Particulate plutonium and americium in Mediterranean surface waters

Plutonium
Americium
Particulate Matter
Terrigenous particle
Biogenic particle
Mediterranean Sea
Plutonium
Americium
Phase particulaire
Particule d'origine terrigène
Particule d'origine biogénique
Mer Méditerranée

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ABSTRACT

Concentrations of ^{238}Pu, $^{239+240}Pu$ and ^{241}Am have been determined on particulate matter collected by filtering through 1.7-7.7 kl of Mediterranean surface water. The results show, on an average, that 3.8 ± 0.7, 2.5 ± 0.6 and $10 \pm 3\%$ of $^{239+240}Pu$, ^{238}Pu and ^{241}Am are respectively retained by the filters. On the basis of $^{241}Am/^{239+240}Pu$ activity ratios in water and particulate, it is estimated that the particles are enriched in ^{241}Am relative to plutonium by a factor of approximately 3 over the water. A possible role played by particles of biogenic and non-biogenic origins in the fractionation between plutonium and americium in the surface layer of the Mediterranean is discussed.

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RÉSUMÉ

État particulaire du plutonium et de l'américium dans les eaux de surface de la Méditerranée

Les concentrations de ^{238}Pu, $^{239+240}Pu$ et ^{241}Am ont été déterminées sur des échantillons de matières en suspension, obtenus par la filtration de 1,7-7,7 kl d'eau de surface en mer Méditerranée. Les résultats montrent, dans l'ensemble, que $3,8 \pm 0,7$, $2,5 \pm 0,6$ et $10 \pm 3\%$ de $^{239+240}Pu$, ^{238}Pu et ^{241}Am sont retenus respectivement sur les filtres. Sur la base des rapports d'activité $^{241}Am/^{239+240}Pu$ dans l'eau et les particules, on peut estimer que les matières en suspension sont enrichies en ^{241}Am d'un facteur 3 environ par comparaison au plutonium et ceci par rapport à l'eau de mer. Le rôle que peuvent jouer les particules d'origine biogénique et non biogénique dans la séparation entre le plutonium et l'américium dans la couche de surface en mer Méditerranée est envisagé.

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INTRODUCTION

The partition of transuranic elements between soluble and particulate phases strongly influences their vertical transport to depth (Noshkin, Bowen, 1973) as well as their behaviour in marine ecosystems (Fowler *et al.*, 1975; Beasley, Fowler, 1976). Whereas the levels and distribution of transuranic elements in unfiltered sea water from the Atlantic and Pacific have been extensively studied (Bowen *et al.*, 1971; Livingston, Bowen, 1976; Miyake, Sugimura, 1976), only a few data are available on transuranics in the particulate fraction in sea water. While Bowen (1975) has reported that $\simeq 70\%$ of the $^{239+240}Pu$ activity in open ocean water samples is retained by 0.45 µm Millipore filters, Krishnaswami *et al.* (1976 *a*, 1976 *b*) using filters, whose efficiency was some 80% of that of 0.45 µm Millipore filters, found that only 1-15% of the $^{239+240}Pu$ in surface samples from the Atlantic and Pacific were retained by filtration.

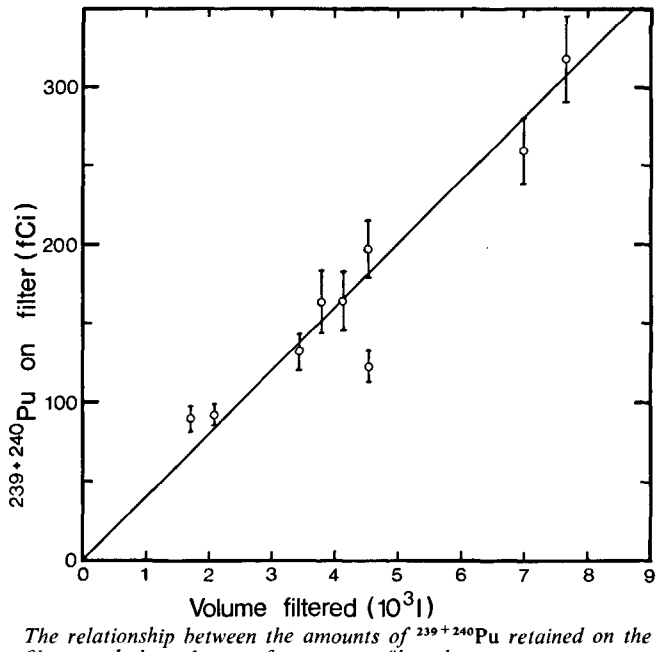
The $^{241}Am/^{239+240}Pu$ activity ratio in global integrated fallout was estimated from soil measurements to be 0.22 in 1974 (Krey *et al.*, 1976). By contrast, the ratios in unfiltered surface water from the Mediterranean (0.06) (Fukai *et al.*, 1976) differ markedly from this value. Since the $^{241}Am/^{239+240}Pu$ activity ratio in the fallout

