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Uranium radioisotopes ^{234}U, ^{235}U and ^{238}U in the environment samples collected near Kowary in the Sudeten Foothills (southwestern Poland)

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Abstract

The paper presents the results of study on the determination of uranium radioisotopes ^{234}U, ^{235}U and ^{238}U in different environmental samples collected near Kowary in the Sudeten Foothills (southwestern Poland). There are uranium mineral deposits in this area, some of which were exploited in the years 1948-63. The aim of the research was to examine the impact of uranium deposits and post-mining waste on the surrounding environment and to identify the mechanism of uranium transfer and potential accumulation in plant organisms. Moreover, due to plans for the development of nuclear energy in Poland, intensive work is underway on the possibility of using the Sudeten uranium deposits for the production of enriched uranium nuclear fuel. The concentration of uranium in the analyzed samples is diverse (by two orders of magnitude). The lowest concentration of uranium occurs in young larch needles from the heap (0.07 ± 0.01 mg/kg), while the highest in rowan leaves at the mining heap (14.8 ± 0.3 mg/kg). This has a direct impact on the activity of ^{238}U, the content of which correlates with the uranium concentration. The radionuclides ^{234}U and ^{238}U in the analyzed samples are not in a state of radioactive equilibrium. A larger disequilibrium concerns the isotopes ^{234}U and ^{238}U (the values of the activity ratio $^{234}U/^{238}U$ are from 0.81 for bracket fungus from a tree at the entrance to the adit to 1.70 for the needles of young larch from the mining heap) and the smaller one the isotopes ^{235}U and ^{238}U. The average value of the activity ratio $^{235}U/^{238}U$ in analyzed samples is about 0.068 ± 0.18 and does not differ significantly from the value of 0.046 typical for natural uranium. Additionally, the $^{235}U/^{238}U$ atomic ratios in the analyzed samples fall within a narrow range, to span to from 0.007257 to 0.00755, and approximate the characteristic value of 0.007255 associated with the natural environment. By contrast, the $^{234}U/^{238}U$ atomic ratios exhibit greater variability, ranging from 0.0000363 to 0.0000784. The study demonstrated that the simultaneous use of alpha spectrometry and mass spectrometry (MS) to determine activity and atomic ratios of uranium isotopes offers immense analytical potential for investigating uranium geochemistry in the natural environment.

1. Introduction

Typical concentration of uranium in rocks is from 0.5 to 4.7 mg/kg (the average value is 2.7 mg/kg). Uranium can be found not only in rocks, but also in soil, water (average of 0.0033 mg/L), plants, animals, and also in human body. However, some types of rocks, e.g. phosphates, black shales, or sandstones, concentrated larger amounts of this element.[1,2] The most important uranium minerals are: pitchblende (60–90% UO_2), uraninite (45–85% UO_2+UO_3) and carnotite [about 45% $K_2(UO_2)_2(VO_4)_2 \cdot 2H_2O$]. Uranium does not occur in nature in a metal, sulfide, arsenide or telluride forms. It is a lipophilic element with a high affinity for oxygen.[3] In geological structures, uranium occurs mainly in two oxidation states: +IV and + VI. Uranium compounds in the + III and + V states may occur in nature as intermediate stages of their formation in the U^{4+} and U^{6+} as oxidation states, but their stable forms can only be obtained in laboratory conditions. Both forms of uranium + IV and + VI are strongly adsorbed by many inorganic and organic compounds.[4] This is due to their large size and high charge density. The mechanism of adsorption of

uranium by oxygen particles is not very well understood.[5] Under reducing conditions, uranium has very low mobility, of the order of a few centimeters, even when uranium U^{4+} ions are stabilized with a chloride and fluoride ion. However, if oxidizing conditions are sufficient to produce the uranyl ion UO_2^{2+} and its complexes, then (in the form of an aqueous solution) it may migrate many kilometers from the original host rock to a place where reduction conditions will cause it to recrystallized. Then the uranyl ion can be reduced to produce e.g. uraninite, coffinite $U[(SiO_4)(OH)_4]$ or brannerite $[(U, Ca, Th, Y)(Ti,Fe)_2O_6]$. The uranyl ion in solution may also encounter conditions in which, due to the evaporation of a large part of the water, minerals that contain the oxidized form of uranium VI.[3,5,6] will be formed. In rocks with a high content of organic compounds, uranium may be combined with organic matter in the form of organometallic compounds or as a substituted ion in the carboxyl groups of humic acids.[3,4]

a) Uranium mineral deposits and its resources in Poland.

