Plutonium
Americium
Activity ratio
Water column
Vertical transport
Mediterranean Sea
Plutonium
Americium
Rapport d'activité
Colonne d'eau
Mouvement vertical
Mer Méditerranée

A note on vertical distribution of plutonium and americium in the Mediterranean Sea

R. Fukai, E. Holm *, S. Ballestra
International Laboratory of Marine Radioactivity. IAEA. Musee Oceanographique. Principality of Monaco
* Present address: Department of Radiation Physics, University of Lund, Lund, Sweden.

Received 11/4/78, in revised form 23/11/78, accepted 28/11/78.

ABSTRACT

The results are presented of ^{137}Cs, ^{238}Pu, $^{239+240}Pu$ and ^{241}Am measurements on a series of water samples taken from a depth profile (0-2 000 m) in the Mediterranean. The data show that the transuranics are vertically transported faster compared with ^{137}Cs in the upper few hundred meters of the Mediterranean under study and the rate of the vertical transport of ^{241}Am is more rapid than that of the plutonium isotopes.

Oceanol. Acta, 1979, **2**, 2, 129-132.

RÉSUMÉ

Note sur la distribution verticale du plutonium et de l'americium en Mer Méditerranée

Les résultats des analyses de ^{137}Cs, ^{238}Pu, $^{239+240}Pu$ et ^{241}Am sur une série d'échantillons d'eau d'un profil (0-2 000 m) en Mer Méditerranée sont présentés. Sur la base des résultats obtenus, les transuraniens sont transportés verticalement plus rapidement que ^{137}Cs dans les premières centaines de mètres de la colonne d'eau et la vitesse du transport vertical de ^{241}Am est plus rapide que celles de ^{238}Pu et $^{239+240}Pu$.

Oceanol. Acta, 1979, **2**, 2, 129-132.

INTRODUCTION

The pattern of vertical distribution of plutonium and americium isotopes in the sea gives information not only on their behaviour in the marine environment but also on the processes of vertical material transport through the water column. Unlike natural α-emitters the major source of plutonium in the oceans is radioactive fallout, and its latitudinal and yearly delivery has been well documented (Hardy *et al.*, 1973; Krey *et al.*, 1976). This makes it possible to use highly reactive plutonium and americium isotopes for tracing the behaviour of the associated particulate matter, both organic and inorganic, from the surface to the bottom of the oceans.

The Mediterranean is closely surrounded by land and generally characterized by low precipitation, high evaporation, low tide and low productivity. Biogeochemical processes prevailing in such a special sea area are considered to be quite different from those in the open oceans. Even within the Mediterranean different local hydrographical conditions make it difficult to generalize observations from one area to another.

While the vertical distribution of plutonium isotopes in the water column has been studied in the Atlantic (Bowen *et al.*, 1971), the Pacific (Livingston, Bowen, 1976; Miyake, Sugimura, 1976) and the Mediterranean (Noshkin, Bowen, 1973; Murray, Fukai, 1978), only a few such studies on americium have been made to date, e.g., in the Atlantic (Livingston *et al.*, 1975) and in the Pacific (Livingston, Bowen, 1976). This paper presents the results of measurements on ^{238}Pu, $^{239+240}Pu$ and ^{241}Am on a series of water samples taken from a depth profile off Monaco in the Mediterranean.

MATERIAL AND METHODS

A series of 200 l water samples was collected at a station located offshore Monaco (43°32'N, 07°32'E) from 9 dif-

ferent depths between surface and 2000 m in August 1976. Using 30 l Niskin sampling bottles, several casts for one depth were necessary to acquire a sufficient volume of water for each analysis. The detailed analytical procedures employed for plutonium and americium measurements have been described elsewhere (Ballestra *et al.*, 1976). Briefly, plutonium and americium were coprecipitated with mixed hydroxides and carbonates of calcium and magnesium from unfiltered seawater; a second coprecipitation was made by scavenging the actinides with ~ 100 mg Fe^{3+}. The separation of iron from the actinides as well as americium from plutonium was achieved by sorption on an anion-exchange column and successive differential elution with changing acid eluents. The separated americium was purified of interferring α-emitters by solvent extraction with HDEHP (di-2-ethylhexyl phosphoric acid)-heptane followed by anion exchange in the nitric acid-methanol medium (Holm, Fukai, 1976). The separated and purified plutonium and americium were respectively electrodeposited onto stainless steel discs and α-spectrometrically determined with a silicon surface barrier detector. In any case, the measurements were completed within 4 months of the sampling date, so that the correction for build-up of ^{241}Am from ^{241}Pu decay during sample storage was negligible, taking into account the ^{241}Pu/$^{239+240}$Pu activity ratio in the fallout delivery (Holm, Persson, 1977).

