

Three Types of Natural Radioactivity in Groundwaters

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Abstract

The authors collected data on concentrations of natural radionuclides (^{222}Rn , ^{226}Ra , ^{228}Ra , ^{238}U , ^{234}U , ^{40}K , ^{210}Pb , ^{210}Po , ^3H , and ^{14}C) in medicinal waters in Poland. Medicinal waters were chosen because they represent an almost complete spectrum of hydrochemical types and groundwater mineralization. The ranges of these concentrations are presented as divided into three regions: the Sudetes, the Carpathians and the Polish Lowlands. Medicinal waters of the Sudetes are characterized by the highest concentrations of ^{222}Rn , ^{238}U and ^{234}U . The radioactivity of Carpathian medicinal waters is associated with the presence of $^{226,228}\text{Ra}$ and ^{40}K and, more rarely, $^{238,234}\text{U}$ or ^{222}Rn . Medicinal waters of the Polish Lowlands are characterized by increased concentrations of $^{226,228}\text{Ra}$ and ^{40}K , while ^{222}Rn and the isotopes $^{238,234}\text{U}$ occur in them in very low concentrations. In terms of natural radionuclide content three types of groundwaters can be defined. Medicinal waters of the Sudetes can be characterized as radium–uranium–radon waters ($\text{Rn} > \text{U} > \text{Ra}$; where $^{234}\text{U} > ^{238}\text{U}$ and $^{226}\text{Ra} > ^{228}\text{Ra}$), of the Carpathians as radium–potassium waters ($\text{K} > \text{Ra}$; where $^{226}\text{Ra} > ^{228}\text{Ra}$), and of the Polish Lowlands as potassium–radium waters ($\text{Ra} > \text{K}$; where $^{228}\text{Ra} > ^{226}\text{Ra}$).

Keywords: ^{222}Rn ; radium; uranium; ^{40}K ; groundwater; brine; thermal water

1. Introduction

Human health and proper functioning are related to using water. Water is essential to life, and it can be used to improve its quality by keeping a person in good psychophysical condition and by restoring health. To achieve this aim, the properties of both water and substances dissolved in it are used. Treatment through contact with water is generally a very safe form of therapy, with a low risk of complications and a short list of contraindications to usage. Hydrotherapy is also used in relaxation treatments, aesthetic medicine and spa treatments helping to maintain youthful appearance. Modern hydrotherapy started to spread in Europe in the early 19th century thanks to people like Vincenz Prisnitz (Vincenz Prißnitz or Vincent Priessnitz). Prisnitz was an illiterate self-taught healer, who popularized treatments using cold spring water (baths and showers) as a form of spa treatment (balneotherapy) in the spa resort Gräfenberg in the Austrian part of Silesia [1], now Lázně Jeseník, a part of the town Jeseník in the northwestern part of the Czech Republic, not far from the Polish border.

In many countries worldwide, medicinal waters are understood as groundwaters containing specific ingredients giving them therapeutic properties, and they include thermal waters and brines. Medicinal waters are used in a range treatments: individual baths in bathtubs, bubble baths, baths in pools, baths in natural springs and pools, showers,



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inhalations or massages (whirlpool, underwater and hydromassage), Scotch hoses, and, very often, drinking treatments. Their usage is often connected with centuries-old tradition, dating back hundreds or even thousands of years. For centuries, in areas with the occurrence of such waters, health resorts, sanatoriums, and leisure and tourist facilities have been set up. Medicinal waters are used in both naturopathy and modern therapeutic (balneotherapeutic) treatments employing contemporary achievements of spa medicine, physical medicine and physical therapy. Such treatments are particularly popular in Europe (e.g., in Germany, Austria, Hungary, the Czech Republic, Poland, Lithuania and Russia) and in Asia (China and Japan) [2–11]. An overview of occurrences of medicinal waters, brines, and thermal waters regarded as medicinal, as well as the ways of their commercial usage in Poland, was presented by Filippovits et al. [12]. As of 31 December 2024, there were 116 deposits of such waters in Poland, most of which were being exploited. The overview does not comprise several exploited deposits of thermal waters which are not classified as medicinal. However, some of them have been included in the current study because of the existing isotopic data. Within one deposit or one locality, water is usually abstracted from one intake (usually a dug or drilled well), several intakes, or, exceptionally, from about a dozen intakes. Among the 116 catalogued Polish deposits of medicinal waters and brines, 5 deposits lie in the area of the East European (Precambrian) Platform, 25 in the West European (Palaeozoic) Platform, 20 deposits in the area of the Sudetes, and 66 in the Carpathians [12]. Due to the small number of available isotopic data, the authors combined all the occurrences (deposits) of medicinal waters on the East European and the West European platforms into one group: deposits in the Polish Lowlands. According to the adopted division, medicinal and potentially medicinal waters of the Sudetes occur in a wide variety of Palaeozoic crystalline rocks of the Variscan orogen and in Carboniferous and Cretaceous sedimentary rocks. In the Carpathians, they are associated with Mesozoic and Early Cenozoic sedimentary rocks of the Alpine orogeny fold structures and, exceptionally, with crystalline rocks. In the Polish Lowlands, medicinal and potentially medicinal waters are found in Mesozoic and Cenozoic platform sediments.

In Poland, groundwaters can be classified as medicinal if they are chemically or microbiologically uncontaminated, characterized by natural variability of physical and chemical properties, and contain no less than 1000 mg/dm³ of dissolved solid minerals or 250 mg/dm³ of free CO₂, 10 mg/dm³ of Fe²⁺, 2 mg/dm³ of F[−], 1 mg/dm³ of I[−], 70 mg/dm³ of metasilicic acid, or 74 Bq/dm³ of radon (isotope ²²²Rn) [13]. Additionally, if they are to be used in balneotherapeutic or physiotherapeutic treatments, they need to have an official certificate confirming the stability of their physicochemical properties, based on the results of at least two years of analyses [14].

The primary goal of the authors' work is to present the current state of knowledge on the occurrence of natural radioactive isotopes in waters recognized as medicinal in Poland. Due to the wide (almost complete) spectrum of hydrochemical types and mineralization of medicinal waters, we will obtain an overview of the content of natural radioactive isotopes in groundwater from a typical area with a platform structure (Polish Lowlands; platform structure—East European (Precambrian) Platform and the West European (Palaeozoic) Platform), an area of young Alpine fold belts (Carpathians) and the Variscan orogen (Sudetes; part of the Bohemian massif). These units represent the major geological units of Central Europe. This study represents the first compilation-based analysis addressing the occurrence of natural radioactive isotopes in groundwater at such a broad regional scale in this part of Europe.

Based on this, the authors aim to identify characteristic groundwater types in terms of their natural radioactive isotope content and their relationships to areas with characteristic geological structures. This is the main goal of the study. Another goal is to present the

gathered information on the role of particular radioactive isotopes in giving groundwaters their medicinal properties or in restricting their usage in balneotherapy and physical therapy in view of their potentially harmful effect on the human body.

1.1. Natural Radioactive Isotopes in Groundwaters

Radioactive constituents found in groundwaters, including medicinal waters, are some of the most important elements contributing to the physical properties of these waters. On the one hand, they can give groundwaters medicinal properties (e.g., radon—the isotope ^{222}Rn) (e.g., [15]) but, on the other, they are undesirable constituents, limiting the possibilities of putting medicinal waters to use. At the same time, radioactive isotopes (e.g., tritium or uranium isotopes) convey information on the genesis, origin, age, and the flow paths and modes of medicinal groundwaters or their components in reservoir rocks (within the rock mass) (e.g., [16–20]).

Radioactive isotopes can occur in the groundwater environment (also in medicinal waters) in ionic form, as constituents of suspensions and colloids, or as dissolved gases. The most significant natural radioactive isotopes dissolved in medicinal waters are those which have the strongest impact on the human body. Such an impact is characteristic of the isotopes which cause the greatest energy transfer to human cells during the shortest possible time. Therefore, these are especially the isotopes whose activity concentrations in groundwaters are the highest and/or those characterized by short half-life (and, consequently, the highest specific activity). Among these isotopes, the most important radioactive constituents of medicinal waters are isotopes of radium and radon. The biggest role is played by two radium isotopes, ^{226}Ra and ^{228}Ra , and the radon isotope with the longest half-life, i.e., ^{222}Rn . In some waters, the uranium isotopes ^{238}U and ^{234}U may also be important. In some medicinal waters, an important role may also be played by radioactive isotopes of light elements, i.e., ^{40}K , ^{14}C and ^3H (T; tritium). It is also possible that radioactive isotopes of heavy metals, being the end links of natural decay chains, especially ^{210}Pb and ^{210}Po from the uranium–radium series, may also be very significant in some medicinal waters [21]. However, it must be emphasized that the adverse impact of uranium isotopes on the human body is usually due to the chemical properties of uranium (a heavy metal) rather than to the emitted ionizing radiation [22,23].

The source of ^{238}U and ^{40}K isotopes in medicinal groundwaters are their reservoir rocks or, more precisely, the minerals building these rocks. The sources of ^{234}U , ^{226}Ra and ^{228}Ra , ^{222}Rn , ^{210}Po and ^{210}Pb can be both reservoir rock minerals and chemical compounds containing the heaviest isotopes from natural decay chains, i.e., uranium, thorium and radium isotopes, secondarily precipitated from groundwaters in cracks and fissures of reservoir rocks. Finally, the lighter uranium isotope, radium isotopes, and, in particular, ^{222}Rn , can be formed in groundwater itself as a result of radioactive decay of uranyl ions ($[\text{UO}_2]^{2+}$) and simple radium ($^{226}\text{Ra}^{2+}$ and $^{228}\text{Ra}^{2+}$) and thorium (Th^{4+}) ions. Also, ^{222}Rn in the form of monatomic gas dissolved in medicinal groundwater may be the source of ^{210}Po and ^{210}Pb isotopes. Tritium (^3H) and ^{14}C are produced as a result of nuclear reactions in the atmosphere, from where they infiltrate with precipitation and enter medicinal groundwaters. The isotope ^{14}C can also be released, as a result of dissolution processes, from young (no more than several dozen thousand years old) reservoir rocks containing carbonate minerals and/or organic matter [24–32].

The radionuclide ^{222}Rn very rarely occurs in groundwaters in a state of radioactive equilibrium with its parent radium isotope, ^{226}Ra [26,33,34]. It is due to the fact that ^{222}Rn dissolves in groundwater as a gas released from the reservoir rocks in which it is formed as a result of ^{226}Ra decay. Rarely, its source in groundwater, also medicinal, is the simple $^{226}\text{Ra}^{2+}$ ion dissolved in this water. Such a situation usually occurs in waters with very

high TDS content and high concentration of dissolved radium, especially in brines. The highest values of ^{222}Rn activity concentration are recorded in low-TDS waters of shallow circulation and modern infiltration [26,33].

As for radium isotopes, they dissolve in groundwater especially when they are close to the surface of grains or crystals of minerals building reservoir rocks. These are often secondary minerals or chemical compounds containing radium, precipitated on the surface of fissures or cracks filled with groundwaters. The highest values of radium isotopes' activity concentration are recorded in high-TDS waters with increased temperature, i.e., in thermal waters and especially in brines [26,33–35]. The world's highest known activity concentration of ^{226}Ra (85.5 Bq/dm^3) has been recorded in medicinal brines of Ustroń in Poland [34,36]. It is probably due to their occurrence in the vicinity of rocks of organic origin, i.e., hard coal deposits. Unpublished data suggest that comparable or even higher activity concentrations of radium isotopes could be expected in brines accompanying oil deposits [37].

