The Distribution and Inventory of Fallout Plutonium in Sediments of the Ligurian Sea near La Spezia, Italy

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ABSTRACT

Pu concentrations in surface sediments of the Ligurian Sea are about ten times higher than in adjacent river sediments and are highly correlated with sediment porosities. The integrated inventory of $^{239,240}Pu$ in a sediment core is calculated to be 3·5 mCi km^{-2}, nearly twice the average input from fallout at these latitudes, apparently because Pu is removed from seawater by particle scavenging.

The sedimentation rate is calculated from the depth of the $^{239,240}Pu$ maximum to be 0·52 ± 0·06 cm y^{-1}.

INTRODUCTION

Recent studies of Pu in coastal environments have revealed discrepancies between inventories of Pu in sediments from the Atlantic continental shelf (Livingston & Bowen, 1979) and the Pacific continental shelf (Beasley *et al.*, 1982). These contrasts have provided a basis to begin understanding the processes that remove Pu to the sediment in shallow water but so far these processes have not received attention in the Mediterranean Sea. Murray & Fukai (1978) pointed out that at the time of their study there were virtually no systematic measurements of Pu in the Mediterranean. Only a few studies since that time have begun to alter the picture (e.g. Livingston *et al.*, 1979; Ballestra *et al.*, 1982; Triulzi *et al.*,

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1982; Thein *et al.*, 1983). Of these, only Triulzi *et al.* (1982) in their work in the Ionian Sea reported sediment profiles.

This work starts to fill that gap. We present the first vertical profile of Pu in Ligurian Sea sediments and begin to build a baseline of Pu concentrations in Mediterranean sediments as a background against which to understand processes controlling the behavior of Pu in the marine environment. We attempt to answer the following questions: (1) How does the pattern of Pu concentrations in sediments change between the Magra River and the Ligurian Sea? (2) What conclusions can we draw about the sedimentation rate and sediment mixing rate from the profile of Pu in the sediments? (3) Does the particle population in the water column control the removal of Pu from the water and, hence, the sediment inventories, as appeared to be the case in the comparison between Atlantic and Pacific shelf sediments?

STUDY AREA

The Ligurian Sea near La Spezia, a region under the influence of the Magra River which supplies a limited input of both water and suspended sediment to the sea (Pierce *et al.*, 1981), forms the area of this study (Fig. 1). The drainage basin of about 2×10^3 km^2 consists of three parts: above its confluence with the Vara River, the Magra itself drains a region dominated by marble, dolomite, limestone and gypsum, whereas the Vara drains a region of quartzite, sandstone and schist; below the confluence the Magra flows through recent alluvial terrace deposits into the sea (Anselmi *et al.*, 1983).

