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Perturbation in the $^{240}Pu/^{239}Pu$ global fallout ratio in local sediments following the nuclear accidents at Thule (Greenland) and Palomares (Spain)

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Abstract

It is well established that the main source of the plutonium found in marinesediments throughout the Northern Hemisphere is global stratospheric fallout, characterized by a typical $^{240}Pu/^{239}Pu$ atom ratio of ~ 0.18. Measurement of perturbations in this ratio at various sites which had been subjected to close-in fallout, mainly from surface-based testing (e.g. Bikini Atoll, Nevada test site, Mururoa Atoll), has confirmed the feasibility of using this ratio to distinguish plutonium from different fallout sources. In the present study, the $^{240}Pu/^{239}Pu$ ratio has been examined in samples of sediment (and soil) collected at Thule (Greenland) and Palomares (Spain), where accidents involving the release and dispersion of plutonium from fractured nuclear weapons occurred in 1968 and 1966, respectively. The $^{240}Pu/^{239}Pu$ ratio was measured by high-resolution alpha spectrometry and spectral deconvolution, and confirmed in the case of the most active samples by high-resolution X-ray spectrometry. Only samples which displayed plutonium heterogeneities, i.e. hot particles or concentrations well in excess (at least two orders of magnitude) of those expected from global fallout, were selected for analysis. The analytical results showed that at Thule the mean $^{240}Pu/^{239}Pu$ atom ratio was 0.033 ± 0.004 ($n = 4$), while at Palomares the equivalent ratio appeared to be significantly higher at 0.056 ± 0.003 ($n = 4$). Both ratios are indicative of low burn-up plutonium and are consistent with those reported for weapons-grade plutonium. It is noteworthy that the mean $^{238}Pu/^{239}Pu$ activity ratio in the Thule samples, at 0.0150 ± 0.0017 ($n = 4$), was also lower than that measured in the Palomares samples, namely, 0.0275 ± 0.0012 ($n = 4$). The $^{241}Pu/^{239}Pu$ ratios were similarly different. Finally, the data show, in contrast to Palomares, that not all of the samples from the Thule accident site were contaminated with plutonium of identical isotopic composition. © 1997 Elsevier Science B.V.

Keywords: Plutonium; Marine sediments; Nuclear fallout

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1. Introduction

In January 1966, four plutonium-bearing nuclear weapons were released at an altitude of 8500 m above the Mediterranean village of Palomares (Spain) following a mid-air collision between two US aircraft, namely a B-52 bomber and a KC-135 refuelling tanker. Although two of the weapons were reported to have been recovered intact (one from the seabed in the nearby Gulf of Vera), the chemical explosive component of the other two detonated on impact on land, and plutonium and uranium were dispersed over an area of approx. 500 ha (NEA, 1981). To date, the quantity of plutonium released does not appear to have been published. However, allowing for clean-up, it has been estimated that the total residual ^{239,240}Pu inventory is in the order of 0.1 TBq (Aarkrog, 1995). A small fraction of this would appear to have found its way to the local marine environment as, recently, it has been reported that traces of plutonium of accident origin have been detected in sediments from the submarine canyon system situated south of the mouth of the (dry) Almanzora river (Romero et al., 1991). Similar traces have been found in marine algae sampled in the vicinity of Palomares (Manjón et al., 1995).

Two years later, a second B-52 bomber also carrying four plutonium-bearing weapons crashed on Arctic ice in Bylot Sound (Greenland), 11 km west of the Thule Air Base. The plane and the chemical explosive component of all four weapons exploded on impact, causing the release of kilogramme quantities of insoluble plutonium oxide to the snow-pack in the locality (Risø, 1970; Aarkrog, 1977; Facer, 1980). Although it has been estimated that ~ 90% of the plutonium was subsequently removed in the ensuing clean-up operation, residual contamination totalling an estimated 1 TBq(^{239,240}Pu) is now known to cover a seabed area in the order of 1000 km^2 (Aarkrog et al., 1984; Smith et al., 1994).

