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The occurrence of ^{226}Ra and ^{228}Ra in groundwaters of the Polish Sudety Mountains

Tadeusz A. Przylibski,
Jerzy Dorda,
Beata Kozłowska

Abstract The paper presents preliminary measurement results of the concentrations of ^{226}Ra and ^{228}Ra isotopes in the groundwaters of the Polish part of the Sudety Mountains. The analysis of sampling results for water from 55 intakes showed that the average concentrations amount to 0.144 Bq/dm^3 for ^{226}Ra and 0.083 Bq/dm^3 for ^{228}Ra, while the extreme values reach 0.007 and 0.92 Bq/dm^3 for ^{226}Ra, and 0.004 and 0.4 Bq/dm^3 for ^{228}Ra. The activity ratio ^{228}Ra/^{226}Ra in the examined groundwaters ranges between 0.099 and 2.059. The result of the conducted research implies that the highest concentrations of ^{226}Ra and ^{228}Ra occur in the waters with the highest general mineralization (the highest values of total dissolved solids (TDS)).

Key words groundwaters • radium • radium waters • the Sudety Mountains • TDS (total dissolved solids)

T. A. Przylibski✉
Faculty of Mining, Division of Geology and Mineral Waters,
Wrocław University of Technology,
27 Wybrzeże S. Wyspiańskiego, 50-370 Wrocław, Poland,
Tel.: +48 71/ 320 68 12, Fax: +48 71/ 344 27 46,
e-mail: tadziop@chaos.ig.pwr.wroc.pl

J. Dorda, B. Kozłowska
Institute of Physics,
Department of Nuclear Physics and Its Applications,
University of Silesia,
4 Uniwersytecka Str., 40-007 Katowice, Poland

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Introduction

The Sudety Mountains are the region of Poland where rocks containing enhanced concentrations of natural radioactive elements occur on the surface or at small depths. Groundwaters flowing through these rocks also contain considerable amounts of dissolved radioactive isotopes, especially radon (^{222}Rn in particular). Consequently, the Sudety Mts. are known for numerous outflows and intakes of groundwaters with significantly increased concentrations of this radioactive gas. Until recently, these waters were wrongly called radioactive, which was also suggested in previous papers [9]. Therefore, in order to characterize the hydrogeochemistry of these waters, it is also important to know the contents of two radium isotopes – ^{226}Ra and ^{228}Ra in these waters. It is especially important as the determinations of the content of these isotopes in groundwaters from the whole Polish part of the Sudety Mts. mentioned in the literature are scarce and scattered, and often isolated [6, 8, 10, 12–14]. These data are insufficient to be fully interpreted without the knowledge of the hydrogeochemical background and a more complete description of radium occurrence in the groundwaters of this region.

Depending on the kind of rock, the type of groundwater and its flow mode, the water can dissolve varying amounts of radium, whose isotopes are formed in all natural radioactive series. The greatest importance in the environment is that of ^{226}Ra (with the longest half-life $T_{1/2}$=1600 years) and ^{228}Ra ($T_{1/2}$=5.76 years) isotopes. The latter is usually in equilibrium with ^{224}Ra ($T_{1/2}$=3.66 days), subsequent in the thorium series. The ^{226}Ra and ^{224}Ra nuclides are alpha-radioactive, while ^{228}Ra is beta-radioactive.

In view of considerable changeability of the chemical composition of groundwaters in the area of the Sudety Mts.,

