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Natural Radioactivity in Thermal Waters: A Case Study from Poland

Chau Nguyen Dinh [1,*] and Jakub Nowak [2]

[1] Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Mickiewicza 30 Av., 30-059 Kraków, Poland
[2] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Mickiewicza 30 Av., 30-059 Kraków, Poland; jakub.nowak@fis.agh.edu.pl
* Correspondence: cnd@agh.edu.pl

Abstract: A natural radioactivity in thermal water was investigated based on 19 selected thermal waters from Poland. The analysed results show that the radionuclides' concentrations in the study waters vary over a wide range. The temperature of the waters varies from above 20 °C to above 80 °C. The waters are characterised by different mineralisation, chemical compositions, and belong to different hydrochemical types. There is a good correlation between the water temperature and the depths of the aquifer formations occurrence, suggesting the thermal energy originates from the thermal geogradient. The concentration of radium is well correlated with the water mineralisation. The ratio of radium activity ($^{226}Ra/^{228}Ra$) in groundwater relates not only the ratio of uranium activity to that of thorium ($^{238}U/^{232}Th$) in aquifer formation, but also depends on the physical and chemical water properties. Based on the concentration of radon and its transport model, the radiation exposures due to inhalation of ^{222}Rn and its progeny for employees and clients of the spa were assessed. The use of the thermal waters as a drinking resource may be problematic due to the possibility of exceeding the recommended annual committed effective dose 0.1 mSv.

Keywords: thermal waters; utilisation; recreational bathing; radioactivity; natural radionuclides

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1. Introduction

Groundwater is classified as thermal when its temperature at the outflow is greater than the annual average air temperature in its region. Due to their physicochemical properties, thermal waters are widely used in balneology, heating and electricity production or as drinking water resources. Since natural radioactive elements commonly occur in the earth's crust, i.e., in aquifers, one of the characteristic features of groundwaters (including thermal ones) is the presence of natural radioactive elements in varying amounts, which basically results from the leachability of the minerals in the aquifer rocks. The concentrations of radioactivity from radium isotopes ($^{226,228}Ra$), uranium ($^{234,238}U$) and radon (^{222}Rn) in groundwater range widely from hundredths of mBq/L to dozens of Bq/L [1]. For example, in thermal waters from northeast Croatia the content of ^{226}Ra is in the range from 0.07Bq/L up to 4.1 Bq/L [2]. In turn, the Massif Central area of France, and in particular the Limagne valley, is known for the presence of CO_2-rich thermal waters with relatively high concentrations of radium isotopes (from 588 mBq/L to 2287 mBq/L for ^{226}Ra and from 260 mBq/L to 1590 mBq/L for ^{228}Ra) [3]. In the thermal waters occurring in northeast India (West Bengal) the radioactivity levels of ^{226}Ra range from 1.18 Bq/L to 1.70 Bq/L and the radon content varies from 3.2 Bq/L to 46.9 Bq/L [4]. In thermal waters from the Petio Region (Taiwan), the concentrations of uranium isotopes ^{234}U and ^{238}U range from 3.7 mBq/Lto 97.7 mBq/L and from 3.3 mBq/L to 99.5 mBq/L, respectively. The thorium content ranges from 2.6 mBq/L to 31.8 mBq/L for ^{232}Th and from 2.2 mBq/L to 33.3 mBq/L for ^{230}Th. The activity concentration of ^{228}Ra ranges from 222 mBq/L to 389 mBq/L and is much higher than that of ^{226}Ra [5]. It is worth noting that activity concentrations of natural radionuclides and chemical composition in groundwater are strongly related to the geological and hydrogeological characteristics of the aquifer, particularly to the content of uranium and thorium in the rock aquifer [6–8].

The presence of natural radionuclides in thermal waters may limit the use of the waters due to the potential radiation exposure which is mainly related to: (1) an external exposure to radiation associated primarily with radon released from thermal water into the air of the pool building; (2) internal exposure as a result of the consumption of thermal water used as drinking water resources. For example, the problem of external exposure was raised by Vogiannis et al. [9], who, based on measurements of the radon content of indoor air in the pool building of the thermal spas on Lesvos Island (Greece), assessed the radiological risk to the bathers during treatment. The estimated annual effective dose was in the range of 0.0067 to 0.1280 mSv [9]. The investigation of radon in indoor air of 14 Portuguese thermal spas showed that the concentration of this isotope exceeded both the national recommended threshold for protection (400 Bq/m^3) and the European Union reference level—300 Bq/m^3 [10,11]. In Poland, Nowak and Nguyen [12], based on measurements of the concentration of ^{222}Rn radioactivity and a model of transfer from the water in the baths to indoor air, estimated the annual effective doses for workers and clients of Polish thermal spas. The results show that for waters with radon contents higher than 18 Bq/L, the annual effective doses for spa employees may exceed 1 mSv—the lower reference limit for category B workers [12].

This work presents the results of measurements of the natural radioactivity in selected thermal waters from Poland. The analyses were carried out for 19 thermal waters occurring in the Polish Carpathians, the Sudetes and the Central Lowlands (Figure 1). The problems connected with the potential radiation hazard resulting from using the thermal waters for recreational purposes and as drinking water resources are discussed.

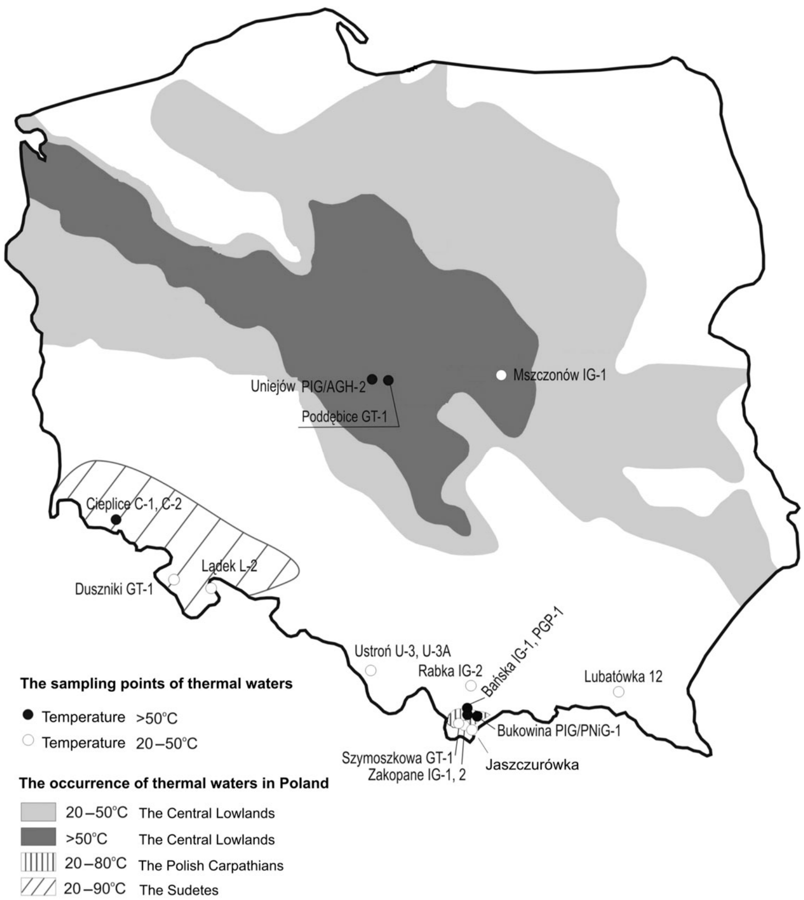

Figure 1. Map of sampling sites of selected thermal waters.