It should also be noted that all radioactive isotopes found in medicinal waters can act as environmental tracers. This means that, by analyzing their contents and their changes, as well as the ratios of the concentrations of their constituents, one can obtain information essential for determining their genesis, age, flow paths and the proportion of components mixing to form the exploited medicinal waters. Particularly useful in such research are the isotopes ^3H and ^{14}C , as well as isotopes of uranium, radium and radon [18–20,38–46]. The use of these isotopes in tracer studies has been well known for many years [16]. What is still open, however, also in Poland, are issues connected with medicinal properties or the groundwaters whose radioactivity is determined by their radon (^{222}Rn) content [15,47], as well as the adverse health effect of medicinal waters containing high concentrations of ^{226}Ra and ^{228}Ra [48,49]. These two issues are significant problems that require scientific, technological and legal solutions. The common lack of radioactive equilibrium between isotopes from natural decay chains found in groundwaters is the reason why it is vital to get to know the activity concentrations of the radioactive isotopes being the last links in natural decay chains, especially lead and polonium isotopes (particularly ^{210}Pb and ^{210}Po), in medicinal waters.

1.2. Harmful and Potentially Beneficial Effects of Radioactive Isotopes on the Human Body

The isotopes ^{226}Ra , ^{228}Ra and ^{222}Rn are recognized as carcinogenic agents by international organizations [30,48,50]. Therefore, Polish law [51] and international recommendations [22,30,52–54] define the levels of allowable activity concentrations of these isotopes in water intended for human consumption and in workplaces (Table 1). Also, measuring their activity concentration in medicinal waters is required [55,56]. Due to the high specific activity of radium, especially of the isotope ^{228}Ra , it should be recognized as a totally undesirable constituent of medicinal waters. Its concentration has to be monitored, and doses received by patients and medical and technical staff involved in administering treatments have to be measured or calculated. Nevertheless, the measures taken in this regard in Poland are rudimentary [57,58] and highly insufficient, not only with regard to European recommendations [54] but also domestic radiological protection regulations [59].

The problem of the effect of ionizing radiation looks slightly different for the radionuclide ^{222}Rn . Based on the theory of radiation hormesis, radon is used as a therapeutic agent in several Polish and many European and non-European health resorts, and it is regarded as a component giving groundwaters medicinal properties [15] and references therein; [26] and references therein. For this reason, medicinal radon waters, as well as radon-enriched air inside underground workings and caves, are used in many radon health resorts worldwide for therapeutic purposes [15]. In view of these facts, it is absolutely

necessary, especially in Polish spa resorts, to implement monitoring of ^{222}Rn activity concentration and its radioactive daughters and to control doses from ionizing radiation emitted by these isotopes. This applies to medicinal materials, i.e., medicinal groundwaters, the air in caves and workings, and hitherto unused though widely available soil air enriched in ^{222}Rn , to spaces intended for therapeutic treatments, and also to medical and technical staff as well as spa clients and patients. It is also possible to employ automatic solutions for monitoring and maintaining highly specified conditions such as the activity concentration of ^{222}Rn and its decay products and the effective dose of ionizing radiation during all possible radon therapy treatments [15]. So far, however, none of the Polish health resorts has fully exploited such possibilities.

Table 1. Radiological requirements that should be met by water intended for human consumption, and derived concentrations for selected natural radioactive isotopes dissolved in water (based on data from [51]).

Radioactive Isotope	Parametric Value (for ^{222}Rn and ^3H) or Derived Concentration ¹ [Bq/dm ³]
^{14}C	240
^3H	100 ²
^{222}Rn	100
^{238}U	3
^{234}U	2.8
^{226}Ra	0.5
^{228}Ra	0.2
^{210}Pb	0.2
^{210}Po	0.1

Notes: ¹ The concentration for which the calculated dose is 0.1 mSv/year with annual water consumption of 730 dm³ and the absorbed-dose coefficient adopted in the Polish atomic law [59]. ² 100 Bq is equivalent to c. 847 TU (tritium units).

Using ^{222}Rn in therapeutic treatments based on the use of medicinal radon waters and identifying the adverse effect of radium isotopes dissolved in medicinal waters are both possible thanks to taking into account the mechanism of transfer of the ionizing radiation energy emitted by these isotopes and absorbed by a patient's cells and tissues. This problem also applies to employees administering therapeutic treatments using radon waters or other radon materials or waters containing increased concentrations of ^{226}Ra and/or ^{228}Ra . Therefore, it is necessary to convert the measured activity concentration of ^{222}Rn , ^{226}Ra and ^{228}Ra to the effective dose of ionizing radiation. Another important issue is the behavior of the very element in the human body. Radon is mostly excreted during breathing and with urine [48]. Radium, on the other hand, can be absorbed into the body, where it can substitute calcium ions (Ca^{2+}) with a similar ionic radius. This results in Ra^{2+} ions being incorporated into bone tissue and significantly modifying its physical properties. The radium isotopes incorporated in tissues are practically unremovable from the body and are an internal source of ionizing radiation for the rest of one's life. They are also the beginning of a chain of successive radioactive transformations causing the formation in the human body of further sources of ionizing radiation—the nuclei of Po, Bi, Tl and Pb isotopes [23,60]. Also, ^{222}Rn , which enters the human body mainly through the respiratory system, besides emitting alpha and gamma radiation during its radioactive decay, causes the formation of further radioactive isotopes of Po, Bi, Tl and Pb, which are solids. They can subsequently dissolve in body fluids, including blood, and undergo radioactive transformations in various organs and tissues, causing principal exposure to ionizing radiation related to the presence of radon [7,8,61,62]. Therefore, it is of paramount importance to standardize radon treatments in a way that will make it possible to estimate

as accurately as possible the dose received from ^{222}Rn and especially from its daughters by spa clients, patients and staff during various balneotherapeutic and physical therapy treatments using radon materials: radon waters and radon-enriched air [63].

As the concentration of potassium, hence also the isotope ^{40}K , is constant in a healthy human body (c. 4000 mmol.; 102 g (women)–134 g (men), which corresponds to ^{40}K content of 3200–4200 Bq, respectively) [64,65] and as the ratio $^{40}\text{K}/\text{K}$ is constant in the environment (0.0117%) [24,27], the isotope ^{40}K is not taken into account when discussing the beneficial or adverse effects of radioisotopes on the human body. Uranium isotopes, due to their low content in medicinal waters (likewise in most groundwaters) and low specific radioactive activity, can only be toxic owing to their chemical properties, and not because of the emitted ionizing radiation [48]. Also, the activity concentrations of the isotopes ^{14}C and ^3H in medicinal waters are too low for the ionizing radiation emitted by these isotopes to have significant effect on the human body [66] (Table 1). As for the isotopes ^{210}Pb and ^{210}Po , our knowledge of their occurrence in medicinal waters is still too limited to say if the ionizing radiation emitted by them has significant effect on the bodies of patients or members of the medical or technical staff employed in health resorts.

For comparison purposes, it is worth citing the parametric values or derived concentrations, i.e., the concentrations for which the calculated effective dose is 0.1 mSv/year, applicable in Poland to water intended for human consumption. These values must not be exceeded in medicinal waters either, especially if they are used in drinking treatment. However, it should be remembered that these levels were calculated for the assumed water intake of 730 L a year. The amount of water drunk by patients is far smaller and, therefore, the parametric values (derived concentrations) for such water should be appropriately larger, and the effective dose for a specific intake ought to be calculated. Nevertheless, the values shown in the table clearly indicate that it is crucial to obtain information on concentrations of potentially most hazardous natural radioactive isotopes, i.e., isotopes of radium, lead and polonium: ^{226}Ra , ^{228}Ra , ^{210}Pb , and ^{210}Po .

2. Materials and Methods

This study is based on a compilation and analysis of published data concerning the occurrence of natural radioactive isotopes in groundwater within three major European geological units: the Sudetes (representing the north-eastern part of the Bohemian Massif), the northern part of the Carpathian arc, and the Polish Lowlands, which include the Paleozoic West European Platform and the Precambrian East European Platform.

The dataset was derived from peer-reviewed scientific publications and includes reported concentration ranges of individual natural radioactive isotopes in groundwater exploited from recognized medicinal water deposits. In addition, the dataset was supplemented with unpublished data obtained from laboratory analyses conducted under the supervision of the first author, as well as archival data derived from hydrogeological documentation of medicinal water deposits. These data correspond to doctoral research conducted under the supervision of the first author and to hydrogeological documentation of four medicinal water deposits. The additional sources were included primarily to complement data on radon and radium isotopes, enabling a more comprehensive representation of their occurrence. Their inclusion made it possible to obtain information for 68 out of 116 medicinal water deposits in Poland. The unpublished data constitute only a minor portion of the overall dataset. Moreover, a substantial portion of the unpublished data has previously been utilized in scientific publications, allowing independent verification and contextualization of the information presented in this review.

To ensure consistency and comparability, all collected data were standardized, including the harmonization of units reported across different studies (e.g., conversion of tritium units to becquerels).

Although the analyzed data originate from the territory of Poland, they are representative of geological formations characteristic of broader European geological units. Medicinal groundwater was selected as the primary data source due to the wide availability of published isotopic data for this category of water. Furthermore, medicinal waters cover nearly the full spectrum of hydrochemical groundwater types occurring within the analyzed geological settings, which makes them suitable for a comprehensive regional assessment.

The compiled dataset spans several decades and includes results obtained using different analytical methods. Despite the temporal and methodological variability, all available data were included in order to achieve a comprehensive assessment of radionuclide occurrence across a geologically diverse and extensive study area. The acquisition of a comparable dataset through original measurements would require long-term monitoring and the involvement of multiple analytical laboratories.

The processed dataset was subsequently analyzed comparatively across the investigated geological units. The results were presented in both tabular and graphical forms. Based on this analysis, groundwater types were identified and characterized in terms of their natural radioactive isotope content, and relationships between radionuclide occurrence and geological settings were established.

