Geological Quarterly, 2017, **61** (4): 771–778
DOI: http://dx.doi.org/10.7306/gq.1365

^{224}Ra and the ^{224}Ra/^{228}Ra activity ratio in selected mineral waters from the Polish Carpathians

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Nguyen Dinh, Ch., Rajchel, L., Duong Van, H., Nowak, J., 2017. ^{224}Ra and the ^{224}Ra/^{228}Ra activity ratio in selected mineral waters from the Polish Carpathians. Geological Quarterly, **61** (4): 771–778, doi: 10.7306/gq.1365

Mineral and therapeutic waters widely occurring in the Polish Carpathians contain a vast amount of biogenic elements. However, radioactive elements like radium isotopes are also found in these waters. This paper presents the first results of the activity concentration measurements of ^{224}Ra in selected mineral waters of the Polish Carpathians. Additionally, the content of ^{226}Ra and ^{228}Ra, and the activity ratios of ^{224}Ra/^{228}Ra, ^{224}Ra/^{226}Ra and ^{226}Ra/^{228}Ra in the waters were determined. The work was based on a method for the simultaneous determination of ^{224}Ra, ^{226}Ra and ^{228}Ra in water samples using the α/β liquid scintillation spectrometer. The results show that the activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra in the mineral waters are comparable and vary from ca. 220 mBq/L to above 1500 mBq/L. The activity ratios of ^{224}Ra/^{228}Ra, ^{224}Ra/^{226}Ra and ^{226}Ra/^{228}Ra are variable within the ranges of 0.68 to 1.48, 0.65 to 1.48, and 0.78 to 2.05, respectively. The committed effective dose resulting from the intake of ^{224}Ra through the water consumption is far lower than that from ^{226}Ra and ^{228}Ra.

Key words: ^{224}Ra, radium, mineral waters, effective dose, LSC method.

INTRODUCTION

The determination of radium isotopes in water samples is very important from the hydrological and radiological point of view. The relation between the radium isotopes' concentration in groundwater and the lithology of the host aquifers were reported by many scientists (e.g., King et al., 1982; Sturchio et al., 1992; Martin and Akber, 1999; Lucivjansky, 1999; Ruberu et al., 2005; Grundl and Cape, 2006, Walencik-Łata et al., 2016). The thermodynamic properties and applications of the radium isotopes for interaction between groundwater and aquifer rock were studied by Davidson and Dickson (1986), Langmuir and Melchior (1985) and Szabo et al. (2012). The contribution of ^{226}Ra and ^{228}Ra to annual committed effective dose resulting from the consumption of mineral and drinking waters amounts to >70% (Bayés et al., 1996; Manjón et al., 1996; Godoy et al., 2001; Waller and Steininger, 2007; Waller et al., 2008; Nguyen et al., 2012).

According to the Council Directive (Euratom, 2013), drinking water is safe from the radiological point of view if with the consumption of two litres per day, the annual committed dose rate originating from the presence of the radioactive elements in this water is <0.1 mSv. In general, in many countries (for example in Poland) there are natural artesian water intakes serving as direct sources of drinking water for population. In that case, the ^{224}Ra should be taken into account in the estimation of committed effective doses.

The Carpathians are the richest region of mineral and therapeutic waters in Poland, where numerous spas and bottling plants are located. A significant number of mineral waters occurring in this region are available for consumers directly from boreholes or springs. The main aim of the work was the determination of ^{224}Ra content in selected mineral waters from the Polish Carpathians. For the first time, the results of the activity concentration of ^{224}Ra in the Polish Carpathian mineral waters are presented. Additionally, the content of other radium isotopes (^{226}Ra and ^{228}Ra) and the activity ratios of ^{224}Ra/^{228}Ra, ^{224}Ra/^{226}Ra and ^{226}Ra/^{228}Ra were determined. In the paper, some geochemical and radiological aspects of the presence of three radium isotopes (^{224}Ra, ^{226}Ra and ^{228}Ra) and their activity ratios in studied mineral waters are also discussed.

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Received: February 14, 2017; accepted: May 28, 2017; first published online: July 3, 2017

