NUKLEONIKA 2004;49(2):69–76

ORIGINAL PAPER

Uranium isotopes in waters and bottom sediments of rivers and lakes in Poland

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Abstract Activity concentrations of ^{238}U, ^{234}U and ^{235}U were determined in waters and bottom sediments in two main rivers in Poland (the Vistula and Odra rivers) with their tributaries, in four coastal rivers and in six lakes. Concentrations of ^{238}U and ^{234}U were compared with the concentrations of ^{226}Ra determined in another study. As compared with concentrations in coastal rivers and in lakes, enhanced concentrations of the radionuclides were observed in water and bottom sediments in the upper and middle courses of the Vistula river, whereas in the Odra river the enhanced concentrations were present only in the bottom sediments. The enhanced concentrations in the Vistula river result from the discharge of coal mine waters from the Upper Silesian Coal Basin, and they indicate that the discharge was continued. The enhanced concentrations in the Odra river observed only in bottom sediments indicate that the discharge occurred in the past. The $^{234}U/^{238}U$ ratio for the bottom sediments was close to unity, indicating that these isotopes were close to equilibrium, whereas for water the average ratio was from 1.2 for lakes to 1.5 for the Vistula river, demonstrating the lack of equilibrium.

Key words activity concentrations • ^{238}U • ^{234}U • water • bottom sediments

Introduction

Three isotopes of uranium exist in nature: ^{238}U with half-life ($T_{1/2}$) of 4.468×10^9 y, ^{234}U ($T_{1/2} - 2.455 \times 10^5$ y) and ^{235}U ($T_{1/2} - 7.038 \times 10^8$ y). Natural uranium contains 99.2745% ^{238}U, 0.0055% ^{234}U and 0.72% ^{235}U [3]. The mass ratio of natural uranium ^{235}U to ^{238}U is about 0.0073 and the activity ratio is 0.046. Many studies on ^{238}U and ^{234}U in natural waters indicate that these isotopes occur in disequilibrium state and that, with a few exceptions, waters contain more ^{234}U than ^{238}U [2, 5, 11–14]. Higher activity of ^{234}U in waters is the result of the ^{234}U atom displacement from the crystal lattice. The recoil atom ^{234}U is liable to be oxidized to the hexavalent stage and can be leached into the water phase more easily than its parent nuclide ^{238}U. The oxidation of U(IV) to U(VI) is an important step in leaching into water, because compounds of U(VI) have a higher solubility in water [4, 5, 11, 16].

The natural level of uranium in water can be enhanced due to human activity which moves naturally occurring radionuclides from inaccessible locations to the environment. In Poland, the enhanced concentration of natural radionuclides occurs in the river Vistula and its tributaries as a result of the discharge of mine waters from the central and eastern part of the Upper Silesian Coal Basin. Mean ^{226}Ra concentrations in discharged water ranged from 0.7 to 28.2 Bq L^{-1} [6]. As a result, the concentrations are enhanced in river waters and in bottom sediments [18, 19]. It can be expected that also uranium isotopes are discharged into surface waters.

Another source of the enhanced level of natural radionuclides in water can be the use of phosphate fertilizers in

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Received: 9 January 2004, Accepted: 14 April 2004

agriculture. The phosphate fertilizers contain uranium which can be leached by moving water from the drainage area to rivers and lakes [17].

The purpose of this study was to determine the concentration of uranium isotopes in waters and in bottom sediments in two main rivers in Poland (the Vistula and Odra rivers) with their tributaries, in four coastal rivers and six lakes. These data were used to determine the influence of the coal mine water discharges on the level of uranium isotopes in the Vistula river, and to estimate the flow of ^{238}U and ^{234}U from the Vistula and Odra rivers catchments to the Baltic Sea. The activities of the uranium isotopes were related to ^{226}Ra.

Materials and methods

Sampling

Samples of water and bottom sediments were collected from two main rivers of Poland: the Vistula river with the tributaries of Bug and Narew, and the Odra river with the tributaries of Nysa Łużycka and Warta. Sampling points were localized in the upper, middle and lower courses of Vistula and Odra. Water and bottom sediments were also collected from four small rivers debouching directly to the Baltic Sea, and from six lakes localized in main lake districts of the country. Samples were gathered in 1999 and 2000. Locations of the sampling points are given in Fig. 1.

Water (10 L) from the rivers was taken from the main streams, whereas water from the lakes was taken from platforms. In the laboratory water samples were filtered through a Whatman No. 42 filter paper, of particle retention 2.5 μm. Bottom sediments were collected from stream beds near the shore line using the Van Veen type sampler. At each location three sub-samples were taken at points 30 m to 50 m apart, to form an averaged sample. The total mass of such a sample was approximately 2 kg (wet weight); it was composed of about equal parts from each point of sampling.

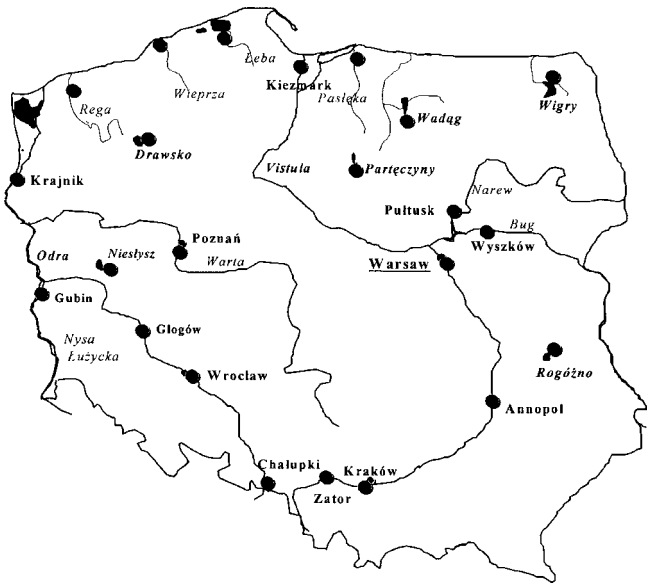

Fig. 1. Sampling locations for water and bottom sediments.