inventory is expected to increase with time till year 2037 due to the *in situ* decay of ^{241}Pu (half-life: 14.8 years) to ^{241}Am (half-life: 433 years), the lower ^{241}Am/$^{239+240}$Pu activity ratio observed in the surface Mediterranean indicates that ^{241}Am fractionates from $^{239+240}$Pu in surface waters. Fractionation was suggested to take place in the Mediterranean based on the measurements of the transuranics in sediments (Livingston *et al.*, 1977) and was confirmed by a depth profile of transuranics in the northwestern Mediterranean (Fukai *et al.*, 1979). The mechanism of the fractionation, however, is not known.

We report here the results of the ^{238}Pu, $^{239+240}$Pu and ^{241}Am measurements on particulate matter from surface waters of the Mediterranean, showing that the particulate matter is significantly enriched in ^{241}Am compared with $^{239+240}$Pu. Possible mechanisms of the fractionation between plutonium and americium in the surface Mediterranean are discussed in relation to the association of these elements with particulates.

MATERIAL AND METHODS

During 1975, samples of unfiltered surface sea water (≃ 200 l) were collected from the western and Tyrrhenian basins in the Mediterranean and measured for transuranic nuclides (Fukai *et al.*, 1976). At the same time, 1.7-7.7 kl of surface water were filtered through 0.45 µm Millipore filters using a large volume filtering apparatus described by Silker (1975), but without the sorption beds. Following gradual incineration of the filters and successive leaching of the residue with aqua regia, the leachate was analyzed for ^{238}Pu, $^{239+240}$Pu and ^{241}Am as previously described (Ballestra *et al.*, 1978). Since more than 1 year elapsed between sample collection and analysis, the ^{241}Am results were corrected for ingrowth from the decay of ^{241}Pu during storage, using a ^{241}Pu/$^{239+240}$Pu activity ratio of 7.0, i.e. the ratio for integrated global fallout (Holm, Persson, 1977).



The relationship between the amounts of $^{239+240}$Pu retained on the filters and the volumes of sea water filtered.

The linear relationship between the $^{239+240}$Pu on the filters and the volume of water filtered shown in the Figure indicates that the efficiency of the filtering system was invariant with the volume of water filtered and that the particulate fraction of $^{239+240}$Pu was rather homogeneously distributed in the area sampled. The observed linearity of filtering efficiency may, however, not apply to filtration of more turbid water or a larger volume-range filtration.

The analytical quality of the data presented was tested repeatedly during the study by analyzing the reference samples such as SW-A-1 (Sargasso Sea water), SW-I-3 (Irish Sea water), SD-B-3 (Bombay sediment), etc., which are available at the IAEA Monaco Laboratory. On the basis of these data the errors in measurement are estimated to be within ± 20% range. In order to obtain

Table 1
Plutonium and americium in Mediterranean surface waters retained by 0.45 µm filters.

