

# Natural radioactive nuclides in the thermal waters of the Polish Inner Carpathians

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**Abstract:** The chemical compositions and activity concentrations of <sup>238</sup>U, <sup>234</sup>U, <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>222</sup>Rn were measured in the thermal waters occurring in the Podhale Trough. This region, part of the Polish Inner Carpathians, is the artesian basin situated between two groundwater recharging zones, the Tatras to the south and the Pieniny Klippen Belt to the north. The thermal water samples were collected from nine selected boreholes with the depths from 1113 m (Zakopane IG-2) to 5526 m (Bańska Niżna IG-1). The waters belong to four hydrochemical types: HCO<sub>3</sub>-SO<sub>4</sub>-Ca-Mg-Na, SO<sub>4</sub>-HCO<sub>3</sub>-Cl-Na-Ca, SO<sub>4</sub>-Ca-Na and SO<sub>4</sub>-Cl-Ca-Na. Their mineralization and temperature range from several hundreds to 2500 mg/l and 23.9 to 86.3 °C, respectively. Excluding the waters from the Szymoszkowa GT-1 and Chochołów PIG-1 boreholes, the activity concentrations of the uranium and radium isotopes in the waters are relatively low and vary from decimals to above ten mBq/l and from several tens to about 600 mBq/l, respectively. They are classified as radon-poor waters. The phenomena mentioned seem to be characteristic of the waters draining limestone formations overlaying the crystalline rocks, namely the principal aquifers in the Tatras. The significant levels of the uranium and radium activity concentrations in the waters from Szymoszkowa GT-1 and Chochołów PIG-1 can be connected with the presences of Lower Triassic black shales with tuffites rich in uranium in the respective recharge areas. Comparing the parameters of the Podhale thermal waters with those of some selected thermal waters occurring in other regions of Poland and in north-west Croatia, the French Massif Central, Spanish Andalusia and north-east Tunisia, the authors found that the temperature of the thermal waters is contained between 16 and about 100 °C; the mineralization and concentrations of radionuclides vary in broad intervals and are considerably affected by the lithology and the geological structure of the region. The <sup>226</sup>Ra activity concentration exceeds that of <sup>228</sup>Ra in almost each of the thermal waters compared, which is similar to the waters from Podhale.

**Key words:** Inner Carpathians, Poland, thermal water, mineralization, natural radioactivity.

## Introduction

Thermal water is defined when the temperature of groundwater at its outflow is higher than the annual average temperature of the air in the region. In Poland groundwater is regarded as thermal if its temperature exceeds 20 °C. Thermal waters were initially used in medicine, then for heating purposes, and nowadays thermal water is also utilized in power plants (Kępińska 2006) and even as drinking water (Marović et al. 1995; Baradács et al. 2001; Gallup 2007). In some countries investigations of the natural radioactive elements in the thermal waters have been carried out in recent years (e.g. Marović et al. 1995; Szerbin 1996). In Poland there were some investigations dealing with the problem of radionuclides in waters, but concerned mainly with mineral waters (Kozłowska 2009; Chau et al. 2010; Grabowski et al. 2010). The contribution of the <sup>226</sup>Ra and <sup>228</sup>Ra isotopes to the total activities of the alpha and beta nuclides in groundwaters is often significantly large in comparison with that of other radioactive elements and concentrations of radium isotopes increase with the aquifer depths (Asikainen & Kahlos 1979; Chau et al. 2011).

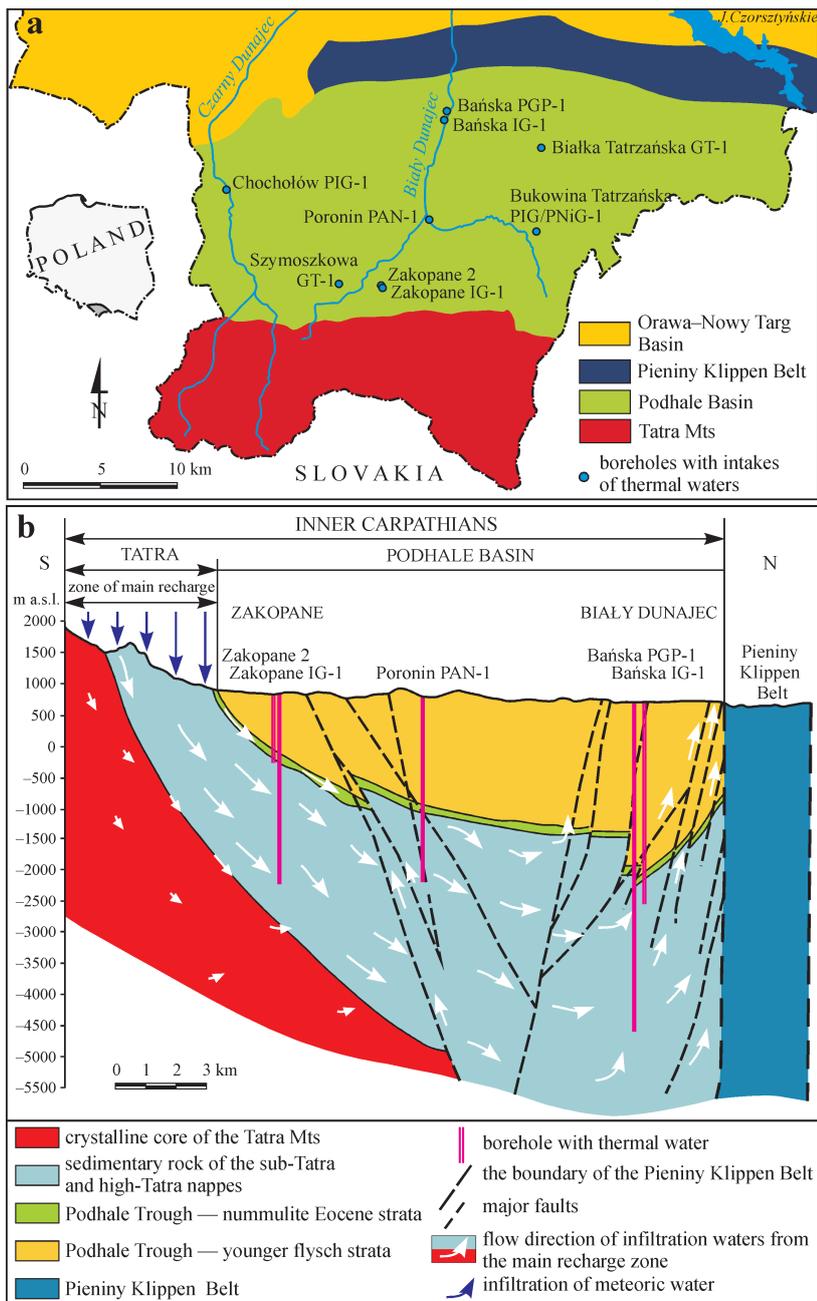
A high temperature of thermal waters is mainly associated with substantial depths of their aquifers and/or is characteristic