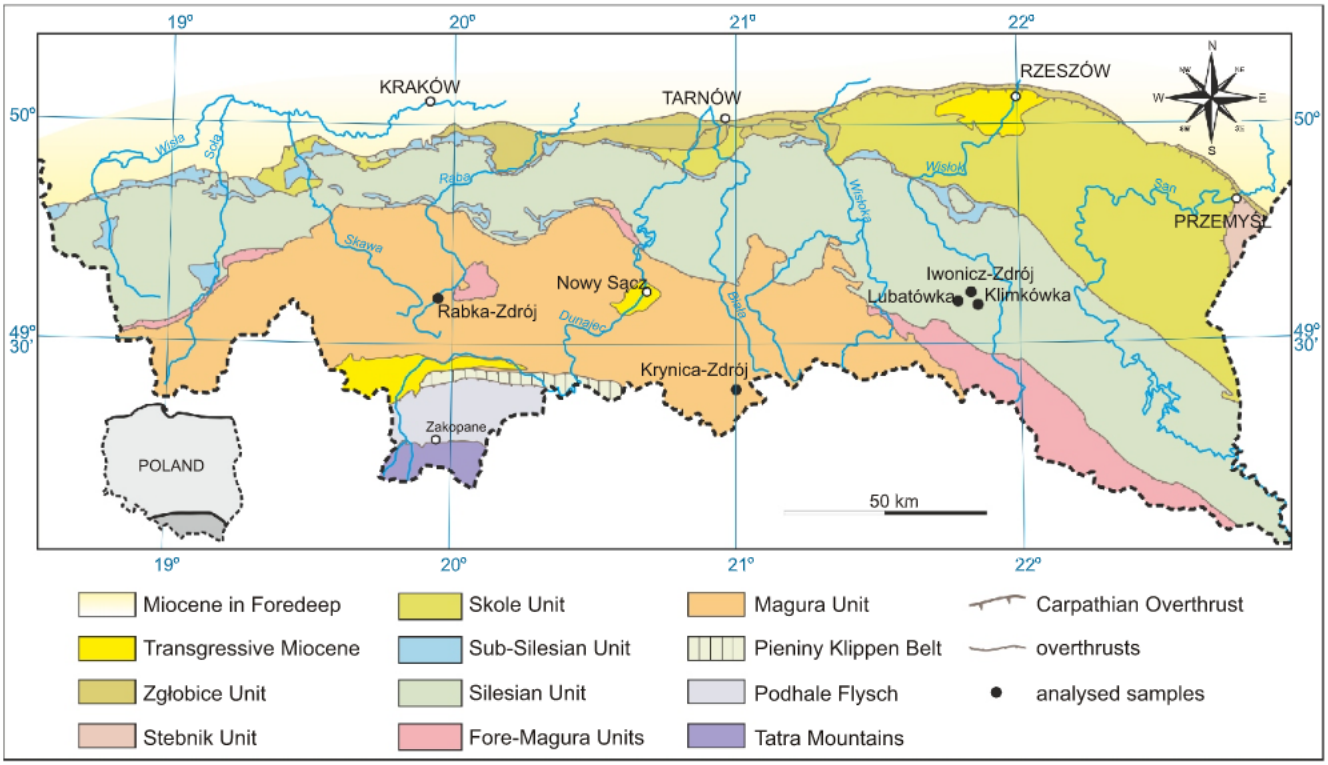

Fig. 1. Map of mineral waters sampling sites

SAMPLING AND ANALYSIS METHOD

STUDY REGION AND SAMPLING

The water samples were collected from several mineral water intakes in the Polish Outer Carpathians (Fig. 1). This region is composed chiefly of Cretaceous and Miocene sandstones and mudstone of flysch origin, in which carbonate and siliceous rocks sporadically occur. The formations are strongly folded and divided onto different units. Due to the very complicated geological structure, the Carpathians are regarded as a region of diverse hydrogeological conditions (e.g., Rajchel, 2012; Rajchel and Czop, 2012). This region hosts many valuable mineral water resources used for balneotherapy and by mineral water plants. The samples were collected from some selected resources of therapeutic bicarbonated waters, waters containing carbon dioxide, and chloride waters from the Magura Unit (Zuber-1 and Zuber-2 boreholes, and Słotwinka spring in Krynica-Zdrój; Krakus, Warzelnia and Rabka IG 2 boreholes in Rabka-Zdrój) and the Silesian Unit (Elin 7 and Emma boreholes in Iwonicz-Zdrój; Klimkówka 27 borehole in Klimkówka; Lubatówka 12 borehole in Lubatówka; Table 1). The waters are diagenetic and mixed with the infiltration water to different degrees (Rajchel and Czop, 2012).

In the Magura Unit (Inoceramian Bed; Fig. 1) the average uranium and thorium concentrations are 2.06 and 8.92 ppm, but in the Silesian Unit (Godula, Istebna, Ciężkowice and Krosno beds; Oszczypko et. al., 2006) they vary from 1.07 to 1.98 and 4.03 to 10.05, respectively (Plewa and Plewa, 1992).

The water samples were placed into 2-litre plastic bottles. Before sampling the bottles were rinsed by HCl 0.1 M and distilled water. To eliminate the remaining liquid, the bottle was rinsed several times with the water intended for analysis at the water intake. The sampling time was recorded and the samples were transported to the laboratory as soon as possible.

METHODOLOGY

At the laboratory, the water samples were weighed and the radium isotopes were co-precipitated from the water sample together with barium as a sulphate compound. The precipitate was placed into the glass vial of volume 22 mL, mixed with 12 mL of the gel scintillation cocktail, and measured by the *Guardian alpha/beta Wallac Scintillation Counter* (LSC method). For every sample, the measurement was performed daily for two hours. The measurement process lasted until the radioactive equilibrium between ^{226}Ra and ^{222}Rn has been established. The applied chemical preparation and measurement procedures were described in detail by Nguyen et al. (1997).