As they enter the sea the suspended particles are transported by the prevailing currents in a north-westerly direction into the Gulf of La Spezia and the Ligurian Sea (Anselmi *et al.*, 1982; Esposito & Manzella, 1982; Astraldi & Manzella, 1983), directly into the south-easterly portion of our study area, which encompassed about 40 km^2 of the continental shelf at water depths from 12 to 100 m. To the north-west of La Spezia along the coastline of the Cinqueterre from Portovenere to Monterosso small streams and direct runoff from the rugged cliffs add only limited amounts of particulate matter and the sediments here are generally more fine-grained and more typical of the Ligurian Sea continental shelf in mineral composition than are those under the direct influence of runoff from the Magra. Grain size of surface sediments generally decreases with
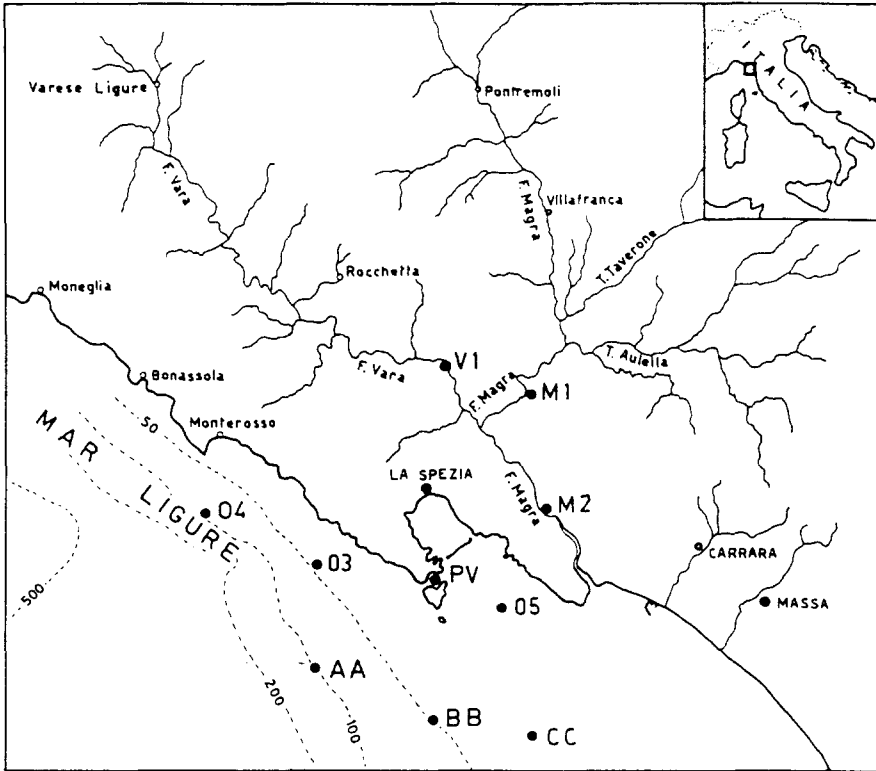
Fig. 1. Sampling sites in the Ligurian Sea and in the Magra and Vara rivers.

distance from the river mouth and beyond 10 km from the river the sediments are predominantly mixed silt and clay, both on the sea floor and inside the Gulf of La Spezia (Anselmi *et al.*, 1983).

METHODS

Sample collection

The marine surface sediments analyzed were collected with a Shipek grab sampler which samples to a depth of 10 cm; in the river, surface sediments were collected by hand. The sediment core was collected in a modified box corer and extruded in the field into 1-cm thick sections with the outer

1 cm of each section removed to eliminate the effects of downtraining. The corer and extruder are new designs which we describe in a separate paper (Papucci *et al.*. 1985). All sediments were weighed wet. dried to a constant weight, reweighed and then ball-milled to a fine, homogeneous powder before analysis. Sediment porosities were calculated for all samples.

Analytical procedures

In a recent exercise to intercalibrate transuranic measurements among several laboratories, the IAEA prepared two marine sediment samples which were extensively analyzed (Fukai *et al.*, 1982). In addition to its primary function of ensuring intercomparison of results among the laboratories, there was an interesting secondary discovery: for one of the standards the measured Pu concentration was about two times higher if the sample was totally dissolved than if it was leached with strong acids. Apparently the standard contained refractory Pu resistant to leaching by strong acids, which, as Sill (1975) reports, is quite easy to form at high temperatures (for example, at temperatures required to ash biological tissue). Since it cannot be known in advance whether or not a sample will contain refractory Pu, we chose to totally dissolve all samples by treatments with HF, HNO_3, HCl and $HClO_4$.

We separated Pu from sediments using a procedure much like the one outlined by Wong (1971) with two changes: (1) we totally dissolved the samples as discussed above and (2) we co-precipitated Pu with CaC_2O_4 before the column extraction. The oxalate co-precipitation removes iron and several other interfering elements from the sample and also allows close control of the normality of the solution before extraction of Pu on the column, a step which is sensitive to acid concentration. The normality was easily controlled with the small quantity of $Fe(OH)_3$ remaining after the oxalate step. Moreover, because interfering ions were removed, the samples always flowed smoothly through the ion exchange columns, which resulted in excellent resolution of the α-spectra. On balance the extra time required for this step was more than compensated by the time saved in the rest of the procedure. The samples were electroplated from a sulfate solution by the procedure of Talvitie (1971) and counted on surface barrier diodes.