RESULTS AND DISCUSSION

The results of the determination of ^{238}Pu, $^{239+240}$Pu and ^{241}Am are given in Table 1, along with the chlorinity and ^{137}Cs values. The data show that a subsurface concentration maximum exists either for $^{239+240}$Pu or ^{238}Pu between 100-250 m, although the uncertainties of the measurements mask the variation of ^{238}Pu below 500 m. In any case, the concentrations of both ^{238}Pu and $^{239+240}$Pu in the upper 250 m tend to be higher than those below 1000 m. This vertical distribution pattern of plutonium is different from that observed in 1973-1974 at the stations located south of the present station, where concentrations of $^{239+240}$Pu as high as those at the surface were found at 2000 m depth (Murray, Fukai, 1978). These high $^{239+240}$Pu concentrations in deep layers were attributed to the intermittent winter sinking of surface water, which is known to take place in the northwestern part of the Mediterranean (Lacombe, Tchernia, 1972; Stanley *et al.*, 1972). Since the present station is located further north than the previous station, the effect of such vertical water movement is considered to be less at this station than that of the previous station. This is supported by the appearance of a chlorinity maximum at this station around 500 m depth, which represents the core of the Levantine intermediate water, as well as the steady decrease of ^{137}Cs between 100 and 1000 m.

The above-mentioned vertical distribution of plutonium at the present station suggests that, whatever the mechanism, the rate of vertical transport of plutonium in the Mediterranean under study is rather slow, compared with the estimated sinking rate of plutonium in the North Atlantic (Noshkin, Bowen, 1973). The depth of the plutonium maxima was deeper in the Atlantic ($\simeq 500$ m) during the period 1968-1972 (Bowen *et al.*, 1971; Livingston *et al.*, 1975) than that observed at the present station. If we integrate the concentration of ^{238}Pu and $^{239+240}$Pu for the entire water column (2200 m), we obtain 71 ± 6 pCi ^{238}Pu/m^2 and 1.39 ± 0.04 nCi $^{239+240}$Pu/m^2. These values correspond respectively to $90 \pm 20\%$ and $70 \pm 10\%$ of the fallout delivery of these isotopes up to 1970 (Hardy *et al.*, 1973) with about 50% of both isotopes above 1000 m. Similar calculations for ^{137}Cs, based on the ^{90}Sr delivery data (Hardy *et al.*, 1972) using ^{137}Cs/^{90}Sr ratio of 1.49 (Volchok *et al.*, 1971), show also that $80 \pm 20\%$ of ^{137}Cs fallout delivered at this latitude is in the water column. Considering the fact that the fallout delivery of the plutonium isotopes has substantially decreased since 1971, it is reasonable to conclude that a major part of ^{238}Pu or $^{239+240}$Pu delivered by fallout is still in the water column.

The vertical distribution of ^{241}Am is more complicated than that for plutonium isotopes. Nevertheless, concentrations of ^{241}Am below 500 m, contrary to those of the plutonium, tend to be higher than those above 250 m. This vertical distribution of ^{241}Am is considered to reflect its complex delivery characteristics; in addition

Table 1

Results of determination of ^{238}Pu, $^{239+240}$Pu and ^{241}Am in seawater samples taken from various depths at a Mediterranean station (offshore Monaco, 43°32'N, 07°32'E August 1976).