Station No.	Position	Date of collection	Volume of sea water filtered (kl)	$^{239+240}$Pu (aCi/l) (*)	$^{239+240}$Pu (% on filter)	^{238}Pu (aCi/l) (*)	^{238}Pu (% on filter)	^{241}Am (aCi/l) (*)	^{241}Am (% on filter)
0	43°11'N, 06°32'E	14 September 1975	4.54	43 ± 4	4.5	1.5 ± 0.3	1.5	4.2 ± 0.8	12
1	42°30'N, 06°30'E	14 September 1975	3.79	44 ± 5	4.3 (***)	1.8 ± 0.3	2.6 (***)	4.8 ± 0.8	8.4 (***)
2	41°30'N, 06°30'E	15 September 1975	4.54	27 ± 2	2.6 (***)	1.3 ± 0.2	1.9 (***)	4.8 ± 0.9	8.4 (***)
3	40°30'N, 06°30'E	16 September 1975	7.00	37 ± 3	3.6 (***)	1.6 ± 0.2	2.4 (***)	3.4 ± 1.0	6.0 (***)
7	37°30'N, 11°00'E	20 September 1975	3.44	39 ± 3	3.5	1.4 ± 0.3	2.5	5.7 ± 0.8	10 (***)
8	38°40'N, 12°00'E	20 September 1975	2.35	35 ± 2	3.4	1.4 ± 0.3	2.8	7.2 ± 0.8	14
9	40°40'N, 11°40'E	20 September 1975	7.68	41 ± 3	3.8	1.7 ± 0.3	3.4	3.4 ± 0.7	4.9
13	42°47'N, 09°25'E	21 September 1975	4.15	40 ± 5	3.6	1.9 ± 0.5	3.2	4.4 ± 1.1	15
14	43°55'N, 09°00'E	22 September 1975	1.70	53 ± 5	4.8	2.0 ± 0.7	2.0	–	–
		Average (**)		40 ± 7	3.8 ± 0.7	1.6 ± 0.2	2.5 ± 0.6	4.7 ± 1.2	10 ± 3

(*) In terms of attocuries (10^{-18} Ci) per litre with 1σ propagated errors.
(**) Uncertainties are given in 1σ standard deviations.
(***) Values for unfiltered sea water were not available. Calculated on the basis of average concentrations in unfiltered water: $^{239+240}$Pu, 1.03 ± 0.05 fCi/l; ^{238}Pu, 0.068 ± 0.007 fCi/l; ^{241}Am, 0.057 ± 0.007 fCi/l (fCi = 10^{-15}Ci; Fukai *et al.*, 1976)

meaningful data for interpreting low-level transuranic behaviour in the environment, our experience shows that constant intra-laboratory analytical quality control is essential. The effort spent in the control measurements on reference samples is always offset by the quality of the environmental data, on which the accuracy of the interpretation depends.

RESULTS AND DISCUSSION

Concentrations of particulate $^{239+240}$Pu, ^{238}Pu and ^{241}Am in Mediterranean surface waters are set out in Table 1, as are the percentages of the particulate fraction to the total amounts present in unfiltered water. These percentages were computed using total unfiltered sea water concentrations (Fukai *et al.*, 1976) for each radionuclide in samples collected at the same time and geographical position. As shown in Table 1, the values of $^{239+240}$Pu or ^{241}Am in unfiltered sea water for three or four stations out of nine are missing. In these cases the average concentrations of these radionuclides in the area under study were used for the computations. The table shows, on the average, that 3.8, 2.5 and 10% of the $^{239+240}$Pu, ^{238}Pu and ^{241}Am are respectively retained by the filters. Judging from the standard deviations associated with the average values, the differences in the percentages for $^{239+240}$Pu and ^{238}Pu are not significant, despite the fact that ^{238}Pu was introduced into the ocean both from the nuclear weapons tests and from the stratospheric injection by the accidental burn-up of the satellite SNAP-9A in 1964 (Hardy *et al.*, 1973). By contrast, the percentage of ^{241}Am retained by the filters is consistently higher than for plutonium isotopes. Clearly, americium associates with particulate matter more than does plutonium. In Table 2, the ^{241}Am/$^{239+240}$Pu activity ratios in the water (based on the data for unfiltered sea water minus those for particulate matter) are compared with those in the particulate fraction. As expected from the data presented in Table 1, the ^{241}Am/$^{239+240}$Pu activity ratios in the particulate fraction are considerably higher than those in the water. Using average values in Table 2, we estimate that the particulates are enriched in ^{241}Am relative to plutonium by a factor of approximately 3 over the water.

Results obtained on particulate $^{239+240}$Pu and ^{241}Am in various regions by different investigators are compared in Table 3 with the present work. The comparisons show that the percentages of particulate $^{239+240}$Pu and ^{241}Am in the surface Mediterranean agree reasonably well with the Pu-range given by Krishnaswami *et al.* (1976 *a*), while they tend to be lower than other values. The values presented in this work indicate that a relatively large fraction of plutonium, and possibly also americium, remains in the solution, at least, in the surface layers of the Mediterranean Sea.

