



²²²Rn Concentration in Groundwaters Circulating in Granitoid Massifs of Poland

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Abstract: The authors' research has shown that the maximum values of ²²²Rn activity concentration in all granitoid massifs of Poland exceed 100 Bq·L⁻¹, i.e., the value allowed for waters intended for human consumption. Such waters should be de-radoned prior to being distributed through the water supply networks. Even more common in these areas is the occurrence of potentially medicinal radon waters, i.e., waters characterized, in accordance with Polish law, by radon activity concentration of at least 74 Bq·L⁻¹. Such waters may be used for balneotherapeutic treatments. For the Karkonosze, Strzegom-Sobótka, Kłodzko-Złoty Stok and Kudowa massifs, the range of hydrogeochemical background of ²²²Rn exceeds both 74 and 100 Bq·L⁻¹. This indicates common occurrence in these areas of both potentially medicinal radon waters and waters which require de-radoning before being supplied for human consumption. More than 50% of groundwaters from the Karkonosze granite area contain over 100 Bq·L⁻¹ of ²²²Rn. This means that these waters are mostly radon and high-radon waters. The remaining massifs contain predominantly low-radon waters and radon-poor waters. The ²²²Rn concentrations obtained by the authors are comparable to values measured in groundwaters in other granitoid massifs in the world, creating both problems and new application possibilities.

Keywords: radon; groundwater; radon water; tap water; medicinal water; granite; granitoid; hydrogeochemical background

1. Introduction

The radon isotope ²²²Rn, alongside radium isotopes ²²⁶Ra and ²²⁸Ra, is the most important natural component of groundwaters, giving them their radioactive properties [1,2]. ²²²Rn is a natural radioactive isotope whose activity concentration in groundwaters varies in a very broad range—from 10^{-4} Bq·L⁻¹ to 102,000 Bq·L⁻¹, hence reaching 9 orders of magnitude [3]. Among the four natural isotopes of radon (with mass numbers 222, 220, 219 and 218), it is only ²²²Rn that, owing to its half-life of slightly more than 3.82 days [4–6], can be transported with groundwater over distances of dozens or even hundreds of metres, and occasionally even further [2,7]. This is the reason for common occurrence of ²²²Rn in groundwater environment [3,8,9]. The activity concentration of this gas in groundwater is mainly due to the parent ²²⁶Ra content in the reservoir rock and the emanation coefficient of this rock [2,10,11] enabling the ²²²Rn formed in it to be released from the structures of rock minerals and grains containing ²²⁶Ra, and then dissolved in water. Therefore, the highest concentrations of radon could be expected in groundwaters flowing through granitoid reservoir rocks. Radon-enriched waters occur particularly in areas of strong brittle tectonic deformations and in zones of fractures and



weathering alterations, hence at small depths of the order of several dozen meters under the ground surface [2,11,12].

From the point of view of radiological protection, ²²²Rn present in groundwater in concentrations higher than 100 Bq·L⁻¹ is hazardous to human health and it should be removed from water before it is used for human consumption. This issue is regulated by appropriate European Union legislation [13], which was the basis for setting this parametric value also in Polish law [14]. At the same time, numerous radon health resorts around the world offer balneotherapeutic treatments using radon waters [12,15–21]. In Poland, groundwaters with ²²²Rn activity concentration of at least 74 Bq·L⁻¹ can be regarded as medicinal in light of geological and mining law [22].

In areas built of granitoid rocks, one can expect the occurrence of radon-enriched waters. This calls for thorough assessment of radon concentration in groundwaters occurring in these areas. On the one hand, it is essential to prevent residents' exposure to increased effective doses of ionizing radiation from radon released from water and inhaled together with its radioactive decay products, isotopes of ^{218,214,210}Po, ^{214,210}Bi, ^{214,210}Pb and ^{210,206}Tl, formed in the air. On the other hand, this information may be significant for medicinal and balneotherapeutic procedures based on the extraction and exploitation of radon-enriched waters in health resorts [12].

The aim of the authors' research is the assessment of the range of ²²²Rn content in groundwaters occurring in these areas of Poland whose geological structure is dominated by granitoid rocks. This information is essential for the needs of groundwater usage planning in these areas and effective radiological protection of their inhabitants.

2. Research Area

In Poland, areas with geological structures dominated by granitoid massifs are found in the south-western and the southern parts of the country (Figure 1). So far, it is mainly the area of Lower Silesia, i.e., the south-western part of the country, where research into radon occurrence in the natural environment has been conducted [23]. The geological structure of this part of Poland is the reason for the occurrence of locally high or very high concentrations of radon. The south-western part of Poland is made up of the so-called Lower Silesian block, whose southern part is composed of the Sudety mountain ranges, and the northern part-of foothills forming the geological structures of the so-called Fore-Sudetic block. These two parts are separated from each other by a regional tectonic dislocation-the Sudetic marginal fault. This region constitutes the north-eastern part of the crystalline Bohemian massif, one of major massifs built of crystalline (igneous and metamorphic) rocks in Europe [24–26]. The structure of this area is characterized by the occurrence at small depths or on the surface of uranium-enriched crystalline rocks, including granitoid massifs [2,23,27,28]. In about a dozen places in the area of the Sudetes, usually small and now unexploited uranium deposits have been documented [29–32]. This is the reason why Lower Silesia is the only area in Poland for which a map of radon potential has been created [33]. The groundwaters of this area have been the main subject of numerous research works on hydrogeochemistry of ²²²Rn and its parent ²²⁶Ra [34–46]. Also, detailed research has been conducted into the occurrence of ²²²Rn in groundwaters flowing through granitoid rocks of three Variscan massifs located in the Sudetes [47].

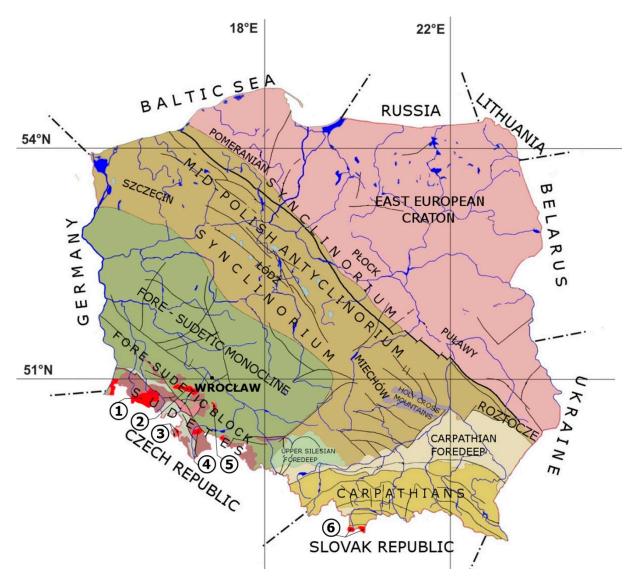


Figure 1. Location of granitoid massifs on a simplified tectonic map of Poland without Cainozoic deposits (according to [48–50]; slightly modified). 1–Karkonosze granite, 2–Strzegom-Sobótka granitoid, 3–Kudowa granitoid, 4–Kłodzko-Złoty Stok granitoid, 5–Strzelin granitoid, 6–Tatra granitoid.

