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Measurement of plutonium isotopes in ground-level air in Northern-Germany – history and recent results

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Abstract The history of plutonium measurements performed on ground-level aerosols is summarised. Recent results are presented, the activity ratios a($^{(239+240)}$Pu)/a(^{137}Cs) and a(^{238}Pu)/a($^{(239+240)}$Pu) measured are discussed and potential sources of ^{238}Pu are considered.

Key words caesium • environmental monitoring • ground-level aerosols • plutonium • radioactivity

Introduction

The radioactivity contained in ground-level aerosols has been measured at the Physikalisch-Technische Bundesanstalt (PTB) since the early sixties. The trace survey station at PTB in Braunschweig is one of the 14 trace survey stations operated within the framework of the German Environmental Radioactivity Monitoring System ("Integriertes Mess- und Informations-System", IMIS). The other stations are operated by the DWD (German Meteorological Service) and by the IAR (Institute for Atmospheric Radioactivity, Federal Office for Radiological Protection).

Methods

Aerosol samples are collected in Braunschweig and Berlin with high-volume aerosol samplers, and the γ-ray spectra of the aerosol ash are measured weekly. The ash samples are combined to form quarterly aerosol ash samples. ^{242}Pu is added as a yield tracer to the quarterly sample which is totally dissolved by means of an open microwave digestion system. The plutonium isotopes are finally electroplated onto a stainless steel disk prior to the α-spectrometric measurements. The radiochemical yields of the total procedure are normally around 90–95 %. The lowest limit of detection (LLD), calculated on the basis of the radiochemical blank in accordance with the Standard ISO 11929-2:2000 [2], was around 0.05 nBq/m^3 in the last two years. The expanded uncertainties assigned to the results are calculated by multiplying the combined standard uncertainty by a coverage factor k=2 in accordance with the "Guide to the Expression of Uncertainty in Measurement" [3]. The uncertainties assigned to the activity ratios are directly calculated from the statistical uncertainty of the net count numbers.

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Results

Fig. 1 shows the graph of the mean activity concentration of $^{(239+240)}$Pu (bold line) in ground-level air in Northern Germany in comparison with that of ^{137}Cs (upper line). The difference between the mean activity concentration levels observed today and those found in the times of nuclear weapons fall-out is quite obvious and impressively underline the "low-level" character of the current measurements. All ^{137}Cs activity concentrations displayed are the results of measurements on aerosol samples taken in Braunschweig and Berlin. In contrast to this, the $^{(239+240)}$Pu graph covers periods of measurements and periods containing calculated $^{(239+240)}$Pu activity concentrations. From 1963 to mid 1969, and from 1974 to 1984, the mean activity concentration of $^{(239+240)}$Pu was calculated with the mean activity ratio a($^{(239+240)}$Pu)/a(^{137}Cs) of 1.50×10^{-2} measured in Braunschweig between 1969 and 1974 [11]. The activity concentration of $^{(239+240)}$Pu calculated for 1984 matches sufficiently the measurement result obtained in Berlin in 1985. From 1985 to 1992 simultaneous measurements of ^{137}Cs were carried out in Braunschweig (line) and Berlin (circles). The results are in good agreement. However, a closer look in particular at the γ-spectrometric measurements performed of the weekly samples, shows that in 1992 a slightly higher ^{137}Cs activity concentration was measured in Berlin, too [12].

After the Chernobyl reactor accident, the annual mean activity concentration of $^{(239+240)}$Pu measured in Berlin increased from 10.5 nBq/m^3 in 1985 to 331 nBq/m^3 in 1986. In 1987 it was 6.99 nBq/m^3. The corresponding values for ^{238}Pu are 0.45 nBq/m^3, 141 nBq/m^3 and 0.56 nBq/m^3, respectively. The influence of the Chernobyl fall-out on the activity ratio a($^{(239+240)}$Pu)/a(^{137}Cs) of 0.015 measured in Berlin in 1985 is characterised by a decrease to about 2.4×10^{-5} at the end of April 1986. At the end of 1986 the ratio was around 1×10^{-3}, again due to re-suspended soil dust contaminated by nuclear weapons fall-out [6, 7]. From 1990 to 1992 the ratio measured in Berlin remained in the range between 1×10^{-3} and 2×10^{-3}. As the routine Pu measurements were started in Braunschweig in 1990, a three-year period of Pu results from both locations is available. The mean activity ratio a($^{(239+240)}$Pu)/a(^{137}Cs) measured in Braunschweig since 1990 is 2.61×10^{-3}. The range of ratios measured in the quarterly samples is from 5.51×10^{-4} to 6.18×10^{-3}.

