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Factors controlling ^{226}Ra, ^{228}Ra and their activity ratio in groundwater – an application in Polish Carpathian mineral waters

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Abstract: The influences of aquifer formations and water chemical composition on the occurrence and activity ratio of radium isotopes in groundwater are discussed. Based on the model of desorption/adsorption processes of natural radionuclides in the rock-water system, the concentrations of radium isotopes and their activity ratio in groundwater are evaluated by the numerical Monte Carlo method (MC). In cases where the groundwater is of a similar age, limited flow (up to several meters/year), the physical conditions and the uranium and thorium activity ratios in host water formations are similar, the activity concentrations of radium isotopes (^{226}Ra, ^{228}Ra) and their activity ratio (^{226}Ra/^{228}Ra) are the highest in the water of high desorption coefficient for chloride sodium water (domination of Cl^-, Na^+ ions), medium in water of moderate desorption (bicarbonate water – HCO_3^-, Ca^{2+}) and the lowest in waters with a low desorption coefficient (sulfate ions prevailing – SO_4^{2-}, Ca^{2-}). The statements are well confirmed in the case of the natural mineral waters from the Polish Outer Carpathians. The total dissolved solids (TDS) of the Polish Carpathians waters varies from several hundred milligrams per liter to several tens of thousands milligrams per liter. The minimum, maximum and average concentrations of ^{226}Ra, ^{228}Ra and their activity ratio (^{226}Ra/^{228}Ra) are 82, 1340, 456 mBq/L, 19, 1240, 354 mBq/L and 0.89, 7.6 and 2.0 for chloride waters; 4, 140, 45.8 mBq/L, 12, 171, 62.7 mBq/L and 0.3, 1.7 and 0.70 for bicarbonate waters and 0.8, 9.3, 3.6 mBq/L, 5.3, 54, 20.1 mBq/L and 0.1, 1.0, 0.3 for sulfate ones, respectively. The desorption coefficients are the highest for the Cl-Na, moderate for the HCO_3-Ca and the lowest for the SO_4-Ca waters (in contrast to the adsorption properties of these waters).

Keywords: radium isotopes, groundwater, recoil effect, desorption/adsorption, Monte Carlo simulation, the Polish Carpathians

INTRODUCTION

In hydrogeology, both stable and radioactive isotopes and relationships between them may serve as reliable investigation tools of groundwater recharge, the main sources of groundwater contamination, groundwater genesis and chemical transformations and interaction of the water with the aquifer formation (Currell et al. 2013, Kasprzyk et al. 2013, d'Obyrn & Postawa 2013). In this paper, the factors controlling the occurrence and activity ratio of the radium isotopes in groundwater were investigated. In nature there are four radium isotopes: ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{223}Ra with half-lifes

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1620 y, 5.75 y, 3.82 d and 11.4 d, respectively. The ^{226}Ra belongs to the uranium series (^{238}U), ^{228}Ra and ^{224}Ra to the thorium one (^{232}Th), and ^{223}Ra belongs to the actinium series (^{235}U). Due to the long half-lifes, ^{226}Ra and ^{228}Ra are the most interesting considering their applications in various fields of Earth sciences.

In groundwater, the concentrations of ^{226}Ra, ^{228}Ra and their activity ratio (^{226}Ra/^{228}Ra) are related to the concentrations of the primordial isotopes (^{238}U, ^{232}Th) in the host aquifers (Asikainen & Kahlos 1979, King et al. 1982, Veterbacka et al. 2006). The radium isotope concentrations are also significantly controlled by chemical water composition and increase with water mineralization (TDS). This fact is attributed to the ion exchange with Ra for the available adsorption sites in the surface of the rock minerals of aquifers (Kraemer & Reid 1984, Lauria et al. 2004). In surface, brackish or shallow groundwater the activity concentrations of ^{226}Ra are often lower than that of ^{228}Ra and the contents of both isotopes are usually very low, ranging from a hundredth to several milibekerels per liter (Elsinger & Moore 1983, Dickson 1985, Krest et al. 1998). Vengosh and co-workers (2009) reported that in fossil groundwater from the Middle East the activity ratio (^{226}Ra/^{228}Ra) in the unconfined zone was lower than that in the confined one, and the radium activity ratio in the confined zone was equal to the adequate activity ratio (^{226}Ra/^{228}Ra) of the host rock aquifer. In several cases the observed radium activity ratios were significantly different than expected from the activity ratios of uranium and thorium (^{238}U/^{232}Th) in the host rocks. For example, Dickson (1985) found that the average activity ratio (^{226}Ra/^{228}Ra) in saline water occurring in south-western Yilgan, Australia, amounted to 0.16, while the activity ratio (^{238}U/^{232}Th) in the rock aquifer amounted to 0.6. Some researchers observed the important role of chloride ions in radium desorption from the aquifer rocks into the groundwater, where the ^{226}Ra content in waters increases with salinity (Martin & Akber 1999, Labidi et al. 2010, Roba et al. 2012, Vinson et al. 2013). The radium concentrations in groundwater are also controlled by the presence of barium and sulfate ions (Sturchio et al. 1993, Grundl & Cape 2006, Szabo et al. 2012). Reynold and co-workers (2003) reported that in Ojo Alamo (northwest New Mexico) aquifer rocks the ^{238}U and ^{232}Th average concentrations amounted to around 40 Bq/kg and 31 Bq/kg respectively, and in the groundwater with a majority of SO_4^{2-} (from 130 mg/L to 883 mg/L) and a minority of Cl^- (from 5.2 mg/L to 70.7 mg/L), the ^{226}Ra and ^{228}Ra activity concentrations ranged from tenths of milibekerels per liter to nearly 10 mBq/L respectively, and their activity ratio (^{226}Ra/^{228}Ra) ranged from 0.2 to 0.6. In contrast to this, in brines at the oil- and gas-field in the Northern Appalachian Basin (USA), the average values of the activity concentrations of ^{226}Ra, ^{228}Ra and their activity ratio are very high and amount to 69.8 Bq/L, 23.7 Bq/L and 4.98 respectively (Rowan et al. 2011). Numerous scientists used the radium isotopes and their activity ratios as indicators of adsorption-desorption interactions and groundwater input into the surface water. (Krest et al. 1999, Martin & Akber 1999). In other cases, Jones et al. (2011) stated that the increased sorption of the ^{226}Ra on the surface of the carbonate minerals with an increasing ^{226}Ra concentration in solution and iron (hydr)oxide played an important role in the sorption processes. Bassot et al. (2000) identified the insignificant role of the perchloric sodium in the radium sorption process. Several studies on radium isotopes in thermal waters show that due to the high temperature the high activities of radium isotopes as well as their large activity ratios (^{226}Ra/^{228}Ra) are often observed (Rihs & Condomines 2002, Whitehead at al. 2007, Nowak et al. 2012). Krishnaswami et al. (1982) investigated radium isotopes in Connecticut groundwater and stated that the desorption coefficient of radium isotopes (k_{ds}) is much lower than the adsorption coefficient (k_{ad}), and the k_{ds} varies in a range of decay constant of ^{228}Ra ($\lambda_{Ra228} - 2.2\cdot10^{-9}$ s) to that of ^{224}Ra ($\lambda_{Ra224} - 3.8\cdot10^{-6}$ s). Davidson & Dickson (1986) and Dickson (1990) identified the alpha recoil as the main mechanism responsible for the migration of radium nuclei from the aquifer rocks into water. Dukat & Kuehl (1995) used the radium activity ratio (^{226}Ra/^{228}Ra) for the estimation of the growth rate of the bottom sediments in the Amazon shelf. Based on the experiments on radium isotopes leaching from sediments and a model of the ion exchange, Webster et al. (1995) stated that the leached radium fraction increases with increasing concentrations of sodium ions in the leaching solution. In the Polish Upper Silesian Coal Basin there are two types of mine brines, distinguished as types A and B (Pluta & Tomza 1988). The TDS of both water types is high, being close to several dozen grams per liter. The A water is characterized by average concentrations of Ba^{2+} (1.5 g/L), Na^+ (37.5 g/L) and no SO_4^{2-}. The B water contains no Ba^{2+}, but is rich in SO_4^{2-} (2.1 g/L), Na^+ (28.0 g/L) and the concentrations of radium isotopes in the water of this type are often much lower than those in the A brine and range from a few tenths to several Bq/L. Except of the mentioned phenomena, the average radium activity ratio (^{226}Ra/^{228}Ra) in the A brines is significantly higher than that in the B type ones (Pluta & Tomza 1988, Tomza 1991, Chałupnik 2005). This fact has been explained as a result of the difference of the barium ion concentrations in the brines (Chałupnik 2005).

The present work aimed at:

- analyzing the main factors controlling concentrations of radium isotopes and their activity ratio in groundwater;
- modeling the processes that control the movement of radium nuclei in the rock-water system;
- estimating concentrations of radium isotopes and their activity ratio in water using the numerical Monte Carlo method;
- verifying the estimated results by comparing them with the measured concentrations of radium isotopes in the mineral waters of different hydrochemical types occurring in the Polish Outer Carpathians.

THEORY AND CALCULATION

Physical background

According to Krishnaswami et al. (1982), the equation describing the rate of radium isotopes per time unit in the groundwater of a water-rock system can be written as:

$$\frac{dN}{dt} = a + k_{ds} \cdot C_{os} - k_{ad} \cdot N - \lambda \cdot N \tag{1}$$

where:

N – number of radium nuclei in a unit volume of water in a time moment t,

A – number of atoms recoiled from solid to liquid per unit volume due to alpha decay,

k_{ds}, k_{ad} – the coefficients of desorption and adsorption of the radium nucleus from the rock surface to the water and from the water to the host matrix respectively; their unit is reciprocal of time [1/s, 1/d, 1/year or so],

λ – the decay constant of the concerned isotope,

C_{os} – the radium isotope concentration in the sediment thin layer contacting with water; the C_{os} is expressed in the equivalent unit volume of water such as [nuclei/L].

