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LONG LIVED NATURAL RADIOACTIVE ELEMENTS IN SPA WATERS OF SOUTHERN POLAND — DOSE ASSESSMENT AND HEALTH HAZARD EVALUATION*

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The aim of this study was to determine the activity concentrations of ^{234,238}U isotopes in mineral, medicinal and spring waters in spas situated in the Sudety and the Outer Carpathian Mountains and to compare the uranium content found in waters from these regions. Samples were collected over a period of 7 years (2005–2011) from 86 water intakes from the Sudety Mountains and Fore-Sudetic block and from 37 water intakes from Outer Carpathians. On the basis of the calculated activity concentrations of ^{234,238}U as well as the existing data on ^{226,228}Ra, the annual effective doses resulting from the consumption of these isotopes were evaluated.

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1. Introduction and methodology

The aim of this study was to determine the activity concentrations of ^{234,238}U isotopes in mineral, medicinal and spring waters in spas situated in the Sudety and the Outer Carpathian Mountains. The sampling sites are presented in Fig. 1. Results concerning the presence of radioactive isotopes in some chosen groundwater intakes of the Outer Carpathian Mountains have already been published [1, 2]. The investigated region is known for a large number of natural water springs and some of these waters have been recognized as either medicinal or potentially medicinal. Apart from mineral elements beneficial for human health, groundwater may contain radioactive isotopes. Long lived uranium: ^{234}U ($T_{1/2} = 2.46 \times 10^5$ yr), ^{238}U ($T_{1/2} = 4.47 \times 10^9$ yr) and radium: ^{226}Ra ($T_{1/2} = 1600$ yr), ^{228}Ra ($T_{1/2} = 5.75$ yr) isotopes are mainly responsible for natural radioactivity

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of groundwater. Measurements of their and their progenies activities may provide information on whether waters, previously classified as mineral or medicinal, are beneficial for humans and whether the quality of these waters will have to be verified in the future.

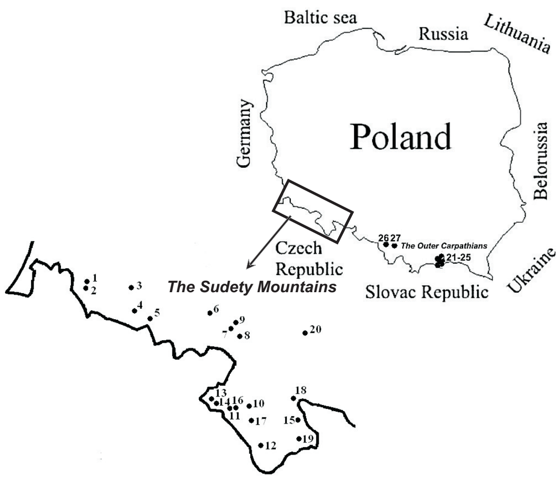

Fig. 1. Sampling sites (number in brackets corresponds to the number of the investigated water intakes): from the Sudety Mountains: 1. Świeradów Spa (15), 2. Czerniawa Spa (5), 3. Cieplice Spa (4), 4. Sosnówka (2), 5. Kowary (3), 6. Szczawno Spa (6), 7. Jedlina Spa (3), 8. Walim (1), 9. Zagórze Śląskie (1), 10. Polanica Spa (5), 11. Duszniki Spa (8), 12. Długopole Spa (3), 13. Kudowa Spa (4), 14. Jeleniów (5), 15. Lądek Spa (6), 16. Bobrowniki Stare (1), 17. Szczawina (1), 18. Złoty Stok (3), 19. Kletno (1); from the Fore-Sudetic block: 20. Przerzeczyn Spa (7); from the Outer Carpathians: 21. Krynica Spa (17), 22. Muszyna (8), 23. Złockie (3), 24. Szczawnik (1), 25. Powroźnik (2); selected saline waters: 26. Dębowiec (4, from the Carpathian Foredeep), 27. Ustroń (2).

The present study contains a full statistical analysis of the activity concentration of the investigated isotopes as well as the comparison of uranium content in waters from the Sudety and the Outer Carpathian Mountains. On the basis of the obtained activities of ^{234,238}U and the previous ^{226,228}Ra data [3], the annual effective doses resulting from the consumption of these isotopes with water both by local people as well as by the tourists and spa patients were evaluated [4]. Uranium isotopes have a harmful effect on human health. Their toxicity is of twofold nature *i.e.* radiological and chemical. The authors have evaluated the risk due to uranium ingestion with water by applying both Polish and foreign standards.

