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^{241}Am concentration and ^{241}Pu/$^{239(240)}$Pu ratios in soils contaminated by weapons-grade plutonium

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^{241}Am and $^{238,239\,(240)}$Pu concentrations have been determined in soil samples from the Atolls of Mururoa and Fagataufa as well as from Palomares for comparison. Mean activity ratios of ^{241}Am/$^{239\,(240)}$Pu for Mururoa, Fangataufa and Palomares with 0.017±0.005, 0.050±0.012 and 0.25±0.07 respectively, show, that also in the most unfavorable case the ^{241}Am contamination remains less than about one third of the $^{239\,(240)}$Pu level. The estimated isotopic composition of the different types of weapons-grade Pu based on these data suggests generally a much lower ^{241}Pu/$^{239(240)}$Pu ratio for Pu used in the first fisson bombs than for the material taken later on for construction of thermonuclear devices. ^{241}Pu/$^{239(240)}$Pu activity ratios of 0.9±0.2 have been found at the safety shot area of the Colette motu and 8.4±0.8 at Palomares, with some hints to a lower one, viz. 5.7±1.5 for at least one of the accidentally involved bombs.

Introduction

During the last few years more and additional information has been published on the radiological situation at nuclear weapon test sites including also the safety shot areas, as for the Nevada Test Site (USA)[1] and Maralinga (Australia),[2] for Semipalatinsk (Kazakhstan),[3,4] the Bikini Atoll (Marshall Islands)[5,6] and the Mururoa Atoll (French Polynesia).[7] Recently on request of the French Government the International Atomic Energy Agency (IAEA) together with an independent International Advisory Committee started such a project for the Atolls of Mururoa and Fangataufa.[8] We took part in this measurement programme, analysing $^{238,239(240)}$Pu and ^{241}Am in soils collected during a sampling campaign organized by the IAEA between July 7 and August 1, 1996. As Pu used for fabrication of nuclear weapons always contains some ^{241}Pu ($T_{1/2}$ = 14.4 y), its progeny ^{241}Am ($T_{1/2}$ = 432 y) can be used for $^{239\,(240)}$Pu monitoring of large contaminated areas by *in situ* γ-spectrometry. For interpretation of such measurements, however, a representative value of the ^{241}Am/$^{239(240)}$Pu activity ratio and a typical depth profile have to be determined. In the following we report some of our experimental results found for soil samples from different areas at the French test sites and for a few ones (n = 5) obtained from Palomares (Spain), where on January 16, 1966 after an air crash and the following explosion of a B 52 bomber nuclear weapons material was spread over an area of about 1–2 km^2. Based on these data the calculated isotopic activity ratios of ^{241}Pu/$^{239(240)}$Pu and ^{238}Pu/$^{239(240)}$Pu is compared for different nuclear devices.

Experimental

Radiochemical analysis of the soil samples was carried out on 0.2–5.0 g aliquotes of the dried material (110 °C), like coral rocks which has been dissolved completely or leached for 3 hours with 200 ml half concentrated nitric acid (7.2M). For the determination of the chemical yield ^{242}Pu and ^{244}Cm was added as a spike. This leaching solution was heated with 0.5 g $NaNO_2$ to give Pu in the Pu(IV) oxidation state and taken for separation of Pu in a first step by anionic exchange with Dowex 1X2 from 7.2M HNO_3.[9] After washing with 10M HCl to remove Th, Pu was eluted with a mixture of 0.36M HCl and 0.018M HF. This fraction was evaporated to dryness and fumed several times with HNO_3 (65%) and some drops of H_2O_2 (30%) to destroy any organic material from the resin and finally with HCl (36%). Samples suited for α-spectrometry were prepared by microprecipitation with NdF_3.[10] From the effluent solution of the first step, ^{241}Am was separated by coprecipitation with calcium oxalate at pH 3.5 and after decomposing this precipitate thermally (500 °C) or by fuming with HNO_3 (65%) purified by anionic exchange with Dowex 1X4 from 4M NH_4SCN and elution with 1M HCl.[11] Samples for α-counting were prepared in the same way as for Pu. Measurements were carried out with a silicon surface barrier detector in combination with a multichannel analyzer system (Canberra S 100) using counting times of 75,000 and 100,000 seconds. More details and our experience with this separation procedure will be published elsewhere.[12]

