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Preliminary studies on natural radioactive nuclides in thermal waters

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Abstract. The paper summaries the data of activity concentrations of uranium, radium isotopes, mineralization and temperature of thermal waters. The data were gathered not only from our measurements of thermal waters occurring in the Polish Carpathians, but also from the attained published references in the world. The graphical relations between concentrations of the uranium and radium isotopes in thermal waters and their parameters such as temperature and mineralization were drawn up and discussed. The relation between the contents of ^{226}Ra and ^{228}Ra for the investigated waters was also analysed. The relations show that the influence of temperature on the mineralization and radioactive elements in thermal waters is complicated.

Key words: thermal water • temperature • mineralization • uranium • radium

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Introduction

Thermal water is defined as a groundwater, if its temperature at the outflow is higher than annual average temperature of the air in the region. In Poland a groundwater is named as thermal if its temperature is larger than 20°C. Thermal water plays a more and more important role in the economy. Since ancient times, thermal water has been used in therapeutic purposes, then as heating sources. Nowadays, thermal water is often utilized as sources of electricity [14], in health centers and even as a drinking water [1]. Though the thermal waters have been well known for a long time, but investigations of their radioactivity have been done since a few years. In Poland there are some works dealt with this topic, but the papers concerning the thermal waters together with the mineral ones were treated as a minor part [4, 12, 15].

High temperature of thermal waters is often connected with the geological formation reservoirs at large depths or in regions of active volcanoes. Therefore, one can expect that the natural radioactivity level of the thermal waters is not only high, but also sensitive to earthquake events. Some scientists reported that the changing radon concentrations in thermal waters should accompany with the events of earthquake and volcanic actives [2, 7, 11, 24].

Based on the data concerning radioactivity, physical and chemical parameters gathered from the available published articles and obtained by our investigation of the thermal waters occurring in the Polish Carpathians, the relations between the uranium, radium isotopes, mineralization, called as total dissolved solids (TDS), and temperature have been drawn up and discussed.

Natural radioactivity in thermal waters

Natural radioactivity in groundwater is principally owing to the occurrence of the ^{40}K and radionuclides generated by successive decays of the radioisotopes: ^{238}U, ^{235}U and ^{232}Th, which are primordial isotopes of the three natural decay series uranium, actinium and thorium, respectively. The annual global mean dose from food and drinking water consumption constitutes near 12% of the total dose from all natural sources estimated at 2.4 mSv [22]. The content of potassium in the body is maintained at a constant level, so the dose of ^{40}K absorbed by the intake of food and drinking water is neglected [22]. According to the European Union legislation as well as to the WHO recommendation, the radon and its decay progenies are excluded from the estimation of the committed dose from the consumption of drinking waters [10, 25]. The share of the uranium and radium isotopes constitute more than 80% of the activity concentration and committed doses in all natural radionuclides occurring in groundwaters [3, 5, 21, 23]. The mentioned reasons prompt us to preliminary deal with uranium and radium in the thermal waters.

Table 1 summarizes the statistic values of the temperature, TDS, uranium and radium isotopes of the thermal waters occurring in several countries.

The data in this table show that the temperature, TDS, uranium and radium isotopes vary in broad ranges and for all the mentioned parameters the mediana values are far smaller than their adequate average ones. In most of the mentioned waters, the radium concentration is larger by one order of magnitude in comparison with uranium concentration. This fact is connected with the reducing conditions prevailing in thermal waters (redox potentials in the deep thermal waters are often negative). These conditions enable the uranium in water to pass from the compounds where uranium ions in the

Table 1. Statistical values of TDS[a], temperature, ^{238}U, ^{226}Ra and ^{228}Ra activity concentrations of thermal waters occurring in some countries