3. Results

3.1. The Occurrence of Natural Radioactive Isotopes in Groundwaters Recognized as Medicinal in Poland

The geological structure of Poland is varied, which is the result of its location at the junction of several big European geological units: the East European Precambrian Platform, the West European Palaeozoic Platform and the areas of the Variscan (the Sudetes) and Alpine (the Carpathians) folding [67]. In accordance with this geological division, Paczyński and Płochniewski [4] distinguished four provinces of mineral water occurrence in Poland (Figure 1): the Precambrian platform (A), the Palaeozoic platform (B), the Sudetes (C), and the Carpathians (D). This division is also used in the classification of medicinal and thermal waters. In view of the small number of deposits, and particularly the amount of data on the concentration of natural radioactive isotopes in groundwaters in the area of the Precambrian (East-European) Platform, the authors analyzed medicinal waters, thermal waters and brines on both platforms jointly, combining them into one area of the Polish Lowlands. In the area of the Sudetes, the following types of medicinal and potentially medicinal waters occur: radon waters (Świeradów-Zdrój, Kowary, Sosnówka, Szklarska Poręba, Jeleniów, Przerzeczyn-Zdrój, and Sobótka), thermal radon waters (Łądek-Zdrój, Karpniki, and Staniszków), thermal waters (Cieplice Śląskie-Zdrój), CO₂-rich waters (Czarniawa-Zdrój, Świeradów-Zdrój, Szczawno-Zdrój, Jedlina-Zdrój, Kudowa-Zdrój, Polanica-Zdrój, Duszniki-Zdrój, and Gorzanów), CO₂-rich radon waters (Świeradów-Zdrój, Szczawno-Zdrój, Bobrowniki Stare, Długopole-Zdrój, Szczawina, and Jeleniów), and sulphide waters (Przerzeczyn-Zdrój). In the Carpathians, CO₂-rich waters prevail (Krynica-Zdrój, Muszyna-Zdrój, Piwniczna-Zdrój, Łomnica-Zdrój, Iwonicz-Zdrój, Rymanów-Zdrój, Lubatówka, Szczawa, Szczawnica, Szczawnik, Tylicz, Wysowa-Zdrój, and Żegiestów), followed by brines (Ustroń, Dębowiec, Zabłocie, Rabka-Zdrój, Rymanów-Zdrój, Lubatówka, and Wełnin), thermal waters (Bańska Niżna, Białka Tatrzańska, Bukowina, Chochołów, Poronin, and Zakopane), sulfide waters (Busko-Zdrój, Solec-Zdrój, Las Winiarski, Dobrowoda, Latoszyn, Mateczny, Swoszowice, and Horyniec-Zdrój) and iodide waters (Polańczyk). In the area of the Polish Lowlands, there are mainly brines (Połczyn-Zdrój,

Sopot, Świnoujście, Kołobrzeg, Kamień Pomorski, and Konstancin-Jeziorna) and thermal brines (Ciechocinek and Grudziądz), as well as thermal waters (Uniejów, Poddębice, and Mszczonów), sulfide waters (Inowrocław and Wieniec) and ferruginous waters (Nałęczów).

Studies on the occurrence of natural radioactive isotopes in groundwaters have been carried out all over Poland. They have covered all of the most important natural radionuclides (^{222}Rn , $^{226,228}\text{Ra}$, $^{238,234}\text{U}$, ^{40}K , ^{210}Pb , ^{210}Po , ^3H , and ^{14}C). The largest number of analyses were conducted in medicinal waters because of the need to assess their safety for patients and to monitor the level of natural radioactivity of waters. The results of such research have made it possible to determine the age of waters, their origin, and geochemical processes occurring in reservoir rocks in particular geological units [16–18,20,36,40,68–78].

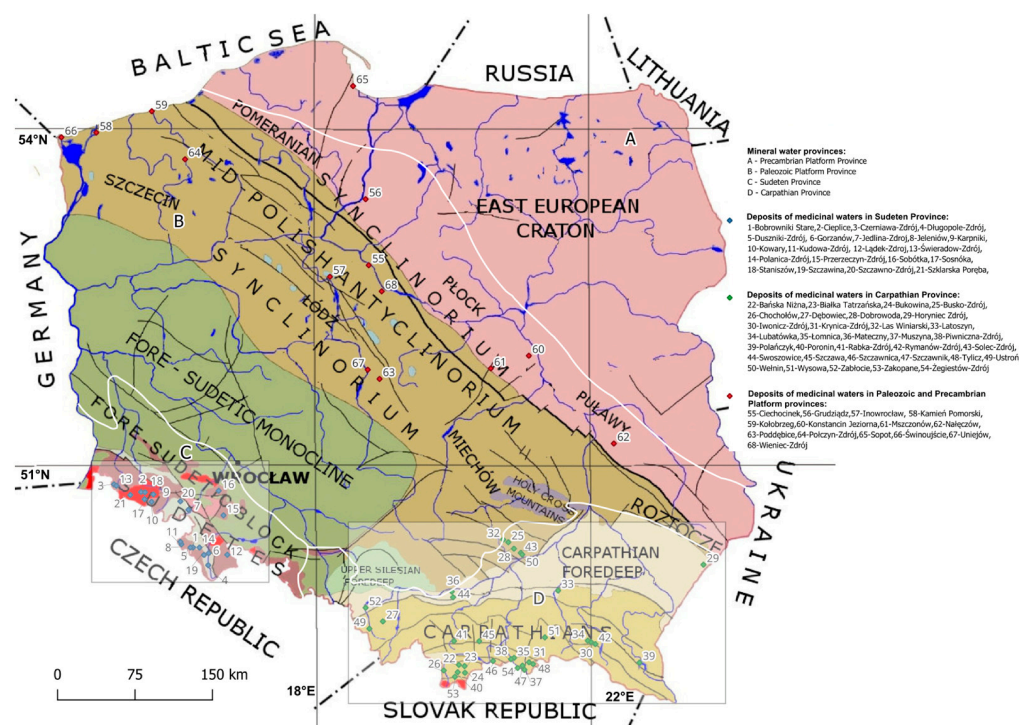


Figure 1. Location of medicinal waters on a simplified tectonic map of Poland without Cenozoic deposits (according to [79–81]; slightly modified by the authors); medicinal and thermal waters and brines are marked as red rhombuses in Polish Lowlands, as blue rhombuses in the Sudetes and as green rhombuses in the Carpathians; numbers describe localization—see descriptions on the figure.

The largest amount of data on the concentration of natural radioactive isotopes in medicinal groundwaters come from the Carpathian (D) and the Sudetic (C) provinces. Province C comprises the Polish Sudetes and the Fore-Sudetic Block (Figure 2). In the Polish part of the Sudetes and in the Fore-Sudetic Block, three main types of medicinal waters are distinguished: the commonest CO_2 -rich waters, thermal waters and radon waters [82]. A lot of data come from province C, especially on isotopes from the uranium–radium series (^{238}U – ^{206}Pb). This is related to the occurrence of uranium- and radium-rich crystalline rocks in this area [68,83–88]. This was the basis of research into concentrations of natural radionuclides, especially ^{222}Rn , $^{226,228}\text{Ra}$ and $^{238,234}\text{U}$ in groundwaters in this area, particularly in medicinal waters used in health resorts and in potentially medicinal waters [26,89]. It is also important that waters with high ^{222}Rn content are treated as medicinal waters [13]. The large number of determinations, especially of the isotope ^{222}Rn (also in radon medicinal waters and potentially medicinal waters), has made it possible to determine the hydrogeochemical background of ^{222}Rn in groundwaters of the Sudetes, the Fore-Sudetic Block, and minor geological units included in them [26,90–92].

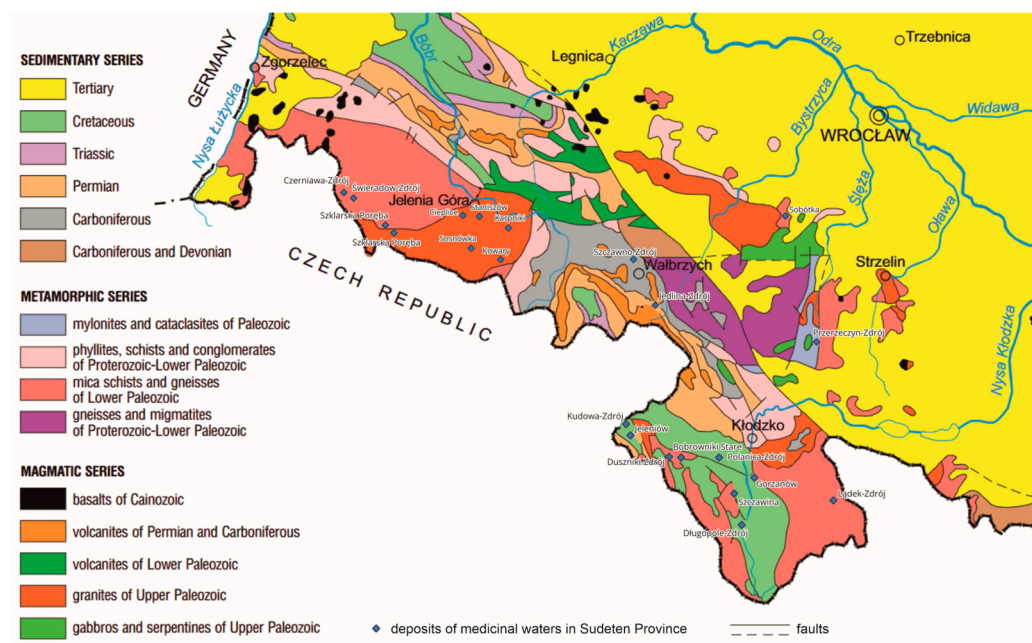


Figure 2. Simplified geological map of the Sudetic province with the most important occurrences of medicinal and thermal waters marked as blue rhombuses with the name of localization (according to [82]; slightly modified by the authors).

3.2. The Sudetes

An analysis of literature data shows varied concentrations of natural radionuclides (^{222}Rn , $^{226,228}\text{Ra}$, and $^{238,234}\text{U}$) in medicinal and potentially medicinal waters in the area of the Sudetes. This is related to the mosaic-like geological structure of the Sudetes, with the presence in neighboring areas of uranium-rich igneous rocks (granites), metamorphic rocks with increased concentrations of this element (orthogneisses), but also igneous and metamorphic rocks with low uranium and radium content (respectively, basalts and paragneisses, mica schists, serpentinites, phyllites, greenstones, quartzites, marbles and others). In other units, there are also sedimentary rocks, including clastic rocks with low uranium and radium content [93–96]. Determination results of these radioactive isotopes' concentrations have been compiled in Table 2.

Table 2. ^{222}Rn , $^{226,228}\text{Ra}$, and $^{238,234}\text{U}$ content in medicinal and potentially medicinal waters of the Sudetes with the hydrogeochemical background and the range of values in particular geological units of the Sudetes (according to [26,37,87,88,91,92,97–112]).

Area, Geological Unit, Spa Town	^{222}Rn		^{226}Ra	^{228}Ra	^{238}U	^{234}U
	Hydrogeochemical Background	Range of Measured Values	Range of Measured Value			
			[Bq/dm ³]	[mBq/dm ³]		
Sudetes:	4–306	0.1–3368	<0.05–1360	<1–840	<0.5–725	<0.5–964
KM	16–690	0.3–1282	<0.05–300	5–380	<0.05–43.38	<0.5–52.08
Cieplice		8.8–163	5–67	5–16	<0.5	<0.5
Śląskie-Zdrój		245–290.1	<0.06	— ¹	—	—
Karpniki		374–650	50	380	2.35–43.38	4.68–52.08
Kowary		177–315	220–300	—	—	—
Sosnówka		116.4–174	—	—	—	—
Staniszów		931–1282	<0.05–0.10	—	—	—
Szklarska Poręba						
KMZ	10–140	1.0–287.3	—	—	—	—

Table 2. Cont.

