

Vertical and horizontal fluxes of plutonium and americium in the western Mediterranean and the Strait of Gibraltar

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Abstract

New data on the vertical distributions of plutonium and americium in the waters of the western Mediterranean and the Strait of Gibraltar are examined in terms of the processes governing their delivery to, transport in and removal from the water column within the basin. Residence times for plutonium and americium in surface waters of ~ 15 and ~ 3 years, respectively, are deduced, and it is shown that by the mid 1990s only ~ 35% of the ^{239,240}Pu and ~ 5% of the ²⁴¹Am deposited as weapons fallout still resided in the water column. Present ^{239,240}Pu inventories in the water column and the underlying sediments are estimated to be ~ 25 TBq and ~ 40 TBq, respectively, which reconcile well with the time-integrated fallout deposition in this zone, taken to be ~ 69 TBq. The data show that there are significant net outward fluxes of plutonium and americium from the basin through the Strait of Gibraltar at the present time. These appear to be compensated by net inward fluxes of similar magnitude through the Strait of Sicily. Thus, the time-integrated fallout deposition in the western basin can be accounted for satisfactorily in terms of present water column and sediment inventories. Enhanced scavenging on the continental shelves, as evidenced by the appreciably higher transuranic concentrations in shelf sediments, supports this contention. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. Physical oceanography of the Mediterranean Sea

The Mediterranean is a mid-latitude, semi-enclosed sea, connected with the Atlantic Ocean only through the narrow and shallow Strait of Gibraltar (Fig. 1). Shallow ridges between Tunisia and Sicily provide the most clear subdivision of the Mediterranean Sea, separating the western and eastern basins. Since evaporation exceeds precipitation and runoff from land, the Mediterranean acts as a negative or concentration basin in which denser and more saline water is continually being formed. To compensate for the loss of water by evaporation and to maintain the salt balance, a two-layer exchange of water takes place through the Strait of Gibraltar, with a surface inflow of less dense Atlantic water (salinity < 37 psu), a bottom outflow of denser Mediterranean water (salinity > 38 psu) and a layer with a strong vertical salinity gradient separating the inflowing and outflowing water masses (Hopkins, 1985; Ambar, 1994).

The Atlantic water which flows into the Mediterranean occupies the top layer (0–200 m) of the Alboran Sea to become the Modified Atlantic Water (MAW) mass. The main path of the Atlantic water coming through the Gibraltar Strait is around two anticyclonic gyres (the western and

the eastern Alboran gyres) that dominate circulation in the Alboran Sea (Heburn and La Violette, 1990). After some meandering in the Alboran Sea, the MAW proceeds along the north African coast to the southern part of the Ionian basin. In the area between Crete and Rhodes, extensive vertical convection gives rise to the formation of more saline (39.0–39.2 psu) and denser Levantine Intermediate Water (LIW) at 200–600 m (Ozsoy et al., 1993). The LIW returns to the western basin through the Strait of Sicily and, after a rather complicated path through the basin, finally flows out of the Mediterranean at a mean depth of more than 150 m, mixed with some underlying western Mediterranean deep water (Bryden et al., 1994). The western Mediterranean deep water (WMDW) is a mass of denser abyssal water, formed in a number of key sites by deep convection. The Gulf of Lions and the Liguro-Provençal basin, in particular, have been identified as the most important of these sites (Ovchinnikov, 1966).

1.2. Global fallout inventories in the western Mediterranean

The major source of transuranium nuclides to the Mediterranean Sea has been global fallout from nuclear weapons tests carried out since the 1950s. The cumulative deposition until 1971 for ^{238}Pu and $^{239,240}\text{Pu}$ (uncorrected for decay) in the 35–45°N latitude belt has been estimated to be

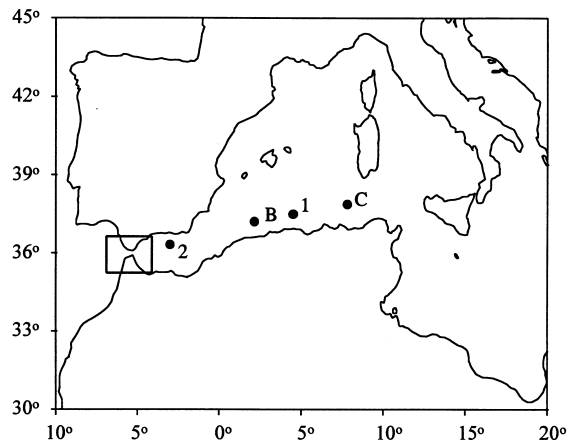
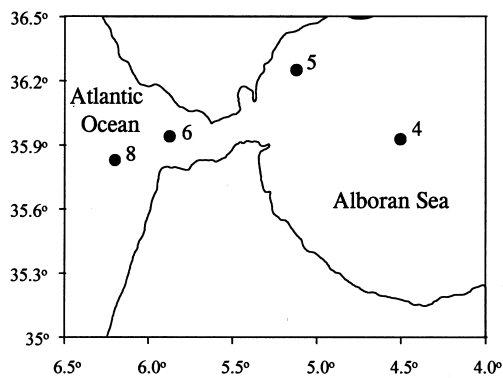


Fig. 1. Sampling sites in the Algerian Basin, Alboran Sea and the Strait of Gibraltar, November 1994.

1.8 and 74.0 Bq m⁻², respectively (Hardy et al., 1973; UNSCEAR, 1982). Although the bulk of global fallout had been deposited by the mid 1960s (Wahlgren et al., 1980), the above values need to be modified to take into account deposition in the period 1972–1994. Measurements carried out on rain water collected at Monaco in the period 1978–1979 (Thein et al., 1980) showed annual fluxes for ²³⁸Pu and ^{239,240}Pu of 0.007 Bq m⁻² and 0.30 Bq m⁻², respectively. If these values are used to calculate the atmospheric input in the period 1972–1994, assuming a constant deposition rate for the 22 years involved, the cumulative deposition to 1994 is estimated to be 1.9 Bq m⁻² for ²³⁸Pu and 80.6 Bq m⁻² for ^{239,240}Pu. An additional 0.94 Bq m⁻² of ²³⁸Pu, introduced by 1971 as a consequence of the accidental re-entry into the atmosphere and subsequent burn up of the SNAP-9A satellite in 1964 (Hardy et al., 1973), has also to be taken into account.