The authors are currently continuing research into ²²²Rn occurrence in groundwater environment. The analysis of results obtained so far has resulted in a decision to extend the research onto all granitoid massifs in Poland. The authors' research is mainly focused on five areas of Variscan granitoid occurrence in Lower Silesia, which has considerably broadened the current knowledge of this problem presented by Przylibski and Gorecka [47]. Moreover, this is the first time that research has covered the area of Variscan granitoids of the Tatras, building the inner part of the Carpathians, an alpine orogen [51,52].

3. Methods of Measurements and Result Calculation

Over the course of fieldwork, the authors collected groundwater samples from accessible springs and wells (usually shallow dug wells), and occasionally also from accessible deep drilled wells. In mountain areas, i.e., in the areas of the Karkonosze granite massif and of the Tatra granitoids, water samples were taken chiefly from springs. In the area of Kudowa granitoids, the proportions of springs and wells in water sampling were comparable while in the remaining granitoid massifs (Kłodzko-Złoty Stok, Strzelin and Strzegom-Sobótka), most groundwater samples were taken from wells. From each well or spring, three groundwater samples of 10 mL each were collected with a disposable syringe. The samples were then injected into scintillation vials, each filled with 10 mL of liquid scintillator Insta-Fluor[™] PLUS. The vials were then sealed and vigorously shaken several times. This enabled the transition of ²²²Rn from the water sample to the scintillator, in which the gas dissolves better than in water.

Thus prepared groundwater samples were transported to the Laboratory of Earth Sciences and Mineral Engineering, Wrocław University of Science and Technology, in whose Isotope Laboratory measurements of ²²²Rn activity concentration were conducted in an ultra-low background liquid-scintillation spectrometer α/β Quantulus 1220. Measurement vials were placed on special templates inside the spectrometer, each able to carry a maximum of 60 vials. The measurement is fully automatic and based on LSC (liquid scintillation counting) technique. It consists of counting the impulses being the light effect of ionizing radiation reaction with the scintillator. Subsequently, the obtained alpha and beta radiation spectrum is analysed.

In the liquid scintillator, the gaseous nuclide ²²²Rn, originating from groundwater reservoir rocks (its activity concentration decreases according to ²²²Rn decay constant from the moment of taking the water sample) and produced as a result of the decay of the parent nuclide ²²⁶Ra dissolved in water (its activity concentration may initially increase until the radioactive equilibrium between ²²⁶Ra and ²²²Rn is reached) is dissolved. For this reason, measurements are performed in two stages. The first stage consists of determining the ²²²Rn activity concentration in the analysed water sample converted to its concentration at the moment of water outflow from the aquifer. The measurement takes place immediately after the samples' arrival in the laboratory. Before the start of the measurements, the samples have to be cooled in the appliance so all the measurement will take place at a stable temperature. The time of about 4 hours, necessary for the settling of the radioactive equilibrium between the radon isotope and its short-lived decay products, has to be allowed. This equilibrium is usually reached while water samples are still being transported to the laboratory. Each of the three vials containing the collected groundwater is subjected to nine 1-hour long measurements. In the case of groundwaters containing considerable concentrations of dissolved radium (²²⁶Ra), radon activity concentration (²²²Rn) may increase over time. This requires correction of the result obtained during the first stage by performing another measurement. The second stage of the measurements takes place after time t, necessary for the complete decay of the ²²²Rn initially present in water to take place and, in practice, to obtain the value of activity concentration below the LLD (lower detection limit) of the spectrometer. Time t can be calculated from formula (1). This makes it possible for the second stage to cover the measurement of the activity concentration of ²²²Rn originating solely from the decay of its parent isotope ²²⁶Ra dissolved in the analysed groundwater. This measurement is performed with the same sealed vials containing scintillator and the collected water. The eventual result for ²²²Rn activity concentration in water is converted to the concentration at the moment of water outflow from the aquifer. It embraces both the ²²²Rn released as gas from reservoir rocks and the ²²²Rn originating directly from the decay of ²²⁶Ra dissolved in the groundwater present in the aquifer. However, it does not comprise the surplus ²²²Rn formed in the collected water from the dissolved ²²⁶Ra during the time between taking the sample and the end of the first stage of the measurement. The applied calculations are based on the radioactive decay law and the equations described by Bateman in 1910 [53], and they take into account the presence of ²²²Rn decay products in the sample. The time t needed for the decay of the ²²²Rn initially present in a water sample below the detection limit of the device is calculated from the formula:

$$t > \log_2(\frac{C_{222_{Rn}}}{LLD}) \cdot t_{\frac{1}{2}(222_{Rn})}$$
(1)

where:

t-time needed for the decay of ²²²Rn nuclei to the activity concentration below the lower detection limit of the spectrometer [24 hours],

 $C_{222_{Rn}}$ -²²²Rn activity concentration [Bq·L⁻¹],

LLD–lower detection limit of the spectrometer; 0.05 Bq·L⁻¹, $t_{\frac{1}{2}(222_{Rn})}^{-222}$ Rn half-life; the duration of 3.8224 days was adopted.

The values of ²²²Rn activity concentration in groundwaters collected from each of the six analysed geological units, i.e., granitoid massifs, constituted the authors' input data set. To provide a coherent presentation, these data were characterized by means of basic descriptive statistic parameters. They comprised such parameters as the minimum and maximum value of a data set, the arithmetic mean, the median, the standard deviation and 95% confidence limit.