Area, Geological Unit, Spa Town	²²² Rn	²²⁶ Ra	²²⁸ Ra	²³⁸ U	²³⁴ U	
	Hydrogeochemical Background	Range of Measured Values	Range of Measured Value			
			[Bq/dm ³]	[mBq/dm ³]		
Sudetes:	4–306	0.1–3368	<0.05–1360	<1–840	<0.5–725	<0.5–964
KUM	3.9–109	0.9–143.9	–	–	–	–
LŚMC		0.3–1852	–	–	–	–
Lądek-Zdrój		110–1413	<3–179	5–13	0.95	0.61
OBMC	8–309	0.3–164	40–139	7–91	<0.5–4.32	<0.5–6.24
Bobrowniki Stare		122–164	94	<20	2.10–4.32	4.73–6.24
Długopole-Zdrój		54.9–137	40–139	17–91	<0.5–0.5	<0.5–1.2
Szczawina		117–152	92	7	1.0	2.1
IMC	17–890	<0.2–3368	11–1360	<6–730	–	–
Czerniawa-Zdrój		14.3–129	11–1250	<6–730	–	–
Szklarska Poręba		19.5–3368	–	–	–	–
Świeradów-Zdrój		<0.2–2005	16–1360	5–670	2.4–29.4	4.3–46.9
RJMC	3–36	3.2–161.3	–	–	–	–
GSGB	6–47	0.6–71.9	–	–	–	–
KŁMC	2.2–13.8	2.2–13.8	–	–	–	–
KMC	3–62	0.6–113	–	–	–	–
BU	4–24	3.8–100.1	–	–	–	–
ISB	4–50	0.1–325.6	22–1260	<1–840	1.0–725	1.9–964
Duszniki-Zdrój		3.8–91.7	32–1260	<20–840	1.1–81	2.5–239
Gorzanów		2.8–17.8	22–80	–	–	–
Jedlina Zdrój		40.2–249	27–170	69–158	1.0–54	2.4–366
Jeleniów		24.8–109	35–550	<6–25	1.1–33	2.6–158
Kudowa-Zdrój		4.3–66.1	50–703	<20–320	1.2–22	1.9–75
Polanica-Zdrój		4.3–27.1	121–1200	<2–143	3.3–8.1	7.3–27
Szczawno-Zdrój		8.8–325.6	39–950	<1–80	4–725	12.1–964
NSB	4–55	1.4–146.8	–	–	–	–
SB	2.6–20.8	2.6–20.8	–	–	–	–
Fore-Sudetic Block:	2–47	0.4–818	–	–	–	–
SSM		0.4–415.5	–	–	–	–
Sobótka		1.0–335	–	–	–	–
SM	1.4–40	0.5–119.4	–	–	–	–
NKMU		0.7–176	–	–	–	–
Przerzeczyn-Zdrój		13–176	18.9–31.5	33–64	3.9–14.8	16.2–55
KMC	2–22	0.4–34.9	–	–	–	–
GSGB	1–35	0.6–65.3	–	–	–	–
SOB	2–18	0.6–41.7	–	–	–	–

Notes: ¹ not available. Background values and ranges were not determined for the areas for which the authors did not have a sufficient amount of data.

The value of the hydrogeochemical background was determined only for the isotope ²²²Rn, as it was the only radionuclide for which a sufficient amount of data was available. The hydrogeochemical background of ²²²Rn for groundwaters of the Sudetes is 4–306 Bq/dm³ and the range of the measured values 0.1–3368 Bq/dm³ (Table 2). Among the geological units of the Sudetes, the highest values of the hydrogeochemical background of ²²²Rn in groundwaters have been determined for the Lądek-Śnieżnik metamorphic complex (36–1250 Bq/dm³), the Izera metamorphic complex (17–890 Bq/dm³)

and the Karkonosze granite (16–690 Bq/dm³) [98,111]. The highest values of ²²²Rn activity concentration were measured in towns situated in the area of the Izera metamorphic complex (Szklarska Poręba, measured value range: 19.5–3368 Bq/dm³, Świeradów-Zdrój, <0.2–2005 Bq/dm³) and the Łądek-Śnieżnik metamorphic complex (Łądek-Zdrój, 110–1413 Bq/dm³), hence in the areas of orthogneiss occurrence in the geological units with the highest hydrogeochemical background of ²²²Rn [98]. Slightly lower values were recorded in the area of the Karkonosze granite occurrence (Szklarska Poręba, 931–1282 Bq/dm³, and Kowary, 374–650 Bq/dm³). Within the fore-Sudetic block, the highest values of ²²²Rn activity concentration were measured in the health resort Przerzecznym-Zdrój (13–176 Bq/dm³) and in Sobótka (1.0–335 Bq/dm³), where only potentially medicinal radon waters occur.

The highest values of ²²⁶Ra activity concentration have been measured in the areas of the Izera metamorphic complex (Świeradów-Zdrój, 16–1360 mBq/dm³, and Szklarska Poręba, 11–1250 mBq/dm³) and the intra-Sudetic basin (Duszniki-Zdrój, 32–1260 mBq/dm³, and Polanica-Zdrój, 121–1200 mBq/dm³). The highest concentrations of ²²⁸Ra (up to 840 mBq/dm³) were measured in the same localities, which suggests a correlation between the presence of both radium isotopes in the same geological units. As both of these radium isotopes belong to different radioactive series (²²⁶Ra to the uranium–radium series and ²²⁸Ra to the thorium series), this also indicates that the concentrations of both radium isotopes in Sudetic groundwaters are determined by the chemical properties of this element and not by the processes related to radioactive transformations.

Although uranium concentrations (^{234,238}U) have been reported less frequently, groundwaters richest in this element are found in the area of the intra-Sudetic basin filled with sedimentary rocks. The highest activity concentrations of uranium isotopes have been recorded in Szczawno-Zdrój (4–725 mBq/dm³ for ²³⁸U and 12.1–964 mBq/dm³ for ²³⁴U), in Duszniki-Zdrój (1.1–81 and 2.5–239 mBq/dm³), and Jedlina-Zdrój (1.0–54 and 2.4–366 mBq/dm³, respectively). It should be emphasized that the concentration ranges of uranium isotopes (²³⁸U and ²³⁴U) in the area of the Sudetes and the fore-Sudetic block are largely unknown due to the limited amount of available data.

In the case of the other analyzed isotopes in the area of Province C, shown in Table 3 (²¹⁰Pb, ²¹⁰Po, ⁴⁰K, ³H, and ¹⁴C), the available amount of data is insufficient to conduct a fuller geochemical analysis and assess mutual correlations between the concentrations of these isotopes. The ²¹⁰Pb isotope content has been measured within just a few geological units. The highest values of lead isotope activity concentration were recorded in the areas of the Bystrzyca and Orlica Mountains metamorphic complex (Szczawina, 485–609 mBq/dm³) and the intra-Sudetic basin (Duszniki-Zdrój, 547 mBq/dm³). No available literature data on the concentration range of ²¹⁰Po in medicinal and potentially medicinal waters in the area of the Sudetes were found. The highest concentrations of the isotope ⁴⁰K were found in the area of the intra-Sudetic basin (Szczawno-Zdrój, 330–740 mBq/dm³, and Jedlina-Zdrój, 250 mBq/dm³). Isolated results were also obtained from several places, including the health resorts in Łądek-Zdrój and Cieplice Śląskie-Zdrój, though the activity concentrations of the isotope ⁴⁰K measured in both localities do not exceed 26 mBq/dm³.

Zero and trace concentrations of tritium have been measured in the area of the Karkonosze granite (Karpniki and Stanisławów, 0.0 TU; Cieplice Śląskie-Zdrój, 0.0–1.7 TU) and the Łądek-Śnieżnik metamorphic complex (Łądek-Zdrój, 0.0–1.0 TU). The results of tritium determination, often over 20 TU, have been obtained in the area of the intra-Sudetic basin (Duszniki-Zdrój, 2.2–35.1 TU; Kudowa Zdrój 0.0–28.8 TU; Polanica-Zdrój, 0.0–23.4 TU), which explicitly indicates the contribution of the modern component (i.e., post-1952) towards recharging these medicinal waters [41,69].

Table 3. ^{210}Pb , ^{210}Po , ^{40}K , ^3H , and ^{14}C content in medicinal and potentially medicinal waters of the Sudetes (according to [20,37,40,76,93,101,102,106,107,110,112–114]).

Area, Geological Unit, Spa town	Range of Measured Values				
	^{210}Pb	^{210}Po	^{40}K	^3H	^{14}C
	[mBq/dm ³]			[TU]	[%modC] ¹
Sudetes:	–	–	18.64–740	–	–
KM	–	–	–	–	–
Cieplice Śląskie-Zdrój	4.1	–	25.1	0.0–1.7	1.1–105
Karpniki	–	–	–	0.0	0.0
Kowary	–	–	–	–	–
Sosnówka	–	–	–	–	–
Staniszów	–	–	–	0.0	5.5
Szklarska Poręba	–	–	–	–	–
KMZ	–	–	–	–	–
KUM	–	–	–	–	–
LŚMC	–	–	–	–	–
Łądek-Zdrój	29.3	–	18.64	0.0–1.0	16.5–32
OBMC	–	–	–	–	–
Bobrowniki Stare	–	–	–	–	–
Długopole-Zdrój	–	–	–	–	–
Szczawina	485–609	–	–	2.2–14.7	–
IMC	–	–	–	–	–
Czerniawa-Zdrój	–	–	–	–	–
Szklarska Poręba	–	–	–	–	–
Świeradów-Zdrój	–	–	–	–	–
RJMC	–	–	–	–	–
GSGB	–	–	–	–	–
KŁMC	–	–	–	–	–
KMC	–	–	–	–	–
BU	–	–	–	–	–
ISB	–	–	23.41–740	0.0–35.1	–
Duszniki-Zdrój	547	–	23.41	2.2–35.1	–
Gorzanów	–	–	–	–	–
Jedlina Zdrój	–	–	250	–	–
Jeleniów	–	–	–	1.9–13.5	–
Kudowa-Zdrój	–	–	–	0.0–28.8	–
Polanica-Zdrój	–	–	–	0.0–23.4	–
Szczawno-Zdrój	–	–	330–740	–	–
NSB	–	–	–	–	–
SB	–	–	–	–	–
Fore-Sudetic Block:	–	–	–	–	–
SSM	–	–	–	–	–
Sobótka	–	–	–	–	–
SM	–	–	–	–	–
NKMU	–	–	–	–	–
Przerzeczyn-Zdrój	–	–	–	–	–
KMC	–	–	–	–	–
GSGB	–	–	–	–	–
SOB	–	–	–	–	–

Notes: ¹ [%modC] the percentage of modern carbon, i.e., the percentage of ^{14}C in a sample relative to international radiocarbon standard (100% modC corresponds to the activity of 0.226 Bq/g C).

The data presented in Tables 2 and 3 indicate that, for the Sudetes region, a relatively extensive dataset is available for isotopes ^{222}Rn , ^{226}Ra , and ^{228}Ra , while data for ^{234}U and ^{238}U are more limited. For other isotopes, such as ^{40}K and ^3H , there is a clear lack of data, whereas, for ^{210}Po , ^{210}Pb , and ^{14}C , the available information is limited and incomplete.

3.3. The Carpathians

Province D is divided into three main regions (Figure 3): the Carpathian Foredeep, the Outer Carpathians and the Inner Carpathians. Particular regions differ in geological setup, both in terms of tectonics and lithology. Geologically, the Carpathians are divided into the Inner Carpathians (the Tatras, the Podhale Basin, and the Pieniny klippen belt) and the Outer Carpathians aka the Flysch Carpathians [67,115]. In this province, occurrences of CO_2 -rich waters and brines are notably frequent. A characteristic feature of this area is cooccurrence of mineral and ordinary waters [116]. In province D, like in provinces A and B, there are no medicinal radon waters, and potentially medicinal radon waters are very rare (cf. Tables 2 and 4). The occurrence of medicinal waters in the area of province D (the Carpathians plus the Carpathian Foredeep) is shown in Figure 3.