Considerable quantities of ²⁴¹Am, mainly formed by ingrowth following the decay of ²⁴¹Pu, are also present in global fallout. Estimates of the deposited ²⁴¹Am inventory, confirmed by measurements on terrestrial soil samples, indicate that by 1974 the ²⁴¹Am inventory represented 22% of the ^{239,240}Pu inventory (Krey et al., 1976). Further calculations using the standard parent–daughter relationship to account for ingrowth, indicate that the ²⁴¹Am inventory in soils will continue to increase until the year 2037, when ²⁴¹Am will represent ~ 42% of the ^{239,240}Pu inventory (Perkins and Thomas, 1980). Using an ²⁴¹Am/^{239,240}Pu activity ratio of 0.37, as determined in soil samples collected at mid-latitudes in the late 1980s (Ryan et al., 1995), the cumulative deposition of ²⁴¹Am in the western Mediterranean to 1994 is estimated to be ~ 29.8 Bq m⁻².

Integration of these deposition values over the western Mediterranean (surface area: 8.5 × 10¹¹ m²) gives estimated fallout inventories for this region of 2.4 TBq, 68.5 TBq and 25.3 TBq for ²³⁸Pu, ^{239,240}Pu and ²⁴¹Am, respectively. The contribution from other sources (riverine inputs, runoff from land, discharges from nuclear installations and accidental releases) are much smaller and do not amount to more than 5% of these

values (Papucci et al., 1996), although they can lead to significant local enhancements in transuranic concentrations near source-terms (e.g. Marcoule, Palomares). Calculation of the total inventories in a given year must, of course, include any contributions which may have arisen via water exchange at the Gibraltar and Sicily Straits, as discussed below.

1.3. Context and background to the present work

The data discussed here were gathered as part of an extensive research project initiated in 1991 by our laboratories within the framework of the EC's Nuclear Fission Safety Research Programme. The overall objective of the project was to study the main processes governing the behaviour and mass-balance of long-lived radionuclides in the western Mediterranean.

Valuable data on the physico-chemical speciation of plutonium and americium in open and coastal waters in the western Mediterranean were gathered in the first part of this project and have been reported in various publications elsewhere (Delfanti et al., 1994; Mitchell et al., 1994, 1995). In particular, the partition of these elements between particulate, colloidal and solution phases was examined and compared with that found in other marine environments. Further, the oxidation state distribution of plutonium in the solution phase was assessed at various depths. These data extended our understanding of the processes controlling the (vertical) distribution of transuranium nuclides in the water column and further highlighted the importance of particle scavenging (especially by biogenic particles) in the removal of transuranium nuclides from surface waters.

In a follow-up study, the concentrations of plutonium and americium in vertical profiles at selected stations in the south-western Mediterranean were determined in the course of an expedition carried out in November 1994 aboard the oceanographic vessel *N.O. Urania*. The objective here was to estimate, on the basis of present concentrations, transuranic inventories in the western Mediterranean water column and, by comparison with data from earlier studies, identify the main processes controlling the removal,

transport and time-trend evolution of these elements within the basin. Special attention was paid to the characterisation of inflowing and outflowing waters through the Strait of Gibraltar with a view to determining radionuclide fluxes and their influence on the transuranic mass-balance in the basin. It is these issues that are the main focus of the present paper.

2. Materials and methods

A total of 16×200 -l (nominal) sea water samples were collected from different depths using 30-l *Niskin* bottles mounted in a rosette sampler at five stations in the vicinity of the Strait of Gibraltar and the Alboran Sea (Fig. 1). The stations were selected, on the basis of their hydrological features, to best characterise the different water masses entering and exiting the Mediterranean through the Strait. Salinity, temperature and density (CTD) profiles, determined immediately prior to sampling, were used to precisely define sampling depths in the water column. A further 3×200 -l samples of sub-surface sea water were collected at Station 1 in the Algerian Basin (Fig. 1). Large volume (400 l) surface samples were also collected at each of these stations using a deck pump. All samples (unfiltered) were pre-concentrated onboard for subsequent total plutonium and americium analysis by co-precipitation with ferric hydroxide after the method of Wong et al. (1970).

In addition, 2×600 -l surface samples were collected in the open waters of the south-western Mediterranean (Stations B and C; Fig. 1). Here, the suspended particulate was separated by filtration through $0.45\text{-}\mu\text{m}$ membrane filters (diameter: 293 mm). The suspended particulate was retained for analysis, as was a representative sub-sample (400 l) of the filtered water.

To effect the pre-concentration of plutonium and americium, samples were acidified with 12 M HCl to a pH of ~ 1.6 . Following addition of ^{242}Pu and ^{243}Am yield monitors and Fe^{3+} carrier (1 mg (Fe) l^{-1} of sea water), samples were vigorously stirred for at least 3 h in order to ensure the complete equilibration of monitor and determi-

nand. The co-precipitation of plutonium and americium with iron(III) hydroxide was then achieved by adjusting the pH of each sample to between 7.5 and 8.0 using 3 M NaOH. Care was taken during the pH adjustment to minimise the formation of insoluble carbonates. Samples were left to settle overnight and the precipitate, containing the plutonium and americium, was collected by filtration through $0.45\text{-}\mu\text{m}$ membranes (diameter: 293 mm) at a flow rate of $\sim 100\text{ l h}^{-1}$ using a peristaltic pump. In most cases, one filter proved sufficient for the filtration of 300 l of treated water.

Sub-samples (0–3 cm) from a sediment core taken at Station 5 (Alboran Sea) were retained for transuranium analysis. Finally, 2×80 -l samples of distilled water (reagent blanks) were processed onboard as part of our quality control programme. These were considered of particular importance, given the low concentrations anticipated in the actual samples. Certified standard reference solutions of ^{242}Pu and ^{243}Am , supplied by the US National Institute of Standards and Technology and measured upon dilution by total α counting in our laboratory, were used as yield monitors throughout the campaign.

In all cases, following radiochemical separation and purification, plutonium and americium were separately plated onto polished stainless-steel discs from a mixed ammonium chloride/ammonium oxalate medium. The activities of α -emitting isotopes in each fraction were then determined by high-resolution α -spectrometry.