2. Geological Characteristics and Radioactivity of the Rock Aquifers

2.1. Polish Carpathians

The Polish Carpathians are located in the south and southeast of Poland. From the tectonic and lithological point of view the Carpathians are divided into inner and outer parts with the Pieniny Klippen Belt as a boundary.

The Inner Carpathians form the region where the most valuable thermal waters occur. This region is composed of the Tatra mountains and Podhale basin. The Tatra mountains are made up of crystalline rocks, which provide a great discharge water zone, and Podhale in the north stands as a great thermal water aquifer. The Podhale basin is composed of the Paleogene flysch formations with up to 3 km of thick, underlain by the Eocene carbonate series [13,14]. The major rocks which make up the Carpathian flysch are intermingling layers of sandstone and slate of Jurassic age. The Podhale flysch is divided into three subfacies: sandstone, normal and slate. In the sandstone subfacies, sandstone and conglomerates are dominant; in the normal facies the contributions of sandstone and mudstone are comparable, and in the slate one, mudstone and shale predominate. The Eocene carbonate series are basically composed of Middle Triassic limestone, conglomerates and dolomite. In both Paleogene Flysch and Eocene formations the fractures and cracks play a role as the main medium of water residence and movement [13,15]. The stratigraphic lithology of the Podhale basin is shown in Figure 2A. In general, the Inner Carpathian structure is a mosaic, which results in every geological fragment being characterised by its specific structure and the groundwater principally being transported in the local area. In consequence, the physical and chemical parameters, as well as the radioactive characteristics, of the Carpathian ground and thermal waters are specific and can change from one local area to another. The Podhale basin is bounded in the north by Pieniny Klippen Belt, which is Tertiary suture zone between Inner and Outer Carpathians. The Pieniny Klippen Belt is chiefly composed of carbonate rocks, trends in E-W direction, being nearly 600 km long, and ranges from a few hundred metres to several kilometres wide [16].

The Outer Carpathians are built up from thick flysch formations formed in the Jurassic to Miocene period. The Outer Carpathians are disturbed tectonically by nappes, scales and folds; structures that generally influence the hydrogeological conditions. Based on their tectonic and lithological characteristics, the Carpathians are divided into several units. Apart from Silesia, until now no thermal water source has been discovered anywhere in the Outer Carpathians. In Silesia there are two thermal water intakes: Ustroń 3 and Ustroń 3A. In Ustroń and its surrounding area, flysch formations from the Silesia and Subsilesia units occur. On the top surface of this area there are Quaternary clays, sands, gravels and colluvium. Below the Quaternary sediments there are shales of the Silesian unit with a thickness near 500 m. Under the Silesian flysch formation there are the shales and variegated sandstones of the Subsilesian unit which is 500 m thick. Below 1000 m deep there are Carboniferous claystones and fine-grained sandstones 200 m thick. Underlying this formation are the Devonian limestones, which are the aquifer of the thermal water (Figure 2B). The high temperature of the thermal waters of this area could be related to the geothermal gradient, which is ~3 °C per 100 m. In consequence, the temperature of the water hosted in the Devonian aquifer can be in the range of 40 °C to 50 °C [17].

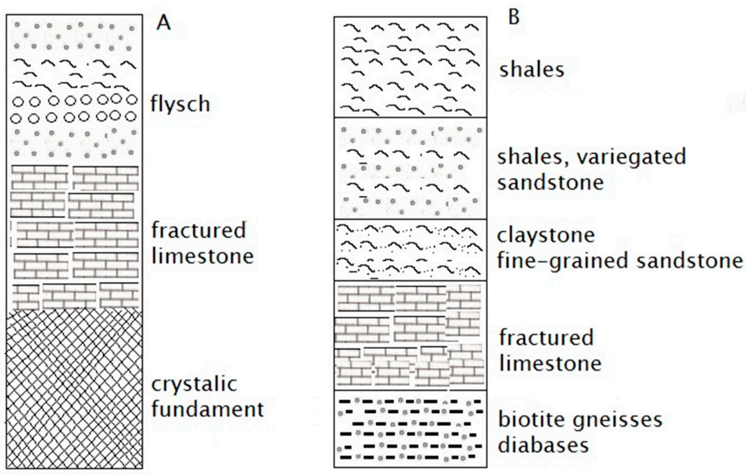

Figure 2. General statigraphic lithology at: Podhale basin—(**A**) follows Chowaniec [13], and Ustroń 3—(**B**) follows Sokołowski and Kempkiewicz [18].

The concentration of natural radioactive elements in the flysch and carbonate formations is low enough. In the Palaeozoic carbonate rocks the concentrations range from below 0.1 ppm (1.2 Bq/kg) to ~4 ppm (49.4 Bq/kg) for uranium and 0.4 (1.6 Bq/kg) to 2.1 ppm (8.5 Bq/kg) for thorium. In sandstone, uranium ranges from 1.6 ppm (19.8 Bq/kg) to 9.8 ppm (121 Bq/kg) and thorium from 6.1 ppm (24.8 Bq/kg) to 12 ppm (48.7 Bq/kg). In the sandstone in the Carpathian Flysch, uranium is found in the range of concentrations from 1.07 ppm (13.2 Bq/kg) to 2.54 ppm (31.37 Bq/kg) and thorium ranges from 4.3 ppm (17.4 Bq/kg) to 8.92 ppm (36.2 Bq/kg). The concentrations of these radioactive elements are higher in mudstone and shale and range from 3.2 ppm (39.5 Bq/kg) to 6.6 ppm (81.5 Bq/kg) for uranium and from 10.2 ppm (41.4 Bq/kg) to 12.8 ppm (52.0 Bq/kg) for thorium [19]. In the crystalline rocks of the Tatra, the uranium and thorium concentrations are 3.2 ppm (39.5 Bq/kg) and 17.9 ppm (72.7 Bq/kg), respectively. The data show that concentrations of both uranium and thorium in the Carpathian aquifer rocks are comparable to the average levels of these elements in the earth's crust; however, they cover a broad range. In the Palaeozoic carbonate the concentration of radioactivity in uranium is higher than that of thorium. In the sandstone, the concentrations of radioactivity of uranium and thorium are comparable and in the crystalline rocks of the Tatra, the concentration of radioactivity in thorium is larger than that of uranium.

