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^{241}Pu in the biggest Polish rivers

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Abstract In the paper the results of ^{241}Pu activity concentration determination in the biggest Polish rivers are presented. The analysis of more than 100 river water samples showed the Vistula and the Odra as well as three Pomeranian Rivers are important sources of ^{241}Pu in the southern Baltic Sea. There were differences in ^{241}Pu activities depending on season and sampling site and the plutonium contamination came mainly from the global atmospheric fallout as well as the Chernobyl accident, which is confirmed by plutonium activity ratios of ^{241}Pu/$^{239+240}$Pu and ^{238}Pu/$^{239+240}$Pu.

Keywords Plutonium ^{241}Pu · ^{241}Pu/$^{239+240}$Pu activity ratio · Rivers · Inflow · Baltic Sea

Introduction

The large amount of radioactive waste produced by human utilization of nuclear power is one of the major problems of environmental pollution in present time. The main sources of plutonium in the marine environment are nuclear weapon tests, satellites and civil nuclear power plant accidents [1–3]. Since 26 April 1986 there has been a new source of plutonium, namely the Chernobyl accident that should be taken into consideration [4, 5]. As reported in 1986, at the time of the accident the total initial core inventory of the Chernobyl reactor was about 4×10^{19} Bq of more than 50 different radioisotopes. During the accident, about 3 % of each isotope was released from the core and plutonium activities were: 3×10^{13} Bq of ^{238}Pu (48 g), 25.5×10^{12} Bq of ^{239}Pu and 3.6×10^{13} Bq of ^{240}Pu (about 18 kg $^{239+240}$Pu) as well as 5.1×10^{15} Bq of ^{241}Pu (1.3 kg) [6].

There are not many data available concerning the measured concentrations of ^{241}Pu in river water samples. Most of them in a large extent referred to soils and local contamination, like Palomares [7], Sellafield [8, 9]; post Chernobyl research in Ukraine [10], Finland [11, 12] and Poland [13–15]. Most of all environmental studies have focused on alpha emitting plutonium isotopes so far. ^{241}Pu is less important in terms of its radiotoxicity than the α-emitting plutonium radionuclides but is quite significant because of its greatest contribution to the whole plutonium fallout. Moreover β-emitting ^{241}Pu ($T_{1/2} = 14.35$ years) decays to the long-living, highly radiotoxic α-emitting ^{241}Am ($T_{1/2} = 432.2$ years) [16]. The principal source of ^{241}Pu on the Polish territory and the southern Baltic area was dry and wet atmospheric fallout from nuclear weapon tests and the Chernobyl accident [4]. After the accident, ^{241}Pu activity deposit in Chernobyl soil was estimated at 2,540 kBq m^{-2} and the value of ^{241}Pu/$^{239+240}$Pu activity ratio was 115 [17]. Our previous experiments on air samples indicated extreme increase of ^{241}Pu amount in atmospheric dust; in April 1986 the ^{241}Pu activity reached 3,643 mBq g^{-1} dw. Starting from May 1986 the ^{241}Pu concentrations in the air dust (33.1 mBq g^{-1} dw) were decreasing systematically and in November 1986 it reached the level close to that before the Chernobyl accident (1.08 mBq g^{-1} dw). The values of ^{241}Pu/$^{239+240}$Pu activity ratio increased from 34 (March 1986) to 56 (April 1986) after the accident and were decreasing slowly achieving 36 in December 1986 [14]. Mietelski and collaborators (1999)

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suggested that the initial (at the moment of the Chernobyl accident) deposition of ^{241}Pu in Poland might have been relatively high, up to the level of 2 kBq m^{-2} [13]. The maximum concentration of ^{241}Pu in forest soil was estimated at 254 Bq kg^{-1} dw and the enhanced levels of this isotope were observed in all samples from the north-eastern Poland. The fallout of ^{241}Pu at that level would result ^{241}Am contamination of up to 70 Bq m^{-2} in the middle of 21st century [17]. Moreover the available information about the bioaccumulation and distribution of ^{241}Pu on Poland territory is still very limited. It is, however, indispensable for the correct assessment of its radioactive contamination and the radiological consequences. ^{241}Pu and its decay product, long-living ^{241}Am, have health hazards even in small concentrations due to their extremely high radiotoxicity [18].

Rivers are important as one of the main sources of drinking water supply and present knowledge on plutonium concentration in Polish rivers is fragmentary and insufficient to estimate water contamination. The main aim of this work was to measure ^{241}Pu activity concentrations in the Vistula, the Odra Rivers and their tributaries as well as in three small Pomeranian Rivers (the Rega, the Parsęta and the Słupia). Further, the research covered: calculation of quarterly and annual ^{241}Pu balance, evaluation of the total ^{241}Pu inflow to the Baltic Sea, estimation of the most important sources of plutonium in the Vistula and the Odra Rivers drainage areas. On the basis of presented results and previously published data [19, 20], the values of ^{241}Pu/$^{239+240}$Pu activity ratios in analyzed river water samples were calculated.

The Vistula, the Odra and the Pomeranian Rivers

Over 95 % of the water supply in Poland originates from atmospheric precipitation. The total annual runoff from Poland to the Baltic Sea is ~60 km^3 per year, and 54 % of this amount is discharged by the Vistula and 34 % with the Odra River [21, 22]. The Vistula and the Odra catchments as well as three Pomeranian rivers cover 90 % of Poland and transport various fluvial material [23]. The Vistula is the biggest Polish river (1047.5 km long) and second largest (after the Neva River) inflowing to the Baltic Sea (Fig. 1). The average water inflow from the Vistula River to the Gulf of Gdańsk was estimated at 30.7 km^3 per year [24]. Annually the Vistula River transports about 1.8×10^6 kg of salt from a coal mine of the Upper Silesian Coal Factory [23, 25]. The Odra River is the second longest river in Poland (after the Vistula River), is 854 km long: 112 km lie in Czech Republic and 742 km in Poland (including 187 km on the border between Germany and Poland) (Fig. 1) [26]. Although the Odra is quite poor in water it regularly floods areas along its course. The largest and the most dangerous was the millennium flood in 1997 called Central European flood. During a week (3–10 of July 1997) local rains were over 500 mm (3–4 times higher than average month precipitation) [27].