of volcanic regions. Some scientists observed that volcanic activity and also earthquakes affect another parameter, namely the radon concentrations of such waters (Belin et al. 2002; Erees et al. 2007; Whitehead et al. 2007; Chaudhuri et al. 2010).

The aims of this work included determinations of the radioactivity (activity concentrations of <sup>222</sup>Rn and radium and uranium isotopes: <sup>228</sup>Ra, <sup>226</sup>Ra, <sup>238</sup>U, <sup>234</sup>U) and chemical composition of thermal waters occurring in the Podhale Trough of the Polish Inner Carpathians. The radioactive data were interpreted regarding the temperature and mineralization of the waters as well as the geological conditions of their aquifers. The data on the Podhale waters were compared with those of the thermal waters occurring in selected regions of Poland and in north-west Croatia, the French Massif Central, Spanish Andalusia and north-east Tunisia.

## Study region

The Podhale Trough is located between the Tatra Mts to the south and the Pieniny Klippen Belt to the north (Fig. 1a). Structurally, the Tatras are composed of the crystalline core, made up of a Carboniferous granitoid intrusion and its meta-



**Fig. 1.** Location of the water sampling points in the Podhale Trough (a) and a geological cross-section of the region (after Chowaniec 2003, modified) (b).

morphic envelope. The crystalline rocks are overlain, but only from the N, by the Permian-Cretaceous sedimentary cover developed structurally as two sub-Tatra and high-Tatra nappes (Książkiewicz 1972).

The Podhale Trough is a broad syncline filled with the Eocene-Oligocene flysch series (Podhale flysch) about 3000 m thick that overlay from the N Tatra nappe structures composed mainly of the Mesozoic carbonate rock sequences. The oldest member of the Trough, directly laying on the Tatra nappe rocks, is represented by the sediments of the so-called nummulite Eocene: a complex of conglomerates, coarse-grained sandstones, detrital limestones, dolomites and num-

mulite limestones. The next in the profile are the Oligocene Szaflary Beds, developed as sandstones, conglomerates, mudstones and shales, followed by the Oligocene Zakopane Beds, represented by shales, conglomerates, sandstones and ferruginous dolomites. The sandstone-mudstone Chochołów Beds make up the upper part of the profile and are overlain in the western part of the Podhale Trough by the thick-bedded sandstones with insets of shales belonging to the Ostrysz Beds (Książkiewicz 1972). Conglomeratic-sandy covers and colluvia are Quaternary deposits.

The massif of the Tatra Mts has most effect on the hydrogeological conditions of the Podhale Trough, which is a classical artesian basin. The origin of the thermal waters is associated mainly with meteoric waters that recharge fractured and karstified Mesozoic and Eocene limestones of the Tatra cover laying on the crystalline core (Fig. 1b). These sediments dip to the north under impermeable and weakly permeable strata of the Podhale flysch. The Pieniny Klippen Belt, which forms the northern closure of the Podhale Trough (Małecka 1981) makes an impermeable barrier for the waters flowing from S. The thermal waters of the Podhale Trough migrate through the rocks of low permeability but a high level of fracturing particularly in fault zones.

**Measurement methods**

*Radionuclides and chemical composition*

To determine the uranium isotopes, the water samples of 5 l were reduced by evaporation to about 1 l and uranium was co-precipitated with MnO<sub>2</sub> in a form of uranyl ammonium [(NH<sub>4</sub>)<sub>2</sub>U<sub>2</sub>O<sub>7</sub>]. The tracer <sup>232</sup>U standard solution of about 100 mBq activity was added to each water sample at the beginning of the evaporation. Then uranium ions were separated out from other

ions in the precipitate using the procedure described in detail by Kronfeld (1974) and modified by Skwarzec (1997). The final precipitate was placed onto a plastic membrane filter with porosity of 0.1 μm. The activity of uranium isotopes was measured using an alpha spectrometer Canberra™ model 7401. The measurement time lasted until a relative standard uncertainty of the net count rates under the <sup>232</sup>U peak lower than 2 % was obtaining.