The accuracy of the method was checked by analyzing three standard reference materials: Columbia River sediment (NBS SRM 4350B) and

TABLE 1

Results of Analysis of Plutonium in Standardized Sediment Samples

Sample	Accepted activity		Measured activity	
	$^{239,240}Pu$ $(dpm\ kg^{-1})$	$^{238}Pu/^{239,240}Pu$	$^{239,240}Pu$ $(dpm\ kg^{-1})$	$^{238}Pu/^{239,240}Pu$
River sediment[a]	$30·5 \pm 1·8$	$0·025 \pm 0·004$	$29·4 \pm 1·4(3)$	$0·038 \pm 0·016$ (3)
SD-B-2	266 ± 67^{b}	$0·43 \pm 0·13^{b}$	351 ± 27 (2)	$0·49 \pm 0·07$ (2)
	422 ± 44^{c}	$0·53 \pm 0·08^{c}$		
SD-B-3	1265 ± 155^{d}	$0·040 \pm 0·007^{d}$	1063 ± 19 (2)	$0·028 \pm 0·002$ (2)

[a]National Bureau of Standards SRM 4350B.
[b]Measured at the International Laboratory of Marine Radioactivity (ILMR) by leaching with hydrochloric and nitric acids.
[c]Measured at ILMR by total dissolution with hydrofluoric, perchloric and nitric acids.
[d]Average result from eight laboratories participating in ILMR intercalibration exercise.

IAEA marine sediments SD-B-2 and SD-B-3. The results are shown in Table 1. As can be seen, we have excellent agreement with the NBS certified sediment and close agreement with the average results on the uncertified IAEA marine sediments. As mentioned above, one of the samples (SD-B-2) apparently contains some refractory Pu and results of its analysis have been variable (Fukai *et al.*, 1982). Overall we feel that our performance on standard reference materials demonstrates the validity of our results, particularly as the range of activities and the sediment matrix in our study were very similar to those of the NBS reference material.

RESULTS

Set out in Table 2 are the concentrations of Pu and the porosities of surface sediments of both the sea floor and the adjacent river (porosity = fraction of sediment volume occupied by water). What is most clearly seen is that the concentrations of Pu in the marine sediments are about ten times higher than in riverine sediments; not unlike the enrichment ratios of 3–15 observed by Beasley *et al.* (1982) between the Columbia River estuary and the Pacific continental shelf. The porosities of the fine sediments collected from protected areas of the rivers were

TABLE 2

Concentrations of Plutonium, Porosities and ^{239,240}Pu/^{137}Cs Ratios in Surface Sediments of the Ligurian Sea Near La Spezia and in Adjacent River Sediments Collected in July, 1984. All Activities are as dpm kg^{-1} Salt-free Dry Wt. Uncertainties are 1σ Propagated Errors

Location	^{239,240}Pu	^{238}Pu × 100/ ^{239,240}Pu	Pu/Cs[a]	Porosity	Depth (m)
SP AA	56 ± 3	3·3 ± 0·6	—	0·629	100
SP BB	26 ± 2	3·4 ± 1·0	—	0·476	47
SP CC	25 ± 2	3·1 ± 0·9	—	0·484	24
SP PV	71 ± 4	2·8 ± 0·5	0·08	0·701	12
SP 03	38 ± 2	3·8 ± 0·8	0·06	0·588	45
SP 04	60 ± 4	4·3 ± 0·7	0·07	0·646	93
SP 05	15 ± 1	3·2 ± 1·0	0·11	nm[b]	18
Vara River (V1)	4·6 ± 0·6	6 ± 3	0·01	0·621	1
Magra River (M1)	1·7 ± 0·5	3 ± 3	0·01	0·790	1
Magra River (M2)	4·9 ± 0·5	7 ± 3	0·03	0·663	1

[a] ^{239,240}Pu/^{137}Cs. The ^{137}Cs data are from Anselmi *et al.* (1982) and are not from the same samples as the Pu data, but from samples collected at the same stations.
[b] nm, Not measured.

high (0·62–0·79), and the porosities of the marine sediments were lower in the region of riverine influence and increased with distance from the river mouth, much as would be predicted from the known sedimentation regime in the region (Anselmi *et al.*, 1982). Clearly the river sediments we collected were representative of only the smallest particle sizes exported by the Magra, for at times of high river flow a sediment load with a large range of particle sizes is carried by the river, the coarser-grained sediments being deposited near the river mouth and smaller particles undoubtedly being carried for some distance. The concordance between our measured porosities and the known sediment regime leads us to believe that our samples, and thus the conclusions from our study, are regionally representative.