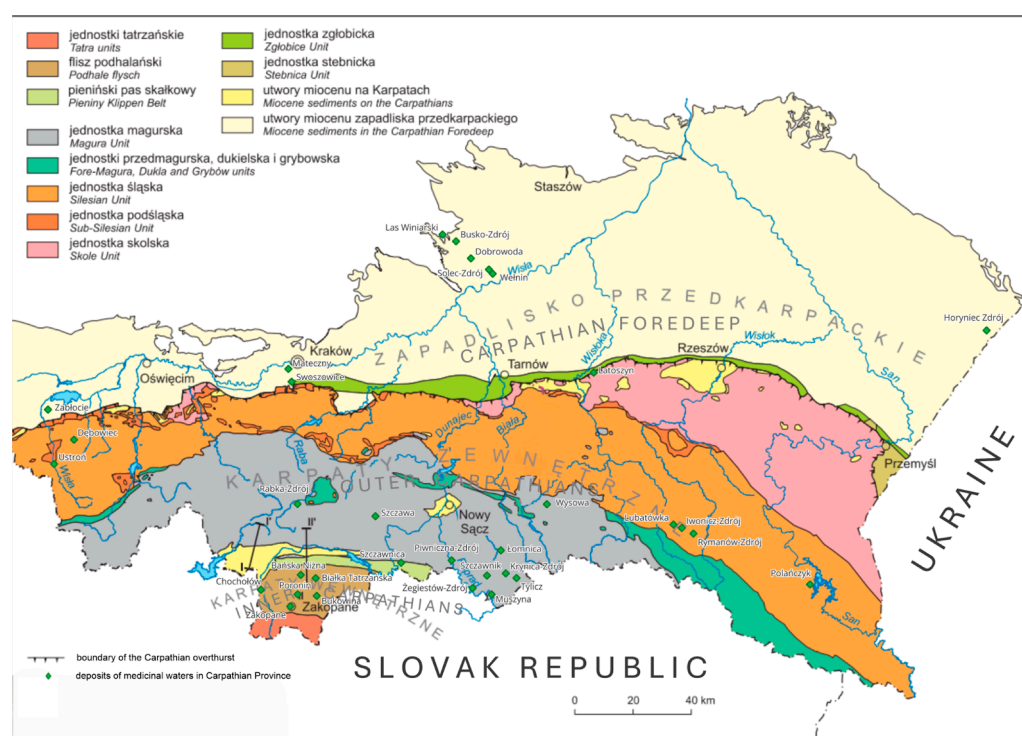


Figure 3. Simplified geological-structural map of the Polish Carpathians and the Carpathian Foredeep with the most important occurrences of medicinal and thermal waters marked as green rhombuses with the name of localization (according to [72,117–119] slightly modified by the authors).

The value of the hydrogeochemical background was determined only for the isotope ^{222}Rn and only in the area of the Variscan granitoids of the Tatra Mountains building the inner part of the Alpine orogen of the Carpathians [103,120]. The hydrogeochemical background of ^{222}Rn in the area of the Tatra granitoids is $0.7\text{--}61\text{ Bq/dm}^3$, and the measured value range is $<0.2\text{--}104.2\text{ Bq/dm}^3$. The results of analyses conducted in the area of the Carpathians and the Carpathian Foredeep show that ^{222}Rn concentration in spring waters and groundwaters usually ranges from several to several dozen Bq/dm^3 and rarely exceeds 80 Bq/dm^3 (Table 4). Such a relationship may be due to a lack of contact between groundwaters and rock formations rich in uranium and radium (^{226}Ra). In the case of the

Tatra granitoids, the relatively low values of ^{222}Rn activity concentration may additionally depend on the degree of erosion of the granitoid massif exposed on the land surface [101].

The highest values of ^{226}Ra activity concentration have been detected in the Outer Carpathians (Ustroń, <3–85 500 mBq/dm³, Lubatówka, 1300–1396 mBq/dm³, and Dębowiec, 190–1270 mBq/dm³). The extreme values measured in the Inner Carpathians are slightly lower (Chochółów, 2260 mBq/dm³). The activity concentration of ^{226}Ra in Ustroń, reaching 85,500 mBq/dm³, is associated with brines that have been in contact with Carboniferous organic sediments (hard coal formations). According to the available literature, this represents the highest value of ^{226}Ra activity concentration in groundwater reported worldwide to date [34]. The highest values of ^{228}Ra activity concentration were also recorded in the Outer Carpathians, in Dębowiec (110–1320 mBq/dm³) and Lubatówka (1100–1271 mBq/dm³). So far, the maximum activity concentrations of ^{226}Ra and ^{228}Ra in mineral waters of the Outer Carpathians (with TDS values characteristic of thermal waters from the Podhale basin) have been c. 170 mBq/dm³ for both isotopes [110]. The increased concentrations of radium isotopes in thermal waters of the Podhale basin are the result of contact between these waters and rocks of the Tatra crystalline massif (including gneisses, granites and schists) and intensified leaching of natural radionuclides out of these rocks by waters with increased temperatures [110].

The highest activity concentrations of uranium isotopes recorded in the Outer Carpathians (for particular water deposits) are 47.7 mBq/dm³ for ^{238}U and 55.6 mBq/dm³ for ^{234}U in Tylicz, and <0.5–15.6 mBq/dm³ for ^{238}U and <0.5–161.7 mBq/dm³ for ^{234}U in Krynica-Zdrój, while, in the Inner Carpathians, they are markedly increased only in the area of Poronin (41.9 mBq/dm³ for ^{238}U and 58.8 mBq/dm³ for ^{234}U).

Table 4. ^{222}Rn , $^{226,228}\text{Ra}$, and $^{238,234}\text{U}$ content in medicinal and potentially medicinal waters of the Carpathians with the hydrogeochemical background and value range in particular geological units of the Carpathians (according to [21,36,92,108,110,113,114,121–125]).

Area, Geological Unit, Spa Town	²²² Rn		²²⁶ Ra	²²⁸ Ra	²³⁸ U	²³⁴ U
	HBV ¹	Range of Measured Values				
	[Bq/dm ³]	[mBq/dm ³]				
Carpathians:	–	<0.2–104.2	<3–85,500	<10–2500	<0.5–47.7	<0.5–161.1
Outer Carpathians		<0.2–76.1	<3–1396	<10–2500	<0.5–47.7	<0.5–161.1
Dębowiec		1.18	190–1270	110–1320	–	1.6
Iwonicz-Zdrój		1.17–5.87	149–575	<20–877	0.5	2.5
Krynica-Zdrój		<1–28.1	6–612	<10–736	<0.5–15.6	<0.5–161.6
Lubatówka		2.32–3.2	1300–1396	1100–1271	2.7–3.1	4.2–7.1
Łomnica		–	65–117	97–171	–	–
Muszyzna		3.0–50.2	4–380	12–270	< 0.5–8.1	0.7–13.1
Piwniczna Zdrój		3.8	15–96	21–73	1.3–25	<0.5–10.4
Polańczyk		3.50	70	–	–	–
Rabka-Zdrój	–	<0.2	246–638	207–616	<0.5–6.2	<0.5–9.3
Rymanów-Zdrój		0.90–9.75	80–758	58–784	–	–
Szczawa		–	91–441	47–340	–	–
Szczawnica		–	14–282	15–167	0.7–7.7	2.0–13.6
Szczawnik		14.2	31	< 30	2.3	8.1
Tylicz		8.3	130	60	15.2–47.7	17–55.6
Ustroń		24.8–76.1	<3–85,500	14.1–17.7	4.6–18.7	3.2–14.0
Wysowa		–	29–106	<20–400	<0.5	0.6–2.1
Zabłocie		–	1600	2500	–	–
Żegiestów-Zdrój		–	<3–56	<10–97	<0.5–3.6	<0.5–7.7

Table 4. Cont.

Area, Geological Unit, Spa Town	²²² Rn		²²⁶ Ra	²²⁸ Ra	²³⁸ U	²³⁴ U
	HBV ¹		Range of Measured Values			
	[Bq/dm ³]		[mBq/dm ³]			
Carpathians:	–	<0.2–104.2	<3–85,500	<10–2500	<0.5–47.7	<0.5–161.1
Inner Carpathians	–	<0.2–18.5	31–2260	<10–339	2.6–41.9	4.5–58.5
Bańska Nizna		<0.2–8.5	560–602	69–161	3.1–3.9	4.7–6.2
Białka Tatrzańska		–	347	116	3.6	5.1
Bukowina		3.1	585	339	1.2	12.5
Chochółów		–	2260	<10	2.9	5.8
Poronin		–	250	<10	41.9	58.8
Zakopane		<0.2–18.5	31–291	19–30	2.6–2.8	4.5–7.5
Tatra granitoids	0.7–61	0.2–104.2	–	–	–	–
Carpathian Foredeep		1.3–9.4	3–500	<10–940	–	–
Busko-Zdrój		–	110–500	240–300	–	–
Dobrowoda	–	–	270	100	–	–
Horyniec Zdrój		3.70–4.00	<5	<10	–	–
Las Winiarski		–	–	–	–	–
Latoszyn		4.60	–	–	–	–
Mateczny		1.30–8.32	–	–	–	–
Solec-Zdrój		–	340	940	–	–
Swoszowice		9–9.4	3–4	31–54	1.3–3.7	3.8–6.2
Wełnin		4.30	–	–	–	–

Notes: ¹ HBV, hydrogeochemical background value.

As for the other studied isotopes in the area of the Carpathian province shown in Table 5, the concentrations of isotope ²¹⁰Pb in medicinal waters were only measured in a few spa towns. The highest values were recorded in Chochółów (102 mBq/dm³), Zakopane (8.2–73.5 mBq/dm³), Szczawnica (<5–56 mBq/dm³), and Rymanów-Zdrój (19–48 mBq/dm³). No available literature data on the ranges of ²¹⁰Po activity concentration in the area of the Carpathian province were found, except for bottled water from Muszyna (Muszynianka), where the activity concentration of this isotope is 0.35 mBq/dm³ [126].

The activity concentrations of the isotope ⁴⁰K in waters from various localities in the Outer Carpathians, the Inner Carpathians and the Carpathian Foredeep have a range of 23–23 400 mBq/dm³, 34.4–1372 mBq/dm³ and 120–5070 mBq/dm³, respectively, with the value of 23 400 mBq/dm³ (in Ustroń) significantly departing from the other results.

No tritium (³H) has been detected in medicinal waters from the area of the Carpathian Foredeep (Busko-Zdrój, Dobrowoda, Horyniec-Zdrój, and Las-Winiarski), which means that these waters have been recharged exclusively with pre-1952 precipitation [69]. Non-detectable to trace concentrations of tritium have been measured in groundwaters from the Inner Carpathians (0.0–0.25 mBq/dm³, except Zakopane (10.6–190 mBq/dm³)). The highest recorded value (190 mBq/dm³) refers to data from 1969. Control data from 2008 point to a marked drop in the so-called tritium curve and its gradual decline to a level close to natural [71,127]. Variability of the isotopic composition of waters over time may be due to the vulnerability of the aquifer system to the size and conditions of exploitation [78]. Results of tritium determination, often over 20 TU, have been obtained in the Outer Carpathians (e.g., in Wysowa, 0.0–63 mBq/dm³, and Krynica-Zdrój, 0.0–45 mBq/dm³), which indicates the contribution of modern (tritium) waters and the age of waters ranging from a few years to a few decades. The amount of available literature data on measured ¹⁴C content

in medicinal and potentially medicinal waters in the area of the Carpathian province is insufficient to enable a satisfactory geochemical analysis.