2.2. Sudetes

The thermal water intakes Cieplice C1, Lądek Zdrój L2 and Duszniki Zdrój GT1 are located in the Sudetes and the Fore-Sudetic block, the Sudetic fault forming a border between these units. The Sudetes and the Fore-Sudetic block are located in the southwest of Poland and belong to the northern and eastern edge zone of the Bohemian crystalline massif. The area of concern is surrounded by dislocations on three sides. In the southwest there is the Lusatian thrust separating from the Bohemian massif, in the east the Sudetes and Sudetic block are bounded with the Moravo–Silesian by the Ramzova thrust. Due to the intensive tectonic movements in the Pre-Cambrian which were accompanied by metamorphic processes and the many repeated intrusive and volcanic activities, the Sudetes and Fore-Sudetic block were displaced by different horizontal and vertical faults. In consequence, the structure of the Sudetes and Fore-Sudetic block can be described as mosaic-like and divided into geological units [20]. In the concerned region there is a great diversity of magmatic and metamorphic rocks with various mineral and chemical compositions. There are lot of dislocations and gaps in the formations; they enable CO_2 to migrate toward surface. The gas significantly influences the chemical composition of the groundwater in this region [21]. The concentrations of radionuclides in the rocks vary over a very broad range even in the rocks of one type, e.g., in Karkonosze granite the concentration of ^{226}Ra is from 1 Bq/kg to 344 Bq/kg with 75.0 Bq/kg being an average; in the rocks of the Lądek-Śnieznik unit the concentration of this isotope varies from 1 to 244 Bq/kg with 43.2 Bq/kg being the average [20]. Both average values are higher than the average of ^{226}Ra in the earth's crust (36 Bq/kg). Malczewski and his group [22] have measured the content of several natural radionuclides in outcrops of crystalline rocks: metamorphic (gneiss, laminated gneiss, mica schists), effusive (basalt) and magmatic (granite) of the Izerski block by a portable field gamma spectrometer with a semiconductor detector. They stated that the concentrations of ^{228}Ac (representing ^{232}Th) varied from 24.9 Bq/kg to 47.9 Bq/kg with 35.6 Bq/kg as an average and ^{226}Ra (representing ^{238}U) from 31.6 Bq/kg to 73.6 Bq/kg with 46.2 Bq/kg on average. The activity ratio between ^{228}Ac and ^{226}Ra (^{228}Ac/^{226}Ra) ranges from 0.41 to 1.3 with an average of 0.77 in the rocks of the Izerski block that were examined.

2.3. The Polish Central Lowlands

The thermal water intakes: Uniejów, Poddębice and Mszczonów are located in the Mongilno-Łódź basin, which is one of three basins of the Szczecin-Miechow region BIII [23]. Over the whole of the Mongilno-Łódź basin there is an occurrence of Cretaceous sediments 200 m to 400 m thick. These sediments stand a major aquifer of the mineral and thermal waters in this region. The water-bearing formations in the Cretaceous sediments are multi-grained sandstone composed of the fine gravel and intermittent black and grey shale with inlays of siderites and ferruginous oolites. In this region there are several salt diapers that have a significant influence on the ground water chemistry [23–25]. The geothermal gradient of this region is 2.8 °C/100 m. However, there is no data concerning the natural radioactive elements in the Cretaceous rocks, but according to Grabowski et al. [26] the average activity ratio of ^{228}Ra/^{226}Ra in the Poddębice and Uniejów groundwaters is 1.64 and 0.64 respectively. The phenomena can be the result of (i): the interaction of the salt diapers; (ii)—mix with surface water; and (iii)—differing relations of the ^{238}U and ^{232}Th in the water hosting formations.

3. Materials and Methods

3.1. Sampling

Water samples were gathered directly from the wellheads into PET (Polyethylene Terephthalate) bottles of volume 5 L and for radon, glass bottles of volume of 0.5 L to avoid an escape of Rn, especially during transport and preparing water sample. Before being used for water collecting, the bottles were washed and rinsed in distilled water. Due to the short half-life of radon, the samples were transported to the laboratory as soon as possible. In order to make a correction for radon decay, the time of collection of every sample was noted down.

The temperature, reduction potential (Eh) and pH index were measured directly at the water outflow using a WTW (Weilheim, Germany) probe.

3.2. Chemical Composition

The chemical elements in the water sample were analysed by ICP-OES (Inductively Coupled Plasma Atomic Emission Spectroscopy) method using an Elkin Elmer 7000 DV spectrometer at the Faculty of Geology, Geophysics and Environmental Protection in AGH University of Science and Technology (FGGEP, AGHUST). A water droplet of the water to be analysed was pumped into the plasma ionisation chamber with a temperature higher than 6000 K, the atoms of the elements in the water droplet were ionised and excited and then emitted light of characteristic wavelengths. Based on the characteristic light wavelengths recorded and the multi-element calibration solution of the Merck Company, the concentrations of the element in the water were calculated. The lower limit of detection (LLD) of the ICP-OES is dependent on the given element and generally is at the level of ppm for major elements (Ca, Mg, Na, K, Fe) and ppb for trace elements (Br, J). The confidence limits of the accuracy of the analysis can be taken as 3% [27].

3.3. Radioactive Isotopes

3.3.1. Uranium Isotopes

For uranium isotopes, a standard uranium (^{232}U) solution with exactly known activity (100 mBq) was initially added to each water sample of 2 L and the samples were reduced by evaporation to around 1 L. Uranium was precipitated from the water by co-precipitating with MnO_2 as uranyl ammonium [$(NH_4)_2U_2O_7$]. Then, uranium ions were separated from the ions of other isotopes in the precipitate, thus being obtained by dissolving it in HCl 9M solution. Following, this the solution was passed through a DOWEX 100–200 mesh anion-exchange column. Next, the eluate with uranium was evaporated to dryness and then the sample was dissolved in HCl 1M. Then, uranium was again precipitated using the Ammonium iron(II) sulfate and neodymium chloride. The final precipitate was placed onto a plastic membrane filter with porosity of 0.1 µm and measured using an alpha spectrometer "Canberra 7401" with silicon semiconductor detector. The resolution of the alpha spectrometer is 17 keV at the line 5500 keV of alpha particles emitted from ^{241}Am. The procedure has been described in detail by Kronfeld [28] and modified by Skwarzec [29]. The measurement time often lasted 72 h; at this time, the uncertainty of assessment amounts of uranium isotopes reached below 5%.

3.3.2. Radium Isotopes

The radium isotopes were precipitated from a 2 L volume of the water sample as sulphate compounds. The sample obtained was cleaned up using distilled water and a centrifuge. Then, the precipitate was separated from other isotopes by dissolving in alkaline EDTA (Ethylenediaminetetraacetic acid) solution. The radium was again precipitated by decreasing the pH of the solution down to 4. The sample thus obtained was again cleaned up using distilled water and a centrifuge, then placed in a specific glass bottle with a 22 mL volume and mixed with 12 mL of a gel scintillation cocktail and measured using the Guardian Wallac 1414 α/β liquid scintillation spectrometer. The detection efficiency for alpha particle is 100%, while beta emitted from the isotopes in the ^{226}Ra and ^{228}Ra groups depends on the isotope and varies from 80% to 85%. The applied chemical preparation, the measurement procedure and the calculation of radium isotopes using the measured count rates were described in detail by Nguyen et al. [30]. The uncertainty for analysed ^{226}Ra and ^{228}Ra depended on their concentrations and varied from 5% to 15%, respectively.

3.3.3. Radiolead

Radiolead was separated from a water sample with a volume of 2 L as a lead sulphate compound by adding lead nitrate solution and sulphuric acid. Then, the precipitate was cleaned up and the lead was separated from the sample following the procedure described above for radium. As a consequence of this procedure a radium precipitate and solution were obtained in which lead was present. The lead was again precipitated from the last solution by adding the sulphuric acid. The sample thus obtained was cleaned up again using distilled water and a centrifuge. The sample was placed in a specific 22 mL plastic bottle and mixed with 12 mL of a gel scintillation cocktail and measured using the Wallac 1414 α/β liquid scintillation spectrometer. The chemical and measurement procedure for determination of ^{210}Pb in the water sample was described in detail by Nguyen et al. [31]. The detection efficiency of the beta particles emitted from the ^{210}Bi (daughter of ^{210}Pb) is nearly 85%. The standard deviation of the method was often at the level of 15%.