After radium precipitation, only radium isotopes (^{226}Ra, ^{228}Ra and ^{224}Ra) occur in the obtained sample. ^{226}Ra belongs to the uranium series with ^{238}U as a primary element, ^{228}Ra and ^{224}Ra are the members of thorium series with ^{232}Th as a first isotope. At the radioactive equilibrium occurring in the ^{226}Ra group, there are four alpha decay isotopes (^{226}Ra, ^{222}Rn, ^{218}Po, ^{214}Po) and two beta decay isotopes (^{218}Pb, ^{214}Bi). In the ^{228}Ra group, there are only two beta decay isotopes (^{228}Ra, ^{228}Ac). The ^{224}Ra group emits four alpha and two beta particles. Four alpha particles are related to ^{224}Ra, ^{220}Rn, ^{216}Po (every isotope emits one α particle per decay), and ^{212}Bi and ^{212}Po with emission of 0.337 α per decay and 0.663 α per decay, respectively. Two beta particles are emitted from ^{212}Pb (one β per decay), ^{212}Bi (0.663 β per decay) and ^{208}Tl (0.337 β per decay; Brown et al. 1986). Since the half-life ($T_{1/2}$) of ^{226}Ra is 1620 y, and the longest daughter in this group is ^{222}Rn with $T_{1/2}$ equal to 3.825 d, so the secular equilibrium in the group is established after nearly 500 h

Table 1

Selected data on boreholes, springs and medicinal waters

Locality/type and name of water intake	Depth [m]	Depth of the water intake [m]	Water type	GPS coordinates
Krynica-Zdrój Zuberb-1 borehole	810.0	696.2–810.0	HCO_3-Na+CO_2	591.2 m a.s.l. 49°24'50''N 20°57'48''E
Krynica-Zdrój Zuber-2 borehole	948.5	586.8–670.0	HCO_3-Na-Mg+CO_2	576.2 m a.s.l. 49°24'53''N 20°57'44''E
Krynica-Zdrój Słotwinka spring	–	–	HCO_3-Mg-Na-Ca+CO_2+Fe	615.0 m a.s.l. 49°25'59''N 20°57'25''E
Rabka-Zdrój Warzelnia borehole	50.2	41.0–45.7	Cl-Na+Fe+I	494.99 m a.s.l. 49°36'36''N 19°58'02''E
Rabka-Zdrój Rabka IG 2 borehole	1215.0	1185–1215	Cl-Na+I+T	563.84 m a.s.l. 49°36'57''N 19°58'30''E
Rabka-Zdrój Krakus borehole	19.0	19.0	Cl-Na+I	495.5 m a.s.l. 49°36'35''N 19°57'58''E
Klimkówka Klimkówka 27 borehole	1255.0	417.0–481.0	HCO_3-Cl-Na+CO_2+I	462.8 m a.s.l. 49°33'26''N 21°47'32''E
Iwonicz-Zdrój Emma borehole	283.7	102.8–263.0	Cl-HCO_3-Na+CO_2+I	435.20 m a.s.l. 49°33'38''N 21°46'58''E
Iwonicz-Zdrój Elin 7 borehole	1030.0	85.0–238.0	Cl-HCO_3-Na+CO_2+I	434.80 m a.s.l. 49°33'39'' N 21°45'02''E
Lubatówka Lubatówka 12 borehole	1151.5	625.0–958.0	Cl-HCO_3-Na+CO_2+I+T	350.7 m a.s.l. 49°33'59''N 21°47'32''E

from the moment of radium precipitation. In the ^{228}Ra group, the activity of ^{228}Ac can reach the ^{228}Ra activity in about 20 h after the precipitation. With reference to the lab time (one month), the ^{228}Th can be regarded as a "stable" isotope due to its $T_{1/2}$ equal to 1.9 y. The $T_{1/2}$ of ^{224}Ra is 3.62 d and the longest lived progeny is ^{212}Pb with the $T_{1/2}$ = 10.6 h, so the transient equilibrium in the group is established after 53 h. Since that moment, the total alpha and beta activities of the ^{224}Ra group decrease in accordance with decay law. After 500 h, the total activity of the ^{224}Ra group is below 2% of the activity of this isotope at the precipitation time. Therefore, the contribution of the ^{224}Ra group to the total alpha and beta count rates after 500 h elapsed from the radium precipitation can be neglected, and the ^{226}Ra and ^{228}Ra can be estimated using the alpha and beta count rates measured after 500 h from the moment of radium precipitation. For every studied sample the dependence of the net alpha and beta intensities (the intensities of the background sample were subtracted from the adequate intensities of the sample) on the time elapsed from the precipitating moment was used to determine the ^{224}Ra, ^{226}Ra and ^{228}Ra contents.