From Fig. 1 one might conclude that, in the period from 1990 to 1992, there is a trend towards a mean activity concentration of $^{(239+240)}$Pu in the air in Berlin which is slightly higher than that in Braunschweig. However, we do not yet know whether this is significant, because the annual mean values from Berlin for these years could be measured on the combined annual samples only whereas they were calculated from the quarterly results from Braunschweig. Collaboration between PTB and DWD was therefore started in order to compare the Pu content of the IMIS aerosol samples quarterly collected in Braunschweig and Berlin. Due to the low air flow rate of the sampler, the ^{238}Pu activities on the counting sources from the Berlin 1999 samples are below LLD. However, the first results indicate that the $^{(239+240)}$Pu activity concentration might be slightly higher in the air in Berlin than in Braunschweig, but this finding needs confirmation by

(i) a very careful evaluation of the radiochemical blank of the filter material used by DWD and
(ii) an investigation on the specific activities of Pu in the aerosol ash (Fig. 2) in order to preclude the effect of different air dust concentrations in Berlin and Braunschweig. The effect of different meteorological conditions, i.e. rainfall duration and rainfall intensity in the sampling period can be minimised as well.

Table 1 shows the results of the Pu analyses available from Braunschweig since 1990 in more detail. Some replicates have been included, because the radiochemical purity of some counting sources which had shown an unexpectedly high isotopic a(^{238}Pu)/a($^{(239+240)}$Pu) ratio had to be checked [13]. The seasonal fluctuation of the mean quarterly activity concentration of $^{(239+240)}$Pu shows a relative minimum in winter and a relative maximum in summer. However, as the quarterly time base is long, it is not possible to specify a month in which the minimum or maximum occurs. The summer maximum is attributable to re-suspended soil dust contaminated mainly by nuclear weapons fall-out. The

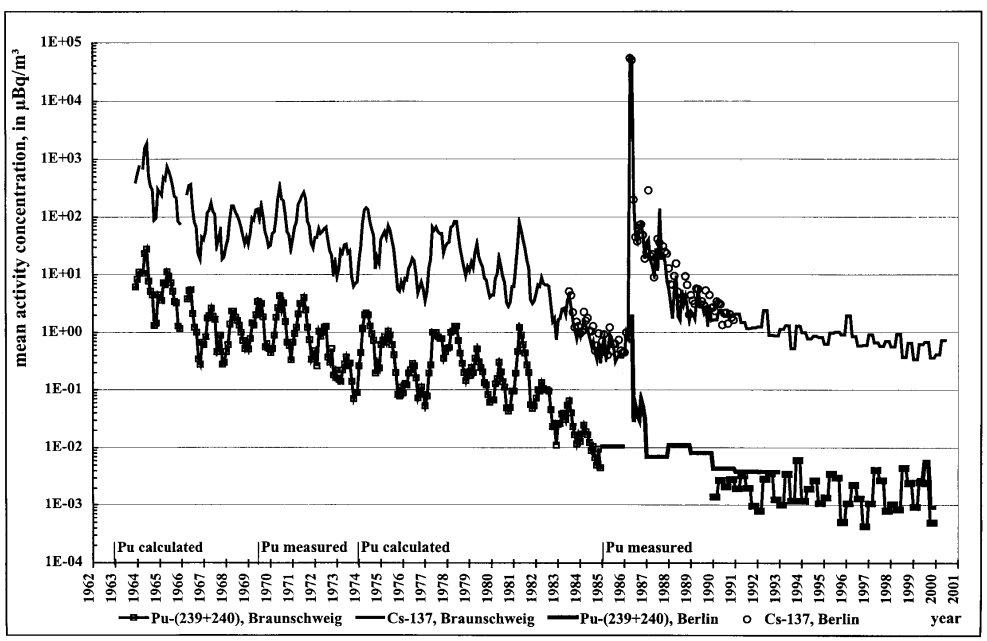

Fig. 1. Mean activity concentrations of ^{137}Cs and $^{(239+240)}$Pu in ground-level air in Northern Germany since 1963.