Based on an analysis of the data shown in Tables 4 and 5, it can be concluded that radioactivity of waters in the area of the Carpathian province is mainly due to the occurrence of the isotopes $^{226,228}\text{Ra}$ and ^{40}K and, more rarely, increased concentrations of $^{238,234}\text{U}$ or ^{222}Rn . In thermal waters within the Podhale basin (e.g., Bańska Niżna and Chochółów), the Magura nappe (Rabka-Zdrój) and the Silesian nappe (Ustroń), the activity concentration of ^{226}Ra is higher than that of ^{228}Ra , while, in thermal waters from the Polish Lowlands (Uniejów, Mszczonów or Grudziądz), an inverse relationship is observed.

Table 5. ^{210}Pb , ^{210}Po , ^{40}K , ^3H , and ^{14}C content in medicinal and potentially medicinal waters in the Carpathians (according to [17,18,35,72–75,77,110,114,122,124,126,128–133]).

Area, Geological Unit, Spa Town	Range of Measured Values				
	^{210}Pb	^{210}Po	^{40}K	^3H	^{14}C
	[mBq/dm ³]			[TU]	[%modC]
Carpathians:	<5–102	–	23–23,400	0–190	0.3–23.2
Outer Carpathians	<5–56.7	–	23–23,400	0–63	–
Dębowiec	–	–	–	–	–
Iwonicz-Zdrój	–	–	260–1220	0.2–7.8	–
Krynica-Zdrój	<5	–	439	0.0–45	–
Lubatówka	56.7	–	596–1210	–	–
Łomnica	10–32	–	–	–	–
Muszyzna	–	0.35	37–396	0.0–13.8	–
Piwniczna-Zdrój	<5	–	554	0.9–16.9	–
Polańczyk	–	–	70–420	–	–
Rabka-Zdrój	<5–16.9	–	2830	–	–
Rymanów-Zdrój	19–48	–	450–1500	0.0–1.0	–
Szczawa	<5–21.4	–	–	–	–
Szczawnica	<5–56	–	359–548	–	–
Szczawnik	–	–	–	–	–
Tylicz	<5	–	40–350	0.0–20	–
Ustroń	–	–	1201–23,400	–	–
Wysowa	–	–	81–223	0.0–63	–
Zabłocie	–	–	–	–	–
Żegiestów-Zdrój	–	–	23–9904	0.3–26	–
Inner Carpathians	8.2–102	–	34.4–1372	0–190	0.3–23.2
Bańska Niżna	30–36	–	1320–1372	0.0–0.2	0.3–3.4
Białka Tatrzańska	9.2	–	1091	–	–
Bukowina	15.3	–	570	0.1	0.8
Chochółów	102	–	570	0.25	3.2
Poronin	–	–	34.4	0.0	23.2
Zakopane	8.2–73.5	–	36.4–107	10.5–190	–
Tatra granitoids	–	–	–	–	–
Carpathian Foredeep	–	–	120–5070	–	–
Busko-Zdrój	–	–	2400	0.0	0.0
Dobrowoda	–	–	–	0.0	0.9
Horyniec-Zdrój	–	–	250–290	0.0	–
Las Winiarski	–	–	3630	0.0	–
Latoszyn	–	–	120	–	–
Mateczny	–	–	–	0.0–14.5	2.1–18.5
Solec-Zdrój	–	–	–	–	–
Swoszowice	9.7	–	–	–	–
Welnin	–	–	5070	–	–

The data presented in Tables 4 and 5 indicate that, for the Carpathian region, relatively extensive datasets are available for isotopes ^{226}Ra , ^{228}Ra , and ^{222}Rn , whereas data for ^{234}U and ^{238}U are more limited. For other isotopes, such as ^{40}K and ^3H , data are largely lacking, while, for ^{210}Po , ^{210}Pb , and ^{14}C , the available information is sparse.

3.4. The Polish Lowlands

Groundwaters in the Polish Lowlands have the smallest amount of data on natural radioactive isotope content (Tables 6 and 7). The medicinal waters, thermal waters, mineral waters and brines occurring in this area circulate in reservoir rocks belonging to two big European geological units: the East European Precambrian Platform and the West European Palaeozoic Platform [4]. Mineral waters in the area of the Polish Lowlands occur at various depths, and the biggest therapeutic significance is characteristic of deposits identified mainly in Lower Cretaceous and Lower Jurassic sandstone formations [134,135]. In the area of the Mid-Polish anticlinorium (in Inowrocław), mineral waters (bitter brines) used in therapeutic treatments are formed as a result of forced leaching of salt deposits [136]. Within the Palaeozoic platform (the Pomerania-Kołobrzeg anticlinorium, Połczyn-Zdrój, and Kamień Pomorski), there are thick Zechstein salt series with salt structures, which determine the predominance of sodium chloride mineral waters in this province [135]. A more detailed analysis of the location of the occurrences of medicinal, thermal and mineral waters and brines in the Polish Lowlands leads to a conclusion that such waters occur mainly in the area of the West European Palaeozoic Platform. The only exception is medicinal waters found in Sopot and Ustka. As the authors did not find any published data on natural radioactive isotope content in the waters from Ustka, Sopot is the only health resort in the area of the East European Precambrian Platform included in this study. This is the reason why the authors describe the medicinal waters, thermal waters, mineral waters and brines from the area of the Polish Lowlands together, without dividing this area into geological units.

The results of the analyses performed in the area of the Polish Lowlands demonstrate that ^{222}Rn activity concentrations in groundwaters usually range from a few to about a dozen Bq/dm^3 (Table 6). The highest values of ^{222}Rn activity concentration have been measured in localities situated in the area of the Mid-Polish anticlinorium (Inowrocław, $17.5 \text{ Bq}/\text{dm}^3$) and the Szczecin-Łódź-Miechów synclinorium (Kołobrzeg, measured value range: $2.20\text{--}8.62 \text{ Bq}/\text{dm}^3$; Połczyn-Zdrój, $9.60 \text{ Bq}/\text{dm}^3$). The highest values of ^{226}Ra activity concentration have been detected in the area of the Kościerzyna-Puławy Synclinorium (Grudziądz, $2160 \text{ mBq}/\text{dm}^3$), the Mid-Polish anticlinorium (Ciechocinek, $1970 \text{ mBq}/\text{dm}^3$) and the Pomeranian anticlinorium (Połczyn-Zdrój, $1120 \text{ mBq}/\text{dm}^3$, and Kamień Pomorski, $660 \text{ mBq}/\text{dm}^3$). The highest activity concentrations of ^{228}Ra (up to $3000 \text{ mBq}/\text{dm}^3$ —Połczyn-Zdrój) have also been measured in these localities, which suggests correlation between the presence of both radium isotopes in groundwaters of the same geological units.

The values of uranium ($^{234,238}\text{U}$) concentration in waters from the Polish Lowlands have been less often published. The highest activity concentration of uranium isotopes has been recorded in the area of the Peribaltic Syncline, in Sopot ($5.1 \text{ mBq}/\text{dm}^3$ for ^{238}U and $45.6 \text{ mBq}/\text{dm}^3$ for ^{234}U), where the main utilized aquifer is associated with Lower-Triassic sediments. However, the limited amount of available data suggests that the range of uranium isotope concentrations in the other geological units stays mostly at low levels ($<0.5\text{--}1.5 \text{ mBq}/\text{dm}^3$ for ^{238}U and $<0.5\text{--}1.19 \text{ mBq}/\text{dm}^3$ for ^{234}U).

Table 6. ^{222}Rn , $^{226,228}\text{Ra}$, and $^{238,234}\text{U}$ content in medicinal and potentially medicinal waters of the Polish Lowlands with the hydrogeochemical background and the range of values in particular geological units (according to [36,37,70,106,110,113,135,137]).

Area, Geological Unit, Spa Town						
	^{222}Rn	^{226}Ra	^{228}Ra	^{238}U	^{234}U	
	HBV	Range of Measured Values				
		[Bq/dm ³]	[mBq/dm ³]			
SŁMC	–	1.9–9.60	40–1120	51–300	<0.5–1.5	<0.5–0.96
Kamień Pomorski		–	660	800	–	–
Kołobrzeg		2.20–8.63	470	–	–	–
Mszczonów		2.9	41	51	1.5	<0.5
Poddębice		5.3	40	62	<0.5	<0.5
Połczyn-Zdrój		9.60	1120	3000	–	–
Świnoujście		3.16–3.47	–	–	–	–
Uniejów		1.9–2.1	560	597–609	<0.5	0.96
KPC		1.36–4.90	70–2160	16–2170	–	–
Grudziądz	–	4.90	2160	2170	–	–
Konstancin Jeziorna		3.88	–	–	–	–
Nałęczów		1.36–1.57	70	16	0.81	1.19
MPA		2.20–17.5	40–1970	14–2100	–	–
Ciechocinek	–	2.40–5.02	1970	2100	–	–
Inowrocław		17.5	–	–	–	–
Wieniec-Zdrój		3.30	40	14	–	–
PS		–	–	–	–	–
Sopot		6.80	470	1020	5.1	45.6

Table 7. ^{210}Pb , ^{210}Po , ^{40}K , ^3H , and ^{14}C content in medicinal and potentially medicinal waters of the Polish Lowlands (according to [106,110,114,126,135,137,138]).

Area, Geological Unit, Spa Town	Range of Measured Values				
	^{210}Pb	^{210}Po	^{40}K	^3H	^{14}C
		[mBq/dm ³]		[TU]	[%modC]
SŁMC	3.2–24	–	164–5860	–	–
Kamień Pomorski	–	–	3100	–	–
Kołobrzeg	–	–	4730	–	–
Mszczonów	3.2	–	930	–	–
Poddębice	5.3	–	164	–	–
Połczyn-Zdrój	–	–	1540	0.0	29.2
Świnoujście	–	–	2760–3070	–	–
Uniejów	24	–	640–5860	–	–
KPC	–	–	100–7110	–	–
Grudziądz	–	–	7110	–	–
Konstancin Jeziorna	–	–	5540	–	–
Nałęczów	–	0.7	100–151	–	–
MPA	–	–	250–5280	–	–
Ciechocinek	–	–	360–5280	0.0–24.2	–
Inowrocław	–	–	<650–2090	–	–
Wieniec-Zdrój	–	–	250	–	–
PS	–	–	–	–	–
Sopot	–	–	–	–	–

As for the rest of the studied isotopes in the area of the Polish Lowlands shown in Table 7, the values of ^{210}Pb concentration were only measured in thermal waters in the area of the Szczecin–Łódź–Miechów synclinorium. The highest activity concentrations of this isotope were recorded in Uniejów (24 mBq/dm³). In the area of the Polish Lowlands, no available literature data on concentration ranges of isotope ^{210}Po were found, except for bottled water from Nałęczów (Nałęczowianka)—0.7 mBq/dm³ [126]. The activity concentrations of the isotope ^{40}K in groundwaters from various localities in the Polish Lowlands stayed in the following ranges: 100–7110 mBq/dm³ in the Kościerzyna–Puławy synclinorium, 250–5280 mBq/dm³ in the Mid-Polish anticlinorium, and 164–5860 mBq/dm³ in the Szczecin–Łódź–Miechów synclinorium. The data for the isotopes ^3H and ^{14}C are currently insufficient for a more comprehensive geochemical analysis, which indicates a need for further systematic isotopic analyses in this region.