Radium isotopes were determined in 2-liter water samples. Radium ions were co-precipitated with barium as a sulphate compound and separated from other isotopes in the precipitate following the procedure described in detail by Tomza

(1975). Next the sample was transferred into a 22 ml glass vial and mixed with 12 ml of the Packard™ gel scintillation cocktail. The radium isotopes activity was measured using a Wallac™ Gardian Liquid Scintillation counter.

Determinations of the  $^{222}\text{Rn}$  activity concentration were made on water samples collected “under the cap” at the laminar water flow (these condition assure that the radon would not escape from the sample) into glass bottles with the volume 0.5 l. The samples were transported to the laboratory as fast as possible. To make a correction for fast radon decay ( $T_{1/2}=3.82$  days), the sample collection times were noted and a time-radon amount correcting factor was introduced. The radon activity was measured in a mixture of 10 ml of the collected water sample with 10 ml of a PerkinElmer™ mineral oil liquid scintillator placed in the glass vial using a Wallac™ Gardian Liquid Scintillation counter.

The chemical composition was determined using a PerkinElmer™ ICP-AES spectrometer with the Merck™ multi-element standards.

The temperature and acidity (pH) of the water were measured directly at the borehole using a WTW™ pH 340/ION device calibrated with the standard Hamilton Duracal™ solution.

#### Detection limits of the methods

The low limit detection (LLD) of a given method was estimated according to the formula described by Currie (1968):

$$LLD = k \cdot \sigma_b$$

where  $k$  — arbitral coefficient equal to 2.75,  $\sigma_b$  — uncertainty of the blank sample measurement. The  $\sigma_b$  value is mainly

controlled by the chemical compounds used in preparation as well as instrumental and measurement conditions. Blank samples were prepared using distilled water. The detection thresholds are: for the uranium isotopes 0.5 mBq, for  $^{222}\text{Rn}$  0.5 Bq and for  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  5 mBq and 10 mBq, respectively (Chau 2010).

The detection threshold of the ICP-AES method depends on the element assayed for and varies from a few to several hundred ppb.

## Results and discussion

### Thermal waters in the Inner Carpathians

The results obtained are presented in Tables 1 and 2. The temperature and mineralization of the waters vary from 26.6 to 86.3 °C and 330 to 2500 mg/l, respectively, and clearly relate both to the depth of the aquifers and the distance between the water wells and the Tatra Mts (Fig. 2a-d). The linear dependence of the water temperature on the depth aquifer reveals that the waters are heated up by geothermal degree.

The activity concentrations of  $^{234}\text{U}$  and  $^{238}\text{U}$  excluding the water from Szymoszkowa GT-1 vary from 1.1 to several tens mBq/l. The uranium concentration neither depends on the water temperature nor on the aquifer formation depth (Fig. 3a,b). In each water the activity concentration of  $^{234}\text{U}$  exceeds that of  $^{238}\text{U}$ , the phenomenon being the consequence of the recoil effect (Osmond 1980).

The activity concentrations of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  range from 29 to over 2200 mBq/l and 25 to 359 mBq/l, respectively

**Table 1:** The physical and chemical properties of the thermal waters of the Podhale Trough.

Borehole	Borehole depth [m]	Temp. [°C]	pH	TDS <sup>1</sup> [mg/l]	Concentrations of major ions [mg/l]						
					SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Bukowina Tatrzańska PIG/PNiG-1	3780	64	7.0	1510	763	159	113	160	17.7	184	15.5
Biała Tatrzańska GT-1	2500	75	6.8	1980	671	252	379	314	33.9	183	42.8
Bańska Niżna PGP-1	3242	86.3	8.2	2500	818	334	492	470	41	188	40.0
Bańska Niżna IG-1	5526	80	6.5	2330	756	285	482	432	42.6	183	34.9
Zakopane IG-2	1113	23.9	7.5	349	16	239	8.60	2.27	1.13	46.0	22.4
Zakopane IG-1	3073	34.2	7.4	368	39.1	220	3.60	10.1	3.32	45.4	20.5
Szymoszkowa GT-1	1737	26.6	7.7	333	4.5	241	3.60	5.35	1.60	40.0	22.8
Poronin PAN-1	3003	63	7.5	1140	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Chochołów PIG-1	3572	82	n/a	1260	607	194	27.2	87.7	18.5	191.9	40.8

<sup>1</sup>TDS — total dissolved solids (mineralization); n/a — not analysed

**Table 2:** The activity concentrations of radon-222, radium and uranium isotopes in the thermal waters of the Podhale Trough.