Following Krishnaswami et al. (1982), the relation between the C_{os} and the concentration of a radium isotope in a host rock can be written as:

$$C_{os} = C_d \left(\frac{\rho(1-\varphi)}{\varphi} \right) \tag{2}$$

where:

C_d – a number of radium isotope nuclei in the solid phase,

φ, ρ – the porosity and density of the rock, respectively.

The rates of the number of radium nuclei due to diffusion and compaction are insignificant, since in the deep aquifers the water can be considered as a homogeneous phase and the horizontal compaction can be neglected (Dickson 1990, Drever 1997). The radium nuclei originating directly from the decay of thorium in water are omitted because most of the thorium compounds are practically insoluble, and the amounts of the thorium isotopes in water usually are significantly lower (Scott 1982, Langmuir & Melchior 1985).

The desorption reactions comprise all the processes increasing the amount of radium isotopes in water, for instance leaching from radium compounds already adsorbed on mineral components of the aquifer, exchange between ions (Na^+, Ca^{2+}) contained in water and radium ions (Ra^{2+}) in rock, and dissolution of solid mineral components of the aquifer. In a similar sense, the adsorption comprises all the processes decreasing the concentration of radium nuclei in water, for instance the precipitation, attaching the radium ions to the suspended particles, ion exchange, etc.

The solution of the differential equation (1) is expressed as:

$$N = \frac{a + k_{ds} \cdot C_{os}}{k_{ad} + \lambda}\left(1 - e^{-(k_{ad}+\lambda)\cdot t}\right) \tag{3}$$

Multiplying both sides of the equation (3) by the decay constant λ, we obtain the time dependence of activity:

$$A = N \cdot \lambda = \lambda \cdot \frac{a + k_{ds} \cdot C_{os}}{k_{ad} + \lambda}\left(1 - e^{-(k_{ad}+\lambda)\cdot t}\right) \tag{4}$$

According to Krishnaswami et al. (1982) and basing on the range of the k_{ds} and k_{ad} values, the expression in the parenthesis of the formulas (3) and (4) reaches the unity if the water retardation time in the host rock is longer than ten years. In this case the radium activity should stabilize. Thus, the activity ratio of radium isotopes (^{226}Ra/^{228}Ra) is:

$$\frac{A_{Ra\,226}}{A_{Ra228}} = \frac{\lambda_{Ra226} \cdot \left(\dfrac{a_{Ra226} + k_{ds} \cdot C_{os\,Ra226}}{k_{ad} + \lambda_{Ra226}}\right)}{\lambda_{Ra228} \cdot \left(\dfrac{a_{Ra228} + k_{ds} \cdot C_{os\,Ra228}}{k_{ad} + \lambda_{Ra228}}\right)} \tag{5}$$

From the formulas (3), (4) and (5) it is seen that the number of Ra nuclei, the activity of radium isotopes and their activity ratio in the stabilized state depend on the concentrations of these isotopes in the host rocks, the recoil factors, the decay constants and the desorption/adsorption coefficients. In the stabilized state (i.e., if the retention time of water in the host rock is long enough), the decay constants of ^{226}Ra and ^{228}Ra are negligible in comparison to the desorption/adsorption factors, thus the equation (5) can be reduced to the form:

$$\begin{aligned} \frac{A_{Ra226}}{A_{Ra228}} &= \frac{\lambda_{Ra226} \cdot (a_{Ra226} + k_{ds} \cdot C_{osRa226})}{\lambda_{Ra228} \cdot (a_{Ra228} + k_{ds} \cdot C_{osRa228})} = \\ &= \frac{\lambda_{Ra226} \cdot a_{Ra226} + \lambda_{Ra226} \cdot k_{ds} \cdot C_{osRa226}}{\lambda_{Ra228} \cdot a_{osRa228} + \lambda_{Ra228} \cdot k_{ds} \cdot C_{Ra228}} \end{aligned} \tag{6}$$

Because of the decay constants λ_{Ra226}, λ_{Ra228} and recoil factors a_{Ra226}, a_{Ra228} are stable and in the unweathered rock the radioactive equilibrium between uranium, thorium and their adequate daughter radium isotopes (^{228}U and ^{226}Ra; ^{232}Th and ^{228}Ra) is often a common phenomenon. The k_{ds} for the groundwater of a given chemical composition is stable. So the equation (6) can be rewritten:

$$\begin{aligned} \frac{A_{Ra226}}{A_{Ra228}} &= \frac{C_1 + \lambda_{Ra226} \cdot k_{ds} \cdot C_{osRa226}}{C_2 + \lambda_{Ra228} \cdot k_{ds} \cdot C_{Ra228}} = \\ &= \frac{C_1 + k_{ds} \cdot A_{osRa226}}{C_2 + k_{ds} \cdot A_{osRa228}} \sim \frac{A_{osU238}}{A_{osTh232}} \end{aligned} \tag{7}$$

where symbols C_1 and C_2 are equal $\lambda_{\mathrm{Ra226}} \cdot a_{\mathrm{Ra226}}$ and $\lambda_{\mathrm{Ra228}} \cdot a_{\mathrm{Ra228}}$ respectively; $A_{os\mathrm{Ra226}}$, $A_{os\mathrm{Ra228}}$, $A_{os\mathrm{U238}}$ and $A_{os\mathrm{Th232}}$ are the activity concentration of ^{226}Ra, ^{228}Ra, ^{238}U and ^{232}Th respectively in the water host formation.

Based on the equation (7) it can be concluded that in the stabilized state the activity ratio of radium isotopes in the groundwater should be proportional to the ratio of these isotopes in the rock and in consequence should be proportional to the activity ratio of the uranium and thorium in the host rock. This phenomenon has been verified by King et al. (1982) and Sturchio et al. (2001) (see chapter "Introduction")

Simulation of the processes controlling the occurrence of radium isotopes (^{226}Ra, ^{228}Ra) and their activity ratio in groundwater using the Monte Carlo method

The concentration of radium isotopes in groundwater is affected simultaneously by many factors. Many combinations of different measured parameters can result in the same effect. Due to that, it would be very difficult to calculate analytically the role of an individual factor mentioned in the equations describing the balance of radium isotopes contained in groundwater. Therefore, the authors tried to consider the role of the controlling components using the Monte Carlo simulation method. The background of this simulation is described in detail in many papers, e.g., in Kalos & Whitlock (2008).

The simulation consists of multiple repetitions of histories, in which the initial nucleus (^{238}U or ^{232}Th) undergoes subsequent decays from ^{238}U to ^{226}Ra or from ^{232}Th to ^{224}Ra, respectively. Its initial position is randomly chosen within a thin rock layer adjacent to the rock surface and later can be changed either by an isotropic alpha decay or, with some probability, due to non-nuclear absorption/desorption processes. Each individual history then describes the movement of the decaying nucleus in the rock-water system and is determined by both the input of data and the sequence of random numbers provided by a random number generator. An example of a possible history in the thorium decay chain is shown in Figure 1. The accuracy of the MC simulation depends both on a precision of the model applied and the number of histories analyzed. For the reasonable interpretation of the results obtained, the number of the histories considered should range from 10^6 to 10^8 or more. In this case the statistical relative standard uncertainty is better than 0.1%.

In our model the following assumptions have been made:

- the system comprises only two phases: water and rock. There is no extra medium (e.g. gas or air) between them;
- in the solid phase there are conditions of the radioactive equilibrium in both the uranium and thorium chains;
- at the very beginning, all the nuclei of ^{238}U and ^{232}Th are contained in the solid phase and there are no nuclei of the isotopes of both series in water;
- the activity concentrations of the ^{238}U and ^{232}Th in the host rock formation are at the same level;
- the nucleus of a given isotope can be moved as a results of the recoil effect following the alpha decay, or by a chemical process; the beta decay does not play any role in the movement of any nucleus;
- the direction of the recoil nucleus is isotropic, and the shift distances of all the nuclei in the same phase are equal; the distances remain independent on the alpha decay energy and the mass of an isotope, being fixed at $0.5 \cdot 10^{-8}$ m (Kigoshi 1971, Fleischer 1980);
- due to Brownian motion, all the nuclei in the water phase can change their positions, but none of them reaches the surface of a solid;
- the nucleus passing from the water to the rock eventually occupies its surface.