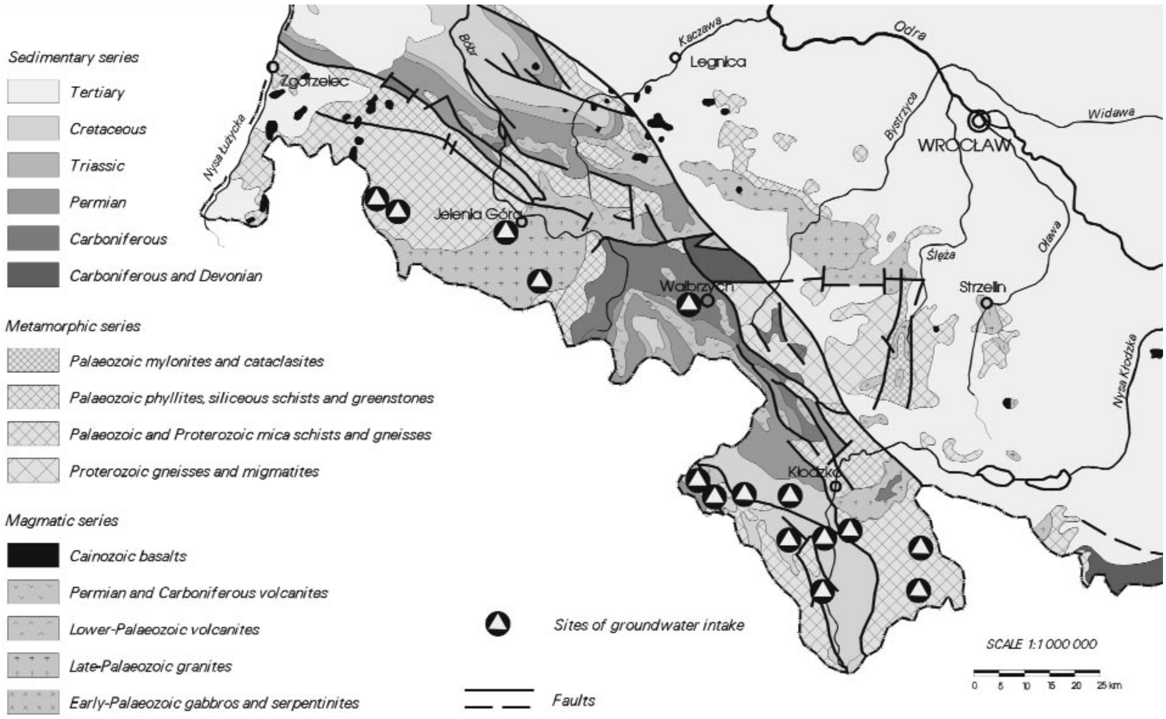

Fig. 1. The distribution of localities where samples of groundwaters were taken for determining ^{226}Ra and ^{228}Ra content, on the background of a simplified geological map of Lower Silesia.

the present authors selected for their research groundwaters extracted or flowing to the surface from different depths, different rocks (with respect to their age and petrologic type), characterized by varying general mineralization – TDS (total dissolved solids), classified within different chemical types and varying in temperature, mean underground flow time (age) and flowing out (or extracted) with varying discharge. Up to now, 55 groundwater springs and intakes from the area of 15 localities in the Polish part of the Sudety Mts. have been examined (Fig. 1). The groundwaters to be analyzed were selected in the way that could enable obtaining possibly wide value range of the aforementioned parameters. The variability range of particular parameters characterizing the examined groundwaters from different intakes and springs have been presented in Table 1, on the basis of the literature data [3, 7, 10–12], archival data from health resorts (Uzdrowisko Świeradów – Czerniawa Sp. z o.o., Uzdrowisko Cieplice Sp. z o.o., Uzdrowisko Szczawno – Jedlina S.A., Zespół Uzdrowisk Kłodzkich S.A., Uzdrowisko Lądek – Długopole S.A.) and data obtained from Prof. Wojciech Ciężkowski (Z.B.U. Zdroje, Wrocław).