Table 1. Mean quarterly activity concentrations of plutonium isotopes and the a(^{238}Pu)/a($^{(239+240)}$Pu) activity ratio in air in Braunschweig since 1990. "p" marks samples taken in parallel.

Year	Quarter	^{238}Pu, in nBq/m^3	$^{(239+240)}$Pu, in nBq/m^3	a(^{238}Pu)/a($^{(239+240)}$Pu)
1990	1	1.00E-01 ± 4.22E-02	1.40E+00 ± 3.08E-01	7.14E-02 ± 3.40E-02
	2	1.53E-01 ± 3.17E-02	2.74E+00 ± 2.79E-01	5.59E-02 ± 1.29E-02
	3	1.20E-01 ± 3.15E-02	2.11E+00 ± 3.01E-01	5.69E-02 ± 1.70E-02
	4	2.80E-01 ± 1.23E-01	2.82E+00 ± 4.84E-01	9.93E-02 ± 4.67E-02
1991	1, p	2.37E-01 ± 6.93E-02	2.19E+00 ± 2.90E-01	1.08E-01 ± 3.47E-02
	2	2.90E-01 ± 5.42E-02	3.30E+00 ± 3.35E-01	8.79E-02 ± 1.87E-02
	3	1.60E-01 ± 5.63E-02	1.99E+00 ± 2.74E-01	8.04E-02 ± 3.04E-02
	4	9.60E-02 ± 4.07E-02	9.60E-01 ± 1.62E-01	1.00E-01 ± 4.56E-02
1992	1	1.40E-01 ± 3.68E-02	7.90E-01 ± 1.15E-01	1.77E-01 ± 5.32E-02
	2	1.70E-01 ± 3.31E-02	2.88E+00 ± 3.08E-01	5.90E-02 ± 1.31E-02
	3	4.60E-01 ± 7.57E-02	3.59E+00 ± 3.59E-01	1.28E-01 ± 2.47E-02
	4	1.90E-01 ± 3.77E-02	1.25E+00 ± 1.39E-01	1.52E-01 ± 3.45E-02
1993	1	2.30E-01 ± 6.71E-02	1.00E+00 ± 1.18E-01	2.30E-01 ± 7.24E-02
	2	6.30E-01 ± 7.78E-02	3.49E+00 ± 3.46E-01	1.81E-01 ± 2.86E-02
	3	1.80E-01 ± 5.10E-02	1.19E+00 ± 1.57E-01	1.51E-01 ± 4.73E-02
	4, p	1.10E-01 ± 2.88E-02	6.90E-01 ± 8.63E-02	1.59E-01 ± 4.62E-02
1994	1	2.60E-01 ± 4.64E-02	1.19E+00 ± 1.35E-01	2.18E-01 ± 4.62E-02
	2	2.30E-01 ± 4.61E-02	1.95E+00 ± 2.20E-01	1.18E-01 ± 2.71E-02
	3	2.50E-01 ± 6.51E-02	2.71E+00 ± 3.22E-01	9.23E-02 ± 2.64E-02
	4	2.50E-01 ± 4.32E-02	1.07E+00 ± 1.23E-01	2.34E-01 ± 4.85E-02
1995	1, p	1.88E-01 ± 3.90E-02	1.35E+00 ± 1.55E-01	1.40E-01 ± 2.00E-02
	2	8.20E-01 ± 1.35E-01	3.53E+00 ± 4.34E-01	2.30E-01 ± 3.00E-02
	3	2.29E-01 ± 6.67E-02	3.02E+00 ± 4.14E-01	8.00E-02 ± 2.00E-02
	4	1.29E-01 ± 4.46E-02	5.10E-01 ± 9.69E-02	2.50E-01 ± 9.67E-02
1996	1	3.31E-01 ± 4.20E-02	1.07E+00 ± 1.08E-01	3.10E-01 ± 3.00E-02
	2	1.63E-01 ± 2.93E-02	2.27E+00 ± 2.23E-01	7.20E-02 ± 1.20E-02
	3	2.01E-01 ± 3.60E-02	1.31E+00 ± 1.42E-01	1.55E-01 ± 2.51E-02
	4	8.99E-02 ± 2.10E-02	4.31E-01 ± 5.52E-02	2.10E-01 ± 4.80E-02
1997	1	1.11E-01 ± 2.74E-02	1.06E+00 ± 1.21E-01	1.05E-01 ± 2.50E-02
	2	2.85E-01 ± 9.73E-02	4.10E+00 ± 6.24E-01	7.20E-02 ± 2.30E-02
	3	4.03E-01 ± 7.68E-02	2.73E+00 ± 3.24E-01	1.50E-01 ± 2.51E-02
	4	1.20E-01 ± 3.38E-02	7.88E-01 ± 1.04E-01	1.62E-01 ± 4.50E-02
1998	1	7.21E-02 ± 2.94E-02	1.02E+00 ± 1.43E-01	7.07E-02 ± 2.80E-02
	2	1.72E-01 ± 4.00E-02	1.73E+00 ± 1.89E-01	1.00E-01 ± 2.20E-02
	3	2.93E-01 ± 5.96E-02	4.47E+00 ± 4.95E-01	6.55E-02 ± 1.10E-02
	4	7.81E-02 ± 2.85E-02	6.77E-01 ± 9.88E-02	1.15E-01 ± 4.20E-02
1999	1	9.96E-02 ± 5.80E-02	9.10E-01 ± 1.60E-01	1.09E-01 ± 5.00E-02
	2	1.88E-01 ± 8.54E-02	2.49E+00 ± 4.08E-01	7.55E-02 ± 2.60E-02
	3	1.51E-01 ± 6.71E-02	2.43E+00 ± 3.25E-01	6.21E-02 ± 2.20E-02
	4	2.80E-02 ± 2.38E-02	4.90E-01 ± 7.96E-02	5.71E-02 ± 4.40E-02
arith, mean		**2.17E-01**	**1.89E+00**	**1.29E-01**
maximum		**8.20E-01**	**4.47E+00**	**3.10E-01**
minimum		**2.80E-02**	**4.31E-01**	**5.59E-02**