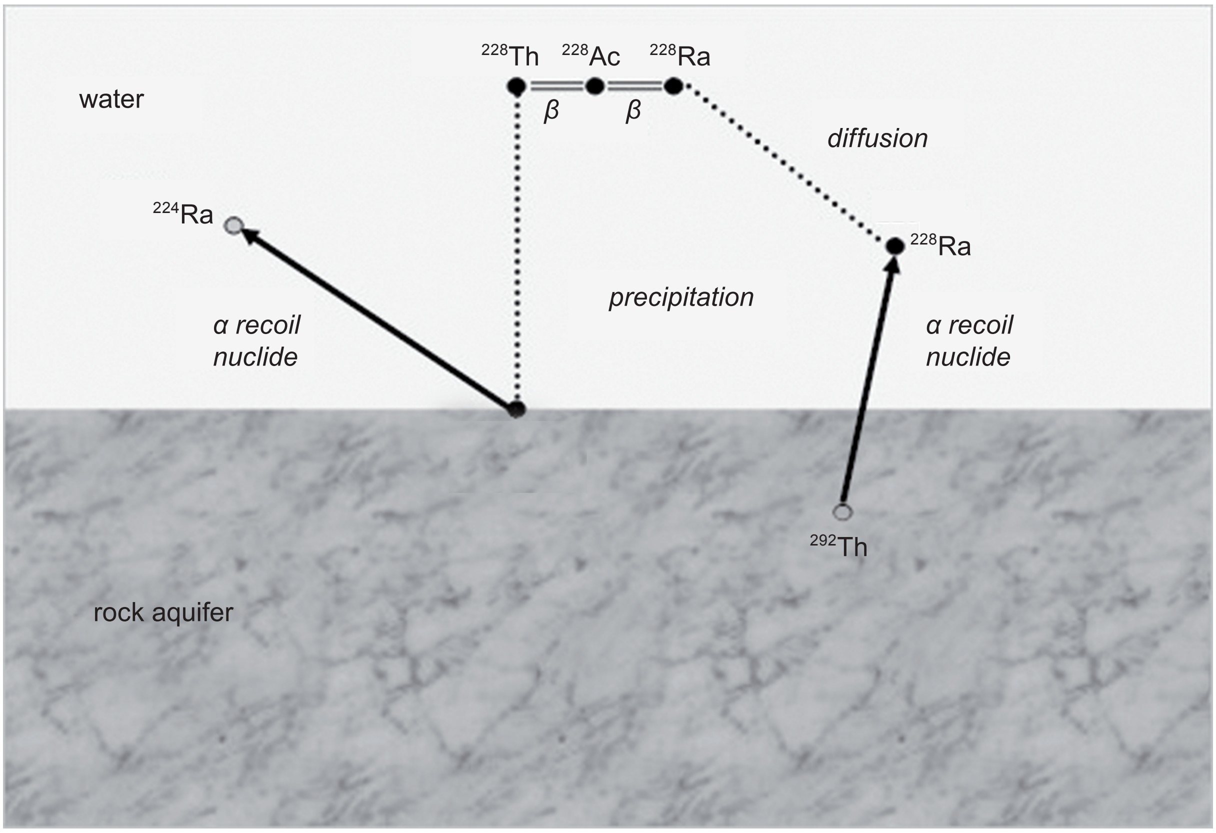

Fig. 1. *An example of the shift path of the nucleus in the thorium decay chain*

On the basis of these assumptions, a computer program has been written where the probabilities of the nucleus passage from the rock to water (and in reverse) due to the nonnuclear processes are given as the data input. In reality these passages between the phases can be caused by many mechanisms but all nonnuclear processes contributing to desorption can be treated as one mechanism and all adsorption processes as another. In this way some particular processes (mechanical leaching, ion exchange, precipitation, attaching to the suspended particles, etc.) do not have to be analyzed individually, simplifying interpretations of the results obtained.

The MC simulation results and discussion

To eliminate the lithology impact, it has been assumed that the both ^{238}U and ^{232}Th are evenly distributed in the solid phase, and their activity concentrations are the same.

Recoil effect. To analyze the recoil effect separately, every passage of any nucleus caused by nonnuclear processes is forbidden, and only the shift caused by recoil is allowed, this model is defined as a simple one. A recoil direction is randomly chosen from an isotropic distribution, and simulation is limited to a layer with a thickness equal to three ranges of the recoil ($3 \cdot 0.5 \cdot 10^{-8}$ m). If any nucleus within a rock is outside this layer, it has no chance to leave the solid phase and its history is terminated. Such a case is denoted as an unsuccessful history. The history is denoted as successful when the radium nucleus concerned occurs in water. In our case, the number of all the histories recorded (successful and unsuccessful) amounted to at least 10^8 in every decay chain (uranium and thorium). The simulated ratio of the activity of radium isotopes ($^{226}Ra/^{228}Ra$) in the water phase is equal to 1.18. This result reflects the fact that ^{226}Ra in the uranium chain forms after three alpha decays starting from the primary isotope (^{238}U), while for the creation of ^{228}Ra in the thorium chain only one alpha decay is required. Therefore, the ^{226}Ra nucleus with three decays has a significantly higher chance to enter the water phase than ^{228}Ra with only one decay.

Desorption/adsorption factors. In this case the data introduced into the simulating program consist of the values of the probabilities of the recoil effect and the values of the desorption/adsorption coefficients. The results of the simulation are referred to the reference system, where the shift of nucleus can be caused only by the recoil effect (see chapter "Recoil effect").

In order to analyze the desorption and adsorption separately, the simulation was carried out for two cases. In the first one, the nucleus shift can happen as a result of recoil and desorption effects, and all passages caused by adsorption processes are forbidden. In the second case, the adsorption is allowed while desorption does not occur at all. The relative concentrations of radium isotopes and the activity ratios ($^{226}Ra/^{228}Ra$), together with their statistical errors, were calculated in a MC simulation for a few representative radium desorption coefficients. The results are shown in Table 1, while Table 2 presents the results for different radium adsorption coefficients. Graphical dependencies of the relative activity concentrations of radium isotopes and their activity ratios on the radium desorption coefficient are presented in Figures 2 and 3. The horizontal axes in these Figures express the reciprocal of the desorption coefficient expressed in the units of time (the time on the X axis refers to the $1/k_{ds}$ and $1/k_{ad}$ but not to the water retention time). The activity concentrations of both radium isotopes increase with an increasing desorption coefficient and reach the stabilized level for k_{ds} higher than 1/y (Fig. 2). The stabilized concentrations are determined by the limit of uranium and thorium activity concentrations in the rock formation. The activity ratio ($^{226}Ra/^{228}Ra$) shown in Figure 3 starts from the value 1.18 for $k_{ds} = 0$ (no desorption), then slowly increases reaching the maximum about 9 at k_{ds} around 1/1000 y and then decreases again to 1 for higher k_{ds} values, so very high desorption can be considered as a mineral dissolution. Figures 4 and 5 present the activities of ^{226}Ra, ^{228}Ra and their activity ratios as the functions of the radium adsorption coefficient k_{ad}. In this case, the concentrations of both radium isotopes and their activity ratio decreases with an increasing k_{ad}. On the left side of Figure 5, where adsorption coefficient is very low and approximates to zero, the $^{226}Ra/^{228}Ra$ ratio returns to 1.18. This value manifests the principal role of the recoil effect, when neither desorption nor absorption processes are present.

Table 1
Activities of the radium isotopes and their activity ratio vs. reciprocal of the radium desorption coefficients, calculated by MC

^{226}Ra, ^{228}Ra activities and their activity ratios vs. radium desorption						
$1/k_{ds}$ [years]	**^{226}Ra act. [relative]**	**uncertainty**	**^{228}Ra act. [relative]**	**uncertainty**	**^{226}Ra/^{228}Ra act. ratio**	**uncertainty**
1.0E-1	1.0E+0	2.0E-3	9.9E-1	2.0E-3	1.1E+0	3.1E-3
3.2E-1	1.0E+0	2.0E-3	9.7E-1	1.9E-3	1.3E+0	3.8E-3
1.0E+0	1.0E+0	2.0E-3	9.0E-1	1.8E-3	2.0E+0	5.6E-3
3.2E+0	1.0E+0	2.0E-3	7.5E-1	1.5E-3	3.6E+0	1.0E-2
1.0E+1	1.0E+0	2.0E-3	5.0E-1	1.0E-3	6.3E+0	1.8E-2
3.2E+1	9.9E-1	2.0E-3	2.7E-1	5.5E-4	8.4E+0	2.4E-2
1.0E+2	9.6E-1	1.9E-3	1.5E-1	3.1E-4	8.0E+0	2.3E-2
3.2E+2	8.9E-1	1.8E-3	1.1E-1	2.1E-4	5.7E+0	1.6E-2
1.0E+3	7.3E-1	1.5E-3	9.1E-2	1.8E-4	3.3E+0	9.2E-3
3.2E+3	4.9E-1	9.7E-4	8.6E-2	1.7E-4	2.0E+0	5.6E-3
1.0E+4	2.7E-1	5.5E-4	8.4E-2	1.7E-4	1.5E+0	4.2E-3
3.2E+4	1.7E-1	3.3E-4	8.4E-2	1.7E-4	1.3E+0	3.8E-3
1.0E+5	1.3E-1	2.5E-4	8.4E-2	1.7E-4	1.3E+0	3.6E-3
3.2E+5	1.1E-1	2.2E-4	8.3E-2	1.7E-4	1.3E+0	3.6E-3
1.0E+6	1.1E-1	2.1E-4	8.4E-2	1.7E-4	1.3E+0	3.6E-3

Table 2
Activities of the radium isotopes and their activity ratio vs. reciprocal of the radium adsorption coefficients, calculated by MC

^{226}Ra, ^{228}Ra activities and their activity ratios vs. radium adsorption						
$1/k_{ad}$ [years]	**^{226}Ra act. [relative]**	**uncertainty**	**^{228}Ra act. [relative]**	**uncertainty**	**^{226}Ra/^{228}Ra act. ratio**	**uncertainty**
1.0E+0	5.0E-5	1.0E-7	8.8E-3	1.8E-5	5.7E-3	1.6E-5
3.2E+0	1.4E-4	2.7E-7	2.3E-2	4.6E-5	5.9E-3	1.7E-5
1.0E+1	4.7E-4	9.5E-7	4.6E-2	9.2E-5	1.0E-2	2.9E-5
3.2E+1	1.4E-3	2.8E-6	6.6E-2	1.3E-4	2.1E-2	6.1E-5
1.0E+2	4.4E-3	8.7E-6	7.7E-2	1.5E-4	5.7E-2	1.6E-4
3.2E+2	1.2E-2	2.5E-5	8.1E-2	1.6E-4	1.5E-1	4.3E-4
1.0E+3	3.1E-2	6.3E-5	8.3E-2	1.7E-4	3.8E-1	1.1E-3
3.2E+3	6.0E-2	1.2E-4	8.3E-2	1.7E-4	7.2E-1	2.0E-3
1.0E+4	8.5E-2	1.7E-4	8.3E-2	1.7E-4	1.0E+0	2.9E-3
3.2E+4	9.7E-2	1.9E-4	8.3E-2	1.7E-4	1.2E+0	3.3E-3
1.0E+5	1.0E-1	2.0E-4	8.3E-2	1.7E-4	1.2E+0	3.4E-3

The relationship between the concentrations of radium isotopes and the uranium desorption coefficient is presented in Figure 6, where only the increase of ^{226}Ra concentration can be observed. In groundwater the positive correlation between U and Ra is very rarely met, since between ^{238}U and ^{226}Ra there are two thorium isotopes (^{234}Th, ^{230}Th, cf. uranium series), which occur as the compounds insoluble in water. On the other hand the chemical properties of uranium significantly differ from that of radium. The positive correlation between ^{238}U and ^{226}Ra can be met only in the experimental conditions, where both uranium and radium isotopes are present in the minerals which easily undergo leaching (Nguyen & Chruściel 2007). There is no special figure for adsorption of uranium, as the concentrations of both radium isotopes are low and almost constant. The numerical data presented in Figure 6, together with their statistical errors, are shown in Table 3.