3.3.4. Radon

To determine the concentration of radon radioactivity, a 10 mL water sample was mixed with 10 mL of PerkinElmer™ Mineral Oil Liquid Scintillation cocktail placed in a glass vial. The mixing time was noted in order to introduce a radon decay correction factor. Each sample was measured for 60 min per day using the Wallac 1414 α/β liquid scintillation spectrometer. The measurement was made continuously for 10 days. The radon content in water samples was calculated based on the curve of the alpha net count rate plotted against time elapsed from the moment of mixing [32]. The uncertainty of the Radon analysis was below 5% for the water with Rn concentration higher than 10 BqL^{-1}; below this level the uncertainty could reach to 10%.

3.3.5. Potassium Isotope (^{40}K)

The concentration of the ^{40}K isotope in water was calculated based on the content of potassium element analysed by the ICP-AES and the stable abundance of ^{40}K in potassium (0.0118%). The standard deviation for analysis of the main elements (Ca, Na, Mg, K) is below 3% [33].

4. Results

4.1. Chemical Composition and Physical Properties of Polish Thermal Waters

The selected physical parameters and main chemical composition of the waters investigated are presented in Table 1.

The temperature and mineralisation of Polish thermal waters range from 21 °C to 86 °C and from 210 mg/L to 120 g/L respectively. Water from the Lądek Zdrój L-2 has the lowest mineralisation (210 mg/L), and the thermal waters from Ustroń have the highest (over 100 g/L). The chemical compositions of the study waters are different, and belong to hydrochemical types such as: HCO3-Ca-Mg, HCO3-Na-Ca, SO4-Cl-Na-Ca, Cl-Na-Ca and Cl-Na. In the case of thermal waters from the Polish Inner Carpathians, the hydrochemical type of water changes from HCO3-Ca-Mg (near the Tatra) to SO4-Cl-Na-Ca (near the Pieniny Klippen Belt).

The depth of the thermal water formations studied varies from 150 m (Poronin PAN-1) to 2986 m (Bańska Niżna PGP-1) below the ground surface; the temperature of the waters at their outflow ranges from 21 °C (Ustroń 3A) to 86.3 °C (Bańska Niżna PGP-1). The pH varies from 6 to 8.2. In most of the waters the reduction condition (negative Eh) applies, but the Eh from the Poronin PAN-1 intake is 227 mV suggesting that the water could be in contact with atmospheric air.

4.2. Natural Radioactivity in Polish Thermal Waters

The measured concentrations of radioactivity of natural radionuclides ($^{234,\,238}U$, $^{226,\,228}Ra$, ^{222}Rn, ^{210}Pb, ^{40}K) in the thermal waters studied are summarised in Table 2.

Excluding the Szymoszkowa water, the concentrations of radioactivity of uranium isotopes are low and range from ≤0.5 mBq/L (lower limit of detection—LLD) to 41 mBq/L (Poronin PAN-1) for ^{238}U and from ≤0.5 mBq/L (LLD) to 58.5 mBq/L (Poronin PAN-1) for ^{234}U. In each water sample the content of ^{234}U exceeds that of ^{238}U, the phenomenon being the consequence of the recoil effect [28]. In the Szymoszkowa water the concentration of ^{238}U and ^{234}U is 328 and 313 mBq/L, respectively. Such a high concentration of radioactivity could be related to the black shale formation occurring in the area [34].

Table 1. The physical parameters and chemical composition of the Polish thermal waters investigated.

Borehole	Location	Depth [1] (m)	Temp. (°C)	Eh (mV)	pH	Concentrations of Major Ions (mg/L)								Type
						TDS	HCO_3^-	Cl^-	SO_4 [2]	Na^+	K^+	Ca^{2+}	Mg^{2+}	
Bukowina PIG/PGNiG-1	IC [2]	2497	64.0	n/a [6]	n/a	1512.3	159	113	763	160	17.7	184	15.5	SO_4-Ca-Na
BiałkaTatrzańska GT-1	IC	2500	73.5	−209	6.83	1982.0	252	379	671	314	33.9	183	42.8	SO_4-Na-Ca
BańskaNiżna PGP-1	IC	2986	86.3	−330	8.2	2502.7	334	492	818	470	41.0	188	40.0	SO_4-Cl-Na
BańskaNiżna IG-1	IC	2626	80.0	n/a	6.5	2333.3	285	482	756	432	42.6	183	34.9	SO_4-Cl-Na
Zakopane 2	IC	1102	23.9	n/a	7.5	349.1	239	8.60	16.0	2.27	1.13	46.0	22.4	HCO_3-Ca
Zakopane IG-1	IC	1580	34.2	n/a	7.4	367.8	220	3.60	39.1	10.1	3.32	45.4	20.5	HCO_3-Ca
Szymoszkowa GT-1	IC	1387	26.6	n/a	7.7	332.7	241	3.60	4.50	5.35	1.60	40.0	22.8	HCO_3-Ca
Poronin PAN-1	IC	150	63.0	227	6	n/a [1]	n/a	n/a	n/a	n/a	n/a	n/a	n/a	-
Chochołów PIG-1	IC	1843	82.0	n/a	n/a	1256.9	194	27.2	607	87.7	18.5	192	40.8	SO_4-Ca-Mg
Rabka IG-2	OC [3]	3395	22.0	n/a	n/a	23,061.4	1487	12,400	4.50	8400	87.9	73.2	39.7	Cl-Na
Lubatówka 12	OC	1205	24.0	−38	7.73	17,700	4270	7090	<0.5	5910	37.3	51.6	57.2	Cl-Na
Ustroń U3	OC	925	23.0	−90	7.1	101,000	79.3	62,400	370	26,400	579	8290	2530	Cl-Na-Ca
Ustroń U3A	OC	1513	21.0	−27.7	7.0	117,000	101	71,700	426	30,800	727	9410	2660	Cl-Na-Ca
LądekZdrój L-2	SU [4]	1320	43.6	−220	6.9	201	24.4	5.60	21.6	49.0	0.78	3.05	<0.01	HCO_3-SO_4-Na
DusznikiZdrój GT-1	SU	425	35.5	8.2	9.4	3430	2330	8.92	72.2	301	182	297	95.1	HCO_3-Na-Ca
Cieplice C-1	SU	1124	65.3	−110	6.9	663	146	42.5	153	153	5.10	7.8	0.02	SO_4-HCO_3-Na
Uniejów PIG/AGH-2	NP [5]	2003	63.9	−150	7.8	6770	296	3770	98.0	2350	28.9	141	27.7	Cl-Na
Poddębice GT-1	NP	1897	49.0	−201	7.2	461	262	21.6	14.3	78.8	4.50	23.9	4.22	HCO_3-Na-Ca
Mszczonów IG-1	NP	1925	41.8	−210	7.5	492	320	7.59	3.37	30.7	11.1	53.1	11.7	HCO_3-Ca-Na

[1] Depth of aquifer. [2] IC—Inner Carpathian. [3] OC—Outer Carpathian. [4] SU—The Sudetes. [5] NP—The Central Lowlands. [6] not analysed.

Table 2. The concentrations of radioactivity of $^{226, 228}$Ra, $^{234, 238}$U, ^{210}Pb, ^{222}Rn and ^{40}K in Polish thermal waters.