Table 3 presents concentrations of Pu and porosities of a sediment core raised at Portovenere (PV). From the porosity of the surface sections of the core it can be seen that the sediments were fine-grained; the average porosity of the upper 9 cm of the core (weighted to correspond to that

TABLE 3

Concentrations of Plutonium and Porosities in a Sediment Core Raised at Portovenere in the Gulf of La Spezia, Ligurian Sea in October, 1983. All Activities are as dpm kg^{-1} Salt-free Dry Wt. Uncertainties are 1σ Propagated Errors

Depth in core (cm)	z' [a] (cm)	$^{239,240}Pu$	$^{238}Pu \times 100/$ $^{239,240}Pu$	Porosity	Date
0–1	0·51	51 ± 2	3·5 ± 0·6	0·709	Oct. 82
2–3	2·8	51 ± 4	4·0 ± 0·6	0·669	Apr. 77
4–5	5·2	52 ± 3	2·6 ± 0·5	0·655	Aug. 73
6–7	7·8	66 ± 3	2·5 ± 0·5	0·656	Jul. 68
7–8	9·1	62 ± 2	3·8 ± 0·4	0·645	Dec. 66
8–9	10·4	75 ± 3	2·8 ± 0·5	0·641	Mar. 63
10–11	13·1	59 ± 2	2·9 ± 0·5	0·612	Feb. 58
12–13	15·7	24 ± 2	3·6 ± 1·3	0·626	Jan. 53
14–15	18·4	20 ± 1	2·4 ± 0·8	0·644	Sep. 47
16–17	21·1	15 ± 1	2·0 ± 0·7	0·637	Jul. 42
19–20	25·1	0·9 ± 0·2	nd [b]	0·636	—
22–23	29·1	0·8 ± 0·2	nd	0·639	—
25–26	33·1	0·5 ± 0·2	nd	0·626	—
30–31	39·8	nd	nd	0·627	—

[a] z' = Sediment depth corrected for compaction by the overburden of sediment.
[b] nd, Not detected.

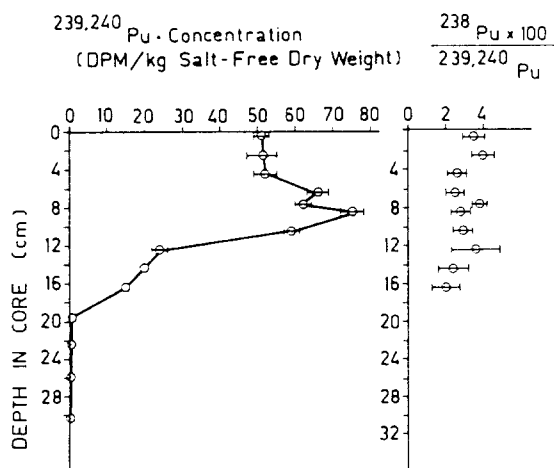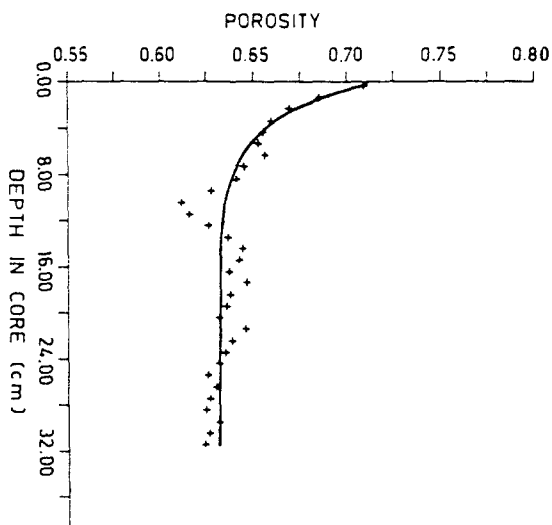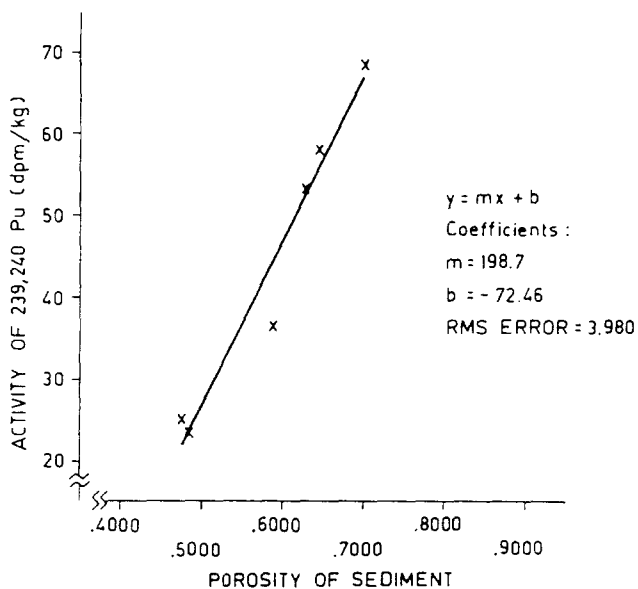**Fig. 2.** Profile of $^{239,240}Pu$ and $^{238}Pu/^{239,240}Pu$ ratios in sediment core PV-04 collected in October 1983 at Portovenere. Uncertainties are 1σ propagated errors.