Depth (m)	Cl (‰)	^{137}Cs* (fCi/l)	^{238}Pu* (fCi/l)	$^{239+240}$Pu* (fCi/l)	^{241}Am* (fCi/l)
Surface	21.00	86±4	0.05 ±0.01	0.9 ±0.1	0.048±0.009
50	20.99	90±6	0.03 ±0.01	0.95±0.06	0.036±0.007
100	21.05	88±3	0.05 ±0.01	1.2 ±0.1	0.07 ±0.01
250	21.29	65±2	0.06 ±0.01	1.2 ±0.1	0.04 ±0.01
500	21.35	56±1	0.029±0.008	0.94±0.09	0.15 ±0.02
750	21.31	39±1	0.036±0.007	0.65±0.04	0.08 ±0.02
1000	21.31	33±2	0.038±0.006	0.47±0.03	0.15 ±0.02
1500	21.28	14±2	0.028±0.005	0.43±0.04	0.12 ±0.02
2000	21.27	21±1	0.014±0.006	0.39±0.03	0.09 ±0.02

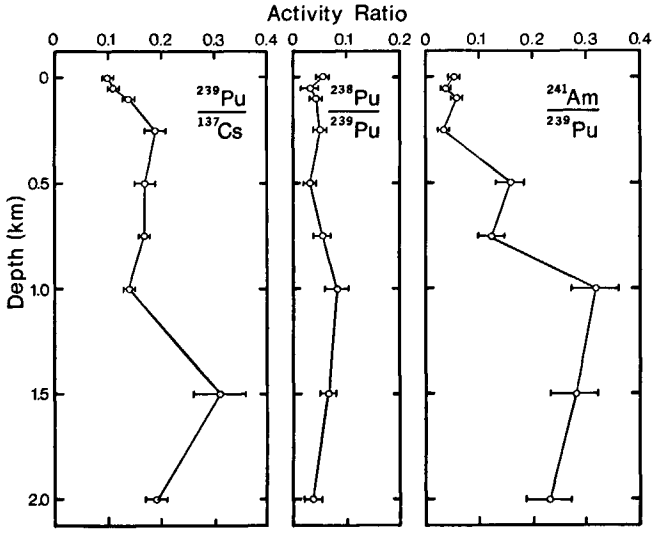
* Uncertainties given are 1 σ propagated errors.

to the fallout supply at the surface followed by the vertical transport through the water column or lateral advective transport, ^{241}Am is also produced *in situ* from the decay of ^{241}Pu (half-life 14.9 years). Thus, an understanding of the increase of ^{241}Am concentration below 500 m, relative to the upper layers, must take both transport and *in situ* build-up into account.

Vertical variations of activity ratios $^{239+240}$Pu/^{137}Cs, ^{238}Pu/$^{239+240}$Pu and ^{241}Am/$^{239+240}$Pu are given in Figure 1.

The $^{239+240}$Pu/^{137}Cs activity ratios increases from 1.0×10^{-2} at the surface to 1.9×10^{-2} at 250 m depth and then remains more or less constant with increasing depth, except for a single high point at 1 500 m, which, due to its larger associated error, may not be significantly different from the other points. This indicates that $^{239+240}$Pu is depleted in near surface layers with respect to ^{137}Cs due probably to its preferential association with sinking particulate matter. Similar differentiation between ^{137}Cs and $^{239+240}$Pu has already been observed in the surface layer in the Atlantic (Bowen *et al.*, 1971), although the average activity ratios both at surface and below 500 m depth in the Atlantic (respectively 0.53×10^{-2} and 1.35×10^{-2}) are significantly lower than the corresponding ratios observed at the present station. The integrated average $^{239+240}$Pu/^{137}Cs ratio at this station below 250 m, $(1.8\pm0.1)\times10^{-2}$, is also higher than the integrated fallout delivery ratio of 1.2×10^{-2} estimated by Holm and Persson (1975), but is close to the range of $(1.9\simeq2.5)\times10^{-2}$ given for Mediterranean sediment (Livingston *et al.*, 1977). This suggests that the behaviour of ^{137}Cs and $^{239+240}$Pu in the deeper layers of the Mediterranean are similar, showing a lack of differentiation in the deeper layers. Thus, it seems that the differentiation between ^{137}Cs and $^{239+240}$Pu takes place only within the upper few hundred meters of the Mediterranean under study. The shallower differentiation depth in this area than that in the Atlantic (Bowen *et al.*, 1971) confirms the slower vertical transport of $^{239+240}$Pu in the Mediterranean compared with that in the Atlantic.