Borehole	Radium Isotopes (mBq/L)		Uranium Isotopes (mBq/L)		^{210}Pb (mBq/L)	^{222}Rn (Bq/L)	^{40}K	^{226}Ra/^{228}Ra	^{234}U/^{238}U	^{226}Ra/^{222}Rn	^{210}Pb/^{222}Rn
	^{226}Ra	^{228}Ra	^{234}U	^{238}U							
Bukowina PIG/PGNiG 1	585	339	12.5	1.2	15.3	3.1	570	1.73	10.4	0.19	0.0049
Białka Tatrzańska GT-1	347	116	5.1	3.6	9.2	n/a [1]	1091	2.99	1.42	n/e [2]	n/e
Bańska Niżna PGP-1	602	69	6.2	3.1	36.0	<0.2	1320	8.72	2.00	n/e	n/e
Bańska Niżna IG-1	560	161	4.7	3.9	30.0	8.5	1372	3.48	1.21	0.066	0.0035
Zakopane 2	291	30	7.5	2.8	73.5	18.5	36.4	9.70	2.68	0.016	0.0040
Zakopane IG-1	31	19	4.5	2.6	8.2	<0.2	107	1.63	1.73	n/e	n/e
Szymoszkowa GT-1	315	35	321	319	30.3	27.1	51.5	9.00	1.01	0.012	0.0011
Poronin PAN-1	250	<10	58.8	41.9	n/a	n/a	34.4	n/e	1.40	n/e	n/e
Chochołów PIG-1	2260	<10	5.8	2.9	102	n/a	570	n/e	2.00	n/e	n/e
Rabka IG-2	608	570	9.3	6.2	16.9	<0.2	n/a	1.07	1.50	n/e	n/e
Lubatówka 12	1396	1271	7.1	3.1	56.7	3.2	596	1.10	2.29	0.44	0.018
Ustroń U3	56,700	14,100	7.0	18.7	n/a	31.5	2830	4.02	0.37	1.80	n/e
Ustroń U3A	66,000	17,700	9.7	4.6	n/a	37.3	1201	3.73	2.11	1.77	n/e
Lądek Zdrój L-2	24	20	0.61	0.95	29.3	148	18,641	1.20	0.64	0.00016	0.00020
Duszniki Zdrój GT-1	3370	940	37.3	14.7	547	3.2	23,406	3.59	2.54	1.05	0.17
Cieplice C-1	21	<10	<0.5	<0.5	4.1	8.0	25.1	n/e	n/e	0.0026	0.00051
Uniejów PIG/AGH-2	560	597	0.96	<0.5	24.0	2.0	5860	0.94	n/e	0.28	0.012
Poddębice GT-1	40	62	<0.5	<0.5	5.3	5.3	164	0.65	n/e	0.0075	0.0010
Mszczonów IG-1	41	51	<0.5	1.5	3.2	2.9	930	0.80	n/e	0.014	0.0011

[1] not analysed. [2] not estimated.

The concentrations of radioactivity of ^{226}Ra and ^{228}Ra vary over a very broad range from 29 mBq/L (Zakopane IG-1) to 64,960 mBq/L (Ustroń 3A) and <10 mBq/L (LDD) to 13,700 mBq/L (Ustroń 3A), respectively. Though the depth of the water hosting the formation at the Zakopane IG-1 intake is over 1500 m, both the mineralisation and $^{226,228}Ra$ concentrations in the water are very low (Tables 1 and 2). In addition, the hydro-chemical type is HCO_3-Ca suggesting a weak interaction between the water and the crystalline limestone in the aquifer. In the case of the water from the Ustroń 3 and Ustroń 3A intakes the concentration of radium isotope is very high, nearly 70 Bq/L for ^{226}Ra and 13 Bq/L for ^{228}Ra. The thermal water is hosted in Devonian limestone. This formation is covered by impermeable shale and variegated sandstone over 1000 m thick, suggesting the water could be isolated from infiltration and mixed with dehydrated water from the impermeable shale [35]. In consequence, the mineralisation and radium concentration are very high. Generally, the concentration of radioactivity of ^{222}Rn in Polish thermal water, excluding the water from Lądek-Zdrój L-2, is low and ranges from 0.2 to ca. 38.0 Bq/L. In the Lądek Zdrój water the Rn concentration is 141 Bq/L. Such a high Rn concentration is linked to the granite aquifer in this area. The strong radioactive disequilibrium between radium and radon ($^{226}Ra/^{222}Rn << 1$) for most of the waters studied suggests that a significant part of the radon in the waters comes directly from the radon emanating from the reservoir rocks [36].

The concentration of radioactivity from ^{210}Pb varies over a wide range from 3.2 mBq/l to 540 mBq/l. The radioactive imbalance between the lead and the radon ($^{210}Pb/^{222}Rn << 1$) suggests that short-lived products of radon decay (^{218}Po, ^{214}Pb, ^{214}Bi and ^{214}Po) form compounds that are insoluble in water.

5. The Radiological Risk Related to the Use of the Thermal Waters Studied

The radiological risk related to exposure to radon for employees and clients of thermal spas was assessed based on the analysis of the content of seven natural radionuclides. An assessment of the radiological risk resulting from the consumption of water as drinking water was also carried out.

5.1. Assessment of the Radiological Risk Resulting from Recreational Bathing

When using thermal waters as a recreational medium, a potential radiological hazard could be generated from radon and its progeny. The effective doses resulting from exposure to radon for "model" clients and employees of thermal spas were evaluated with the following assumptions: (1) water from the thermal intake is directly used to fill the swimming pool, (2) radon in the indoor air of a swimming pool building only came from the thermal water as a result of radon exhalation processes, (3) employees spend their whole working time (2000 h per year) in a swimming pool building, (4) the client is defined as an adult who spends 3 h at a spa for recreational bathing once a month (36 h per year). The radon transfer coefficient (T_{Rn}) described by Nowak and Nguyen [12] and the concentration of radon radioactivity in thermal water were used to evaluate the radon content in the indoor air of the swimming pool. According to UNSCEAR (United Nations Scientific Committee on the Effects of Atomic Radiation) [37], the annual effective dose (D_{Rn}) was calculated by the following formula:

$$D_{Rn} = C_{air} \cdot F_{eq} \cdot K_{Rn} \cdot t, \quad (1)$$

where C_{air} is the radon content in the indoor air of the swimming pool, F_{eq} stands for the indoor radon equilibrium factor, which is equal to 0.4 [32], K_{Rn} is the dose conversion factor, and amounts to 9 nSv (Bq h m^{-3})$^{-1}$ [37], t stands for the annual occupancy time at the swimming pool.

Generally, the estimated annual effective doses for clients and employees vary from 0.27 to ca. 50.0 µSv and from 0.015 to 2.8 mSv, respectively (Table 3).

Table 3. The annual effective doses for thermal spa clients and employees and the committed effective dose resulting from consumption.

Borehole	Method of Utilisation	Annual Effective Dose [a] for Clients (µSv)	Annual Effective Dose [a] for Employees (mSv)	Committed Effective Dose [b] (mSv)
Bukowina PIG/PGNiG 1	Recreational bathing. heating	4.14	0.23	0.30
Białka Tatrzańska GT-1	Recreational bathing	n/e [c]	n/e	0.13
Bańska Niżna PGP-1	Recreational bathing. heating	0.27	0.015	0.18
Bańska Niżna IG-1	Heating	11.4	0.63	0.21
Zakopane 2	Recreational bathing	24.7	1.37	0.11
Zakopane IG-1	Recreational bathing	0.27	0.015	0.02
Szymoszkowa GT-1	Recreational bathing	36.2	2.01	0.12
Poronin PAN-1	Not used	n/e	n/e	0.060
Chochołów PIG-1	Recreational bathing	n/e	n/e	0.52
Rabka IG-2	Balneological treatment	0.27	0.015	0.42
Lubatówka 12	Balneological treatment	4.28	0.24	0.95
Ustroń U3	Balneological treatment	42.1	2.34	n/e
Ustroń U3A	Balneological treatment	49.8	2.77	n/e
Lądek Zdrój L-2	Balneological treatment	198	11.0	0.030
Duszniki Zdrój GT-1	Balneological treatment	4.28	0.24	1.44
Cieplice C-1	Balneological treatment	10.7	0.59	0.011
Uniejów PIG/AGH-2	Recreational bathing. heating	2.67	0.15	0.43
Poddębice GT-1	Recreational bathing. heating	7.08	0.39	0.04
Mszczonów IG-1	Recreational bathing. heating	3.87	0.22	0.04

[a] resulted as inhalation, [b] resulted as consumption, [c] not estimated.