The similarities between these accidents is apparent. Both involved the dispersion of insoluble plutonium oxide from fractured nuclear weapons fabricated in the US, probably in the early- to mid-1960s (Livingston et al., 1975; Aarkrog et al., 1984; Holm et al., 1988). Both were similarly well defined in time and space. Follow-up studies by several researchers established the initial boundaries of the contamination zones at each location (Ramos and Iranzo, 1966; Aarkrog, 1971) and identified the ^{238}Pu/^{239,240}Pu ratio characteristic of each event (Aarkrog, 1971, 1977; Aarkrog et al., 1984; Romero et al., 1991). Furthermore, the presence of so-called hot particles, containing anomalously high plutonium concentrations, was confirmed in samples of seabed sediment from both locations (Risø, 1970; Aarkrog et al., 1984; Romero et al., 1991).

In this paper, we report the determination of the ^{240}Pu/^{239}Pu atom ratio by high-resolution alpha spectrometry and spectral deconvolution in a limited selection of sediment samples, each containing an undetermined number of hot particles, from the Palomares and Thule zones. The ^{238}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios at both locations are also given and comparisons made with previously published data for both sites, data for nuclear test sites and global fallout ratios for similar latitudes. Our principal objective in carrying out these measurements was to determine, with improved precision, the plutonium isotopic signature of each of these source-terms.

2. Experimental

In the present exercise, sources (discs) containing plutonium plated in the course of previous studies of sediment contamination at Palomares (C. Gascó and J. Sánchez-Cabeza, personal communications, 1994) and Thule (Aarkrog et al., 1984; Smith et al., 1994), were retrieved from our archives and re-measured by high-resolution alpha spectrometry with a PIPS detector of the highest quality (active area of 100 mm^2 and certified resolution of < 12 keV FWHM). Prior to re-measurement, plutonium was stripped from each disc and re-purified to eliminate ingrown ^{241}Am. Only discs prepared from samples which displayed plutonium heterogeneities, i.e. hot particles, or concentrations well in excess (at least two orders of magnitude) of those expected from global fallout, were selected for analysis. In the case of Palomares, two of the samples were recov-

ered in 1991 by coring from between the 6- and 8-cm sediment horizons, approximately 5 km offshore at a water depth of 44 m, while the remaining two were taken on land close to the village of Palomares from what had been one of the most heavily contaminated zones prior to clean-up. At Thule, two of the samples were taken in 1979 from the top 3 cm of the most contaminated area of the seabed, close to the original impact site, while the remainder were recovered more than a decade later between the 7- and 10-cm sediment horizons in the same area.

The complex ^{239,240}Pu multiplet was unfolded using a simple deconvolution technique based on commercially-available software (MicroSAMPO) originally developed for gamma spectrometry (Aarnio et al., 1987). Full details of the technique have been described elsewhere (León Vintró et al., 1996). Suffice, that in our approach the analytical or peak-shape function is defined (for each spectrum) by fitting a modified gaussian function with left- and right-handed exponential tails to the partially resolved ^{242}Pu doublet (used as tracer) and, if present, the ^{238}Pu doublet. The peaks so fitted are used to create an energy calibration file with which, using published energy data, the positions (in channels) of the component peaks of the ^{239,240}Pu multiplet are predicted. These positions are not altered subsequently when MicroSAMPO's interactive multiplet analysis facility is employed to quantify the relative spectral intensities of the component peaks (Fig. 1). The ^{240}Pu/^{239}Pu ratio is then readily determined from the fitted areas after applying a small correction ($\sim 1\%$) for the coincidence summing of alpha particles and conversion electrons. Although not essential, this correction leads to an improvement in the agreement between the measured alpha-emission probabilities and published values. Such agreement represents a useful test of the efficacy of the method.

In the case of the most active (> 5 Bq) samples, the ratio was confirmed by measuring the Lx/α-ray activity ratio using the method of Komura et al. (1984). Finally, the ^{241}Pu/^{239}Pu ratio was determined in most of the samples by the technique of supported-disc liquid scintillation counting (Ryan et al., 1993; Condren et al., 1996). Note that all ratios have been decay corrected to the respective accident dates.

