

## Temporal variations in plutonium and americium inventories and their relation to vertical transport in the northwestern Mediterranean Sea

Scott W. Fowler, Victor E. Noshkin,<sup>1</sup> Jacques La Rosa, and Janine Gastaud

IAEA Marine Environment Laboratory, P.O. Box 800, 4 Quai Antoine 1<sup>er</sup>, MC-98012 Monaco

### Abstract

Vertical fluxes of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  and temporal changes in their inventories in the northwestern Mediterranean Sea have been examined through high-resolution water column sampling coupled with direct measurements of the vertical flux of particle-bound transuranics using time-series sediment traps. Water column profiles of both radionuclides showed well-defined sub-surface maxima ( $^{239+240}\text{Pu}$  between 100–400 m;  $^{241}\text{Am}$  at 100–200 m and 800 m), the depths of which are a result of the different biogeochemical scavenging behavior of the two radionuclides. Comparison of deep water column (0–2,000 m) transuranic inventories with those derived from earlier measurements demonstrate that the total  $^{239+240}\text{Pu}$  inventory had not substantially changed between 1976–1990 whereas  $^{241}\text{Am}$  had decreased by approximately 24%. Enhanced scavenging of  $^{241}\text{Am}$  and a resultant, more rapid removal from the water column relative to  $^{239+240}\text{Pu}$  was also supported by the observation of elevated Am/Pu activity ratios in sinking particles collected in sediment traps at depth. Direct measurements of the downward flux of particulate  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  compared with transuranic removal rates derived from observed total water column inventory differences over time, show that particles sinking out of deep waters (1,000–2,000 m) could account for 26–72% of the computed total annual  $^{239+240}\text{Pu}$  loss and virtually all of the  $^{241}\text{Am}$  removal from the water column. Upper water column (0–200 m) residence times based on direct flux measurements ranged from 20–30 yr for  $^{239+240}\text{Pu}$  and 5–10 yr for  $^{241}\text{Am}$ . The observation that  $^{241}\text{Am}/^{239+240}\text{Pu}$  activity ratios in unfiltered Mediterranean seawater are six times lower than those in the north Pacific suggests the existence of a specific mechanism for enhanced scavenging and removal of  $^{241}\text{Am}$  from the generally oligotrophic waters of the open Mediterranean. It is proposed that atmospheric inputs of aluminosilicate particles transported by Saharan dust events which frequently occur in the Mediterranean region could enhance the geochemical scavenging and resultant removal of  $^{241}\text{Am}$  to the sediments.

One of the main objectives of current oceanic flux studies is to examine spatial and temporal variability of the downward vertical transport of key elements and radionuclides involved in marine biogeochemical cycles. Two long-lived transuranic elements, plutonium and americium, have entered the marine environment as contaminants primarily via fallout from atmospheric weapons testing. The different chemical behaviors of these two artificial radionuclides in seawater have made them unique tools for studying various particle-related processes in the ocean (Fukai et al. 1979, 1983; Holm et al. 1980; Bowen et al. 1980; Beasley et al. 1982; Fowler et al. 1983, 1990a,b, 1991; Molero et al. 1995a,b).

As a result of increasing interest in such anthropogenic

tracers, a substantial database has accrued on the distribution and behavior of plutonium and americium in seawater, suspended particulates, and sediments. However, direct measurements of the particle-associated vertical flux of plutonium and americium remain rare, even though such information is essential for quantifying their residence times and removal rates in the water column (Fowler et al. 1983, 1990a,b, 1991; Livingston and Anderson 1983; Bacon et al. 1985; Fowler 1987). Another method for deriving the downward movements of surface-introduced transuranic elements is to compare seawater radionuclide inventories for given depth intervals over different periods of time. Based solely on seawater profiles measured in the mid-1970s and early 1980s, it has been postulated that the association of transuranics with sinking particles is likely responsible for the slow downward displacement of plutonium and americium in Mediterranean waters (Fukai et al. 1983). This approach depends on the accuracy of the derived inventory differences over relatively short periods of time which, in turn, is a function of the resolution of the measurements with depth. In order to refine such critical comparisons, we have measured high-resolution depth profiles of plutonium and americium in the northwestern Mediterranean basin during a series of cruises in 1989–1990. The profiles were taken at two offshore stations (Fig. 1) where time-series sediment trap experiments were carried out at the same time to quantify the present downward vertical flux of transuranium nuclides and other elements (see Peinert et al. 1992; Miquel et al. 1994). The goal of the study was to compare direct measurements of transuranium nuclide sedimentation via sinking

<sup>1</sup>Present address: Lawrence Livermore National Laboratory, Health and Ecological Assessment Division, University of California, P.O. Box 808, Livermore, California 94550.

### Acknowledgments

This work was supported in part by the French JGOFS Program “DYFAMED” and the CEC Marine Science and Technology Program under contract MAST-0016-C (EBD) as part of the EROS-2000 project. We thank the crews of the R/V *Marion Dufresne*, *Georges Petit*, *Korotneff*, and *Catherine Laurence* for their assistance in deploying and recovering the sediment trap moorings. Useful comments on the manuscript from J. K. Cochran, H. D. Livingston, and two anonymous referees are greatly appreciated. The IAEA Marine Environment Laboratory operates under an agreement between the International Atomic Energy Agency and the Government of the Principality of Monaco.

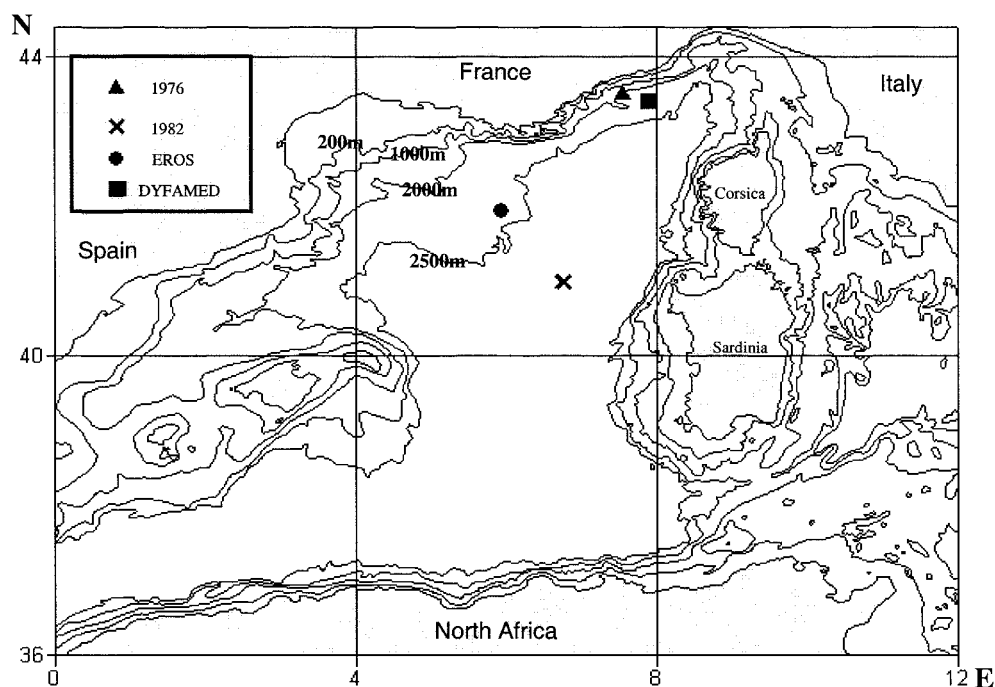


Fig. 1. Location of DYFAMED and EROS-2000 stations in northwestern Mediterranean Sea where water column and sinking particles were sampled in 1989–1990 for transuranic analyses. Neighboring stations where similar water column measurements were made in 1976 and 1982 are also shown.

particulate matter with independent estimates of radionuclide removal to the sediments based on temporal changes in the water column transuranic inventories.

#### Methods and materials

**Seawater profiles**—Unfiltered seawater samples were collected during three separate cruises at two locations in the northwestern Mediterranean basin (Fig. 1). During May and November 1989, two sampling cruises on board the R/V *Pr. Georges Petit* were undertaken at the French DYFAMED station (43°25'N, 07°53'E) located approximately 28 nautical miles southeast of Cap Ferrat, France. On each occasion seawater was collected at 17 depths by casts employing 30-liter Niskin bottles mounted on a Rosette sampler. Approximately 60 liters of seawater were taken at each depth to a maximum depth of 2,250 m. In addition, on two occasions in January and February 1999, 70 liters of surface water were collected at the DYFAMED site to further assess any changes in transuranic content in surface waters over the last two decades. During the May 1990 'CYBELLE' cruise on board R/V *Marion Dufresne*, 19 depths were sampled by taking similar casts down to a depth of 2,470 m at the EROS-2000 'ETRO' station (41°57'N, 05°56'E) in the Gulf of Lions approximately 60 nautical miles south of Toulon, France. The DYFAMED and EROS-2000 stations are about 124 nautical miles apart (Fig. 1).

**Particle fluxes**—Automated time-series sediment traps (cylindro-conical type, 0.125 m<sup>2</sup> opening) were used to collect sinking particles at both stations during various periods

between June 1988 and July 1990. At the DYFAMED station (2,260 m bottom depth) from June 1988 to December 1989, traps moored at 100, 200, 1,000, and 2,000 m collected material for various time intervals ranging from 14 to 27 days. In spring–summer of 1990, similar automated sediment traps were moored at the EROS-2000 'ETRO' station in the Gulf of Lions (2,475 m bottom depth) at depths of 200, 500, 1,000, and 2,000 m. Each of the six collection cups sequentially sampled a 13-day period between 14 April and 1 July 1990. Trap design, sample preservation methodology, and protocols for treatment and preparation of the particulate samples have been described in detail elsewhere (Fowler et al. 1990b; Peinert et al. 1992; Miquel et al. 1994).