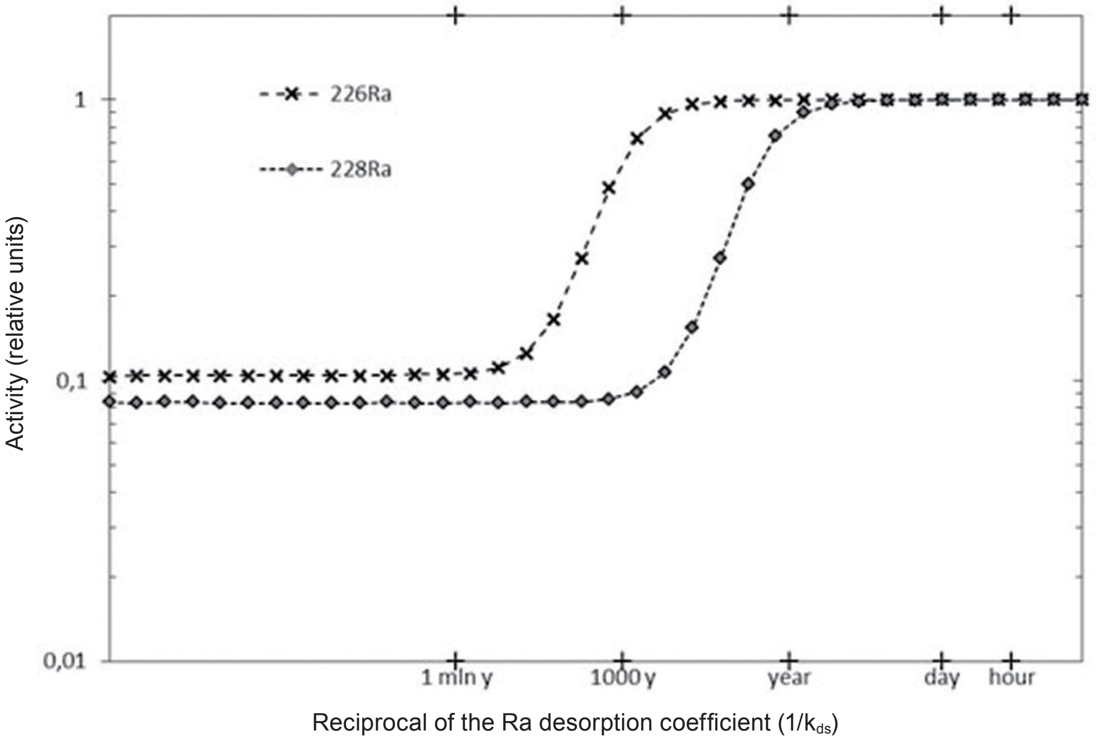

Fig. 2. *Relation between relative activity concentrations of* ^{226}*Ra,* ^{228}*Ra and the reciprocal of the radium desorption coefficient*

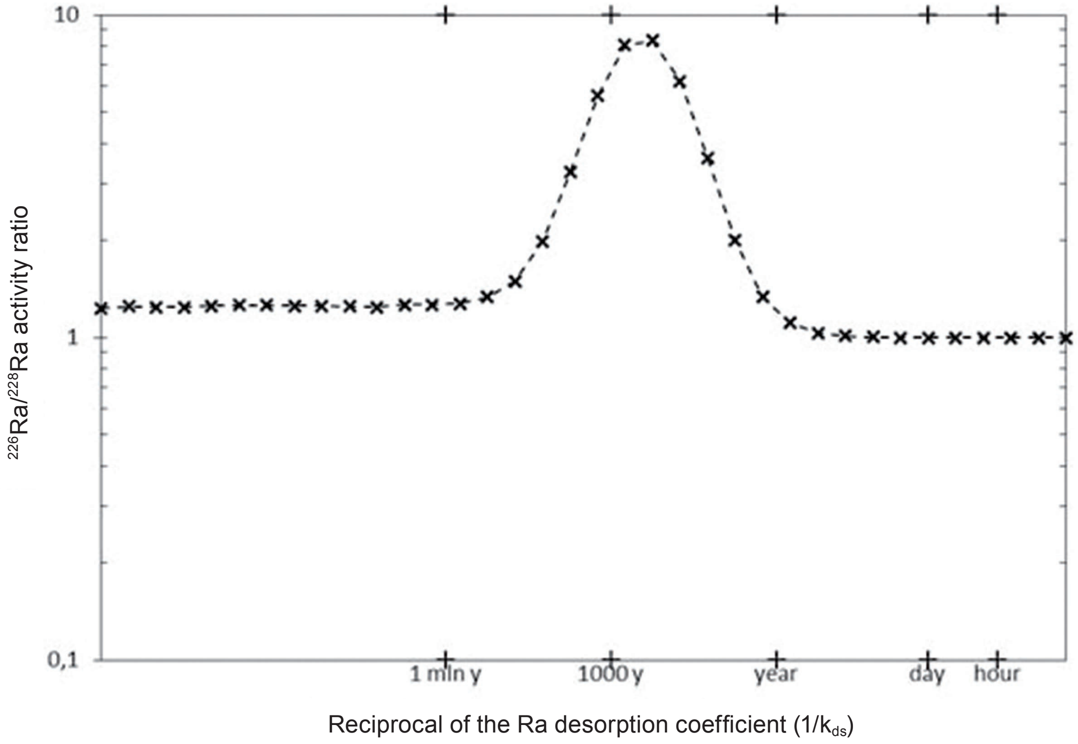

Fig. 3. *Relation between the activity ratio of radium isotopes (*^{226}*Ra/*^{228}*Ra) and the reciprocal of the radium desorption coefficient*

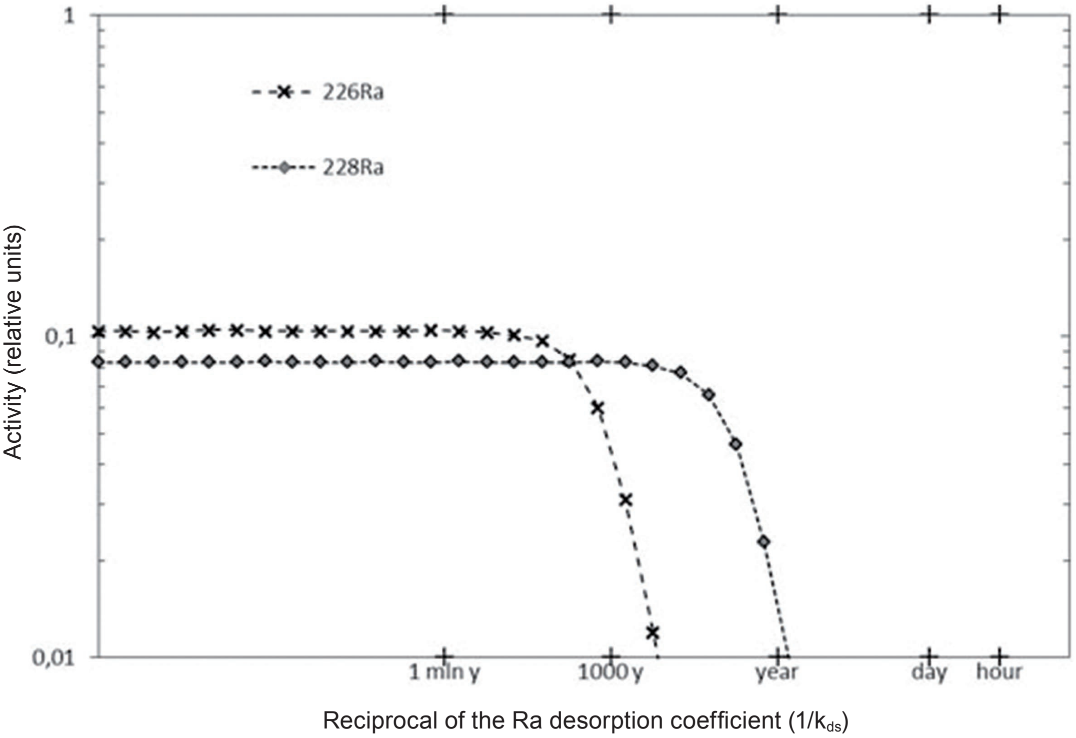

Fig. 4. *Relation between the relative activity concentrations of ^{226}Ra, ^{228}Ra and the reciprocal of the radium adsorption coefficient*