Below: Results of samples suspected to contain one (or more) "hot" particle(s). They have been checked for radiochemical purity of the Pu α-counting source. These results are not taken into account in the arithmetic mean value calculation.

1991	1; 1st run	7.60E-01 ± 1.21E-01	1.64E+00 ± 2.18E-01	2.18E-01 ± 9.61E-02
	1; 2nd run	8.16E-01 ± 1.05E-01	1.96E+00 ± 2.09E-01	2.09E-01 ± 6.94E-02
1993	4; 1st run	2.50E-01 ± 4.28E-02	5.50E-01 ± 7.20E-02	4.55E-01 ± 9.80E-02
	4; 2nd run	2.56E-01 ± 3.01E-02	6.06E-01 ± 5.63E-02	4.22E-01 ± 6.33E-02
1995	1; 1st run	4.87E-01 ± 7.54E-02	1.36E+00 ± 1.59E-01	3.70E-01 ± 5.00E-02
	1; 2nd run	5.62E-01 ± 8.46E-02	1.36E+00 ± 1.18E-01	4.13E-01 ± 1.00E-02

The combined expanded uncertainty is calculated by multiplication of the combined standard uncertainty by a coverage factor k=2 [3]

mean quarterly activity concentration of ^{238}Pu seems like having reached a maximum around 1995/1996. It is sometimes close to the LLD. The activity ratios a(^{238}Pu)/a($^{(239+240)}$Pu) of about 0.4 measured in quarterly samples in 1991, 1993, and 1995 (enlarged separate dots in Fig. 3) obviously are outside the range of ratios normally measured. After these results had been confirmed by re-analysis and re-purification, we believed that the aerosol samples of concern had contained a "hot" particle. We checked the "hot" particle hypothesis by analysis of a second air dust sample collected with another sampler operated in parallel. The results are marked by a "p" in Table 1. As all the available aerosol ash of a sample had to be completely dissolved at the beginning of the procedure, it is impossible to measure sub-samples in order to detect a "hot" particle.