Materials and methods

The grab surface river water samples 60–200 dm^3 volume (3–5 samples per sampling location) were taken every quarter from five Polish rivers (the Vistula, the Odra and the Pomeranian—the Rega, the Pasłęka, the Słupia) from November 2002 to November 2004 (Fig. 1). Each unfiltered water sample (all were poor in suspended matter) was prepared for radioanalytical procedure the same way. In the laboratory, the analyzed samples were spiked immediately after their delivery (5.69 mBq of ^{242}Pu) adequate amount for the measurements, was added as a yield tracer to each sample before the radiochemical analysis. All plutonium nuclides in river water samples was coprecipitated with manganese dioxide and further separated and purified on Dowex anion exchange resins. Finally, the plutonium was electrodeposited on a steel discs [4, 28, 29]. The first the activities of ^{238}Pu and $^{239+240}$Pu radionuclides were measured in alpha spectrometry and the minimum detectable activity for $^{239+240}$Pu was 0.05 mBq. After 5–8 years the determination of ^{241}Pu was done indirectly by measuring the increment in ^{241}Am from the decay of β-emitting ^{241}Pu using an alpha spectrometer Canberra Packard Alpha Analyst equipped with 12 PIPS detectors (300 and 450 mm^2 area each, FWHM = 17–18 keV). The currently acquired spectra were compared with those obtained earlier [19, 20]. A comparison of the obtained spectra allowed us for the calculation of the ^{241}Pu content based on the increment of the 5.49 MeV peak of ^{241}Am, taking into account the ^{238}Pu present in the samples from the Chernobyl accident and its decay. The ^{241}Pu activity concentrations were recalculated on the time of the original sampling. The calculation of the ^{241}Pu activity was based on the following formula:

$$A_{\mathrm{Pu}_0} = 30.11409 \cdot \frac{A_{^{241}\mathrm{Am}} \cdot e^{+\lambda_{\mathrm{Am}} \cdot t}}{(1 - e^{-\lambda_{\mathrm{Pu}} \cdot t})}$$

where A_{Pu_0} ^{241}Pu activity in the time of sampling, 31.11409 constant value ($\lambda_{\mathrm{Pu}}/\lambda_{\mathrm{Am}}$), $A_{^{241}\mathrm{Am}}$ ^{241}Am activity increment measured after 10 years, λ_{Pu} and λ_{Am} 0.048303 year^{-1} (counted for 14.35 years half-life time) and 0.001604 year $^{-1}$ (counted for 432.2 years half-life time) respectively, t time from sampling to ^{241}Am measurement (10 years).

The accuracy and the precision of the radiochemical methods of plutonium analysis were satisfactory (<7 %) and estimated by analysis of IAEA standard materials