The determination of uranium ^{234,238}U was performed with the use of the α spectrometer 7401VR from Canberra–Packard, USA and the silicon surface barrier detector with a surface area of 300 mm^2 (Ortec Instruments).

The chemical separation of uranium from other radionuclides present in water was conducted on a slightly modified procedure published by Suomela [5]. Uranium was separated and purified on an anion exchange resin Dowex 1×8 (Cl-type, 200–400 mesh). The α-spectrometry source was prepared from the uranium fraction by co-precipitation with NdF_3 [6].

2. Results and discussions

The evaluated activity concentrations of $^{234,238}U$ and statistical analyses are presented in Table I. From among 86 investigated water samples from the the Sudety Mountains 9 results for ^{238}U and 3 for ^{234}U exhibited activity concentration under Minimum Detectable Activity (MDA, 0.5 mBq/l). From among 37 investigated water samples from the Outer Carpathians 15 results for ^{238}U and 5 for ^{234}U exhibited activity concentration under MDA (0.5 mBq/l). The medians calculated for all ^{238}U and ^{234}U results were lower than the arithmetic means which shows that both distributions are not only abnormal but also asymmetric. The skewness parameters were different from zero and positive. This is reflected in the long right-sided tail of the distribution. Moreover, a significant number of results are much above the arithmetic mean. Comparing the statistical data of ^{238}U and ^{234}U for the Sudety Mountains with those for the Outer Carpathians it can be seen that the median of ^{238}U activity concentrations in the Sudetic waters is almost 7 times higher than the one in Carpathian waters. The median of ^{234}U activity concentrations in the Sudetic springs is about 6 times higher than that in Carpathian springs.

TABLE I

Statistical analyses of uranium activity concentrations (in [mBq/l]) and $^{234}U/^{238}U$ activity ratio in the studied groundwaters of the Sudety and the Outer Carpathian Mountains [4] (on the basis of Statistica 7.0 software). AM — arithmetic mean, SD — standard deviation, SP — skewness parameter.

Izotope/ Izotope ratio	AM	SD	SD Mean	Median	Quartile I	Quartile III	Value min	Value max	SP
The Sudety Mountains									
^{238}U	42	193	22	7.9	3.0	16.6	0.5	1529	6.9
^{234}U	90	440	49	14.8	3.4	30.2	0.6	3850	8.1
$^{234}U/^{238}U$	2.4	1.2	0.1	2.2	1.5	3.0	0.8	6.8	1.1
The Outer Carpathians									
^{238}U	2.5	3.6	0.8	1.2	0.6	2.5	0.5	16	3.1
^{234}U	9.5	29.1	5.3	2.4	1.0	7.8	0.7	162	5.3
$^{234}U/^{238}U$	4.4	3.3	0.7	3.0	2.1	6.8	1.2	13.5	1.4

No radioactive equilibrium between the parent nuclide ^{238}U and its daughter ^{234}U was observed in the investigated waters (Table I). The activity ratio ^{234}U/^{238}U > 1 indicates that ^{234}U atoms leach more easily from the mineral structures to water than ^{238}U. A full description of the state of disequilibrium in water and the processes responsible for it are discussed in details in [7].

In order to evaluate the correlation between two variables, one can calculate the Pearson correlation coefficient which is a measure of their linear dependence. A high positive correlation between ^{238}U and ^{234}U was observed in the studied waters (Table II). This proves that there is an almost linear dependence between uranium isotope activity concentrations. The comparison of ^{222}Rn isotope with ^{238,234}U for both the Sudety and the Outer Carpathian Mountains shows there is no or a very weak negative correlation between them. Similar dependencies were observed for ^{226}Ra and ^{234,238}U. This points to a different geochemical behavior of these isotopes and a radioactive disequilibrium among ^{238}U and its progenies in the decay chain. The higher the Total Dissolved Solids (TDS) in waters, the higher the amount of radium leached from the rocks. However, a higher TDS does not mean that the uranium content is also higher. In contrast to the behavior of radium, the ^{222}Rn activity concentrations were observed in waters with low TDS.

TABLE II

Correlation coefficients between activity concentrations of ^{238}U, ^{234}U, ^{222}Rn, ^{226}Ra, ^{228}Ra, and the total mineralization of water (TDS) for the investigated waters from Sudety and Outer Carpathians.