Analytical methods

Uranium isotopes were determined separately in the filtered water, the suspended matter retained on the filter paper and in bottom sediments. Determinations were performed in 5 L of water and in 2 g samples of the bottom sediments. ^{232}U was used as an internal tracer for counting of alpha activity and chemical recovery. To the samples of water ^{232}U tracer and concentrated HNO_3 were added, then the samples were evaporated to dryness. To the residue, 8 M HNO_3 was added and heated until the residue was dissolved. Suspended matter was dried, ^{232}U tracer was added, suspension with filter was incinerated and the remainder was dissolved in 8 M HNO_3. Samples of the bottom sediments were dried in air, sieved through a 2 mm mesh to remove the roots of plants and stones and then dried at 105°C. The 2 g dry samples were placed in a muffle furnace and ignited at 450°C until the organic matter was ashed, then transferred to a PTFE beaker. ^{232}U tracer was added and silica was removed by digestion with HNO_3 and HF. Finally, the residue was dissolved in 8 M HNO_3.

The following step of the analysis was the same for waters, suspended matters and bottom sediments. The 8 M HNO_3 solutions were passed through an anion exchange column (Dowex 1 × 8, 50–100 mesh) converted to the nitric form. The eluate was evaporated to dryness and the residue was dissolved in a solution of $Al(NO_3)$ in nitric acid and transferred to a separatory funnel to which TBT in kerosene was added. Uranium was extracted to the organic phase and then reextracted to water. The aqueous phase was evaporated to dryness and the residue was dissolved in sulphuric acid. Uranium was electrodeposited on a stainless steel disc of 17 mm in diameter at a current of 1 A for 1.5 h. Details of the analytical procedure were described elsewhere [10]. Activity of the deposited uranium was measured by an alpha spectrometry system. PIPS detectors for alpha spectrometry placed in a vacuum chamber were connected with a multichannel analyzer Multiport II MCA (Canberra MP2-GE) with GENIE 2000 spectroscopy software.

Average uranium tracer recovery was approx. 77%, lower limit of detection (LLD) with the counting time of 82.000 s was equal to 0.22 mBq/sample for ^{234}U and 0.29 mBq/sample for ^{238}U and ^{235}U. The reliability of the applied method was checked in Proficiency Test organized by the IAEA in 2003; the reference water samples designated with codes IAEA-421, IAEA-423 and IAEA-431 were analysed. For these samples, the average relative bias between our values and the IAEA values was 6.5% for ^{238}U, 2.7% for ^{234}U and the average precision was about 4.5%.

Results

Activity concentration of uranium in the filtered water fluctuated depending on the sampling point and year. Activity concentrations of ^{234}U, ^{235}U and ^{238}U in the Vistula river and its tributaries, and in the Odra river with tributaries are given in Table 1. Activity concentrations of ^{234}U ranged from 3.47 ± 0.27 mBq L^{-1} in the Warta river (Poznań) up to 21.7 ± 1.59 mBq L^{-1} in Vistula at Zator, whereas concentrations of ^{238}U ranged from 3.05 ± 0.24 mBq L^{-1} in Warta to 13.1 ± 0.75 mBq L^{-1} in Bug at Wyszków. The

Table 1. Activity concentrations of ^{234}U, ^{235}U and ^{238}U in filtered water and suspended matter of Vistula and 2 tributaries, and Odra and 2 tributaries in 1999 and 2000 (mBq L^{-1}).