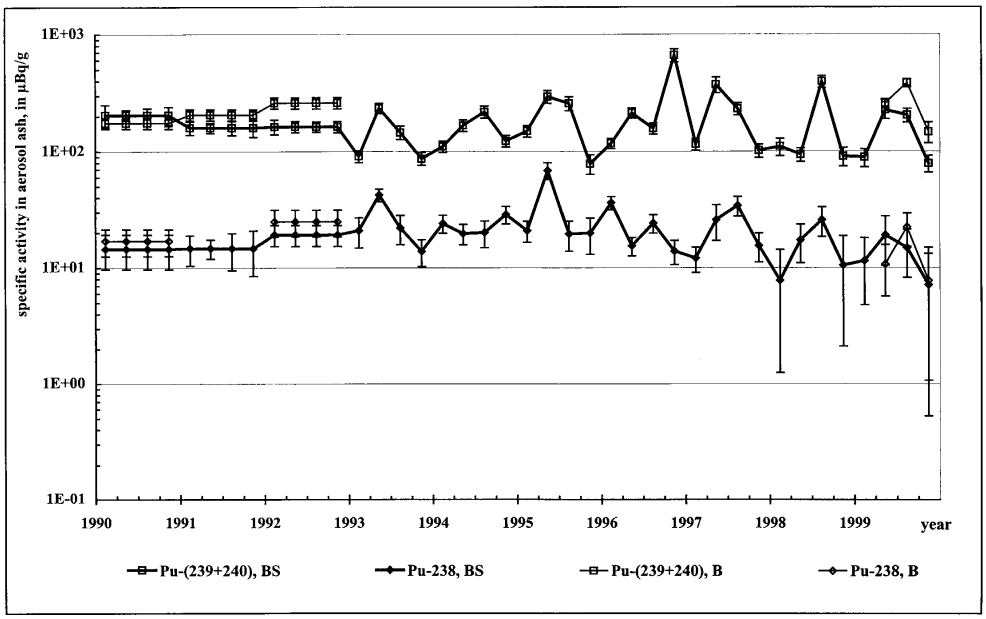

Fig. 2. Mean specific activity of ^{238}Pu, $^{(239+240)}$Pu, in ground-level aerosol ash in Braunschweig (BS) and Berlin (B) since 1990.

Discussion

The first potential source of "hot" particles is the Chernobyl fall-out deposited in Europe [1, 5, 9]. In Berlin the annual mean value of the activity ratio had increased by a factor of about 10 from 0.042 to an annual mean value of 0.43 in 1986 due to the influence of the Chernobyl reactor accident. Before 1992, the annual mean value of the ratio had remained between 0.08 and 0.10 [7]. This indicates that the probability of collecting a "hot" particle in high-volume aerosol sampling may not be negligible, especially if snow--out or rain-out events occur after prolonged periods during which dry wind from Eastern Europe prevails. We expect to observe activity ratios in samples taken in Berlin, which are higher than those of samples from Braunschweig after the LLD for the Berlin samples will have improved.

The second potential source of ^{238}Pu are discharges of nuclear fuel reprocessing plants. Although the emissions from the Western European reprocessing plants are decreasing, it is possible that marine sediment particles can get re-suspended and added to the ground-level aerosols by storms, thus adding ^{238}Pu from the "old" inventory formerly deposited in the English Channel and the North Sea.

And, last but not least, it might be possible that there are still satellite fuel particles in the environment, which stem from re-entries of ^{238}Pu-powered satellites.

A few more activity ratios a(^{238}Pu)/a($^{(239+240)}$Pu) of about 0.4 were also observed in aerosols (Spain, Poland, Czech Republic) and in a sediment of a river (Southern Germany) in recent years. However, they have not yet been published because one expects activity ratios in environmental samples, which are typical of weapons fall-out. As the interest in the radioecology of "hot" particles is increasing [10], information about potential patterns of the environmental distribution of ^{238}Pu-containing particles in Europe is helpful. Knowledge of the activity ratio a(^{238}Pu)/a($^{(239+240)}$Pu) observed in ground-level aerosols from different sites in Northern Germany was urgently required, for example, in late 1998, when potential Pu emissions from a nuclear