Mineral deposits with high uranium content are not always of the greatest economic importance. There are 13 basic uranium-bearing deposits in the world, which differ in rock mineralogy.[2,7,8] Due to the uranium content, its ores can be divided into:

- - very rich, where the U content is above 15% by weight,
- - rich, 1–15% U,
- - medium quality, 0.1-1% U,
- - poor, 0.01–0.1% U,
- - very poor, 0.001–0.01% U.

The first mention of occurring of uranium in Poland appeared in the description of Stanisław Staszic in 1815. In the 1920s, uranium deposits in Kowary were exploited, mainly because of the radium they contained.[9] Uranium in the Sudeten Foothills area occurs mainly in vein-type deposits on the Karkonosze Mountains granite base. In the years 1948-63, a total of almost 700 ton of uranium were extracted from the Sudeten Mountains deposits, the most in Radoniów (about 345 tons), then Pogórze and Wolność in Kowary (about 300 tons), and Kopaliny in Kladno (about 30 tons) and Miedzianka (about 20 tons). Most of this uranium was exported to the Soviet Union, where it was used in military programs and arms race. The post-mining waste in Kowary and Radoniów still have a relatively high uranium content (from 300 to 800 mg/kg), hence the interest in them as potential sources of uranium for the development of nuclear energy. On the other hand, the presence of uranium deposits and heaps creates opportunities to conduct research on their impact on the surrounding ecosystems and possible transfer od uranium and its concentration in endemic plants. Intensive study in the area of Poland in the 1980s and 1990s led to the discovery of uranium mineralization in variegated sandstone formations in the Fore-Sudetic Monocline and the Low and Middle Triassic sediments in the Peribaltic Syneclise and in the Ordovician Dictyonema Shales of the Podlasie Depression, as well as in the copper-bearing shales of the Legnica district.[9,10] The uranium deposits in Poland are located in several large areas, The primary examples are: Sudetic minaral deposits (around Kowary, Radoniów, Wambierzyce, Okrzeszyn and Grzmiące), the Oligocene Mennilite

Shales of the Carpathians (in the Bezmichowa-Monastery area), the Holy Cross Mountains (Staszic pyrite deposit in Rudki), in Podlasie (Rajsk) and in Warmia (in the area between Krynica Morska and Pasłęk). The uranium content in uranium ore in Polish mineral deposits ranges from 250 to 1100 mg/kg of rock. Additional unconventional uranium resources are also found in our country in copper deposits, waste from the production of artificial fertilizers and in hard coal. The uranium content in Polish coals is only 1–9 mg/kg, while the uranium content in copper ore is approximately 60 mg/kg of rock (from 13 to 360 mg/kg), with a Cu content of about 2%. The total ore resources are 2,400 million tons, including 48 million tons of copper and 144 thousand tons of uranium.[11] The International Atomic Energy Agency estimates that Poland has a total of approximately 100,000 tons of natural uranium (so-called forecasted resources):[9,12]

b) Uranium radioisotopes in the natural environment

Natural uranium consists of three alpha radioisotopes with the following composition: ^{238}U (99.2745%), ^{235}U (0.7200%) and ^{234}U (0.0055%). In nature, isotopes ^{234}U and ^{238}U are not in a state of radioactive equilibrium, which means that the activities of both isotopes are not equal. Greater imbalance occurs in the aquatic environment than in soils and bottom sediments. There are many scientific hypotheses about the fractionation of radioactive decay products of ^{238}U, which assume the possibility of gradual oxidation of $^{234}Th(VI)$ to $^{234}U(VI)$ during radioactive decay. Moreover, the energy of the radioactive decay of ^{238}U is sufficient not only to break the chemical bond, but also to deprive the ^{234}U atoms of two electrons. Generally, there are three main causes of radioactive disequilibrium.[13,14,15,16,17,18]