River	Sampling location	^{234}U		^{235}U		^{238}U	
		water	suspended matter	water	suspended matter	water	suspended matter
				1999			
Vistula	Zator	18.7 ± 1.24[a)]	1.19 ± 0.10	0.28 ± 0.05	<0.06	9.34 ± 0.66	0.75 ± 0.07
	Kraków	13.6 ± 0.92	0.94 ± 0.08	0.46 ± 0.09	<0.06	7.16 ± 0.51	0.53 ± 0.05
	Annopol	9.42 ± 0.68	0.45 ± 0.09	0.26 ± 0.05	<0.06	6.72 ± 0.51	1.07 ± 0.07
	Warszawa	10.9 ± 0.76	1.08 ± 0.12	0.30 ± 0.04	<0.06	7.57 ± 0.54	0.92 ± 0.09
	Kiezmark	15.3 ± 1.06	2.20 ± 0.18	0.49 ± 0.08	0.10 ± 0.02	11.5 ± 0.81	1.98 ± 0.16
Bug	Wyszków	9.38 ± 0.25	2.98 ± 0.25	0.28 ± 0.05	0.07 ± 0.02	6.77 ± 0.50	2.33 ± 0.20
Narew	Pułtusk	8.61 ± 0.61	1.52 ± 0.12	0.33 ± 0.06	<0.06	7.12 ± 0.52	1.37 ± 0.11
Odra	Chałupki	5.79 ± 0.30	0.30 ± 0.03	0.14 ± 0.02	<0.06	3.79 ± 0.21	0.23 ± 0.03
	Wrocław	6.93 ± 0.50	2.28 ± 0.15	0.19 ± 0.04	<0.06	4.51 ± 0.35	1.54 ± 0.11
	Głogów	6.72 ± 0.50	1.45 ± 0.12	0.22 ± 0.05	<0.06	4.58 ± 0.36	1.02 ± 0.09
	Krajnik	12.8 ± 0.82	2.56 ± 0.19	0.44 ± 0.06	0.09 ± 0.02	10.6 ± 0.68	2.32 ± 0.17
Nysa Łużycka	Gubin	4.70 ± 0.40	0.16 ± 0.02	0.20 ± 0.05	<0.06	3.79 ± 0.33	0.17 ± 0.02
Warta	Poznań	15.6 ± 0.95	1.62 ± 0.09	0.39 ± 0.07	<0.06	12.8 ± 0.79	1.15 ± 0.08
				2000			
Vistula	Zator	21.7 ± 1.59	1.57 ± 0.11	0.48 ± 0.07	<0.06	11.1 ± 0.85	0.92 ± 0.07
	Kraków	16.2 ± 1.13	1.84 ± 0.16	0.34 ± 0.06	<0.06	8.64 ± 0.64	1.18 ± 0.11
	Annopol	11.2 ± 0.90	2.41 ± 0.15	0.44 ± 0.08	0.07 ± 0.02	8.04 ± 0.67	2.01 ± 0.12
	Warszawa	10.8 ± 0.80	2.55 ± 0.19	0.33 ± 0.06	0.07 ± 0.02	7.81 ± 0.60	1.90 ± 0.15
	Kiezmark	11.8 ± 0.83	3.11 ± 0.27	0.36 ± 0.07	0.12 ± 0.02	9.43 ± 0.74	2.54 ± 0.22
Bug	Wyszków	16.5 ± 0.93	5.23 ± 0.44	0.54 ± 0.06	0.16 ± 0.03	13.1 ± 0.75	3.97 ± 0.34
Narew	Pułtusk	12.7 ± 0.89	1.80 ± 0.14	0.37 ± 0.06	0.08 ± 0.02	10.3 ± 0.73	1.62 ± 0.12
Odra	Chałupki	8.00 ± 0.41	1.07 ± 0.10	0.20 ± 0.03	0.29 ± 0.04	5.24 ± 0.28	0.81 ± 0.08
	Wrocław	14.2 ± 1.06	3.63 ± 0.25	0.46 ± 0.08	0.09 ± 0.02	9.00 ± 0.70	2.42 ± 0.17
	Głogów	8.56 ± 0.62	2.26 ± 0.17	0.20 ± 0.05	<0.06	6.21 ± 0.46	1.62 ± 0.13
	Krajnik	10.7 ± 0.75	2.43 ± 0.17	0.35 ± 0.06	<0.06	8.85 ± 0.63	1.88 ± 0.14
Nysa Łużycka	Gubin	6.33 ± 0.37	0.78 ± 0.08	0.30 ± 0.04	<0.06	5.14 ± 0.31	0.64 ± 0.06
Warta	Poznań	3.47 ± 0.27	1.73 ± 0.13	0.12 ± 0.03	0.08 ± 0.02	3.05 ± 0.24	1.32 ± 0.11

[a)] Value ± counting error at confidence level of 95%.

range of ^{234}U activity concentrations in coastal rivers was much smaller, being from 4.32 ± 0.27 in Wieprza to 8.66 ± 0.68 mBq L^{-1} in Łeba; for ^{238}U it was from 3.42 ± 0.28 mBq L^{-1} to 7.02 ± 0.56 mBq L^{-1} in the same rivers (Table 2). Among lakes, the lowest values of ^{234}U and ^{238}U activity concentrations in filtered water were observed in Rogóźno, being 1.07 ± 0.13 mBq L^{-1} and 0.77 ± 0.06 mBq L^{-1}, respectively; the highest concentrations were in Wadąg: 10.0 ± 0.55 mBq L^{-1} for ^{234}U and 8.80 ± 0.49 mBq L^{-1} for ^{238}U (Table 3). Uranium in the suspended matter constituted about 18% of that in the filtered water for the rivers and about 40% for the lakes. The different amounts may be due to different contents of the suspended matter in the water samples. The samples from the rivers were collected from bridges over the main streams, whereas the samples from the lakes were collected from platforms, where the water level was closer to the bottom. Therefore, in the latter case the bottom sediments could get more easily into the collected samples.

Activity concentrations of ^{234}U, ^{235}U and ^{238}U in the bottom sediments of rivers and lakes are presented in Tables 4 and 5, respectively. Enhanced contents of uranium were observed in the bottom sediments in the upper Vistula, upper and middle Odra and Nysa Łużycka. The lowest activity concentrations of ^{234}U and ^{238}U in the bottom sediments were found in the mouth of the Vistula river (Kiezmark) and of the Odra river (Krajnik). In sediments of the tributaries (Bug, Narew, Warta), the concentrations of uranium isotopes were similar to that in the mouths of the main rivers, and in the coastal rivers. Activity concentrations of ^{234}U in the bottom sediments of lakes ranged from 2.87 ± 0.22 Bq kg^{-1} dry weight (d.wt.) in Rogóźno to 15.1 ± 0.89 Bq kg^{-1} d.wt. in Wigry; concentrations of ^{238}U ranged in these lakes from 3.05 ± 0.23 Bq kg^{-1} d.wt. to 15.1 ± 0.88 Bq kg^{-1} d.wt.

Activity concentrations of ^{234}U and ^{238}U in the filtered water and in the bottom sediments of rivers and lakes are presented in Fig. 2. The highest activity concentrations in water were found in the Vistula river and its tributaries, whereas the highest concentrations in the bottom sediments were observed in the Odra river with tributaries.