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Spike recoveries of 85±9% and 83±20% were obtained for Pu and Am respectively in coral rock samples from Mururoa (n=20) and of 89±6% and only 37±6% respectively for soil samples from Palomares (n=10). All determinations were performed in duplicate or triplicate together with analyses of reference materials and a chemical blank as part of the validation and quality measures. Detection limits ranged between 0.04–1.0 Bq/kg depending on the sample amounts used.

Results and discussion

Soil concentrations of ^{241}Am and $^{238,\ 239\ (240)}$Pu found for different areas at the Atolls of Mururoa and Fagataufa are given in Tables 1 and 2. The depth profile of one core taken at the Colette motu, where in the context together 4 safety shots have been carried out (the first on July, 21 1966; the last one on July, 28 1974),[13] shows that the weapon material remained in the upper surface layer. The ^{241}Am concentration reaches there 0.10 kBq/kg, whereas the $^{239\ (240)}$Pu activity amounts to 4.8±0.2 kBq/kg. Maximum values for bedrock samples from this site are reported with 2.36±0.06 and 74± 8 kBq/kg for ^{241}Am and $^{239(240)}$Pu respectively.[8] From our results a mean ^{241}Am/$^{238,239(240)}$Pu=0.017±0.005 activity ratio can be calculated (n=11). Top soil samples collected at Faucon, an area of the Mururoa Atoll situated in the south west, which was striken by the first fission bombs tested on a barge (July 2, 1966),[13] show values of 1.8–3.5 Bq/kg for ^{241}Am and 130–292 Bq/kg for $^{239\ (240)}$Pu. At Fangataufa, an other Atoll where on August 24, 1968 the first French test with a thermonuclear device was conducted, the ^{241}Am concentration in loose coral rocks was approximately in the same range as mentioned above, $^{239\ (240)}$Pu somewhat lower, viz. 20–93 Bq/kg. Therefore, the mean ^{241}Am/$^{239(240)}$Pu ratio was significantly higher with 0.050±0.012 (n=11). Quite different, however, was the ^{238}Pu/$^{239(240)}$Pu ratio. Corrected for the radioactive decay of ^{238}Pu ($T_{1/2}$=87.7 y) with reference date July, 1966 a ratio of 0.476±0.027 (n=8) occurred here, compared with only 0.007±0.002 (n=12) for the samples from Collette and Faucon at the Mururoa Atoll.

^{241}Am and $^{238,239(240)}$Pu concentrations determined in soil samples from Palomares are presented in Table 3. As seen from these results, particles of accidentally released weapons material are distributed sometimes very inhomogeneously. Samples from station 2–1, 2–2 and 3–1 have been contaminated mainly in context with the impact of 2 from 4 different bombs involved in this air crash, stations 5–1 and 5–2 are situated between these two impact points.[14] The highest concentration found in an aliquote of a sample from station 2–2, was 17±5 and 113±3 kBq/kg for ^{241}Am and $^{239(240)}$Pu respectively, most probably due to contamination of the soil with hot particles. In this case an ^{241}Am/$^{239(240)}$Pu ratio of 0.15± 0.04 was obtained. This ratio seems to be somewhat lower, than those determined from all our other analyses ranging up to 0.36±0.04, with a mean value of 0.25±0.07 (n=10). Provided there is no discrimination between Am and Pu caused by different migration behavior in soil, when weathering there nearly over 2 decades before sampled, this can be seen as a hint, that the weapons Pu used for manufacturing these 4 bombs was not always of the same origin. The ^{238}Pu/$^{239(240)}$Pu ratio back dated to January 16, 1966 was 0.023±0.003 and agrees with published values about the US bomb material.[15]

Table 1. ^{241}Am and $^{238,239(240)}$Pu concentrations in soil from the Atoll of Mururoa (French Polynesia)