**Radionuclide analysis**—Immediately after sampling, the unfiltered seawater was acidified with HNO<sub>3</sub> to pH 1 and then spiked with appropriate yield determinants (<sup>242</sup>Pu and <sup>243</sup>Am). Following transport to the laboratory the transuranium nuclides were co-precipitated and settled with Fe(OH)<sub>3</sub>. The precipitate was subsequently dissolved and <sup>239+240</sup>Pu and <sup>241</sup>Am chemically separated and purified by methodologies described previously (Ballestra et al. 1978; Fukai et al. 1979; Ballestra and Fukai 1983). Freeze-dried particulate samples from the sediment traps (20–110 mg dry) were ground to a fine powder in an agate mortar. Aliquots of the powder were spiked with yield determinants, digested in a concentrated HNO<sub>3</sub>-HClO<sub>4</sub> mixture and evaporated to dryness. Any siliceous residue remaining after the initial dissolution was further treated with HF until a clear solution was obtained. All samples were subsequently taken to dryness, brought to volume with dilute HNO<sub>3</sub> and co-precipitated with Fe(OH)<sub>3</sub>.

The separated and purified  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  from all samples were electrodeposited onto stainless steel discs and measured by alpha spectrometry using silicon barrier detectors (Fowler et al. 1983). Counting errors associated with all radiometric measurements were propagated and are reported at the  $1\sigma$  level.

## Results and discussion

*Vertical distributions of transuranic concentrations*—Both the DYFAMED and EROS stations are located in the central zone of the northwestern basin which is characterized by a permanent cyclonic gyre (Millot 1987). The main hydrographic feature in this region, the Ligurian Current, flows in a southwesterly direction along the coast within a band about 15 nautical miles wide. These open water stations are therefore sufficiently distant from the continental slope, Ligurian Current, and frontal zone to be considered relatively free from the influence of any major lateral advective processes which might affect the transuranic profiles (*see e.g.*, Lévy et al. 1998). Consequently we feel it justified to interpret profile distributions in the first instance within a 1-D framework.

Concentrations of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  at the EROS-2000 station and  $^{239+240}\text{Pu}$  at the DYFAMED station are set out in Table 1. Corresponding concentration profiles for the radionuclides are shown along with the  $^{241}\text{Am}/^{239+240}\text{Pu}$  activity ratios in Fig. 2. These profiles, which are comprised of measurements from 17–19 depths, offer the greatest resolution to date of plutonium concentration changes over depth in the Mediterranean Sea. All three profiles of  $^{239+240}\text{Pu}$  show a distinct subsurface maximum in concentration. The DYFAMED November 1989 and EROS plutonium profiles are quite similar in shape with subsurface maxima (one broad and the other sharp) evident between 100–400 m. The May 1989 profile at the DYFAMED site was somewhat different from that taken at the same station six months later. In May the sharp subsurface maximum was centered at 100 m, whereas in November 1989 it had shifted to a depth of 400 m. Furthermore, the elevated Pu concentration at 2,230 m from May 1989 was likely due to a local sediment resuspension event since the sample was taken only 30 m from the bottom.

Previously reported profiles for plutonium in the Mediterranean have identified a subsurface maximum at similar depths although with much less resolution (Fukai et al. 1979, 1983; Fowler et al. 1990b; Merino et al. 1997). This feature, which has also been observed in other seas, is generally attributed to the downward vertical transport and subsequent mineralization of plutonium-enriched organic particulates which release the radionuclide back into the water column (Bowen et al. 1980; *see* Sholkovitz 1983, for review). With the aid of our high-resolution profiles, one can see that the subsurface  $^{239+240}\text{Pu}$  maximum does not always correspond to the depth of the core of the Levantine Intermediate Water (~400 m) which is characterized by a salinity maximum (Fig. 2). Any major control of the  $^{239+240}\text{Pu}$  distribution by this hydrographic feature is unlikely. The depth of the subsurface maximum observed at the DYFAMED station is more probably related to temporal changes in primary pro-

Table 1. Concentrations of plutonium and americium in seawater from two stations in the northwestern Mediterranean basin.

Location (depth, m)	Concentration (mBq m <sup>-3</sup> )		$^{241}\text{Am}/^{239+240}\text{Pu}$ ratio
	$^{239+240}\text{Pu}$	$^{241}\text{Am}$	
EROS-2000, ETRO Station (41°57'N, 05°56'E), May 1990			
Surface	22.5±2.5	1.31±0.48	0.06±0.02
100	31.9±3.3	3.04±0.80	0.10±0.03
200	31.9±3.6	3.12±0.85	0.10±0.03
250	27.6±2.9	2.47±0.62	0.09±0.02
300	31.8±3.3	2.72±0.63	0.09±0.02
400	25.3±2.8	1.26±0.98	0.05±0.04
500	25.5±2.9	2.40±0.48	0.09±0.02
600	22.6±3.1	2.57±0.50	0.11±0.03
700	16.9±2.0	3.21±0.45	0.19±0.03
800	21.6±2.5	4.90±0.78	0.23±0.04
900	21.8±3.0	2.66±0.42	0.13±0.03
1,000	20.2±2.5	2.83±0.44	0.14±0.03
1,200	21.0±1.5	3.40±0.20	0.16±0.02
1,400	21.3±1.6	3.01±0.59	0.14±0.03
1,600	24.1±1.7	3.91±0.76	0.16±0.03
1,800	20.4±1.7	3.43±0.93	0.17±0.05
2,000	20.1±1.5	3.36±0.69	0.17±0.04
2,200	26.3±1.8	3.02±0.63	0.11±0.03
2,470	22.8±1.5	2.50±0.55	0.11±0.03
DYFAMED Station (43°25'N, 07°53'E), May 1989			
Surface	21.4±2.0		
100	34.9±4.7		
200	27.7±2.5		
300	26.9±2.8		
400	25.2±2.7		
500	20.6±2.3		
600	22.3±2.1		
700	18.5±1.9		
800	19.9±2.2		
900	22.3±2.9		
1,000	19.4±1.8		
1,200	18.1±1.8		
1,400	19.2±1.9		
1,600	21.0±1.8		
1,800	20.4±1.6		
2,000	23.3±2.7		
2,230	31.8±5.7		
DYFAMED Station (43°25'N, 07°53'E), November 1989			
Surface	17.8±2.8		
100	18.5±2.0		
200	21.9±3.5		
300	30.4±3.2		
400	36.2±4.3		
500	30.4±3.1		
600	25.4±4.2		
700	26.2±2.6		
800	22.5±2.7		
900	23.9±2.8		
1,000	18.4±2.3		
1,200	20.3±2.1		
1,400	24.4±2.2		
1,600	22.5±2.8		
1,800	19.3±1.7		
2,000	21.0±2.4		
2,250	23.6±2.6		