To explain the reason for the fractionation between plutonium and americium in the Mediterranean water column, Livingston *et al.* (1977) postulated that the inorganic component of the Mediterranean particle population is much higher than in the Atlantic, and that these inorganic particles preferentially retain americium over plutonium, leading to greater vertical transport of americium. Since, generally speaking, biological productivity is observed to be low (Brouardel, Rink, 1956) and terrigenous detritus tends to be high (Emelyanov, Shimkus, 1972) in Mediterranean waters, our finding of relative enrichment of ^{241}Am in particulate matter from these waters supports the above hypothesis, if the affinity of ^{241}Am to associate itself with terrigenous

Table 2
^{241}Am/$^{239+240}$Pu *activity ratios in surface Mediterranean.*

Station No.	(^{241}Am/$^{239+240}$Pu) × 100 (*)	
	Water (**)	Particulates
0	3 ± 1	10 ± 2
1	–	11 ± 2
2	–	18 ± 4
3	–	9 ± 3
7	–	15 ± 2
8	4 ± 2	21 ± 3
9	6 ± 2	8 ± 2
13	3 ± 1	11 ± 3
14	4 ± 1	–
Average (***)	4 ± 1	13 + 5

(*) Uncertainties are given in 1 σ propagated errors.
(**) Computations were made based on the data on unfiltered water minus those on particulate matter.
(***) Uncertainties are given in 1 σ standard deviations.

Table 3
Particulate $^{239+240}$Pu *and* ^{241}Am *in surface water from different regions.*

Region	Concentration in unfiltered sea water		Particulate fraction (> 0.45 μm)		Reference
	$^{239+240}$Pu (*) (fCi/l)	^{241}Am (*) (fCi/l)	$^{239+240}$Pu (%)	^{241}Am (%)	
Open Ocean (****)	≃ 1	0.05-0.3	≃ 70	–	Bowen (1975)
Bikini Atoll	50	30	≃ 40	≃ 90	Nevissi, Schell (1975)
Lake Michigan	0,6	0.02	5-40	–	Wahlgren, Marshall (1975)
Irish Sea	100	70	≃ 30 (**)	–	Hetherington *et al.* (1976)
Atlantic Ocean	–	–	(1-15) (***)	–	Krishnaswami *et al.* (1976 *a*)
Irish Sea	2 400	1 700	36 (**)	80 (**)	Hetherington, Harvey (1978)
	20	15	36 (**)	52 (**)	
Mediterranean Sea	1	0.06	4	10	This work

(*) fCi = 10^{-15} Ci.
(**) 0.22 μm filters were used.
(***) Based on Bowen's value. TAMIL cotton-fibre filters were used.
(****) Location not specified.

detritus is actually higher than that of plutonium and the sinking rates of the americium-bearing particles are faster than plutonium-bearing particles, the majority of which may possibly be biogenic.

In laboratory experiments with ^{237}Pu, Murray and Fukai (1975) showed that the particulate formation of hexavalent plutonium in sea water (30% at pH 8) is much less than either quadrivalent plutonium or trivalent americium (> 90% at pH 8). Hetherington *et al.* (1975) found that the "soluble" plutonium (that which passes a 0.22 μm Millipore filter) behaves in a more or less conservative manner like ^{137}Cs in the Irish Sea. Lovett and Nelson (1978) stated that the soluble plutonium in Lake Michigan is predominantly hexavalent (75%). They also measured the *in situ* distribution coefficients of plutonium and americium between particulates and Irish Sea water, giving the values of $\simeq 10^5$ and 10^6, respectively. These results suggest that a major portion of the "soluble" plutonium in sea water, at least that originated from the Windscale reprocessing plant, occurs in hexavalent form, while americium is considered to be in trivalent form. If this is the case also for the fallout transuranics, the difference in the oxidation state must substantially influence the fractionation between plutonium and americium in the sea water medium.

As the particulate matter on the filters was not analyzed for the ratio of biogenic to terrigenic matter in the present work, we cannot conclusively state that ^{241}Am is preferentially enriched in one or the other. Thus, it appears that defining the composition of the particulate matter as well as determining relative enrichment of transuranics in particulates are key factors for understanding transuranic element behaviour in the oceans.

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