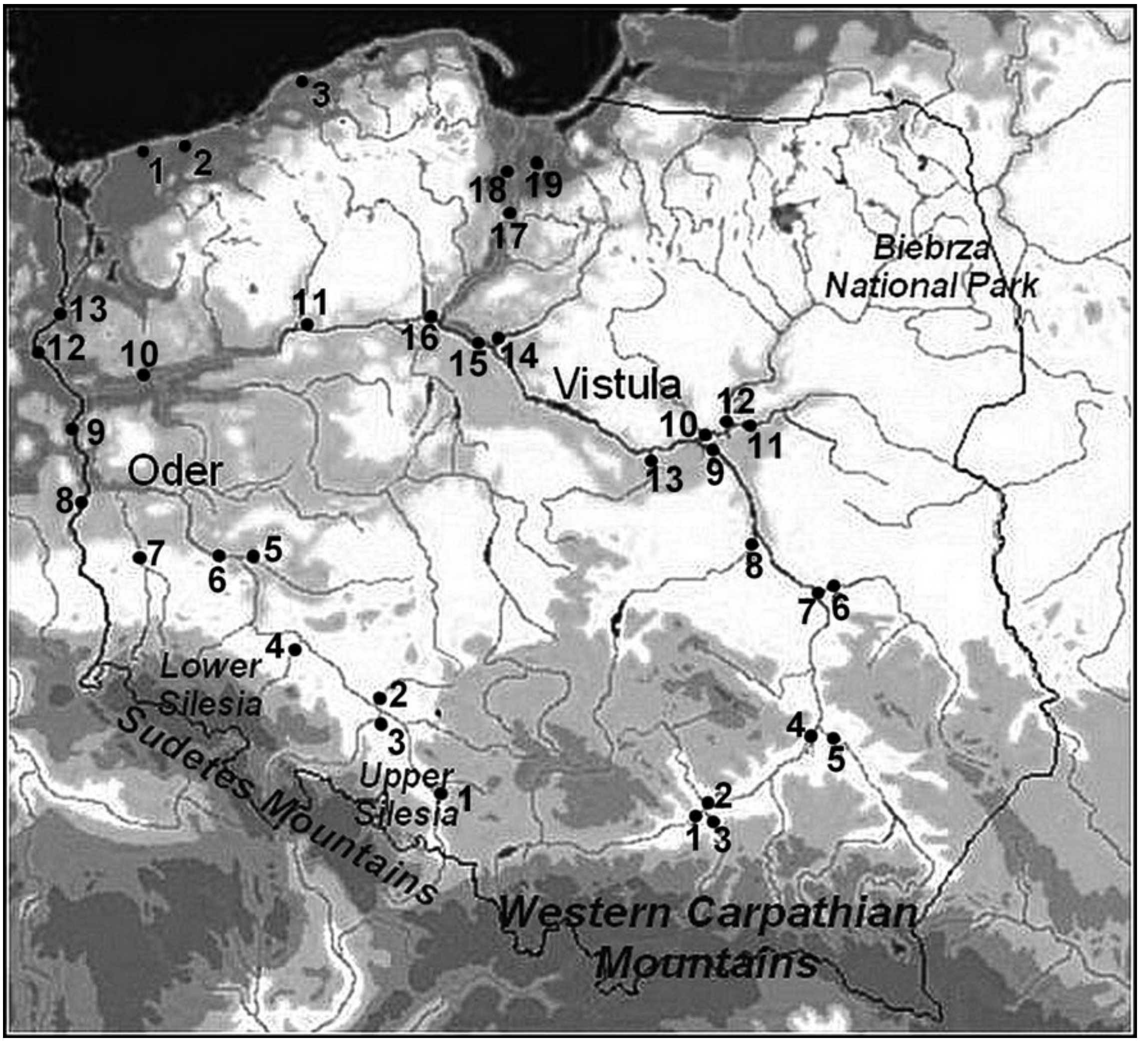

Fig. 1 Sampling sites. The Vistula: *1* Kraków, *2* Nida, *3* Dunajec, *4* Sandomierz, *5* San, *6* Wieprz, *7* Dęblin, *8* Pilica, *9* Warszawa, *10* Bug & Narew, *11* Bug, *12* Narew, *13* Bzura, *14* Drwęca, *15* Toruń, *16* Brda, *17* Grudziądz, *18* Leniwka, *19* Nogat. The Odra: *1* Chałupki, *2* Mała Panew, *3* Nysa Kłodzka, *4* Bystrzyca, *5* Barycz, *6* Głogów, *7* Bóbr, *8* Nysa Łużycka, *9* Słubice, *10* Warta, *11* Noteć, *12* Gozdowice, *13* Widuchowa. The Pomeranian Rivers: *1* Rega, *2* Parsęta, *3* Słupia

(IAEA-367, IAEA-384). The plutonium chemical yield varied from 60 to 90 %. The results of ^{241}Pu activity concentration in river water samples are given with their 2σ SD confidence intervals.

Results and discussion

The Vistula River

The activity concentrations of ^{241}Pu in water samples from the Vistula River and its tributaries and the values of the ^{241}Pu/$^{239+240}$Pu activity ratios are presented in Tables 1, 2, 3 and 4.

In the winter the highest ^{241}Pu concentration in the Vistula River was in river water taken from Sandomierz (105 ± 17 mBq m^{-3}) (Table 1). This value corresponds to high ^{241}Pu concentration measured in water samples taken from its tributary the San (150 ± 18 mBq m^{-3}) while the highest was observed in the Bug (165 ± 20 mBq m^{-3}). The Vistula tributaries lie on Paleogene sedimentary rock rich in sand and loess from river accumulation processes mostly and during analyzed period had high precipitation (50–90 mm) which allows for bigger and faster runoff, probably increasing dilution and desorption processes, especially in mountain rivers [19, 22, 30]. The concentrations of plutonium in freshwater reflect the current inputs from the atmosphere and effluents plus the amount of plutonium eroded from the catchment [31].

During the spring snowmelt, the highest ^{241}Pu activities in the main stream of the Vistula River were noticed in samples taken in Dęblin (102 ± 16 mBq m^{-3}) (Table 2).

Table 1 Average ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Vistula River waters and its tributaries in the winter

Sampling site	^{241}Pu (mBq m^{-3} ± SD)	$^{238}Pu/^{239+240}Pu$[a]	$^{241}Pu/^{239+240}Pu$[a]
Vistula River			
Malbork (Nogat)	69 ± 11	0.28 ± 0.06	33 ± 6
Kiezmark (Leniwka)	65 ± 10	0.26 ± 0.09	34 ± 8
Grudziądz	40 ± 5	0.14 ± 0.02	17 ± 2
Toruń	82 ± 13	0.17 ± 0.04	19 ± 3
Warszawa	83 ± 10	0.31 ± 0.07	44 ± 7
Dęblin	95 ± 12	0.23 ± 0.11	22 ± 5
Sandomierz	105 ± 17	0.11 ± 0.06	18 ± 4
Kraków	63 ± 8	0.08 ± 0.04	20 ± 4
Vistula tributaries			
Brda	82 ± 12	0.09 ± 0.05	14 ± 3
Drwęca	60 ± 9	0.15 ± 0.08	17 ± 4
Bzura	19 ± 3	0.18 ± 0.08	5 ± 1
Narew (Pułtusk)	97 ± 15	0.26 ± 0.12	25 ± 6
Bug	165 ± 20	0.26 ± 0.12	33 ± 8
Bug and Narew (NDM)	103 ± 17	0.26 ± 0.12	33 ± 7
Pilica	84 ± 10	0.18 ± 0.07	7 ± 1
Wieprz	118 ± 12	0.04 ± 0.03	14 ± 2
San	150 ± 18	0.20 ± 0.22	10 ± 5
Nida	74 ± 9	0.25 ± 0.20	23 ± 9
Dunajec	96 ± 21	0.43 ± 0.17	39 ± 12

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Skwarzec et al. [19])

Among the Vistula tributaries higher values of ^{241}Pu concentrations were measured in samples taken from the Narew and the Pilica (177 ± 19 and 165 ± 20 mBq m^{-3} respectively). Analyzed areas had the average maximum snow depth of 60 cm during winter what could cause huge amount of snowmelt as well as were rich in prolonged rain (lasting continuously 30–60 days) what increased atmospheric fallout and plutonium runoff [30].