Location	Sample Code	Aliquot, g	Activity concentration,[8] Bq/kg±1 σ ^{241}Am	$^{239(240)}$Pu	^{238}Pu	Activity ratio, ×100 ^{241}Am/$^{239(240)}$Pu	^{238}Pu/$^{239(240)}$Pu
Colette depth profile: (coral bedrock)	0–1 cm	5.0	100.1 ± 5.1	4814 ± 225	27.8 ± 6.7	2.08 ± 0.14	0.58 ± 0.14
			102.7 ± 6.2	4184 ± 194	22.3 ± 4.8	2.45 ± 0.19	0.53 ± 0.12
	1–2 cm		9.23 ± 0.63	540 ± 34	2.52 ± 1.27	1.71 ± 0.16	0.47 ± 0.24
			8.09 ± 0.61	525 ± 27	3.89 ± 1.24	1.54 ± 0.14	0.74 ± 0.24
	2–16 cm		1.71 ± 0.22	134 ± 5	0.60 ± 0.20	1.28 ± 0.17	0.45 ± 0.15
			2.55 ± 0.27	95 ± 4	0.89 ± 0.27	2.67 ± 0.30	0.93 ± 0.28
Faucon (top soil)	9.3.6	5.0	3.01 ± 0.21	222 ± 9	0.92 ± 0.16	1.36 ± 0.11	0.42 ± 0.07
			3.50 ± 0.24	258 ± 11	0.93 ± 0.16	1.36 ± 0.11	0.36 ± 0.06
	9.3.18		1.80 ± 0.20	133 ± 6	0.49 ± 0.12	1.36 ± 0.16	0.37 ± 0.09
			2.50 ± 0.20	130 ± 6	0.79 ± 0.17	1.92 ± 0.18	0.61 ± 0.13
	9.3.25		2.70 ± 0.40	292 ± 15	1.26 ± 0.16	0.92 ± 0.14	0.43 ± 0.06
			–	265 ± 13	1.42 ± 0.19	–	0.54 ± 0.08
Arithmetic mean (reference date 1997 04 30):						1.69 ± 0.51	0.54 ± 0.16

Table 2. ^{241}Am and $^{238,239(240)}$Pu concentrations in soil from the Atoll of Fangataufa (French Polynesia)

Location	Sample Code	Aliquot, g	Activity concentration,[8] Bq/kg±1 σ ^{241}Am	$^{239(240)}$Pu	^{238}Pu	Activity ratio, ×100 ^{241}Am/$^{239(240)}$Pu	^{238}Pu/$^{239(240)}$Pu
Kilo	11.5.1						
depth profile:	0–1 cm	5.0	0.49 ± 0.15	11.6 ± 0.5	2.82 ± 0.18	4.2 ± 1.3	24.6 ± 1.9
coral bedrock			0.69 ± 0.16	12.8 ± 0.5	3.21 ± 0.21	5.4 ± 1.3	25.1 ± 1.9
	1–2 cm		≤0.10	0.60 ± 0.09	0.11 ± 0.04	–	18.3 ± 7.2
			≤0.10	0.96 ± 0.11	0.13 ± 0.04	–	13.5 ± 4.4
	2–10 cm		0.16 ± 0.13	4.29 ± 0.25	0.97 ± 0.11	3.7 ± 3.0	22.6 ± 2.9
			≤0.10	3.70 ± 0.22	0.89 ± 0.10	–	24.1 ± 3.1
Loose	11.4.1	5.0	1.84 ± 0.19	48.2 ± 1.4	17.8 ± 0.6	3.8 ± 0.4	36.9 ± 1.7
coral rocks			2.03 ± 0.15	43.2 ± 1.4	15.0 ± 0.6	4.7 ± 0.4	34.7 ± 1.7
	11.4.2		1.20 ± 0.17	21.4 ± 0.7	9.0 ± 0.4	5.8 ± 0.8	42.0 ± 2.3
			0.89 ± 0.10	22.5 ± 0.8	8.0 ± 0.3	4.9 ± 0.6	35.6 ± 1.8
	11.4.3		1.37 ± 0.13	20.8 ± 0.6	7.8 ± 0.4	6.6 ± 0.7	37.5 ± 2.2
			0.86 ± 0.12	20.3 ± 0.8	7.6 ± 0.4	4.2 ± 0.6	37.6 ± 2.4
	11.4.4		3.87 ± 0.23	92.7 ± 2.3	35.6 ± 0.9	4.2 ± 0.3	38.4 ± 1.4
			6.39 ± 0.46	83.0 ± 2.5	31.9 ± 1.1	7.7 ± 0.6	38.4 ± 1.8
Arithmetic mean (reference date 1997 04 30):						5.0 ± 1.2	30.7 ± 8.6