Based on the registered values of ²²²Rn activity concentration in groundwaters, ranges of the hydrogeochemical background of ²²²Rn were determined for the analysed granitoid massifs. This required the performance of several operations aimed at verifying the available data and analysing the type of statistical distribution of these values. At the first stage, Graf's test was used to verify the data for the presence of possible gross errors. Then extreme values and outliers were identified and removed from the data sets. In order to standardize these sets, logarithmic transformation of variables was performed. Values greater than three times the interquartile range were regarded as extreme values, and those greater than 1.5 times the interquartile range from the lower or upper quartile–as outliers [54]. For the thus modified data sets, log-normal data distribution was confirmed at the adopted significance level of 0.05, based on compliance test χ^2 . The next stage consisted of calculating the hydrogeochemical background, for which the most reliable method is computational method $Z \pm 1.28\sigma$, where Z is the mean value and σ -the standard deviation [55]. Only in the case of the Karkonosze granite massif, values did not demonstrate a log-normal distribution. The range of hydrogeochemical background for this unit was calculated based on the median M and its standard deviation $\sigma_M (M \pm \sigma_M)$.

4. Results and Discussion

The authors measured ²²²Rn activity concentration in groundwaters collected at 493 points in the area of 6 granitoid massifs in Poland (Figures 2–7). Such wide-ranging measurements had not been performed in Poland before. The authors sought to make sure that groundwater sampling was relatively uniform within each granitoid massif. As a result, they discovered that none of the analysed massifs comprised areas with particularly high occurrence of waters with low or high ²²²Rn content (cf. Figures 2–7). The results of the conducted analyses are shown in Table 1. It contains selected descriptive statistics characterizing sets of data on ²²²Rn activity concentration in groundwaters in particular granitoid massifs. The obtained results demonstrate maximum values exceeding 100 Bq \cdot L⁻¹ in all granitoid massifs in Poland. It indicates a possibility of capturing groundwaters with ²²²Rn activity concentrations exceeding the value allowable for waters intended for human consumption in all areas with granitoid rocks playing an important part in their structures. This points to the necessity of de-radoning such water before it is distributed through a water supply network. What is even more likely is the occurrence within Polish granitoid massifs of waters regarded as potentially medicinal due to the 222 Rn content reaching, according to Polish law, at least 74 Bq·L⁻¹. This means that 222 Rn content determination in groundwaters is essential in these areas, both in terms of radiological protection and possible use of such waters in balneotherapy (radonotherapy).

Among all the studied granitoid massifs, the highest mean, median and maximum values of ²²²Rn activity concentration are characteristic of groundwaters in the Karkonosze, followed by those in the Strzegom-Sobótka and Kłodzko-Złoty Stok massifs. The lowest values of these statistical parameters were found in groundwaters from the granitoids of the Tatras and the Strzelin massif. The obtained results are consistent with the results of earlier research conducted on fewer groundwater samples from the Karkonosze, Strzegom-Sobótka, Strzelin and Kłodzko-Złoty Stok granitoid massifs [42,47]. These archival data are shown in Table 2.

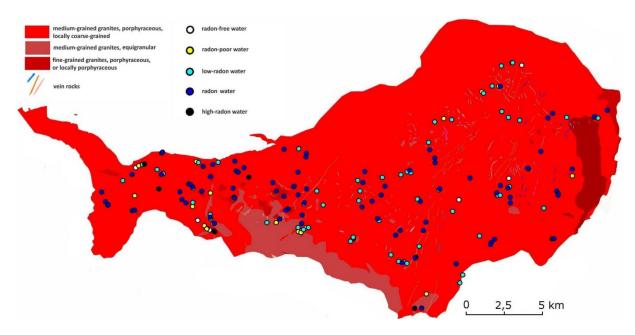


Figure 2. The Karkonosze granites. Groundwater sampling sites plotted together with the types of collected water by ²²²Rn content according to Przylibski's classification [2].

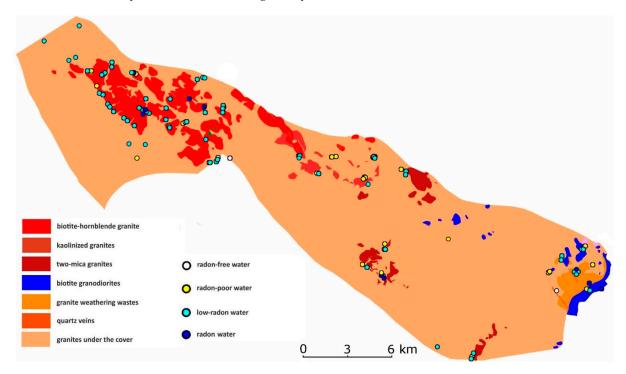


Figure 3. Strzegom-Sobótka granitoids. Groundwater sampling sites plotted together with the types of collected water by ²²²Rn content according to Przylibski's classification [2].

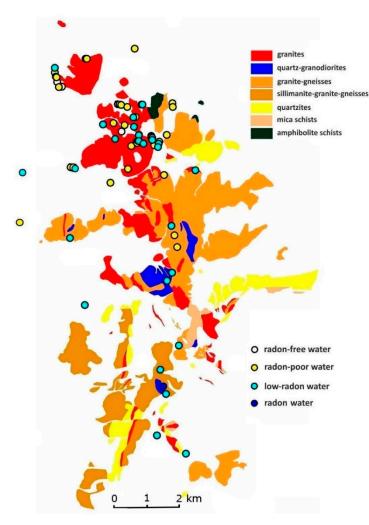


Figure 4. Strzelin granitoids. Groundwater sampling sites plotted together with the types of collected water by ²²²Rn content according to Przylibski's classification [2].

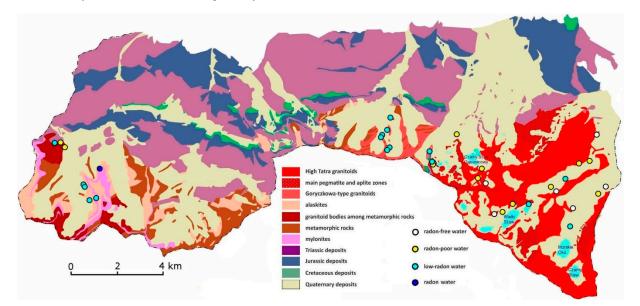


Figure 5. The Tatra granitoids. Groundwater sampling sites plotted together with the types of collected water by ²²²Rn content according to Przylibski's classification [2].