The summer is characterized by the lowest plutonium concentrations of all the seasons and this situation also had the reflection in previously measured $^{239+240}Pu$ activities [19]. The highest ^{241}Pu concentration was found in water taken from Warszawa (71 ± 10 mBq m^{-3}) (Table 3). Among the Vistula tributaries the highest ^{241}Pu activity was in the Pilica (131 ± 16 mBq m^{-3}) as well as in the Bzura (131 ± 13 mBq m^{-3}). Summer 2004 had was the poorest in rain among the seasons sampled, and this could decrease possible plutonium runoff [30].

The autumn was very rainy what influenced on plutonium concentrations in water samples; much higher plutonium concentrations were found at north-eastern Poland. In the Vistula River during autumn the highest ^{241}Pu activity was measured in Malbork (133 ± 13 mBq m^{-3}) (Table 4). Among the Vistula tributaries, the highest ^{241}Pu concentrations were found in river samples taken from the Drwęca and the Narew (249 ± 27 and 233 ± 28 mBq m^{-3} respectively). Generally, the concentrations of ^{241}Pu in all analyzed seasons corresponded with previously measured $^{239+240}Pu$.

On the basis of average seasonal plutonium concentrations in the Vistula River and its tributaries, average annual values of ^{241}Pu activities were calculated (Table 5). Higher plutonium concentrations in water from the Vistula River and its tributaries are the result of atmospheric fallout as well as watershed and underground flow connected to rains and snowmelt [19, 32]. These processes occur at lower range during summer seasons, typical in Poland, and as follows we can observe lower plutonium concentration in river water.

Seasonal runoff

On the basis of the seasonal and the annual inflows of the Vistula River waters and its tributaries [22] as well as the average seasonal and the annual plutonium concentrations (Table 5) the seasonal and the annual runoff of plutonium ^{241}Pu from the Vistula drainage were calculated (Table 6). During the winter, the largest flow of ^{241}Pu in the main stream of the Vistula River was estimated in Toruń (460 MBq quarter^{-1}). The runoff noticed in Toruń is connected to huge runoff from the Bug and the Narew Rivers (253 MBq quarter^{-1})—these rivers has the biggest drainage area from all analyzed watersheds and constitutes 59 % of total Vistula drainage area. In the spring, among the Vistula tributaries the highest ^{241}Pu flow was also observed in the Bug and the Narew (278 MBq quarter^{-1}) what influenced on its high runoff in Toruń (503 MBq quarter^{-1}) and further

Table 2 Average ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Vistula River waters and its tributaries in the spring

Sampling site	^{241}Pu (mBq m^{-3} ± SD)	$^{238}Pu/^{239+240}Pu$[a]	$^{241}Pu/^{239+240}Pu$[a]
Vistula River			
Malbork (Nogat)	71 ± 8	0.19 ± 0.08	13 ± 3
Kiezmark (Leniwka)	65 ± 10	0.10 ± 0.07	14 ± 4
Grudziądz	51 ± 8	0.12 ± 0.04	16 ± 3
Toruń	52 ± 6	0.15 ± 0.05	21 ± 4
Warszawa	26 ± 3	0.11 ± 0.08	15 ± 4
Dęblin	102 ± 16	0.09 ± 0.04	12 ± 2
Sandomierz	50 ± 6	0.06 ± 0.03	10 ± 2
Kraków	24 ± 3	0.04 ± 0.04	9 ± 2
Vistula tributaries			
Brda	145 ± 16	0.43 ± 0.30	12 ± 5
Drwęca	130 ± 16	0.14 ± 0.09	22 ± 5
Bzura	103 ± 12	0.38 ± 0.27	20 ± 8
Narew (Pułtusk)	177 ± 19	0.20 ± 0.09	30 ± 6
Bug	84 ± 12	0.33 ± 0.16	25 ± 7
Bug and Narew (NDM)	83 ± 9	0.07 ± 0.05	26 ± 6
Pilica	165 ± 20	0.16 ± 0.10	26 ± 7
Wieprz	127 ± 15	0.48 ± 0.17	15 ± 4
San	111 ± 14	0.14 ± 0.09	10 ± 2
Nida	144 ± 19	0.28 ± 0.22	18 ± 8
Dunajec	74 ± 9	0.17 ± 0.06	17 ± 3

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Skwarzec et al. [19])

parts of the Vistula. Springs are mostly rich in rains, the snow melts increasing the water inflow from watersheds while the summer was characterized by the lowest plutonium flow among all analyzed seasons what is connected with the low amount of precipitation [30]. During the autumn season, among the Vistula tributaries the biggest ^{241}Pu flow in was observed, similarly to $^{239+240}Pu$, in wide lowland Narew River (209 MBq quarter^{-1}) [19]. Annually, the biggest ^{241}Pu flow occurs near the Vistula River delta zone, in Kiezmark (1601 MBq year^{-1}) and also in the lower part, in Toruń (1392 MBq year^{-1}) connected to the big watershed of the Bug and the Narew rivers rich in precipitation, flat and wet, lying at the eastern part of Poland (Table 6).

Inflow to the Baltic Sea

On the basis of the annual flow of plutonium from the Vistula River, the annual inflow of ^{241}Pu to the southern Baltic was calculated and presented in Table 7. The Vistula River is an important source of plutonium radionuclides in the southern Baltic environment. Annually, the southern Baltic Sea—concretely the Gdańsk Basin—is enriched with 1,653 MBq of ^{241}Pu and from this amount 1601 MBq of ^{241}Pu (96.8 %) go to the Gulf of Gdańsk via the main river branch, the Leniwka River, as well as 52 MBq of ^{241}Pu (3.2 %) go to the Vistula Lagoon via the Nogat and the contribution of ^{241}Pu in individual branches is the same in comparison with $^{239+240}Pu$ [19]. Plutonium from the Vistula River drainage is transported to deeper regions of the Gulf of Gdańsk and the Gdańsk Deep and deposited in sediments [33–36]. The largest amount of ^{241}Pu was calculated in spring (695 MBq) and winter (547 MBq). Generally, lowland rivers from the eastern part of Poland (the Narew and the Bug) are characterized by higher values of total plutonium runoff and the values of the $^{241}Pu/^{239+240}Pu$ activity ratio suggested the highest impact of the Chernobyl accident on this territory. The enhanced concentrations of plutonium in water from the Vistula River were the result of the atmospheric fallout, its rinsing off from the catchment area, from snowmelt, enhanced precipitation and materials leached from soil and river bed [19]. In river systems about 70 ± 20 % of the whole plutonium was transported to the estuary, but rest 30 ± 20 % stays in the river, probably connected to suspended matter [37]. But sediments do accumulate in large, deep rivers; however the average rate of plutonium removal from surface waters (about 0.3 % per day) is too slow relative to the hydrologic flow rate to efficiently deposit [31, 38].