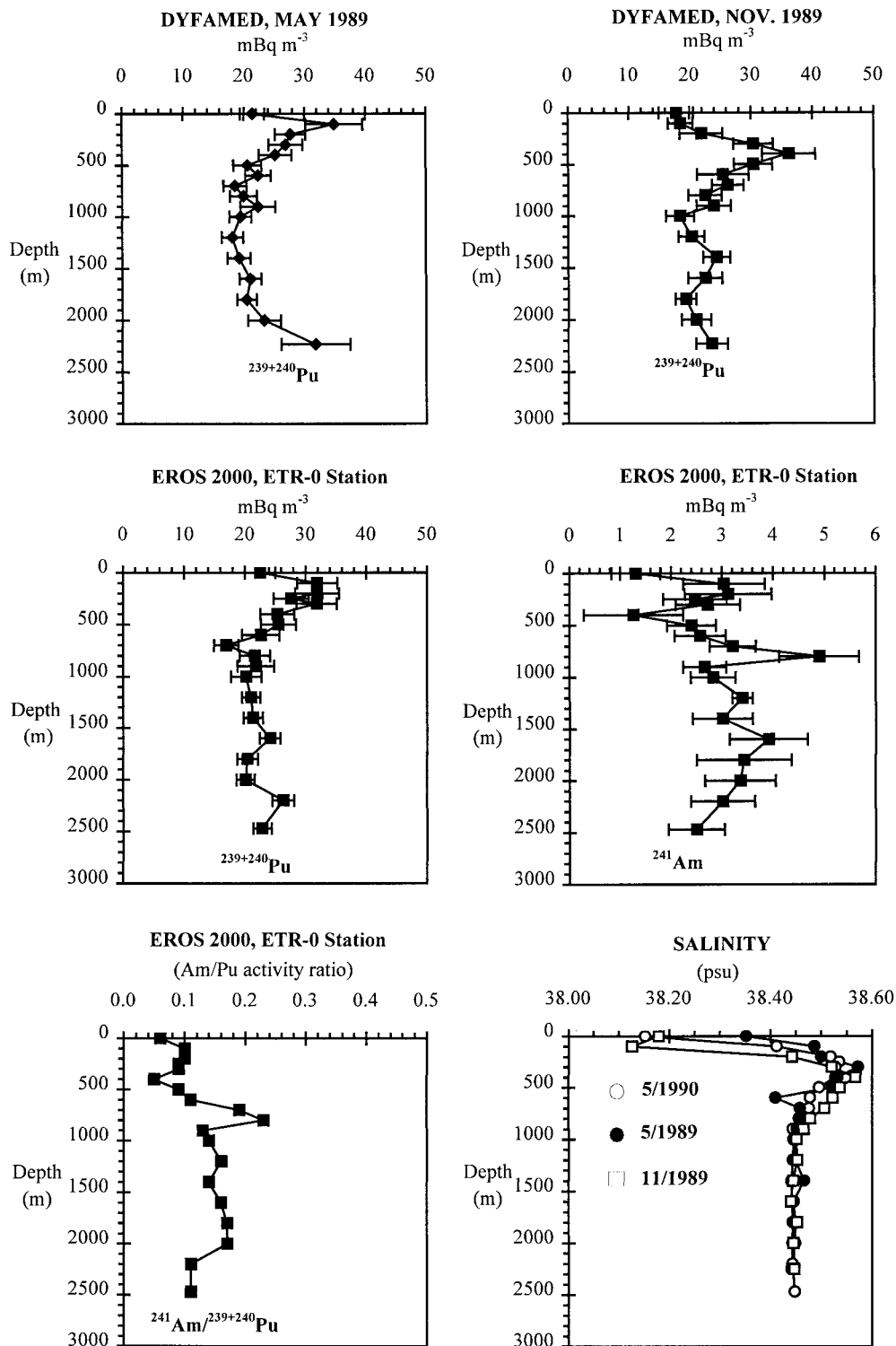


Fig. 2. Vertical profiles of  $^{239+240}\text{Pu}$  (DYFAMED and EROS-2000 stations),  $^{241}\text{Am}$  (EROS-2000) and salinity (both stations) measured during 1989–1990 in the northwestern Mediterranean Sea.

duction and particle formation in these waters. In the northwestern basin, primary production is characterized by a strong spring bloom which normally occurs during the period April–May (Brouardel 1971; Jacques 1988; Morel and

André 1991). During May in the central zone of the gyre near the DYFAMED station, this bloom is evidenced by high phytoplankton concentrations in the upper 100 m (Goffart et al. 1995) which in turn presumably result in enhanced plu-

tonium scavenging by these organic particles. Such a scenario may account in part for the sharp maximum  $^{239+240}\text{Pu}$  concentration in unfiltered water at 100 m observed during May 1989 at the DYFAMED site.

A high-resolution profile for  $^{241}\text{Am}$  was also obtained at the EROS station for purposes of comparison with earlier data (Fig. 2). The profile shows two subsurface maxima, a smaller one between 100–200 m that corresponds to the depth of the Pu subsurface maximum, and a much sharper maximum centered at 800-m depth. The significance of the deep subsurface maximum is not clear but may be related to enhanced scavenging of  $^{241}\text{Am}$  by certain types of particles at this depth; nevertheless, whatever the process involved, it does not affect the corresponding vertical distribution of  $^{239+240}\text{Pu}$  (Fig. 2). Fukai et al. (1983) reported the presence of subsurface  $^{241}\text{Am}$  maxima at one station in Catalan Sea, another in the Ionian Sea, and two in the eastern Mediterranean although they recognized that the low resolution of their profiles made it difficult to define precisely the actual depth of this feature. In the Catalan Sea in 1981 (ibid.), an apparent  $^{241}\text{Am}$  peak was noted at the 500-m sampling depth with a relatively high concentration of approximately  $17 \text{ mBq m}^{-3}$ . From samples taken at a station in the same area during 1991, Molero et al. (1995a) present an  $^{241}\text{Am}$  profile of four depths to 1,000 m which is nearly flat with a maximum concentration at 500 m of only  $1.9 \text{ mBq m}^{-3}$ . Unfortunately, neither study sampled between 500 and 1,000 m, thus it is not possible to corroborate the deep subsurface  $^{241}\text{Am}$  maximum ( $4.9 \text{ mBq m}^{-3}$ ) at 800 m we measured at the EROS station further east. However, one  $^{241}\text{Am}$  profile presented by Fukai et al. (1983) from the eastern Mediterranean basin in which water was sampled at five depths between 250 and 1,500 m shows a marked subsurface maximum at about 750 m ( $\sim 22 \text{ mBq m}^{-3}$ ), a depth very similar to that observed in our profile but with an  $^{241}\text{Am}$  concentration four times higher. Clearly, more high-resolution sampling at these deeper depths is needed to resolve the exact position of this feature, if indeed it is stable throughout the Mediterranean.

*Transuranium inventories*—The deep water concentration profiles for  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the northwestern Mediterranean (Fig. 2) are the first detailed measurements made in this region for some time. Our understanding of plutonium and americium biogeochemistry would be greatly facilitated by knowledge of how the concentrations have changed at various depths in the water column over time. To do this, historical data prior to 1989 from the entire western Mediterranean were assembled and inventories for various depth intervals computed. The older profiles have been compiled in IAEA (1991) and include several studies carried out between 1969–1986 (Noshkin and Bowen 1972; Ballestra et al. 1984; Livingston et al. 1979; Fukai et al. 1979, 1983; Fowler et al. 1990b). Most of these earlier profiles were comprised of very few sampling depths, which limits the accuracy of determining water column inventories. Therefore, only two deep-water column profiles, which were taken very near our 1989–1990 stations and included at least seven sample depths, were selected for purposes of detailed inventory comparisons. In this way, the best possible degree of

accuracy could be achieved in assessing temporal changes at depth.

The mean transuranium concentrations ( $\text{mBq m}^{-3}$ ) between each depth sampled were first computed. These values were then used to estimate inventories per unit area between two successive depths. For example, the  $\text{Bq m}^{-2}$  for  $^{239+240}\text{Pu}$  (shown in Table 2) within the 0–200 m interval of the May 1989 station using data given in Table 1 was determined as:

$$5.9 \text{ Bq m}^{-2} = [(21.4 + 34.9) + (34.9 + 27.7)] \\ \times 100 \div (1,000 \times 2).$$

The total inventory to depths of 1,000 and 2,000 m below the surface were computed and shown in Table 2. These values were obtained by summing the  $\text{Bq m}^{-2}$  in the respective preceding 200-m depth intervals. Interpolation was required to estimate the total inventory reported to 500- and 1,500-m depth. Using this procedure, unique comparative results can be generated to assess changes in water column inventory over time even with earlier, more poorly defined data sets. Considering the major errors involved in sampling and radioanalyses, the precision of these inventories is estimated to be within  $\pm 10\%$ . Inspection of the 0–2,000 m inventories shows that on average very little, if any, decrease in total inventory had occurred during roughly the decade over which the measurements were made. However,  $^{239+240}\text{Pu}$  inventories in the lower 1,000–2,000-m interval of the 2,000-m water column have clearly increased over that time period. Computations indicate that in the 1976–1982 time frame only 33% of the  $^{239+240}\text{Pu}$  water column inventory resided within the lower 1,000-m depth interval, and by 1989–1990 the percentage had increased to 46%. In conjunction with the increase in deep-water plutonium inventories, there was a concomitant decrease of approximately 35% in the upper mixed layer (0–200 m) during this time. A similar decrease in plutonium is evident from recent surface water data collected from the DYFAMED station. In January and February 1999,  $^{239+240}\text{Pu}$  concentrations were 16 and 12  $\text{mBq m}^{-3}$ , respectively. Comparing the mean concentration for these two surface samples with that measured at the same location some 10 years earlier suggests an approximate 30% decrease during the last decade. It is evident from these data that plutonium is slowly being removed from the surface layers and accumulating in the deeper waters of the western Mediterranean.

A profile of the  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratio in seawater at the EROS station is also shown in Fig. 2. Of particular note is the well-defined, enhanced ratio at the depth of the subsurface  $^{241}\text{Am}$  maximum. There is also an overall tendency for an increase in the ratio with depth, a feature which has been observed in other studies and is attributed to the more rapid vertical transport of  $^{241}\text{Am}$  through the water column compared to  $^{239+240}\text{Pu}$  (Fukai et al. 1979). The range in  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratios we measured in 1990 (0.06–0.23) is within the range of those (0.03–0.32) reported for two nearby locations sampled in 1976 and 1981 (Fukai et al. 1979, 1983).

$^{241}\text{Am}$  inventories in different depth intervals from the EROS station were calculated and compared with those from a detailed  $^{241}\text{Am}$  profile also taken in the northwestern basin nearly 14 years earlier by Fukai et al. (1979). The data in

Table 2.  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  inventories ( $\text{Bq m}^{-2}$ ) in seawater between depth intervals at stations in the western Mediterranean (1976–1990). Locations of stations are shown in Fig. 1.