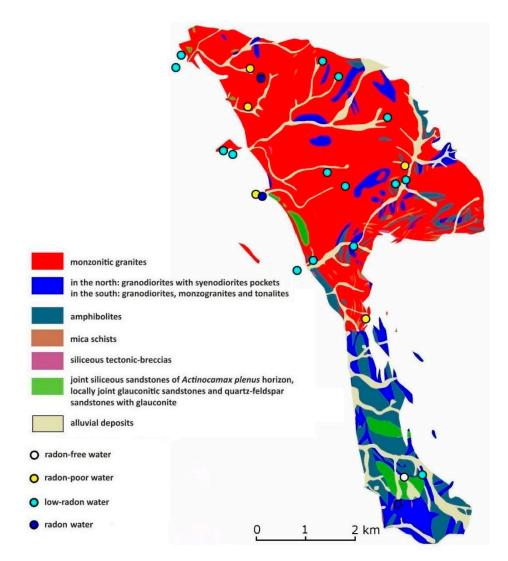


Figure 6. Kudowa granitoids. Groundwater sampling sites plotted together with the types of collected water by ²²²Rn content according to Przylibski's classification [2].

Table 1. Selected descriptive statistic values for ²²² Rn activity concentration in groundwaters from
granitoid massifs of Poland.

Granitoid Massif	Number of Data	Min.	Max.	Arithmetic Mean	Standard Deviation	Median	The Lower	The Upper
							95% Confidence Limit	
	(-)		(Bq·L ⁻¹)					
Karkonosze	203	0.3	1465	217	280	106	76.0	137.6
Strzegom-Sobótka	115	0.4	415.5	43.5	68.5	19.1	15.0	28.1
Strzelin	69	0.5	119.4	15.7	21.8	7.9	5.4	12.5
Kłodzko-Złoty Stok	45	1.0	287.3	57.6	57.0	36.3	20.8	65.6
Kudowa	25	0.9	143.9	38.5	40.9	20.6	14.2	61.2
Tatra	36	0.2	104.2	18.6	23.8	9.5	2.9	16.1

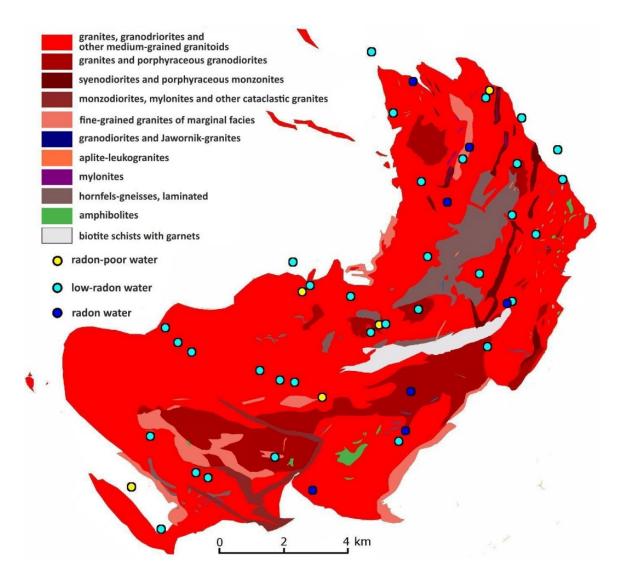


Figure 7. Kłodzko-Złoty Stok granitoids. Groundwater sampling sites plotted together with the type of collected water by ²²²Rn content according to Przylibski's classification [2].

Granitoid Massif	Number of Data	Minimum	Maximum	Arithmetic Mean	Standard Deviation	Median
	[-]			$[Bq \cdot L^{-1}]$		
Karkonosze	199 ^a 58 ^b	0.3 ^a 0.3 ^b	1391.5 ^a 1716 ^b	212 ^a 293 ^b	275.1 ^a 367 ^b	106 ^a 179 ^b
Strzegom-Sobótka	95 ^a	0.3 ^a	415.5 ^a	42.4 ^a	64.0 ^a	19.1 ^a
Strzelin	55 ^a	0.5 ^a	95.1 ^a	14.2 ^a	19.1 ^a	7.9 ^a
Kłodzko-Złoty Stok	22 ^b	1.5 ^b	228 ^b	65.5 ^b	57.0 ^b	34.5 ^b

Table 2. Archival descriptive statistic values for ²²²Rn activity concentration in groundwaters from granitoid massifs of Poland.

a-data according to [47]. b-data according to [42].

Even more clearly, the necessity of determining ²²²Rn content in groundwaters captured in the areas of granitoid massifs of Poland is demonstrated by the recorded values of ²²²Rn hydrogeochemical background. The calculated values of the background with reference to archival values, obtained for far smaller data sets [55] are shown in Table 3. For 4 massifs: the Karkonosze, Strzegom-Sobótka,

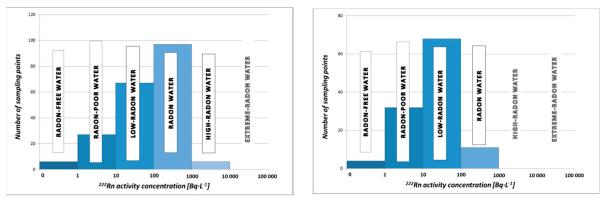
Kłodzko-Złoty Stok and Kudowa massifs, the range of hydrogeochemical background exceeds both 74 and 100 Bq·L⁻¹. This indicates common occurrence in these areas of both potentially medicinal radon waters and waters which require de-radoning before being supplied for human consumption. Therefore determination of ²²²Rn activity concentration should be also common in groundwater intakes supplying individual residential buildings in these areas.

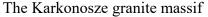
Table 3. Ranges of hydrogeochemical background of ²²²Rn in groundwaters from granitoid massifs of Poland.

Granitoid massif	Hydrogeochemical background of ²²² Rn (Bq·L ⁻¹)		
Karkonosze	$16 \div 690$ $21 \div 868^{a}$		
Strzegom-Sobótka	3÷112		
Strzelin	$1.4 \div 40$		
Kłodzko-Złoty Stok	$10 \div 140 \\ 6 \div 242^{a}$		
Kudowa	3.9 ÷ 109		
Tatra	$0.7 \div 61$		
	data assauding to [55]		

a-data according to [55].

