NUKLEONIKA 2010;55(4):519–522

ORIGINAL PAPER

Uranium, radium and radon isotopes in selected brines of Poland

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Abstract. Natural radioactive isotopes were studied in nine different types of brines from four locations in Poland. Investigated brines are exploited from various geological structures composed of the rocks of different chemical and mineral composition as well as different age and depth. All investigated brines are used in balneotherapy (i.e. baths, inhalations, showers). The main goal of this study was to obtain some basic knowledge on the activity range of natural elements such as uranium, radium and radon in different brine types in Poland and their variability depending on their location in certain geological structures. Activities of ^{234,238}U, ^{226,228}Ra and ^{222}Rn isotopes were measured with the use of two nuclear spectrometry techniques: liquid scintillation and alpha spectrometry. The activity concentrations of ^{222}Rn vary from below 1 to 76.1±3.7 Bq/l, for the ^{226}Ra isotope from 0.19±0.01 to 85.5±0.4 Bq/l and for ^{228}Ra from below 0.03 to 2.17±0.09 Bq/l. For uranium isotopes, the concentrations are in the range from below 0.5 to 5.1±0.4 mBq/l for ^{238}U and from 1.6±0.4 to 45.6±2.0 mBq/l for ^{234}U. The obtained results indicate high radium activity concentrations corresponding to high mineralization of waters.

Key words: uranium • radium • radon • brines

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Received: 30 June 2009
Accepted: 30 December 2009

Introduction

Brine is a highly mineralized groundwater (total dissolved solids, TDS > 30 g/l) often containing also higher amounts of natural radioactive isotopes. Concentration of Cl^- ions and some other hydrochemical indicators together with the isotopic data of brines from the studied Upper Silesia Basin (USB) region indicate that their salinity has its origin in leaching the Miocene sediments [6, 7]. Another evidence come from the considerable differences in Cl^- concentrations accompanying the constant isotopic composition. Thus, the salinity of deep Carboniferous brines from the USB has its origin in leaching with possible secondary enrichment in infiltration processes.

Brines studied in this work are exploited from various geological structures composed of the rocks of different chemical and mineral composition. Investigated brines are not natural springs, but they are obtained from boreholes at a depth of 500–1800 m. Water drillings at Ustroń were performed in 1962–1992. Brines from U-3 and U-3a intakes are of Cl-Na-Ca, Br, I, Fe, Sr type with temperatures of 50°C and 22°C, respectively. They were obtained from the Upper and Middle Devonian layers. Borehole C-1 was drilled for secondary forced water and brine from this intake has a similar chemical type as from U-3 and U-3a and the temperature about 20°C. Podbasenie is the place for water usage. Qualities

Fig. 1. Localization of the investigated regions on the map of Poland. 1 – Ustroń health resort (U-3, U-3a, Podbasenie, C-1 brines); 2 – Dębowiec health resort (D-2, ST-5, Thermal Brine Zabłocka); 3 – Grudziądz (IG-1); 4 – Sopot (Zdrój Św. Wojciecha).

and values of brines from Dębowiec were discovered in the year 1912 when the investigations performed by Chemisch-Mikroskopische Laboratorium from Vienna showed that they contain the highest concentrations of I and Br in Europe. The exploited brines led to the production of specific, for human health, thermal brine Zabłocka with very rich mineral composition. Therapeutic water of chemical type Cl-Na, Br, I, Fe, B was found in the borehole Grudziądz IG-1. This is the "old" water of the pre-Quaternary infiltration which contains an admixture of other waters, e.g. probably relict marine waters. The brine Zdrój Św. Wojciecha from Sopot is of Cl-Na, Br, I type. Investigated brines represent different chemical types and mineralization and are used in balneotherapy in baths, inhalations, showers, etc. Their localization on the map of Poland is presented in Fig. 1.

Experimental procedures

Studies of natural radioactivity in nine brines from four resorts in Poland were performed with the use of two different nuclear spectrometry techniques. The measurement of radon ^{222}Rn and radium ^{226,228}Ra activity concentrations in investigated samples were performed with the use of a 1414 WinSpectral α/β liquid scintillation counter (LSC) from Wallac. ^{222}Rn concentration in water samples was determined according to the procedure worked out by Suomela [12]. A sample of 10 ml of water was drawn by a disposable syringe and transferred to a scintillation vial filled with 10 ml of a scintillation cocktail Insta-Fluor (Canberra, Packard). ^{222}Rn activity concentration was calculated from the α part of the spectrum originating from this isotope and its α-radioactive daughters. The minimum detectable activity (MDA) was calculated according to Curie's publication [3] and was equal to 1 Bq/l at 1 h counting time.