	$^{239+240}\text{Pu}$					$^{241}\text{Am}$	
	43°32'N	41°00'N	43°25'N	43°25'N	41°57'N	43°32'N	41°57'N
Longitude	07°32'E	06°45'E	07°53'E	07°53'E	05°56'E	07°32'E	05°56'E
Collection date	Aug 76	Apr 82	May 89	Nov 89	May 90	Aug 76	May 90
Max. sample depth (m)	2,000	2,000	2,230	2,250	2,470	2,250	2,500
Bottom depth (m)	2,250	2,600	2,260	2,260	2,500	2,000	2,470
No. sample depths*	9	7	17	17	19	9	19
Reference†	1	2	3	3	3	1	3
Depth interval (m)							
0–200	8.1	8.5	5.9	4.2	5.9	0.38	0.53
200–400	8.2	6.7	5.3	6.1	5.8	0.64	0.47
400–600	6.9	5.9	4.4	5.7	5.0	0.78	0.43
600–800	5.5	4.8	4.0	5.1	3.9	0.85	0.70
800–1,000	4.2	4.7	4.2	3.9	4.3	0.85	0.65
1,000–1,200	3.3	3.1	3.8	4.3	4.1	1.0	0.62
1,200–1,400	3.3	3.2	3.7	4.5	4.2	1.0	0.64
1,400–1,600	3.2	3.0	4.0	4.5	4.5	0.89	0.69
1,600–1,800	3.0	2.7	4.1	4.1	4.5	0.78	0.73
1,800–2,000	3.0	3.0	4.4	3.9	4.1	0.78	0.68
0–500	20.3	18.8	13.6	13.3	14.3	1.4	1.2
0–1,000	32.8	30.6	23.6	25.0	24.9	3.5	2.8
0–1,500	41.1	38.6	33.1	36.1	35.5	6.0	4.4
0–2,000	48.7	45.6	43.6	46.3	46.3	8.0	6.1
>2,000	—	—	49.0	48.9	57.5	—	7.6
1,000–2,000	15.9	15.0	20.0	21.3	21.4	4.5	3.4
1,000–2,000 (%)‡	33%	33%	46%	46%	46%	56%	56%

\* Number of data points used to construct inventory profile.

† 1. Fukai et al. 1979; 2. Ballestra et al. 1984; 3. This study.

‡ Percentage of total inventory (0–2,000 m) in 1,000–2,000-m depth interval.

Table 2 show that the depth distributions of  $^{241}\text{Am}$  are more complex than those of plutonium. Except for the upper mixed layer (0–200 m), there has been a clear decrease in the inventories over time at the depth intervals examined. The entire 2,000-m water column inventories indicate that there was roughly a 24% loss in  $^{241}\text{Am}$  during the period 1976–1990. Nevertheless, the fraction of that inventory residing in the deeper 1,000–2,000-m depth interval was the same (~56%) at both times. While  $^{239+240}\text{Pu}$  has shown a slow increase in the amount retained in the lower half of the 2,000-m water column over this time period, the corresponding  $^{241}\text{Am}$  data suggest a rapid transfer from the water column, most probably into the sediments. This is consistent with the hypothesis put forward by others that  $^{241}\text{Am}$  is transported downward in Mediterranean waters more rapidly than  $^{239+240}\text{Pu}$  (Livingston et al. 1977; Fukai et al. 1979, 1983; Holm et al. 1980; Molero et al. 1995*a,b*). Furthermore,  $^{241}\text{Am}$  levels have continued to decrease over the last decade as demonstrated by the observation that  $^{241}\text{Am}$  concentrations in surface waters from the DYFAMED station in early 1999 (0.50  $\text{mBq m}^{-3}$  for both the January and February samples) were ~62% lower than the level measured at the nearby EROS station in May 1990 (Table 1).

The inventories of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  deal only with the measured concentrations within the upper 2,000 m of the water column in the western Mediterranean. However, nearly one-half of the surface area of this region is represented by

depths greater than 2,000 m (Christensen et al. 1989); thus, any realistic computation of total transuranic inventories (TBq) for the western Mediterranean must include inventories for these deeper depths. In order to estimate inventories at depths greater than 2,000 m, the cumulative inventories for  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  at each station were plotted and were found to increase linearly with depth. Therefore, based on the observed linearity to 2,000 m, inventories below this depth were derived by extrapolation of this relationship. In the case of our 1989–1990  $^{239+240}\text{Pu}$  data, average values of inventories from the three separate profiles were plotted and regression equations relating the cumulative inventory with depth were developed so that inventories to 3,500 m could be more accurately estimated. These regression equations as well as those determined for inventories from previous years are given in the footnotes to Table 3.

For  $^{239+240}\text{Pu}$ , where far more historical profile data are available, inventories to depth were determined in this fashion for three separate time periods, i.e., 1976, 1981–1982, and 1989–1990 (Table 3). The cumulative inventories in different depth intervals were then multiplied by the areas of those depth intervals in the western Mediterranean basin (Christensen et al. 1989) to arrive at estimates of the total water column transuranic inventory (TBq) for each time period. Comparable  $^{241}\text{Am}$  profile data for the western basin are fewer; hence, a comparison of total water column inventories has only been made (Table 3) using the measured in-

Table 3. Mean total  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  inventories (TBq) for different intervals in the western Mediterranean basin (Alboran, Balearic, and Ligurian Seas).

Depth interval (m)	Area <sup>†</sup> $\text{m}^2 \times 10^9$	$^{239+240}\text{Pu}$						$^{241}\text{Am}$			
		1976 <sup>‡</sup>		1981–1982 <sup>§</sup>		1989–1990 <sup>  </sup>		1976 <sup>‡</sup>		1990 <sup>  </sup>	
		$\text{Bq m}^{-2}$	# TBq	$\text{Bq m}^{-2}$	# TBq	$\text{Bq m}^{-2}$	# TBq	$\text{Bq m}^{-2}$	# TBq	$\text{Bq m}^{-2}$	# TBq
0–200*	105.1	8.1	0.86	8.0	0.84	5.3	0.56	0.38	0.04	0.53	0.06
200–500*	59.5	20.3	1.21	18.2	1.08	13.5	0.80	1.41	0.08	1.22	0.07
500–1,000*	63.5	32.8	2.08	31.5	2.00	24.5	1.56	3.50	0.22	2.78	0.18
1,000–1,500*	51.0	41.1	2.10	38.6	1.97	34.9	1.78	5.95	0.30	4.39	0.22
1,500–2,000*	48.4	48.7	2.36	45.6	2.21	45.4	2.20	7.95	0.39	6.15	0.30
2,000–2,500	83.9	63.3	5.31	61.9	5.19	57.5	4.82	10.10	0.85	7.61	0.64
2,500–3,000	267.8	74.6	20.00	73.6	19.71	68.8	18.42	12.24	3.28	9.18	2.46
3,000–3,500	2.2	85.9	0.19	85.3	0.19	80.1	0.18	14.38	0.03	10.76	0.02
Total	681.4		34.1		33.2		30.3		5.19		3.95

\* Depths for which actual measured values were used to compute inventories (see Table 2). Inventories for remaining depths were derived from regression equations (see text and footnotes to this Table).

† Area of depth intervals as defined and computed by Christensen et al. (1989). Note that the Tyrrhenian Sea is not included.

‡ Computed from data of Fukai et al. (1979). Inventories below 2,000 m derived from regression equations (see text):  $^{239+240}\text{Pu}$  ( $\text{Bq m}^{-2}$ ) = 0.0226 (Depth) + 6.67;  $^{241}\text{Am}$  ( $\text{Bq m}^{-2}$ ) = 0.00429 (Depth) – 0.631.

§ Mean values computed from data in Fukai et al. (1983) and Ballestra et al. (1984). Inventories below 2,000 m derived from regression equations (see text):  $\text{Bq m}^{-2}$  = 0.0234 (Depth) + 3.34. The original 1981 data used from these sources are not presented in Table 2.

|| Mean values computed from data in Table 2, this study. Inventories below 2,000 m derived from regression equations (see text):  $^{239+240}\text{Pu}$  ( $\text{Bq m}^{-2}$ ) = 0.0226 (Depth) + 1.02;  $^{241}\text{Am}$  ( $\text{Bq m}^{-2}$ ) = 0.00315 (Depth) – 0.268.

¶ Represents cumulative inventory per unit area ( $\text{Bq m}^{-2}$ ) from the sea surface to the maximum depth (m) for the interval shown in Column 1. Values of  $\text{Bq m}^{-2}$  to 2,000 m are from Table 2. Regression equations are used to estimate the inventory per unit area to depths below 2,000 m.

# The total inventory (TBq shown in Columns 4, 6, 8, 10, and 12) to the maximum depth indicated in Column 1 is the product of the  $\text{Bq m}^{-2}$  (shown in Columns 3, 5, 7, 9, and 11) and the area of the different depth zones shown in Column 2.

inventories from the two stations reported in Table 2. The differences in total water column inventories of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  over time and the computed mean annual loss of these radionuclides from the water column are given in Table 4. From this assessment it is evident that a greater fraction of the  $^{241}\text{Am}$  inventory has been removed from the water column over the years than for  $^{239+240}\text{Pu}$ .

Other computations based on total integrated fallout deposition in the Mediterranean region lead to the same conclusion. For example, from the data of Hardy et al. (1973) total integrated  $^{239+240}\text{Pu}$  deposition until 1971 in the Mediterranean region ( $35^\circ$ – $45^\circ$  Lat. band) is estimated to be approximately  $74 \text{ Bq m}^{-2}$ . Based on annual  $^{239+240}\text{Pu}$  wet de-

position rate estimates for the northwestern basin (Thein et al. 1980), we can add  $5.7 \text{ Bq m}^{-2}$  to that amount for the 19-year period until our water column profiles were determined. This results in a total integrated  $^{239+240}\text{Pu}$  deposition by 1990 of  $79.7 \text{ Bq m}^{-2}$ . Estimating total  $^{241}\text{Am}$  deposition, which involves taking into account ingrowth of  $^{241}\text{Am}$  from the  $^{241}\text{Pu}$  deposited, is more difficult; however, if we use an  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratio of 0.37 measured in mid-latitude soils in the late 1980s (Ryan et al. 1995), an integrated  $^{241}\text{Am}$  deposition of  $29.5 \text{ Bq m}^{-2}$  can be derived from the known  $^{239+240}\text{Pu}$  deposition. Comparing these integrated deposition inventories with the 1989–1990 water column inventories given in Table 3 indicates that in the deepest areas of the

Table 4. Summary of total water column inventories (TBq) for transuranics in the western Mediterranean Sea and mean annual transuranic loss ( $\text{Bq m}^{-2} \text{ yr}^{-1}$ ) derived for different time intervals.