3. Results and discussion

Plutonium and americium concentrations in (unfiltered) sea water sampled at various depths in the Alboran Sea, the Strait of Gibraltar and the Algerian Basin are given in Tables 1 and 2.

3.1. ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am concentrations and isotopic ratios in surface sea water

The mean $^{239,240}\text{Pu}$ concentration in surface water of the Atlantic Ocean near Gibraltar was found to be $5.7 \pm 1.2\text{ mBq m}^{-3}$, while for the

Table 1
Plutonium and americium concentrations ($\pm 1\sigma$) in sea water in the Alboran Sea and in the vicinity of the Strait of Gibraltar, November 1994

Location Depth (m)	Concentration (mBq m^{-3})			$\frac{^{238}\text{Pu}}{^{239,240}\text{Pu}}$	$\frac{^{241}\text{Am}}{^{239,240}\text{Pu}}$
	^{238}Pu	$^{239,240}\text{Pu}$	^{241}Am		
<i>Station 2 (36°20.00' N, 02°59.92' W; 1000 m)</i>					
20	0.46 ± 0.08	11.1 ± 0.4	< 0.32	0.041 ± 0.007	< 0.029
300	0.49 ± 0.09	20.8 ± 0.7	0.41 ± 0.06	0.024 ± 0.004	0.020 ± 0.003
500	0.52 ± 0.11	19.6 ± 0.8	0.92 ± 0.11	0.027 ± 0.006	0.047 ± 0.006
700	0.64 ± 0.12	24.5 ± 0.9	0.67 ± 0.14	0.026 ± 0.005	0.027 ± 0.006
977	0.61 ± 0.13	20.9 ± 0.9	1.48 ± 0.14	0.029 ± 0.006	0.071 ± 0.007
<i>Station 4 (35°56.00' N, 04°30.00' W; 1280 m)</i>					
10	0.30 ± 0.05	8.5 ± 0.3	< 0.32	0.035 ± 0.007	< 0.038
200	0.72 ± 0.11	15.9 ± 0.6	0.50 ± 0.06	0.046 ± 0.007	0.031 ± 0.004
300	0.50 ± 0.09	18.9 ± 0.7	1.04 ± 0.10	0.026 ± 0.005	0.055 ± 0.006
400	0.55 ± 0.09	23.5 ± 0.7	0.31 ± 0.10	0.024 ± 0.004	0.013 ± 0.004
500	0.50 ± 0.10	19.0 ± 0.7	0.93 ± 0.10	0.027 ± 0.005	0.049 ± 0.006
650	0.55 ± 0.09	17.5 ± 0.6	1.08 ± 0.11	0.032 ± 0.005	0.061 ± 0.007
800	0.55 ± 0.12	19.8 ± 0.8	0.25 ± 0.09	0.028 ± 0.006	0.013 ± 0.005
1000	0.21 ± 0.06	16.9 ± 0.7	1.28 ± 0.17	0.013 ± 0.004	0.076 ± 0.010
1200	0.30 ± 0.08	18.9 ± 0.8	1.16 ± 0.12	0.016 ± 0.005	0.061 ± 0.007
<i>Station 5 (36°14.92' N, 05°07.01' W; 356 m)</i>					
5	0.16 ± 0.04	10.0 ± 0.4	< 0.33	0.016 ± 0.004	< 0.033
120	0.76 ± 0.11	19.2 ± 0.7	1.30 ± 0.15	0.040 ± 0.006	0.068 ± 0.008
330	0.55 ± 0.11	26.7 ± 1.0	0.47 ± 0.09	0.021 ± 0.004	0.018 ± 0.004
<i>Station 6 (35°56.42' N, 05°52.15' W; 296 m)</i>					
5	0.21 ± 0.05	4.8 ± 0.3	0.11 ± 0.03	0.044 ± 0.011	0.022 ± 0.006
225	0.62 ± 0.10	20.9 ± 0.7	0.34 ± 0.06	0.030 ± 0.005	0.016 ± 0.003
<i>Station 8 (35°50' N, 06°12' W; 428 m)</i>					
5	0.17 ± 0.03	6.5 ± 0.2	< 0.25	0.026 ± 0.005	< 0.038
350	0.54 ± 0.08	19.0 ± 0.6	0.67 ± 0.08	0.029 ± 0.004	0.035 ± 0.004

Table 2
Plutonium and americium concentrations ($\pm 1\sigma$) in sea water in the Algerian basin, November 1994

Location Depth (m)	Concentration (mBq m^{-3})			$\frac{^{238}\text{Pu}}{^{239,240}\text{Pu}}$	$\frac{^{241}\text{Am}}{^{239,240}\text{Pu}}$
	^{238}Pu	$^{239,240}\text{Pu}$	^{241}Am		
<i>Station 1 (37°30.00' N, 04°30.00' E; 2733 m)</i>					
5	0.11 ± 0.03	8.1 ± 0.3	0.14 ± 0.04	0.014 ± 0.004	0.017 ± 0.005
650	0.73 ± 0.12	15.8 ± 0.7	1.24 ± 0.10	0.046 ± 0.008	0.078 ± 0.007
1000	0.22 ± 0.08	14.6 ± 0.7	2.0 ± 0.2	0.015 ± 0.005	0.133 ± 0.014
2500	0.93 ± 0.17	20.7 ± 0.9	1.74 ± 0.14	0.045 ± 0.008	0.084 ± 0.008
<i>Station B (37°12.51' N, 02°08.38' E; 2700 m):</i>					
5	0.51 ± 0.07	7.7 ± 0.3	< 0.25	0.066 ± 0.009	< 0.032
<i>Station C (37°52.48' N, 07°48.82' E; 2750 m)</i>					
5	0.32 ± 0.06	7.6 ± 0.3	< 0.25	0.042 ± 0.008	< 0.033

Alboran Sea and the Algerian Basin a mean value of 8.8 ± 1.4 mBq m^{-3} was recorded. The latter can be taken as representative of the $^{239,240}\text{Pu}$ concentration in the MAW mass. These concentrations are lower than those recorded in previous studies carried out by other workers in the same general zone. When our data are combined with previously published $^{239,240}\text{Pu}$ concentrations spanning the period 1970–1993, an exponential decrease in surface concentration with time is apparent (Fig. 2).

