Pilot study of ^{222}Rn and ^{226}Ra activity concentrations in groundwaters of Roztocze region, Poland

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Abstract. Authors selected 5 intakes of groundwaters outflowing from carbonate rocks in Roztocze region in Poland and measured activity concentrations of ^{222}Rn and ^{226}Ra. The average values of ^{222}Rn and ^{226}Ra activity concentrations were: 5.3 (min. 2.0, max. 8.3 Bq/dm^3) and 0.06 Bq/dm^3 (from <0.06 to 0.07 Bq/dm^3) respectively. To make a comparison authors made also investigations in groundwaters from other regions built of carbonate rocks in Poland (Sudetes, Kraków-Częstochowa Upland, Lublin Upland, Tatra Mountains). In groundwaters from these regions, ^{222}Rn activity concentration was from 2.2 to 47.8 Bq/dm^3, while mean value was 16.0 Bq/dm^3. All of ^{226}Ra activity concentration values measured in these regions were below LLD (< 0.05 Bq/dm^3). Results from Roztocze and other regions are comparable. All of investigated waters according to new polish regulations about limits of ^{222}Rn and ^{226}Ra activity concentrations could be used as drinking waters (the limits of ^{222}Rn and ^{226}Ra activity concentrations are 100 Bq/dm^3 and 0.5 Bq/dm^3 respectively).

1 Introduction

^{222}Rn and ^{226}Ra isotopes are the most important natural sources of ionizing radiation in the environment, and especially in the human environment. For this reason also in Poland extensive research is carried out on various aspects of their occurrence, and especially ^{222}Rn, in all geospheres: the lithosphere, the hydrosphere, the atmosphere, and also in residential buildings and building materials, health resorts and underground tourist objects [1–5].

^{222}Rn and ^{226}Ra isotopes play special role in the groundwater environment [6, 7]. Studies on the occurrence of ^{222}Rn and ^{226}Ra isotopes in groundwaters conducted in Poland have not only pure scientific character but they have also practical applications. These practical aspects are related to the use of the groundwater as a source of water supply for the population intended for consumption. In this respect, recently amended law is in force in Poland. They regulate the maximum permissible content of both of these isotopes in water. For ^{222}Rn isotope it is 100 Bq/dm^3, and for ^{226}Ra it is 0.5 Bq/dm^3 [8].

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Due to the geological structure of Poland and the geochemistry of ^{222}Rn and ^{226}Ra both of these isotopes are present in particularly huge concentrations in the environment of Lower Silesia [3, 9]. For this reason, until now, in the area of Lower Silesia, especially in the Sudetes, extensive research into the occurrence of ^{222}Rn and ^{226}Ra in groundwaters has been carried out [3, 9–19]. Outside this area, similar studies were conducted much less frequently and to a less comprehensive extent [18, 20–28]. For this reason, to date, we do not have knowledge about the occurrence of these radioisotopes in groundwaters of many other areas of Poland, including Roztocze region, that are often exploited and used in households, as well as for human consumption. To complete this knowledge, the authors began research on the occurrence of ^{222}Rn and ^{226}Ra isotopes in Poland's groundwaters outside Lower Silesia, including in the area of Roztocze region.