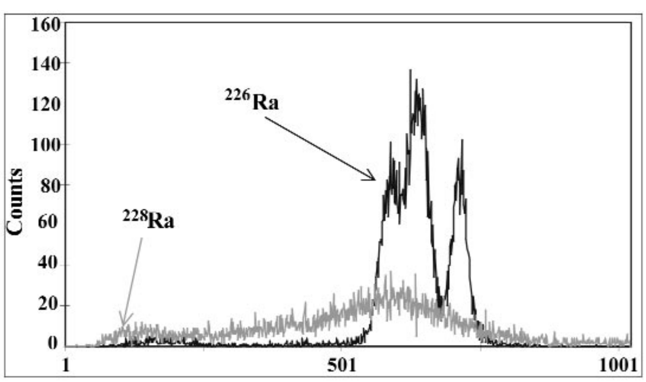

Fig. 2. The pulse-height radium spectrum obtained for the spring water sample Jan Kazimierz (Duszniki Zdrój).

Method of determining ^{226}Ra and ^{228}Ra concentrations

In order to determine the content of radium isotopes in the groundwaters of the analysed intakes, 5 dm^3 samples were taken twice or three times at minimum 6-month intervals. The liquid-scintillation technique was used to measure the contents of ^{226}Ra and ^{228}Ra in the water samples with the use of a 1414WinSpectral α/β counter produced by Wallac. The counter is equipped with a system of electronic separation of impulses coming from α- and β-radioactive isotopes. The system enables simultaneous determination of the activity of isotopes containing both radioactivity components. In order to determine the activity of radium isotopes, the water samples were treated chemically, in compliance with a slightly modified (only EDTA was used as a complexing compound) Polish norm [2]. In this method, radium isotopes are separated from water by co-precipitation with barium and purified of its derivatives. The radium and barium precipitate is then transferred to a scintillation vessel and mixed with a gelling scintillator. The samples prepared in this way were placed in the liquid-scintillation counter. The activity of ^{226}Ra nuclide was determined from the α-radioac-

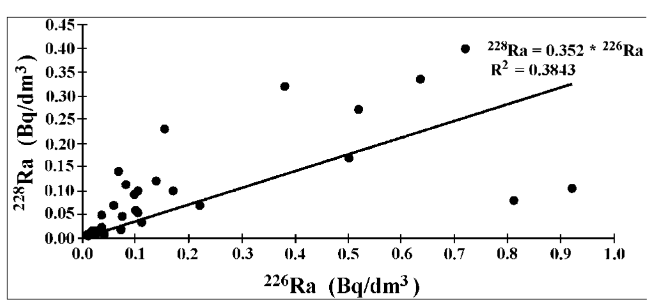

Fig. 3. The concentrations of ^{226}Ra and ^{228}Ra in the groundwaters of the Polish part of the Sudety Mts. and their mutual proportions. The graph presents the value of the linear correlation coefficient (R) and the trend line equation for 55 groundwater springs and intakes.

Table 1. Variability ranges of the selected geological, physical and chemical parameters characterizing the analyzed groundwaters from different springs and intakes. Based on literature data [3, 7, 10–12], health-resorts' archival data (Uzdrowisko Świeradów – Czerniawa Sp. z o.o., Uzdrowisko Cieplice Sp. z o.o., Uzdrowisko Szczawno – Jedlina S.A., Zespół Uzdrowisk Kłodzkich S.A. and Uzdrowisko Lądek – Długopole S.A.) and data obtained from Prof. Wojciech Ciężkowski (Z.B.U. Zdroje, Wrocław).

Parameter		Minimum value		Maximum value	
Depth of the intake	(m u.g.l.)	0	springs	750	Cieplice Śląskie Zdrój
Mineralization (TDS)	(g/dm^3)	0.06	Świeradów Zdrój	3.43	Kudowa Zdrój
Discharge	(m^3/h)	0.03	Szczawno Zdrój	32.9	Gorzanów
Temperature	(°C)	6.7	Kowary	59.5	Cieplice Śląskie Zdrój
Time of the underground flow	(years)	4–5	Świeradów Zdrój	~28000	Cieplice Śląskie Zdrój
Chemical type of water		Considered: acidulous and acido-carbonic waters (CO_2 rich waters), thermal waters and low mineralized waters.			
Type of resorvoir rock		Applied division into: magmatic, sedimentary and metamorphic rocks.			

tivity spectrum component, while the activity of ^{228}Ra – from the β-radioactivity spectrum component [5] (Fig. 2).