A similar trend had been observed for ^{137}Cs prior to the deposition of Chernobyl fallout in 1986 (Papucci et al., 1996). As radiocaesium behaves conservatively within the water column, physical processes (such as the formation of intermediate and deep water by convection) are largely responsible for the transfer of this element from surface to depth. Although the same physical processes will contribute to the removal of transuranium nuclides from surface waters, the strong affinity of the transuranics for suspended particulate matter and subsequent sedimentation, must also be taken into account.

From the best fit to the data compiled in Fig. 2, a mean residence time for plutonium in the surface layer of 15 years is indicated, in good agreement with the value of 12.3 years suggested by Thein et al. (1980) on the basis of plutonium

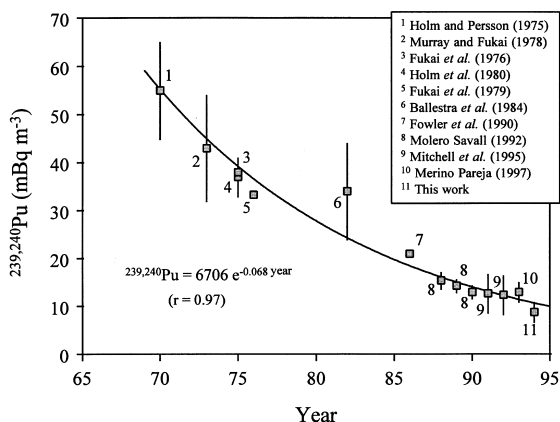


Fig. 2. Temporal evolution of $^{239,240}\text{Pu}$ concentrations in surface waters of the western Mediterranean in the period 1970–1994.

delivery and estimated inventories in the mixed layer (0–100 m). The mean $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio in surface waters, at 0.035 ± 0.017 ($n = 8$), is indicative of global fallout and statistically consistent with that reported previously for the western Mediterranean (Ballestra, 1980; Vives i Batlle, 1988, 1993; Molero i Savall, 1992; Merino Pareja, 1993, 1997; Manjón and García León, 1995; Mitchell et al., 1995).

Concentrations of ^{241}Am in surface waters were, in most cases, below our limit of detection. In the two samples where ^{241}Am could be measured, a mean value of 0.13 ± 0.02 mBq m^{-3} was determined. Again, this value is lower than that reported in previous studies. Comparison with the corresponding levels in 1975 (Fukai et al., 1976), namely 2.1 ± 0.3 mBq m^{-3} ($n = 9$), indicate that americium levels in surface waters of the Mediterranean have fallen by over an order of magnitude (factor of 16) in the past two decades. If, as in the case of plutonium, an exponential decrease with time is assumed, a mean residence time for americium of ~ 7 years can be derived. This is, however, an overestimation of the true residence time, as ^{241}Am is continually produced in the surface layer via the decay of ^{241}Pu . Taking this into account, the mean residence time for americium in the Mediterranean surface mixed layer is estimated to be ~ 3 years (Thein et al., 1980).

The mean $^{241}\text{Am}/^{239,240}\text{Pu}$ activity ratio in surface waters, at 0.020 ± 0.004 ($n = 2$), is approximately an order of magnitude lower than the value of 0.22 reported by Krey et al. (1976) for global fallout in the mid-1970s and the value of 0.37 reported for mid-latitude soils in the late 1980s by Ryan et al. (1995). It is also lower than the mean of 0.055 ± 0.007 reported for Mediterranean surface waters in 1975 by Fukai et al. (1976). This decrease in the $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio is further evidence of the considerably shorter mean residence time of americium with respect to plutonium in the surface layer. Indeed, the difference in the residence times of a factor of five can readily be explained if removal by sinking particles is the dominant mechanism controlling the vertical flux of transuranium nuclides, as the

percentage of americium associated with the particulate fraction is 2–6 times higher than that of plutonium (Holm et al., 1980; Molero et al., 1995a). The enrichment of americium with respect to plutonium is believed to be due to the preferential association of americium to inorganic particles which, in a zone of low productivity such as the Mediterranean, are more abundant than biogenic particles (Livingston et al., 1977).

This enrichment results in an increase in the $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio in seabed sediments (Livingston et al., 1977; Antón et al., 1994; Molero et al., 1995b). In fact, measurements on surface (0–3 cm) sediment collected at Station 5 (Table 3) show that while the $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratio, at 0.031 ± 0.003 , is identical to the corresponding ratio in surface sea water, the $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio, at 0.279 ± 0.012 , is an order of magnitude higher than that (0.020 ± 0.004) observed in surface waters at the same location.

The preferential removal of transuranium nuclides with respect to the more conservative nuclide ^{137}Cs from the surface mixed layer is evident when the $^{239,240}\text{Pu}/^{137}\text{Cs}$ ratios in surface waters and in fallout are analysed. The mean $^{239,240}\text{Pu}/^{137}\text{Cs}$ ratio in fallout over the Mediterranean area was 0.023 in the period 1978–1979 (Thein et al., 1980) and 0.026 in 1994 (Piemonte Regional Agency for Environmental Protection, personal communication). The corresponding ratios in surface sea water are much lower and have decreased significantly with time, falling from 0.009 ± 0.003 ($n = 9$) in the period 1977–1982 (Fukai et al., 1982) to 0.0033 ± 0.0010 ($n = 6$) by 1994 (Papucci and Delfanti, in press). This reduction exceeds that expected on the basis of radioactive decay alone and confirms that plutonium is being removed from surface waters more rapidly than ^{137}Cs .

3.2. Proportion of plutonium in dissolved and particulate forms

The partition of plutonium between particulate ($> 0.45 \mu\text{m}$) and solution phases in surface waters was examined at two locations (Stations B and C) in the Algerian Basin. The percentage of $^{239,240}\text{Pu}$ in particulate form was in the range 2–4% and is in good agreement with the percentages recorded in a previous expedition to the western Mediterranean, namely $5 \pm 3\%$ ($n = 12$), by Mitchell et al. (1995). It is also similar to the values reported for open Mediterranean waters by other workers (Holm et al., 1980; Molero et al., 1995b). At all stations, measured suspended loads were very low, being typically 0.1–0.5 mg l^{-1} . Plutonium-238 concentrations in the particulate fraction were below our limit of detection.