Average values of the activity ratio of ^{234}U to ^{238}U in the filtered water, suspended matter and bottom sediments are given in Table 6. These data show that the largest disequilibrium occurred for the Vistula river with its tributaries (1.50 ± 0.29 in water), a smaller disequilibrium was

Table 2. Activity concentrations of ^{234}U, ^{235}U and ^{238}U in filtered water and suspended matter of coastal rivers in 1999 and 2000 (mBq L^{-1}).

River	Sampling location	^{234}U		^{235}U		^{238}U	
		water	suspended matter	water	suspended matter	water	suspended matter
				1999			
Rega	Trzebiatów	7.42 ± 0.57[a)]	0.51 ± 0.05	0.37 ± 0.07	<0.06	6.98 ± 0.54	0.39 ± 0.04
Wieprza	St. Kraków	4.32 ± 0.27	0.33 ± 0.04	0.12 ± 0.03	<0.06	3.42 ± 0.28	0.28 ± 0.03
Łeba	Cecenowo	8.66 ± 0.68	0.78 ± 0.06	0.32 ± 0.07	<0.06	7.02 ± 0.56	0.64 ± 0.06
Pasłęka	N. Pasłęka	7.68 ± 0.61	0.88 ± 0.08	0.21 ± 0.05	<0.06	6.98 ± 0.56	0.75 ± 0.07
				2000			
Rega	Trzebiatów	8.11 ± 0.58	1.05 ± 0.10	0.31 ± 0.06	<0.06	6.90 ± 0.50	0.88 ± 0.09
Wieprza	St. Kraków	6.20 ± 0.39	1.60 ± 0.16	0.22 ± 0.04	<0.06	4.86 ± 0.32	1.51 ± 0.15
Łeba	Cecenowo	6.63 ± 0.48	0.58 ± 0.06	0.23 ± 0.05	<0.06	5.73 ± 0.42	0.52 ± 0.05
Pasłęka	N. Pasłęka	7.10 ± 0.42	1.56 ± 0.13	0.25 ± 0.04	<0.06	6.48 ± 0.39	1.30 ± 0.11

[a)] Value ± counting error at confidence level of 95%.

observed in the Odra river and its tributaries (1.35 ± 0.16 in water). The activity ratios in the coastal rivers and lakes were similar, being 1.17 ± 0.06 and 1.19 ± 0.14, respectively. In the suspended matter, the $^{234}U/^{238}U$ ratio was similar to that in the filtered water what indicates that uranium in the suspended matter was adsorbed from water. In the bottom sediments, the average $^{234}U/^{238}U$ ratio were close to unity, indicating that these isotopes are closer to the equilibrium than in water and suspended matter. The $^{234}U/^{238}U$ ratio of about unity in the bottom sediments and above unity in water were also reported by Plater *et al*. [11] in the Wash and Fenland drainage basin, UK. The $^{234}U/^{238}U$ ratio over unity in waters can be explained by the preferential solubility of ^{234}U from uranium minerals, and the ratio closer to unity in the bottom sediments can be explained by leaching of ^{234}U from sediments by water.

Annual flow of ^{234}U and ^{238}U to the Baltic Sea was estimated from uranium concentration in water (dissolved and suspended) in the mouth of Vistula (Kiezmark) and Odra (Krajnik). The average flow of water to the Baltic Sea from these rivers in 1999 and 2000 was taken from a publication of Central Statistical Office [1]. The estimated total flow of ^{234}U from the catchments of these rivers was 1.10 TBq in 1999 and 0.88 TBq in 2000; the flow of ^{238}U was 0.84 TBq in 1999 and 0.67 TBq in 2000 (Table 7). The contribution of the Vistula river to the total flow was about

Table 3. Activity concentrations of ^{234}U, ^{235}U and ^{238}U in filtered water and suspended matter of lakes in 1999 and 2000 (mBq L^{-1}).

Lake	^{234}U		^{235}U		^{238}U	
	water	suspended matter	water	suspended matter	water	suspended matter
			1999			
Partęczyny	5.18 ± 0.40[a)]	3.81 ± 0.29	0.15 ± 0.04	0.14 ± 0.03	4.12 ± 0.33	3.33 ± 0.25
Drawsko	2.17 ± 0.21	1.12 ± 0.08	0.06 ± 0.02	0.21 ± 0.03	1.74 ± 0.18	1.03 ± 0.06
Wadąg	8.39 ± 0.64	5.31 ± 0.42	0.30 ± 0.05	0.16 ± 0.03	7.99 ± 0.55	4.69 ± 0.37
Rogóżno	1.19 ± 0.09	0.26 ± 0.03	<0.06	<0.06	0.77 ± 0.06	0.20 ± 0.03
Niesłysz	1.25 ± 0.14	0.21 ± 0.03	<0.06	<0.06	1.10 ± 0.13	0.19 ± 0.02
Wigry	3.05 ± 0.27	0.70 ± 0.05	0.10 ± 0.03	0.09 ± 0.02	2.55 ± 0.23	0.63 ± 0.16
			2000			
Partęczyny	10.8 ± 0.79	2.15 ± 0.18	0.40 ± 0.07	0.08 ± 0.02	10.1 ± 0.74	1.81 ± 0.16
Drawsko	4.55 ± 0.24	2.82 ± 0.18	0.18 ± 0.03	0.11 ± 0.02	4.26 ± 0.23	2.58 ± 0.16
Wadąg	10.0 ± 0.55	2.27 ± 0.19	0.42 ± 0.05	0.27 ± 0.04	8.80 ± 0.49	2.06 ± 0.17
Rogóżno	1.07 ± 0.13	0.40 ± 0.05	<0.06	<0.06	0.93 ± 0.12	0.31 ± 0.04
Niesłysz	3.80 ± 0.28	1.54 ± 0.16	0.12 ± 0.03	<0.06	2.93 ± 0.23	1.29 ± 0.14
Wigry	6.29 ± 0.55	3.70 ± 0.22	0.25 ± 0.05	0.11 ± 0.02	5.77 ± 0.52	3.37 ± 0.20

[a)] Value ± counting error at confidence level of 95%.

