

Activity concentration of plutonium in atmospheric precipitation

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Abstract. Activity concentrations of plutonium isotopes (^{238}Pu , $^{239+240}\text{Pu}$) were determined in atmospheric precipitation samples collected in Kraków from August 2005 to December 2007. The volume of 29 samples varied in the range 14–269 dm³. The method of samples collection, preparation and radiochemical analysis proper for the separation of plutonium are indicated in brief. Monthly plutonium deposition showed seasonal variation for $^{239+240}\text{Pu}$ the first maximum was observed in August 2005 and amounted to about 2.65 ± 0.31 mBq/m², the second one in July 2006 – 0.371 ± 0.063 mBq/m² and the third one in April 2007 – 0.859 ± 0.075 mBq/m² and for ^{238}Pu in September 2005 – 0.090 ± 0.038 mBq/m², July 2006 – 0.177 ± 0.074 mBq/m² and the third maximum in May 2007 – 0.333 ± 0.028 mBq/m². Similar behaviour of activity concentration of plutonium was also observed in other parts of the earth. Anomalously high deposition of $^{239+240}\text{Pu}$ (2.65 ± 0.31 mBq/m²) was found in August 2005. The $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratios higher than the global fallout value ~ 0.55 (in Poland) suggested participation from different sources of plutonium.

Key words: activity ratio $^{238}\text{Pu}/^{239+240}\text{Pu}$ • atmospheric precipitation • global fallout • Chernobyl

Introduction

The atmospheric precipitation is any product of the condensation of atmospheric water vapour that is deposited on the earth surface. It consists of many different forms of water: rain, freezing rain, drizzle, ice needles, snow, ice pellets, etc. [2] and many various aerosols for instance: soil aerosols (resuspended particles which are a result of wind erosion – containing mainly silicates) [6], biological (plants, for instance) aerosols as well as anthropogenic aerosols like those coming from thermal power stations. Multiplicity of forms of atmospheric precipitation made it the most important source of very interesting information concerning transport of trace elements, including plutonium.

The appearance of plutonium in the air is connected with human activity like: atmospheric nuclear weapon tests in the past (Novaya Zemlya, Semipalatynsk, Bikini Atoll, Nevada, etc.) – resulted in the so-called global fallout, production and reprocessing of nuclear fuel (Sellafield, La Hague, Majak, etc.), nuclear accidents (Chernobyl (1986), etc.) or disintegration of satellites (American satellite equipped with SNAP 9A (1963) or Russian Cosmos-954 (1978)) [4]. Most of the artificial radionuclides injected into the atmosphere were eventually deposited on the earth surface by wet and dry deposition processes [3].

The sources of plutonium in atmosphere can be verified by the ratio of $^{238}\text{Pu}/^{239+240}\text{Pu}$ which is like a fingerprint for each origin. The value of activity ratio

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of plutonium coming from global fallout is 0.03 [12], 0.55 [10] or 0.60 [7] for the Chernobyl deposition in Poland and for Sellafield 0.18–0.21 [8].

The aim of this work is to determine the activity concentrations of ^{238}Pu and $^{239+240}\text{Pu}$ in atmospheric precipitation samples collected in Kraków in the period from August 2005 to December 2007.

Analytical procedure

Sampling

The atmospheric precipitation collector was located in Kraków (50°04'N 19°58'E), Poland in the area of the Henryk Niewodniczański Institute of Nuclear Physics Polish Academy of Sciences very close to the nearest farmland. Wet and dry deposition was collected using a 2.28 m² stainless-steel collector in the form of rectangular container with a small outflow connecting tube. The atmospheric deposition was then transported through a rubber tube to two polyethylene barrels of 160 dm³ capacity. The sampling was performed monthly from August 2005 to December 2007. In this way a total number of 29 samples was collected. Sample volume varied in the range 14–269 dm³.

Pretreatment of the samples

The monthly wet and dry deposition samples were, after sampling, acidified with about 2 cm³ of concentrated HNO₃ per litre. Next, the sample was evaporated to small volume (200 cm³) on a hot plate using a stainless-steel pot. The plastic barrel was then washed using a small amount of 0.1 M HNO₃ and an ash-less (analytical) filter paper which was afterwards ashed in a muffle furnace at 400°C. In the end, three fractions obtained (sample, ashed filters and acid from washing) were combined into one sample, mixed and evaporated to dryness initially in an evaporation dish on a hot plate and, after quantitative transfer to a final polyethylene vial under an infrared lamp.