The procedure for radium ^{226,228}Ra determination was based on radiochemical preconcentration by coprecipitation with $BaSO_4$ and purification of its derivatives. This method is based on the Polish Norm [8]. The measurements were performed once a day (1 h counting time) over the period of a month, until the secular equilibrium between radium and its derivatives is reached. ^{226}Ra was calculated from the α part of the spectrum. ^{228}Ra content was estimated from a high-energy β daughter ^{228}Ac in the radioactive equilibrium state with ^{228}Ra. Theoretical calculations were based on Bateman's equations [1]. The MDA was equal to 0.01 Bq/l for ^{226}Ra and 0.03 Bq/l for ^{228}Ra for 1 h counting time and 3 l of water sample.

The uranium ^{234,238}U determination was performed with the use of a α-spectrometer 7401VR (Canberra, Packard, USA) and a silicon surface barrier detector with a surface area of 300 mm^2 (Ortec Instruments). Prior to the radiochemical treatment of samples, the standard of ^{232}U National Institute of Standards and Technology (NIST), USA of well known activity was added to each 0.5 l water sample. Uranium was separated on the anion-exchange resin Dowex 1×8 (Cl^-, 200–400 mesh) on the basis of a slightly modified procedure worked out by Soumela [13]. A thin α-spectrometry source was prepared from a uranium fraction by coprecipitation with NdF_3 [11]. The MDA was equal to 0.5 mBq/l for ^{234,238}U for a measurement lasting two days.

Samples from Ustroń and Dębowiec Health Resorts were collected four times over the period of 3 years (2005–2007). Sampling at Grudziądz and Sopot was performed once in 2007. The samples were collected in polyethylene bottles and acidified in order to avoid radionuclide precipitation and adsorption on the walls of the containers.

Results and discussion

Brines from eight intakes and one bottle from four different spas were investigated for radon, radium and uranium isotopes (Table 1). Concerning their high mineralization up to 120 g/l, special care was needed during radiochemical procedures.

As can be seen in Table 1, activity concentrations of the radon isotope ^{222}Rn (from below 1 to 76.1±3.7 Bq/l) are always close to that of its parent radionuclide radium ^{226}Ra. For investigated brines from Ustroń and from Dębowiec health resorts, the ^{222}Rn activity concentrations are equal to or a little lower than ^{226}Ra. For the remaining brines (IG-1, Zdrój Św. Wojciecha) from Grudziądz and Sopot, the ^{222}Rn values are a little higher than ^{226}Ra, but still of the same order of magnitude. The correlation coefficient between these two isotopes is equal to $r = +0.98$ (Table 2) what indicates a strong positive correlation. It seems that in all investigated brines radon originates from radium dissolved in water, not from surrounding reservoir rocks. The opposite result was obtained previously for mineral and spring groundwaters of different origin in Poland [4, 9, 10].

The activity concentrations for uranium isotopes varied from below 0.5 mBq/l to 5.1±0.4 mBq/l and from 1.6±0.4 mBq/l to 45.6±2.0 mBq/l for ^{238}U and ^{234}U,

Table 1. Mineralization and activity concentration of ^{222}Rn and ^{226,228}Ra in Bq/l and of ^{234,238}U in mBq/l for studied brines. For ^{222}Rn, ^{226,228}Ra and ^{234,238}U values ± SD (n)*. The uncertainty of a single measurement was calculated as a square root of the sum of uncertainties in all quantities in quadrate