- - differences in the chemical properties of the decay products (mainly thorium ^{234}Th and protactinium ^{234}Pa),
- - the recoil of an alpha particle from the crystal lattice, which makes it easier for the ^{234}U isotope to pass into water.
- - isotopes created as a result of the decay of their parent predecessors in the radioactive series assume an oxidation state that is dictated by the redox potential (Eh) of the surrounding environment. This energy allows the ^{234}Th or ^{234}U isotope to pass from the places occupied in the crystallographic lattice by the atoms of the initial ^{238}U isotope to the grains and intergranular gaps.

In natural waters (seas and oceans), an excess of activity of the ^{234}U isotope is usually observed in relation to ^{238}U. For example, the activity ratio of $^{234}U/^{238}U$ in the water of the Baltic Sea is 1.17, and in the water of the Atlantic Ocean it reaches the value of 1.14, while in the bottom sediments of both water areas it oscillates around 1.00 (from 0.83 to 1.28). Also in basalts and marine concretions, the values of this quotient are approximately 1.00 (from 0.70 to 1.36). In sea and ocean water, uranium concentration increases with salinity. For ocean waters, this relationship is described by the equation: $U(mg/m^3) = (0.0934 \pm 0.056) \cdot S$ (where S is salinity in ‰ or PSU), while in the Baltic water the uranium concentration

increases according to the relationship: U(mg/m^3) = 0.10·S ± 0.11. However, the value of the activity ratio $^{234}U/^{238}U$ in marine waters, decreases with salinity.[19,20]

In turn, in river and lake waters, even higher values of the activity ratio $^{234}U/^{238}U$ are recorded, ranging from 1.20 to 1.50.[20,21,22] In the aquatic environment, uranium occurs in two oxidation states: U(IV) and U(VI). Compounds in which + 4 occurs in the reduced form are slightly soluble, while compounds in which it occurs at the + 6 oxidation stage are easily soluble because it occurs in the form of soluble anionic carbonate complexes: $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_2]^{2-}$, which do not sorb on suspensions, but accumulate in plants, because it has a tendency to accumulate organic matter.[23,24,25]

Much greater radioactive disequilibrium, between uranium isotopes was found in groundwater and brine water, where the values of the $^{234}U/^{238}U$ activity ratio range from 0.52 to 9.02 and from 1.11 to 5.14, respectively. In general, it can be said that the radioactive imbalance in the natural environment between uranium isotopes depends on many factors, among which the most important is the redox potential (Eh).[16,17,20]

c) Uranium $^{235}U/^{238}U$ atomic ratio in environment

The uranium isotopes ^{235}U and ^{238}U differ significantly in their half-lives, which are $7.038 \cdot 10^8$ and $4.468 \cdot 10^9$ years, respectively. This means that the $^{235}U/^{238}U$ atomic ratio also changes over time. Currently, it is 0.00725, while during the operation of the natural nuclear reactor in Oklo (Gabon, approximately 1.8 billion years ago), it was much higher at 0.0368. At that time, a slow chain reaction of fission of the uranium ^{235}U nucleus began in uranium-rich ore deposits that were flooded with water (as a moderator). As the reaction intensified, the temperature increased, causing the water to evaporate and the reaction to slow down. As the temperature dropped, the water returned to the reactor, and the reaction increased again until the water evaporated again. Samples from Oklo showed a deficiency of ^{235}U in the magnesite uranate, with ^{235}U contents of 0.440%, 0.592%, and 0.625%, respectively. Samples with very high uranium content (approximately 46%) showed the presence of elements with masses of 80–105 and 130–150, which correspond to two peaks in the ^{235}U fission yield. The natural nuclear reactor at Oklo operated for between 100,000 and 500,000 years until the ^{235}U content in the uranium ore dropped below 3.5%.[26,27]