Radiochemical preparation

The evaporated samples were transferred to polytetrafluoroethylene (PTFE) beakers and spiked with a ^{242}Pu tracer with an activity ranging from 0.0035 Bq/sample to 0.013 Bq/sample. Then, the silica and organic matrix of the sample were destroyed by successively treatment with 70 cm³ of concentrated hydrofluoride acid (HF) 50 cm³ of HNO₃ (three times) and 70 cm³ of HCl. The mineralization process was finished by adding 3 g of HBO₃ to the sample to bind fluoride ions [4]. Then, the Pu oxidation state was stabilized as +4 by adding 0.5 cm³ of hydrazine and 2 g of NaNO₂. Finally, the sample was contained in 200–250 ml of 8 M HNO₃.

Plutonium was separated on an anion-exchange column filled with Dowex 1 × 8 resin from 8 M HNO₃. At the beginning, thorium was eluted using 12 M HCl and then the plutonium was stripped from the column with a solution of 0.1 M HF and 0.1 M HCl [11].

The source for alpha spectrometric measurement was prepared by the NdF₃ co-precipitation method [5].

Measurements

Alpha-particle spectra were obtained by measuring the plutonium sources with a Silena Alpha-Quatro spectrometer with passivated ion-implanted silicon detectors (Canberra) of 450 mm² active area.

The average counting time was about 10 days, and the limit of detection amounted to 0.15 mBq/sample.

All alpha spectrometry sources were measured after about one month from the separation of plutonium when the radioactive equilibrium state between ^{228}Th and ^{224}Ra was achieved. In spite of radiochemical purification, traces of ^{228}Th very often disturbed determination of ^{238}Pu . Thus, the presented results for ^{238}Pu are corrected for any traces of ^{228}Th . This correction increases sometime the uncertainty of ^{238}Pu activity concentration determination.

Results and discussion

The total $^{239+240}\text{Pu}$ and ^{238}Pu activity concentration of wet and dry deposition in Kraków found for the years 2005–2007 are summarized in Table 1. The results of the measurements from the years 2005–2006 have been published earlier [4]. The obtained values of ^{238}Pu deposition ranged from below 0.003 mBq/m² to 0.333 ± 0.028 mBq/m² and $^{239+240}\text{Pu}$ from 0.039 ± 0.010 mBq/m² to 2.65 ± 0.31 mBq/m². The maxima and minima for $^{239+240}\text{Pu}$ and ^{238}Pu did not coincide with the ones in the same time period. This suggested that at least two different sources of ^{238}Pu and $^{239+240}\text{Pu}$ were observed. The next fact confirming this observation was the lack of correlation between the activity concentration and a total volume of collected atmospheric water sample (the square of Pearson's correlation coefficient for $^{239+240}\text{Pu}$ and volume of collected sample amounted to 0.18 when for ^{238}Pu 0.05) (Table 1).

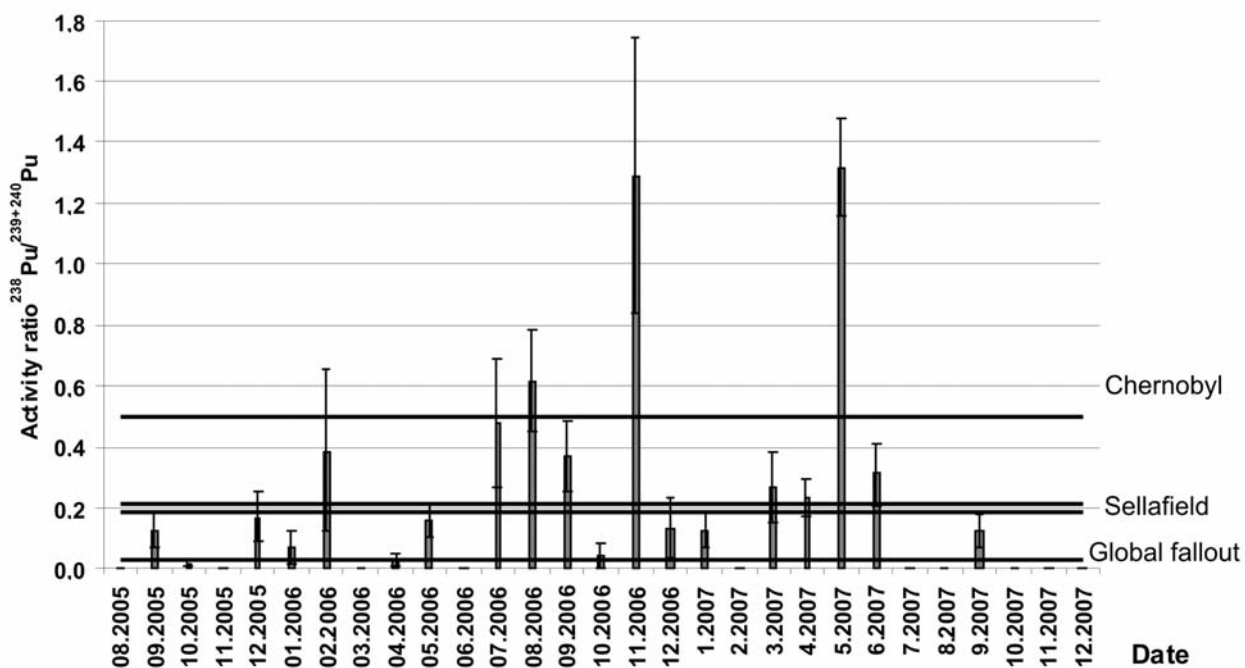
The interesting result was a seasonal variation of activity concentration of $^{239+240}\text{Pu}$ and ^{238}Pu observed, what confirmed literature data from other parts of the earth [1, 9]. The maximum appeared in August 2005, July 2006 and April 2007 for $^{239+240}\text{Pu}$ and September 2005, July 2006 and May 2007 for ^{238}Pu – the summer season in Poland. These high values might be correlated with agricultural activities of farmers in these seasons at the nearest farmland what could increase resuspension effect in the air.