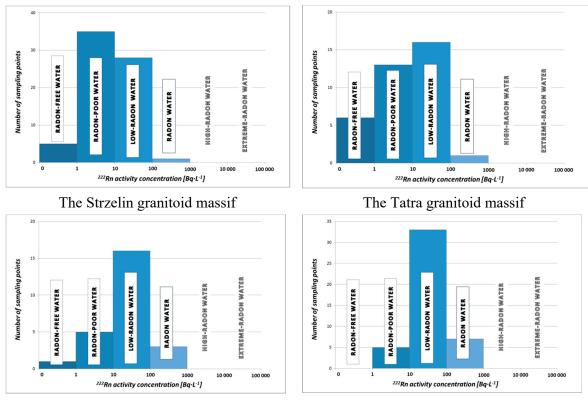
The occurrence of groundwaters with ²²²Rn activity concentration of more than 100 Bq·L⁻¹ in particular granitoid massifs in Poland is presented by histograms shown in Figure 8. In the case of the Karkonosze massif, such waters account for over 50% of all groundwaters while in the areas of the remaining granitoid massifs, they make up from several to about a dozen per cent of all groundwaters. The number of potentially medicinal radon groundwater occurrences is even higher and it is 117 (57.6%), 19 (16.5%), 2 (2.9%), 14 (31.1%), 5 (20%), and 1 (2.8%) for the granitoid massifs of the Karkonosze, Strzegom-Sobótka, Strzelin, Kłodzko-Złoty Stok, Kudowa and the Tatra mountains respectively. In the Karkonosze massif, radon waters predominate. According to Przylibski's classification [2], they contain from 100 to 999.99 Bq·L⁻¹ of ²²²Rn. In the remaining granitoid massifs, low-radon waters, with ²²²Rn content from 10 to 99.99 Bq·L⁻¹ predominate, and in the granitoid massif of Strzelin—waters poor in radon, with ²²²Rn content between 1 and 9.99 Bq·L⁻¹ (cf. Figure 8).

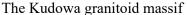




The Strzegom-Sobótka granitoid massif

Figure 8. Cont.





The Kłodzko-Złoty Stok granitoid massif

Figure 8. Histograms of ²²²Rn activity concentration in groundwaters from granitoid massifs of Poland. Names of groundwater types by ²²²Rn content by Przylibski [2].

The obtained results indicate that in every granitoid massif in Poland one may expect the occurrence of both potentially medicinal radon waters and waters with ²²²Rn activity concentration exceeding the value allowable for waters intended for human consumption, i.e., 100 $Bq L^{-1}$. Nevertheless, the frequency of such groundwater occurrence depends on the concentration of uranium and parent ²²⁶Ra in granitoid rocks, on the grade of weathering and erosion, and on granitoid massif exposure on the earth's surface [47]. Among Polish granitoids, it is undoubtedly the granite massif of the Karkonosze which has the highest prospect of the occurrence of potentially medicinal radon waters and of groundwaters that require de-radoning before being used as the source of water intended for human consumption. In the area of this massif itself, more than half of groundwater occurrence are potentially medicinal radon waters and waters with 222 Rn activity concentration above 100 Bq·L⁻¹. It is also the only Polish granitoid massif with the occurrence of high-radon groundwaters, containing, according to Przylibski's classification [2] from 1 000 to 9 999.99 Bq·L⁻¹ of ²²²Rn. The second highest occurrence of radon waters, and possibly also high-radon waters, should be expected in the areas of Strzegom-Sobótka, Kłodzko-Złoty Stok and Kudowa granitoid massifs. The smallest proportion of radon groundwaters was identified in the areas of the granitoid massifs of Strzelin and the Tatra mountains. The performed measurements indicate that further research and measurements aimed at documenting the occurrence of potentially medicinal radon waters should be conducted especially in the massifs of the Karkonosze, Strzegom-Sobótka and, subsequently, Kłodzko-Złoty Stok and Kudowa. At the same time, in view of radiological protection of residents, groundwater analyses for ²²²Rn content should be conducted in the area of all granitoid massifs in Poland.

Similar conclusions could be extended onto all granitoid massifs of all ages, lying on all continents, as the ²²²Rn concentrations measured by the authors in groundwaters circulating in granitoid massifs in Poland are comparable to the values measured in groundwaters in other granitoid massifs in the world. Example values of ²²²Rn activity concentration in groundwaters circulating in granitoid massifs

on various continents have been compiled in Table 4. Granitoid massifs can be treated as some of the areas with the most likely occurrence of both potentially medicinal radon waters and waters with ²²²Rn activity concentrations excluding them from being intended as drinking water or from household usage inside residential buildings. In areas whose geological structures are dominated by granitoid rocks, ²²²Rn activity concentration in groundwaters may exceed even 100,000 Bq·L⁻¹, and radon groundwater occurrence is common. In this respect, groundwaters flowing through granitoid massifs in Poland are not different from similar massifs in Europe and on the other continents.

Granitoid Massif Location	²²² Rn activity Concentration [Bq·L ⁻¹]	References
	EUROPE	
	Sweden	
Stripa granite	Max. 102,000	[56,57]
	Norway	
Iddefjord granite	65–8,500	[58]
	Germany	
Bad Brambach	Max. 25,000	[59]
	Austria	
Bohemian Massif	Max. 793	[60]
Variscan meta-granites in the Alps	Max. 120	[60]
	Denmark	
Bornholm	Max. 1070	[61]
	Portugal	
Vila Real (northern Portugal); springs	Max. 938	[62]
	United Kingdom	
Carnmenellis Granite	Max. 740	[8]
	ASIA	
	Korea	
Korea: Jurassic Granite Area, Icheon, Middle Korea	Max. 865.8	[63]
	India	
Tumkur district	Max. 253	[64]
Himalaya Munsiari Fm. and Bhatwari Fm.	Max. 887	[65]
	AFRICA	
	Ghana	
Aprade-Mesuam	Dug well (mean): 41.26 Borehole (mean): 46.16	[66]
	Nigeria	
Gubrunde	15.8 ± 0.2	[67]
Kundiga	26.6 ± 0.3	[67]
0	AMERICAS	r 1
	Brasil	
Águas de Lindóia	22.1 ± 1.1	[68]
	USA	
Maine	Max. 55,000	[69]

Table 4. ²²²Rn activity concentration in groundwaters from selected granitoid massifs of the world.

5. Conclusions

The results obtained by the authors demonstrate that the maximum values of 222 Rn activity concentration in all granitoid massifs in Poland exceed 100 Bq·L⁻¹. This indicates a possibility of capturing groundwaters with 222 Rn activity concentration beyond the value allowable for waters intended for human consumption in the areas of the studied granitoid massifs. Such waters should be de-radoned prior to being distributed through water supply networks. What is even more common is the occurrence in these areas of potentially medicinal radon waters, i.e., waters characterized, according to Polish law, by 222 Rn activity concentration of at least 74 Bq·L⁻¹. This means that 222 Rn content determination in groundwaters is essential in these areas, both from the point of view of radiological protection and possible use of radon waters in balneotherapy (radonotherapy).