We were also unable to detect ^{241}Am in either the particulate or the filtered fraction at these two stations. However, in coastal waters, where suspended loads are usually higher, up to 10% of the plutonium and 45% of the americium have been reported to be in particulate form (Molero et al., 1995a).

3.3. Vertical distributions of plutonium and americium in the water column

The vertical distributions of $^{239,240}\text{Pu}$ at different stations in the Algerian Basin, the Alboran Sea and the Strait of Gibraltar are shown in Fig. 3, together with the corresponding salinity and temperature profiles.

In the open waters of the Algerian Basin and the Alboran Sea (Stations 1, 2 and 4), plutonium profiles resemble those reported in earlier studies at different locations throughout the western

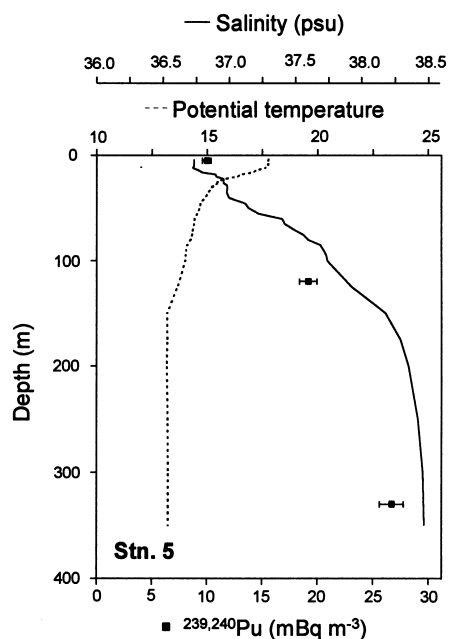
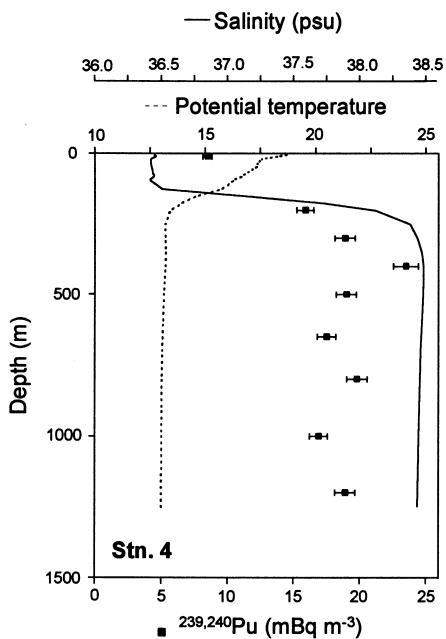
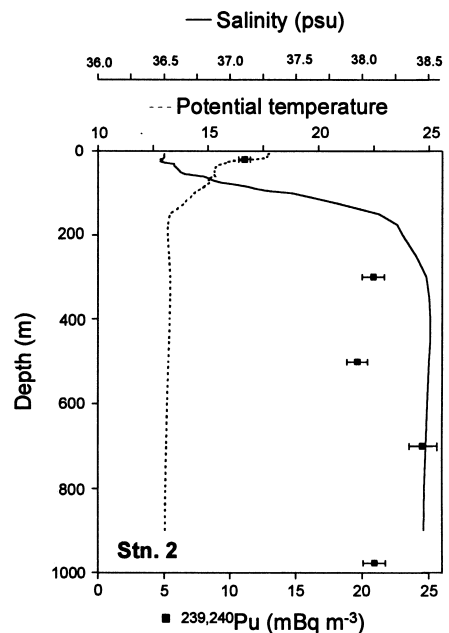
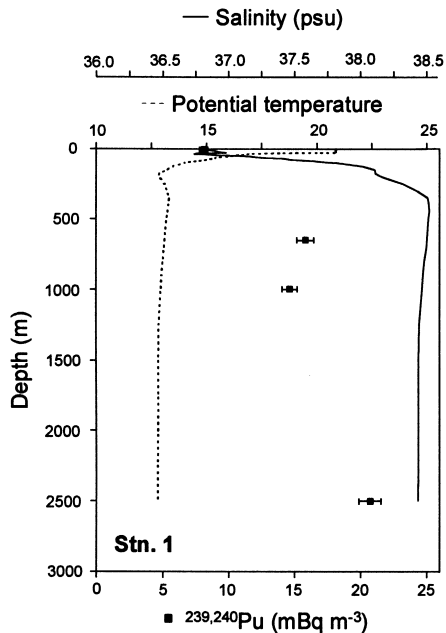
Table 3

Plutonium and americium concentrations ($\pm 1\sigma$) in seabed sediment (0–3 cm) collected at Station 5 in the Alboran Sea, November 1994

Concentration (mBq kg^{-1} , dry wt.)			$^{238}\text{Pu}/^{239,240}\text{Pu}$	$^{241}\text{Am}/^{239,240}\text{Pu}$
^{238}Pu	$^{239,240}\text{Pu}$	^{241}Am		
17.3 ± 1.7	550 ± 12	154 ± 6	0.031 ± 0.003	0.279 ± 0.012

Mediterranean (Fukai et al., 1979; Fowler et al., 1990; IAEA, 1991; Mitchell et al., 1995; Merino et al., 1997), with lowest concentrations being recorded in the surface layers. As discussed above,

this can be attributed to the vertical transport of plutonium associated with sinking particles and to the presence of MAW. Typically, concentrations in surface waters were about half of those in



