9.6\cdot10^{-7}$	$9.2\cdot10^{-8}$	$3.6\cdot10^{-6}$

* ^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U.

from 1.0±0.3 mBq/l to 725±36 mBq/l for ^{238}U. The uncertainty of a single measurement was calculated as a square root of the sum of uncertainties in all quantities in quadrate. Four out of ten water samples have activity concentrations below MDA for ^{228}Ra. The highest values of radon, radium and uranium activity concentrations were obtained for Marta spring. For this, water activity of natural uranium corresponds to the mass of 58.4±2.9 µg/l, which considerably exceeds the limit for drinking waters (<15 µg/l) [10].

The activity ratio ^{226}Ra/^{228}Ra in investigated samples varied from 0.6±0.2 to 5.8±1.7 (Table 1b), and there is a high positive correlation (r=+0.5, N=6) between these isotopes. This means that the chemical properties of radium are responsible for the concentration of these isotopes in waters. The activity ratio ^{226}Ra/^{238}U varied in a range from 1.1±0.1 to 144±41, which indicates that radium is much easier transported to water than uranium (Table 1b).

The uranium activity ratio ^{234}U/^{238}U in investigated samples varied from 1.3±0.1 to 6.8±0.5 (Table 1b), which indicates a lack of radioactive equilibrium in theses waters. An activity ratio ^{234}U/^{238}U higher than 1 indicates that ^{234}U atoms are easier leached from rocks than ^{238}U nuclei. (A full description of the mechanism responsible for the state of uranium disequilibrium in waters is discussed elsewhere [11].)

Total effective radiation doses were calculated for eight samples used for daily consumption by citizens and patients. In Szczawno spa there are medicinal and/or mineral waters, so daily consumption of 0.5 l was taken for calculations. Since waters from Jedlina and Zagórze Śląskie are drinking waters from free intakes, 2l consumption per day was assumed. The summed effective doses were calculated on the basis of dose conversion factors equal to $2.8\cdot10^{-7}$Sv/Bq, $6.9\cdot10^{-7}$Sv/Bq, $4.9\cdot10^{-8}$Sv/Bq and $4.5\cdot10^{-8}$Sv/Bq for ^{226}Ra, ^{228}Ra ^{234}U and ^{238}U, respectively [10] (Table 1b). Some of these waters are consumed directly from the water intakes. The effective doses from ^{222}Rn were additionally calculated on the basis of the dose conversion factor $3.5\cdot10^{-9}$ Sv/Bq [12] and 0.5 liter of water consumption per day. The highest dose from ^{222}Rn equal to 145 µSv/year was obtained for Marta spring (Table 1b).

The last exercise concerning investigated waters was to evaluate the carcinogenic risk effect arising from the radioactive substance present in water samples that can be calculated according to U.S. Environmental Protection Agency recommendations [13]. The carcinogenic risk effect R_{SRN} arising from the radioactive substance found in water sample is defined by the following equation [14]:

$$R_{SRN} = SF_0 \cdot RW \cdot IR_w \cdot EF \cdot ED$$

...where:

R_{SRN}	– risk caused by the ingestion of a given radionuclide in water,
SF_0	– ingestion cancer slope factor in [risk/pCi] (radionuclide specific) [15],
RW	– activity concentration in [pCi/l],
IR_w	– daily ingestion rate of water in [l/day],
EF	– exposure frequency in [days/yr],
ED	– exposure duration in [yr].

R_{SRN} – expresses the average carcinogenic risk over a lifetime (i.e. 60 years) calculated for each underground water from Jedlina Spa and Zagórze Śląskie of each specific radionuclide (^{226}Ra, ^{228}Ra, ^{238}U, ^{234}U), separately. Since waters from Szczawno Spa are medical, a time duration of 30 years was assumed (Table 1b).

The estimated total risk value (TR) concerns a hypothetical population and is defined as a sum of risks calculated for each radionuclide separately, i.e ^{226}Ra, ^{228}Ra, ^{234}U and ^{238}U:

$$TR = \sum_{SRN=1}^{4} R_{SRN} = R_{226Ra} + R_{228Ra} + R_{238U} + R_{234U}$$

Health risk assessment was conducted according to the presently accepted general trend of a probabilistic approach. The idea of this approach together with Monte Carlo simulations as a calculation technique both in carcinogenic and non-carcinogenic (toxic) aspect was previously discussed in [14, 16]. Gaseous ^{222}Rn was not taken into account. TR's were calculated with the Monte Carlo simulations performed with the use of the software package Cristal Ball 2000 ver. 5.0. The computational procedure was repeated 50,000 times. In consequence, 50,000 element classes of TR values was obtained and the probability distributions fitting was performed using the Kolomogrov-Smirnov test. The output TR results were given in the form of beta probability distributions. Exposure assumptions such as daily and yearly consumption and time duration were regarded as random variables characterized by the probability distribution functions (Table 1b). Due to the lack of knowledge about these assumptions, they were modeled with uniform probability distributions presented in Table 1b. An expected value and a lower and upper limit of an interval confidence were calculated for each probability distribution separately. The obtained results represented the average value and its uncertainty of cancer risk assessment in a hypothetical population. The lower and upper limits of the confidence intervals were regarded as 2.5 and 97.5 percentiles of a given probability distribution (p-level = 0.05).

All the data analyses performed for mineral, medicinal and table waters from the investigated region showed that the radiological risks do not exceed current lifetime "acceptable risk" equal to 10^{-3} [17]. The value 10^{-3} represents an approach not taking into account the ALARA (as low as reasonably achievable) principle [18, 19]. The EPA prefers to apply 10^{-4} to 10^{-6} incremental lifetime target risk range in managing radiation risk [19, 17]. The values obtained in the present work are all above the "lower bound" goal, so the radiological risk of the investigated isotopes is acceptable.

Conclusions

The measurements of natural radioactivity in groundwaters from Szczawno-Jedlina health resort and Zagórze Śląskie were performed. Some of these waters are bottled as mineral or medicinal and are commercially available on the market, and some of them are used as medicinal waters in health spas during medical treatment for patients or are available for free for citizens.

In order to obtain activity concentrations of natural radionuclides, two different nuclear spectrometry techniques were applied. The highest value of uranium radioactivity content was obtained for medicinal Marta water from Szczawno health resort with activity concentration equal to 964±48 mBq/l for ^{234}U and 725±36 mBq/l for ^{238}U. This water has ^{222}Rn concentration equal to 227±12 Bq/l and is classified as radon-enriched water (with radon content > 74 Bq/l) and also contains the highest value of ^{226}Ra content equal to 808±80 mBq/l from all obtained results. With the obtained concentration results, the summed effective doses from radium and uranium were evaluated and they varied from 2.8 to 73 µSv/year (Table 1b). The doses obtained for all waters except Marta do not exceed the limit of 100 µSv/year, which is established for drinking water by the World Health Organization [10]. The highest value equal to 73 µSv/year was obtained for medicinal water Marta, which is used only for balneological purposes.

Additionally, the annual effective dose due to radon ingestion was also estimated. Only Marta spring, which is radon medicinal water, gives a higher value of annual effective dose from ^{222}Rn equal to 145 µSv/year.

Risk levels due to the carcinogenic effect of ^{226,228}Ra and ^{234,238}U radionuclides consumed with water were evaluated, but it should be emphasized that these values are only estimates. All values obtained in the present work fall within the EPA incremental limits from 10^{-4} to 10^{-6}.

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