In the area of Poland, the highest mean, median and maximum values of ²²²Rn activity concentration have been found in groundwaters in the Karkonosze massif, followed by the massifs of Strzegom-Sobótka and Kłodzko-Złoty Stok. For the four Polish massifs: the Karkonosze, Strzegom-Sobótka, Kłodzko-Złoty Stok and Kudowa, the range of hydrogeochemical background of ²²²Rn exceeds both 74 and 100 Bq·L⁻¹. This indicates common occurrence in these areas of both potentially medicinal radon waters and waters requiring de-radoning before being supplied for human consumption. More than 50% of groundwaters from the Karkonosze granite area contain over 100 Bq·L⁻¹ of ²²²Rn. This means that waters circulating in the rocks of this massif are mostly radon and high-radon waters. The remaining massifs contain predominantly low-radon and radon-poor waters. Nevertheless, the number of potentially medicinal radon groundwater occurrences is 117 (57.6%), 19 (16.5%), 2 (2.9%), 14 (31.1%), 5 (20%), and 1 (2.8%) for the granitoid massifs of the Karkonosze, Strzegom-Sobótka, Strzelin, Kłodzko-Złoty Stok, Kudowa and the Tatra mountains respectively. Therefore granitoid massifs of Poland are characterized by the occurrence of potentially medicinal radon waters. They could supply the existing and future health resorts with the necessary resources.

The ²²²Rn concentrations measured by the authors in groundwaters circulating in granitoid massifs in Poland are comparable to values measured in groundwaters in other granitoid massifs in the world. Granitoid massifs can be treated as some of the areas with the most likely occurrence of both potentially medicinal radon waters and waters whose ²²²Rn activity concentrations could exclude them from being intended as drinking water or from household usage inside residential buildings.

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References

- 1. Chau, N.D.; Dulinski, M.; Jodlowski, P.; Nowak, J.; Rozanski, K.; Sleziak, M.; Wachniew, P. Natural radioactivity in groundwater—A review. *Isotopes Environ. Health Stud.* **2011**, *47*, 415–437. [CrossRef]
- 2. Przylibski, T.A. *Radon. Specific Component of Medicinal Waters in the Sudety Mountains*; Oficyna Wydawnicza Politechniki Wrocławskiej: Wrocław, Poland, 2005. (In Polish)

- 3. Girault, F.; Perrier, F.; Przylibski, T.A. Radon-222 and radium-226 occurrence in water: A review. In *Radon*, *Health and Natural Hazards*; Gillmore, G.K., Perrier, F.E., Crockett, R.G.M., Eds.; Geological Society of London: London, UK, 2018; Volume 451, pp. 131–154. [CrossRef]
- 4. Collé, R. A precise determination of the ²²²Rn half-life by $4\pi \alpha\beta$ liquid scintillation measurements. *Radioact. Radiochem.* **1995**, *6*, 16–29.
- 5. Collé, R. Critically evaluated half-life for ²²²Rn radioactive decay and associated uncertainties. *Radioact. Radiochem.* **1995**, *6*, 30–40.
- 6. Bellotti, E.; Brogan, C.; Di Carlo, G.; Laubenstein, M.; Menegazzo, R. Precise measurement of the ²²²Rn half-life: A probe to monitor the stability of radioactivity. *Phys. Lett. B* **2015**, *743*, 526–530. [CrossRef]
- 7. Przylibski, T.A. Size estimation and protection of the areas supplying radon to groundwater intakes. *Arch. Environ. Prot.* **2000**, *26*, 55–71.
- 8. Ball, T.K.; Cameron, D.G.; Colman, T.B.; Roberts, P.D. Behaviour of radon in the geological environment: A review. *Q. J. Eng. Geol. Hydrogeol.* **1991**, *24*, 169–182. [CrossRef]
- Appleton, J.D. Radon in air and water. In *Essentials of Medical Geology*; Selinus, O., Alloway, B., Centeno, J.A., Finkelman, R.B., Fuge, R., Lindh, U., Smedley, P., Eds.; Springer: Dordrecht, The Netherlands, 2013; pp. 239–277.
- 10. Przylibski, T.A. Estimating coefficient of radon emanation from crystalline rocks into groundwater. *Appl. Radiat. Isot.* **2000**, *53*, 473–479. [CrossRef]
- 11. Przylibski, T.A. Shallow circulation groundwater—The main type of water containing hazardous radon concentration. *Nat. Hazards Earth Sys.* **2011**, *11*, 1695–1703. [CrossRef]
- Przylibski, T.A. Radon. A radioactive therapeutic element. In *Radon, Health and Natural Hazards*; Gillmore, G.K., Perrier, F.E., Crockett, R.G.M., Eds.; Geological Society of London: London, UK, 2018; Volume 451, pp. 209–236. [CrossRef]
- 13. Council Directive 2013/51/EURATOM of 22 October 2013. Laying down requirements for the protection of the health of the general public with regard to radioactive substances in water intended for human consumption. *Off. J. Eur. Union* **2013**, *7*, 56.
- 14. Regulation by the Minister of Health of 7 December 2017 on the quality of water intended for human consumption. *J. Laws* **2017**, Item 2294. (In Polish)
- 15. Kochański, J.W. A review of research into medicinal applications of radon-222 in Polish health resorts. *Folia Med. Lodz.* **2002**, *29*, 31–68. (In Polish)
- 16. Becker, K. One century of radon therapy. Int. J. Low Radiat. 2004, 1, 334–357. [CrossRef]
- Falkenbach, A.; Kovacs, J.; Franke, A.; Jörgens, K.; Ammer, K. Radon therapy for the treatment of rheumatic diseases—Review and meta-analysis of controlled clinical trials. *Rheumatol. Int.* 2005, 25, 205–210. [CrossRef]
- 18. Erickson, B.E. The therapeutic use of radon: A biomedical treatment in Europe; An "alternative" remedy in the United States. *Dose-Response* 2007, *5*, 48–62. [CrossRef] [PubMed]
- Nagy, K.; Kávási, N.; Kovács, T.; Somlai, J. Radon therapy and speleotherapy in Hungary. *Press Th. Clim.* 2008, 145, 219–225.
- 20. Franke, A.; Franke, T. Long-term benefits of radon spa therapy in rheumatic diseases: Results of the randomized, multi-centre IMuRa trial. *Rheumatol. Int.* **2013**, *33*, 2839–2850.
- 21. Kapetanović, A.; Hodžić, S.; Avdić, D. The effect of mineral radon water applied in the form of full baths on blood pressure in patients with hypertension. *J. Health Sci.* **2013**, *3*, 38–40. [CrossRef]
- 22. Law of 9 June 2011: Geological and mining law. J. Law 9 Febr. 2015 2011, Item 196. (In Polish)
- 23. Przylibski, T.A. Radon research in Poland: A review. Solid State Phenom. 2015, 238, 90–115. [CrossRef]
- 24. Kryza, R.; Mazur, S.; Oberc-Dziedzic, T. Sudetic geological mosaic: Insight into the root of the Variscan orogeny. *Prz. Geol.* 2004, *52*, 761–773.
- Żelaźniewicz, A.; Aleksandrowski, P. Tectonic subdivision of Poland: Southwestern Poland. *Prz. Geol.* 2008, 56, 904–911, (In Polish with English abstract).
- 26. Mazur, S.; Aleksandrowski, P.; Szczepański, J. Outline structure and tectonic evolution of the Variscan Sudetes. *Prz. Geol.* **2010**, *58*, 133–145, (In Polish with English abstract).
- 27. Bareja, E.; Jęczmyk, M.; Banasiewicz, J.; Lis, J.; Miecznik, J.B.; Ałdan, M. Radioactive elements in the Sudetes. *Biul. Inst. Geol.* **1982**, *341*, 259–272. (In Polish)