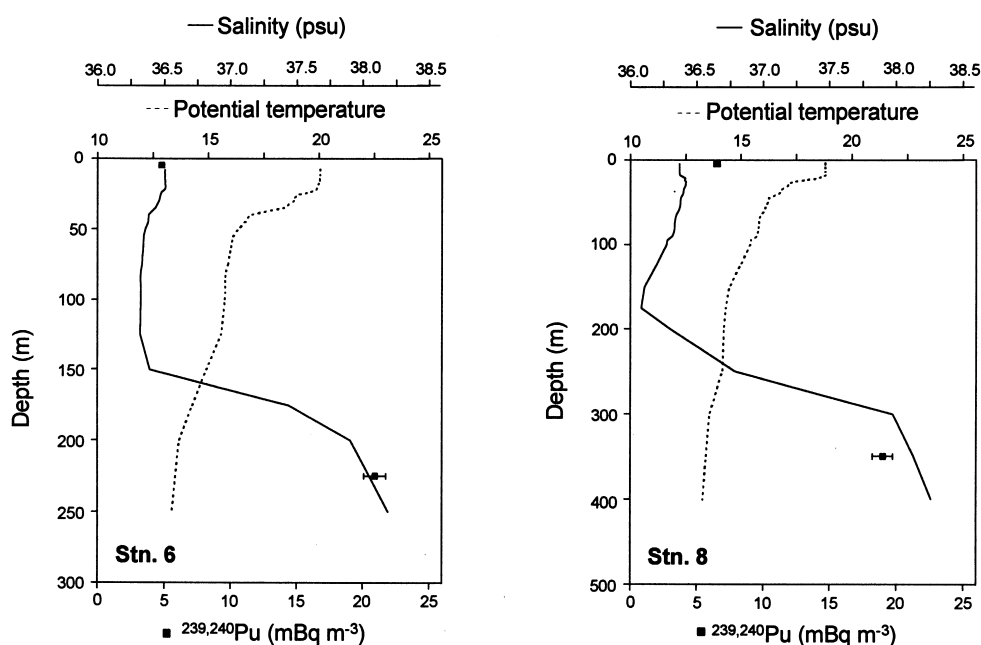


Fig. 3. Vertical distribution of $^{239,240}\text{Pu}$ in the water column at selected stations in the Algerian Basin, Alboran Sea and Strait of Gibraltar. The corresponding temperature and salinity profiles are also shown.

sub-surface layers. For the vertical profile with the highest sampling resolution (Station 4), a sub-surface maximum in the total plutonium concentration was observed at a depth of approximately 400 m. Similar, shallow sub-surface maxima have also been observed at depths of some few hundreds of metres in the western Mediterranean (Ballestra, 1980; IAEA, 1991; Mitchell et al., 1995; Merino et al., 1997) and in open waters in the Atlantic and Pacific oceans (Bowen et al., 1980; Nelson et al., 1984; Cochran et al., 1987). Although the depth of the sub-surface maximum is very similar to that observed in the past, the corresponding plutonium concentration is now much lower, being half of that reported for the period 1977–1981 by Fukai et al. (1982) at five stations in the western Mediterranean. In contrast, concentrations recorded in deeper layers (1000–2000 m) have doubled over the past 15 years.

Various suggestions have been advanced to account for this maximum. However, there appears to be a consensus that it is related to the vertical transport and the dissolution/remineralisation of

biogenic debris and organic matter, with the return of plutonium into solution (Sholkovitz, 1983). Analysis of the distribution of the chemical forms of plutonium in the Mediterranean water column has provided further evidence for this hypothesis. Besides confirming the presence of a sub-surface concentration maximum at depths between 250

Table 4
Percentage ($\pm 1\sigma$) of Pu(V) in filtered sea water sampled throughout the western Mediterranean in July–August 1991 and 1992 (source: Mitchell et al., 1995)

Depth (m)	$^{239,240}\text{Pu}$ (mBq m^{-3})	% $^{239,240}\text{Pu(V)}$
<i>Algerian Basin (37°49' N, 02°32' E; 2770 m)</i>		
15	12.6 ± 0.5	70.7 ± 1.6
515	29.1 ± 0.8	87.0 ± 0.8
1200	21.3 ± 1.8	92.2 ± 0.9
2745	24.8 ± 1.2	94.8 ± 0.6
<i>Catalan-Balearic Sea (42°00' N, 03°40' E; 931 m)</i>		
3.5	16.1 ± 0.7	62.8 ± 1.9
50	14.8 ± 0.6	28.2 ± 1.8
250	33.4 ± 1.3	80.3 ± 1.0
911	24.3 ± 0.9	88.0 ± 0.8

and 500 m, detailed measurements of the oxidation state distribution of plutonium in filtered sea water by Mitchell et al. (1995) showed the predominance of the Pu(V) oxidation state in the solution phase to be reversed at 50 m (Table 4). This reversal in oxidation state characterisation has been attributed to the reduction of oxidised plutonium by phytoplankton forming in a biologically productive layer near the surface, i.e. the euphotic zone.

There appeared to be no statistically significant variation in the $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio with depth. Measured ratios were in the range 0.014–0.046, with an overall mean of 0.029 ± 0.010 ($n = 18$). Similar variations have been reported in rain water sampled at Monaco in the late 1970s (Thein et al., 1980). In contrast, $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios were appreciably higher in deeper waters compared to surface waters, in agreement with previous observations (Fukai et al., 1979).

These results confirm that in the open waters of the Alboran Sea and the Algerian Basin, the removal of americium (and to a lesser extent plutonium) by sinking particles is the dominant mechanism governing the vertical transport of both elements in the water column.

3.4. Present and past plutonium and americium inventories in the water column

The inventories of $^{239,240}\text{Pu}$ and ^{241}Am were calculated at each of the above stations by simply integrating the concentration profiles, assuming a linear variation in concentration between sampling depths. For the calculation, vertical profiles

from studies conducted in the period 1990–1994 throughout the western Mediterranean were also included (Mitchell et al., 1995; Merino Pareja, 1997). The $^{239,240}\text{Pu}$ inventories were found to vary between 2.4 Bq m^{-2} (50-m water column) and 63.9 Bq m^{-2} (2700-m water column). The corresponding figures for ^{241}Am were 0.05 Bq m^{-2} and 3.3 Bq m^{-2} , respectively. A linear increase in the respective inventories with depth is evident from these profiles (Fig. 4). Using the mean depths and surface areas for each western Mediterranean sub-division as defined in the ATOMED-3 regional model (Ortins de Betten-court et al., 1994), estimates of 24.8 TBq ($^{239,240}\text{Pu}$) and 1.2 TBq (^{241}Am) were derived for the total inventories in the water column of the western Mediterranean (Table 5). On the basis of the estimated delivery figures given earlier, this implies that approximately 35% of the plutonium and 5% of the americium still resided in the water column in 1994.