The Odra River

The activity concentrations of ^{241}Pu in analyzed water samples from the Odra River and its tributaries and the values of $^{241}Pu/^{239+240}Pu$ activity ratios are presented in Tables 8, 9, 10, and 11.

Table 3 Average ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Vistula River waters and its tributaries in the summer

Sampling site	^{241}Pu (mBq m^{-3} ± SD)	$^{238}Pu/^{239+240}Pu^{a}$	$^{241}Pu/^{239+240}Pu^{a}$
Vistula River			
Malbork (Nogat)	43 ± 6	0.07 ± 0.03	15 ± 3
Kiezmark (Leniwka)	21 ± 2	0.09 ± 0.06	17 ± 4
Grudziądz	24 ± 3	0.18 ± 0.08	21 ± 4
Toruń	57 ± 9	0.33 ± 0.22	21 ± 8
Warszawa	71 ± 10	0.14 ± 0.06	23 ± 5
Dęblin	54 ± 6	0.24 ± 0.07	17 ± 3
Sandomierz	43 ± 5	0.14 ± 0.05	22 ± 4
Kraków	39 ± 5	0.38 ± 0.16	38 ± 9
Vistula tributaries			
Brda	165 ± 18	0.17 ± 0.18	26 ± 11
Drwęca	93 ± 10	0.29 ± 0.16	37 ± 11
Bzura	131 ± 13	0.11 ± 0.08	21 ± 5
Narew (Pułtusk)	110 ± 18	0.06 ± 0.06	33 ± 10
Bug	109 ± 13	0.05 ± 0.04	19 ± 4
Bug and Narew (NDM)	67 ± 7	0.24 ± 0.12	27 ± 7
Pilica	131 ± 16	0.17 ± 0.09	20 ± 5
Wieprz	48 ± 5	0.56 ± 0.31	42 ± 15
San	90 ± 10	0.25 ± 0.28	20 ± 10
Nida	43 ± 5	0.15 ± 0.12	23 ± 7
Dunajec	32 ± 4	0.17 ± 0.13	21 ± 6

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Skwarzec et al. [19])

Table 4 Average ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Vistula River waters and its tributaries in the autumn

Sampling site ($n = 3$)	^{241}Pu (mBq m^{-3} ± SD)	$^{238}Pu/^{239+240}Pu^{a}$	$^{241}Pu/^{239+240}Pu^{a}$
Vistula River			
Malbork (Nogat)	133 ± 16	0.08 ± 0.03	19 ± 3
Kiezmark (Leniwka)	84 ± 13	0.08 ± 0.02	19 ± 3
Grudziądz	39 ± 5	0.17 ± 0.18	17 ± 7
Toruń	69 ± 10	0.22 ± 0.05	18 ± 3
Warszawa	49 ± 8	0.11 ± 0.04	6 ± 1
Dęblin	71 ± 8	0.16 ± 0.06	20 ± 4
Sandomierz	40 ± 5	0.13 ± 0.08	25 ± 6
Kraków	62 ± 8	0.20 ± 0.09	29 ± 7
Vistula tributaries			
Brda	152 ± 17	0.12 ± 0.09	20 ± 5
Drwęca	248 ± 27	0.15 ± 0.06	8 ± 1
Bzura	137 ± 15	0.08 ± 0.06	16 ± 4
Narew (Pułtusk)	233 ± 28	0.07 ± 0.02	16 ± 2
Bug	106 ± 14	0.24 ± 0.13	11 ± 3
Bug and Narew (NDM)	49 ± 6	0.29 ± 0.16	13 ± 4
Pilica	101 ± 11	0.07 ± 0.07	12 ± 3
Wieprz	81 ± 9.7	0.20 ± 0.09	12 ± 3
San	90.9 ± 11	0.11 ± 0.04	20 ± 3
Nida	124 ± 20	0.33 ± 0.39	20 ± 2
Dunajec	155 ± 23	0.14 ± 0.15	32 ± 13

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Skwarzec et al. [19])

Table 5 Average annual concentration of ^{241}Pu concentrations as well as ^{241}Pu/$^{239+240}$Pu activity ratios in the Vistula River and its tributaries

Sampling location	^{241}Pu (mBq m^{-3} ± SD)	^{241}Pu/$^{239+240}$Pu[a]
The Vistula River		
Malbork (Nogat)	79 ± 10	18 ± 3
Kiezmark (Leniwka)	59 ± 9	19 ± 4
Grudziądz	38 ± 5	17 ± 4
Toruń	65 ± 9	19 ± 4
Warszawa	57 ± 8	16 ± 3
Dęblin	81 ± 11	16 ± 3
Sandomierz	60 ± 8	17 ± 3
Kraków	47 ± 6	21 ± 5
Vistula Tributaries		
Brda	136 ± 16	17 ± 6
Drwęca	133 ± 16	13 ± 3
Bzura	97 ± 11	17 ± 5
Narew (Pułtusk)	154 ± 20	22 ± 4
Bug	116 ± 15	20 ± 5
Bug and Narew (NDM)	75 ± 10	24 ± 6
Pilica	120 ± 14	14 ± 3
Wieprz	94 ± 10	15 ± 2
San	110 ± 13	12 ± 4
Nida	96 ± 13	20 ± 9
Dunajec	89 ± 14	27 ± 8