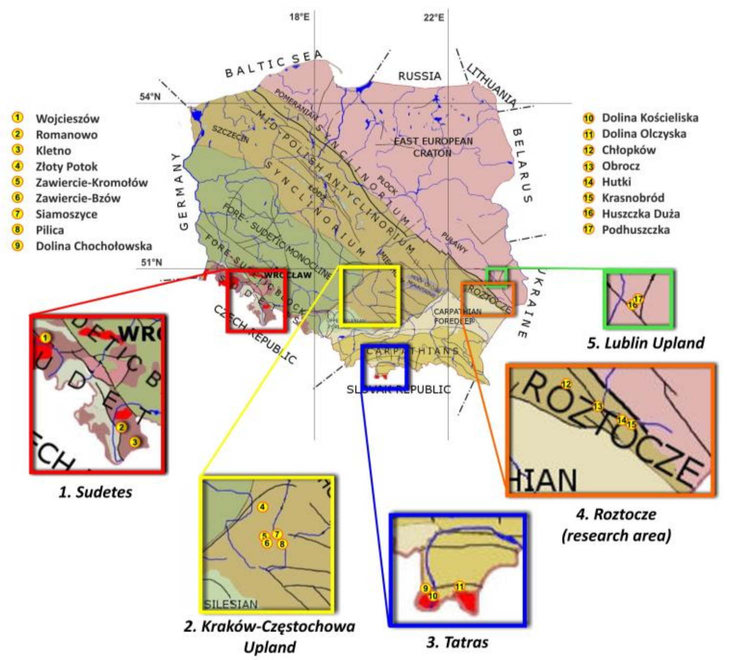

Fig. 1. Location of the authors' research areas against a simplified geological map of Poland.

2 Research area and measurement methods

Roztocze region is located in south-eastern Poland and is part of the Lublin-Lviv Upland [29]. The deep geological structure is the boundary between the Pre-Cambrian Eastern European Platform and the younger structures of Western Europe. This is the tectonic suture zone, the so-called Teisseyre-Tornquist zone. Over the older rocks there are Upper Paleozoic (Devonian and Carboniferous) sedimentary deposits filling the Lublin Basin forming on the foreland of the Variscan orogen [30, 31]. Paleozoic structures are covered by a complex of Jurassic and Cretaceous sediments, forming the Mesozoic Puławy Basin, part of the so-called marginal trough [30, 32]. The thickness of the Jurassic sediments reaches up to 300 m and the Upper Cretaceous deposits lying on them range from 300 to over 1000 m thick. These are marls, opoka, limestones, gaize, and chalkstone. On the Mesozoic sediments lie the Paleogene rocks, forming one non-separated carbonate rocks complex. These rocks are covered locally with Oligocene-Miocene sands, muds and clays of a thickness not exceeding 40 m. Quaternary gravels, sands, muds, clays and loess are also found locally on these rocks. The rocks of the Cretaceous, Paleogene and Neogene form a capacious fissure basin of groundwater. In these rocks there are mainly HCO_3-Ca type waters, sometimes also HCO_3-Ca-Mg type waters, with mineralization from 210 to 879 mg/dm^3 (hydrogeochemical background is in the range of 200−600 mg/dm^3). Groundwaters have a pH in the range of 6.5−8.15. These are good quality water that can be used as water intended for human consumption without treatment or require only a simple treatment. The Roztocze aquifer system belongs to the hydrogeological region of Lublin and Radom, which is part of the southern (Mesozoic) hydrogeological province of Poland [33].

The authors measured ^{222}Rn and ^{226}Ra activity concentrations in groundwaters by the technique of Liquid Scintillation Counting (LSC), using Ultra Low Level Liquid Scintillaton Spectrometer Quantulus 1220 α/β. This method is based on scintillation and the external photoelectric effect. Liquid scintillator, excited by energy of radioactive decay event, emits photons of light. They are visible and detectable for photomultipliers, that convert the light flashes into a measurable electrical signal. Number of registered photons is proportional to the number of radioactive decay events in the sample. Each time three samples of groundwater with a volume of 10 cm^3 were taken from a water intake and injected to a special glass vial under the layer of 10 cm^3 of liquid scintillator InstaFLUOR Plus. Multiple shaking with a sample provides transition of ^{222}Rn from the aqueous layer to organic phase of the scintillator and ensure that all radioactive decays are registered by a spectrometer. Each sample is subjected to nine 1-hour measurements, which gives 27 results of ^{222}Rn activity concentration. The same samples as for ^{222}Rn analyses are used to measure ^{226}Ra activity concentration and are subjected to the same tests. However, the measurement begins only after the time required to achieve a state of radioactive equilibrium between ^{222}Rn and ^{226}Ra. Making such number of measurements allow statistical reducing of indication uncertainty to less than 1%. The lower limit of detection (LLD) of this method is 0.05 Bq/dm^3.