The origin of the activity concentration variation of plutonium in collected samples can be explained based on the activity ratios of $^{238}\text{Pu}/^{239+240}\text{Pu}$ which are shown in Fig. 1. The whole results could be divided into three groups. The first group includes points with the activity ratio typical of global fallout, the second – with $^{238}\text{Pu}/^{239+240}\text{Pu}$ above the value characteristic of Chernobyl fallout (these result have not been explained up till now). The third contains the results with activity ratios between the global fallout and the Chernobyl one. Such results were observed usually in summer. The first suggestion was an explanation for the third

Table 1. Activity concentration of ^{238}Pu and $^{239+240}\text{Pu}$ in atmospheric precipitation (mBq/m^2) and sample volume (dm^3)

	Name of sample	Activity concentration (mBq/m^2) ^a		Volume of sample (dm^3)
		^{238}Pu	$^{239+240}\text{Pu}$	
1	08.2005	< 0.013	2.65 ± 0.31	269
2	09.2005	0.090 ± 0.038	0.719 ± 0.079	100
3	10.2005	0.004 ± 0.003	0.264 ± 0.050	19
4	11.2005	< 0.019	0.277 ± 0.035	60
5	12.2005	0.026 ± 0.012	0.152 ± 0.020	198
6	01.2006	0.010 ± 0.008	0.157 ± 0.023	64
7	02.2006	0.015 ± 0.010	0.039 ± 0.010	113
8	03.2006	< 0.012	0.067 ± 0.010	75
9	04.2006	0.005 ± 0.003	0.166 ± 0.024	255
10	05.2006	0.029 ± 0.009	0.180 ± 0.021	137
11	06.2006	< 0.013	0.268 ± 0.027	209
12	07.2006	0.177 ± 0.074	0.371 ± 0.063	87
13	08.2006	0.047 ± 0.011	0.076 ± 0.010	52
14	09.2006	0.028 ± 0.008	0.076 ± 0.011	100
15	10.2006	0.011 ± 0.010	0.253 ± 0.028	19
16	11.2006	0.088 ± 0.023	0.068 ± 0.016	98
17	12.2006	0.019 ± 0.014	0.146 ± 0.017	19
18	01.2007	0.018 ± 0.008	0.146 ± 0.025	57
19	02.2007	< 0.014	0.077 ± 0.010	36
20	03.2007	0.061 ± 0.026	0.231 ± 0.034	59
21	04.2007	0.198 ± 0.049	0.859 ± 0.075	15
22	05.2007	0.333 ± 0.028	0.253 ± 0.022	29
23	06.2007	0.087 ± 0.027	0.282 ± 0.033	79
24	07.2007	< 0.017	0.194 ± 0.026	68
25	08.2007	< 0.031	0.173 ± 0.025	125
26	09.2007	0.022 ± 0.009	0.183 ± 0.028	154
27	10.2007	< 0.035	0.125 ± 0.018	49
28	11.2007	< 0.028	0.191 ± 0.023	76
29	12.2007	< 0.009	0.046 ± 0.009	14
	Arithmetic mean	0.067	0.299	91
	SD	0.085	0.486	68
	Median	0.028	0.180	–

^a For all cases, the mean value uncertainties are connected with ^{238}Pu or $^{239+240}\text{Pu}$ and ^{242}Pu statistical measuring errors.