3. Results and discussion

It has been shown that the main source of the plutonium found in marine sediments throughout the Northern Hemisphere, well removed from the influence of local sources, is global stratospheric fallout, characterized by a typical ^{240}Pu/^{239}Pu atom ratio of 0.18 ± 0.01 (Buesseler and Sholkowitz, 1987). As one might expect, this value is indistinguishable from the global fallout mean of 0.176 ± 0.014 established following a worldwide survey of terrestrial soils in 1970–1971 (Krey et al., 1976).

In contrast, the mean ^{240}Pu/^{239}Pu atom ratio observed in this study of marine sediments and soils containing hot particles sampled in the vicinity of Palomares was 0.056 ± 0.003 (Table 1), while the corresponding ratio for Thule, with one important exception, was considerably lower at 0.033 ± 0.004 (Table 2). It is noteworthy that the exception (Sample 1) gave a ratio of 0.055 ± 0.002 which, clearly, is indistinguishable from the Palomares mean. High-resolution X-ray spectrometry on this, our most active sample from Thule, provided confirmation of this result, giving 0.064 ± 0.008. A similar measurement on sediment (Sample 1) from Palomares gave an almost identical result, namely 0.054 ± 0.004. These values are in good agreement with the value of 0.058 ± 0.008 reported for a sample of sediment from Thule by Komura et al. (1984), who also used X-ray spectrometry. Somewhat lower values have been recorded in three samples from Thule by Kolb and Arnold (1993), using a similar technique (Arnold and Kolb, 1995).

Statistically, the samples from Palomares are isotopically identical, whereas this is evidently not the case at Thule. In summary, our admittedly limited data would appear to suggest that not all of the weapons involved in the Thule accident contained plutonium of identical isotopic composition. Although unlikely, we can not exclude the possibility that the isotopic homogeneity observed in the samples from Palomares is related to factors other than the isotopic composition of the