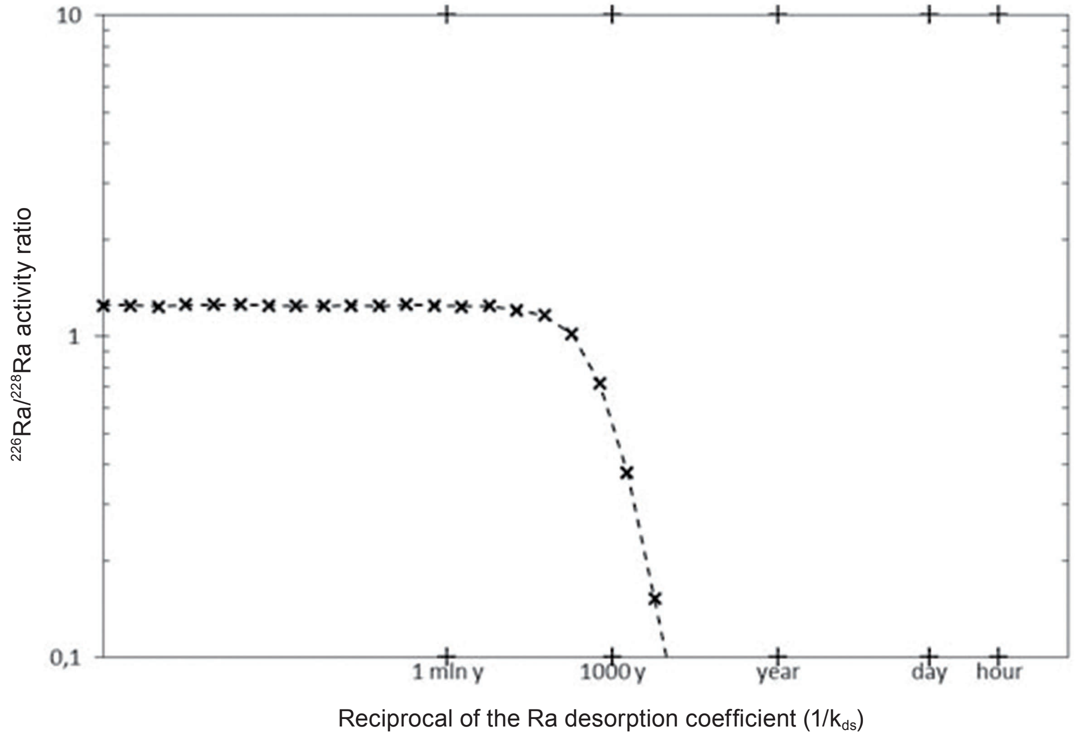

Fig. 5. *Relation between the activity ratio of radium isotopes (^{226}Ra/^{228}Ra) and the reciprocal of the radium adsorption coefficient*

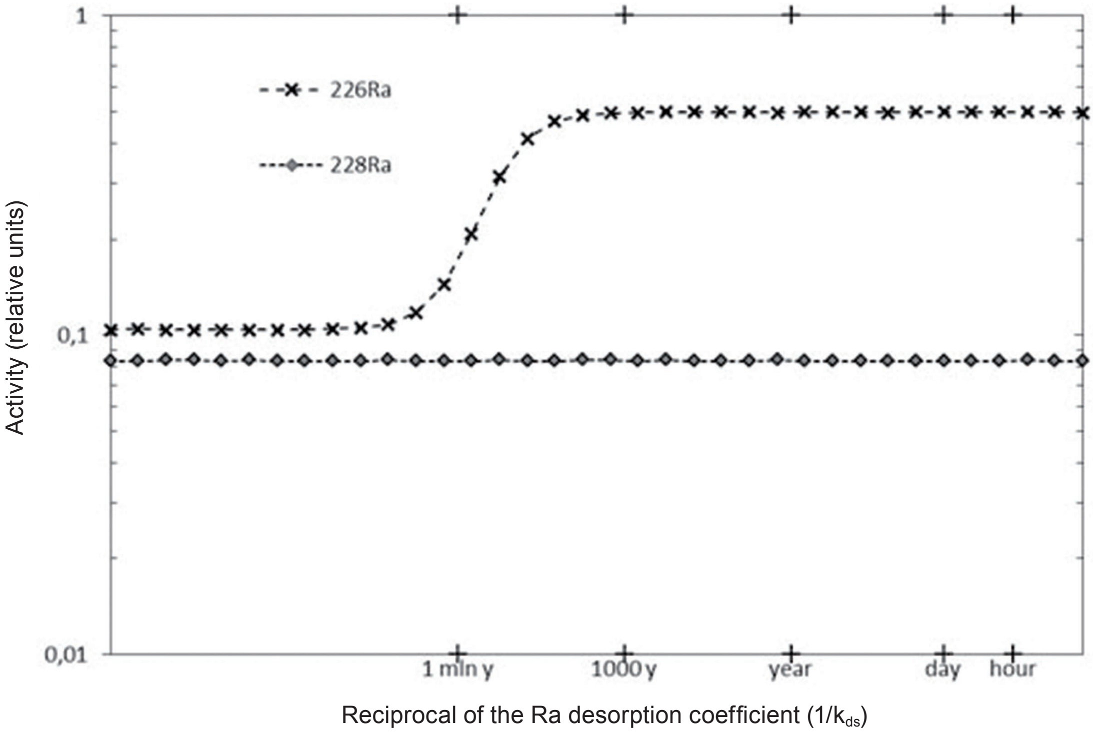

Fig. 6. *Relation between the relative activity concentrations of ^{226}Ra, ^{228}Ra and the reciprocal of the uranium desorption coefficient*

Table 3
Activities of the radium isotopes vs. reciprocal of the uranium desorption/adsorption coefficients, calculated by MC

Radium activity vs. uranium desorption				
U 1/k_{ds} [years]	**^{226}Ra act. [relative]**	**uncertainty**	**^{228}Ra act. [relative]**	**uncertainty**
1.0E+3	5.0E-1	1.0E-3	8.3E-2	1.7E-4
3.2E+3	5.0E-1	9.9E-4	8.4E-2	1.7E-4
1.0E+4	4.9E-1	9.8E-4	8.4E-2	1.7E-4
3.2E+4	4.7E-1	9.4E-4	8.3E-2	1.7E-4
1.0E+5	4.1E-1	8.3E-4	8.3E-2	1.7E-4
3.2E+5	3.1E-1	6.3E-4	8.4E-2	1.7E-4
1.0E+6	2.1E-1	4.2E-4	8.3E-2	1.7E-4
3.2E+6	1.4E-1	2.9E-4	8.3E-2	1.7E-4
1.0E+7	1.2E-1	2.4E-4	8.3E-2	1.7E-4
3.2E+7	1.1E-1	2.2E-4	8.4E-2	1.7E-4
Radium activity vs. uranium adsorption				
U 1/k_{ad} [years]	**^{226}Ra act. [relative]**	**uncertainty**	**^{228}Ra act. [relative]**	**uncertainty**
1.0E+0	1.0E-1	2.1E-4	8.3E-2	1.7E-4
3.2E+0	1.0E-1	2.1E-4	8.3E-2	1.7E-4
…				
1.0E+7	1.0E-1	2.1E-4	8.4E-2	1.7E-4
3.2E+7	1.0E-1	2.1E-4	8.3E-2	1.7E-4

Since all the thorium and actinium compounds are practically insoluble in water, their adsorption and desorption do not affect the radium isotope concentration in groundwater.

Some remarks on the results of MC simulation. When the uranium and thorium activity concentrations in the aquifer are at the same level, from the results of the MC simulations the following conclusions can be made:

- if alpha recoil is the sole mechanism responsible for the migration of nuclei (desorption/adsorption neglected), the radium isotope activity ratio (^{226}Ra/^{228}Ra) in groundwater is close to 1.2;
- concentrations of radium isotopes and their activity ratio in groundwater increase with a growing desorption coefficient but decrease with an increasing adsorption coefficient;
- since many thorium and actinium compounds are practically insoluble in water, their influences on the radium isotope concentration in groundwater are not observed.

ACTIVITY CONCENTRATIONS OF RADIUM ISOTOPES IN MINERAL WATERS OF VARIOUS HYDROCHEMICAL TYPES IN THE POLISH OUTER CARPATHIANS

Geological setting

The Polish Outer Carpathians are situated in the south-east of Poland. This region, with an area of about 19,000 km^2 and constituting only 6% of Poland, contains rich resources of mineral waters of high quality (Fig. 7). The Outer Carpathians are built of Paleocene flysch series composed of sandstones, mudstones, shales and conglomerates. Most of the aquifers with mineral waters are Paleocene sandstones (Porowski 2006). The porosity of the water-bearing formations ranges from a few percent to above ten percent, and the rocks are intersected by many fissures through which groundwater can migrate and in which it can be retained. This is a reason that the Polish Outer Carpathians are so rich in mineral waters and, from the hydrochemical point of view, the waters in this region are mainly bicarbonate waters, subordinately they belong to the chloride or sulfate types (Paczyński & Płochniewski 1996, Chowaniec 1998). The TDS of the waters varies from a few hundred miligrams per liter to several dozen grams per liter. The uranium and thorium mass concentrations in the host Paleocene aquifers range from 1.07 ppm (13.2 Bq/L) to 1.98 ppm (24.5 Bq/L) and from 4.3 ppm (15.2 Bq/kg) to 5.88 ppm (20.8 Bq/kg), respectively (Plewa & Plewa 1992). These ranges of activity concentrations are equivalent to the ratios of the uranium-thorium activity concentrations (^{238}U/^{232}Th) from 0.53 to 1.2.