Results and discussion

Table 2 contains basic statistical parameters related to the occurrence of both radium isotopes in the groundwaters of the Polish part of the Sudety Mts., as well as their mutual proportions. A considerable range of concentrations, both of ^{226}Ra and ^{228}Ra, is discernible, in both cases reaching two orders of magnitude. As shown in Fig. 3, most of the recorded concentrations of both isotopes are lower than the arithmetic mean value. One can also notice a large number of intakes where ^{226}Ra content is higher than the content of ^{228}Ra. Nevertheless, there are also intakes whose waters contain higher concentrations of ^{228}Ra than ^{226}Ra, which is clearly demonstrated by the value range and the mean value of ^{228}Ra/^{226}Ra activity ratio (Fig. 3, Table 2).

Figure 4 presents the dependence of ^{226}Ra and ^{228}Ra concentrations on the TDS value of the groundwater. The graphs very clearly depict higher concentration values of radium isotopes in the waters with higher TDS values. This means that one should expect higher concentrations of radium isotopes in waters containing large amounts of dissolved mineral substances. On the other hand, no regularity has been noticed in the changes of ^{226}Ra and ^{228}Ra concentration values in relation to the extraction depth of a particular groundwater (Fig. 5), the discharge of the intake (Fig. 6), water temperature (Fig. 7), or the mean underground flow time (the age of the groundwater) (Fig. 8). The apparent regularity in the occurrence of the highest concentration values of radium isotopes in the waters at a temperature over ten degrees Celsius (Fig. 7) results from the fact that such temperatures are characteristic of waters with the highest TDS values in the Sudety Mts. No influence of the kind of reservoir rock or the type of the groundwater on the measured concentration values of ^{226}Ra and ^{228}Ra in the groundwaters of the Polish part of the Sudety Mts. has been noticed, either. The absence of the observed correlations might result from the fact that too few groundwater springs and intakes have been taken into consideration so far. In the case of some groundwater types and some kinds of reservoir rocks, it was only possible to correlate 3 to 7 data.

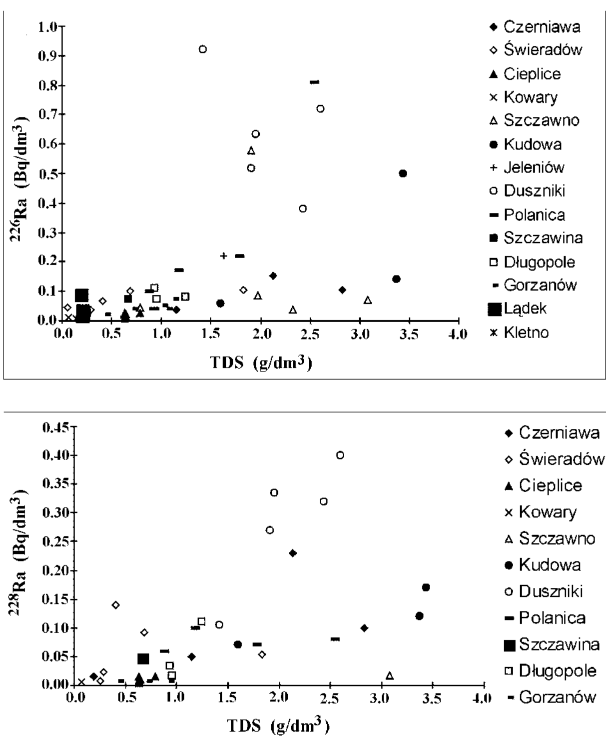

Fig. 4. The correlation between ^{226}Ra and ^{228}Ra concentrations and the TDS value of water for 55 groundwater springs and intakes in the Polish part of the Sudety Mts.