[a] On the basis of ^{238}Pu and $^{239+240}$Pu concentrations (Skwarzec et al. [19])

In the autumn, the highest ^{241}Pu concentration in the Odra River was found in water sample taken in Chałupki (170 ± 27 mBq m^{-3}) (Table 8). Such situation, the highest plutonium concentration at the river stream, corresponds to this observed previously in the Vistula drainage, in a case of ^{241}Pu as well as $^{239+240}$Pu [19, 20]. The Odra source, similarly to the Vistula, lies on the Paleogene sedimentary rock rich in sand and loess coming from a river accumulation processes and goes through an area of loess and loess-like clay characterized by high precipitation when compared to the other regions [30]. The autumn 2003 was very rainy, monthly precipitation over the Odra's source was 75–100 mm [30] and such high precipitation increased the atmospheric fallout as well as allowed for bigger and faster runoff, probably increasing the dilution and the desorption processes, especially in mountain Sudetian rivers. Plutonium washed out from the soil by rains is predominantly rainwater or dry atmospheric fallout origin. The southern tributaries had the highest ^{241}Pu concentrations and the biggest had the Bóbr (67 ± 7 mBq m^{-3}).

In the winter, the highest ^{241}Pu concentration in the Odra River was found in water samples taken in Gozdowice (135 ± 21 mBq m^{-3}). Among the tributaries, similarly to the autumn season, the highest ^{241}Pu concentration was found in the Bóbr (200 ± 32 mBq m^{-3}) (Table 9). The Odra River source area is characterized by the longest snow season—average 100–110 days [30].

During the spring snowmelt, the highest ^{241}Pu concentrations in the main stream of the Odra River were noticed in the samples taken from the southern mountain part, the closest to the stream, namely in Głogów and Chałupki (105 ± 14 and 98 ± 15 mBq m^{-3} respectively), while among the tributaries the highest ^{241}Pu concentration was measured in the water samples taken from the Nysa Łużycka (131 ± 14 mBq m^{-3}) (Table 10). This river carries a lot of snowmelt, enriched in desorbed or dissolved soil compounds. Moreover, this area in the spring 2004 was very rainy (50–100 mm) what could increase the plutonium dilution processes as well as atmospheric fallout and its total runoff [30].

The summer, similarly as the Vistula River, is characterized by the lowest plutonium concentrations of all the seasons. The highest ^{241}Pu activity concentrations was found in water sample taken in Słubice (127 ± 16 mBq m^{-3}) (Table 11). Among the Odra tributaries the highest ^{241}Pu concentration was in huge lowland Warta (144 ± 23.0 mBq m^{-3}), the longest and the biggest tributary which contributes 45.9 % of the total Odra watershed [22]. Similar situation was observed in previously measured $^{239+240}$Pu concentrations [20]. The summer 2004 was the poorest in rains among all seasons sampled as well, and this could decrease possible plutonium runoff and atmospheric fallout [30]. Generally, similarly to the Vistula River, the concentrations of ^{241}Pu in the Odra river water correspond with previously measured $^{239+240}$Pu activities [19, 20].

On the basis of the average seasonal plutonium concentrations in the Odra River and its tributaries, the average annual values of ^{241}Pu activities as well as the values of the ^{241}Pu/$^{239+240}$Pu activity ratios were calculated (Table 12). Higher annual plutonium concentrations in the water from the Odra River and its tributaries were found, similarly to $^{239+240}$Pu, in the Nysa Kłodzka (98 ± 11 mBq m^{-3}), the Bóbr (94 ± 13 mBq m^{-3}) and the Nysa Łużycka (91 ± 11 mBq m^{-3}). Higher plutonium concentrations in these rivers could be a result of the atmospheric fallout mainly as well as more intensive flow connected with rains and snowmelt [19, 20, 32]. The average values of the ^{241}Pu/$^{239+240}$Pu activity (Table 12) indicated different plutonium origin in the Odra River—not only nuclear weapon tests and the Chernobyl accident, also Sellafield and Cap de la Hague influence [39].

Table 6 Seasonal and annual flow rate of ^{241}Pu in the Vistula River and its tributaries

Sampling site	Winter (MBq quarter^{-1})	Spring (MBq quarter^{-1})	Summer (MBq quarter^{-1})	Autumn (MBq quarter^{-1})	All year (MBq year^{-1})
Vistula					
Malbork	11	12	7	22	52
Kiezmark	547	695	57	302	1601
Grudziądz	348	525	63	100	1036
Toruń	460	503	261	168	1392
Warszawa	294	170	115	131	710
Dęblin	353	632	106	163	1253
Sandomierz	174	225	42	36	478
Kraków	33	15	6	22	76
Vistula Tributaries					
Brda	21	31	20	33	104
Drwęca	15	33	11	57	116
Bzura	4	23	6	13	46
Narew	75	248	31	209	563
Bug	119	209	31	69	428
Bug and Narew	253	278	42	66	639
Pilica	38	84	22	33	177
Wieprz	42	40	7	17	106
San	157	227	31	46	461
Nida	10	24	4	7	45
Dunajec	74	156	12	54	297

Table 7 Annual flux of ^{241}Pu from the Vistula and the Odra River to the Baltic Sea

Season	Vistula (MBq)			Odra (MBq)
	Total runoff	Into		Total runoff
		Gulf of Gdańsk	Vistula Lagoon	
Winter	558	547	11	105
Spring	707	695	12	164
Summer	64	57	7	102
Autumn	324	302	22	245
Annual	1,653	1,601	52	616