Borehole	$^{222}\text{Rn}$ [Bq/l]	Radium isotopes [mBq/l]			Uranium isotopes [mBq/l]		
		$^{226}\text{Ra}$	$^{228}\text{Ra}$	$^{226}\text{Ra}/^{228}\text{Ra}$	$^{234}\text{U}$	$^{238}\text{U}$	$^{234}\text{U}/^{238}\text{U}$
Bukowina Tatrzańska PIG/PNiG-1	2.9	595	359	1.66	13	1.1	11.8
Biała Tatrzańska GT-1	n/a <sup>1</sup>	342	106	3.22	5.3	3.4	1.58
Bańska Niżna PGP-1	0.2	589	79	7.45	5.9	3.1	1.90
Bańska Niżna IG-1	8	570	171	3.33	4.8	3.7	1.30
Zakopane IG-2	18.7	294	32	9.20	7.6	2.9	2.62
Zakopane IG-1	0.2	29	25	1.16	4.7	2.5	1.88
Szymoszkowa GT-1	25.4	309	34	9.08	313	328	0.95
Poronin PAN-1	n/a	254	25	10.2	58.5	41	1.43
Chochołów PIG-1	n/a	2250	25	90	5.9	2.7	2.19

<sup>1</sup>n/a — not analysed

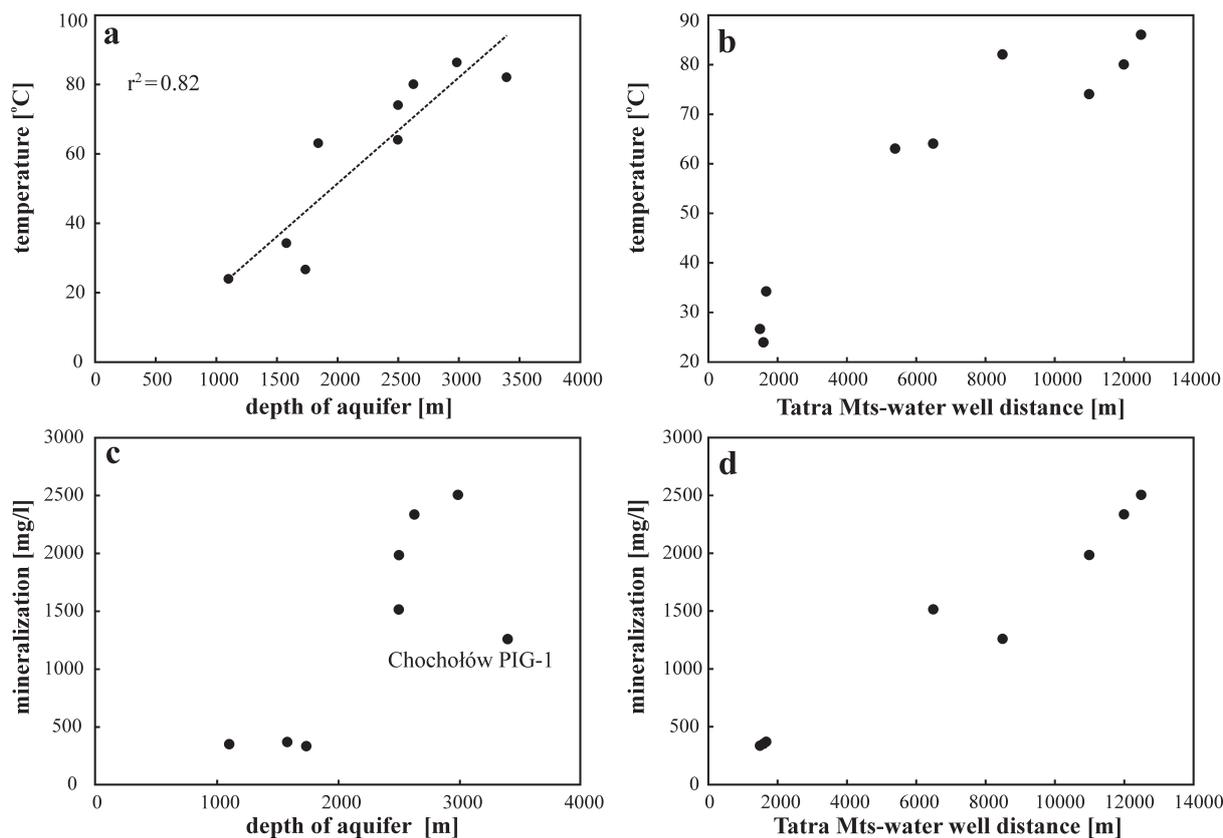


Fig. 2. Temperature and mineralization of the analysed thermal waters versus aquifer depth (a, b) and the Tatra Mts-water well distances (c, d).