Table 4. Activity concentrations of ^{234}U, ^{235}U and ^{238}U in bottom sediments of rivers in 1999 and 2000 (Bq kg^{-1} dry weight).

River	Sampling location	1999			2000		
		^{234}U	^{235}U	^{238}U	^{234}U	^{235}U	^{238}U
Vistula	Zator	31.1 ± 2.44[a)]	1.16 ± 0.21	26.5 ± 2.11	30.1 ± 2.39	0.97 ± 0.07	28.5 ± 2.19
	Kraków	20.7 ± 1.57	0.89 ± 0.17	20.2 ± 1.54	21.5 ± 1.59	0.78 ± 0.14	22.4 ± 1.64
	Annopol	18.1 ± 1.36	0.72 ± 0.14	17.9 ± 1.35	9.26 ± 0.77	0.35 ± 0.10	9.71 ± 0.80
	Warszawa	22.1 ± 1.59	0.65 ± 0.12	20.6 ± 1.49	9.59 ± 0.79	0.35 ± 0.07	9.34 ± 0.77
	Kiezmark	7.73 ± 0.71	0.43 ± 0.11	7.99 ± 0.73	5.97 ± 0.56	0.31 ± 0.09	5.60 ± 0.53
Bug	Wyszków	9.64 ± 0.76	0.31 ± 0.09	9.27 ± 0.73	6.83 ± 0.61	0.26 ± 0.08	7.06 ± 0.63
Narew	Pułtusk	8.32 ± 0.72	0.42 ± 0.13	8.32 ± 0.72	10.2 ± 0.83	0.37 ± 0.08	9.27 ± 0.77
Odra	Chałupki	32.2 ± 2.25	1.50 ± 0.21	34.0 ± 2.37	24.9 ± 2.09	1.21 ± 0.22	24.4 ± 2.04
	Wrocław	46.5 ± 3.77	1.43 ± 0.22	48.0 ± 3.44	24.0 ± 1.52	0.94 ± 0.14	23.0 ± 1.46
	Głogów	24.6 ± 1.92	1.31 ± 0.22	24.0 ± 1.87	10.0 ± 0.83	0.52 ± 0.12	10.8 ± 0.89
	Krajnik	7.39 ± 0.69	0.23 ± 0.08	7.73 ± 0.70	7.06 ± 0.62	0.30 ± 0.09	7.23 ± 0.63
Nysa Łużycka	Gubin	16.6 ± 1.26	0.90 ± 0.16	16.7 ± 1.27	40.2 ± 2.74	1.83 ± 0.24	39.1 ± 2.67
Warta	Poznań	8.27 ± 0.73	0.35 ± 0.09	8.30 ± 0.73	5.81 ± 0.40	0.32 ± 0.07	5.57 ± 0.39
Rega	Trzebiatów	10.3 ± 0.82	0.46 ± 0.09	9.34 ± 0.76	8.56 ± 0.58	0.42 ± 0.08	7.89 ± 0.54
Wieprza	St. Kraków	8.96 ± 0.84	0.35 ± 0.11	7.93 ± 0.76	6.83 ± 0.58	0.31 ± 0.09	6.99 ± 0.59
Łeba	Cecenowo	8.60 ± 0.77	0.33 ± 0.08	7.90 ± 0.72	9.00 ± 0.62	0.40 ± 0.08	9.14 ± 0.62
Pasłęka	N. Pasłęka	12.9 ± 1.05	0.45 ± 0.09	12.4 ± 1.02	12.4 ± 0.94	0.52 ± 0.10	11.8 ± 0.91

[a)] Value ± counting error at confidence level of 95%.

Table 5. Activity concentrations of ^{234}U, ^{235}U and ^{238}U in bottom sediments of lakes in 1999 and 2000 (Bq kg^{-1} dry weight).

Lake	1999			2000		
	^{234}U	^{235}U	^{238}U	^{234}U	^{235}U	^{238}U
Partęczyny	8.60 ± 0.68[a)]	0.35 ± 0.07	8.30 ± 0.66	7.65 ± 0.69	0.33 ± 0.10	7.54 ± 0.68
Drawsko	6.77 ± 0.67	0.32 ± 0.01	7.44 ± 0.72	9.49 ± 0.71	0.38 ± 0.09	9.25 ± 0.70
Wadąg	8.60 ± 0.72	0.32 ± 0.09	8.70 ± 0.72	10.1 ± 0.80	0.53 ± 0.12	9.53 ± 0.76
Rogóźno	2.87 ± 0.22	<0.15	3.05 ± 0.23	4.22 ± 0.46	<0.15	4.48 ± 0.48
Niesłysz	9.47 ± 0.77	0.28 ± 0.08	8.51 ± 0.70	4.87 ± 0.47	0.20 ± 0.07	4.72 ± 0.46
Wigry	15.1 ± 0.89	0.77 ± 0.11	15.1 ± 0.88	8.23 ± 0.69	0.26 ± 0.08	9.05 ± 0.74

[a)] Value ± counting error at confidence level of 95%.

70%. The data on the inflow of uranium isotopes from the Vistula river water to the Baltic Sea are comparable with the data obtained by Skwarzec [13].