In the case of the Lądek-Zdrój L-2 water, both clients and employees would receive significantly higher doses of 198 µSv and 11.0 mSv, respectively. Due to the short time in the bathing hall, the calculated doses for clients are much lower than the annual dose limit for members of the public: 1 mSv [38]. For most of the waters investigated, the doses do not exceed 5% of the annual dose limit (1 mSv). Considering employees, for the five waters with a radon content higher than 18 Bq/l (Zakopane 2, Szymoszkowa GT-1, Ustroń U3, Ustoń U3A and Lądek-Zdrój L-2), the annual effective doses exceed 1 mSv, the lower reference limit for Category B workers. For water from Lądek-Zdrój L-2, the annual effective dose is higher than 6 mSv and workers working under such conditions are classified under the A category, and according to the EU and Polish legislation they are obliged to wear a personal dosimeter [38–42].

From the radiological point of view, recreational bathing with thermal water is not a health hazard for clients. However, in the case of health centres using thermal water with a radon content higher than 18 Bq/L the doses for employees may exceed the lower reference level for workers of Category B. Therefore, some development in ventilation of the swimming pool buildings should be recommended in order to reduce the radon content in the indoor air.

5.2. Assessment of Radiological Risk Resulting from the Consumption of Water as Drinking Water

The estimated mean effective dose resulting from the absorption of radioactive elements through the consumption of food and drinking water is 0.29 mSv/year. This value constitutes ca. 12% of the total dose from natural sources—2.4 mSv [40]. In accordance with quality standards laid down in European Union legislation [41], water can be treated as drinking water if the annual dose caused by radionuclides taken in with the water is below 0.1. Therefore, before the use of thermal water as drinking water is considered, an analysis should be undertaken in terms of radiological hazards. The committed effective dose D resulting from the intake of radionuclides occurring in drinking water can be estimated by the following formula:

$$D = V \cdot \sum_{i=1}^{n} A_i \cdot e(g)_i \quad (2)$$

where: V is the annual consumption of water, A_i is the activity concentration of the given radionuclide in water expressed in Bq/L and $e(g)_i$ stands for the dose in Sv resulting from the ingestion of 1 Bq of the given radionuclide [42].

In accordance with WHO Guidelines for Drinking Water Quality [43] an annual water consumption of 730 L (2 L/day) was assumed for the calculations. The estimated committed effective doses range from 0.011 mSv/year (Cieplice C-1) to 1.44 mSv/year (Duszniki GT-1). For six waters, the estimated doses do not exceed the level of 0.1 mSv/year (Table 3). As the above analysis shows, from the radiological point of view the use of thermal waters as drinking water resources may result in a problem associated with exceeding the annual permissible dose of 0.1 mSv. It should be emphasised that most of the waters studied would need to undergo a water purification process, which is also necessary due to their chemical composition (overly high content of other elements, among them chlorine and boron ions [44]. The water purification processes would result in partial removal of radionuclides from the water, and as a consequence, reduce the committed effective dose related to the consumption of waters. For example, the research of Gafvert et al. [45], Kleinschmidt and Auber [46] and Tomaszewska and Bodzek [47] show that the reduction of the natural radionuclide content in water as a result of water purification processes may even reach 90% of the initial content.

6. Discussion

The dependence of water temperature on the depth of the water hosting formation is shown in Figure 3.

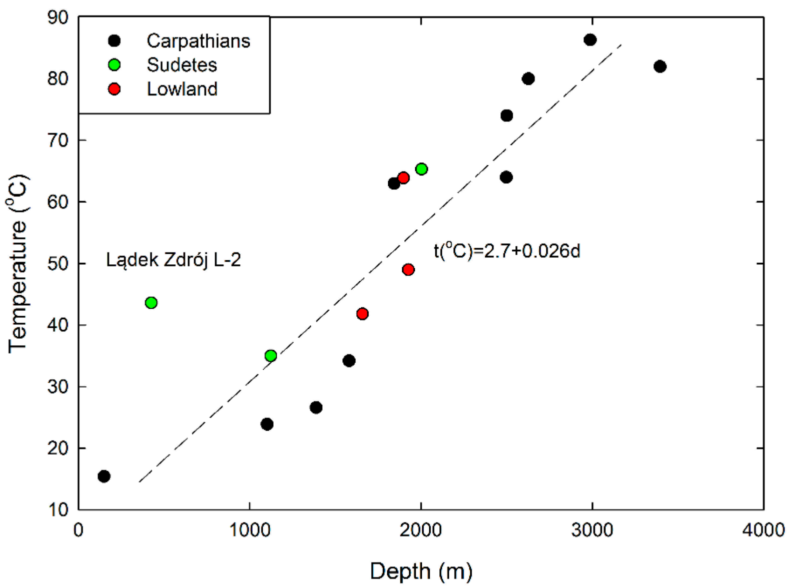

Figure 3. Relationship between water temperature and aquifer depth.

Excluding the water from the Lądek L-2 intake, all the points are scattered on the line t (°C) = 2.7 + 0.026 d (m) where d is the depth expressed in metres. Assuming that there is a thermal equilibrium between the thermal water and the rock aquifer, the coefficient at depth d can be regarded as the geothermal gradient and equal to 2.6 ± 0.4 °C per 100 m. This value is comparable with that earlier published for these regions [18,19].

There is no clear dependence of water mineralisation on the depth of the water hosting formation (Figure 4) but there is an increasing tendency to mineralisation.

This fact can be related to a different interaction between the water and rock aquifer due to differences in the physical and chemical characteristics of the water hosting formations and the physical and chemical properties of the waters in the regions studied.

The low uranium concentration in thermal water is linked to the reduction condition prevailing in groundwater in general and in the specific case of thermal water in particular. In all the waters studied, excluding the water from the Poronin PAN-1 intake, the Eh ranges from −27.7 mV up to −330 mV. In reduction conditions uranium forms insoluble compounds and disappears from the water.

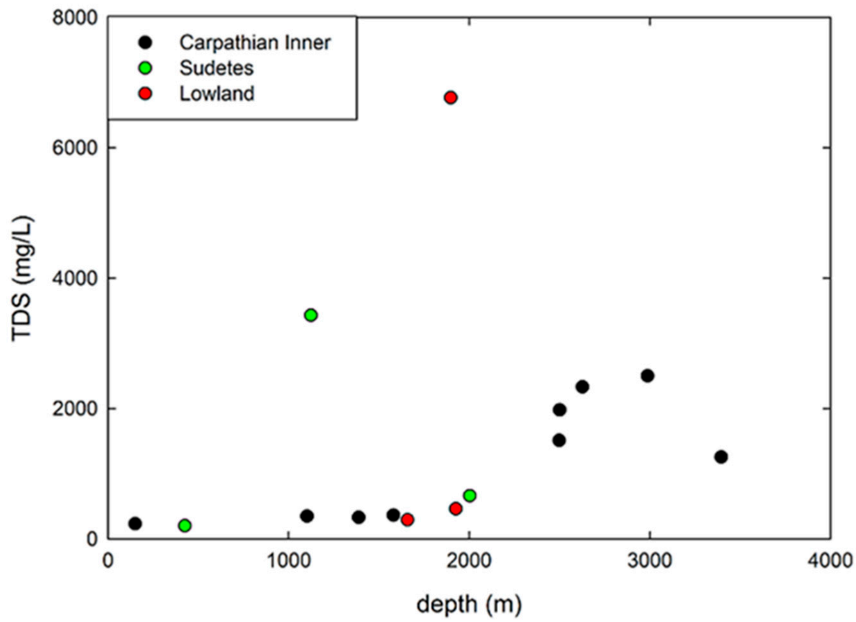

Figure 4. Relationship between water mineralisation and depth aquifer.