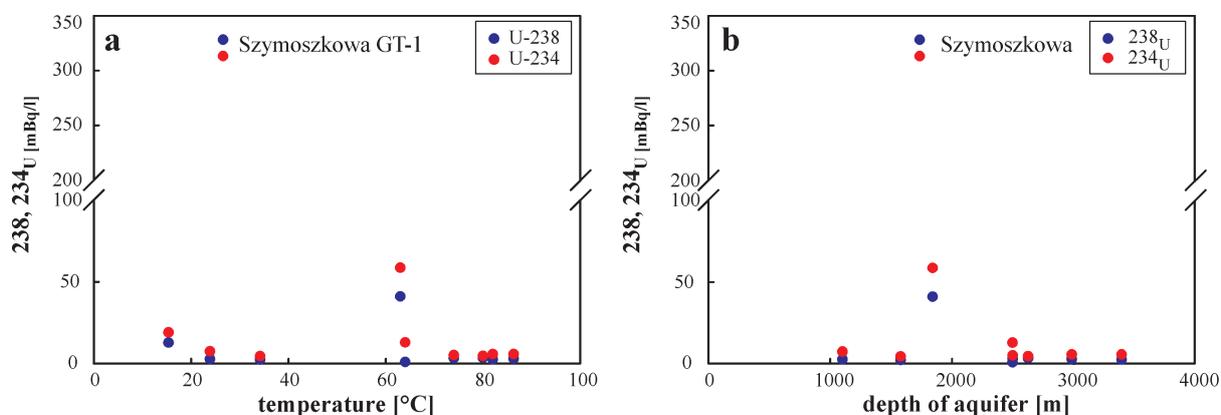


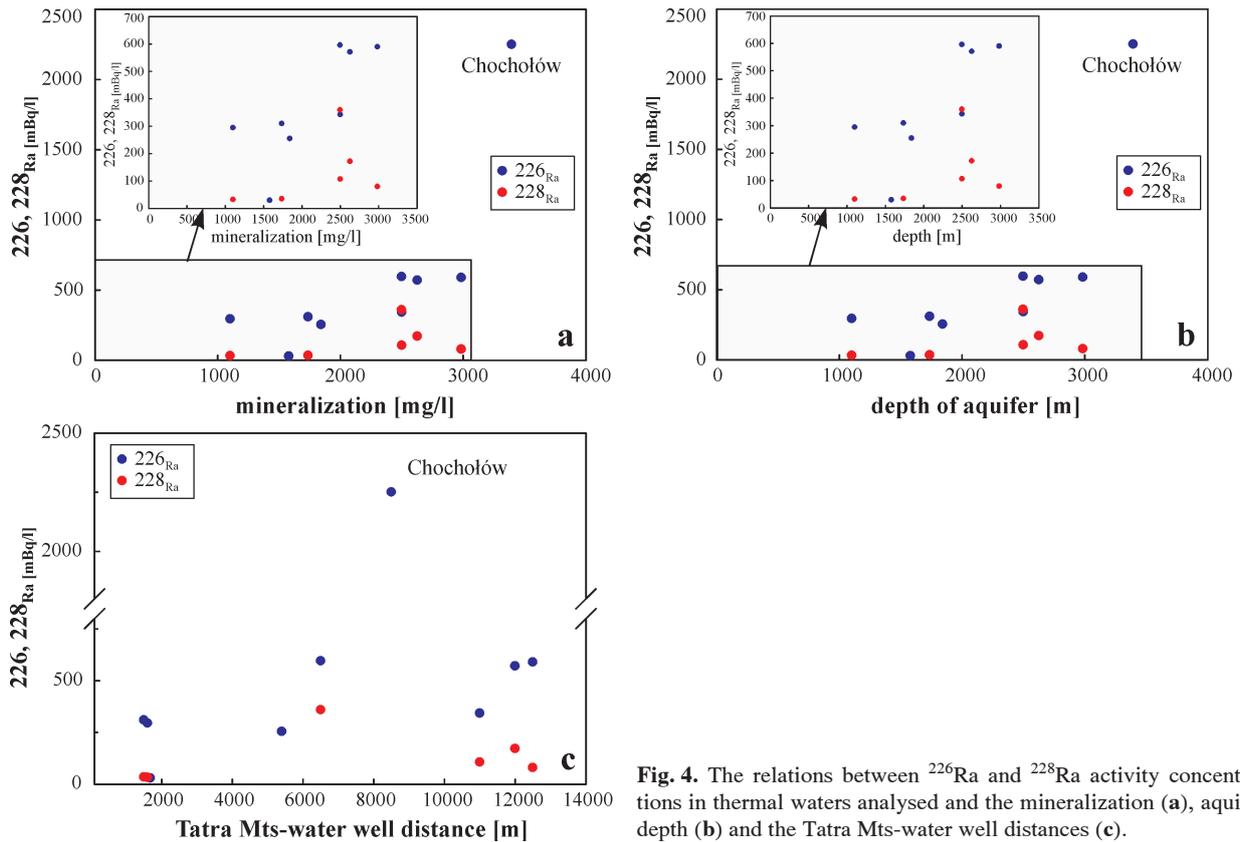
Fig. 3. The relations between the activity concentration of uranium isotopes and temperature (a) and depth of the aquifer formation (b).

(Table 2), and in each thermal water the activity concentration of  $^{226}\text{Ra}$  exceeds, usually considerably, that of  $^{228}\text{Ra}$ . The data reported by Lućivjanski (1999) and Chau et al. (2012), show that in the Carpathian waters we can observe that if the mineralizations of the thermal and mineral waters are comparable, the radium isotope concentrations in thermal waters are often significantly higher than those in mineral ones. On the other hand, the uranium activity concentrations are in the same range in both types of waters and vary from decimals mBq/l to several tens mBq/l. Radium belongs to the group of the alkaline earth elements and its geochemical properties are similar to those of calcium and magnesium,

whose ions are major components of water. Therefore, the radium activity concentration should increase with water mineralization and with the depths of the water-bearing formations as well as with the distance between the water wells and the Tatra Mts (Fig. 4a-c).

The  $^{222}\text{Rn}$  concentrations in the waters studied are low and vary from tenths Bq/l to 30 Bq/l. Such low levels are characteristic of the limestone aquifer and, additionally, of high temperatures of the water.