The average activity ratio of ^{235}U to ^{238}U for the water samples was equal to 0.042 ± 0.007 and for the bottom sediments 0.043 ± 0.08; these values are close to the value 0.046 for uranium in nature.

In the samples in which analyses of uranium isotopes were performed, ^{226}Ra was also determined in the previous study [18]. The comparison of the activity concentrations of ^{226}Ra (data from [18]) with those of the uranium isotopes (this study) has indicated that ^{226}Ra and ^{238}U in the waters and sediments are not in equilibrium. However, the statistical analysis of the results indicates the occurrence of

Table 6. Activity concentration ratios of $^{234}U/^{238}U$ in filtered water, suspended matter and bottom sediments.

Rivers and lakes	Filtered water (mean ± SD)	Suspended matter (mean ± SD)	Bottom sediment (mean ± SD)
Vistula river and tributaries	1.50 ± 0.29	1.35 ± 0.22	1.03 ± 0.06
Odra river and tributaries	1.35 ± 0.16	1.31 ± 0.16	0.99 ± 0.04
Coastal rivers	1.17 ± 0.06	1.22 ± 0.06	1.06 ± 0.05
Lakes	1.19 ± 0.14	1.15 ± 0.07	1.00 ± 0.06

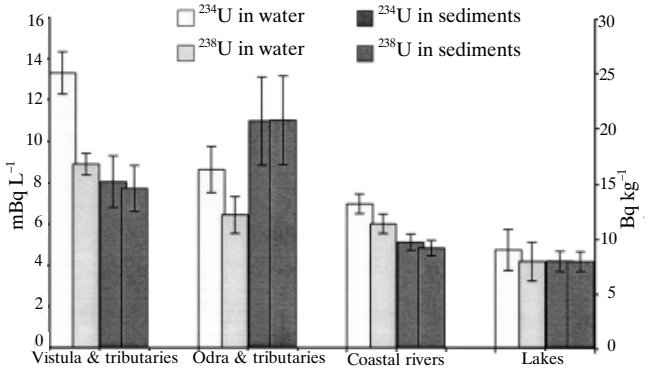

Fig. 2. Mean concentrations of ^{234}U and ^{238}U in waters (mBq L^{-1}) and in bottom sediments (Bq kg^{-1} dry weight) in rivers and lakes. Bars show standard error of the mean.

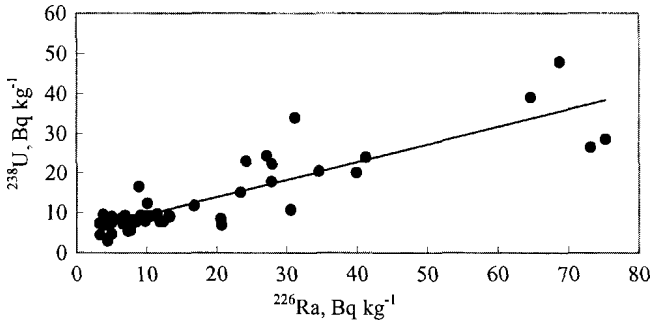

Fig. 3. Relationship between ^{238}U and ^{226}Ra concentrations in bottom sediments of rivers and lakes. Data for ^{226}Ra are from [18].

a relationship between these isotopes in the bottom sediments. Figure 3 shows such a relationship between ^{238}U and ^{226}Ra; it is expressed by the equation:

$$y = 0.344x + 6.6327$$

where: y is the activity concentration of ^{238}U in bottom sediments; x – activity concentration of ^{226}Ra. The correlation coefficient, r, is 0.80.

The activity concentrations of ^{234}U, ^{238}U and ^{226}Ra in the filtered water along the Vistula river from the zero point to the mouth are given in Fig. 4. The zero point was assumed by the waterways authorities to lie at the mouth

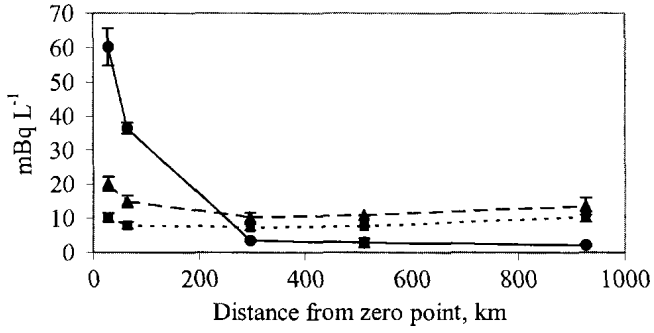

Fig. 4. Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra in filtered water along the Vistula river; –▲– ^{234}U, ···■··· ^{238}U, –●– ^{226}Ra [18]. Bars show standard deviation (SD). Zero point is 130 km from the sources of the Vistula river.

Table 7. Estimated flow of ^{234}U and ^{238}U from the Vistula and Odra rivers catchments to the Baltic Sea in 1999 and 2000 (TBq).