**Fig. 1.** Activity ratios of $^{238}\text{Pu}/^{239+240}\text{Pu}$ in atmospheric precipitation.

group of results and the interference of Chernobyl and global fallout (which can be enhanced by resuspension effect). However, research of activity concentration of plutonium in soil samples collected from the cultivated area nearby this possibility was rejected. It was found that the origin of plutonium in the area of Kraków was just the global fallout. Other most important feature of results from the third group was that they could be observed also in winter time when the snow cover (in Poland as well as around Chernobyl) significantly reduces resuspension. Due to these facts, the assumption that the interference of the Chernobyl and global fallouts is not true in this case. Therefore, it is likely that the Sellafield emission via sea spray could be the source of plutonium with increased activity ratio. However, this is only a supposition. To prove this hypothesis mass spectrometry was planned, which would provide values for another isotopic ratio $^{239}\text{Pu}/^{240}\text{Pu}$ (not provided by alpha spectrometry). This would be helpful in verification of the above hypothesis.

Conclusions

The activity ratios for many samples of atmospheric deposition were found to be much higher than the typical values for the global fallout and lower than revealed by the Chernobyl deposition in Poland. It seems to be unlikely that the reason of the observed ratios were resuspension or the influence by Chernobyl fallout. It was supposed that the observed higher isotopic ratios resulted from Sellafield emission. However, this should be verified.

The seasonal variation of activity concentration of $^{239+240}\text{Pu}$ and ^{238}Pu suggested the existence of two different sources of plutonium in the atmospheric air. Correlation between the plutonium activity and the volume of sample was not observed. The problem with the unusually high value of $^{238}\text{Pu}/^{239+240}\text{Pu}$ activity ratio above 0.5 is still open.

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References

1. Hirose K, Kim CK, Kim CS, Chang BW, Igarashi Y, Aoyama M (2004) Wet and dry deposition patterns of plutonium in Daejeon, Korea. *Sci Total Environ* 332:243–252
2. <http://amsglossary.allenpress.com/glossary/>
3. Katsuragi Y, Hirose K, Sugimura Y (1982) A study of plutonium fallout in Tokyo. *Pap Met Geophys* 33:85–93
4. Kierepko R, Mietelski JW, Borowiec W, Tarasiewicz S, Błażej S, Kapała J (2009) Plutonium traces in atmospheric precipitation and in aerosols from Kraków and Białystok. *Radiochim Acta* 97;4/5:253–255
5. LaRosa JJ, Cooper E, Ghods-Esphahani A *et al.* (1992) Radiochemical methods used by the IAEA's Laboratories at Seibersdorf for the determination of ^{90}Sr , ^{144}Ce and Pu radionuclides in the environment samples collected for the International Chernobyl Project. *J Environ Radioactiv* 17:183–209
6. Lehto J, Salminen S, Jaakkola T *et al.* (2006) Plutonium in the air in Kurchatov, Kazakhstan. *Sci Total Environ* 366:206–217
7. Mietelski JW (2003) Nuclear spectrometry applied to studies of bioavailability of radionuclides from “fuel-like hot particles” in forest environment. (DSc Thesis). IFJ Report no. 1921/B. IFJ, Kraków (in Polish)
8. Mitchell PI, Battle J Vives i, Downes AB, Condren OM, Leon Vintro L, Sanchez-Cabeza JA (1995) Recent observation on the physico-chemical speciation of plutonium in the Irish Sea and the western Mediterranean. *Appl Radiat Isot* 46:1175–1190
9. Montero MPR, Sanchez AM (2001) Activity of $^{239+240}\text{Pu}$ and ^{238}Pu in atmospheric deposits. *Appl Radiat Isot* 55:97–102
10. Pietruszewski A, Bojanowski R (1990) Plutonium in air in Warsaw after Chernobyl accident. In: *Proc of the Int Symp on Post-Chernobyl Environmental Radioactivity Studies in East European Countries*, Kazimierz nad Wisłą, Poland, 17–19 September 1990. Lublin, pp 118–126
11. Sill CW (1987) Precipitation of actinides as fluorides or hydroxides for high resolution alpha spectrometry. *Nucl Chem Waste Mgmt* 7:201–215
12. UNSCEAR (1982) Report with annexes. United Nations sales publ. E.82.IX.8. New York