Generally, the Podhale Trough is composed of flysch formations (sandstones and shales, minor conglomerates). The uranium and thorium contents of these rocks range from a



**Fig. 4.** The relations between  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity concentrations in thermal waters analysed and the mineralization (a), aquifer depth (b) and the Tatra Mts-water well distances (c).

few to ca. 30 Bq/kg (Plewa & Plewa 1992), but the concentrations of natural radionuclides in the water samples from Szymbark GT-1 and Chochółów PIG-1 are elevated in comparison to those in the waters from other sampling sites. Such relations must be connected with the lithology and geological structure of the Tatras and, particularly with a presence of rocks of significant uranium concentrations drained by the two waters. It is worth adding that in the Dolina Białego Valley of the Tatras the exploitation work for uranium was carried out in Lower Triassic black shales with tuffites in the 1950s. Considering only minor amounts of this element, its exploitation stopped, but is witnessed by two adits ca. 500 m long (Grodzicki 1993; Szczepanek 2003; Bac-Moszaszwili & Jurewicz 2010). The radon concentrations and gamma ray dose rates measured in these adits are significantly high and range from 600 to 15,000  $\text{Bq/m}^3$  and from 40 to above 5500  $\text{nSv/h}$ , respectively (Kozak et al. 2010).

### Comparisons

In order to understand better the factors controlling the level of the radioactive nuclides, dissolved materials and temperature of the thermal waters concerned, the authors attempted to compare the data obtained with those already published.

#### *Some examples from Poland*

In Poland apart from the Inner Carpathians, thermal waters also occur in some regions such as the Outer Carpathians, the Sudetes and central Poland.

The Outer Carpathians localized north of the Inner Carpathians are composed principally of the thick Cretaceous-Miocene flysch formations folded in different forms. On the basis of the sediment type and the shape of folds, the Outer Carpathians are divided into different units. In contrast to the Inner Carpathians, the Outer Carpathians are very rich in mineral waters, whereas thermal waters can be found in only a few places such as Lubatówka and Ustroń. Both sites belong to the Silesian Unit, Lubatówka being situated in its eastern part, and Ustroń in the western part. The groundwaters occurring in the Eastern Outer Carpathians often belong to the  $\text{Cl-HCO}_3\text{-Na}$  hydrochemical type and their mineralization ranges from a few to 20 grams/l. Oil and gas deposits also occur in this region. The waters in the Outer Western Carpathians often belong to the  $\text{Cl-Na-Ca}$  type, their mineralization is considerably higher than that of the Outer Eastern Carpathians and reaches even above 100 g/l (Ciężkowski et al. 2010).

The Sudetes are composed mainly of a complex mosaic of essentially igneous and metamorphic rock types and, as a result, water migrates horizontally and vertically through fractures connecting very different rock formations. The mineralization of the groundwater of the region is generally low and ranges from a few tenths to a few g/l (Ciężkowski et al. 2010).

The central part of Poland belongs to the so-called hydrological province of the Paleozoic Platform. The sandstone formations are major aquifers in the province and the  $\text{Cl-Na}$  is the common hydrochemical type of the groundwaters in the region (Paczyński & Płochniewski 1996).

The measured physical parameters, chemical composition as well as activity concentrations of some selected thermal

**Table 3:** The physical and chemical properties of some selected thermal waters of Poland (Przylibski et al. 2012).

Borehole	Geological unit	Borehole depth [m]	Temp [°C]	pH	TDS [mg/l]	Concentrations of major ions [mg/l]						
						SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Lubatówka 12	Outer Carpathians	960	24	7.1	17700	0.5	4270	7090	5910	37.3	51.6	57.2
Ustroń U-3		1728	23	6.9	101000	370	79	62400	26400	579	8290	2530
Ustroń U-3A		17310	21	6.7	117000	426	101	71700	30800	727	9410	2660
Lądek Zdrój L-2	Sudetes (Lower Silesia)	700	43.6	9.2	201	21.6	24	5.6	49	0.78	3.05	0.01
Duszniki Zdrój GT-1		1695	28.3	6.8	3430	72.2	2330	8.92	301	182	297	95.1
Cieplice C-1		2002	65.3	7.8	663	153	146	42.5	153	5.1	7.8	0.02
Uniejów PIG/AGH-2	central region of Poland	2025	63.9	7.0	6770	98.0	296	3770	2350	28.9	141	27.7
Poddebice GT-1		2039	49.0	7.3	461	14.3	262	21.6	78.8	4.50	23.9	4.22
Mszczonów IG-1		1793	41.8	7.3	292	3.37	320	7.59	30.7	11.1	53.1	11.7

TDS — Total dissolved solids

**Table 4:** The activity concentrations of radon-222, radium and uranium isotopes of some selected thermal waters of Poland (Przylibski et al. 2012).

Borehole	<sup>222</sup> Rn [Bq/l]	Radium isotopes [mBq/l]			Uranium isotopes [mBq/l]		
		<sup>226</sup> Ra	<sup>228</sup> Ra	<sup>226</sup> Ra/ <sup>228</sup> Ra	<sup>234</sup> U	<sup>238</sup> U	<sup>234</sup> U/ <sup>238</sup> U
Lubatówka 12	2.9	1420	1390	1.02	7.7	2.7	2.85
Ustroń U-3	33	57700	13100	4.41	7.7	22.1	0.35
Ustroń U-3A	36	65000	13700	4.74	9.6	4.8	2.09
Lądek Zdrój L-2	145	23	23	1.00	0.62	0.91	0.68
Duszniki Zdrój GT-1	3.4	3270	910	3.59	32.3	14.5	2.23
Cieplice C-1	8.1	19	≤ 10	n/e <sup>1</sup>	≤ 0.5	≤ 0.5	n/e
Uniejów PIG/AGH-2	2.1	532	609	0.87	0.95	≤ 0.5	n/e
Poddebice GT-1	5.1	41	60	0.68	≤ 0.5	≤ 0.5	n/e
Mszczonów IG-1	3.1	42	50	0.84	≤ 0.5	1.49	0.34