Based on an analysis of the data shown in Tables 6 and 7, it can be concluded that radioactivity of waters in the area of the Polish Lowlands is mainly due to the occurrence of isotopes ^{40}K and $^{226,228}\text{Ra}$ and, more rarely, increased concentrations of ^{222}Rn or $^{238,234}\text{U}$.

4. Discussion

The natural radioactive isotopes occurring in groundwaters regarded as medicinal waters in Poland can be divided into four groups: A. isotopes giving water its medicinal properties (^{222}Rn), B. isotopes potentially harmful to the human body (^{222}Rn , $^{226,228}\text{Ra}$, $^{238,234}\text{U}$, ^{210}Pb , and ^{210}Po), C. isotopes neutral to the human body (^{40}K , ^{14}C , and ^3H) and D. isotopes used as tracers in hydrogeological analyses enabling characterizing the genesis of these waters, their age (groundwater transit time), intake recharge areas, flow paths, vulnerability to anthropogenic contamination, etc. (^3H , ^{14}C , ^{222}Rn , $^{238,234}\text{U}$, $^{226,228}\text{Ra}$, ^{210}Pb , and ^{210}Po). ^{222}Rn can be classified into all the groups, and its harmful or beneficial effect on the human body depends on the size of the effective dose, for which mainly its radioactive decay products are responsible. The ^{40}K isotope is neutral to the human body, and ^{14}C and ^3H can be classified as tracer isotopes, neutral to the human body. The other isotopes can and do act as environmental tracers and, in increased concentrations, they can emit radiation carrying so much energy that absorbing it by a human may result in exceeding the allowable effective dose and cause undesirable effects, harmful to the human body (Figure 4). It should be noted here that the chemical effect of uranium, being a heavy metal, is more adverse to the human body than the physical effect of its isotopes, related to the emitted ionizing radiation.

NATURAL RADIOACTIVE ISOTOPES	
GIVING GROUNDWATER MEDICINAL PROPERTIES	POTENTIALLY HARMFUL TO HEALTH
^{222}Rn	^{222}Rn ^{226}Ra ^{228}Ra ^{238}U ^{234}U ^{210}Pb ^{210}Po
^{238}U ^{234}U ^{228}Ra ^{226}Ra ^{222}Rn ^{210}Pb ^{210}Po ^{14}C ^3H	^{40}K ^{14}C ^3H
USED AS ENVIRONMENTAL TRACERS	NEUTRAL TO HEALTH (in natural conditions and concentrations)

Figure 4. Division of natural radioactive isotopes occurring in medicinal waters according to their use and the effect on the human body.

While analyzing the available data on natural radioactive isotope content in medicinal waters including thermal waters and brines in the territory of Poland, it should be noted that very few analyses have been conducted and very few results are available. The data are particularly scarce in the area of the Polish Lowlands. The amount of existing and published data, i.e., data readily available for analyses, does not enable a broader in-depth interpretation either in hydrogeological or radiological terms, especially with regard to radiological protection. Only the aspect of ^{222}Rn content in the area of the Sudetes is better documented due to recognizing this isotope as an agent giving a large number of groundwaters in this area medicinal properties. The broader scope of research into ^{222}Rn hydrogeochemistry in the area of the Sudetes has made it possible to determine the hydrogeochemical background of ^{222}Rn both for the whole unit and its smaller constituent geological units.

The highest values of ^{222}Rn activity concentration have been recorded in the Sudetic province (C). From an analysis of data shown in Tables 2 and 3, it can be concluded that the largest concentrations of the isotopes ^{222}Rn and $^{226,228}\text{Ra}$ occur in geological units built of uranium- and radium-rich crystalline rocks. Radium and radon are rarely found to enrich groundwaters circulating within sedimentary rocks (the Intrasudetic Basin). On the other hand, the highest concentrations of the isotopes $^{238,234}\text{U}$ in groundwaters are found in the area of a unit built of sedimentary rocks, characterized by much lower Rn and Ra content [85]. This proves a significant influence of hydrochemical characteristics of groundwaters on the transport of natural radioactive isotopes. Specific concentrations of radon, radium and uranium isotopes are characteristic of particular constituent geological units of the Sudetes. Characterizing these concentrations could be a tool enabling distinguishing groundwaters from different geological units of the Sudetes. This is one of the numerous manifestations of the mosaic-like geologic setup of the Sudetes, where the neighboring units are characterized by significantly different mineral and chemical composition of rocks, including the reservoir rocks of groundwaters, also medicinal waters. In the area of the Sudetes, radioactivity of groundwaters, including medicinal waters, is related primarily to the concentration of ^{222}Rn dissolved in it, while waters containing large concentrations of the isotopes $^{226,228}\text{Ra}$ are much less common and those with increased concentrations of $^{238,234}\text{U}$ even rarer. The data on ^{222}Rn , ^{226}Ra , and partly ^{228}Ra , are the main database of knowledge on radionuclides dissolved in spa waters in the area of the Sudetes. Determinations of uranium isotopes are much less complete, and data for the isotopes ^{210}Pb , ^{210}Po , ^3H and ^{14}C are currently insufficient for a more complete geochemical analysis. This is a significant limitation in the assessment of the influence of geological environment on radioactivity of groundwaters, which points to a need for conducting further systematic isotopic analyses in the region so that their results can be used for describing the hydrogeochemical and radiological characteristics of particular isotopes and groundwaters recognized as medicinal and potentially medicinal and their reservoir rocks. A characteristic feature of the Sudetes is the occurrence of medicinal and potentially medicinal waters with the highest concentrations of radon (the isotope ^{222}Rn) and uranium isotopes, both ^{238}U and ^{234}U , in Poland. It should also be noted that, in some medicinal waters in the area of the Sudetes, the activity concentrations of ^{222}Rn , ^{226}Ra and ^{228}Ra exceed the parametric values and derived concentrations for waters intended for human consumption. In one case, a ^{210}Pb concentration in excess of the derived concentration was also recorded.

Based on an analysis of the data shown in Tables 4 and 5, it can be concluded that the radioactivity of waters in the area of the Carpathian province is mainly due to the occurrence of the isotopes $^{226,228}\text{Ra}$ and ^{40}K and, more rarely, increased concentrations of $^{238,234}\text{U}$ or ^{222}Rn . Increased concentrations of the isotopes ^{40}K and $^{226,228}\text{Ra}$ are associated

chiefly with brines and thermal waters with increased TDS content. Thermal waters and brines also occur in the Polish Lowlands, where they are also characterized by increased concentrations of primarily ^{40}K and $^{226,228}\text{Ra}$. It is worth noting, however, that, in thermal waters within the Carpathians, in particular in the Podhale Basin (e.g., Bańska Niżna and Chochółów), the Magura nappe (Rabka-Zdrój) and the Silesian nappe (Ustroń), the activity concentration of ^{226}Ra is higher than that of ^{228}Ra , while, in thermal waters from the Polish Lowlands (Uniejów, Mszczonów or Grudziądz), an inverse relationship is observed. The highest concentrations of the isotopes ^{40}K and $^{226,228}\text{Ra}$ are characteristic of waters with the highest TDS content, i.e., brines and thermal brines. Although both brines and thermal waters can be used in drinking treatments only exceptionally, it must be remembered that, in the Carpathians, derived concentrations of ^{226}Ra and ^{228}Ra in medicinal waters, including brines and thermal waters, are very often exceeded. A similar situation is also observed in the Polish Lowlands, where the concentrations of both radium isotopes also exceed the values of derived concentrations.

In the area of the Sudetes, medicinal waters are usually characterized by a smaller circulation depth and lower TDS content and temperature than waters from the area of the Carpathians and the Polish Lowlands. They are also characterized by increased concentrations, often in excess of the parametric values and derived concentrations for waters intended for human consumption, of such natural radioactive isotopes as ^{222}Rn , ^{226}Ra and ^{228}Ra and, more rarely, ^{210}Pb , as well as markedly increased concentration of ^{238}U and ^{234}U . In comparison, medicinal waters in the Carpathians and in the Polish Lowlands, including thermal waters and brines, are characterized by larger circulation depths and higher TDS content and temperature than waters from the Sudetes. What distinguishes medicinal waters from these areas from Sudetic waters are ^{226}Ra and ^{228}Ra concentrations exceeding the values of derived concentrations for waters intended for human consumption, as well as markedly increased concentrations of the isotope ^{40}K . Additionally, waters of the Carpathians and waters from the Polish Lowlands differ in the ratio of radium isotope concentrations. In the Carpathians, ^{226}Ra activity concentration is higher than that of ^{228}Ra , whereas, in the waters of the Polish Lowlands, ^{226}Ra activity concentration is lower than ^{228}Ra activity concentration. This means that the decisive role in radium isotope transport is played by the chemical properties of this element and the physicochemical conditions in (medicinal) groundwaters and not by the processes related to radioactive transformations of the isotopes ^{226}Ra and ^{228}Ra belonging to different radioactive series (uranium–radium and thorium, respectively).

Differences in the ranges of activity concentrations of selected natural radioactive isotopes occurring in groundwaters regarded as medicinal and potentially medicinal waters in Poland divided into particular provinces, the Sudetes, the Carpathians and the Polish Lowlands, are shown in the diagrams in Figure 5.

The undetected or very low concentrations of the isotope ^3H (tritium) usually indicate water recharged before the period of atmospheric nuclear testing, i.e., before 1952. Its presence, on the other hand, even in trace amounts, may indicate an admixture of modern waters [19,40,69]. The results of tritium determinations at a level between a few and c. 20 TU (2.36 Bq/dm^3) suggest modern recharge of medicinal waters, i.e., after the start of atmospheric nuclear testing in 1952. As a rule, in each of the discussed geological units of Poland, waters with high TDS content and large circulation depths contain no tritium. These waters are mainly brines and some thermal waters with high TDS content. The maximum tritium content in medicinal waters in Poland is an order of magnitude lower than the parametric value for waters intended for human consumption, i.e., 100 Bq/dm^3 .

The scarcity of data on natural radioactive isotope content in groundwaters regarded as medicinal waters makes it difficult not only to fully describe the hydrogeochemical

characteristics of these waters but especially to ensure the radiological safety of spa clients, patients and staff involved in using these waters in balneotherapeutic treatments. In order to define the specific requirements for radionuclide content in these waters, it would be necessary to start by defining limits of the activity concentration of particular isotopes in water intended for drinking treatment (internal exposure) based on the parametric values and derived concentrations defined for waters intended for human consumption. For other treatments, i.e., baths, showers, water jets, massages, etc. (external exposure), parametric values should be defined based on the measurements and calculations of the effective dose for each kind of treatment. To achieve these aims, extensive and methodical research as well as standardization of methods of administering treatments are necessary. Only based on the results of such work, the appropriate legal regulations could be introduced.