2. Materials and methods

Environmental samples (rocks, uranium mine waste, soils, plants) were collected in 2023 near the former uranium mine near Kowary in the Sudetes Foothills (southwestern Poland, Fig. 1). The radioanalytical methods for the determination of uranium are based on mineralization and sequential separation and purification of the uranium on anion exchange resin. Before analysis, samples were added ^{232}U as an recovery internal tracers. After mineralization the solution was evaporated and dissolved in 8 M nitric acid and the solution passed through anion exchange resin (Dowex 1x8) column. The uranium adsorbed

on the resin was eluted using 0,5 M nitric acid and solution was evaporated to dryness. The residue was dissolved in 5 mL 1 M $(NH_4)_2SO_4$ (pH = 1,5) and uranium fraction was purified (from iron, cobalt and copper) on a column containing Dowex 1x8 in the sulphate form. Uranium after desorption and elution from column was electroplated on a polished stainless steel disc.[20,28,29]

The activities of ^{234}U, ^{235}U and ^{238}U radionuclides in analysis samples were measured using alpha spectrometry equipped in a surface barrier PIPS (passivated implanted planar silicon) detector with active surface of 300 mm^2 (Canberra-Packard, Ortec). The radiochemical method of the analysis of polonium and uranium samples ensures high recovery (between 85–97%). Analytical quality control of the entire radiochemical procedure was regularly performed through participation in IAEA intercomparison exercises and using CRM (certified reference materials, SD-N1/2, SD-A-1, IAEA-327, IAEA-384, IAEA-414). In addition, the radioanalytical process was validated. Precision and accuracy of radiochemical determination of uranium isotopes were satisfactory (precision error less than 3% and accuracy error less than 2.4%) and measurement uncertainty was approximately 4%. The values of the limit of detection (L_d), limit of concentration (L_c) and minimum detectable activity (MDA) were determined from blank samples according to procedure presented by Hurtgen et al.[30] as a modification of the Currie method.[31] For the analyzed uranium isotopes the average obtained MDA values were as follows: 0,15 mBq/g for ^{234}U, 0,10 mBq/g for ^{235}U and 0,12 mBq/g for ^{238}U.

The atomic ratios of $^{235}U/^{238}U$ and $^{234}U/^{238}U$ were determined employing an Agilent 8900#100 ICP-MS/MS instrument (Agilent Technologies). Prior to analysis, a dry-mass aliquot of mineral and organic samples, ranging from 0.5 to 1 g, was incinerated at 600°C within a muffle furnace. Subsequently, total digestion was performed using the M6 microwave digestion system (PreeKem) to convert the solid material into a clear liquid by heating at 200°C with a mixture of 40% HF, 70% HNO_3, 36% HCl, and 30% H_2O_2.[32] The resultant solution was transferred to a plastic Falcon vial, diluted with ultrapure water to 40 mL, and centrifuged at 4000 rpm for 10 min. For isotopic analysis of ^{234}U, ^{235}U, and ^{238}U via ICP-MS/MS, 1.5 mL of the sample, solution was pipetted into a plastic Falcon vial (total volume 15 mL), spiked with 50 µL of internal standards In and Re (each at 0.5 µg/g; CPAChem), and further diluted to 9 mL with ultrapure water to produce a mixture of 4% HNO_3 and 0.75% HCl.