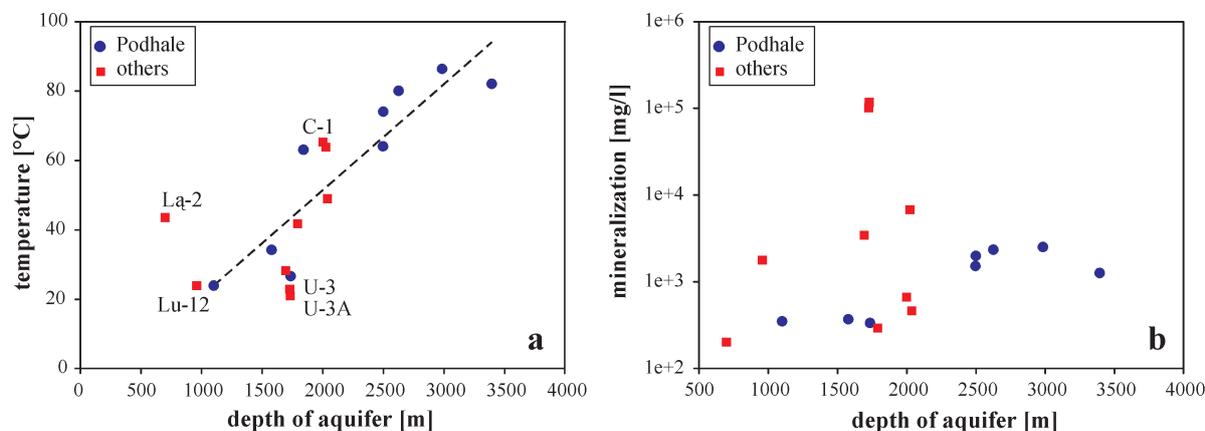
<sup>1</sup> not estimated

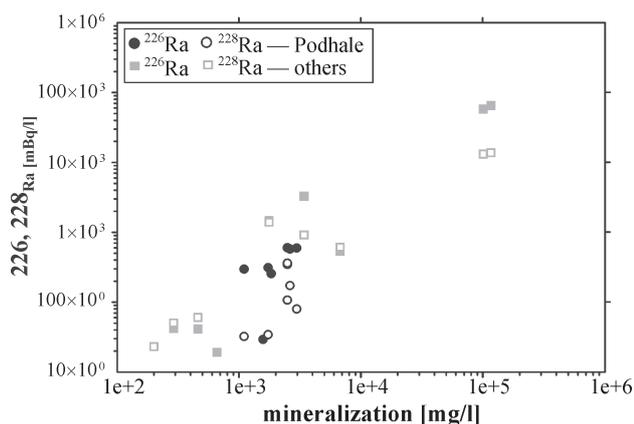
waters occurring in the mentioned regions are summarized in Tables 3 and 4. The temperatures of the waters from other regions of Poland are contained within the same interval of those of the waters of Podhale (Table 3). The mineralization values of the waters from the Sudetes are similar, but those from central Poland and, particularly, from the Outer Carpathians (Lubatówka and Ustroń) are considerably higher in comparison with those obtained for the waters from the Podhale Trough. Generally, the uranium activity concentrations of the Polish waters compared are low and contained within the same range, however the activity concentrations of radium isotopes vary considerably in a wide interval (from ca.

20 to 65,000 mBq/l). The radon activity concentration in the water from Lądek (the Sudetes) is the highest and amounts to 145 Bq/l. Such high values must be connected with emanations of radon from uranium-rich granites into the water.

The relations between the temperature, mineralization and the aquifer depth for all the Polish thermal waters are shown in Figure 5a and 5b. Except for the water of Lądek (L-2), the water temperature increases with the depth of aquifer (Fig. 5a), which can be explained by the geothermal gradient (Fig. 5a), which can be explained by the geothermal gradient. Though the depth of the aquifer in Lądek Zdrój (the Sudetes) is shallow in comparison with other aquifers (700 m), the water temperature is relatively high (43 °C). This could result from ascension of waters from deeper formations migrating through rock fissures (Ciężkowski et al. 2011). The relation between the water mineralization and the aquifer depth seems to be complicated and depends on the geology of the individual region (Fig. 5b).

The activity concentrations of radium isotopes increase with the mineralization for all Polish thermal waters in question (Fig. 6). It is worth adding that the activity concentration of <sup>226</sup>Ra is lower than that of the <sup>228</sup>Ra for the waters from the central region of Poland. This is probably related to the <sup>232</sup>Th activity concentration exceeding that of the <sup>238</sup>U in the sandstone formation, which is the main aquifer in the central region of Poland.

**Fig. 5.** The relations between the temperature (a) and mineralization (b) of some Polish thermal waters and the depths of the aquifer formations.



**Fig. 6.** The relations between activity concentrations of radium isotopes and mineralization of some Polish thermal waters.