Fig. 3. Profile of porosity in sediment core PV-04 collected in October 1983 at Portovenere. The solid line is a non-linear least squares fit to the equation of Matsumoto & Wong (1977) (see text).

Fig. 4. The relationship between porosity and the concentration of ^{239,240}Pu in surface sediments of the Ligurian Sea.

collected by the Shipek grab sampler) was 0·667, similar to porosities from our other stations with fine-grained sediments. In profile (Fig. 2), there was a well-preserved Pu maximum corresponding to the peak fallout input in 1963. The porosity profile (Fig. 3) shows evidence of compaction at depth by the sediment overburden; the porosity profile was calculated by a non-linear least squares fit to the equation of Matsumoto & Wong (1977) presented in our discussion of sedimentation rate below.

DISCUSSION

Plutonium concentration and porosity of surface sediments

The concentration of ^{239,240}Pu in surface sediments appears to be highly correlated to the porosity of the sediments which, in turn, is related to the grain size. This can be seen from the good fit when ^{239,240}Pu is plotted versus porosity (Fig. 4). The line through the points is the least squares best fit to a straight line. Data from station SP 05 are excluded from the plot because inclusion of superficial water in the drying tray prohibited measurement of porosity. Laboratory notes on this sample, however, identify it as a sandy sample which should have low porosity, which most probably accounts for its low Pu concentration. Hetherington *et al.* (1975) demonstrated the relationship between grain size and Pu concentration for the Ravenglass estuary; the relationship between Pu concentration and porosity which we report here confirms that the trend of higher concentrations in samples of smaller grain size is valid also for the Ligurian Sea but shows further that, in surface sediments, porosity is equally useful in predicting Pu concentrations and it is easily measured from the wet and dry weights. Although the relationship between porosity and Pu concentration could be accurately described by a linear relationship over the range in this study (Fig. 4), there is no theoretical reason to expect that the relationship will be linear outside this range. In fact, Hetherington *et al.* (1975) found the concentration of Pu to be nearly independent of grain size for particles greater than about 20 μm in diameter.

  Although in surface sediments the concentration of plutonium is highly correlated with porosity, we would not expect porosity to correlate well with the depth profile of Pu in the sediment core and indeed it does not (see Figs 2 and 3). The changing porosity with depth is affected not only

by grain size but also by compaction from the overburden of sediment. Moreover, the depth profile of Pu concentrations arises mainly from the input of fallout which has varied over the years; the record of its input is preserved in the sedimentary column.