Figure 1
Vertical variations of activity ratios $^{239+240}$Pu/^{137}Cs, ^{238}Pu/$^{239+240}$Pu and ^{241}Am/$^{239+240}$Pu in a Mediterranean water column (in the figure $^{239+240}$Pu is expressed as ^{239}Pu).



The ^{238}Pu/$^{239+240}$Pu activity ratios vary little with depth and the integrated average ratio with respect to the entire water column, $(5.1\pm0.5)\times10^{-2}$, is not significantly different from the average ratio, $(6.6\pm0.8)\times10^{-2}$, reported for Mediterranean surface waters (Fukai *et al.*, 1976).

The vertical variations of ^{241}Am/$^{239+240}$Pu activity ratio are complicated. Nevertheless, the ratios at various depths can be systematically divided into three groups: $\simeq5\times10^{-2}$ between surface and 250 m, $\simeq15\times10^{-2}$ between 500-750 m and $(20\text{-}30)\times10^{-2}$ below 1 000 m. The lower ratios in the upper layers, $\simeq5\times10^{-2}$, are consistent with the average ratio of $(5.5\pm0.7)\times10^{-2}$ reported for the surface waters covering the much broader western Mediterranean area (Fukai *et al.*, 1976). Since the ^{241}Am/$^{239+240}$Pu activity ratio in the integrated global fallout in 1974 was estimated to be 22×10^{-2} (Krey *et al.*, 1976), the lower ratios obtained for the upper layers in the Mediterranean suggest that americium is transported downwards from this layer more rapidly than plutonium. This is consistent with the conclusion obtained by Livingston *et al.* (1977) on the basis of ^{241}Am/$^{239+240}$Pu ratios found in the Mediterranean sediments, or the estimated loss of ^{241}Am originating from the Windscale discharge in currents travelling along the British coast (Livingston, Bowen, 1977). This relatively rapid vertical transport of americium plus the *in situ* build-up of ^{241}Am from ^{241}Pu should result in an increase of the ^{241}Am/$^{239+240}$Pu activity ratios in the deeper layer. In addition, the advective transport may also change the ratio at certain depths. All these factors complicate the interpretation of the vertical variations of ^{241}Am/$^{239+240}$Pu ratios.

The water column inventories of $^{239+240}$Pu above and below a depth of 875 m (middle of 750 and 1 000 m) are calculated to be respectively 830 ± 30 pCi/m^2 and 570 ± 30 pCi/m^2. The corresponding inventories for ^{241}Am are 80 ± 10 pCi/m^2 and 160 ± 20 pCi/m^2. If we apply the ^{241}Am/$^{239+240}$Pu activity ratio in the integrated global fallout of 22×10^{-2} (Krey *et al.*, 1976) and assume an equal vertical transport rate for $^{239+240}$Pu and ^{241}Am, it follows that 180 pCi/m^2 and 110 pCi/m^2 of ^{241}Am should be present respectively above and below 875 m. Since, in reality, the rate of vertical transport for ^{241}Am is faster than that for $^{239+240}$Pu, the difference of the transport rates results in a deficiency of ^{241}Am in the upper layer and the excess of ^{241}Am in the lower layer compared with the computed ^{241}Am inventories. This deficiency or excess of ^{241}Am is calculated to be respectively -100 pCi/m^2 or $+50$ pCi/m^2. The difference between deficiency and excess, approximately 50 pCi ^{241}Am/m^2, should have been lost from the water column through the preferential deposition of ^{241}Am to the bottom. This should result in substantial increase of ^{241}Am/$^{239+240}$Pu activity ratio for the bottom sediments, compared with that for the water column. This elucidation is consistent with the finding

by Livingston *et al.* (1977) for the Mediterranean sediments.

The mechanism of the differentiation between plutonium and americium in the water column and the question of how far we can generalize the observed processes at the present station to other areas of the Mediterranean are open to future studies.

Acknowledgement

The authors wish to thank Drs. C. L. Osterberg and S. W. Fowler of the Monaco Laboratory for their critical reading of the manuscript. The International Laboratory of Marine Radioactivity operates under a tripartite agreement between the International Atomic Energy Agency, the Government of the Principality of Monaco and the Oceanographic Institute at Monaco. Support for the present work is gratefully acknowledged.