The ^{226}Ra concentration in a water sample is estimated by the formula:

$$^{226}\mathrm{Ra} = \frac{I^{\alpha}_{500}}{F^{\mathrm{Ra-226}}_{\alpha-500} \times 60 \times \varepsilon_{\alpha} \times V} \quad [1]$$

where: I^{α}_{500} – net count rate (cpm) of the sample measured in the alpha channel after 500 h from the moment of radium precipitation; $F^{\mathrm{Ra-226}}_{\alpha-500}$ – factor corresponding to relative alpha activity of the ^{226}Ra group at 500 h elapsed from the sample preparation; this factor can be obtained from the Bateman equation or empirically using the sample prepared from the ^{226}Ra standard solution; ε_{α} – the detection efficiency of the liquid scintillation detector for alpha particle and can be estimated using the sample of ^{226}Ra standard solution or arbitrarily taken to be equal to 100% (Horrocks, 1974); V – water sample volume; the 60 is the number of seconds in one minute.

The ^{228}Ra concentration in the water sample is determined using the beta count rate. The total beta count rate at 500 h elapsed time consists of both beta count rates from the ^{228}Ra and ^{226}Ra groups. The count rate of the beta particles emitted from the ^{226}Ra group is calculated by the following formula:

$$I^{\mathrm{Ra-226}}_{\beta-500} = I^{\alpha}_{500} \times C_{\beta\alpha} \quad [2]$$

where: $C_{\beta\alpha} = \frac{I^{st}_{\beta-500}}{I^{st}_{\alpha-500}}$; $I^{st}_{\beta-500}$ and $I^{st}_{\alpha-500}$ is the count rates for the ^{226}Ra standard sample after 500 h from the moment of radium precipitation measured in the beta and alpha channels, respectively.

The count rate from the ^{228}Ra group in the sample is equal to:

$$I^{\mathrm{Ra-228}}_{\beta-500} = I^{total}_{\beta-500} - I^{\mathrm{Ra-226}}_{\beta-500} \quad [3]$$

where: $I_{\beta-500}^{total}$ – the count rate measured in the beta channel for the sample.

The ^{228}Ra concentration in water sample is estimated by the formula:

$$^{228}\mathrm{Ra} = \frac{I_{\beta-500}^{\mathrm{Ra}-228}}{F_{\beta-500}^{\mathrm{Ra}-228} \times 60 \times \varepsilon_{\beta} \times V} \quad [4]$$

where: $F_{\beta-500}^{\mathrm{Ra}-228}$ – the factor corresponding to the relative beta activity of the ^{228}Ra group after 500 h from the moment of radium precipitation, ε_{β} – the efficiency of the detection of beta particles emitted from the ^{228}Ra group. The other symbols denote the same as in Formula [1].

The count rates measured daily in the alpha channel consist of the count rate originating from both the ^{226}Ra and ^{224}Ra groups, so the count rate measured at the *t*-moment from the ^{224}Ra content in the prepared water sample is determined as follows:

$$I_{\alpha}^{\mathrm{Ra}-224}(t) = I_{\beta}^{total}(t) - I_{\alpha}^{\mathrm{Ra}-226}(t) \quad [5]$$

where: $I_{\alpha}^{total}(t)$, $I_{\alpha}^{\mathrm{Ra}-226}(t)$ are the total alpha count rate and the alpha count rate originating from the ^{226}Ra group, respectively; t – the elapsed time from the moment of radium precipitation.

The $I_{\alpha}^{\mathrm{Ra}-226}(t)$ can be calculated by the formula:

$$I_{\alpha}^{\mathrm{Ra}-226}(t) = {}^{226}\mathrm{Ra} \times 60 \times V \times F_{\alpha}^{\mathrm{Ra}-226}(t) \quad [6]$$

where: ^{226}Ra – the activity concentration determined by Formula [1], is the factor corresponding to the relative alpha activity for the ^{226}Ra group at the time (t) elapsed from the sample.

$F_{\alpha}^{\mathrm{Ra}-226}(t)$ can be calculated using the Bateman equation or determined empirically using the sample prepared from the ^{226}Ra standard solution. The α and β spectra of the prepared ^{228}Ra standard sample measured at 50 and 265 h elapsed from the radium precipitation are presented in Figure 2 and Figure 3, respectively. The figures show that the alpha activity decreased in agreement with the ^{224}Ra decay and the beta activity decreased clearly more slowly in comparison with the alpha one.