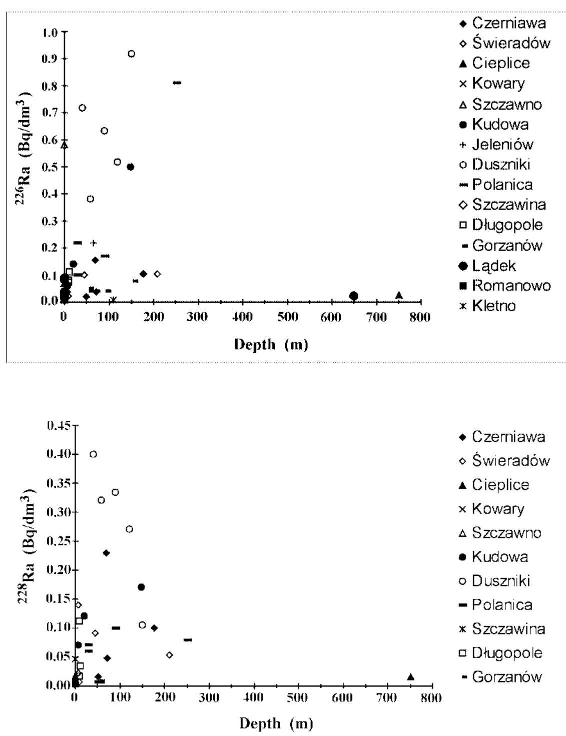

Fig. 5. The correlation between ^{226}Ra and ^{228}Ra concentrations and the depth of water extraction for 55 groundwater springs and intakes in the Polish part of the Sudety Mts.

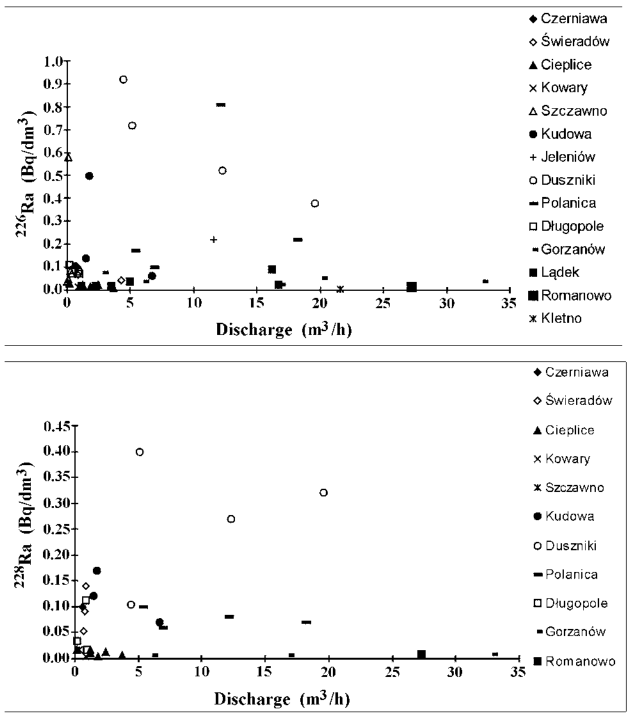

Fig. 6. The correlation between ^{226}Ra and ^{228}Ra concentrations and the discharge of the water intakes for 55 groundwater springs and intakes in the Polish part of the Sudety Mts.

The observed relationship between ^{226}Ra and ^{228}Ra concentrations and the TDS values proves that one may expect larger amounts of dissolved radium in waters with the highest general mineralization, whose value depends, most of all, on its temperature, underground flow time (the impact on the reservoir rocks), capability of dissolving minerals (facilitated e.g. by the presence of dissolved carbon dioxide), as well as on the mineral composition of the reservoir rocks (containing minerals easily or poorly soluble in water). It is possible that the absence of recorded relationships between particular factors influencing the TDS value

Table 2. The content of ^{226}Ra and ^{228}Ra in the analyzed groundwaters of the Polish Sudety Mts.