Table 3. ^{241}Am and $^{238,239(240)}$Pu concentrations in soil from Palomares (Spain)

Location	Sample Code	Aliquot, g	Activity concentration, Bq/kg±1 σ ^{241}Am	$^{239(240)}$Pu	^{238}Pu	Activity ratio, ×100 ^{241}Am/$^{239(240)}$Pu	^{238}Pu/$^{239(240)}$Pu
Station	2–1	1.0161	23.4 ± 2.0	124.2 ± 5.3	2.2 ± 0.4	18.8 ± 2.0	1.77 ± 0.33
		1.1037	55.0 ± 4.1	–	–	–	–
	2–2	0.5536	17 100 ± 4 500	112 900 ± 2 600	1700 ± 100	15.1 ± 4.0	1.50 ± 0.09
		0.1665	133 ± 13	394 ± 14	8.3 ± 1.5	33.8 ± 4.0	2.10 ± 0.38
		0.2330	92 ± 9	257 ± 10	3.9 ± 0.7	35.8 ± 4.0	1.52 ± 0.28
	3–1	0.4903	105 ± 8	474 ± 15	8.7 ± 0.9	22.2 ± 2.0	1.84 ± 0.20
		0.2214	103 ± 9	463 ± 17	8.9 ± 1.3	22.2 ± 2.0	1.92 ± 0.29
	5–1	1.1167	9.2 ± 1.2	46.0 ± 1.9	1.1 ± 0.2	20.0 ± 3.0	2.40 ± 0.45
		1.9203	16.2 ± 1.3	58.6 ± 2.1	1.0 ± 0.2	27.6 ± 2.0	1.70 ± 0.35
	5–2	1.1420	6.0 ± 0.8	30.2 ± 1.4	0.50 ± 0.10	19.9 ± 3.0	1.66 ± 0.34
		1.8783	17.6 ± 1.4	50.1 ± 1.8	0.88 ± 0.13	35.1 ± 3.0	1.76 ± 0.28
Arithmetic mean (reference date 1997 03 30):						25.1 ± 7.0	1.82 ± 0.26

Based on the experimentally determined ^{241}Am/$^{239(240)}$Pu ratios also the original ^{241}Pu/$^{239(240)}$Pu activity ratios can be calculated according to the radioactive decay equation of a short living mother- and a long living daugther-nuclide by the formula:

$$(^{241}\text{Pu}/^{239(240)}\text{Pu}) = (^{241}\text{Am}_t/^{239(240)}\text{Pu}) \cdot (432/14.4) \cdot f_{corr}$$

with: $1/f_{corr} = 1 - e^{-\ln 2 \cdot (t/14.4)}$

as correction factor for the incompletelly ingrown ^{241}Am after a period of t years since plutonium production. For Palomares such ratios varied between 5.7±1.5 for the hot particle contamination at station 2–2 and 14.0±1.5 at the same station, with an over all mean of 9.6±2.7 referred to the year 1966. The most reliable value, however, was 8.4±0.8 at station 3–1. Assumed that the Pu production for these weapons took place more likely in the early sixties (1960), the ^{241}Pu/$^{239(240)}$Pu activity ratio was originally 5.4±1.4 (station 2–2) and 7.9±0.7 (station 3–1). Similar results can be derived from sediment analyses measuring ^{241}Pu directly by liquid scintillation counting. ROMERO et al.[16] reported a ratio of 1.42±0.46 (reference date 1989) for hot spots in sediments of the Almanzora river mouth and from marine sediments off shore near Palomares a ratio of 2.6±0.5 (August, 1993) has been obtained.[17]