River	1999		2000	
	^{234}U	^{238}U	^{234}U	^{238}U
Vistula	0.77	0.60	0.64	0.51
Odra	0.33	0.28	0.20	0.16
Total	0.10	0.88	0.84	0.67

of the river Przemsza to Vistula, about 130 km from the sources of Vistula. Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra decreased with the river course from 27 km (Zator) to 295 km (Annopol) from the zero point and then they remained almost unchanged. The biggest decrease occurred from Zator (27 km) to Kraków (63.7 km); it was about 20% for uranium isotopes and about 40% for ^{226}Ra. Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra in the bottom sediments along the Vistula river are shown in Fig. 5. Concentrations of ^{234}U and ^{238}U were almost the same. Similarly as for the water samples, the highest activity concentrations were observed at Zator. In the course from Zator to Kraków, the concentrations of uranium isotopes dropped by about 25%, whereas that of ^{226}Ra dropped by about 60%. At Annopol, the sediments contained less uranium by about 35% and less ^{226}Ra by about 40% in comparison to Kraków. In samples collected in Warsaw (510 km from the zero point), concentrations of the radionuclides remained at the level similar as in Annopol. The "normal" level of the radionuclides, as that in the Bug,

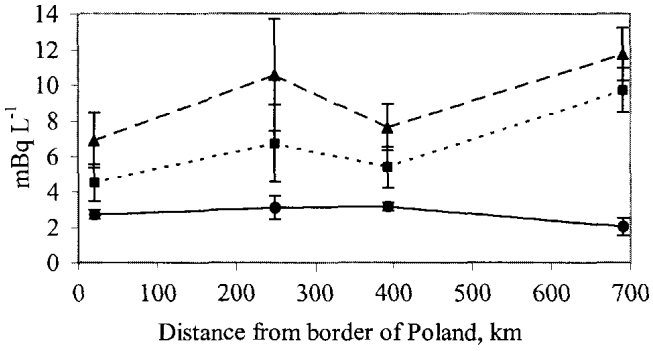

Fig. 5. Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra in filtered water along the Odra river; –▲– ^{234}U, ···■··· ^{238}U, –●– ^{226}Ra [18]. Bars show SD.

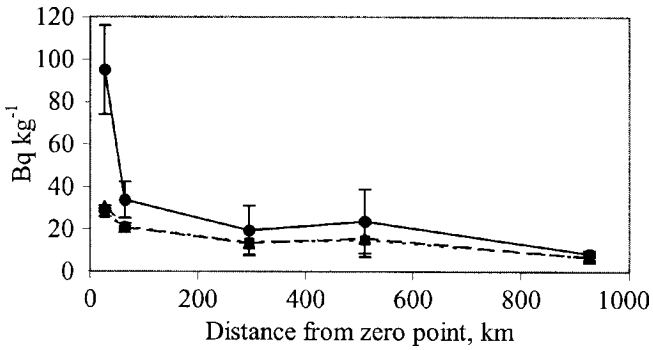

Fig. 6. Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra in bottom sediments along the Vistula river; –▲– ^{234}U, ···■··· ^{238}U, –●– ^{226}Ra [18]. Bars show SD.

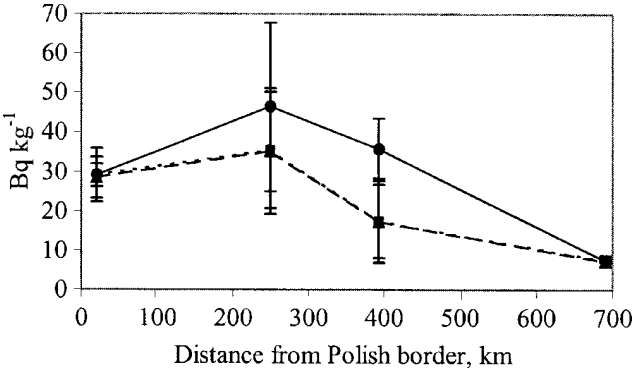

Fig. 7. Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra in bottom sediments along the Odra river; –▲– ^{234}U, ···■··· ^{238}U, –●– ^{226}Ra [18]. Bars show SD.

Narew and Warta rivers was found at Kiezmark (926 km from the point zero).

Activity concentrations of ^{234}U, ^{238}U and ^{226}Ra concentrations in the filtered water and bottom sediments in the Odra river, being the second main river in Poland, are presented in Figs. 6 and 7, respectively. In water, the concentrations of uranium along the river change within a narrow range and are similar to that in the tributaries of the Vistula and Odra rivers and coastal rivers (Tables 1 and 2). Activity concentrations of ^{226}Ra [18] are lower than those of uranium isotopes. They are similar to the ^{226}Ra concentrations in other rivers, with the exception of Vistula at Zator and Kraków. In the bottom sediments, the enhanced level of uranium and ^{226}Ra was observed in the upper and middle course of Odra. At Chałupki (20 km from the border with Czech Republic) and Krajnik (690 km) activity concentrations of uranium isotopes are close to that of ^{226}Ra, whereas in Wrocław (249 km) and Głogów (393 km), the concentration of ^{226}Ra is about 1.3 times and about two times higher, respectively. Taking into account the "normal" concentrations of the radionuclides in water and their enhanced concentrations in the bottom sediments it is supposed that mine waters were discharged to this river and/or its tributaries in the past.

Discussion

In Poland the enhanced level of uranium in waters can be due to human activity. The most important is the discharge of coal mine waters with an elevated level of natural radionuclides to the surface waters. The use of phosphate fertilizers in agriculture may result in the increase of uranium and radium. In natural waters, bottom sediments are a sink for uranium and radium and from the study of concentration of these radionuclides in sediments the information on the past release may be obtained.

The present study shows that the concentrations of uranium in the filtrated water and bottom sediments are enhanced in the upper Vistula river (Zator and Kraków). The enhanced concentrations can be attributed to the discharge of mine water from the Upper Silesian Coal Basin. These waters contain uranium isotopes, however, their concentrations are much lower than those of ^{226}Ra [18, 19]. The concentration of uranium isotopes in the filtered water of the middle and lower Vistula were higher than in other rivers and lakes. Probably, this can be ascribed to the use of phosphate fertilizers in agriculture.