Health resort	Brand name of brine	TDS (g/l)	^{222}Ra (Bq/l)	^{226}Ra (Bq/l)	^{228}Ra (Bq/l)	^{238}U (mBq/l)	^{234}U (mBq/l)
Ustroń	U-3	101	47.2 ± 10.1 (4)	68.6 ± 3.0 (4)	< MDA	2.7 ± 0.9 (1)	14.0 ± 1.9 (1)
	U-3a	122	76.1 ± 3.7 (4)	85.5 ± 0.4 (4)	< MDA	0.5 ± 0.2 (1)	3.2 ± 0.4 (1)
	Podbasenie	NA	25.3 ± 0.5 (4)	25.9 ± 0.6 (4)	< MDA	0.9 ± 0.3 (1)	4.8 ± 0.5 (1)
	C-1	NA	24.8 ± 0.4 (4)	25.2 ± 0.7 (4)	< MDA	0.5 ± 0.2 (1)	4.2 ± 0.5 (1)
Dębowiec	D-2	32	1.16 ± 0.04 (1)	1.07 ± 0.01 (3)	1.20 ± 0.04 (1)	0.8 ± 0.2 (1)	2.6 ± 0.4 (1)
	ST-5	36	1.18 ± 0.10 (1)	1.27 ± 0.04 (2)	1.32 ± 0.06 (1)	< MDA	1.6 ± 0.4 (1)
	Thermal Brine Zabłocka	44	< MDA	0.19 ± 0.01 (1)	0.11 ± 0.03 (1)	NA	NA
Grudziądz	IG-1	79	4.90 ± 0.50 (1)	2.16 ± 0.07 (1)	2.17 ± 0.09 (1)	NA	NA
Sopot	Zdrój Św. Wojciecha	44	6.80 ± 0.60 (1)	0.47 ± 0.02 (1)	1.02 ± 0.05 (1)	5.1 ± 0.4 (1)	45.6 ± 2.0 (1)

* (n) – number of individuals. NA – not available.

Table 2. Correlation coefficients and the number of correlated pairs

Correlated elements	Number of correlated pairs	Correlation coefficient
^{222}Rn-^{226}Ra	8	0.98
^{226}Ra-^{228}Ra	5	0.95
^{226}Ra-^{238}U	6	–0.30
TDS-Ra_{total}	7	0.91
TDS-^{226}Ra	7	0.91
TDS-^{228}Ra	5	0.61

respectively. For radium isotopes, the concentrations ranged from 0.19±0.01 Bq/l to 85.5±0.4 Bq/l for ^{226}Ra and from below 0.03 to 2.17±0.9 Bq/l for ^{228}Ra. The isotopic ratio of ^{234}U/^{238}U in the investigated samples varied from 3±1 to 9±1, which means that ^{234}U isotope is more easily leached from a solid matrix to water than ^{238}U. The ^{234}U excess in water is caused by the direct transfer of ^{234}U across the crystalline matrix by alpha recoil or by increased vulnerability to waters related to the oxidation of uranium from the valence state +4 to +6.

The correlation coefficient between two radium isotopes was equal to $r = +0.95$ (Table 2), which indicates a statistically strong positive correlation. This may mean that chemical properties of radium are responsible for its content in the investigated water and, therefore, independent of the mass of the isotope and its attachment to the radioactive decay series. Low negative correlation ($r = –0.30$) was observed between ^{226}Ra and its parent nuclide ^{238}U. Thus, different chemical properties of radium and uranium are the reason for their different behaviour in the environment of brine water. Although the TDS values are incomplete, it can be observed that the higher TDS of the water, the higher activity concentration of the measured radium ($r = +0.91$), Table 2. Previous investigations showed similar dependences, especially for ^{226}Ra [4] $r = +0.6$ for the Sudety Mts and $r = +0.71$ for the Outer Carpathians groundwaters, [5] $r = +0.82$, [14] $r = +0.72$, [2] $r = +0.97$. The data presented here are only preliminary indicating an important role of chemical type of studied brines and probably also the lithology of its reservoir rocks on the wide concentrations of investigated radionuclides. Obtained results indicated the necessity of further and more detailed research on this scope.

Conclusions

The main goal of this research was to contribute to the knowledge about the distribution of radioactive isotopes in brines in Poland. Studied brines represent different localities and were obtained from different geological structures from the depths of 500–1800 m.

The obtained results indicate high radium activity concentrations corresponding to high mineralization of waters (TDS). As the natural radioactivity of brines seems to be related to the brine chemical type and its total mineralization, its identification may be useful for the general prediction of radiological hazards to miners and patients. It is also necessary to carry out more detailed geochemical investigations due to lithology of the reservoir rocks of brines.

Obtained interesting results point out the necessity of undertaking wider and more complex research on the natural radionuclides present in different chemical types of brines exploited from various geological structures in Poland. It is important concerning both the practical point of view (radiation protection) and scientific one (geochemistry of U, Ra and Rn isotopes).

Acknowledgment. One of the authors (A.W.) would like to thank the Polish Ministry of Science and Higher Education for financial support (project: 1010/B/P01/2008/35, PhD grant).

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