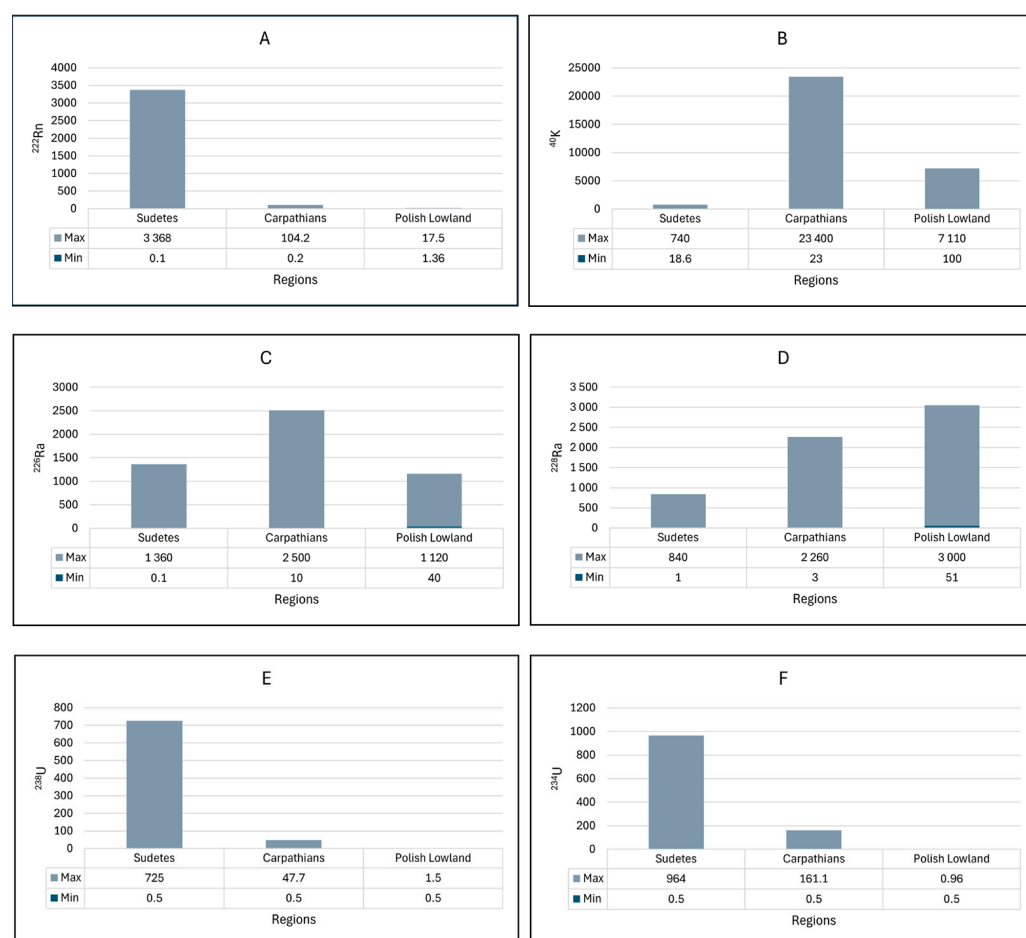


Figure 5. Diagrams showing ranges of activity concentrations (for ^{222}Rn in Bq/dm³; for other isotopes in mBq/dm³) of selected natural radioactive isotopes in medicinal waters of Poland, divided into particular provinces: the Sudetes, the Carpathians and the Polish Lowlands. Subfigures: A for ^{222}Rn , B for ^{40}K , C for ^{226}Ra , D for ^{228}Ra , E for ^{238}U and F for ^{234}U .

The authors propose that, in the case of the isotope ^{222}Rn , which, as recognized by law in some countries including Poland, gives groundwaters medicinal properties according to the radiation hormesis theory, the maximum allowable activity concentration in water intended for drinking treatment should prevent patients from receiving an effective dose higher than half of the annual dose received by the general public from drinking water with ^{222}Rn activity concentration equal to the parametric value, i.e., 100 Bq/dm³. With the assumed annual intake of 730 L, the maximum absorption of this isotope could reach 73,000 Bq. Assuming also that drinking treatment in a health resort requires drinking about 10 liters of water, the maximum activity concentration of ^{222}Rn in medicinal radon water

intended for drinking treatment should not exceed 3650 Bq/dm³. For the other natural radioactive isotopes, with unquestionably adverse effect on the human body, the authors propose that the maximum value of the activity concentration of each of these isotopes (^{238,234}U, ^{226,228}Ra, ²¹⁰Pb, and ²¹⁰Po) in medicinal water intended for drinking treatment should be the derived concentration resulting in receiving 20% of the annual effective dose from consuming 730 L of water (i.e., 0.02 mSv). Assuming the intake of 10 L of water during spa treatment, the maximum activity concentrations of ²³⁸U, ²³⁴U, ²²⁶Ra, ²²⁸Ra, ²¹⁰Pb and ²¹⁰Po in medicinal water intended for drinking treatment should be 43.8 Bq/dm³, 40.9 Bq/dm³, 7.3 Bq/dm³, 2.9 Bq/dm³, 2.9 Bq/dm³ and 1.5 Bq/dm³, respectively.

5. Conclusions

Among the catalogued 116 medicinal water deposits in Poland, the authors obtained data on natural radioactive isotope content in these waters only for 68 localities, also including thermal waters from several deposits not recognized as medicinal and several areas with the occurrence of potentially medicinal waters (e.g., radon waters in the area of the Sudetes and in the Tatra Mts in the Carpathians). These localities include 1 out of 5 deposits in the area of the East European (Precambrian) Platform, 13 localities out of 25 deposits in the area of the West European (Palaeozoic) Platform, 21 localities out of 20 deposits and several occurrences of potentially medicinal waters in the Sudetes, and 33 localities in the Carpathians out of 66 catalogued deposits in this mountain range. This overview shows how many medicinal water deposits and areas with the occurrence of potentially medicinal waters, and thermal waters not recognized as medicinal, lack data on natural radioactive isotope content. The largest number of available results of isotopic analyses in the area of Poland come from the Sudetes; a large amount of data was also obtained for the Carpathians, whereas the worst situation, in terms of our knowledge of the occurrence of natural radioactive isotopes in medicinal waters, is in the area of the Polish Lowlands, i.e., in the West-European and East-European platforms. As a result, it has only been possible so far to determine the hydrogeochemical background for ²²²Rn, and only in the area of the Sudetes and their constituent geological units, and one small geological unit of the Carpathians (the Tatra granitoids).

The collected and analyzed data allow a conclusion that we can distinguish three types of groundwater in terms of the content of natural radioactive isotopes associated with their occurrence in areas with different types of geological structure:

- Medicinal waters in the area of **the Sudetes (the Variscan orogen)** are characterized by the highest values of the activity concentrations of ²²²Rn and the isotopes ²³⁸U and ²³⁴U in Poland. In some medicinal waters in the area of the Sudetes, the activity concentrations of ²²²Rn, ²²⁶Ra and ²²⁸Ra exceed the parametric values and derived concentrations for waters intended for human consumption. In one case, an exceeded derived concentration of ²¹⁰Pb was also recorded. In terms of natural radioactive isotope content, medicinal waters of the Sudetes can be characterized as **radium–uranium–radon waters (Rn > U > Ra; where ²³⁴U > ²³⁸U and ²²⁶Ra > ²²⁸Ra)**.
- The radioactivity of medicinal waters of **the Carpathians (the Alpine orogen)** is mainly associated with the occurrence of the isotopes ^{226,228}Ra and ⁴⁰K and more rarely with increased concentrations of ^{238,234}U or ²²²Rn. Increased concentrations of the isotopes ⁴⁰K and ^{226,228}Ra are associated chiefly with brines and thermal brines. A characteristic feature of Carpathian medicinal waters is the occurrence of ²²⁶Ra activity concentration higher than ²²⁸Ra activity concentration. In medicinal waters from this area, the derived concentrations of ²²⁶Ra and ²²⁸Ra defined for waters intended for human consumptions are very often exceeded. In terms of natural radioactive

isotope content, medicinal waters of the Carpathians can be characterized as **radium–potassium waters** ($K > Ra$; where $^{226}Ra > ^{228}Ra$).

- Medicinal waters occurring in the **Polish Lowlands (the East European Precambrian Platform and the West European Palaeozoic Platform)** are characterized by increased concentrations of the isotopes $^{226,228}Ra$ and ^{40}K , whereas the concentrations of ^{222}Rn and the isotopes $^{238,234}U$ in these waters are very low. A characteristic feature of medicinal waters occurring in the Polish Lowlands is the presence of ^{228}Ra activity concentration higher than ^{226}Ra activity concentration, i.e., the opposite to the situation in Carpathian waters. In medicinal waters of this area, the derived concentrations of ^{226}Ra and ^{228}Ra defined for waters intended for human consumptions are also very often exceeded. In terms of natural radioactive isotope content, medicinal waters of the Polish Lowlands can be characterized as **potassium–radium waters** ($Ra > K$; where $^{228}Ra > ^{226}Ra$).

Based on the above discussion it can be concluded that natural radioactive isotopes occurring in groundwaters recognized as medicinal or potentially medicinal in Poland can be divided into four groups. These are: A. isotopes giving waters medicinal properties (^{222}Rn), B. isotopes potentially harmful to the human body (^{222}Rn , $^{226,228}Ra$, $^{238,234}U$, ^{210}Pb , and ^{210}Po), C. isotopes neutral to the human body (^{40}K , ^{14}C , and 3H), and D. isotopes used as tracers in hydrogeological studies (3H , ^{14}C , ^{222}Rn , $^{238,234}U$, $^{226,228}Ra$, ^{210}Pb , and ^{210}Po).

Because of the insufficient number of research results concerning natural radioactive isotope content in medicinal waters in Poland, a complete and detailed description of their hydrogeochemical characteristics is currently impossible. It is also impossible to assess the potential radiation exposure of patients and treatment staff or to take appropriate radiological protection measures. The first and the easiest step to take based on guidelines on waters intended for human consumption should be to define the concentration limits of particular radioactive isotopes in groundwaters regarded as medicinal waters intended for drinking treatment. The authors propose setting the maximum content limits for ^{222}Rn , ^{238}U , ^{234}U , ^{226}Ra , ^{228}Ra , ^{210}Pb , and ^{210}Po as 3650 Bq/dm³, 43.8 Bq/dm³, 40.9 Bq/dm³, 7.3 Bq/dm³, 2.9 Bq/dm³, 2.9 Bq/dm³ and 1.5 Bq/dm³, respectively.

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Abbreviations

The following abbreviations are used in this manuscript:

HBV	Hydrogeochemical background value
KM	Karkonosze Massif
KMZ	Kłodzko-Złoty Stok Masif
KUM	Kudowa Massif
LŚMC	Łądek-Śnieżnik Metamorphic Complex
OBMC	Orlica-Bystrzyca Metamorphic Complex
IMC	Izera Metamorphic Complex
RJMC	Rudawy Janowickie Metamorphic Complex
GSGB	Sowie Góry Gneissic Block
KŁMC	Metamorphic Kłodzki Complex
KMC	Metamorfik Kaczawski Complex
BU	Bardo Unit
ISB	Intra-Sudetic Basin
NSB	North Sudetic Basin
SB	Świebodzice Basin
SSM	Strzegom-Sobótka Massif
SM	Strzelin Massif
NKMU	Niemcza-Kamieniec Metamorphic Unit
SOB	Silesian-Opole Basin
ŚLMC	Szczecin-Łódź-Miechów Synclinorium
KPC	Kościerzyna-Puławy Synclinorium
MPA	Mid-Polish Anticlinorium
PS	Peribaltic Syncline

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