Enhanced levels of uranium isotopes occurred in the bottom sediments in the upper and middle Odra and Nysa Łużycka rivers, but not in the filtrated water. This suggests that the discharge of uranium containing waters took place in the past; these data are in accordance with the low values of the radium activity concentrations in waters of the Odra river and its tributaries in 1994–1995 [19], and the Odra and Nysa Łużycka rivers in 1994–2000 [18].

In the present study, the average activity concentrations of the total uranium in water ranged from about 9 mBq L^{-1} (about 4 mBq L^{-1} of ^{238}U) in lakes to about 22 mBq L^{-1} (about 9 mBq L^{-1} of ^{238}U) in the Vistula river with tributaries (Fig. 2). This is less than the average uranium concentrations in the USA in surface waters (37 mBq L^{-1}; range from 0.37 to 25.234 mBq L^{-1}) [9] and less than activity concentrations of ^{238}U in Canada (14.8 mBq L^{-1} in Milliken lake, 40.2 mBq L^{-1} in Fredette lake and 17.3 mBq L^{-1} in Fredette creek) [15]. Activity concentrations of ^{238}U in river waters of the Wash and Fenland drainage basin in UK range from 7.9 mBq L^{-1} to 14.4 mBq L^{-1} [11] and in five German rivers they range from 8.8 mBq L^{-1} to 43.2 mBq L^{-1} [8].

Average activity concentrations of ^{238}U in bottom sediments in the present work were from about 8 Bq kg^{-1} d.wt. in lakes to about 20 Bq kg^{-1} d.wt. in the Odra and Nysa Łużycka rivers (Fig. 2). At the same level were ^{238}U concentrations in the bottom sediments of the rivers of the Wash and Fenland drainage basin in UK (range from 9 Bq kg^{-1} d.wt. to 18 Bq kg^{-1} d.wt.) [11], where the ^{238}U concentrations in water were also similar. However, in Spain in a bottom sediment of the Maderos river at the site above the uranium mine the ^{238}U concentration was much higher, namely, 125 Bq kg^{-1} d.wt., though the ^{238}U concentration in water was 16 mBq L^{-1} [7], being similar as in waters in Poland. Evidently, the uranium concentration in bottom sediments cannot be directly related to its concentration in water, because the absorption of uranium depends mainly on the kind of sediment; for the removal of uranium from waters important are especially humic substances and clay minerals [11].

References

1. Central Statistical Office (2001) Environment 2001. Information and statistical papers. Central Statistical Office (GUS), Warsaw (in Polish)
2. Cothern CR, Lappenbusch WL (1983) Occurrence of uranium in drinking water in the US. Health Phys 45:89–99
3. Firestone RB (1998) Table of isotopes. John Wiley & Sons, Inc., New York
4. Fleischer RL (1980) Isotopic disequilibrium of uranium: alpha-recoil damage and preferential solution effects. Science 207:979–981
5. Hess CT, Michel J, Horton TR, Prichard HM, Coniglio WA (1985) The occurrence of radioactivity in public water supplies in the United States. Health Phys 48:553–586
6. Lebecka J, Tomza I, Pluta I (1986) Natural radionuclides in off-waters from coal mines. Postępy Fizyki Medycznej 21:255–261 (in Polish)
7. Lozano JC, Blanco Rodriguez P, Vera Tome F (2002) Distribution of long-lived radionuclides of the ^{238}U series in the sediments of a small river in a uranium mineralized region of Spain. J Environ Radioact 63:153–171

8. Mangini A, Sonntag C, Bertsch G, Müller E (1979) Evidence for a higher natural uranium content in world rivers. Nature 278:337–339
9. NCRP (1984) Exposures from the uranium series with emphasis on radon and its daughter. NCRP Report No. 77. National Council on Radiation Protection and Measurements, Bethesda, MD
10. Pietrzak-Flis Z, Suplińska MM, Rosiak L (1997) The dietary intake of ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, ^{228}Th, and ^{226}Ra from food and drinking water by inhabitants of Walbrzych region. J Radioanal Nucl Chem 222:189–193
11. Plater AJ, Ivanovich M, Dugdale RE (1992) Uranium series disequilibrium in river sediments and waters: the significance of anomalous activity ratios. Appl Geochem 7:101–110
12. Shiraishi K, Igarashi Y, Yamamoto M *et al*. (1994) Concentrations of thorium and uranium in freshwater samples collected in the former USSR. J Radioanal Nucl Chem 185:157–165
13. Skwarzec B (1995) Polonium, uranium and plutonium in ecosystem of the Southern Baltic Sea. Rozprawy i Monografie IO PAN. Vol. 6. Institute of Oceanology PAS, Sopot (in Polish)
14. Skwarzec B, Boryło A, Strumińska D (2002) ^{234}U and ^{238}U isotopes in water and sediments of the southern Baltic. J Environ Radioact 61:345–363
15. Swanson SM (1985) Food-chain transfer of U-series radionuclides in a Northern Saskatchewan aquatic system. Health Phys 49:747–770
16. UNSCEAR (1977) Sources and effects of ionizing radiation. United Nations, New York
17. UNSCEAR (1982) Ionizing radiation: sources and biological effects. United Nations, New York
18. Wardaszko T, Radwan I, Pietrzak-Flis Z (2001) Radioactive contamination of rivers and lakes in Poland 1994–2000. Inspekcja Ochrony Środowiska, Warsaw (in Polish)
19. Wysocka M, Lebecka J, Skubacz K, Mielnikow A, Chałupnik S, Michalik B (1996) Behaviour of radium isotopes released from coal mines in rivers. In: Proc of the Int Conf Technologically Enhanced Natural Radiation Caused by Non-Uranium Mining, 16–19 October 1996, Szczyrk, Poland, pp 295–306