REFERENCES

Ballestra S., Holm E., Fukai R., 1976. Measurements of transuranic elements in the Mediterranean, 1976 Report, Activ. Intern. Lab. Mar. Radioact.. IAEA. Monaco. 133-136.

Bowen V. T., Wong K. M., Noshkin V. E., 1971. Plutonium-239 in and over the Atlantic Ocean, *J. Mar. Res.*, **29,** 1-9.

Fukai R., Ballestra S., Holm E., 1976. ^{241}Americium in Mediterranean surface waters, *Nature*, **264,** 739-740.

Hardy E. P., Krey P. W., Volchok H. L., 1972. Global inventory and distribution of Pu-238 from SNAP-9A, US-AEC Rep. HASL-250, 32 p.

Hardy E. P., Krey P. W., Volchok H. L., 1973. Global inventory and distribution of fallout plutonium, *Nature*, **241,** 444-445.

Holm E., Fukai R., 1976. Determination of americium and curium by using ion-exchange in nitric acid-methanol medium for environmental analysis, *Talanta*, **23,** 853-855.

Holm E., Persson R. B. R., 1975. Transfer of fallout plutonium in the food-chain lichen – reindeer – man, "Transuranium Nuclides in the Environment", IAEA. Vienna, 435-446.

Holm E., Persson R. B. R., 1977. Pu-241 and Am-241 in the environment, *Proc. 4th Intern. Congr. IRPA*, **3,** 845-848.

Krey P. W., Hardy E. P., Pachucki C., Rourke F., Coluzza J., Benson W. K., 1976. Mass isotopic composition of global fall-out plutonium in soil, "Transuranium Nuclides in the Environment", IAEA. Vienna, 671-678.

Lacombe H., Tchernia P., 1972. Caractères hydrologiques et circulation des eaux en Méditerranée in *The Mediterranean Sea: A natural Sedimentation Laboratory*, edited by D. J. Stanley, Dowden, Hutchinson and Ross Inc., Stroudsburg, Pennsylvania, 25-36.

Livingston H. D., Mann D. R., Bowen V. T., 1975. Analytical procedures for transuranic elements in seawater and marine sediments, "Analytical Methods in Oceanography", *Adv. Chem. Ser.* 147, American Chem. Soc., Washington, DC, 124-138.

Livingston H. D., Bowen V. T., 1976. Americium in the marine environment – Relationship to plutonium, "Environmental Toxicity of Aquatic Radionuclides: Models and Mechanisms", *Ann Arbor Sci. Publ. Inc., Ann Arbor, Mich.*, 107-130.

Livingston H. D., Bowen V. T., Burke J. C., 1977. Fallout radionuclides in Mediterranean sediments, *Rapp. Comm. int. Mer Médit.*, **24,** 3, 37-40.

Livingston H. D., Bowen V. T., 1977. Windscale effluent in the waters and sediments of the Minch, *Nature*, **269,** 586-588.

Miyake Y., Sugimura Y., 1976. The plutonium content of Pacific Ocean waters, "Transuranium Nuclides in the Environment". IAEA. Vienna 91-105.

Murray C. N., Fukai R., 1978. Measurements of $^{239+240}$Pu in the northwestern Mediterranean, *Estuarine Coast. Mar. Sci.*, **6,** 145-151.

Noshkin V. E., Bowen V. T., 1973. Concentrations and distributions of long-lived fallout radionuclides in open ocean sediments, "Radioactive Contamination of the Marine Environment", IAEA. Vienna, 671-686.

Stanley D. J., Cita M. B., Flemming N. C., Kelling G., Lloyd R. M., Milliman J. D., Pierce J. W., Ryan W. B. F., Weiler Y., 1972. Guidelines for future sediment-related research in the Mediterranean Sea, in *The Mediterranean Sea: A Natural Sedimentation Laboratory*, edited by D. J. Stanley, Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania, 723-741.

Volchok H. L., Bowen V. T., Folsom T. R., Broecker W. S., Schuert E. A., Bien G. S., 1971. Oceanic distributions of radionuclides from nuclear explosions, in *Radioactivity in the Marine Environment*, edited by A. H. Seymour, NAS-NRS, Washington, DC, 42-89.