Seasonal runoff

On the basis of the seasonal and the annual inflows of the Odra River waters and its tributaries [22] as well as the average seasonal and the annual plutonium concentrations (Table 12) the seasonal and the annual runoff of ^{241}Pu from the Odra drainage were calculated (Table 13). During the autumn season, among the Odra tributaries the highest ^{241}Pu inflow was observed in the longest and the biggest tributary the Warta (11 MBq quarter^{-1}), while the lowest, similarly to $^{239+240}Pu$, in the Barycz and the shortest Bystrzyca (both 1 MBq quarter^{-1}). The highest flow of ^{241}Pu in the main stream of the Odra River was estimated, similarly to $^{239+240}Pu$, in Gozdowice (321 MBq quarter^{-1}) and this value was the

Table 8 Average values of ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Odra waters and its tributaries in autumn

Sampling site	^{241}Pu (mBq m^{-3})	$^{238}Pu/^{239+240}Pu^{a}$	$^{241}Pu/^{239+240}Pu^{a}$
Odra River			
Chałupki	170 ± 27	0.27 ± 0.11	37 ± 9
Głogów	163 ± 24	0.33 ± 0.22	47 ± 17
Słubice	99 ± 15	0.33 ± 0.22	35 ± 13
Gozdowice	163 ± 20	0.30 ± 0.11	43 ± 9
Widuchowa	123 ± 13	0.13 ± 0.07	46 ± 10
Odra tributaries			
Mała Panew	50 ± 6	0.19 ± 0.09	24 ± 5
Nysa Kłodzka	57 ± 6	0.38 ± 0.11	18 ± 3
Bystrzyca	49 ± 5	0.40 ± 0.14	47 ± 10
Barycz	53 ± 6	0.25 ± 0.14	24 ± 7
Bóbr	67 ± 7	0.20 ± 0.10	6 ± 1
Nysa Łużycka	14 ± 2	0.20 ± 0.04	3 ± 0.4
Warta	13 ± 1	0.10 ± 0.06	10 ± 2
Noteć	11 ± 1	0.12 ± 0.06	3 ± 1

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Strumińska-Parulska et al. [20])

Table 9 Average values of ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Odra waters and its tributaries in winter

Sampling site	^{241}Pu (mBq m^{-3})	$^{238}Pu/^{239+240}Pu$[a]	$^{241}Pu/^{239+240}Pu$[a]
Odra River			
Chałupki	118 ± 14	0.24 ± 0.08	16 ± 3
Głogów	101 ± 13	0.30 ± 0.14	34 ± 7
Słubice	87 ± 10	0.26 ± 0.09	38 ± 7
Gozdowice	135 ± 21	0.18 ± 0.11	38 ± 11
Widuchowa	53 ± 7	0.31 ± 0.17	43 ± 13
Odra tributaries			
Mała Panew	17 ± 2	0.40 ± 0.24	20 ± 7
Nysa Kłodzka	179 ± 18	0.11 ± 0.05	30 ± 5
Bystrzyca	120 ± 18	0.11 ± 0.05	17 ± 3
Barycz	34 ± 5	0.23 ± 0.15	17 ± 5
Bóbr	200 ± 32	0.24 ± 0.12	23 ± 6
Nysa Łużycka	143 ± 17	0.11 ± 0.04	29 ± 5
Warta	76 ± 9	0.22 ± 0.14	32 ± 9
Noteć	7 ± 1	0.33 ± 0.22	4 ± 1

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Strumińska-Parulska et al. [20])

Table 10 Average values of ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Odra waters and its tributaries in spring

Sampling site	^{241}Pu (mBq m^{-3})	$^{238}Pu/^{239+240}Pu$[a]	$^{241}Pu/^{239+240}Pu$[a]
Odra River			
Chałupki	98 ± 15	0.20 ± 0.13	42 ± 13
Głogów	105 ± 14	0.36 ± 0.13	33 ± 8
Słubice	77 ± 9	0.30 ± 0.12	17 ± 4
Gozdowice	43 ± 6	0.19 ± 0.07	13 ± 3
Widuchowa	83 ± 12	0.37 ± 0.16	41 ± 11
Odra tributaries			
Mała Panew	88 ± 11	0.15 ± 0.05	32 ± 6
Nysa Kłodzka	102 ± 13	0.21 ± 0.07	24 ± 5
Bystrzyca	43 ± 6	0.35 ± 0.15	23 ± 6
Barycz	17 ± 2	0.38 ± 0.26	38 ± 14
Bóbr	51 ± 6	0.16 ± 0.07	7 ± 1
Nysa Łużycka	131 ± 14	0.14 ± 0.06	31 ± 6
Warta	67 ± 7	0.33 ± 0.27	22 ± 9
Noteć	48 ± 5	0.31 ± 0.10	11 ± 2

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Strumińska-Parulska et al. [20])

highest among all analyzed seasons and sampling sites and could be connected to a huge runoff from the Warta [20]. During the winter, among the Odra tributaries, the highest flow of ^{241}Pu was also calculated for long and wide Warta River

Table 11 Average values of ^{241}Pu concentrations as well as $^{238}Pu/^{239+240}Pu$ and $^{241}Pu/^{239+240}Pu$ activity ratios in the Odra waters and its tributaries in summer

Sampling site	^{241}Pu (mBq m^{-3})	$^{238}Pu/^{239+240}Pu$[a]	$^{241}Pu/^{239+240}Pu$[a]
Odra River			
Chałupki	117 ± 18	0.37 ± 0.18	30 ± 9
Głogów	48 ± 7	0.41 ± 0.15	28 ± 7
Słubice	127 ± 16	0.33 ± 0.26	35 ± 13
Gozdowice	91 ± 12	0.23 ± 0.10	25 ± 6
Widuchowa	51 ± 7	0.38 ± 0.16	26 ± 8
Odra tributaries			
Mała Panew	75 ± 12	0.23 ± 0.09	25 ± 8
Nysa Kłodzka	52 ± 8	0.23 ± 0.08	14 ± 3
Bystrzyca	43 ± 5	0.34 ± 0.25	37 ± 6
Barycz	77 ± 11	0.38 ± 0.21	41 ± 15
Bóbr	57 ± 6	0.29 ± 0.12	36 ± 7
Nysa Łużycka	75 ± 9	0.16 ± 0.10	36 ± 9
Warta	144 ± 23	0.40 ± 0.21	35 ± 12
Noteć	64 ± 10	0.10 ± 0.06	17 ± 5