The first measurement sequence acquired ^{235}U and ^{238}U in tandem (MS/MS) scan mode and kinetic energy discrimination (KED) mode with He as the collision gas within the collision/reaction cell (CRC). During the second sequence, the mass spectrometer was integrated with an APEX 2IR desolvation nebulizer (Elemental Scientific Inc.) to enhance the instrument's sensitivity (up to 20x). For quantification of ^{234}U and ^{235}U, tandem (MS/MS) scan mode was employed alongside a mass-shift mode (m/z + 32), where O_2 served as the reaction gas in the CRC. The $^{234}U/^{238}U$ atom ratio was determined indirectly by multiplying the measured $^{234}U/^{235}U$ and $^{235}U/^{238}U$ values. External mass bias correction was performed using the exponential law,[33] based on repeated measurements of the IRMM-074/6 ($^{235}U/^{238}U$ = 1.000259 ± 0.000015, k = 2) and IRMM-3636b ($^{233}U/^{236}U$ = 1.01906 ± 0.00016, k = 2) certified standards

(EC JRC). Method validation used the certified reference material IRMM-3020a (EC JRC), with atom ratios of $^{235}U/^{238}U = 0.254264 \pm 0.000041$ and $^{234}U/^{238}U = 0.000004931 \pm 0.000000035$ (k = 2). The obtained results aligned with the certified values.[32] Detection limits, calculated as three times the standard deviation (3×SD) of procedural blanks, were as follows: 0.4 pg/g for ^{238}U, 0.04 pg/g for ^{235}U, and 0.003 pg/g for ^{234}U.

3. Results and discussion

The results of the determination of uranium isotopes ^{234}U, ^{235}U, ^{238}U, as well as activity ratios: $^{234}U/^{238}U$ and $^{235}U/^{238}U$ in the analyzed samples from the Kowary area are presented in Table 1.

Table 1
Uranium content (mg/kg) and radioactivity of its radionuclides (mBq/g) as well as values of activity ratios $^{234}U/^{238}U$ and $^{235}U/^{238}U$ in samples from the Kowary area

Sample	**^{234}U [mBq/g]**	**^{235}U [mBq/g]**	**^{238}U [mBq/g]**	**$^{234}U/^{238}U$ Activity ratio**	**$^{235}U/^{238}U$ activity ratio**	**Uranium [mg/kg]**
Leaves from the young European rowan tree on the heap	173.2 ± 3.7	7.50 ± 0.66	181.1 ± 3.6	0.96 ± 0.02	0.041 ± 0.005	14.8 ± 0.3
Bracket fungus from a tree at the entrance to the adit	3.85 ± 0.50	0.31 ± 0.01	4.79 ± 0.36	0.81 ± 0.12	0.065 ± 0.016	0.39 ± 0.03
Plant growing at the entrance to the adit	2.34 ± 0.15	0.12 ± 0.04	1.57 ± 0.12	1.49 ± 0.13	0.076 ± 0.017	0.13 ± 0.01
Plant growing near Jelenia Struga	3.98 ± 0.21	0.25 ± 0.08	2.70 ± 0.17	1.47 ± 0.11	0.092 ± 0.020	0.22 ± 0.03
Field buttercup plant near Jelenia Struga	11.54 ± 0.37	0.22 ± 0.04	9.24 ± 0.30	1.25 ± 0.05	0.043 ± 0.015	0.75 ± 0.03
Young larch from the heap - needles	1.49 ± 0,05	0.03 ± 0,01	0.88 ± 0.04	1.70 ± 0.08	0.039 ± 0.010	0.07 ± 0.01
Young larch from the heap – stem and trunk	1.68 ± 0.08	0.14 ± 0.02	1.61 ± 0.07	1.04 ± 0.05	0.087 ± 0.020	0.13 ± 0.02

Uranium concentration was calculated on the basis of the activity of its isotope ^{238}U using the conversion factor: activity of 1 Bq ^{238}U = 81,6 µg uranium.[19]