		$^{239+240}\text{Pu}$	$^{241}\text{Am}$
Inventory for years	1976 ( $T_1$ )	34.1 TBq	5.19 TBq
	1981–1982 ( $T_2$ )	33.2 TBq	—
	1989–1990 ( $T_3$ )	30.3 TBq	3.95 TBq
Inventory decrease between years	$T_2 - T_1$	0.9 TBq	—
	$T_3 - T_2$	2.9 TBq	—
	$T_3 - T_1$	3.8 TBq	1.24 TBq
Mean per loss per year for different time intervals*	$T_2 - T_1$	$0.24 \text{ Bq m}^{-2} \text{ yr}^{-1}$	—
	$T_3 - T_2$	$0.53 \text{ Bq m}^{-2} \text{ yr}^{-1}$	—
	$T_3 - T_1$	$0.41 \text{ Bq m}^{-2} \text{ yr}^{-1}$	$0.13 \text{ Bq m}^{-2} \text{ yr}^{-1}$
Overall mean loss		$0.39 \text{ Bq m}^{-2} \text{ yr}^{-1}$	$0.13 \text{ Bq m}^{-2} \text{ yr}^{-1}$

\* The difference in total inventories between any two-year intervals is computed as the inventory decrease divided by the total surface area of the western Mediterranean basin ( $681 \times 10^9 \text{ m}^2$ ) divided by the average time interval between the years when measurements were made (i.e., 5.5, 8, or 13.5 yr).

Table 5. Concentrations and vertical fluxes of transuranics in sinking particles from the northwestern Mediterranean Sea.

Experiment/ (Location)	Date	*Depth (m)	Mass flux (mg m <sup>-2</sup> d <sup>-1</sup> )	<sup>239+240</sup> Pu		<sup>241</sup> Am		<sup>241</sup> Am/ <sup>239+240</sup> Pu activity ratio	
				(Bq kg <sup>-1</sup> )	(mBq m <sup>-2</sup> d <sup>-1</sup> )	(Bq kg <sup>-1</sup> )	(mBq m <sup>-2</sup> d <sup>-1</sup> )		
EROS-2000									
(Gulf of Lions, 1990)	14–27 Apr	200	128	1.92	0.245	0.46	0.059	0.24	
		27 Apr–10 May	200	309	3.83	1.183	3.29	1.016	0.86
			500	48.6	2.82	0.137	1.48	0.072	0.52
			1,000	242	4.73	1.146	2.50	0.606	0.53
			2,000	241	3.36	0.809	3.33	0.802	0.99
		10–23 May	200	182	5.28	0.960	0.32	0.058	0.06
			1,000	121	3.33	0.402	1.85	0.224	0.56
	23 May–05 Jun		2,000	174	3.02	0.527	2.40	0.418	0.79
			200	71.8	5.91	0.424	2.14	0.154	0.36
		15–18 Jun	200	61.4	7.60	0.467	2.52	0.155	0.33
	18 Jun–01 Jul	200	101	8.45	0.849	1.92	0.193	0.23	
	DYFAMED								
	(Ligurian Sea, 1988– 1989)	05 Jun–15 Jul 1988	100	221	4.43	0.979	0.73	0.161	0.16
			200	96	8.20	0.787	2.01	0.193	0.25
1,000			151	6.70	1.012	3.22	0.486	0.48	
5–30 May 1989		200	137	5.12	0.701	2.17	0.297	0.42	
		1,000	45.5	4.70	0.214	3.90	0.178	0.83	
3 Nov–1 Dec 1989		100	47	2.60	0.122	3.70	0.174	1.42	
		2,000	42.5	2.35	0.100	5.70	0.242	2.43	
1–15 Dec 1989		100	254	1.34	0.340	0.81	0.206	0.60	
		200	155	2.37	0.367	0.85	0.132	0.36	
		1,000	151	2.18	0.329	1.76	0.266	0.81	
		2,000	230	1.88	0.432	3.63	0.835	1.93	

\* Missing depths = insufficient sample for transuranic analyses.

western Mediterranean (3,000–3,500 m) virtually all the deposited <sup>239+240</sup>Pu remained in the water column in 1990, whereas only 37% of the deposited <sup>241</sup>Am was still present.

Temporal changes in inventories are more evident when examined through specific depth intervals where most previous measurements have been made. Using similar reasoning for computing integrated <sup>239+240</sup>Pu deposition inventories for a given year, it can be calculated from the data of Livingston et al. (1979) that for a water column profile measurement made in the northwestern basin in 1975, about 74% of the deposited <sup>239+240</sup>Pu was retained in the upper 2,600 m. From a similar profile measured nearby in 1976 by Fukai et al. (1979) (Table 2), we estimate that approximately 65% of the deposited <sup>239+240</sup>Pu was located in the upper 2,000 m at that time. Over the same 2,000-m depth range for the three profiles we measured (Table 2), on average only 57% of the deposited <sup>239+240</sup>Pu remained by 1989–1990. Hence, from these data sets there is further indication of the slow downward movement of plutonium in the water column during that 15-yr period.

We can also estimate the total removal of <sup>239+240</sup>Pu and <sup>241</sup>Am from the water column by computing the total fallout inventories for the basin and comparing these with the transuranic inventories remaining in the water column of the entire basin. To compute the fallout inventories, the deposition values over the western basin given above are integrated over the total surface area of the basin shown in Table 3

(681.4 × 10<sup>9</sup> m<sup>2</sup>). This results in total integrated delivery over the basin of 54.3 TBq of <sup>239+240</sup>Pu and 20.1 TBq of <sup>241</sup>Am. Comparing the total water column inventories for 1989–1990 (Table 3) with the total delivery values indicates that 56% and 20% of the deposited <sup>239+240</sup>Pu and <sup>241</sup>Am, respectively, were still present in the water column at that time.

*Vertical fluxes*—Plutonium and americium concentrations in sinking particles and corresponding radionuclide fluxes are given in Table 5. Concentrations of both radionuclides in the particulate matter were similar at the two stations and ranged from approximately 0.3 to 8 Bq kg<sup>-1</sup>. During the DYFAMED experiment <sup>239+240</sup>Pu concentrations varied by a factor of 6 and <sup>241</sup>Am by a factor of 8. Furthermore, the highest plutonium fluxes were in part due to the high <sup>239+240</sup>Pu concentrations in the particles as is evident from the data for June–July 1988 and May 1989. The <sup>241</sup>Am/<sup>239+240</sup>Pu ratios in the particles were all higher than were observed in bulk seawater, and some very high ratios (1.9–2.4), more typical of Mediterranean sediments (Livingston et al. 1977), were recorded in particles fluxing through 2,000 m.

During the course of the 2½-month EROS experiment from April to July, the <sup>239+240</sup>Pu concentrations in particles at 200 m steadily increased from 1.92–8.45 Bq kg<sup>-1</sup>. Corresponding <sup>241</sup>Am levels varied by a factor of 10 throughout this period but did not follow the same increasing trend as

Table 6. Mean annual transuranic fluxes measured by sediment traps in the western Mediterranean Sea.

Location/(Program)	Trap depth (m)	Mean $^{239+240}\text{Pu}$ flux ( $\text{Bq m}^{-2}\text{yr}^{-1}$ )	Mean $^{241}\text{Am}$ flux ( $\text{Bq m}^{-2}\text{yr}^{-1}$ )	Reference
Lacaze-Duthiers Canyon (ECOMARGE)	300	2.7	2.8	Fowler et al. 1990b
Cañon de Foix, Balearic Sea (FLUBAL '93)	710	0.71	—	Merino 1997
	1,180	1.08	—	
Ligurian Sea, Corsica (DYFAMED)	200	0.16	0.048	Fowler et al. 1990a
Ligurian Sea, Villefranche (DYFAMED)	1,000	0.19	0.081	This study
	2,000	0.10	0.20	
Gulf of Lions (EROS)	1,000	0.28	0.15	This study
	2,000	0.24	0.22	

$^{239+240}\text{Pu}$ . From the end of April until the end of May, no clear trend in radionuclide concentration with depth was evident except for  $^{241}\text{Am}$  immediately following the major sedimentation pulse of phytoplankton aggregates, which swept the water column between 27 April and 10 May 1990 (Peinert et al. 1992). At this time (10–23 May) both  $^{241}\text{Am}$  concentration and flux increased with depth, suggesting enhanced scavenging of the radionuclide throughout the water column. Preferential scavenging of  $^{241}\text{Am}$  relative to  $^{239+240}\text{Pu}$  is also reflected in the increasing  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratio in the sinking particles with depth (Table 5). During both these periods, microscopic and chemical analyses of the trap material indicated the presence of large amounts of diatom cells and phyto-detritus, which served as the primary transport vector for the radionuclides (Peinert et al. 1992). With the exception of the period of rapid mass flux and enhanced  $^{241}\text{Am}$  scavenging associated with the crash of a phytoplankton bloom, the  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratio in particles fluxing through 200 m more closely reflected the ratio in fallout ( $\sim 0.3\text{--}0.4$ ).

The maximum fluxes of both  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  at both stations generally coincided with the periods of maximum sedimentation, demonstrating that particle flux was the primary factor controlling transuranic flux. Transuranic fluxes measured at both stations were similar to those recorded in the same general region off Corsica during spring 1986 (Fowler et al. 1990a), but they were an order of magnitude lower than  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  fluxes measured during fall 1983 in the high sedimentation regime of the Lacaze-Duthiers Canyon in the Gulf of Lions (Fowler et al. 1990b). Clearly, variations in the flux of these radionuclides to a large extent depend on the sedimentation rate.