- Borucki, J.; Głowacki, Z.; Masłowski, W.; Sałdan, M.; Uberna, J.; Zajączkowski, W. Assessment of Prospects for Exploration of Uranium Ore Deposits in Poland; Institute of Nuclear Chemistry and Technology: Warszawa, Poland, 1967. (In Polish)
- 29. Zdulski, M. Sources for History of Uranium Mining in Poland; Wydawnictwo DiG: Warszawa, Poland, 2000.
- 30. Klementowski, R. *In the Shadow of Sudetic Uranium. Uranium Mining in Poland in 1948–1973*; IPN: Wrocław, Poland, 2010. (In Polish)
- Solecki, A.; Śliwiński, W.; Wojciechowska, I.; Tchorz-Trzeciakiewicz, D.; Syryczyński, P.; Sadowska, M.; Makowski, B. Assessment of a possibility of uranium mineralization occurrence in Poland on the basis of results of geological and prospection work. *Prz. Geol.* 2011, *59*, 98–110. (In Polish)
- 32. Miecznik, J.B.; Strzelecki, R.; Wołkowicz, S. Uranium in Poland—History of prospecting and chances for finding new deposits. *Prz. Geol.* **2011**, *59*, 688–697, (In Polish with English abstract).
- Wołkowicz, S. Radon potential of Sudetes and selected units of Fore-Sudetic Block. In *Radon Potential of the Sudetes with Determination of Potentially Medicinal Radon Water Areas;* Wołkowicz, S., Ed.; Państwowy Instytut Geologiczny: Warszawa, Poland, 2007; pp. 5–106, (In Polish with English summary).
- 34. Ciężkowski, W.; Przylibski, T.A. Radon in waters from health resorts of the Sudety Mts. (SW Poland). *Appl. Radiat. Isot.* **1997**, *48*, 855–856. [CrossRef]
- 35. Przylibski, T.A.; Żebrowski, A. Origin of radon in medicinal waters of Świeradów Zdrój. *Nukleonika* **1996**, *41*, 109–115.
- 36. Przylibski, T.A.; Żebrowski, A. Origin of radon in medicinal waters of Lądek Zdrój (Sudety Mountains, SW Poland). J. Environ. Radioact. 1999, 46, 121–129. [CrossRef]
- Przylibski, T.A. ²²²Rn concentration changes in medicinal groundwaters of Lądek Zdrój (Sudety Mountains, SW Poland). J. Environ. Radioact. 2000, 48, 327–347. [CrossRef]
- Przylibski, T.A.; Mroczkowski, K.; Żebrowski, A.; Filbier, P. Radon-222 in medicinal groundwaters of Szczawno Zdrój (Sudety Mountains, SW Poland). *Environ. Geol.* 2001, 40, 429–439. [CrossRef]
- 39. Przylibski, T.A.; Dorda, J.; Kozłowska, B. The occurrence of ²²⁶Ra and ²²⁸Ra in groundwaters of the Polish Sudety Mountains. *Nukleonika* **2002**, *47*, 5–64.
- Przylibski, T.A.; Kozłowska, B.; Dorda, J.; Kiełczawa, B. Radon-222 and ²²⁶Ra concentrations in mineralized groundwaters of Gorzanów (Kłodzko Basin, Sudeten Mountains, SW Poland). *J. Radioanal. Nucl. Chem.* 2002, 253, 11–19. [CrossRef]
- Przylibski, T.A.; Mamont-Cieśla, K.; Kusyk, M.; Dorda, J.; Kozłowska, B. Radon concentrations in groundwaters of the Polish part of the Sudety Mountains (SW Poland). *J. Environ. Radioact.* 2004, 75, 193–209. [CrossRef] [PubMed]
- Przylibski, T.A.; Adamczyk-Lorenc, A.; Żak, S. Areas of the occurrence of potentially medicinal radon water in the Sudetes. In *Radon Potential of the Sudetes with Determination of Potentially Medicinal Radon Water Areas*; Wołkowicz, S., Ed.; Państwowy Instytut Geologiczny: Warszawa, Poland, 2007; pp. 107–167, (In Polish with English summary).
- 43. Przylibski, T.A.; Fijałkowska, L.; Bielecka, A. Potentially medicinal radon waters of the Śleża massif. *Prz. Geol.* **2008**, *56*, 763–771, (In Polish with English abstract).
- 44. Przylibski, T.A.; Gorecka, J.; Kula, A.; Fijałkowska-Lichwa, L.; Zagożdżon, K.; Zagożdżon, P.; Miśta, W.; Nowakowski, R. ²²²Rn and ²²⁶Ra activity concentrations in groundwaters of southern Poland: New data and selected genetic relations. *J. Radioanal. Nucl. Chem.* **2014**, *301*, 757–764. [CrossRef]
- 45. Walencik, A.; Kozłowska, B.; Przylibski, T.A.; Dorda, J.; Zipper, W. Natural radioactivity of groundwater from the Przerzeczyn-Zdrój Spa. *Nukleonika* **2010**, *55*, 169–175.
- 46. Walencik-Łata, A.; Kozłowska, B.; Dorda, J.; Przylibski, T.A. The detailed analysis of natural radionuclides dissolved in spa waters of the Kłodzko Valley, Sudety Mountains, Poland. *Sci. Total Environ.* **2016**, *569–570*, 1174–1189. [CrossRef]
- 47. Przylibski, T.A.; Gorecka, J. ²²²Rn activity concentration differences in groundwaters of three Variscan granitoid massifs in the Sudetes (NE Bohemian Massif, SW Poland). *J. Environ. Radioact.* **2014**, *134*, 43–53. [CrossRef]
- 48. Znosko, J. Map of tectonic units of Poland. In *Tectonic atlas of Poland*; Znosko, J., Ed.; Polish Geological Institute: Warsaw, Poland, 1998.
- 49. Narkiewicz, M.; Dadlez, R. Geological regional subdivision of Poland-general guidelines and proposed schemes of sub-Cenozoic and sub-Permian units. *Prz. Geol.* **2008**, *56*, 391–397, (In Polish with English abstract).