Analytical techniques

In the period 2006–2008, mineral water samples from several dozen water intakes from the Outer Carpathians were collected (see Fig. 7). For every water sample the TDS, chemical composition and radium isotopes were analyzed. Water TDS and chemical composition were determined using the ICP-AES 40 and multi-element standard solution of Merck® company. The cooling argon gas flow rate of 14 L/min was used for the induced couple plasma instrument, the power of 1350 W for reflected RF. Both auxiliary gas and nebulizer flow rate amounted to 1.0 L/min, water sample uptake of 0.8 mL/min. Depending on the element, the low limit detection varied from a few ppb to ppm with 3% of uncertainty (Murray et al. 2000, Oliveira & Sarkis 2001).

The water sample of five liters of volume was reduced to nearly one liter by evaporation at 80°C, then the radium isotopes were co-precipitated together with barium carrier as a sulfate compound. To eliminate ^{210}Pb from the obtained sample, the precipitate was washed and dissolved in EDTA solution, the radium was again precipitated by adding acetic acid. The precipitate was washed using distilled water and centrifuged. Finally, the obtained precipitate near 0.5 g of mass was placed in the glass vial of 22 mL and mixed with 4 mL distilled water and 12 mL of Instal-Gel plus scintillation cocktail of Perkin Elmer®. The sample was measured every day using alpha/beta spectrometer Quantulus® for two hours, the number of measurements should amount at least 20. The ^{226}Ra and ^{228}Ra were determined using the dependence of alpha and beta count rates on the time elapsed from the preparation ending.

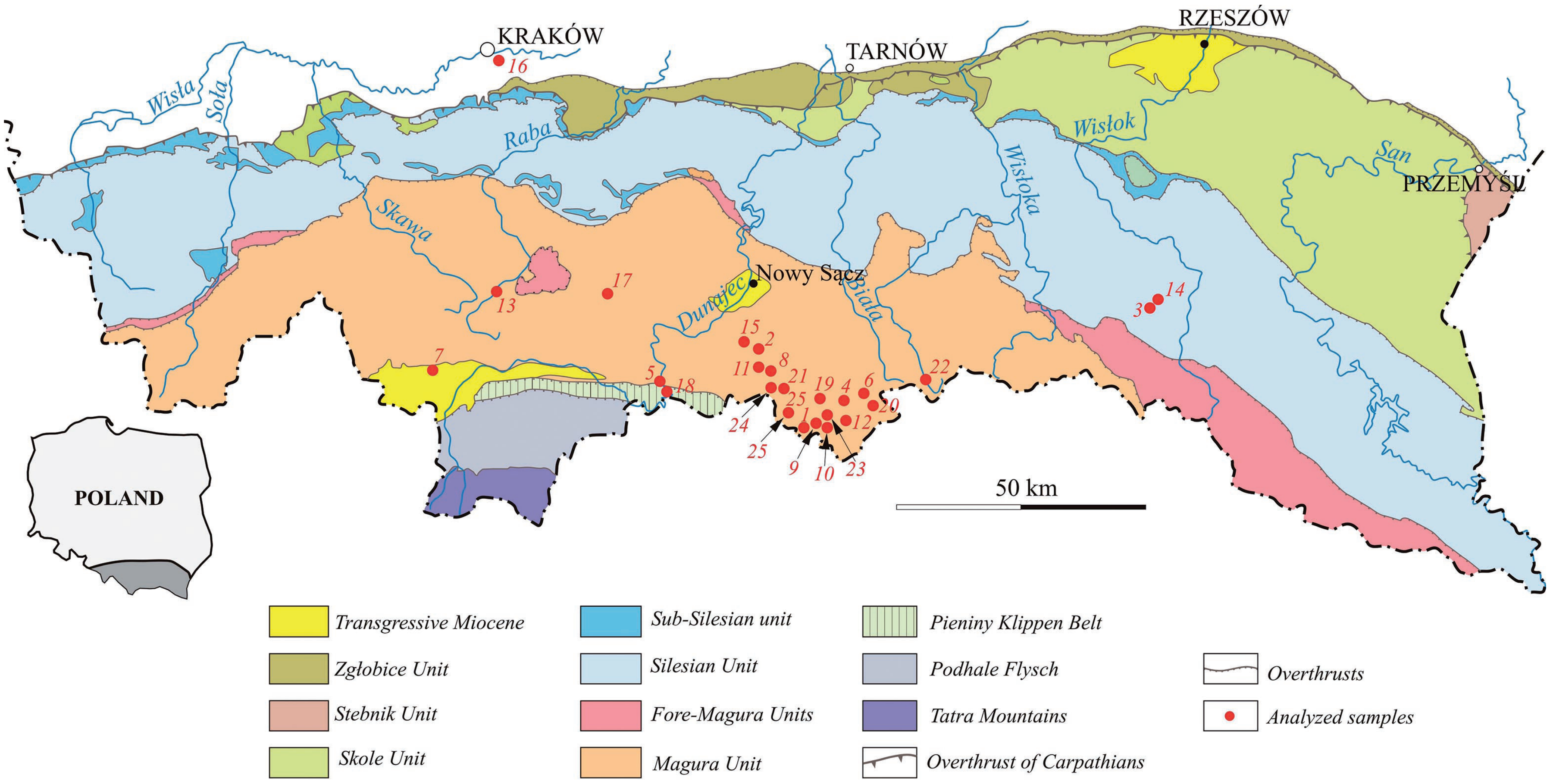

Fig. 7. *Map of the Polish Carpathians with localizations of the studied water intakes: 1 – Andrzejówka, 2 – Głębokie, 3 – Iwonicz-Zdrój, 4 – Jastrzębik, 5 – Krościenko, 6 – Krynica-Zdrój, 7 – Lipnica na Orawie, 8 – Łomnica, 9 – Milik, 10 – Muszyna-Zdrój, 11 – Piwniczna-Zdrój, 12 – Powroźnik, 13 – Rabka-Zdrój, 14 – Rymanów-Zdrój, 15 – Rytro, 16 – Swoszowice, 17 – Szczawa, 18 – Szczawnica, 19 – Szczawnik, 20 – Tylicz, 21 – Wierchomla, 22 – Wysowa-Zdrój, 23 – Złockie, 24 – Zubrzyk, 25 – Żegiestów*

Table 4

Concentrations of the dominating ions [mg/L], activities concentrations of 226Ra and 228Ra [mBq/L] and their activity ratios in the waters studied