Nuclide	Minimum	Arithmetic mean	Maximum	Median	Standard deviation
	(Bq/dm^3)				
^{226}Ra	0.007	0.144	0.92	0.051	0.22
^{228}Ra	0.004	0.083	0.4	0.048	0.10
^{228}Ra/^{226}Ra	0.10	0.64	2.06	–	–

of water and the concentrations of ^{226}Ra and ^{228}Ra should be partly attributed to the scanty number of sampled groundwater intakes. Nevertheless, it is also possible that each of these factors has a different influence on the TDS value of groundwaters in particular intakes and springs, at the same time influencing the concentration of radium isotopes. This does not allow the observation of statistically significant correlations between particular factors, considering all the intakes of analyzed groundwaters.

The mean concentration of radium in groundwaters all over the world reaches the order of 10^{-9} mg/dm^3, i.e. 3.7×10^{-2} Bq/dm^3 [1]. The conversion of radium concentration (in mg/dm^3) into its activity (in Bq/dm^3) implies that only the ^{226}Ra nuclide was taken into consideration. In light of the results presented above, this seems problematic. According to currently used classification by Alekin [1], waters containing enhanced radium concentrations – radium waters – can be divided into weak-radium waters (containing up to 10^{-7} mg/dm^3, i.e. up to 3.7 Bq/dm^3 of radium), medium-radium waters (containing from 10^{-7} to 10^{-6} mg/dm^3, i.e. from 3.7 to 37 Bq/dm^3 of radium) and strong-radium waters (containing more than 10^{-6} mg/dm^3, i.e. more than 37 Bq/dm^3 of radium). According to this classification, all the examined groundwaters of the Sudety Mts. belong to weak-radium waters. Nevertheless, it must be noted that this classification requires some modifications. Firstly, the hydrochemical radium background of the Sudety Mts. should be determined to enable the identification of radium waters in general, i.e. the waters

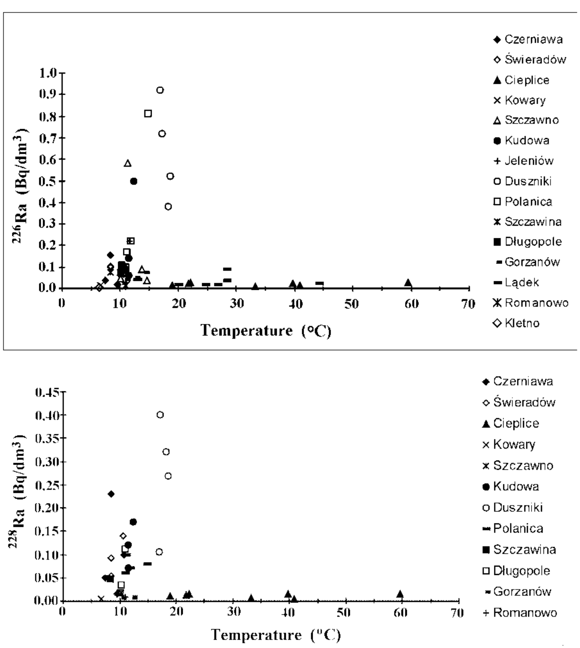

Fig. 7. The correlation between ^{226}Ra and ^{228}Ra concentrations and the temperature of water for 55 groundwater springs and intakes in the Polish part of the Sudety Mts.