The concentrations of radium isotopes in thermal waters increase with their mineralisation (Figure 5).

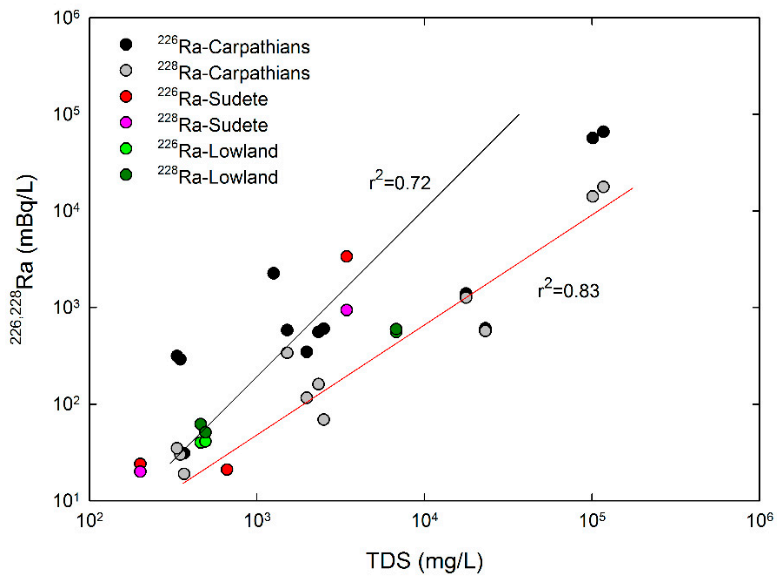

Figure 5. Relationship between the log of radium isotopes' concentrations and mineralisation (TDS) in Polish thermal waters.

The correlation coefficient is $r^2 = 0.83$ for ^{228}Ra (dark red line) and $r^2 = 0.73$ for ^{226}Ra (black line). Additionally, there is a clear linear correlation between the concentration of radioactivity of radium isotopes and the concentration of Ca^{2+} ions (Figure 6).

This fact is a consequence of a similarity in geochemical properties of radium with those of calcium. The radium isotope contents are very well correlated with hardness calculated using concentration of Ca^{2+} and Mg^{2+} expressed in mval unit (Figure 7).

Though ^{226}Ra is the number of the uranium series and ^{228}Ra is the element of the thorium series, there is a real correlation between them (Figure 8).

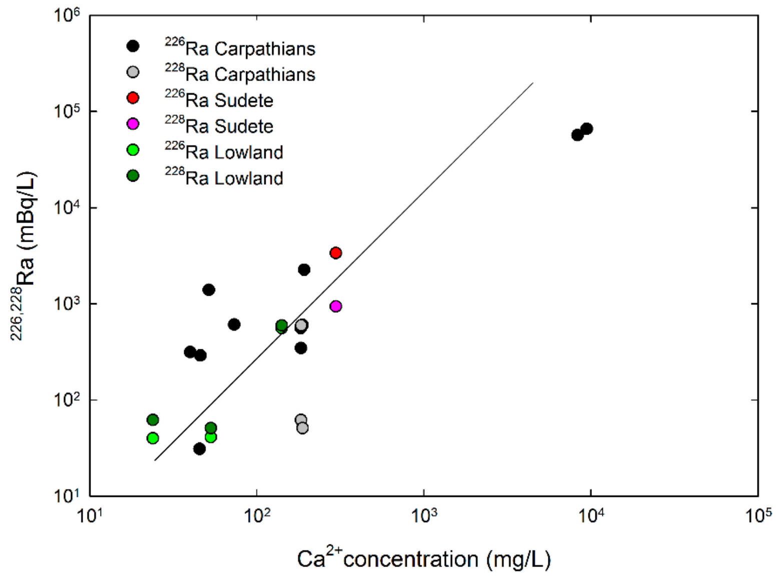

Figure 6. Relationship between radium content in Polish thermal waters and Ca^{2+} concentration (excluding Cieplice C-1 and Lądek-Zdój L-2).

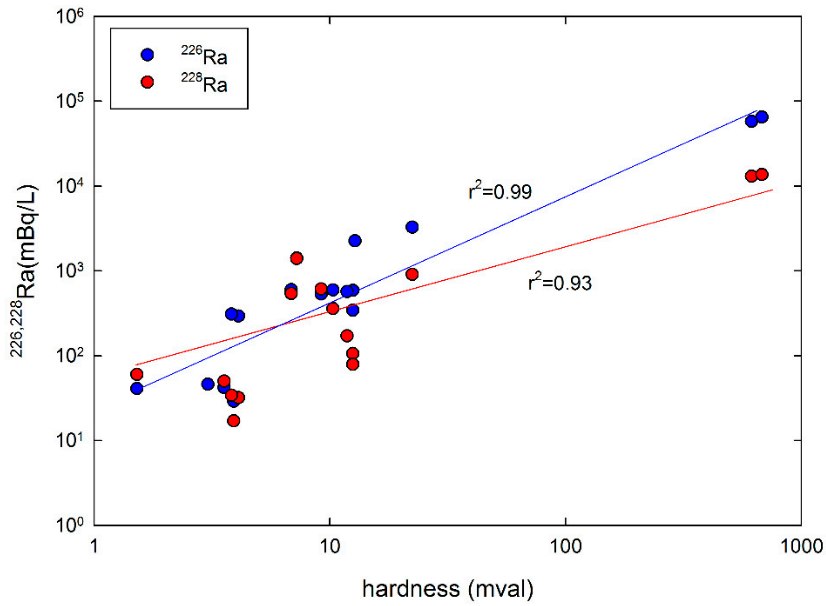

Figure 7. Relationship between water hardness and the concentrations of radium isotopes in the studied waters.

The ratio of the radioactivity concentration of radium isotopes ($^{226}Ra/^{228}Ra$) in groundwater is not only related to the relationship between the uranium and thorium content in the aquifer rocks, but also to the residence time in the underground aquifer as well as to the desorption/absorption coefficient of the groundwater [48,49]. In the case of the Carpathian and the Sudeten regions, the occurrence of thermal waters is mostly in limestone aquifers where the concentration of radioactivity of uranium is often higher than that of thorium (the ratio of concentration of radioactivity of $^{232}Th/^{238}U$ is 0.8). This is more due to the desorption coefficient of the thermal water being higher at high temperature than that of the water with low temperature. In consequence, the concentration of ^{226}Ra is higher than that of ^{228}Ra. In the case of waters from the Polish Lowlands, the concentration of radioactivity of ^{226}Ra is lower than that of ^{228}Ra (the $^{226}Ra/^{228}Ra$ ratio is less than one). This fact can be related to the content of uranium and thorium in the sandstone aquifer of the thermal water in this region in which the average activity ratio of $^{232}Th/^{238}U$ is approximately 2.3 [26]. Additionally, in this area the groundwater is probably mixed with infiltration water [26], resulting in the radium concentration being low and only reaching several tens of mBq/L.