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Strumińska-Parulska et al. [20])

Table 12 Average annual values of ^{241}Pu concentrations as well as $^{241}Pu/^{239+240}Pu$ activity ratios in the Odra waters and its tributaries

Sampling site	^{241}Pu (mBq m^{-3})	$^{241}Pu/^{239+240}Pu$[a]
Odra River		
Chałupki	126 ± 18	28 ± 7
Głogów	104 ± 14	37 ± 10
Słubice	98 ± 13	29 ± 8
Gozdowice	108 ± 15	31 ± 7
Widuchowa	78 ± 10	39 ± 10
Odra tributaries		
Mała Panew	57 ± 8	26 ± 7
Nysa Kłodzka	98 ± 11	23 ± 4
Bystrzyca	67 ± 9	24 ± 5
Barycz	45 ± 6	28 ± 9
Bóbr	94 ± 13	13 ± 3
Nysa Łużycka	91 ± 11	23 ± 4
Warta	75 ± 10	28 ± 9
Noteć	32 ± 4	9 ± 2

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Strumińska-Parulska et al. [20])

(64 MBq quarter^{-1}). The highest flow of ^{241}Pu in the main stream of the Odra was calculated again in Gozdowice (263 MBq quarter^{-1}). In the spring, among the Odra tributaries the highest ^{241}Pu flow was observed, similarly to previous seasons, in the Warta (56 MBq quarter^{-1}). Polish springs are

Table 13 Seasonal and annual inflow of ^{241}Pu in the Odra and its tributaries

Sampling site	Autumn (MBq quarter^{-1})	Winter (MBq quarter^{-1})	Spring (MBq quarter^{-1})	Summer (MBq quarter^{-1})	All year (MBq year^{-1})
Odra					
Chałupki	26	18	15	18	76
Głogów	106	65	67	31	269
Słubice	93	81	71	119	364
Gozdowice	321	263	84	179	848
Widuchowa	245	105	164	102	616
Odra Tributaries					
Mała Panew	1	0.3	2	1	4.3
Nysa Kłodzka	5	16	9	5	34
Bystrzyca	1	2	7	1	4
Barycz	1	0.4	0.2	1	2.6
Bóbr	8	23	6	7	43
Nysa Łużycka	1	10	9	5	26
Warta	11	64	56	122	254
Noteć	4	3	18	24	49

Table 14 ^{241}Pu concentrations as well $^{241}Pu/^{239+240}Pu$ activity ratios and seasonal inflow of ^{241}Pu from the Pomeranian Rivers in the spring

River	Length (km)	^{241}Pu concentration (mBq m^{-3})	$^{241}Pu/^{239+240}Pu$[a]	Seasonal ^{241}Pu flow (MBq quarter^{-1})	Annual ^{241}Pu flow (MBq year^{-1})
Rega	199	106 ± 16	31 ± 10	5	20
Parsęta	139	106 ± 17	9 ± 3	17	68
Słupia	138.6	146 ± 17	37 ± 11	13	52

[a] On the basis of ^{238}Pu and $^{239+240}Pu$ concentrations (Strumińska-Parulska et al. [20])

often rainy, the snow melts, what increases the water inflow from watersheds and the Warta covers huge part of Polish lowlands. The summer was characterized by the lowest plutonium flow among all analyzed seasons what is connected with the low amount of precipitation, however very high and the highest among all seasons was observed in the Warta tributary (122 MBq quarter^{-1}). Annually, the highest ^{241}Pu flow in the main stream of the Odra River, similarly to $^{239+240}Pu$, occurs in Gozdowice (848 MBq year^{-1}) and among the tributaries in the Warta (254 MBq year^{-1}) (Table 13).

Inflow to the Baltic Sea

On the basis of the annual flow of plutonium from the Odra River, the annual inflow of ^{241}Pu to the southern Baltic (the Pomeranian Bay) was calculated and presented in Table 7. The Odra River, similarly to the Vistula, is an important source of plutonium radionuclides in the southern Baltic environment. Annually, the Pomeranian Bay is enriched with 616 MBq of ^{241}Pu. Generally, mountain Odra tributaries from "the Opole anomaly" area carry the biggest amount of plutonium.

The Pomeranian Rivers

Three Pomeranian Rivers (the Słupia, the Parsęta and the Rega) were examined in the spring 2004 and the results of ^{241}Pu activities measurements are presented in Table 14. The highest ^{241}Pu concentration was measured in the water samples taken from the Słupia (146 ± 17 mBq m^{-3}). Annually, these three Pomeranian Rivers carry 140 MBq of ^{241}Pu (Table 14).

Conclusions

On the basis of the study we can conclude that the annual surface runoff of ^{241}Pu were higher in big lowland catchments, in both the Vistula and the Odra drainage. The results of our investigation indicated the Vistula, the Oder and to a lesser extent the Pomeranian Rivers as important sources of plutonium ^{241}Pu in the southern Baltic Sea environment and annually, the southern Baltic Sea is enriched by 2,418 MBq of ^{241}Pu. The biggest inflow from the Vistula River was estimated for spring season, while for the Odra River in autumn.

In Poland, the plutonium contamination comes mainly from global atmospheric fallout resulting from nuclear weapon tests with huge impact of the Chernobyl accident, which is confirmed by plutonium activity ratios.

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