Among the analyzed samples, the lowest uranium concentration are in plant growing at the entrance to the needles of a young larch growing on a heap 0.07 ± 0.01 mg/kg, while the highest in rowan leaves at the heap 14.8 ± 0.3 mg/kg. Large amounts of uranium contained in rowan leaves come mainly from the

post-mining uranium deposits. The uranium contents in the tree bracket fungus as well as in the plants growing near the tunnel and near the stream differ slightly. This has a direct impact on the activity of ^{238}U, the content of which correlates with the concentration of elemental uranium. The radionuclides ^{234}U and ^{238}U in the analyzed samples are not in a state of radioactive equilibrium. A larger disequilibrium concerns the isotopes ^{234}U and ^{238}U (the values of the $^{234}U/^{238}U$ activity ratio are from 0.81 ± 0.12 for bracket fungus from a tree at the entrance to the uranium mine adit to 1.70 ± 0.08 for needles of young larch from the mining heap. The average value of the activity ratio $^{235}U/^{238}U$ in analyzed samples is about 0.068 ± 0.018 and does not differ significantly from the value of 0.046, typical for natural uranium. In turn, the results of the $^{235}U/^{238}U$ activity ratio measurements obtained using a mass spectrometer (MS) show less variation than those obtained using an alpha spectrometer and fall within a narrow range of values from 0.0460 ± 0.0001 to 0.0479 ± 0.0002 (Table 2).

The values of $^{234}U/^{238}U$ activity ratios are typical for the values occurring in rock and soil and indicated the process of uranium isotopic fractionation in the analyzed samples occurs to a small extent.[20] The highest uranium concentration in rowan leaves *Sorbus aucuparia L*. at the heap samples indicated that they may be a potential source of technological uranium for industrial purposes and nuclear energy. The results of uranium isotope determinations in the needles, stem, and trunk of a young larch tree growing on the heap are interesting. Differences in the values of $^{234}U/^{238}U$ activity ratio indicate that the uranium in the larch needles comes from rainfall (values 1.70 ± 0.08 is typical for rainwater and surface water), while the uranium in the larch stem and trunk is transported from the heap floor (values 1.04 ± 0,05 are typical for soil). In turn, the values of $^{234}U/^{238}U$ activity ratio in the analyzed samples, measured using a mass spectrometer (MS), show greater variation, ranging from 0.66 ± 0.05 to 1.42 ± 0.10 (Table 2). Both the lowest and highest values of this ratio were determined in rock samples collected at the entrance to the uranium mine and from the surface of the heap. It is difficult to state conclusively why such significant differences in the values of $^{234}U/^{238}U$ activity ratio are observed within the same type of samples; however, the surface of the waste pile is continuously exposed to atmospheric factors, including rainfall, which contribute to an increase in ^{234}U activity relative to ^{238}U.

The results of the $^{235}U/^{238}U$ and $^{234}U/^{238}U$ atomic ratios in the examined materials, as determined by mass spectrometry (MS) were presented in Table 2. The values of $^{235}U/^{238}U$ atomic ratio in analyzed samples fall within a narrow range, spanning from 0.007257 to 0.00755, and approximate the characteristic value of 0.007255 associated with the natural environment.[35] The highest value of this ratio was measured in a rock sample collected from the surface of the waste. At the same time the $^{234}U/^{238}U$ atomic ratio findings exhibit greater variability, ranging from 0.0000363 to 0.0000784.

Table 2

Uranium atomic and activity ratios of $^{235}U/^{238}U$ and $^{234}U/^{238}U$ in samples from the Kowary area. The values of activity ratios are calculated from the measured atomic ratios by mass spectrometry (MS)