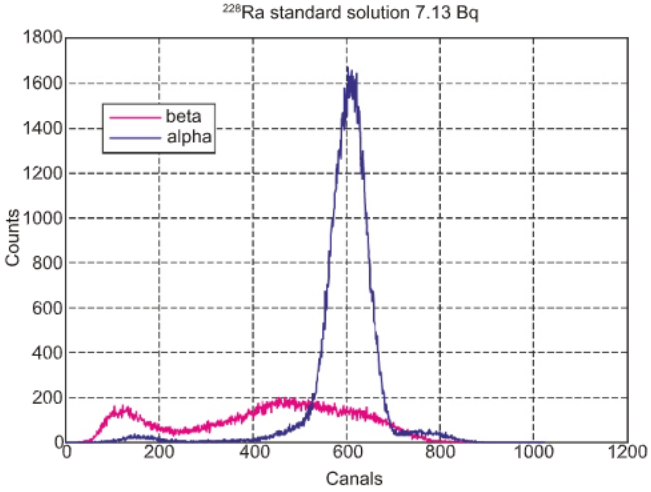

Fig. 2. Alpha and beta spectra of the ^{228}Ra standard solution measured by *Wallac Winspectral 1414* alpha and beta liquid scintillation counter at 50 h elapsed from the radium precipitation

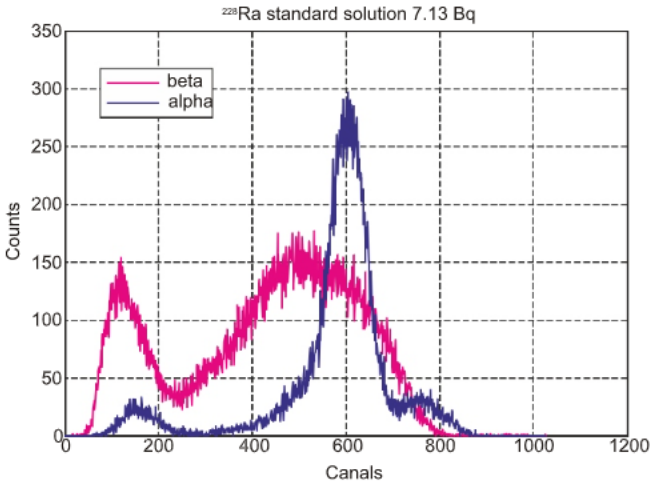

Fig. 3. Alpha and beta spectra of the ^{228}Ra standard solution measured by *Wallac Winspectral 1414* alpha and beta liquid scintillation counter at 265 h elapsed from the radium precipitation

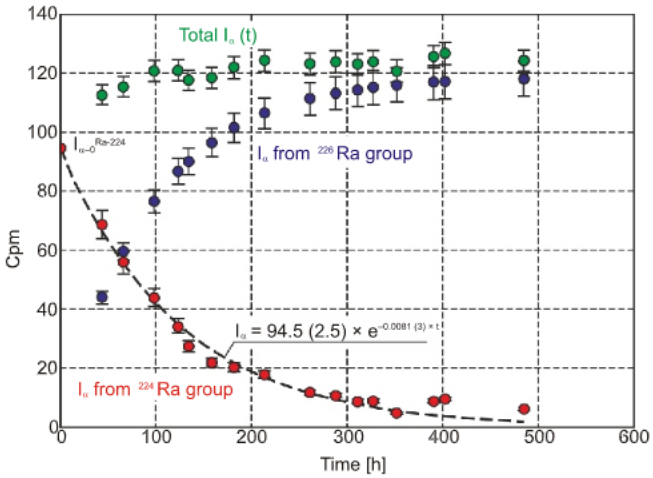

Fig. 4. Total alpha count rates and its components of ^{226}Ra and ^{224}Ra groups for the water sample collected from the Zuber-2 intake (for the fitting curve value of λ = 0.0081 h^{-1} corresponding to $T_{1/2}$ equal to 3.57 days)

This fact is related to both the constant beta activity of the ^{228}Ra group and the decreasing beta activity of the ^{224}Ra group. The measured total alpha count rate as a function of the elapsed time and its separated components originating from the ^{226}Ra and ^{224}Ra groups for the sample collected from the Zuber-2 water intake is shown in Figure 4 as an example. In order to estimate the ^{224}Ra content, the curve (according to the decay form – ae^{-bt}) presenting the relation between the component of the alpha count rate of the ^{224}Ra group and time elapsed from the precipitating moment (after 53 h) is fitted. The content of ^{224}Ra is calculated using the decay law of the ^{224}Ra group and $I_{\alpha-0}^{\mathrm{Ra}-224}$ which is an ordinate of the intersection point of the above-mentioned fitted curve on the y-coordinate.

$$^{224}\mathrm{Ra} = \frac{I_{\alpha-0}^{\mathrm{Ra}-224} \times e^{-\lambda_{\mathrm{Ra}\cdot 224} \times 53}}{60 \times F_{\alpha-53}^{\mathrm{Ra}-224} \times \varepsilon_{\alpha} \times V} \times e^{\lambda_{\mathrm{Ra}\cdot 224} \times (\Delta t + 53)} =$$

$$= \frac{I_{\alpha-0}^{\mathrm{Ra}-224} \times e^{-\lambda_{\mathrm{Ra}\cdot 224} \times \Delta t}}{60 \times F_{\alpha-53}^{\mathrm{Ra}-224} \times \varepsilon_{\alpha} \times V} \quad [7]$$

where: λ_{Ra-224} [h^{-1}] – the fitted value of the ^{224}Ra decay constant, and F^{Ra-224}_{53} the factor corresponding to the relative alpha activity of the ^{224}Ra group at 53 hours elapsed from the precipitating water sample, and can be estimated using the Bateman equation for the ^{224}Ra group or determined empirically using the sample prepared from the ^{232}Th standard solution, where there is radioactive equilibrium between ^{228}Ra and ^{224}Ra. Δt [h] – the time elapsed from the water sampling moment to the precipitation point.