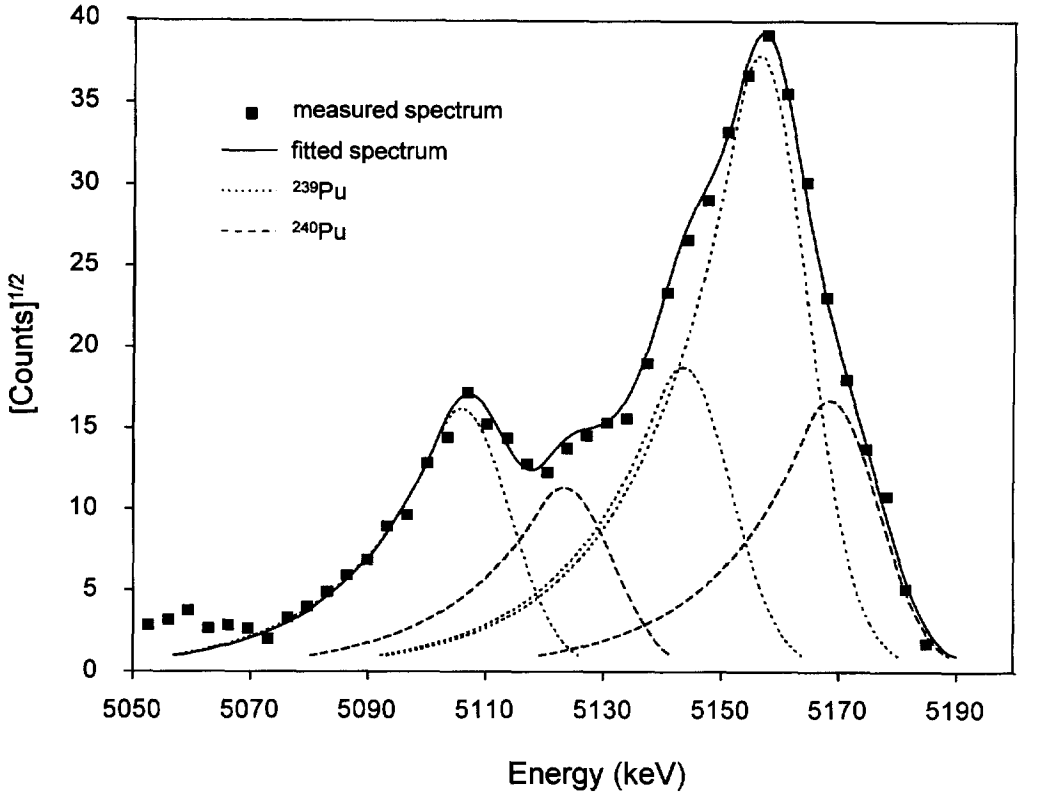

Fig. 1. Unfolding the ^{239,240}Pu multiplet. The spectrum shown is that of Sediment Sample 1 from Thule recorded at an energy dispersion of 3.4keV/channel (note that the ordinate is non-linear, being a square-root scale). The listed energies of the component peaks are 5105.5, 5123.7, 5143.8, 5156.7 and 5168.2 keV (components with relative intensities < 0.1% are not considered in the fitting).

two weapons which reportedly disintegrated on impact with the ground approximately 2.5 km apart (Iranzo et al., 1987).

Overall, our ^{240}Pu/^{239}Pu data are virtually indistinguishable from those reported for samples from low-yield nuclear weapons (and safety shots) test-sites. For example, a ^{240}Pu/^{239}Pu ratio of $\sim 0.0315 \pm 0.0004$ has been measured at Mururoa Atoll (León Vintró et al., 1996), while a mean of 0.035 has been reported for the Nevada test site (Krey et al., 1976). Similar values have been reported at former UK nuclear weapons test sites in Australia (Burns et al., 1994). Further, measurements on surface soil collected in 1979 from the Nishiyama area in Nagasaki gave a ratio of 0.042 ± 0.014 (Komura et al., 1984). The Nishiyama area had been heavily contaminated, having been subjected to 'black rain' precipitation shortly after the nuclear weapon explosion of 9 August1945. Clearly, the measured ^{240}Pu/^{239}Pu ratios are typical of much of the weapons-grade plutonium produced in western countries since the mid-1940s and are quite distinct from the global fallout ratio of ~ 0.18 (Krey et al., 1976; Buesseler and Sholkowitz, 1987).

The mean ^{238}Pu/^{239}Pu activity ratio in the Thule samples was found to be 0.0150 ± 0.0017 (Samples 2–5), while the corresponding ratio in the Palomares samples was 0.0275 ± 0.0012, in broad agreement with previously published data for both zones (Aarkrog et al., 1984; Holm et al., 1988; Romero et al., 1991). These values are clearly inferior to the cumulative (through 1971) global fallout means of 0.041 and 0.061 reported

Table 1
Plutonium isotopic ratios in contaminated Palomares sediment and soil sampled in 1991. Quoted uncertainties are 1 S.D. (reference date: 17 January 1966)

Sample coordinates	$^{239,240}Pu$ (Bq)[a]	$^{240}Pu/^{239}Pu$ atom ratio	$^{240}Pu/^{239}Pu$ activity ratio	$^{238}Pu/^{239}Pu$ activity ratio
1991				
Sediment 1 37°10′N 01°49′W	8.6	0.059 ± 0.003	0.219 ± 0.010	0.0271 ± 0.0012
Sediment 2 37°10′N 01°49′W	1.5	0.057 ± 0.002	0.209 ± 0.008	0.0266 ± 0.0010
1991				
Soil 1 37°15′N 01°52′W	7.6	0.052 ± 0.001	0.192 ± 0.004	0.0269 ± 0.0007
Soil 2 37°15′N 01°52′W	2.8	0.055 ± 0.002	0.203 ± 0.007	0.0292 ± 0.0014
Mean (n = 4)	—	0.056 ± 0.003	0.206 ± 0.011	0.0275 ± 0.0012

[a] The activity on each disc.