Localization and name of the intake	Sample ID	Hydrochemical water type	TDS*	SO_4^{2-}	Cl^-	HCO_3^-	Na^+	Ca^{2+}	Mg^{2+}	^{226}Ra	^{228}Ra	$^{226}Ra/^{228}Ra$
Bicarbonate water												
Jastrzębik G-8	J-55	HCO_3-Ca-Mg	1250	19.5	5.50	918	14.0	222	38.6	15± 2	41 ± 7	0.37 ± 0.08
K-8	K-33	HCO_3-Ca	2650	1.20	1.70	1940	11.5	561	41.8	37 ± 4	65 ± 9	0.57 ± 0.10
K-3	K-34	HCO_3-Ca-Mg	3870	4.34	1.90	2880	30.4	729	118	140 ± 11	106 ± 11	1.32 ± 0.17
Jacek	L-25	HCO_3-Ca-Na	500	56.6	41.7	264	38.6	70.3	14.9	21 ± 3	26 ± 5	0.81 ± 0.19
SL-3	Sz-61	HCO_3-Ca-Mg	900	23.7	8.60	640	49.2	114	37.9	22 ± 2	58 ± 6	0.38 ± 0.05
Hanna	W-16	HCO_3-Ca-Mg	1690	0.40	2.10	1250	71.7	254	63.2	113 ± 9	66 ± 6	1.71 ± 0.21
Złockie 8	Z-54	HCO_3-Ca-Mg	1130	20.5	3.70	828	49.8	164	33.5	45 ± 5	65 ± 9	0.69 ± 0.12
Anna	Ż-47	HCO_3-Ca-Mg	2570	17.0	8.70	1910	28.0	445	116	32 ± 3	46 ± 6	0.70 ± 0.11
Słomniczanka	Ł-9	HCO_3-Ca-Mg	2500	1.84	1.60	1870	44.6	446	75.3	65 ± 5	120 ± 11	0.57 ± 0.06
Górne	Ł-10	HCO_3-Ca-Mg	2240	5.10	7.20	1660	34.5	420	65.0	65 ± 6	97 ± 17	0.67 ± 0.13
Stanisław	Ł-11	HCO_3-Ca-Mg	2900	0.10	11.0	2160	133	401	115	117 ± 8	171 ± 15	0.68 ± 0.08
P-1	M-49	HCO_3-Ca-Mg	620	33.0	25.0	399	18.4	102	28.6	6 ± 1	18 ± 3	0.33 ± 0.08
P-2	M-50	HCO_3-Mg-Ca	1840	32.0	13.3	1380	54.5	158	174	24 ± 3	36 ± 5	0.67 ± 0.12
Łukasz	M-51	HCO_3-Ca-Mg	720	33.0	12.6	498	16.2	119	33.1	12 ± 2	21 ± 3	0.57 ± 0.13
Grunwald	M-56	HCO_3-Ca-Mg	2390	13.8	9.10	1800	90.0	332	104	31 ± 5	74 ± 8	0.42 ± 0.08
Józef	M-59	HCO_3-Ca-Mg	1200	30.5	7.70	873	17.1	193	49.1	12 ± 1	40 ± 5	0.30 ± 0.05
Stanisław	M-60	HCO_3-Ca	2730	55.0	13.9	1970	6.10	557	66.5	4 ± 1	12 ± 3	0.33 ± 0.12
Piwniczanka-5	P-21	HCO_3-Ca-Mg	1150	47.1	14.2	798	64.0	139	52.4	22 ± 3	31 ± 4	0.71 ± 0.13
Piwniczanka-6	P-22	HCO_3-Ca-Mg	1240	67.9	12.9	853	55.6	160	54.4	15 ± 2	21 ± 3	0.71 ± 0.14
Piwniczanka-11	P-24	HCO_3-Ca-Mg	1180	29.7	9.20	848	48.3	160	49.3	96 ± 8	73 ± 7	1.32 ± 0.17
P-I	P-57	HCO_3-Ca-Mg	2430	21.3	11.9	1780	88.8	408	71.2	31 ± 3	74 ± 8	0.42 ± 0.06
P-III	P-58	HCO_3-Ca	2250	6.30	8.40	1660	47.3	434	45.3	30 ± 3	60 ± 7	0.50 ± 0.08
Min			500	0.1	1.6	264	6.1	70.3	14,9	4	12	0.3
Max			3870	67.9	41.7	2880	155	729	196	140	171	1.71
Average			1876	23.1	10.4	1326	50.7	299.7	71.4	45.8	62.7	0.70
Chloride water												
Sól-źr. Warzelnia	S-15	Cl-Na	41370	0.2	23600	886	15720	320	89.6	1280 ± 130	1240 ± 190	1.03 ± 0.19
Iwonicz Emma	J-2	Cl-Na	4280	0.2	1480	1220	1430	37	8.5	156 ± 14	100 ± 26	1.56 ± 0.43
Iwonicz -Elin	J-3	Cl-Na	5440	0.2	1950	1440	1870	34	8.4	156 ± 12	86 ± 21	1.81 ± 0.46
Iwonicz -Iza 19	J-7	Cl-Na	832	2.6	66.7	472	185	36.6	8.5	82 ± 6	19 ± 5	4.3 ± 1.20
Klimkówka 25	J-8	Cl-Na	13020	0.2	2850	5950	4090	19.5	28.3	415 ± 16	158 ± 50	2.63 ± 0.84
Lubatówka 14	J-9	Cl-Na	18770	0.2	7750	3970	6590	40	37	1340 ± 70	893 ± 220	1.50 ± 0.38
Rymanów C	R-13	Cl-Na	6230	0.2	915	3210	1940	7.6	3.0	753 ± 29	624 ± 140	1.20 ± 0.27
Rymanów Rz-4	R-15	Cl-Na	6170	0.2	1651	2240	2030	39	5.2	198 ± 10	26 ± 10	7.6 ± 2.9
Siary	L-27	Cl-Na	2700	21.1	1500	178	8800	63.5	20.7	169 ±19	130 ± 20	1.30 ± 0.25
Warzelnia	R-38	Cl-Na	13100	6.54	6550	1280	4780	46.5	23.3	246 ± 18	207 ± 19	1.19 ± 0.14
Helena	R-42	Cl-Na	17400	3.93	9700	750	6670	31.7	27.0	243 ± 18	190 ± 17	1.28 ± 0.15
Rabka-19	R-40	Cl-Na	19700	3.10	10500	1320	7400	49.2	33.6	334 ± 25	376 ±32	0.89 ± 0.10
Krakus	R-39	Cl-Na	21400	17.1	11400	1360	7880	78.5	41.0	384 ± 27	292 ±24	1.32 ± 0.14
Rabka-18	R-41	Cl-Na	24600	3.27	13500	1310	9010	70.6	38.6	638 ± 43	616 ± 47	1.04 ± 0.11
Min			832	0.2	66.7	178	185	7.6	3	82	19	0.89
Max			41370	21.1	23600	5950	15720	320	89.6	1340	1240	7.6
Average			13929	4	6672	1828	5600	62	27	456.7	354.1	2.0
Sulfate waters												
Napoleon	S-12	SO_4-Ca-Mg	2220	1220	2.50	350	62.3	430	98.4	4 ± 1	41 ± 9	0.10 ± 0.03
Główny	S-13	SO_4-Ca-Mg	2380	1280	24.8	380	41.4	499	92.4	3 ± 1	54 ± 9	0.06 ± 0.02
Oaza		HCO_3-SO_4-Ca	260	23	5	171	2	52	7	0.8 ± 0.1	8.2 ± 1.1	0.10 ± 0.02
Kinga		HCO_3-SO_4-Ca	490	28	7	336	5	98	13	3.2 ± 0.4	5.3 ± 0.7	0.60 ± 0.11
Kazimierka		HCO_3-SO_4-Ca	560	35	7	388	10	88	29	0.8 ± 0.1	5.0 ± 0.5	0.16 ± 0.03
Hermes		HCO_3-SO_4-Ca	504	117	36	214	10	109	17	3.8 ± 0.4	17.8 ± 2.3	0.21 ± 0.04
Jan		HCO_3-SO_4-Ca	790	51	18	525	15	152	25	9.3 ± 1.0	9.2 ± 1.0	1.00 ± 0.15
Min			260	23	5	171	2	52	7	0.8	5.3	0.1
Max			2380	1280	36	525	15	409	29	9.3	54.0	1.0.
Average			1029	393.4	14.6	337.7	8.4	204	18.2	3.6	20.1	0.3

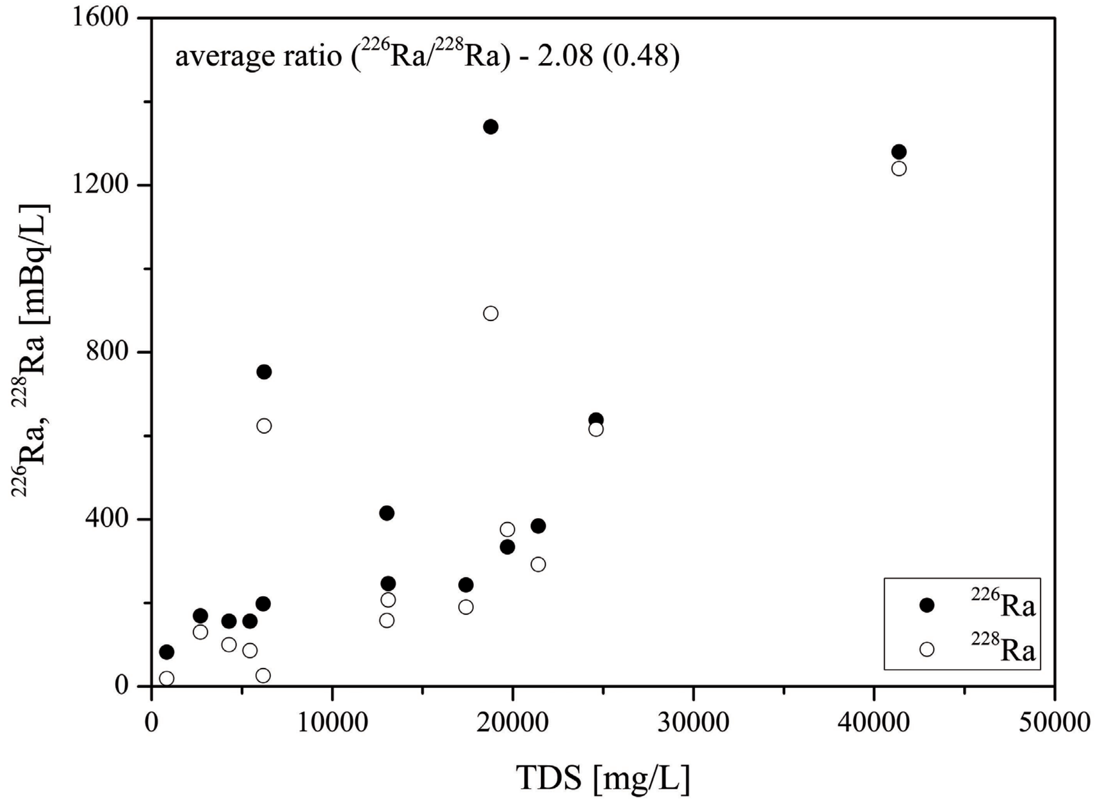

Fig. 8. *Relation between the activity concentrations of radium isotopes and TDS in the chloride waters of the Polish Carpathians*

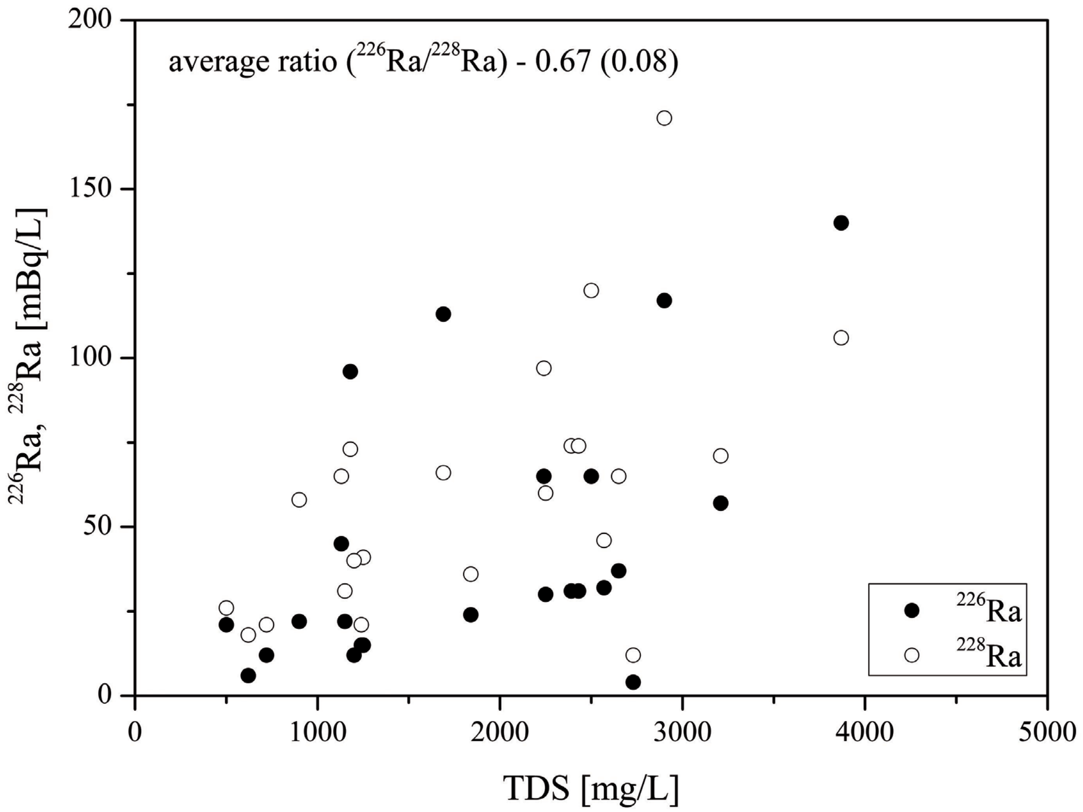

Fig. 9. *Relation between the activity concentrations of radium isotopes and TDS in the bicarbonate waters of the Polish Carpathians*