The degree to which large particle transport is responsible for the removal of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  from the water column can be examined by comparing direct measurements of mean annual transuranic fluxes, particularly those in deep waters, with the estimates of changes in total water column plutonium and americium inventories over time (Table 4). In Table 6 a summary of mean annual  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  fluxes computed from time-series sediment trap data is given for various areas of the western Mediterranean. Excluding high-

energy canyon systems where fluxes are extremely high, a comparison of deep water (1,000–2,000 m) particulate transuranic fluxes in the open waters of the western basin with the derived annual loss rates given in Table 4 suggests that on average 26–72% of the estimated plutonium loss can be accounted for by the sinking out of large particles, whereas virtually all of the  $^{241}\text{Am}$  loss could have occurred by this mechanism. This observation points to a relatively slow removal of the standing stock of plutonium in western Mediterranean waters compared with that of americium.

The average  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  flux through 200 m during the 2½-month EROS-2000 study was 0.688 and 0.273  $\text{mBq m}^{-2}\text{d}^{-1}$ , respectively (Table 5). Transuranic concentration profiles in seawater measured at this site during early May resulted in corresponding radionuclide inventories above 200 m of 5.9 and 0.53  $\text{Bq m}^{-2}$  (Table 2). Under the assumption of steady state conditions, such fluxes would result in a residence time for  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the upper mixed layers of approximately 24 and 5.3 yr, respectively. These residence times are considerably longer than those (2.5 and 0.14 yr, respectively) reported for a 17-d deployment in the Lacaze-Duthiers Canyon (Fowler et al. 1990b) and are probably more representative of average transuranic flux in open waters of the northwestern Mediterranean basin.

Mean upper layer (0–200 m) residence times of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  have been computed in this fashion for various areas in the northwestern Mediterranean (Table 7). Residence times in the high sedimentation, Lacaze-Duthiers Canyon regime in the Gulf of Lions are typically very short, on the order of 1–2 months for  $^{241}\text{Am}$ , and 2–3 yr for  $^{239+240}\text{Pu}$ . In contrast, in the open Mediterranean where particle fluxes are lower, mean residence times are much longer, i.e., approximately 5–10 yr for  $^{241}\text{Am}$  and 20–30 yr for  $^{239+240}\text{Pu}$ . These latter values are in fair agreement with corresponding estimates of 2.9 and 12.3 yr for this region based on atmospheric delivery rate data and mixed layer (0–100 m) transuranic inventories from the mid-1970s (Thein et al. 1980).

It is of particular interest to compare similar transuranic residence time estimates derived from Pacific Ocean data. Also given in Table 7 are the upper mixed-layer residence times for plutonium and americium at three VERTEX sta-

Table 7. Mean residence times (years) for plutonium and americium in the upper water column of the northwestern Mediterranean Sea and the northeast Pacific Ocean.

	ECO-MARGE Lacaze-Duthiers Canyon (300 m) (42°40'N, 03°22'E)	DYFA-MED Corsica (200 m) (42°44'N, 08°31'E)	DYFAMED Ville-franche (200 m) (43°25'N, 07°53'E)	EROS-2000 ETRO (200 m) (41°57'N, 5°56'E)
Northwestern Mediterranean Sea (1986–1990)*				
<sup>239+240</sup> Pu	2.5	32‡	22	24
<sup>241</sup> Am	0.14	11§	6.9§	5.3
	N. Pacific			
	VERTEX 1 (250 m) (35°48'N, 123°35'W)	GYRE (150 m) (28°N, 155°W)	VERTEX Time Series (150 m) (33°N, 139°W)	
Northeast Pacific Ocean (1980–1988)†				
<sup>239+240</sup> Pu	13	16	4.1 ± 1.8 (2.6–6.8)	
<sup>241</sup> Am	1.5	37	5.8	

\* Data taken from Fowler et al. 1990a,b; this study.

† Data taken from Fowler et al. 1983, 1991; Fowler 1987.

‡ Based on mean inventory in upper 200 m water column at DYFAMED station in 1989 (see Table 2).

§ Based on water column inventory (0–200 m) measured at EROS station in 1990 (see Table 2).

tions in the open northeast Pacific. For all three stations the residence times for <sup>239+240</sup>Pu were shorter than those measured at the open Mediterranean sites. Comparable data for <sup>241</sup>Am are fewer; nevertheless, in oligotrophic waters of the north Pacific gyre station, the <sup>241</sup>Am residence time (37 yr) is roughly twice as long as that of <sup>239+240</sup>Pu, which is opposite to the relationship observed in the western Mediterranean. Thus, it appears that the biogeochemical behavior of these fallout radionuclides in the upper water column of oligotrophic waters from these two open ocean regions are quite different. At the VERTEX 1 station, the pattern of residence times more closely approximates that found in the Mediterranean, with <sup>241</sup>Am being removed from the upper water column much more rapidly than <sup>239+240</sup>Pu. However, the VERTEX 1 station is situated in the highly productive California Current and, during the time of the 2-week sediment trap experiment, a phytoplankton bloom with associated grazing activity was present (Fowler et al. 1983). Therefore, the qualitative and quantitative aspects of the particle flux at this station were quite different from those at the other two open Pacific sites shown in Table 7.

**Transuranic ratios**—Ratios of <sup>241</sup>Am/<sup>239+240</sup>Pu and the differential behavior of these radionuclides in the marine environment have been the focus of much discussion (Fukai et al. 1979; Koide et al. 1981; Fowler et al. 1983; Livingston et al. 1977, 1987; León Vintró et al. 1999). From the present study as well as earlier work on transuranics in water column profiles and sediment cores from the western Mediterranean, it is now well-established that <sup>241</sup>Am is removed from the

water column and transferred to the sediments much more rapidly than <sup>239+240</sup>Pu. However, one aspect of this differential behavior which has not been examined in detail is how downward transport and removal processes in the Mediterranean compare with those in other oceanic areas. To obtain some insight into this question, <sup>241</sup>Am/<sup>239+240</sup>Pu activity ratios in unfiltered seawater have been compiled for the western Mediterranean and the north Pacific ocean, two regions where a considerable amount of water column data on transuranics has been obtained (Table 8). This compilation from mid-latitudes in the northern hemisphere is not all inclusive of those existing in various publications and reports, however, we consider it to be representative of the most in-depth studies carried out in areas subject only to inputs of atmospheric fallout from previous nuclear tests. Furthermore, the data in Table 8 include both surface water measurements as well as those in profiles to a maximum depth of 3,000 m. Although several studies cited above have shown that <sup>241</sup>Am/<sup>239+240</sup>Pu ratios often increase with depth, for the purposes of this analysis measurements from all depths have been lumped together for comparison. From both the average values and ranges of ratios given, it is evident that <sup>241</sup>Am/<sup>239+240</sup>Pu ratios in unfiltered seawater are considerably lower in the Mediterranean than in north Pacific waters. If all the compiled data are treated together, the mean ratio in the western Mediterranean (0.097) is approximately six times lower than that in north Pacific waters (0.57). Given this difference and the fact that fallout introduced to these two oceanic areas contains the same Am/Pu signature (Table 8, ~0.3), the question arises as to the cause of this apparent difference in geochemical behavior.

In contrast to the north Pacific ocean, the semi-enclosed Mediterranean basin is unique in that it receives frequent atmospheric inputs of mineral aerosol particles transported via Saharan dust storms in Africa (Moulin et al. 1997). Furthermore, the mass of this dust is large at roughly one billion tonnes per year, and it has been shown that deposition of these fine particles can profoundly influence the geochemistry and sedimentology of the Mediterranean Sea (Loÿe-Pilot et al. 1986; Buat-Menard et al. 1989). Buat-Menard et al. (1989) have demonstrated a close coupling between the large atmospheric inputs of aluminosilicates and their rapid removal from surface waters, and vertical flux to depth in the northwestern Mediterranean basin. In fact, their time-series sediment trap studies indicate that aluminosilicate minerals alone can account for 5 to 76% of the downward mass flux in this region, and that zooplankton grazing activities and resultant fecal pellet production are largely responsible for the aggregation of the aluminosilicates and their rapid transport to depth.

The majority of data from both field and laboratory experiments demonstrates that <sup>241</sup>Am is more particle reactive than plutonium (see e.g., IAEA 1985). In the case of aluminosilicate particles, which form the deep ocean sediments in many areas, the difference in the two radionuclide distribution coefficients between sediments and water ( $K_d$ ) may be as much as one to two orders of magnitude, depending upon particle type (IAEA 1985; Aston and Fowler 1987). Therefore, it seems highly plausible that in the Mediterranean region which is continually receiving such high atmo-

Table 8.  $^{241}\text{Am}/^{239+240}\text{Pu}$  activity ratio in unfiltered seawater from various locations and depths (surface – 3,000 m) in the western Mediterranean Sea and north Pacific Ocean.