Region	No. of samples	Statistic parameters	Temperature (°C)	TDS (mg/L)	^{238}U (mBq/L)	^{234}U (mBq/L)	^{226}Ra (mBq/L)	^{228}Ra (mBq/L)
Croatia [18]	12	min	22				87	
		max	96				6 200	
		average	46				1 322	
		MD[b]	40				283.5	
		SD[c]	23.3				895.8	
France [20]	6	min	16	3 608	5		588	260
		max	41	5 608	27		2 287	1 590
		average	30	4 137	15		1 158	854
		MD	24	4 137	16		947	794
		SD	9.4	746.2	8.4		627.8	452.5
Poland*	9	min	22	54	1.1	4.1	12	25
		max	86	22 599	324	303	598	540
		average	47.9	3 511.9	39.5	44.3	370.9	150.6
		MD	34	1 449	2.8	10.9	342.9	79
		SD	27	7 214.4	106.8	97.4	235.9	182.2
Spain [9]	19	min	15	289			15	
		max	52	14 790			1 367	
		average	28	3 702			263	
		MD	21	2 070			157	
		SD	12.4	4 432.8			328.5	
Tunisia [16]	24	min	21	200	1.2	1.3	2	2
		max	75	24 600	69.1	153.4	1 630	1 032
		average	46	6 604	9.6	18.3	507	177
		MD	45	2 840	4.3	7.0	358	113
		SD	15.9	7 606.3	15.5	33.0	489	217.6
Turkey [2]	36	min	29				120	
		max	90				700	
		average	51				337	
		MD	47				315	
		SD	13.3				156.7	

[a] TDS – total dissolved solids.
[b] MD – median.
[c] SD – standard deviation.
[*] The data obtained by our measurements.

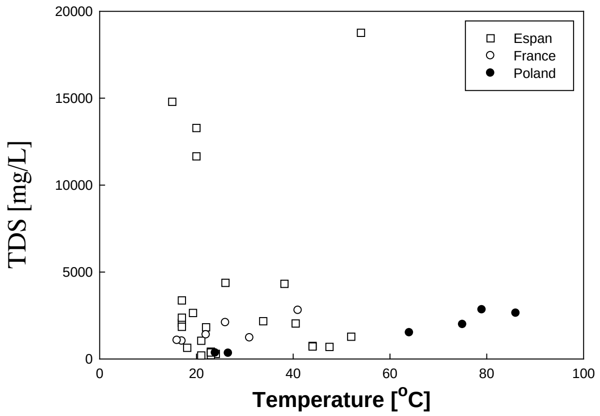

Fig. 1. Relation between the TDS and temperature of the thermal waters.

sixth valence state to the fourth one and are easy to be precipitated. On the other hand, the radium ions are not sensitive to the redox conditions.

Mineralization

The dissolved materials in groundwaters are mostly due to the interaction of water with rocks during its migration and residence time in formation reservoirs. Consequence, the hydrochemical type of thermal water can be changed with depth [8]. According to the chemical theory, the dissolve factors increase with solutions temperature. Mineralizations of the most thermal waters are lower than 5000 mg/L with the exception of two waters from Paterna and Chiclana (Spain) whose TDS are larger than 11 000 mg/L. The relation between the TDS and water temperature is presented in Fig. 1, which shows that the influence of temperature on the mineralization in thermal waters is not apparent.

Radionuclides

Uranium

In the environment, uranium appears in the fourth or sixth valence states. Under reducing conditions the fourth state is a dominant form for a broad range of pH. In the aquatic environment it forms insoluble compounds attaching with the suspended particles, adsorbed by organic matter or precipitated on the mineral surfaces. Uranium in the sixth state of valence prevails under oxidation conditions. In the aquatic environment uranium often occurs as uranyl ions (UO_2^{2+}) and has a high mobility.

The redox potential of the thermal waters often is negative indicating that the reducing conditions are prevailing, and as a result of that, the uranium content in waters are very limited. Though in some cases, such as in uranium deposits or in the aquifers of the elevated uranium contents, concentration of this element in water may reach several hundreds mBq/L [4, 17].