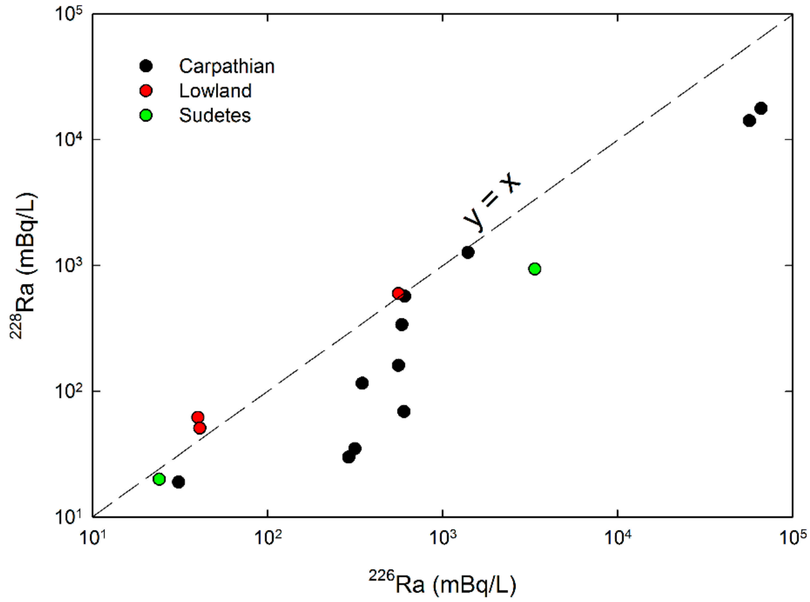

Figure 8. Relationship between ^{226}Ra concentration and ^{228}Ra concentration in the studied waters.

The uncertainties of the analysed radionuclides are invisible on all figures showing the relationships of their concentrations in the system with logarithmic ordinate.

Due to the low concentration of uranium in limestone and sandstone water aquifers, the radon concentration in the thermal waters studied is low and therefore they can be classified as low radon waters.

There is no correlation between ^{226}Ra and ^{222}Rn and weak correlation between ^{226}Ra and ^{210}Pb (Figure 9) suggest ^{222}Rn and ^{210}Pb are not directed from the radioactive decay of the ^{226}Ra in water.

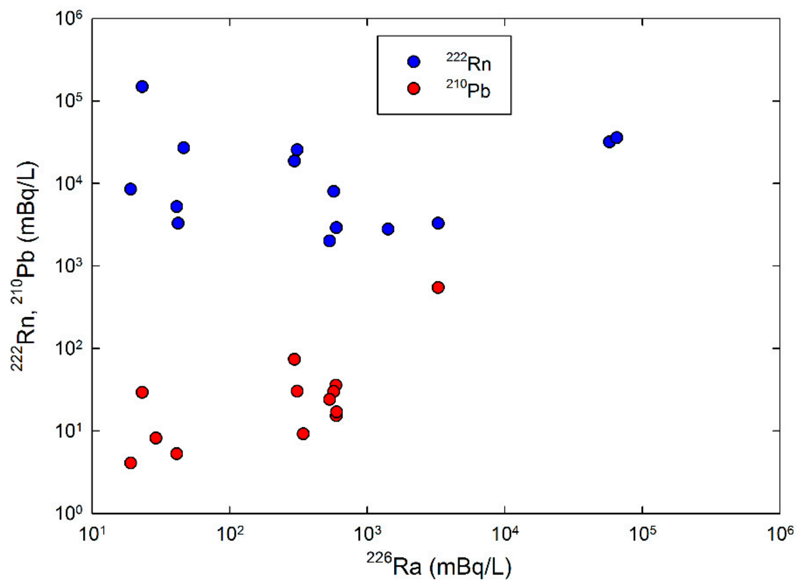

Figure 9. ^{226}Ra concentration vs. ^{222}Rn and ^{210}Pb concentrations.

Comparing the ^{226}Ra concentration with those of ^{222}Rn in the water from the Ustroń intakes (Table 2), we can see that the concentration of ^{222}Rn is far lower than that of ^{226}Ra, which is very rarely observed in groundwater. Since Rn in groundwater is often generated from an emanation process in the rock aquifer and the Ra in groundwater is discharged by the leachability of the minerals of the aquifer rock, in consequence the concentration of Rn is far higher than that of Ra (Table 2). The problem of ^{222}Rn in the Ustroń intake thermal water should be given serious consideration. In the case of the Ustroń intake, the Rn could be generated from the radioactive decay of the ^{226}Ra in the water and a certain fraction of the Rn gas formed can escape from the water into the surrounding rocks.

Excluding the water from Lądek Zdrój L-2, the measured Rn concentrations in the studied thermal waters are low enough and the calculated annual effective doses for occupants range from 0.022 mSv/year to 2.7 mSv/year. These effective doses fit well in the dose range estimated by Walczak and co-workers for nine selected Polish spa centres [50]. In consequence, the employees in spas with annual committed dose above 1 mSv/year are classified to the B category, who should undergo an annual medical examination, and the Rn in spa air should be monitored. In the Lądek Zdrój the calculated annual dose reached nearly 11 mSv/year; the employees of this spa are classified to the A class. In this case, the employee should bear a personnel dosimeter and the spa air should be treated to decrease the Rn level.

A lung dose in mSv/year is calculated by multiplying the Rn concentration in water (Bq/L) by the factor $1.1. \times 10^{-2}$ mSv/Bq [51]. In this case, the calculated lung dose ranged from 0.002 mSv/year to 1.48 mSv/year. However according to UNCEAR [40], the lung cancer resulting from the radon in water is nearly 0.1% in comparison with that resulting from the inhalation of radon in the air and it can be neglected in comparison with that resulting from tobacco smoking.

Because of the assumed short residence time in spa, the effective dose predicted for client is in order of tens µSv/year and can be ignored in the hazard assessment.

7. Conclusions

The temperature of the thermal waters in the study increases with depth of occurrence, suggesting that the temperature measurement of the thermal waters can serve as a method for determination of the geothermal gradient. In some cases, knowing the water temperature allows us to predict the degree of interaction between thermal water and rock aquifer [52].

There is no clear correlation between water mineralisation and aquifer depth, suggesting a significant difference in the rock aquifers and in the chemical and physical properties of the thermal waters studied as well as in the residence time of the thermal waters.

The thermal waters analysed are characterised by high variability of the content of natural radioactive elements. The concentration of radium isotopes generally increases with mineralisation, which is a feature of most groundwaters. In addition, a linear correlation has been found between the concentration of radium radioactivity and Ca^{+2} ion concentrations and water hardness.

It is probable that most of the Rn in the water from the Ustroń intakes originates from the Ra within it; this fact is very rarely observed in groundwater.

In the case of recreational bathing, the calculated annual doses for clients of thermal water spas using the waters studied are much lower than the annual radiation dose limit for members of the public (1 mSv). Generally, the thermal waters studied do not pose a radiological risk for clients of spas when used for recreational purposes. In the case of spa workers, the calculated annual effective doses may exceed the lower reference limit for category B workers (1 mSv) when considering thermal water with a radon content higher than 18 Bq/l. Therefore, some action should be undertaken to reduce the radon content in the indoor air of swimming pool buildings.

From a radiological point of view, the use of the thermal waters studied as a drinking water resource may be problematic, given the possibility of exceeding the recommended annual committed effective dose (0.1 mSv).

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