Ocean	Location/Date	$^{241}\text{Am}/^{239+240}\text{Pu}$		Reference
		$\bar{X} + \sigma$	(Range)	
Western Mediterranean	Gulf of Lions, Ligurian Sea, Tyrrhenian Sea, surface, 1975	0.06±0.027	(0.027–0.10)	Fukai et al. 1976
	Ligurian Sea, 1976	0.14±0.11	(0.033–0.32)	Fukai et al. 1979
	Gulf of Lions, 1981	0.13±0.08	(0.03–0.20)	Fukai et al. 1983
	Gulf of Lions, 1986	0.067±0.021	(0.038–0.098)*	Fowler et al. 1990b
	EROS Station, 1990	0.13±0.05	(0.049–0.22)	This study
	Catalan coast, 1989, 1991	0.16±0.09	(0.09–0.38)	Molero et al. 1995b
	Catalan Sea, 1991	0.068±0.017	(0.051–0.09)	Molero et al. 1995a
	Alboran Sea, 1994	0.044±0.023	(0.013–0.076)	León Vintró et al. 1999
	Algerian Basin, 1994	0.078±0.048	(0.017–0.133)	León Vintró et al. 1999
	DYFAMED Station, surface, 1999	0.036±0.015	(0.031–0.041)	This study
North Pacific	Northwest, 1977–1978	0.36±0.37	(0.05–1.5)	Miyaki et al. 1988
	Central, deep, 1979–1980	0.33±0.082	(0.20–0.51)*	Livingston et al. 1987
	California current, surface, 1979	0.36±0.12	(0.26–0.59)	Livingston et al. 1987
	California current, 1980	0.64±0.39	(0.28–1.1)	Fowler et al. 1983
	Central gyre, surface, 1980	0.18±0.05	(0.14–0.24)	Livingston et al. 1987
	Off central Mexico, 1981–1982	1.57±1.52	(0.49–4.6)	Fowler unpubl. results
	Central gyre, 1983	0.60±0.27	(0.28–1.1)	Fowler unpubl. results
	Central Northeast, 1986–1988	0.72±0.38	(0.24–1.3)	Fowler et al. 1991
FALLOUT in soils (mid-latitude)	Mid-1970s		0.22–0.25	Krey et al. 1976
	Late 1980s		0.37	Ryan et al. 1995

\* Some near bottom depths excluded because of potential high sediment load or boundary layer effects such as radionuclide dissolution from sediments.

spheric inputs of aluminosilicates, the sinking particle field would scavenge more  $^{241}\text{Am}$  relative to  $^{239+240}\text{Pu}$ , thus rendering  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratios in unfiltered seawater uniformly low. Bulk water depleted in  $^{241}\text{Am}$  relative to  $^{239+240}\text{Pu}$  throughout the water column suggests that  $^{241}\text{Am}$  is being delivered to the sediments more rapidly than plutonium. Such a scenario would indeed account for the very high  $^{241}\text{Am}/^{239+240}\text{Pu}$  ratios (0.7–1.8) which have been measured in deep Mediterranean sediments (Livingston et al. 1977). This particle scavenging model for transuranics, based on qualitative differences in the particle field, could be tested during a Saharan dust event by intensive sampling of the suspended particulate and rapidly sinking particle fields using large volume filtration pumps and sediment traps.

## Summary and conclusions

Only very few high-resolution data sets can be used to adequately assess temporal trends in changes of the plutonium and americium inventories in the Mediterranean Sea. In all our 1989–1990 profiles a subsurface maximum of  $^{239+240}\text{Pu}$  was observed between 100–400 m. Measurements made at a single station during two different times of the year indicate that the position of the subsurface maximum may be closely controlled by the degree of primary production occurring in the upper water column. The profile for  $^{241}\text{Am}$  revealed two subsurface maxima, one between 100–200 m, and a stronger peak at 800 m, suggesting a different geochemical behavior of this radionuclide compared with plutonium.

An assessment of  $^{239+240}\text{Pu}$  inventories derived from the

profiles demonstrates that while deep water column inventories (e.g., 0–2,000 m) have not substantially changed over the 10–15 yr period examined, the fraction of the  $^{239+240}\text{Pu}$  inventory at a given depth interval in the deeper layers has increased considerably, demonstrating the slow, downward movement of  $^{239+240}\text{Pu}$  in the northwestern Mediterranean. This increase at depth is commensurate with an approximate 35% decrease in the  $^{239+240}\text{Pu}$  inventory in the upper mixed layer (0–200 m) during the same period. In contrast,  $^{241}\text{Am}$  is removed much more rapidly from the water column than  $^{239+240}\text{Pu}$ , as is evident from the increased  $^{241}\text{Am}/^{239+240}\text{Pu}$  activity ratio in bulk seawater at depth, as well as the approximately 24% decrease in the  $^{241}\text{Am}$  inventory (0–2,000 m) over the 13.5-yr period. Temporal changes are also evident from total water column transuranic inventories derived for the entire western Mediterranean basin, which indicate a small but consistent decrease from 34.1 to 30.3 TBq for  $^{239+240}\text{Pu}$  and 5.19 to 3.95 TBq for  $^{241}\text{Am}$  between 1976 and 1989–1990, resulting in an approximate annual loss from the water column of  $0.39 \text{ Bq m}^{-2} \text{ y}^{-1}$ , and  $0.13 \text{ Bq m}^{-2} \text{ y}^{-1}$ , respectively. Time-series measurements of the vertical flux of particulate  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  made at the same stations during 1988–1990 demonstrated that particles sinking through deep waters (1,000–2,000 m) could account for 26 to 72% of the derived annual  $^{239+240}\text{Pu}$  loss and virtually all the  $^{241}\text{Am}$  removal from the water column. Coupling the measured upper water transuranic fluxes with upper mixed-layer transuranic inventories results in upper mixed-layer (0–200 m) residence times of approximately 20–30 yr and 5–10 yr for  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$ , respectively. Furthermore, the residence times for  $^{239+240}\text{Pu}$  in the Mediterranean are longer

than those in the open waters of the northeast Pacific Ocean, whereas the corresponding residence time for  $^{241}\text{Am}$  in the open Pacific (37 yr) is longer than that of  $^{239+240}\text{Pu}$ . Such observations suggest different scavenging rates and transport behaviors for the two radionuclides in these oligotrophic areas. An examination of  $^{241}\text{Am}/^{239+240}\text{Pu}$  activity ratios in a variety of unfiltered seawater samples from the two oceans has shown that ratios in western Mediterranean waters are on average some six times lower than those in the north Pacific. Such a large impoverishment of  $^{241}\text{Am}$  relative to  $^{239+240}\text{Pu}$  in Mediterranean seawater argues for a mechanism that effects much more rapid removal of  $^{241}\text{Am}$  in the Mediterranean basin. The frequent atmospheric inputs of massive amounts of aluminosilicate particles to the Mediterranean via Saharan dust events furnishes a particle type for which  $^{241}\text{Am}$  has a greater binding affinity than  $^{239+240}\text{Pu}$ . This, in turn, could lead to higher vertical transport rates of  $^{241}\text{Am}$  relative to  $^{239+240}\text{Pu}$  and higher  $^{241}\text{Am}$  transport in general compared with that in the open north Pacific where large-scale dust inputs are rare.