In an attempt to establish the temporal evolution of the plutonium inventory in the water column, similar calculations were carried out for previous years using vertical profiles measured in earlier studies throughout the western Mediterranean (IAEA, 1991). The results are plotted in Fig. 5. As in the case of surface water concentrations, the plutonium inventory has diminished exponentially from $\sim 50 \text{ TBq}$ in 1971 to $\sim 25 \text{ TBq}$ in 1994. From the best fit to the data, a mean residence time for plutonium in the water column of ~ 35 years is derived, which is about twice as long as the residence time in the surface layer. The annual loss for a particular year is,

Table 5

Estimated plutonium and americium inventories in the water column in the different sub-divisions of the western Mediterranean

Zone	Area (m^2)	Mean depth (m)	Inventory (TBq)	
			$^{239,240}\text{Pu}$	^{241}Am
Alboran Sea	5×10^{10}	575	0.64	0.03
Liguro-Provençal Sea	2.81×10^{11}	1500	8.6	0.41
Algerian Basin	2.69×10^{11}	1500	8.2	0.40
Tyrrhenian Sea	2.40×10^{11}	1500	7.3	0.35
Gulf of Lions	6.7×10^9	80	0.02	0.01
Western Mediterranean	8.5×10^{11}	1433	24.8	1.2

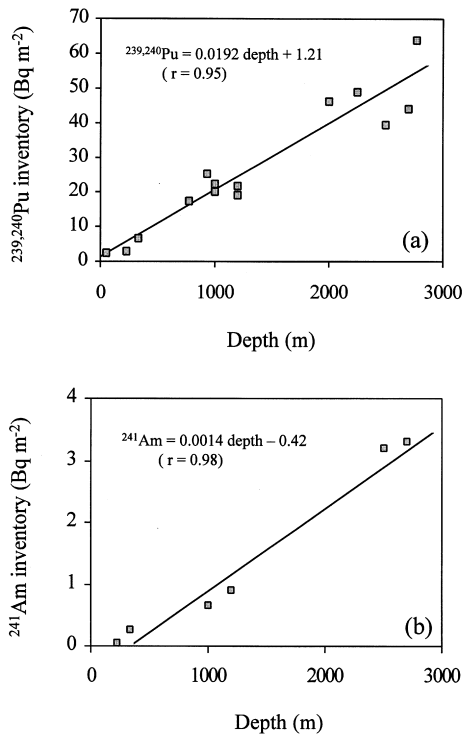


Fig. 4. Variation of the water column inventories of (a) $^{239,240}\text{Pu}$ and (b) ^{241}Am with depth.

thus, estimated to be $\sim 3\%$ of the water column inventory at that year. For 1994, this corresponds to a loss of 0.77 TBq ($^{239,240}\text{Pu}$).

Data derived from sediment trap experiments

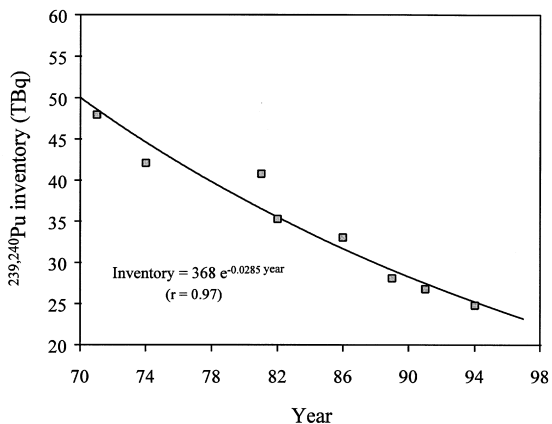


Fig. 5. Temporal evolution of the $^{239,240}\text{Pu}$ inventory in the western Mediterranean water column.

by IAEA-MEL at deep stations in the north-western Mediterranean suggest a representative value for plutonium loss from the water column in association with sinking particles of $\sim 0.25 \text{ Bq m}^{-2} \text{ year}^{-1}$ (Baxter et al., 1995; Fowler et al., in press). However, enhanced scavenging of transuranics has been reported on the continental shelves which account for $\sim 20\%$ of the total surface; $^{239,240}\text{Pu}$ inventory calculations based on measured concentrations in coastal sediments show levels two to three times higher than the integrated fallout deposition (Antón et al., 1994; Delfanti and Papucci, 1995; Merino Pareja, 1997). Thus, the quantities of the transuranics removed from the water column and trapped in coastal sediments is significant.

Using published inventories at a small number of well scattered sites in both coastal and deep waters, and some interpolation, we have estimated the total $^{239,240}\text{Pu}$ inventory in the sediments of the western Mediterranean to be $\sim 40 \text{ TBq}$ at the present time. When added to the $\sim 25 \text{ TBq}$ remaining in the overlying water column, we arrive to an overall total of $\sim 65 \text{ TBq}$, which is similar to that of the integrated fallout deposition discussed above (i.e. 69 TBq).

From the vertical profiles in the vicinity of the Strait of Gibraltar (Table 1), it is clear that the concentrations of transuranium nuclides in inflowing Atlantic waters are lower than those in outflowing Mediterranean waters at the present time. If similar volumes of water are exchanged through the Strait, this will result in a net outward flux of transuranium nuclides from the basin. Although few (if any) data are available on the vertical distributions of these nuclides in the eastern basin, it is unlikely that they differ significantly from those in the western basin (i.e. depleted concentrations in surface waters and enhanced concentrations at mid depths). Accordingly, a net flux of transuranium nuclides is also to be expected between these basins, as a similar two-layer exchange of water takes place through the Strait of Sicily. Here, however, surface water from the western basin flows into the eastern basin, while intermediate water from the eastern basin pours over the sill into the western basin. As similar water volumes are exchanged, this will

result in a net flux of transuranium nuclides into the western basin. Moreover, as these volumes are almost identical to those exchanged at the Strait of Gibraltar, the transuranic flux into the western Mediterranean is likely to be comparable to the flux out of the latter through the Strait of Gibraltar. This explains why the mass balance in the basin can effectively be accounted for on the basis of the sediment and water column inventories alone.

3.5. Plutonium and americium fluxes through the Strait of Gibraltar

Water exiting the Mediterranean via the Strait of Gibraltar is roughly a mix of 2/3 LIW (300–600-m depth) and 1/3 WMDW (600 m to bottom). Based on the vertical profiles in the Alboran Sea (Stations 2, 4 and 5), we can assume a mean $^{239,240}\text{Pu}$ concentration of 21.5 mBq m^{-3} in LIW and 19.8 mBq m^{-3} in WMDW, giving a representative (weighted) concentration of 20.9 mBq m^{-3} in outflowing water.