In accordance with the definition described by Currie (2008) and propagation law, the limit of detection was calculated based on the average uncertainty of the count rates in the alpha and beta channels for the background sample, and is equal to 11 mBq/dm^3 for ^{224}Ra, 7 mBq/dm^3 for ^{226}Ra, and 30 mBq/dm^3 for ^{228}Ra.

RESULTS AND DISCUSSION

The activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra in the studied waters vary from 206 to 1116 mBq/L, from 213 to 1545 mBq/L, and from 186 to 752 mBq/L, respectively (Table 2). Figures 5, 6 and 7 show the relationships between ^{226}Ra and ^{224}Ra, between ^{228}Ra and ^{224}Ra, and between ^{228}Ra and ^{226}Ra, respectively. All points (excluding the water from Lubatówka 12) in the figures are scattered between line 1:1. There are strong linear correlations between the studied radium isotopes. The Pearson correlation coefficient for the relations between ^{226}Ra and ^{224}Ra, between ^{228}Ra and ^{224}Ra, and between ^{228}Ra and ^{226}Ra is equal to 0.94, 0.88 and 0.85, respectively. The three analysed isotopes are variants of the same chemical element (radium); thus, their chemical properties and behaviour in groundwater are the same.

The activity ratios of ^{224}Ra/^{228}Ra and ^{226}Ra/^{228}Ra range in the intervals of 0.68–1.48 and 0.78–2.05, respectively. The average value of ^{224}Ra/^{228}Ra activity ratio is 1.09, and, if we exclude the water from Lubatówka 12, this ratio decreases to 1.04. The observed phenomena indicate that the activity concentration of ^{224}Ra in groundwater is generally slightly higher than that of ^{228}Ra, which is related to the recoil effect. In the thorium decay chain, ^{224}Ra is followed by two alpha decays, while ^{228}Ra is followed only by one alpha decay. Therefore, ^{224}Ra shows higher probability of migration due to direct transfer of the atom across the solid/liquid phase boundary or lattice destruction by recoil effect than ^{228}Ra. It is the same process which causes uranium isotopes disequilibrium (the activity ratio of ^{234}U/^{238}U is generally >1) in groundwater (Osmond and Cowart, 1976; Nguyen et al., 2011).

In such mineral waters, the chemical processes dominate the recoil effect and radium isotopes migrate mainly from host rocks to water due to leaching processes. The lower content of ^{224}Ra than ^{228}Ra can be associated with the fact that thorium (^{228}Th is progeny of ^{228}Ra and parent of ^{224}Ra) forms low-soluble and highly adsorbed compounds in contrast to radium (Langmuir, 1997; Nguyen et al., 2011).

The observed average activity ratio values (^{226}Ra/^{228}Ra) for all studied waters are 1.2, being typical for highly mineralised groundwater in the Polish Carpathians (Nguyen et al., 2016). Generally, the activity concentrations of ^{226}Ra, ^{228}Ra and their activity ratio (^{226}Ra/^{228}Ra) in groundwater are related to the adequate content and activity ratio of their primordial isotopes (^{238}U, ^{232}Th, ^{238}U/^{232}Th) in the host aquifers (Asikainen and Kahlos, 1979; King et al., 1982; Vesterbacka et al., 2006; Nguyen et al., 2012). For six waters from the Magura Unit and three waters from the Silesian Unit, the average activity concentration ratios (^{226}Ra/^{228}Ra) are 1.04 and 1.47, respectively. The values correspond, to a certain degree, to the ratios of the average uranium and thorium concentrations in the Magura and Silesian units. The highest activity concentrations of the radium isotopes and their activity ratios (^{226}Ra/^{228}Ra and ^{224}Ra/^{228}Ra) were observed

Table 2

The activity concentrations of ^{224}Ra, ^{226}Ra and ^{228}Ra and their activity ratios in the studied Carpathian mineral waters