Figure 2 presents the relation between the uranium concentration and temperature. Similarly to the mineralization, the temperature does not indicate any visible influence on the uranium content in the mentioned

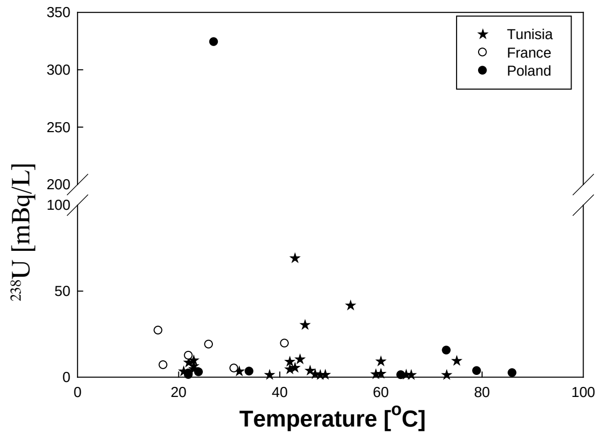

Fig. 2. Relation between ^{238}U concentration and temperature in thermal waters.

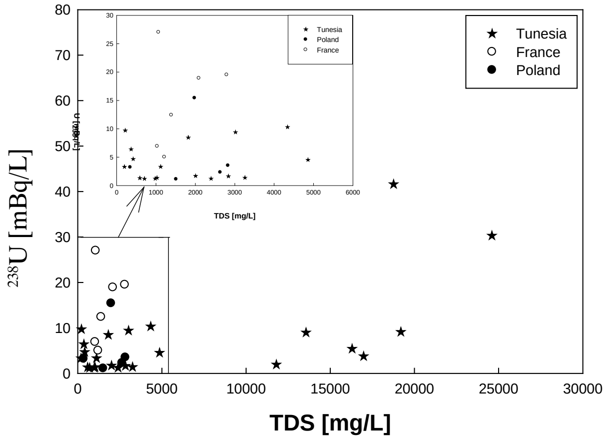

Fig. 3. The relation between ^{238}U concentration and TDS.

waters. The formation reservoir of water, where the ^{238}U concentration amounts to 330 mBq/L, is localized near the uranium vein at the Polana Szymoszkowa at Zakopane (Fig. 2, Ref. [4]).

There is no apparent relationship between the uranium concentration in thermal waters and their mineralization (Fig. 3). The phenomena can be explained by the fact that the uranyl ions basically are sensitive to the redox potential (Eh) and CO_2 gas content in water (Fig. 3, Refs. [13, 19]).

Radium

In the natural environment there are four radium isotopes (^{226}Ra, ^{228}Ra, ^{224}Ra, ^{223}Ra), two of them (^{226}Ra, ^{228}Ra) are most important in groundwater systems. ^{226}Ra with $T_{1/2}$ = 1620 years belongs to the ^{238}U series, while ^{228}Ra with $T_{1/2}$ = 5.75 years is a daughter of ^{232}Th. The chemical properties of radium are similar to the elements of alkaline metals (Ba, Ca and so on), therefore radium often accompanies with these elements in the environment. Radium isotopes in the aquatic environment appear as Ra^{2+} ions, their presence in groundwaters being controlled by (i) leaching of host rocks, (ii) desorption/adsorption processes governed by physical and chemical parameters of water, (iii) recoil effect. Consequently, the radium isotope concentration should be related, to some extent, to the uranium and thorium content in formation reservoir. According to the chemical background, the leaching of the host rocks

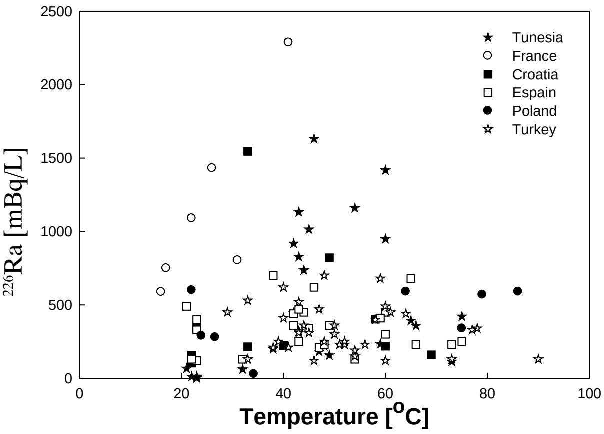

Fig. 4. ^{226}Ra concentration in thermal waters as a function of temperature.