Sample	$^{235}U/^{238}U$ atomic ratio	$^{235}U/^{238}U$ activity ratio	$^{234}U/^{238}U$ atomic ratio	$^{234}U/^{238}U$ activity ratio
Bilberry	0.007257 ± 0.000021	0.0460 ± 0.0001	0.0000556 ± 0.0000024	1.01 ± 0.04
Broom fork-moss from heap	0.007272 ± 0.000041	0.0461 ± 0.0003	0.0000635 ± 0.0000010	1.15 ± 0.02
Grooved shield lichen	0.007266 ± 0.000061	0.0461 ± 0.0004	0.0000631 ± 0.0000019	1.15 ± 0.03
Leaves from the young European rowan tree	0.007283 ± 0.000054	0.0462 ± 0.0003	0.0000557 ± 0.0000021	1.01 ± 0.04
Stinging nettle	0.007267 ± 0.000039	0.0461 ± 0.0002	0.0000573 ± 0.0000030	1.04 ± 0.06
Soil from under nettles	0.007400 ± 0.000045	0.0469 ± 0.0003	0.0000618 ± 0.0000030	1.12 ± 0.06
Soil (bottom layer)	0.007325 ± 0.000032	0.0464 ± 0.0002	0.0000620 ± 0.0000027	1.13 ± 0.05
Soil from under plant	0.007309 ± 0.000025	0.0463 ± 0.0002	0.0000565 ± 0.0000023	1.03 ± 0.04
Rock from the heap	0.007550 ± 0.000031	0.0479 ± 0.0002	0.0000784 ± 0.0000057	1.42 ± 0.10
Rock from the mine entrance	0.007267 ± 0.000029	0.0461 ± 0.0002	0.0000363 ± 0.0000025	0.66 ± 0.05

The occurrence of uranium and its radioisotope content has been fairly well studied in Poland and the ecosystem of the southern Baltic Sea. Typical concentrations of this element in soils and Baltic bottom sediments range from 2 to 12 mg/kg. Both uranium isotopes, ^{234}U and ^{238}U, are in relative radioactive equilibrium in soils and sediments.[19] Regardless of geographic variation, diffusion of uranium from bottom sediments into water via pore water and diagenetic changes in the sedimentary material is observed throughout the southern Baltic Sea. Similarly, in river sediments, uranium can diffuse into water and flow downstream into the Baltic Sea. In the examined waters of the Vistula and Oder river basins, we observe a significant predominance of the ^{234}U isotope over ^{238}U, and the activity ratio values range from 1.20 to 1.60. Uranium concentrations in Polish river waters range from 3.83 Bq/m^3 (0.32 mg/m^3) to 11.50 Bq/m^3 (0.93 mg/m^3), with the exception of the Bystrzyca river basin (the Sudeten Foothills), where its content is much higher and averages 68.24 Bq/m^3 (5.57 mg/m^3). Very high uranium contents in the Bystrzyca river basin are the result of natural weathering and erosion processes of the Sudeten rocks,

which contain elevated contents of this element, as well as human activity related to the mining and processing of uranium ores and quarries.[20]

The results of uranium content obtained in samples collected from the Kowary area indicate that they do not differ significantly from those found in soils and bottom sediments, while the values of the $^{234}U/^{238}U$ activity ratio oscillating around 1.0 indicate the terrigenous origin of this element in the tested samples.

4. Conclusions

The lowest uranium concentration, i.e. 0.07 ± 0.01 mg/kg, occurs in the needles of a young larch growing on a heap, while the highest in rowan leaves *Sorbus aucuparia L*. at the post-mining uranium heap 14.8 ± 0.3 mg/kg. This has a direct impact on the activity of ^{238}U, the content of which correlates with the concentration of elemental uranium. The radionuclides ^{234}U and ^{238}U in the analyzed samples are not in a state of radioactive equilibrium. The values of the activity ratio $^{234}U/^{238}U$ are of larger disequilibrium. They range from 0.81 ± 0.12 for bracket fungus from a tree at the entrance to the uranium mine adit to 1.70 ± 0.08 for needles of young larch from the mining heap. The average value of the activity ratio $^{235}U/^{238}U$ in analyzed samples is about 0.068 and does not differ significantly from the value of 0.046 typical for natural uranium. In turn, the results of the $^{235}U/^{238}U$ activity ratio measurements obtained using a mass spectrometer (MS) show less variation than those obtained using an alpha spectrometer and fall within a narrow range of values from 0.0460 ± 0.0001 to 0.0479 ± 0.0002. The values of $^{235}U/^{238}U$ atomic ratio in analyzed samples fall within a narrow range, spanning from 0.007257 to 0.00755, and approximate the characteristic value of 0.007255 associated with the natural environment. The highest value of this ratio was measured in a rock sample collected from the surface of the waste. At the same time the $^{234}U/^{238}U$ atomic ratio findings exhibit greater variability, ranging from 0.0000363 to 0.0000784. The highest uranium concentration in the samples collected around the post-mining uranium area indicated that the heap in Kowary may be a potential source of technological uranium for industrial purposes and nuclear energy in Poland.