No.	Locality/ water intake	TDS [g/L]	Activity concentration [mBq/L]			Activity concentration ratio		
			^{224}Ra	^{226}Ra	^{228}Ra	^{224}Ra/ ^{228}Ra	^{224}Ra/ ^{226}Ra	^{226}Ra/ ^{228}Ra
1	Krynica-Zdrój Zuber-1	23.2	428 ± 38	568 ± 24	530 ± 38	0.81	0.75	1.07
2	Krynica-Zdrój Zuber-2	20.5	460 ± 32	447 ± 23	312 ± 34	1.47	1.03	1.43
3	Krynica-Zdrój Słotwinka	3.52	420 ± 17	284 ± 19	362 ± 30	1.16	1.48	0.78
4	Rabka-Zdrój Warzelnia	20.6	216 ± 17	314 ± 19	312 ± 25	0.70	0.69	1.01
5	Rabka-Zdrój Rabka IG 2	23.5	722 ± 45	619 ± 25	598 ± 39	1.21	1.17	1.04
6	Rabka-Zdrój Krakus	23.8	331 ± 23	442 ± 30	485 ± 41	0.68	0.75	0.91
7	Klimkówka Klimkówka 27	12.2	218 ± 34	333 ± 15	215 ± 25	1.01	0.65	1.55
8	Iwonicz-Zdrój Emma	5.92	206 ± 13	213 ± 8	203 ± 18	1.01	0.97	1.05
9	Iwonicz-Zdrój Elin 7	5.80	245 ± 23	231 ± 17	186 ± 19	1.31	1.06	1.24
10	Lubatówka Lubatówka 12	20.5	1116 ± 71	1545 ± 88	752 ± 61	1.48	0.72	2.05