Two stations in the Atlantic Ocean (Stations 6 and 8) and one in the Alboran Sea (Station 5) were selected in an attempt to characterise plutonium concentrations in the Atlantic and Mediterranean waters before and after flowing through the Strait. At these stations, CTD profiles show the presence of two well-defined water masses: surface Atlantic water, characterised by salinities in the range 36.4–36.7 psu and underlying Mediterranean water, with salinities of 38.0–38.4 psu (Fig. 3). The concentration of plutonium in surface water at Station 5 (10.0 mBq m^{-3}) is significantly higher than the corresponding concentrations at Stations 6 and 8 on the Atlantic side of the Strait (4.8 and 6.5 mBq m^{-3} , respectively). This is partly due to mixing with underlying Mediterranean water at the Gibraltar sill, but might also be related to upwelling at the northern boundaries of the anticyclonic gyre in the western Alboran Sea. Plutonium concentrations in the core of the Mediterranean water at Stations 6 and 8 on the Atlantic side are 20.9 and 19.0 mBq m^{-3} , respectively, and are very similar to the values for the water leaving the Mediterranean.

The exact amount of water flowing through the Strait of Gibraltar is difficult to estimate as the net flow represents only approximately 5% of the total flow in either direction (Cruzado, 1985). In this work, values of 1.39 Sv ($1 \text{ Sv} = 1 \times 10^6 \text{ m}^3 \text{ s}^{-1}$) and 1.32 Sv for the inflowing and outflowing fluxes, respectively, have been assumed (Hopkins, 1985). The resulting net flow, at 0.07 Sv , is compatible with other values reported in the literature (Béthoux, 1977) and consistent with values deduced from evaporation, precipitation and runoff. On this basis, an annual inflow of 0.22 TBq ($^{239,240}\text{Pu}$) from the Atlantic and an outflow of 0.87 TBq ($^{239,240}\text{Pu}$) from the Mediterranean results in an annual (net) flux of 0.65 TBq ($^{239,240}\text{Pu}$) from the Mediterranean, representing $\sim 2.5\%$ of the present water column inventory in the western Mediterranean and $\sim 85\%$ of the present annual loss in the basin. A similar calculation for ^{241}Am , taking the inflowing and outflowing concentrations to be 0.11 mBq m^{-3} and 0.8 mBq m^{-3} , respectively, suggests an annual (net) flux of $\sim 0.03 \text{ TBq}$ (^{241}Am) from the Mediterranean, which also represents $\sim 2.5\%$ of the present americium inventory.

Interestingly, no net flux was found for ^{137}Cs in the course of this same campaign (Papucci et al., 1996). This has been attributed to the conservative nature of ^{137}Cs and its virtual ‘homogenisation’ in the water column as a result of diffusion and convection processes. By 1994, ^{137}Cs profiles in the Alboran Sea showed little or no vertical structure (Papucci et al., 1996). In fact, ^{137}Cs concentrations in surface Mediterranean and Atlantic sea water are very similar to those in LIW and only slightly higher than those in WMDW (Papucci and Delfanti, in press). Consequently, at the Strait, concentrations in inflowing and outflowing waters are indistinguishable.

We are confident that the observed difference between Atlantic and Mediterranean $^{239,240}\text{Pu}$ concentrations at the Strait of Gibraltar is a genuine feature of these waters at the present time and not a sampling artefact. Indeed, a more recent study carried out by Gascó and Antón (in press) has confirmed the observed difference, with $^{239,240}\text{Pu}$ concentrations again reported as being two to three times higher in outflowing Mediter-

ranean water compared to inflowing Atlantic water.

4. Conclusions

By examining the vertical distribution of transuranium nuclides in selected zones of the western Mediterranean at the present time and comparing our results with those obtained in earlier studies, it has been possible to establish the time-trend evolution of these nuclides and the key processes controlling their transport in the western Mediterranean basin.

The data show that, as a consequence of the removal of transuranium nuclides in association with sinking particles, plutonium and americium concentrations in surface waters have decreased substantially in recent decades, with preferential removal of americium with respect to plutonium. Residence times for these elements in the surface mixed layer are estimated to be ~ 15 years and ~ 3 years, respectively.

Vertical profiles in open waters of the western Mediterranean have confirmed the presence of a sub-surface maximum in plutonium concentrations at a depth of several hundreds of metres and have emphasised the role played by sinking particles in first scavenging transuranium nuclides from surface waters and then returning them to solution upon dissolution at intermediate depths.

Inventory calculations from the vertical profiles have revealed an effectively linear relationship between inventories and depth, which has allowed the determination of present water column inventories in the basin. In this context, it has been estimated that, by November 1994, approximately 35% of the plutonium and 5% of the americium still resided in the water column. A study of the temporal evolution of plutonium inventories in the water column has established a residence time for this element of approximately 35 years, which is approximately twice as long as the plutonium residence time in the surface mixed layer. On this basis, the annual loss of plutonium for a

particular year has been estimated to be $\sim 3\%$ of the water column inventory at that year. For 1994, this corresponded to a loss of 0.77 TBq ($^{239,240}\text{Pu}$).

From the analysis of vertical profiles in the vicinity of the Strait of Gibraltar, it is clear that inflowing Atlantic waters have lower transuranic concentrations than outflowing Mediterranean waters. As comparable amounts of water are exchanged through the Strait, this results in a net outward flux of transuranium nuclides from the basin. For 1994, the flux of transuranium nuclides through the Strait has been estimated to be 0.65 TBq for $^{239,240}\text{Pu}$ representing $\sim 85\%$ of the present annual loss, and 0.03 TBq for ^{241}Am . These losses, however, are likely to be compensated by comparable influxes from the eastern basin via the Strait of Sicily. Although the latter assumption has yet to be confirmed experimentally, if true, the decline in the water column inventory can only be attributed to removal of these nuclides to the underlying sediments, mainly along the coastal margins. Enhanced scavenging on the continental shelves, as evidenced by the appreciably higher transuranic concentrations in shelf sediments, supports this hypothesis, and suggests that despite net transuranic fluxes through the Gibraltar and Sicily Straits, the time-integrated transuranium fallout deposition in the western basin can effectively be accounted for in terms of present water column and sediment inventories.

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