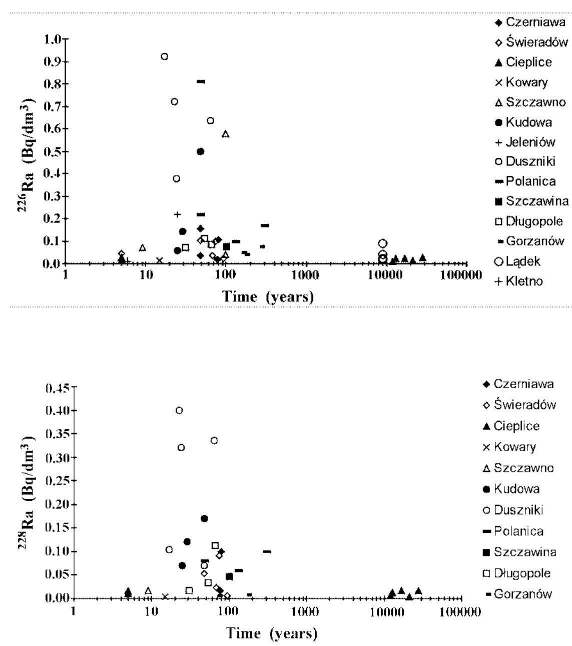

Fig. 8. The correlation between ^{226}Ra and ^{228}Ra concentrations and the mean underground water flow time (water age) for 55 groundwater springs and intakes in the Polish part of the Sudety Mts.

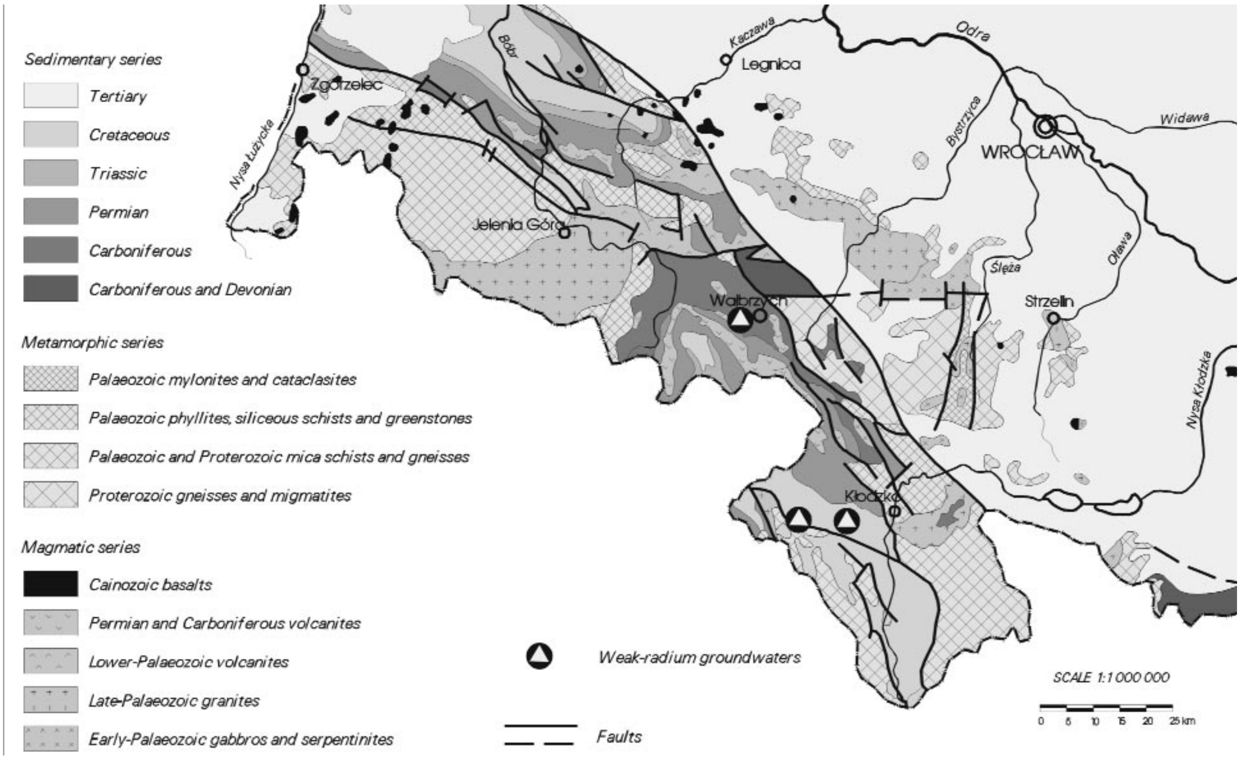

Fig. 9. The occurrence of weak radium groundwaters (with ^{226}Ra concentration between 0.37 and 3.7 Bq/dm^3) in the Polish part of the Sudety Mts., on the background of a simplified geological map of Lower Silesia.