Correlated elements	Correlation coefficient	Number of correlated pairs	Correlation coefficient	Number of correlated pairs
	The Sudety Mountains		The Outer Carpathians	
^{238}U–^{234}U	0.98	75	0.89	20
^{222}Rn–^{238}U	−0.01	73	−0.01	12
^{222}Rn–^{234}U	−0.03	79	−0.08	22
^{226}Ra–^{238}U	0.05	69	−0.12	15
TDS–^{238}U	0.06	68	−0.02	20
TDS–^{234}U	0.03	72	0.12	30
TDS–^{222}Rn	−0.46	72	−0.42	23
TDS–^{226}Ra	0.62	70	0.93	29
TDS–^{228}Ra	0.37	56	0.75	18

The annual effective radiation doses were calculated by assuming that the daily consumption of mineral or medicinal waters amounts to 0.5 l. Since some of the waters are drinking water from free intakes for local inhabitants or from municipal water supplies a consumption of 2 l per day was assumed.

The dose conversion factors used for the calculation were taken from the WHO publication [8]. Since the medicinal waters from Ustroń and Dębowiec are only used for balneotherapy and not drinking their effective doses were not determined in our study.

According to the decree of the Polish Ministry of Health [9] and WHO Guidelines [8] concerning the requirements for drinking water the total annual effective dose from all radionuclides except for ^{3}H, ^{40}K and ^{222}Rn cannot exceed the value of 100 μSv/yr.

The maximum values of the calculated effective doses from uranium and radium consumption with water together with the summed up effective doses are presented in Table III. On adding the effective doses from radium and uranium, it turned out that the total effective doses from the consumption of these isotopes with water for some of the intakes from the Sudety Mountains (Table III) exceeded the limit for drinking water. Detailed investigations of the effective doses arising from consumption of uranium and radium isotopes with the particular waters can be found in [4].

TABLE III

Effective doses in [μSv/yr] resulting from radionuclide consumption (max. values). For waters from the Sudety Mountains only the summed effective doses values exceeding the limit of 100 μSv/yr are presented.

Name of the water intake/spa	Daily consumption	Effective doses in [μSv/yr](max. values) ^{238}U	^{234}U	^{226}Ra	^{228}Ra	Ra+U
The Sudety Mountains						
P-1/Czerniawa	0.5 [l/day]	0.2	0.8	35	67	103
B-3/Duszniki	2 [l/day]	2.5	8.1	145	121	277
No. 39/Duszniki	2 [l/day]	0.1	0.4	114	106	221
K-200/Kudowa	2 [l/day]	0.6	1.9	131	60	194
The Outer Carpathians						
Zuber III/Krynica	0.5 [l/day]	0.005	0.04	25	50	75
No. 1/Muszyna	2 [l/day]	0.015	0.03	35	—	35

On taking the chemical toxicity of uranium into account it was estimated, that the concentration of uranium in drinking water cannot exceed the limit of 15 μg/l [8]. Uranium content in the investigated waters from the Sudety Mountains ranged from 0.04 μg/l to 124 ± 3 μg/l, whereas the median and arithmetic mean were equal to 0.64 μg/l and 3.4 ± 1.8 μg/l, respectively. The highest uranium content was observed in the spring water from the Cieplice Spa and this water is currently not used for drinking. Medicinal water Marta from Szczawno Spa with the uranium content equal to 59 ± 3 μg/l also exceeded the limit for drinking waters (15 μg/l). Nowadays this water is only used for balneological purposes.

Uranium content in the investigated waters from the Outer Carpathians varied from $0.04\,\mu$g/l to $1.3 \pm 0.1\,\mu$g/l whereas the median and arithmetic mean were equal to $0.10\,\mu$g/l and $0.20 \pm 0.06\,\mu$g/l, respectively. None of the waters from the Outer Carpathians exceeded the limit of 15 μg/l.

3. Summary and conclusions

The waters from the Sudety Mountains and from the Outer Carpathians were compared in relation to their uranium content. The investigated waters from the Sudety Mountains exhibited higher uranium content than waters from the Outer Carpathians. Moreover, activity concentrations of ^{234,238}U were lower than 0.5 mBq/l in a significant number of water intakes from the Outer Carpathians. Effective radiation doses, due to radionuclide ingestion with drinking water, were also estimated. The doses related to uranium isotopes did not exceed the limit of $100\,\mu$Sv/yr for all samples. Radium isotopes constitute the main contribution to the total effective dose. In the case of some of the water intakes from the Sudety Mountains the total effective radiation doses exceeded the limit of $100\,\mu$Sv/yr. However, the doses obtained for all waters from the Outer Carpathians did not exceed the limit of $100\,\mu$Sv/yr. Since uranium presents not only radiological but also chemical hazard, the estimated uranium content in the investigated waters was compared with the currently valid regulations concerning the quality of drinking water. From our comparison it resulted that only two waters from the Sudety Mountains exceeded the limit of $15\,\mu$g/l.

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