### References

- ASTON, S. R., AND S. W. FOWLER. 1987. Bioavailability of technetium, plutonium and americium from deep-sea sediments to the clam *Tapes decussatus* L., p. 209–220. In T. P. O'Connor, W. V. Burt, and I. W. Duedall [eds.], *Oceanic processes in marine pollution, V. 2. Physicochemical processes and wastes in the ocean*. R. E. Krieger. Publ. Co.
- BACON, M. P., C.-A. HUH, A. P. FLEER, AND W. G. DEUSER. 1985. Seasonality in the flux of natural radionuclides and plutonium in the deep Sargasso Sea. *Deep-Sea Res.* **32**: 273–286.
- BALLESTRA, S., R. BOJANOWSKI, R. FUKAI, AND D. VAS. 1984. Behaviour of selected radionuclides in the northwestern Mediterranean basin influenced by river discharge, p. 215–232. In A. Cigna and C. Myttenaere [eds.], *International symposium on the behaviour of long-lived radionuclides in the marine environment*. Commission of the European Communities.
- , AND R. FUKAI. 1983. An improved radiochemical procedure for low-level measurements of americium in environmental matrices. *Talanta* **30**: 45–48.
- , E. HOLM, AND R. FUKAI. 1978. Low level determination of transuranic elements in marine environmental samples, 9 pp. In *Proceedings of a symposium on determination of radionuclides in environmental materials*. Central Electricity Generating Board, London, Paper No. 15 (nonpaginated).
- BEASLEY, T. M., R. CARPENTER, AND C. D. JENNINGS. 1982. Plutonium,  $^{241}\text{Am}$ , and  $^{137}\text{Cs}$  ratios, inventories and vertical profiles in Washington and Oregon continental shelf sediments. *Geochim. Cosmochim. Acta* **46**: 1931–1946.
- BOWEN, V. T., V. E. NOSHKIN, H. D. LIVINGSTON, AND H. L. VOLCHOK. 1980. Fallout radionuclides in the Pacific Ocean: Vertical and horizontal distributions, largely from GEOSECS stations. *Earth Planet. Sci. Lett.* **49**: 411–434.
- BROUARDEL, J. 1971. Variations dans le temps de la production primaire de la mer au voisinage de Monaco. *Mém. Inst. Océanogr. Monaco* **3**: 1–20.
- BUAT-MENARD, P., J. DAVIES, E. REMOUDAKI, J. C. MIQUEL, G. BERGAMETTI, C. E. LAMBERT, U. EZAT, C. QUETEL, J. LA ROSA, AND S. W. FOWLER. 1989. Non-steady-state biological removal of atmospheric particles from Mediterranean surface waters. *Nature* **340**: 131–134.
- CHRISTENSEN, J. P., T. T. PACKARD, F. Q. DORTCH, H. J. MINAS, J. C. GASCARD, C. RICHEZ, AND P. C. GARFIELD. 1989. Carbon oxidation in the deep Mediterranean sea: Evidence for dissolved organic carbon source. *Glob. Biogeochem. Cycles* **3(4)**: 315–335.
- FOWLER, S. W. 1987. VERTEX: Factors affecting the vertical flux of  $^{239+240}\text{Pu}$  and  $^{241}\text{Am}$  in the upper layers of the Northeast Pacific Ocean. *Colloque Internationale d'Océanologie, ECO systems des MARGES continentales*, Perpignan, C.I.E.S.M. Monaco, p. 82.
- , S. BALLESTRA, J. LA ROSA, AND R. FUKAI. 1983. Vertical transport of particulate-associated plutonium and americium in the upper water column of the northeast Pacific. *Deep-Sea Res.* **30**: 1221–1233.
- , ———, ———, E. HOLM, AND J. J. LOPEZ. 1990a. Flux of transuranium nuclides in the northwestern Mediterranean following the Chernobyl accident. *Rapp. Comm. Internat. Mer. Médit.* **32(1)**: 317.
- , ———, AND J.-P. VILLENEUVE. 1990b. Flux of transuranium nuclides and chlorinated hydrocarbons in the northwestern Mediterranean. *Continental Shelf Res.* **10(9–11)**: 1005–1023.
- , S. W., L. F. SMALL, J. LA ROSA, J.-J. LOPEZ, AND J.-L. TEYSSIE. 1991. Interannual variation in transuranic flux at the Vertex time-series station in the northeast Pacific and its relationship to biological activity, p. 286–298. In P. J. Kershaw and D. S. Woodhead [eds.], *Radionuclides in the study of marine processes*. Elsevier Applied Science.
- FUKAI, R., S. BALLESTRA, AND E. HOLM. 1976.  $^{241}\text{Americium}$  in Mediterranean surface waters. *Nature* **264**: 739–740.
- , ———, AND D. VAS. 1983. Characteristics of the vertical transport of transuranic elements through the Mediterranean water column, p. 95–101. In VI<sup>es</sup> Journées d'Etudes sur les Pollutions Marines en Méditerranée. *Comm. Internat. Explorat. Scientif. Mer Médit.*, Monaco.
- , E. HOLM, AND S. BALLESTRA. 1979. A note on vertical distribution of plutonium and americium in the Mediterranean Sea. *Oceanol. Acta* **2**: 129–132.
- GOFFART, A., J.-H. HECQ, AND L. PRIEUR. 1995. Contrôle du phytoplancton du bassin Ligure par le front liguro-provençal (secteur Corse). *Oceanol. Acta* **18**: 329–342.
- HARDY, E. P., P. W. KREY, AND H. L. VOLCHOK. 1973. Global fallout inventory and distribution of fallout plutonium. *Nature* **241**: 444–445.
- HOLM, E., S. BALLESTRA, R. FUKAI, AND T. M. BEASLEY. 1980. Particulate plutonium and americium in Mediterranean surface waters. *Oceanol. Acta* **3**: 157–160.
- IAEA. 1985. Sediment  $K_d$ s and concentration factors for radionuclides in the marine environment. *Technical Reports Series No. 247*. IAEA, Vienna.
- . 1991. IAEA marine environment laboratory. *Biennial Report 1989/1990*. IAEA, Vienna.
- JACQUES, G. 1988. Flux de carbone en milieu pélagique de Méditerranée occidentale lors de la floraison printanière, *Océanographie pélagique méditerranéenne*, H. J. Minas and P. Nival [eds.], *Oceanologica Acta*, sp. Vol. **9**: 143–148.
- KOIDE, M., P. W. WILLIAMS, AND E. D. GOLDBERG. 1981. Am-241/Pu-239+240 ratios in the marine environment. *Mar. Environment. Res.* **5**: 241–246.
- KREY, P. W., E. P. HARDY, C. PACHUCKI, F. ROURKE, J. COLUZZA, AND W. K. BENSON. 1976. Mass isotopic composition of global fall-out plutonium in soil, p. 671–678. In *Transuranium Nuclides in the Environment*, International Atomic Energy Agency, Vienna.
- LEÓN VINTRÓ, L., P. I. MITCHELL, O. M. CONDREN, A. B. DOWNES, C. PAPUCCI, AND R. DELFANTI. 1999. Vertical and horizontal fluxes of plutonium and americium in the western Mediterranean and the Strait of Gibraltar. *Sci. Tot. Environ.* **237**: 77–91.

- LÉVY, M., L. MÉMERY, AND J.-M. ANDRÉ. 1998. Simulation of primary production and export fluxes in the northwestern Mediterranean Sea. *J. Mar. Res.* **56**: 197–238.
- LIVINGSTON, H. D., AND R. F. ANDERSON. 1983. Large particle transport of plutonium and other fallout radionuclides to the deep ocean. *Nature* **303**: 228–231.
- , V. T. BOWEN, AND J. C. BURKE. 1977. Fallout radionuclides in Mediterranean sediments. *Rapp. Comm. Internat. Explorat. Scientif. Mer Médit.* **24**: 37–40.
- , S. A. CASSO, V. T. BOWEN, AND J. C. BURKE. 1979. Soluble and particle-associated fallout radionuclides in Mediterranean water and sediments. *Rapp. Comm. Internat. Explorat. Scientif. Mer Médit.* **25/26(5)**: 71–76.
- , D. R. MANN, S. A. CASSO, D. L. SCHNEIDER, L. D. SURPRENANT, AND V. T. BOWEN. 1987. Particle and solution phase depth distributions of transuranics and <sup>59</sup>Fe in the north Pacific. *Mar. Environment. Res.* **5**: 1–24.
- LOÏE-PILOT, M. D., J. M. MARTIN, AND J. MORELLI. 1986. Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. *Nature* **321**: 427–428.
- MERINO, J. 1997. Estudios sobre el ciclo del plutonio en ecosistemas acuáticos. Tesis Doctoral, Facultat de Ciències, Universitat Autònoma de Barcelona.
- , J. A. SANCHEZ-CABEZA, J. M. BRUACH, P. MASQUE, AND LL. PUJOL. 1997. Artificial radionuclides in a high resolution water column profile from the Catalan Sea (the northwestern Mediterranean). *Radioprot.-Colloques* **32**: C2, 85–90.
- MILLOT, C. 1987. Circulation in the western Mediterranean Sea. *Oceanol. Acta* **10**: 143–149.
- MIQUEL, J.-C., S. W. FOWLER, J. LA ROSA, AND P. BUAT-MENARD. 1994. Dynamics of the downward flux of particles and carbon in the open northwestern Mediterranean Sea. *Deep-Sea Res. I* **41(2)**: 243–261.
- MIYAKE, Y., K. SARUHASHI, Y. SUGIMURA, T. KANAZAWA, AND K. HIROSE. 1988. Contents of <sup>137</sup>Cs, plutonium, and americium isotopes in the southern ocean waters. *Papers in Meteorology and Geophysics* **39**: 95–113.
- MOLERO, J., J. A. SANCHEZ-CABEZA, J. MERINO, LL. PUJOL, P. I. MITCHELL, AND A. VIDAL QUADRAS. 1995a. Vertical distribution of radiocesium, plutonium, and americium in the Catalan Sea (Northwestern Mediterranean). *J. Environ. Radioact.* **26**: 205–216.
- , ———, ———, J. VIVES BATLLE, P. I. MITCHELL, AND A. VIDAL QUADRAS. 1995b. Particulate distribution of plutonium and americium in surface waters from the Spanish Mediterranean coast. *J. Environ. Radioact.* **28**: 271–283.
- MOREL, A., AND J.-M. ANDRÉ. 1991. Pigment distributions and primary production in the western Mediterranean, as derived and modeled from coastal zone color scanner observations. *J. Geophys. Res.* **96**: 12685–12698.
- MOULIN, C., C. E. LAMBERT, F. DULAC, AND U. DAYAN. 1997. Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation. *Nature* **387**: 691–694.
- NOSHKIN, V. E., AND V. T. BOWEN. 1972. Concentrations and distributions of long-lived fallout radionuclides in open ocean sediments, p. 671–686. *In* Radioactive contamination of the marine environment. IAEA, Vienna.
- PEINERT, R. D., S. W. FOWLER, J. LA ROSA, J.-C. MIQUEL, AND J.-L. TEYSSIE. 1992. Vertical flux and microplankton assemblages in the Gulf of Lions during spring 1990, p. 413–424. *In* J.-M. Martin and H. Barth [eds.], EROS-2000 (European River Ocean System). Third workshop on the north-west Mediterranean Sea, Water pollution research report 28. CEC, Brussels, Belgium.
- RYAN, T. P., P. I. MITCHELL, J. A. SANCHEZ-CABEZA, V. SMITH, AND J. VIVES I BATLLE. 1995. Distribution of radioactive fallout throughout Ireland, p. 276–282. *In* Proc. Int. Tyndall School and National Environment Week, Carlow (Ireland), 11–19 September 1993. Science, green issues and the environment: Ireland and the global crisis.
- SHOLKOVITZ, E. R. 1983. The geochemistry of plutonium in fresh and marine environments. *Earth-Sci. Reviews* **19**: 95–161.
- THEIN, M., S. BALLESTRA, A. YAMATO, AND R. FUKAI. 1980. Delivery of transuranic elements by rain to the Mediterranean Sea. *Geochim. Cosmochim. Acta* **44**: 1091–1097.

Received: 8 February 1999

Accepted: 13 September 1999

Amended: 6 October 1999