Part of measurements from Sudetes were carried out using the AlphaGUARD™ equipment. It consists of four elements: the portable device AlphaGUARD™, the pump - AlphaPUMP™ and two glass vessels - AquaKIT™. The crucial measurement takes place inside the AlphaGUARD™ device. It uses a pulse-counting ionization chamber. A sample of water with volume of 100 cm^3 is injected by the use of syringe into an emanation vessel, equipped with a degassing tube and aerator. Switching on the pump, causes turbulence of the water sample and - as a result - releasing of radon dissolved in water. Then radon, through the tubing system, gets into the safety vessel for drying, and then goes to the AlphaGUARD™ device. The whole measurement lasts for 30 minutes. Measurements of ^{222}Rn activity concentration take place in one-minute intervals.

In order to measure temperature (T), electrical conductivity (EC), pH and oxidation-reduction potential (ORP) of water, portable multi-parameter device - WTW Multi 3430 - equipped with three probes was used. Probes for measuring pH and ORP are integrated. They contains built-in reference and measurement electrodes, while the measurement of the EC is carried out by a conductometric probe.

3 Results

Authors collected 11 groundwater samples from five chosen intakes in Roztocze region and measured ^{222}Rn and ^{226}Ra activity concentrations in these waters. The study was carried out since 2010. Authors sampled two intakes in Krasnobród: Kaplica na wodzie spring (2013, 2015 and 2016) and St. Roch spring (in 2016). In 2013–2016 they took groundwaters' samples from karst spring Belfont (Hutki) and from spring in Obrocz, near by the crossroad. In 2010 they took also one sample from the spring in Chłopków.

In the field, when it was possible, authors, while sampling, measured also basic water's parameters as: T, pH, ORP and EC (Table 1). Based on the correlation between conductivity and total dissolved solids (TDS) authors calculated mineralisation of the water (equation 1). All of investigated waters are fresh and ultra-fresh. According to Hem statement, the factor f is between 0.54 and 0.96, but rather narrowed to 0.55–0.75 [34]. Authors based on their own research, assumed $f = 0.75$.

$$TDS = f \cdot EC \tag{1}$$

where: TDS – total dissolved solids, [$mg \cdot dm^{-3}$], f – conversion factor, [$cm \cdot mg \cdot S^{-1} \cdot dm^{-3}$], EC – electrical conductivity, [$S \cdot cm^{-1}$].

All of investigated groundwaters are cold, neutral or low alcaline. Positive values of ORP could prove that these waters are rich in oxygen and are probably shallow circulation waters.

The values of ^{222}Rn activity concentration measured in groundwaters taken from Roztocze region are from 2.0 to 8.3 Bq/dm^3. The arithmetic mean is 5.3 Bq/dm^3, geometric mean is 4.8 Bq/dm^3, and other descriptive statistics of ^{222}Rn activity concentration, as median and standard deviation are 5.1 and 2.1 Bq/dm^3 respectively.

Table 1. ^{222}Rn and ^{226}Ra activity concentrations and basic physico-chemical parameters of groundwaters occurring in Roztocze region.