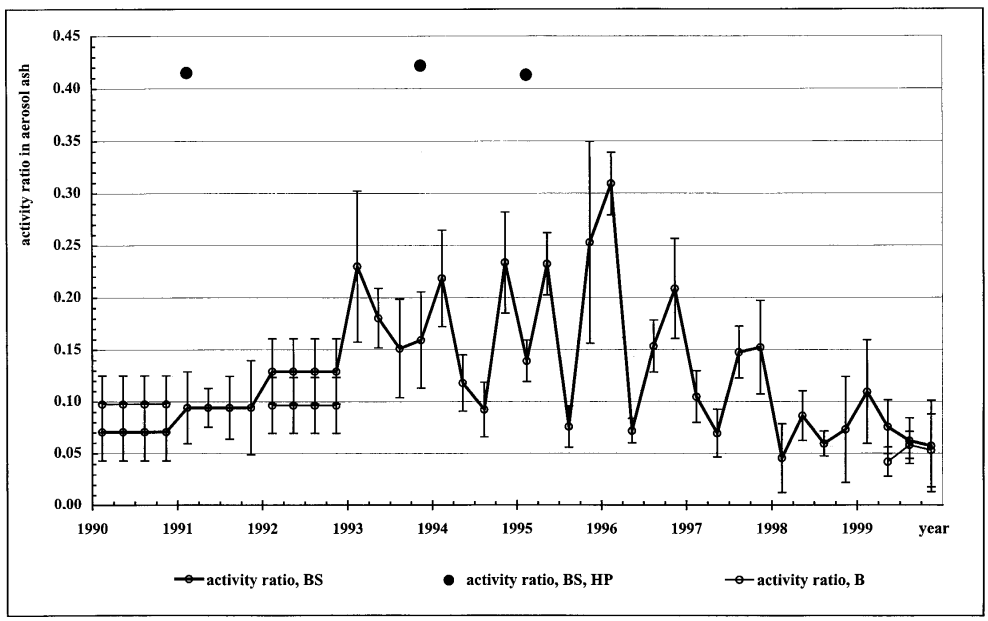

Fig. 3. The activity ratio a(^{238}Pu)/a($^{(239+240)}$Pu) in ground--level aerosol ash in Braunschweig (BS) and Berlin (B) since 1990. "HP" marking samples suspected to contain a "hot" particle.

power plant located near the city of Hamburg were controversially discussed in Germany.

In order to discriminate possible sources of ^{238}Pu, a multi-correlation analysis was performed [8], but the results for the Pu isotopes are contradictory because of the number of potential sources and the quarterly time basis necessary to collect significant ^{238}Pu activities: On the one hand, higher $a(^{238}Pu)/a(^{(239+240)}Pu)$ ratios can be observed in winter when prolonged periods with prevailing wind from the east occur in Northern Germany. But on the other hand, the conclusion can be drawn that the higher ratios are correlated with the weather conditions when the wind comes from directions around south-west. Potential sources of ^{238}Pu located in that direction are the nuclear fuel reprocessing plants operated in France and Great Britain. Plutonium ratios measured in North Sea waters by the Federal Maritime and Hydrographic Agency of Germany ("Bundesamt für Seeschifffahrt und Hydrographie", BSH) within the framework of IMIS were around unity at the beginning of the nineties and had decreased to values around 0.13 to 0.55 in 1998 [4]. It is not clear whether and to what extent the mean plutonium activity concentrations in air in Braunschweig are influenced by direct airborne contributions and/or by re-suspended intertidal sea sediment particles. As both reprocessing plants have reduced the discharges, also those to the atmosphere, for about 15 to 20 years, this might explain to some extent the decrease of the mean activity concentration of ^{238}Pu and of the activity ratio $a(^{238}Pu)/a(^{(239+240)}Pu)$ observed in the air in Braunschweig since about 1995/1996.

Conclusions

Long-term measurement series on plutonium isotopes in ground-level aerosols from Northern Germany show that the measurements today, carried out on a real "low-level" activity scale are a helpful tool to monitor the environmental plutonium contamination and to obtain information about its variation. As it is difficult to identify the potential source of ^{238}Pu, it is at present impossible to attribute the increase in the activity ratio $a(^{238}Pu)/a(^{(239+240)}Pu)$ observed in quarterly aerosol samples from Braunschweig to a certain ^{238}Pu source.

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