Table 4. Activity ratios of $^{241}Pu/^{239\,(240)}Pu$ in different nuclear weapons devices

Location	Date	$^{241}Pu/^{239\,(240)}Pu$ ratio	Remarks	Reference
Safety trials:				
Nevada Test Site (USA)	1956–1957[13]	4.3–7.5	Thermonuclear devices	FONG and ALVAREZ[1]
Emu	1953 10 14/26[13]	0.75–0.90	Totem 1 and 2	JOHNSTON et al.[23]
Maralinga (Australia)	1960–1963	0.95	Tadje (main test site)	JOHNSTON et al.[2]
Mururoa (French Polynesia)	1974 07 01/28[13]	0.9±0.2	Colette motu	This work
Pu fission bombs:				
Nagasaki (Japan)	1945 08 09	1.5±0.1	^{241}Am measured	YAMAMOTO et al.[22]
Nishiyama area		2.2±0.5	^{241}Pu directly	
Semipalatinsk (Former Soviet Union)	1949 08 29	1.52±0.04	^{241}Pu directly	YAMAMOTO et al.[3]
Accidents with thermonuclear devices:				
Palomares	1966 01 16	8.2±0.8	($^{241}Pu/^{239}Pu$)	GASCÓ et al.[21]
		8.4±0.8		This work
		5.7±1.5	Hot particles	This work
Thule	1968 01 21	4.2±0.5		LIVINGSTONE et al.[18]
		3.3±0.4		AARKROG et al.[19]

The lower value, perhaps for one of the bombs, can be compared with a ratio of about 4.2 found at Thule,[18–20] where on January 21, 1967 also an aircraft accident occurred with thermonuclear devices from the USA. The higher ratio confirms earlier findings, by e.g., GASCÓ et al.[21] and agrees with data about the isotopic composition of weapons plutonium manufactured in Rock Flats given by KREY and KRAJEWSKY.[15] Looking to ^{241}Am and $^{239(240)}Pu$ contaminations of the safety shot areas at Nevada Test Site, however, two typical $^{241}Pu/^{239(240)}Pu$ activity ratios of about 4.3 and 7.5 can be expected for the weapons material used in thermonuclear devices of the US bombs.[1] At contrary the first fission bombs generally showed much lower ratios. Samples from Nishiyama area,[22] which was contaminated by debris of the first plutonium bomb dropped on Nagasaki (August 9, 1945) suggest a ratio of 1.5±0.1, exactly the same as observed for Pu applied in the first Soviet test at Semipalatinsk (August 29, 1948).[3] The $^{241}Pu/^{239(240)}Pu$ activity ratios estimated from our investigations on the Mururoa and Fagataufa samples are compared in Table 4 with data derived from different studies about nuclear test sites published in the literature. From the safety trials at Colette motu a ratio of 0.9±0.2 (ref. 1966) can be estimated for the material used in the first French nuclear weapons experiments. This agrees also with values of 0.75–0.9 at Emu – Totem 1 and 2 experiments[23] in Oct., 1953 – and of 0.95 occuring at Maralinga (Taranaki), where such safety tests have been performed between 1960–1963 by the UK Atomic Weapons Research Establishment.[2] With the further development of the weapons technology and enhanced production of fusion bombs, obviously the Pu material need not necessarily achieve those high purity standards with regard to the isotopic Pu composition as at the beginning. ^{241}Am contaminations due to nuclear weapons tests always remain below about one third of the $^{239(240)}Pu$ levels, also in the case of higher activity ratios of $^{241}Pu/^{239(240)}Pu$ and accidents with such devices. From a radiological point of view the ^{241}Am concentration in surface soil can be rather ignored, whilst $^{239(240)}Pu$ must be seen as a serious contaminant, which has to be removed very often by expensive cleanup operations.

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