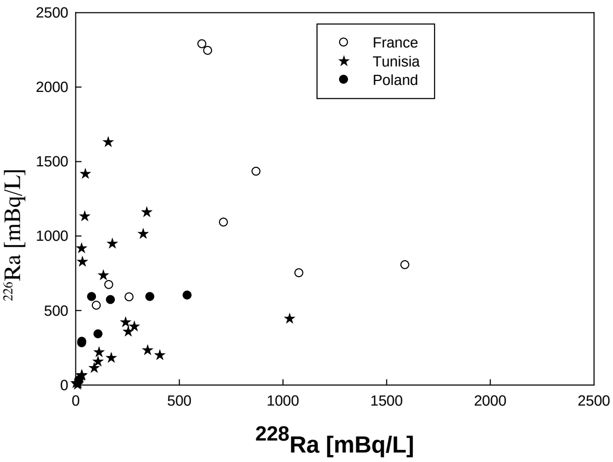

Fig. 5. The relation between ^{226}Ra and ^{228}Ra concentrations.

can increase with increasing solution temperature. So, the content of radium isotopes in thermal waters should increase with its temperature. Figure 4 reveals that the ^{226}Ra content is not apparently related with temperature. This fact has also been observed by Dueñas *et al.* (Fig. 4, Ref. [9]).

Figures 1, 2 and 4 reveal that the influence of temperature on the concentrations of radium, uranium isotopes and the mineralization of thermal waters is complicated.

The relation between ^{226}Ra and ^{228}Ra activity concentrations in the investigated thermal waters is presented in Fig. 5. This figure shows that in most of the investigated thermal waters (~90%) the ^{226}Ra activity concentration is larger than those of ^{228}Ra. This phenomenon can be connected with the high deposition coefficient of the thermal water of the radium from the rock aquifer and in consequence, the activity ratio of radium isotopes (^{226}Ra/^{228}Ra) is often higher than one (Fig. 5, Ref. [6]).

Generally, the radium activity concentration in thermal water increases with their mineralization (Fig. 6), though in every region, the dependence may have specific shape upon the geological properties of the investigated region.

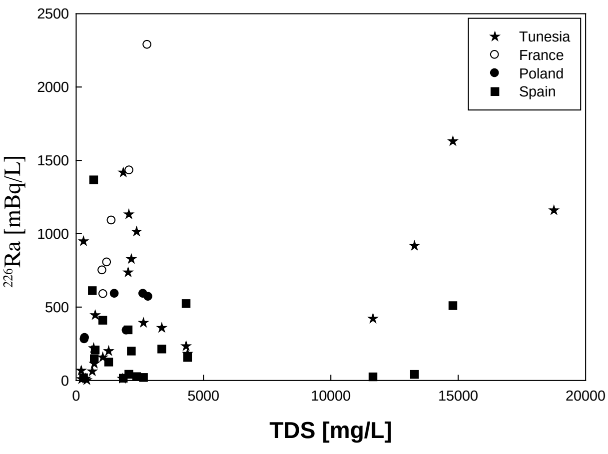

Fig. 6. The relation between ^{226}Ra concentration and TDS.

Conclusion

Thermal waters have been discovered in ancient times, and play a more and more important role in economy. They are often used for heating purposes, in relaxation, in therapeutic centers, in some countries thermal waters serve as the sources of energy. Nowadays, several sources of waters of this kind are used in plants of drinking water. The data concerning the radioactive elements in thermal waters from several countries as well as from the Polish Carpathians show that the influence of water temperature on the mineralization, uranium and radium isotope concentrations is not clearly apparent. In the majority of thermal waters the activity concentration of ^{226}Ra is larger than the ^{228}Ra one.

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