*Some examples from outside Poland*

On the basis of the data concerning the temperature, mineralization and uranium and radium activity concentrations of some selected thermal waters from north-west Croatia (Marović et al. 1996), the French Massif Central (Rihs & Condomines 2002), Spanish Andalusia (Dueñas et al. 1998) and from north-east Tunisia (Labidi et al. 2002), the values of statistical parameters were estimated and summarized (Table 5). The following remarks have arisen from the analy-

sis of these data. (1) The temperature of the thermal waters compared ranges from 15 to near 100 °C. (2) The mineralization and radium isotopes concentrations vary in broad intervals. (3) The median values of mineralization and the activity concentrations of radium and uranium isotopes are much lower than average, so we can state that for every region the number of the waters with low mineralization and low radioactivity level is far larger than that of the waters with high mineralization and high radioactivity level. (4) Generally, the activity concentrations of uranium isotopes are far lower than those of radium isotopes. (5) In most of the thermal waters compared, the activity concentration of <sup>228</sup>Ra is lower than that of <sup>226</sup>Ra. This must be connected with radioactive characteristics of most aquifers, in which the <sup>238</sup>U concentrations are higher than those of <sup>232</sup>Th.

**Conclusions**

For several years the Podhale thermal waters have been well known and used in heating and for therapeutic purposes, but their radioactive properties have been investigated for a relatively short time.

The temperature of the waters of the Podhale Trough ranges from 26 to about 100 °C and increases with the depth of the host rock formations.

The mineralization of the Podhale Trough thermal waters is relatively low, and varies from 330 to 2550 mg/l. The con-

**Table 5:** Statistical values of TDS (total dissolved solids), temperature, <sup>238</sup>U, <sup>226</sup>Ra and <sup>228</sup>Ra activity concentrations of some selected thermal waters occurring outside Poland (Marović et al. 1996; Dueñas et al. 1998; Rihs & Condomines 2002; Labidi et al. 2002).

Region	No. of samples	Statistic paramet.	Temperature [°C]	TDS [mg/l]	<sup>238</sup> U [mBq/l]	<sup>234</sup> U [mBq/l]	<sup>226</sup> Ra [mBq/l]	<sup>228</sup> Ra [mBq/l]
Croatia [Marović et al. 1996]	12	min	22				87	
		max	96				6200	
		average	46				1322	
		median	40				283.5	
		stand. dev.	23.3				895.8	
France [Rihs & Condomines 2002]	6	min	16	3608	5		588	260
		max	41	5608	27		2287	1590
		average	30	4137	15		1158	854
		median	24	4137	16		947	794
		stand. dev.	9.4	746.2	8.4		627.8	452.5
Poland	18	min	22	201	≤0.5	≤0.5	19	23
		max	86	117000	328	313	65000	13700
		average	47.9	14405	29	32	7404	1806
		median	34	1385	3.1	7.6	437	79
		stand. dev.	27	34766	83.4	79.2	19684	4382
Spain [Dueñas et al. 1989]	19	min	15	289			15	
		max	52	14790			1367	
		average	28	3702			263	
		median	21	2070			157	
		stand. dev.	12.4	4432.8			328.5	
Tunisia [Labidi et al. 2002]	24	min	21	200	1.2	1.3	2	2
		max	75	24600	69.1	153.4	1630	1032
		average	46	6604	9.6	18.3	507	177
		median	45	2840	4.3	7.0	358	113
		stand. dev.	15.9	7606.3	15.5	33.0	489	217.6
Turkey [Belin et al. 2002]	36	min	29				120	
		max	90				700	
		average	51				337	
		median	47				315	
		stand. dev.	13.3				156.7	

centrations of radium isotopes are relatively high and increase with mineralization and temperature. In the thermal waters of Podhale the  $^{226}\text{Ra}$  activity concentration is considerably higher than that of  $^{228}\text{Ra}$ . The fact is connected with much higher activity concentrations of uranium than thorium in the limestone aquifer.

The temperature, mineralization and radium activity concentration of the thermal waters increase with the distance between the well pumping the water and the Tatra Mts.

Generally the uranium concentrations in the investigated waters are low, ranging from decimals to tens mBq/l, and depend neither on the aquifer depth nor on the water temperature or its mineralization. Most of the investigated waters are classified as radon-poor ones.

The concentrations of the natural radionuclides in the waters in sedimentary rocks of the sub-Tatra and high Tatra nappes from Szymoszkowa GT-1 and Chochołów PIG-1 are significantly higher in comparison with those in waters from other places in the Podhale Trough. It may result from a presence of specific, uranium-rich rocks strata drained by the water pumped from these two localities.

The mineralization, activity concentrations of the natural radioactive nuclides in the thermal waters occurring in the other regions in Poland as well as in some other countries range within far broader intervals in comparison with the respective parameters of the waters from the Podhale Trough.

Generally, the heat of the thermal waters, particularly the Polish ones, results from the geothermal gradient. The radium activity concentrations increase with water mineralization.

Usually in thermal water the  $^{226}\text{Ra}$  activity concentration is far larger than that of  $^{238}\text{U}$ . This phenomenon is explained by the differences of geochemical properties of radium and uranium in groundwaters, where the reduction conditions are often prevailing, under such conditions uranium is insoluble, on the other hand the radium is not effected by the environment.

The activity content of  $^{226}\text{Ra}$  is higher than that of  $^{228}\text{Ra}$  in most of the waters. This is probably connected with the relation between the uranium and thorium contents in the rock aquifers.

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