The study demonstrated that the simultaneous use of alpha spectrometry and mass spectrometry (MS) to determine activity and atomic ratios of uranium isotopes offers immense analytical potential for investigating uranium geochemistry in the natural environment.

Declarations

Author Contribution

K.L.B. conceived the study concept and design, coordinated the research, supervised the project, performed data interpretation, and served as the corresponding author. B.S. drafted the original manuscript. A.B. contributed to field sampling, laboratory analyses, and data interpretation. B.S. participated in laboratory measurements, validation of analytical methods, and interpretation of results.

A.C. contributed to sample preparation, data analysis, and critical revision of the manuscript. E.Ł. and B.S. contributed to the interpretation of results, critically reviewed and edited the manuscript, and provided scientific supervision. All authors discussed the results, contributed to the final version of the manuscript, and approved the submitted version.

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Figures

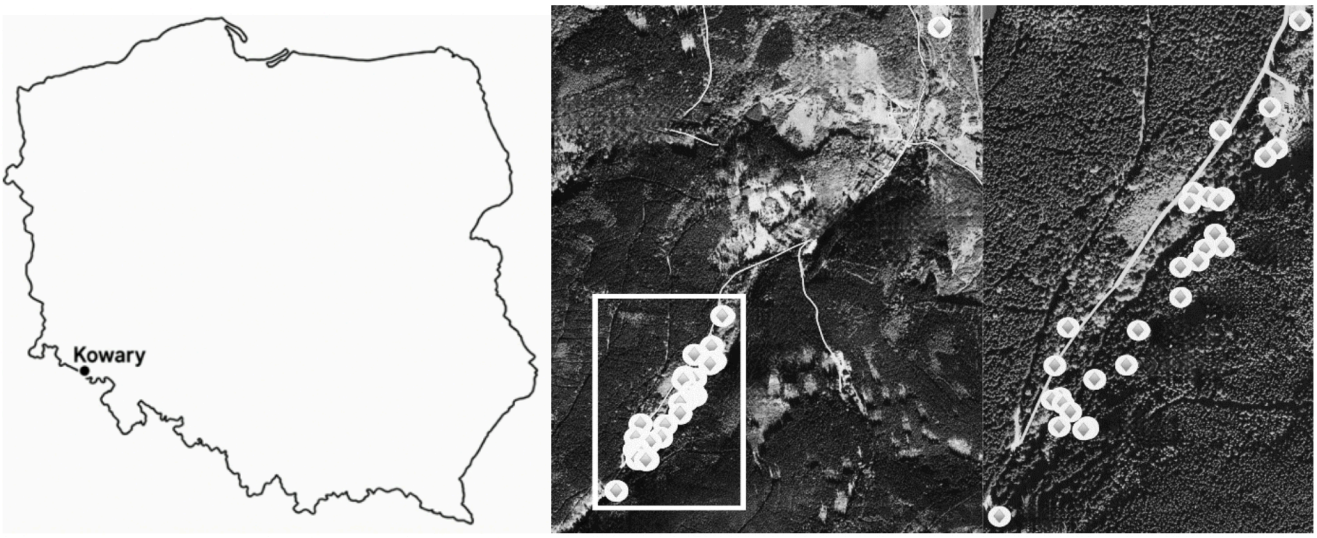


Figure 1

Sample collection locations in the Sudetes Foothills (southwestern Poland)