Region	**Outflow/ intake location**	**Outflow/ intake name**	**Date of sampling**	**Basic water parameters**				**Activity concentration [Bq/dm^3]**			
				pH	ORP	T	EC				
				[–]	[mV]	[°C]	[µS/cm]	^{222}Rn	Uncertainty	^{226}Ra	Uncertainty
Roztocze	**Krasnobród**	Kaplica na wodzie spring	06.10.2013	n.d.	n.d.	n.d.	n.d.	4.4	0.2	<0.06	LLD
			22.08.2015	8.1	177	12.6	550	2.3	0.2	<0.06	LLD
			21.04.2016	7.7	141.5	8.8	442	4.5	0.2	<0.06	LLD
			mean					3.7			
		St. Roch spring	21.04.2016	6.9	221.9	7.3	121	2.0	0.1	<0.06	LLD
	Hutki	Karst spring Belfont	06.10.2013	n.d.	n.d.	n.d.	n.d.	5.2	0.2	0.07	0.06
			22.08.2015	7.9	229.1	9	483	4.4	0.4	0.06	0.01
			21.04.2016	7.3	224.7	8.8	481	5.1	0.2	<0.06	LLD
			mean					4.9			
	Obrocz	Spring near by crossroad	08.09.2013	8.1	148.1	8.9	428	7.2	0.3	0.06	0.06
			24.08.2015	7.9	79.8	8.8	436	7.4	0.5	<0.06	LLD
			21.04.2016	7.4	202.6	8.7	437	7.2	0.2	<0.06	LLD
			mean					7.3			
	Chłop-ków	Spring	17.08.2010	n.d.	n.d.	n.d.	n.d.	8.3	0.5	<0.06	LLD

n.d. – no data; LLD – lower limit of detection

According to Przylibski's classification [3] all of investigated groundwaters are radon-poor waters (Fig. 2a).

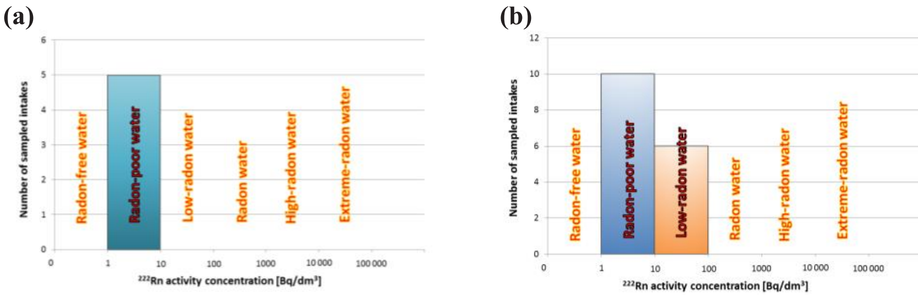

Fig. 2. Histograms of ^{222}Rn activity concentration in groundwaters of **(a)** Roztocze region and **(b)** regions built of carbonate rocks with the exception of Roztocze region.

In most of the samples taken from Roztocze region ^{226}Ra activity concentration was less than 0.06 Bq/dm^3. In cases that the value was above LLD, authors registered 0.06 Bq/dm^3 (spring nearby crossroad in Obrocz and karst spring Belfont in Hutki) or 0.07 Bq/dm^3 (karst spring Belfont, Hutki) (Table 1).

At the same time, from 2003, authors conducted research in other karst regions in Poland: Lublin Upland, Kraków-Częstochowa Upland, Tatras and Sudetes [11, 35]. Average values of activity concentrations of ^{222}Rn and ^{226}Ra in groundwaters outflowing from carbonate rocks from Roztocze and from other regions are presented in Table 2.

Table 2. Average values of ^{222}Rn and ^{226}Ra activity concentrations in all investigated groundwaters (authors' own unpublished data and [11, 35]).

Region	Location	Outflow/ intake name	Time of sampling	Number of measure-ments	Average value of activity concentration [Bq/dm^3]	
					^{222}Rn	^{226}Ra
Roztocze	Krasnobród	Kaplica na wodzie spring	06.10.2013–21.04.2016	3	3.7	< 0.06
		St. Roch spring	21.04.2016	1	2.0	< 0.06
	Hutki	Karst spring Belfont	06.10.2013–21.04.2016.	3	4.9	0.07
	Obrocz	spring nearby crossroad	08.09.2013–21.04.2016	3	7.3	0.06
	Chłopków	spring	17.08.2010	1	8.3	< 0.06
Lublin Upland	Huszczka Duża	spring	17.08.2010	1	9.8	<0.06
	Podhuszczka	Karst spring	17.08.2010	1	5.0	< 0.06
Kraków-Częstochowa Upland	Złoty Potok	Zygmunt spring	27.05.2012	1	5.2	n.d.
		Spełnione Marzenia spring	27.05.2012	1	5.9	n.d.
	Zawiercie-Kromołów	Warta spring	27.05.2012	1	6.4	n.d.
	Zawiercie-Bzów	Czarna Przemsza spring	27.05.2012	1	28.7	n.d.
	Pilica	Pilica spring	27.05.2012	1	2.2	n.d.
	Siamoszyce	Krztynia spring	27.05.2012	1	3.8	n.d.