that contain radium concentrations higher than the background value. As no results of such studies are available (they are still in progress), weak-radium waters should be considered the waters including radium concentrations at least one order of magnitude higher than the mean values registered in groundwaters. Then, the waters regarded as weak-radium waters could contain from 10^{-8} to 10^{-7} mg/dm^3, i.e. from 0.37 to 3.7 Bq/dm^3 of radium (or, more specifically, ^{226}Ra nuclide). According to these criteria, weak-radium groundwaters would occur in the Polish part of the Sudety Mts. only in three out of the fifteen localities, in which the research has been conducted (Fig. 9). The waters occurring in the other areas probably contain ^{226}Ra and ^{228}Ra isotopes in the concentrations characteristic of the background of the Sudetic groundwaters. Further research will enable the identification of particular areas within the Sudety Mts., where determining characteristic values of ^{226}Ra and ^{228}Ra concentrations in groundwaters will be possible. A larger number of sampled intakes of waters flowing through rocks of various types will make it possible to relate characteristic concentration values of these isotopes recorded in this groundwaters to the geological structure of particular areas. Similar studies were carried out in the USA almost 20 years ago [4], so it will be possible to compare the results obtained in the Sudety Mts. to those from the United States. However, the research in the Sudety Mts. has barely been initiated now.

Conclusions

The obtained measurement results of ^{226}Ra and ^{228}Ra concentrations in the groundwaters of 55 selected intakes in the Polish part of the Sudety Mts. oscillate between 0.007 and 0.92 Bq/dm^3 for ^{226}Ra, and between 0.004 and 0.4 Bq/dm^3 for ^{228}Ra. The average values amount to 0.144 Bq/dm^3 and 0.083 Bq/dm^3, respectively. The isotopic composition of radium dissolved in groundwaters is quite variable: $2.059 > {}^{228}Ra/{}^{226}Ra > 0.099$. However, the waters that prevail have higher concentration of ^{226}Ra nuclide than that of ^{228}Ra nuclide.

No statistically significant values of the correlation coefficient between the concentration changes of the examined radium isotopes in the groundwaters and the changes in the depth of water extraction, the discharge of the intake, underground flow time (the age of the water) or water temperature have been noted. Nor has been noticed any influence of the kind of the reservoir rock or the type of groundwater on the registered concentration values of ^{226}Ra and ^{228}Ra isotopes. The lack of observable correlations of this kind may result partly from the fact that not enough groundwater springs and intakes have been taken into consideration.

Any observable regularities in the content of radium isotopes in the groundwaters of the Polish part of the Sudety Mts. are the consequence of the noted interdependence between the TDS value of the water and the concentrations of these isotopes. Waters with the highest TDS value also contain the highest observed ^{226}Ra and ^{228}Ra concentrations. In light of these facts, it seems that the most significant factors for the contents of ^{226}Ra and ^{228}Ra in the groundwaters of the Polish part of the Sudety Mts. are those determining the general mineralization of the water (TDS), while the dominant role might be played by only some of them, depending on the local geological and hydrogeochemical conditions. One may expect the highest concentrations of these radium isotopes in the chemically aggressive waters flowing through easily soluble reservoir rocks containing increased amounts of radium (uranium and thorium).

It is essential to carry out further, more extensive and detailed research of the occurrence of radium (particularly of ^{226}Ra and ^{228}Ra isotopes) in the groundwaters of the Polish part of the Sudety Mts., in order to characterize precisely the hydrogeochemistry of this element. It is particularly important to determine the radium hydrogeochemical background, and on this basis, to define the potential areas of radium waters occurrence. This will also enable a proposal of a new classification of radium waters, considering the current results of hydrogeochemical research.

The results of further research will enable rational management of groundwaters of the Sudety Mts., the Polish region where the occurrence of strongly radioactive waters, including radium waters, is the most probable.

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