Sedimentation rate

Identification of the subsurface maximum of fallout radionuclides in sediment cores, corresponding to the peak fallout in 1963 (Perkins & Thomas, 1980), has been used to calculate average sedimentation rates in regions of rapid sedimentation (Robbins & Edgington, 1975; Olsen *et al.*, 1981; Beasley *et al.*, 1986), but it has not been found effective for sedimentation rates less than 1 cm y^{-1} because sediment mixing often alters the radionuclide profile at sites of low sedimentation. In model calculations of the distribution of fallout radionuclides in sediments of the Hudson estuary, for example, Olsen *et al.* (1981) showed that, for sedimentation rates greater than 1 cm y^{-1}, sediment mixing rates had little effect on radionuclide distributions but, for a sedimentation rate of 0·3 cm y^{-1}, the fallout maximum was smeared at mixing rates deemed to be reasonable for the Hudson estuary. Even then, however, the location of the subsurface peak did not change greatly but it lost definition. The Pu profile from our Portovenere core in Fig. 2 shows a clearly defined subsurface maximum corresponding to the 1963 fallout peak suggesting that the mixing rate at this station was low. The low tidal and wave energy and a paucity of benthic organisms would lead us to a prediction of low mixing rate which, indeed, seems to be the case at this station. Because of these conditions we feel confident in using the subsurface maximum to estimate the average sedimentation rate.

In calculating the average surface sedimentation rate we have first corrected the depth of each horizon for compaction by the overburden of sediment as described by Matsumoto & Wong (1977). The porosity data were fitted by a non-linear least squares fit to eqn (1)

$$\phi = (\phi_0 - \phi_\infty) \exp(-\alpha z) + \phi_\infty \tag{1}$$

where ϕ_0 and ϕ_∞ are porosities of sediments at the interface ($z = 0$) and final compaction ($z = \infty$) respectively. The compaction corrected depth, z', was calculated from eqn (2)

$$z' = z + \int_0^z [(\phi_0 - \phi)/(1 - \phi_0)] dz \tag{2}$$

Dividing the compaction-corrected depth of $10 \cdot 4$ cm by the 20 y between the fallout peak and our sampling date gives an average surface sedimentation rate of $0 \cdot 52 \pm 0 \cdot 06$ cm y^{-1}, the uncertainty being calculated from our sampling at 1 cm horizons.

As this is one of the first radiometric calculations of sedimentation rate in the Ligurian Sea, it could aid in the understanding of the fate of many particle-reactive pollutants, including heavy metals such as Fe, Po, Pb, Am, Cr(III) and Hg (Santchi *et al.*, 1980) in these waters. At a depth of 200 m offshore from Monaco, Burns & Villeneuve (1983) reported a sedimentation rate of $0 \cdot 1$ cm y^{-1} measured by ^{210}Pb but this difference between the sedimentation rates at the two stations is easily understood because our station is in shallower water near a source of suspended sediment.

Plutonium inventory

The inventory of Pu in sediments at the coring site was calculated to be $3 \cdot 5$ mCi km^{-2} by summing the products of the Pu concentration and the total weight of each horizon divided by the cross-sectional area of the core; Pu concentrations were interpolated for horizons which were not analyzed. (Over the continental shelf less than $0 \cdot 01$ mCi km^{-2} is contained in the water column or less than $0 \cdot 3\%$ of the sediment inventory, a negligible part of the total inventory.) This inventory is compared with other published reports of sediment inventories in Table 4. In general, it is far greater than those found in deep water sediments of the Atlantic and Mediterranean but comparable to inventories measured in other shallow water marine sediments. All of the reported inventories in Table 4 were measured at locations from 30 to 50° N latitude, a band in which the cumulative delivery of fallout Pu up to 1971 was $1 \cdot 8$–$2 \cdot 2$ mCi km^{-2} (Hardy *et al.*, 1973) and which has not increased substantially since 1971 because present day deposition is only a fraction of that near the peak in 1963 (Perkins & Thomas, 1980). The inventory in our study area, like those in most other shallow marine environments, is substantially higher (about two times) than would be expected from the cumulative fallout deposition. Deep water sediments have only a fraction of fallout delivery, the bulk of the inventory being retained in the water column. And even at deep water stations calculations of inventories in the water column are sometimes higher than fallout delivery (Livingston *et al.*, 1979; Bowen *et al.*, 1980). Inventory calculations in the water column have a potential for