- 50. Karnkowski, P.H. Tectonic subdivision of Poland—Polish lowlands. *Prz. Geol.* **2008**, *56*, 895–903, (In Polish with English abstract).
- Gaweda, A.; Burda, J.; Klötzli, U.; Golonka, J.; Szopa, K. Episodic construction of the Tatra granitoid intrusion (Central Western Carpathians, Poland/Slovakia): Consequences for the geodynamics of the variscan collision and the Rheic Ocean closure. *Int. J. Earth Sci.* 2016, 105, 1153–1174. [CrossRef]
- 52. Aleksandrowski, P.; Mazur, S. On the new tectonic solutions in "Geological Atlas of Poland". *Prz. Geol.* **2017**, 65, 1499–1510, (In Polish with English abstract).
- 53. Miliszkiewicz, A. Radon; PWN: Wrocław, Poland, 1978. (In Polish)
- 54. Janica, D. Natural Hydrogeochemical Background of the Quaternary Groundwaters of North-Eastern Poland. Ph.D. Thesis, University of Warsaw, Warsaw, Poland, 2002. (In Polish).
- 55. Adamczyk-Lorenc, A. Hydrogeochemical Background of Radon in Groundwaters of the Sudetes. Ph.D. Thesis, Wrocław University of Technology, Wrocław, Poland, 2007. (In Polish).
- Andrews, J.N.; Giles, I.S.; Kay, R.L.F.; Lee, D.J.; Osmond, J.K.; Cowart, J.B.; Fritz, P.; Barker, J.F.; Gale, J. Radioelements, radiogenic helium and age relationship for groundwaters from the granites at Stripa, Sweden. *Geochim. Cosmochim. Acta* 1982, 46, 1533–1543. [CrossRef]
- 57. Andrews, J.N.; Ford, D.J.; Hussain, N.; Trivedi, D.; Youngman, M.J. Natural radioelement solution by circulating groundwaters in the Stripa granite. *Geochim. Cosmochim. Acta* **1989**, *53*, 1791–1802. [CrossRef]
- 58. Banks, D.; Royset, O.; Strand, T.; Skarphagen, H. Radioelement (U, Th, Rn) concentrations in Norwegian bedrock groundwaters. *Environ. Geol.* **1995**, *25*, 165–180. [CrossRef]
- 59. Heinicke, J.; Koch, U.; Hebert, D.; Martinelli, G. Simultaneous measurements of radon and CO₂ in water as a possible tool for earthquake prediction. In *Gas Geochemistry*; Dubois, C., Ed.; Science Reviews: Northwood, UK, 1995; pp. 295–303.
- Schubert, G.; Berka, R.; Katzlberger, Ch.; Motschka, K.; Denner, M.; Grath, J.; Philippitsch, R. Radionuclides in groundwater, rock and stream sediments in Austria—Results of a recent survey. In *Radon, Health and Natural Hazards*; Gillmore, G.K., Perrier, F.E., Crockett, R.G.M., Eds.; Geological Society of London: London, UK, 2018; Volume 451, pp. 83–112. [CrossRef]
- 61. Ulbak, K.; Klinder, O. Radium and radon in Danish drinking water. *Radiat. Prot. Dosim.* **1984**, *7*, 87–89. [CrossRef]
- 62. Gomes, M.E.P.; Neves, L.J.P.; Coelho, F.; Carvalho, A.; Sousa, M.; Pereira, A.J.S.C. Geochemistry of granites and metasediments of the urban area of Vila Real (northern Portugal) and correlative radon risk. *Environ. Earth Sci.* **2011**, *64*, 497–502. [CrossRef]
- 63. Cho, B.W.; Choo, C.O. Geochemical behavior of uranium and radon in groundwater of jurassic granite area, Icheon, middle Korea. *Water* **2019**, *11*, 1278. [CrossRef]
- 64. Md, N.K.; Vinayachandran, N.; Jose, B.; Vashistha, R. Radon in groundwater in Tumkur District of Karnataka with special reference to sampling sensitivity. *J. Geol. Soc. India* **2014**, *83*, 665–668. [CrossRef]
- 65. Choubey, V.M.; Bartarya, S.K.; Ramola, R.C. Radon in Himalayan springs: A geohydrological control. *Environ. Geol.* **2000**, *39*, 523–530. [CrossRef]
- Asare-Donkor, N.K.; Poku, P.A.; Addison, E.C.D.K.; Wemengah, D.D.; Adimado, A.A. Measurement of radon concentration in groundwater in the Ashanti region of Ghana. *J. Radioanal. Nucl. Chem.* 2018, 317, 675–683. [CrossRef]
- Arabi, A.S.; Funtua, I.I.; Dewu, B.B.M.; Kwaya, M.Y.; Kurowska, E.; Hauwau Kulu, S.; Abdulhamid, M.S.; Mahed, G. Geology, lineaments, and sensitivity of groundwater to radon gas contamination. *Sustain. Water Resour. Manag.* 2018, 4, 643–653. [CrossRef]
- 68. Bonotto, D.M. ²²²Rn, ²²⁰Rn and other dissolved gases in mineral waters of southeast Brazil. *J. Environ. Radioact.* **2014**, *132*, 21–30. [CrossRef] [PubMed]
- 69. Michel, J. Relationship of radium and radon with geological formations. In *Radon, Radium and Uranium in Drinking Water*; Cothern, C.R., Rebers, P.A., Eds.; Lewis Publishers: Boca Raton, FL, USA, 1990; pp. 83–95.



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