Sudetes	Western Sudetes	Wojcieszów	Miłek spring	13.09.2003–03.07.2012	4	28.3	< 0.05
			Zamek spring	13.09.2003	1	33.6	< 0.05
	Eastern Sudetes	Romanowo	Romanowskie spring, outflow no. 1	29.09.2002–03.07.2012	4	25.6	< 0.05
		Kletno	Karst spring Kletno I	02.07.2003–02.06.2004	2	8.5	< 0.05
			Marianna spring	02.06.2004–15.05.2012	2	4.1	< 0.05
Tatras		Kościeliska valley	Lodowe spring	27.08.2012	1	2.6	n.d.
		Chochołowska valley	Karst spring Chochołowskie	27.08.2012	1	25.5	n.d.
		Olczyska valley	Karst spring Olczyskie	27.08.2012	1	13.8	n.d.

n.d. – no data

Groundwaters occurring in regions analysed to compare with Roztocze are radon poor-waters and low-radon waters (Fig. 2b).

The biggest values of ^{222}Rn activity concentrations were registered in groundwater in Miłek spring, Zamek spring, both located in Wojcieszów (Sudetes) and Czarna Przemsza spring in Zawiercie-Bzów (Kraków-Częstochowa Upland). The values of ^{222}Rn activity concentration measured in 24 groundwaters' samples taken from regions built of carbonate rocks (with the exception of Roztocze) are from 2.2 to 47.8 Bq/dm^3. The arithmetic mean is 16.0 Bq/dm^3, geometric mean is 11.0 Bq/dm^3, and other descriptive statistics of ^{222}Rn, as median and standard deviation are respectively 9.9 and 13.2 Bq/dm^3. ^{226}Ra activity concentration in all of investigated waters from these regions was below 0.05 Bq/dm^3.

All registered values of ^{222}Rn activity concentration are typical for groundwaters occurring in karst regions, outflowing from carbonate rocks in Poland.

4 Conclusions

Groundwaters taken from Roztocze region are poor-radon waters. In other regions built of carbonate rocks most of groundwaters are also poor-radon and in some cases low-radon waters. Average values of ^{222}Rn and ^{226}Ra activity concentrations in Roztocze region are: 5.3 and 0.06 Bq/dm^3, respectively. Maximum activity concentrations' values are 8.3 and 0.07 Bq/dm^3 for ^{222}Rn and ^{226}Ra, respectively, minimum: 2.0 and 0.06 Bq/dm^3 for ^{222}Rn and ^{226}Ra respectively. In groundwaters taken from regions built of carbonate rocks excluding Roztocze average value of ^{222}Rn activity concentration is 16.0 Bq/dm^3, minimum value is 2.2, Bq/dm^3 and maximum is 47.8 Bq/dm^3. ^{226}Ra activity concentration was below LLD.

All results from Roztocze and other regions built of carbonate rocks in Poland are similar and comparable. Authors are going to continue this study expanding research area to another regions of similar geology in Poland (e.g. Pieniny Mountains).

Levels of ^{222}Rn and ^{226}Ra activity concentrations measured in all investigated groundwaters are even 10 times less than the limits set by polish law regulations which are 100 Bq/dm^3 and 0,5 Bq/dm^3 for ^{222}Rn and ^{226}Ra respectively. It means that except of sanitary or other reasons all of tested groundwaters could be intended for human consumption.

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