Table 2
Plutonium isotopic ratios in contaminated Thule sediment sampled in 1979 and 1991. Quoted uncertainties are 1 S.D. (reference date: 21 January 1968)

Sample coordinates	$^{239,240}Pu$ (Bq)[a]	$^{240}Pu/^{239}Pu$ atom ratio	$^{240}Pu/^{239}Pu$ activity ratio	$^{238}Pu/^{239}Pu$ activity ratio
1979				
Sediment 1 76°30′N 69°25′W	5.9	0.055 ± 0.002	0.202 ± 0.006	0.0248 ± 0.0007
Sediment 2 76°31′N 69°17′W	0.6	0.037 ± 0.003	0.137 ± 0.009	0.0171 ± 0.0006
1991				
Sediment 3 76°31′N 69°17′W	2.4	0.029 ± 0.001	0.107 ± 0.003	0.0131 ± 0.0004
Sediment 4 76°31′N 69°17′W	1.4	0.031 ± 0.002	0.113 ± 0.009	0.0144 ± 0.0006
Sediment 5 76°31′N 69°17′W	0.8	0.034 ± 0.001	0.125 ± 0.003	0.0155 ± 0.0006
Mean (n = 4) Samples 2–5	–	0.033 ± 0.004	0.121 ± 0.013	0.0150 ± 0.0017

[a] The activity on each disc.

for the latitude bands 70–80°N and 30–40°N, respectively (Hardy et al., 1973; Krey et al., 1976; Perkins and Thomas, 1980). Again, the $^{238}Pu/^{239}Pu$ activity ratio in the atypical sample from Thule (Sediment 1) was statistically indistinguishable from the mean Palomares ratio. Similar differences were found in the case of the $^{241}Pu/^{239}Pu$ activity ratio, where the respective means were 2.3 ± 0.9 (Thule Samples 2–5) and 6.1 ± 0.5 (Palomares Samples 1–2), with the atypical sample from Thule giving 4.1 ± 0.2.

Although small, these differences are significant and more than likely reflect variations in the conditions under which the plutonium was originally produced (type of reactor, operating history, integrated neutron flux, etc.). This may be the explanation for the considerable scatter in the values of the $^{238}Pu/^{239,240}Pu$ ratio reported by previous researchers in samples of sediment and biota from the Thule impact zone (Aarkrog, 1971, 1977; Aarkrog et al., 1984; Risø, 1988; Kolb and Arnold, 1993). Again, we stress that in each of the samples analysed in this study, the contribution from global fallout was insignificant being less, and in most cases much less, than 1%.

Finally, the mass isotopic composition of the plutonium in the samples from Palomares and Thule is given in Table 3. Note that in all cases the percentages of ^{241}Pu and ^{238}Pu are very low, being less than 0.5% and 0.01%, respectively. For comparison, data for contaminated soils at Rocky Flats, Colorado (Krey and Krajewski, 1972) and the Nevada Test Site (Krey et al., 1976), as well as for sediments from Chernaya Bay on the SW coast of Novaya Zemlya (Smith et al., 1995), have also been included.

Table 3
Mass isotopic composition of weapons-grade plutonium at Palomares and Thule

Zone	Percentage of total plutonium			
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
Palomares 1–4	0.0094	94.4	5.3	0.34
Thule 1	0.0085	94.6	5.2	0.23
Thule 2–5	0.0053	96.7	3.2	0.13
Rocky Flats	0.04	93.3	6.0	0.58
Nevada Test Site	—	93.8	6.0	0.25
Chernaya Bay	—	97.0	2.9	0.12

4. Conclusions

The mean $^{240}Pu/^{239}Pu$ ratios observed at Palomares and Thule, though distinct, are both indicative of weapons-grade plutonium. Similar observations apply to the $^{238}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios. However, in contrast to the Palomares data which showed that the samples from this zone were isotopically homogeneous, significant variations were identified in the isotopic ratios for the Thule samples. It is suggested that these can be attributed to the use of plutonium produced under different conditions in at least one of the weapons which disintegrated in the Thule accident. It is, therefore, appropriate to caution against the adoption of a 'unique' isotopic ratio when attempting to 'fingerprint' a potentially complex source-term.

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