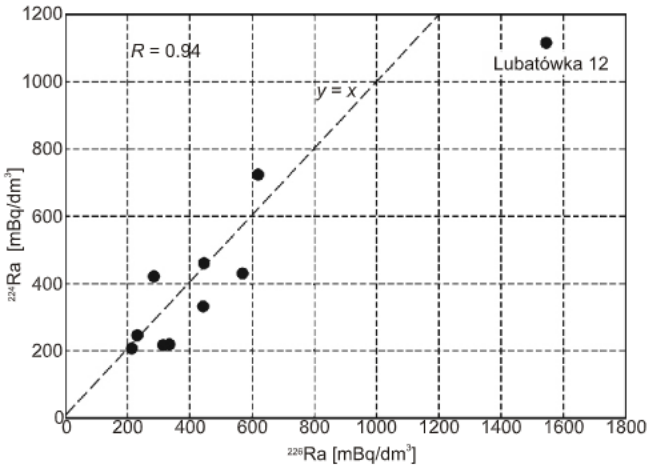

Fig. 5. ^{226}Ra concentration vs. ^{224}Ra concentration in the water samples

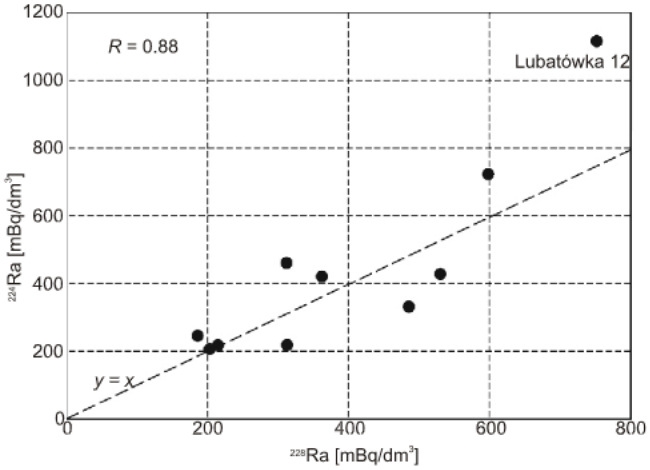

Fig. 6. ^{228}Ra concentration vs. ^{224}Ra concentration in water samples

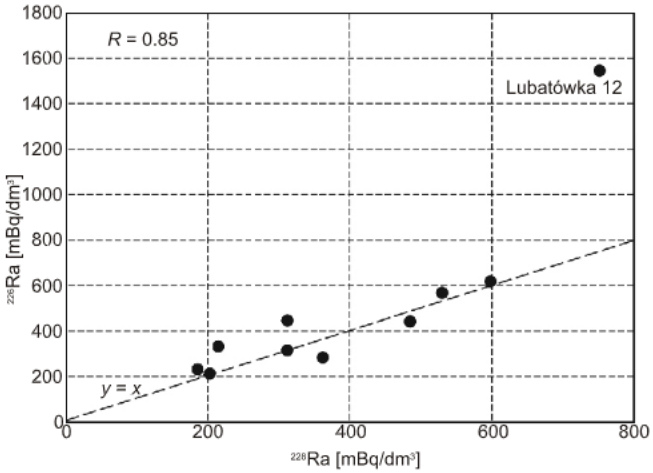

Fig.7. ^{226}Ra concentration vs. ^{228}Ra concentration in the water samples

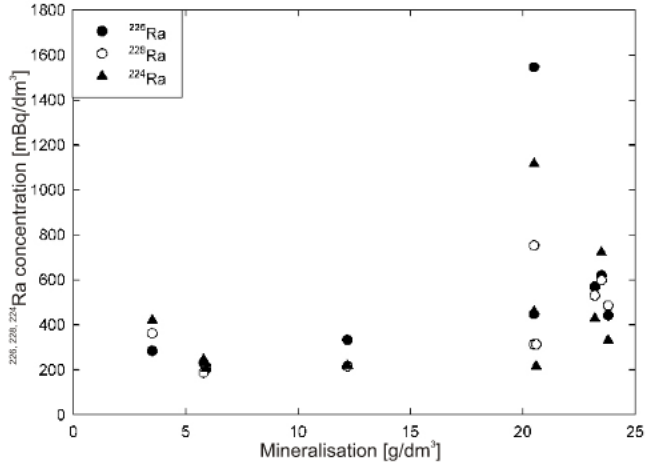

Fig. 8. Activity concentrations of radium isotopes (^{224}Ra, ^{226}Ra and ^{228}Ra) vs. TDS in the water samples

in the water from Lubatówka 12. This fact can be related to the local geology and hydrogeological conditions in this area.

The TDS in the investigated groundwater varies from 3.5 to 23.8 g/L. The relations between activity concentrations of three radium isotopes (^{224}Ra, ^{226}Ra and ^{228}Ra) and TDS are presented in Figure 8. There is no clear relation between the radium content in investigated waters and TDS, or it is difficult to notice because of the small amount of data.

Based on the obtained activity concentrations of the radium isotopes, the annual committed effective doses (E) resulting from consumption of two litres of the mineral waters a day for adults were calculated using the following equation:

$$E = V \times \sum_{i=1}^{N} (A_i \times DCF_i) \quad [8]$$

where: V stands for consumption of water (2L per day), A_i – the activity concentration of the given radionuclide in water expressed in Bq/L, and DCF_i stands for the DCFs (Dose Conversion Factor) for ingestion by humans belonging to the given age group (adults in this case). The DCF is equal to the dose in Sv resulting from the ingestion of 1Bq of the given radionuclide (ICRP, 1995; WHO, 2008).

The calculated committed effective dose from ^{226}Ra and ^{228}Ra changes in the range from 44 to 316 μSv/year and from 94 to 379 μSv/year, respectively. The data show that the dose from the ^{224}Ra varies from 7.5 to 53 μSv/year and its contribution to the total annual committed effective dose is <8% (Table 3). Thus, the intake of ^{224}Ra with consumed water does not pose a significant radiological risk to human health in comparison with other two radium isotopes (^{226}Ra and ^{228}Ra).

CONCLUSIONS

The activity concentrations of ^{224}Ra in the studied mineral waters are comparable to that of ^{226}Ra and ^{228}Ra. There is a

Table 3

The annual committed effective doses for adults resulting from intake of the waters, calculated for three radium isotopes (^{224}Ra, ^{226}Ra and ^{228}Ra)

No.	Town/ water intake	Annual committed effective dose [μSv]			Contribution of ^{224}Ra to the total effective dose [%]
		^{224}Ra	^{226}Ra	^{228}Ra	
1	Krynica-Zdrój Zuber-1	15	116	267	3.8
2	Krynica-Zdrój Zuber-2	20	86	302	7.1
3	Krynica-Zdrój Słotwinka	15	58	182	6.0
4	Rabka-Zdrój Warzelnia	8.4	64	157	3.7
5	Rabka-Zdrój Rabka IG 2	34	127	301	7.4
6	Rabka-Zdrój Krakus	12	90	244	3.6
7	Klimkówka Klimkówka 27	11	68	108	5.9
8	Iwonicz-Zdrój Emma	7.5	44	102	4.9
9	Iwonicz-Zdrój Elin 7	10	47	94	6.7
10	Lubatówka Lubatówka 12	53	316	379	7.1

strong linear correlation between ^{224}Ra and the other two radium isotopes.

The average value of the observed activity ratio (^{224}Ra/^{228}Ra) is slightly above 1 (1.04). This is related to the recoil effect; the same process which causes the disequilibrium of uranium isotopes in groundwater. The activity ratio of ^{224}Ra/^{228}Ra lower than 1 can be related to the fact that thorium forms low-soluble and highly adsorbed compounds in an aqueous environment. The activity ratios of ^{226}Ra/^{228}Ra in the Magura and Silesian units are related to the average concentrations of uranium and thorium in water-bearing formations occurring in the units.

The intake of ^{224}Ra with consumed water does not pose a significant radiological risk to human health in comparison with ^{226}Ra and ^{228}Ra.

The LSC method is clearly useful for the simultaneous determination of ^{224}Ra, ^{226}Ra and ^{228}Ra in water samples.

Acknowledgements. The authors would like to express their thanks to the anonymous reviewers for their valuable remarks. This work was supported by the AGH University of Science and Technology projects Nos.: 11.11.140.645, 11.11.140.862 and 15.11.220.717.

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