greater error than do sediment calculations, however, because the concentration of Pu at a single depth is chosen to be representative of large volumes of water. A small analytical error or a small misrepresentation in the average Pu concentration because of the sampling depth is magnified when multiplied over large volumes. That problem aside, reported data from the water column show some locations with higher and some with lower inventories than fallout delivery. In general, then, the distribution of Pu is not simply a matter of only vertical transport of fallout delivered to the sea surface but involves advection and removal processes which modify the inventories giving some locations higher and others lower inventories.

It is apparent from Table 4 that the lowest sediment inventories are found in the deep ocean, with intermediate values in slope sediments, and the highest inventories in shallow marine environments where the inventories are usually higher than fallout delivery. That the inventories are greater than delivery in both Mediterranean and Pacific shelf sediments indicates that it is a general and not a local phenomenon. This confirms the assertion by Beasley *et al.* (1982) that the high inventories on the Pacific shelf are not due to close-in fallout from the Pacific Proving Ground, an explanation advanced by Bowen *et al.* (1980) to explain the inventory excesses in the Pacific water column, but that they result from the processes by which Pu is removed from seawater. In particular, this seems to be controlled in large measure by the particle populations. The lower inventories on the Atlantic continental shelf measured by Livingston & Bowen (1979) run counter to this trend and we will discuss possible reasons for this below.

Although it is difficult to be definitive from a single core, it is confirmed by the work of Triulzi *et al.* (1982) and by other work underway in our laboratory that the Pu inventories are lower in Mediterranean than in Pacific shelf sediments despite surface water concentrations which are even higher in the Mediterranean and particle populations which are about the same. Ballestra *et al.* (1982) report the average concentration of Pu to be 2×10^{-3} dpm litre^{-1} in the north-western Mediterranean, while concentrations in Pacific surface waters are in the range of $0.7–1 \times 10^{-3}$ dpm kg^{-1} (Bowen *et al.*, 1980; Nielsen, 1982). Although particle populations in the Ligurian Sea are variable, Pierce *et al.* (1981) found the average concentrations to be slightly higher than for the Oregon shelf; Corradi *et al.* (1982) found an average of 1.2 mg litre^{-1} suspended load in our study area compared to about 1 mg litre^{-1} on the Pacific shelf.

TABLE 4

Inventories of $^{239.240}$Pu in Marine Sediments Collected From Different Environments. Inventories in mCi km^{-2}

Location and environment	$^{239.240}$Pu inventory	Reference
Ligurian Sea continental shelf	3·5	This work
Ionian Sea continental shelf	2–6	Triulzi *et al.* (1982)
Buzzards Bay shallow water	1·6 – 2·5	Noshkin (1972)
NE Pacific Ocean continental shelf	4·1 – 14·2	Beasley *et al.* (1982)
NE Pacific Ocean continental slope	1·5	Beasley *et al.* (1982)
Atlantic and Mediterranean deep water sediments	0·2 – 0·3	Noshkin & Bowen (1973)
Mediterranean deep water sediments	0·06 – 0·18	Livingston *et al.* (1979)
NW Atlantic continental shelf	0·6 ± 0·3	Livingston & Bowen (1979)

We propose as an explanation for the difference in sediment inventories the lower energy for physical and biological mixing of the sediments in the Mediterranean. As we discussed above, it is evident that sediment mixing rates are lower in the Ligurian Sea than in the Hudson estuary and they should likewise be lower than those on the Pacific shelf. Although the sedimentation rates in the two locales are similar, the subsurface Pu maximum is completely obliterated in Pacific shelf sediments but is well defined in the Ligurian Sea because of its low mixing rate. This may also provide a clue to understanding why the inventories of Pu measured by Livingston & Bowen (1979) on the Atlantic continental shelf were so low while the inventories in nearby Buzzards Bay were higher (Noshkin, 1972): their cores were all raised from depths greater than 200 m where, as in the Ligurian Sea, the energy for physical mixing would be very low. Perhaps this is a contributing factor along with the low particle population and sedimentation rate suggested by Beasley *et al.* (1982) in explaining the low inventories.