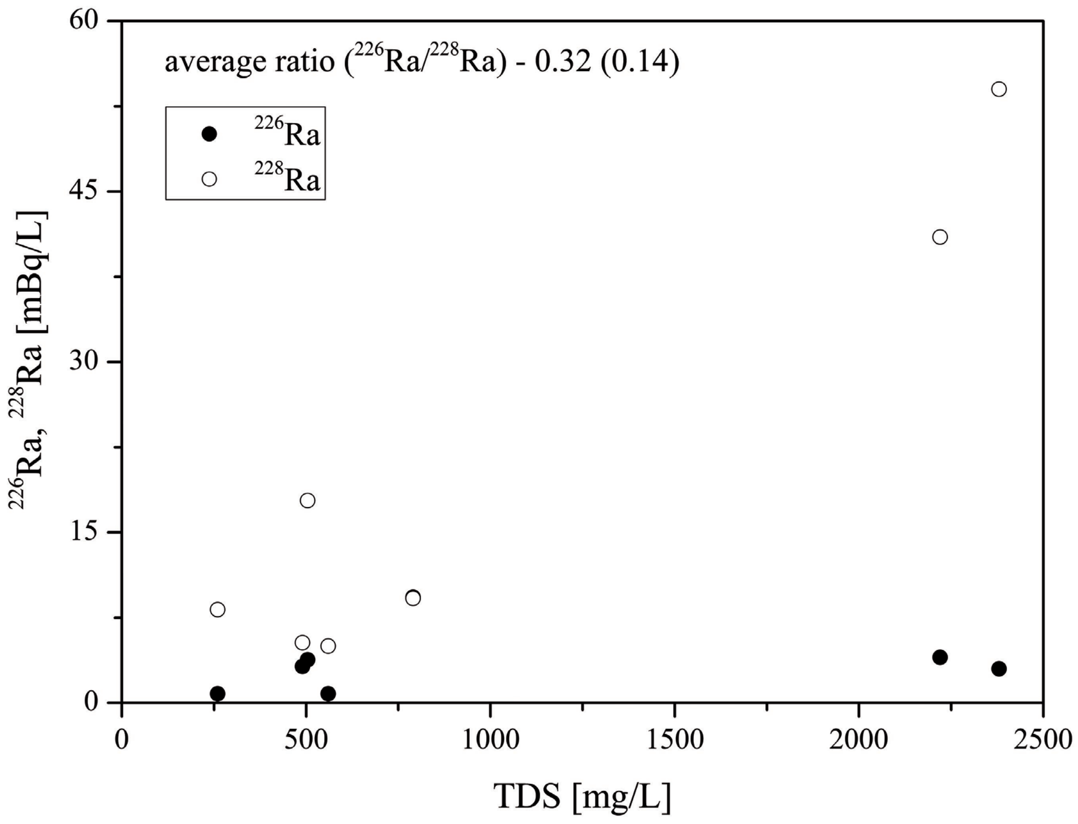

Fig. 10. *Relation between the activity concentrations of radium isotopes and TDS in sulfate waters of the Polish Carpathians*

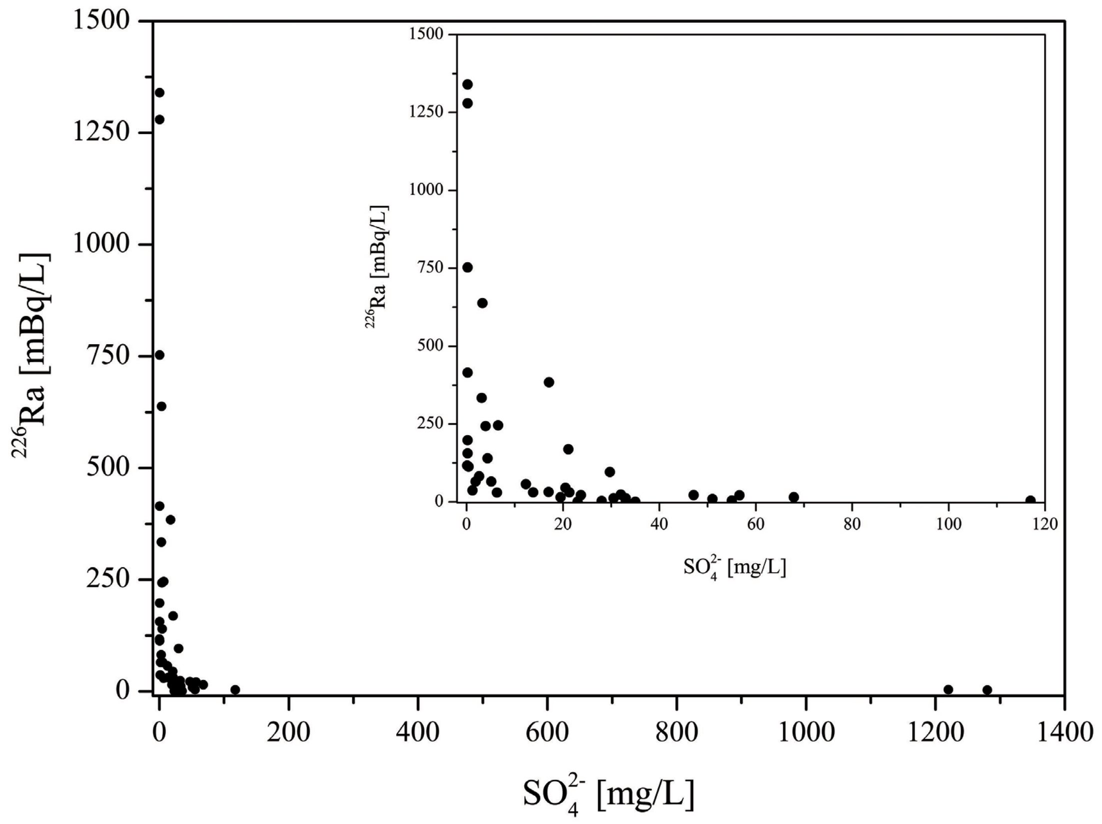

Fig. 11. *Relation between the ^{226}Ra activity concentrations and the SO_4^{2-} concentration in mineral waters of the Polish Carpathians*

The limit of detection and relative uncertainty amount to 5 mBq/sample and near 10% and 10 mBq/sample and near 15% for ^{226}Ra and ^{228}Ra respectively. The preparing, measuring and calculating the contents of radium isotopes in water samples are described by Nguyen et al. (1997).

Results and discussion

The hydrochemical types, pH of water, concentrations of major ions, TDS contents, concentrations of radium isotopes and their activity concentration ratios in the water samples are presented in Table 4. These data show that the TDS, as well as concentrations of radium isotopes, are the highest in the chloride-sodium waters, medium in the bicarbonate waters and the lowest in the sulfate waters. The relations between the radium isotope concentration and TDS for the chloride, bicarbonate and sulfate waters are presented in Figures 8–10, respectively. The average activity ratio amounts to 2.0, 0.70 and 0.30 for chloride, bicarbonate and sulfate water types, respectively. These results are probably attributed to the desorption/adsorption factors of the waters investigated. The largest desorption and the least adsorption factors have been established for the chloride water types, the medium factors for the bicarbonate water types, and the least desorption and the largest adsorption for the sulfate water types. The observed phenomena confirms the results of the MC simulations (cf. chapter "The MC simulation results and discussion"). The TDS, as well as the radium concentration of the mineral water, decreases with an increasing SO_4^{2-} concentration (Fig. 11). This fact is connected with the insolubility of many sulfate compounds.

CONCLUSIONS

The concentrations of radium isotopes and their activity ratios in the groundwater are useful in various scientific and practical fields, for instance in the determination of mixing zones, in estimations of the sedimentation rates, and in the appraisal of the committed doses resulting from drinking mineral waters.

Based on the investigations carried out in this work, the following conclusions can be drawn:

1. in the groundwater of moderate desorption and adsorption coefficients, the radium isotope activity ratio (^{226}Ra/^{228}Ra) should reflect the ratio of the activity concentrations of uranium and thorium (^{238}U/^{232}Th) in host aquifer rocks;
2. the ^{226}Ra and ^{228}Ra activity concentrations and their ratio depend not only on the uranium and thorium concentrations in the aquifer rocks, but also on the desorption/adsorption properties of the groundwater;
3. for the mineral Polish Carpathian waters, the radium isotope activity concentrations and their ratio are the highest in chloride waters, medium in the bicarbonate waters and the lowest in the sulfate waters;
4. for the mineral waters of the Polish Carpathians, the TDS values and the concentrations of radium isotopes decrease with an increasing SO_4^{2-} concentration.

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