In a high energy environment like the Pacific shelf, on the other hand, the resuspension of particles at the sediment–water interface could provide the mechanism to remove more of the Pu from the water and generate higher inventories. The suggestion that particles entering the ocean in river runoff scavenge Pu from seawater is supported by ratios of $^{239,240}Pu/^{137}Cs$ in surface sediments both in this work and in the work of Beasley *et al.* (1982). Although we did not measure ^{137}Cs in our samples, we estimated the ratios from the data of Anselmi *et al.* (1982) who reported ^{137}Cs at some of the same stations which we sampled. These ratios are summarized in Table 2. The average ratio of the river stations is 0·016 while the average from the marine stations is 0·08. Since the change in ratio from river to sea is caused more from an increase in Pu than from a decrease in Cs we conclude that the primary mechanism for the change is adsorption of Pu onto the particles as they contact seawater.

We do not believe that the difference between Ligurian Sea and Pacific shelf Pu inventories can be attributed to differences in particle size or mineralogical composition. The porosities are similar or even higher in our core which, if anything, should lead to higher concentrations of Pu based on the evidence of higher distribution coefficients (K_ds) at smaller grain size (Hetherington *et al.*, 1975), but in fact the concentrations in our core are somewhat lower. Since it has been shown (Beasley *et al.*, 1982) that Pu in sediments is associated primarily with hydrous Fe and Mn coatings on the particle surfaces, the number of particles is more important than their composition in removing Pu from the water column. In line with this view, one might predict that the high sediment load from the Columbia River could supply sufficiently large numbers of particles to effect the inventory differences observed between the Pacific study and this study, but neither the sedimentation rates nor the reported populations of both biogenic and inorganic particles support this idea. For, unless the published reports of particle populations are in error or we have vastly overestimated the sedimentation rate, these two parameters are similar for the Ligurian Sea and the Pacific shelf and some additional mechanism is required to explain continental shelf inventory differences. We think that resuspension of sediments in higher energy environments is the likely explanation.

Reconstruction of Pu concentrations in surface waters

Using the surface sedimentation rate and assuming that it had been constant over the length of the core, we dated each horizon and then

attempted to back-calculate what the concentration of Pu in Mediterranean surface water would have been at that time. In doing so we assumed that, in addition to the sedimentation rate, the K_ds and particle populations in surface waters were likewise constant. These calculations, even though they involve rather sweeping assumptions, reveal two things: (1) that Pu was measured below the 1945 horizon when the first nuclear weapon was tested at Alamogordo, and (2) that the 1963 peak in calculated seawater concentration was less than 50% higher than at present.

The most reasonable conclusion from the first observation is that, although the sediment mixing rate is low enough to preserve a well-defined 1963 fallout peak in Ligurian Sea sediments, there has, nevertheless, been some sediment mixing to carry Pu to depths below the 1945 horizon. The source of this mixing could be either physical processes or bioturbation or both, but as yet we have no way of distinguishing these. In either case it does not compromise our measurement of sedimentation rate.

The second conclusion which could be drawn is that the concentration of Pu in Mediterranean surface waters has not varied much since about 1958. During that time we calculate that the range has been only from a maximum of $2 \cdot 9 \times 10^{-3}$ dpm litre^{-1} to its present low of $2 \cdot 0 \times 10^{-3}$ dpm litre^{-1} (Ballestra *et al.*, 1982). Even taking into account some smearing which took Pu below the 1945 horizon and thus left the maximum concentration in 1963 slightly lower than would otherwise be calculated, the conclusion remains that the Mediterranean probably never had concentrations of Pu in seawater substantially greater than at present. This conclusion is not in conflict with measurements in the Pacific Ocean from early 1964 (Pillai *et al.*, 1964) to 1980 (Nielsen, 1982) which show very similar Pu concentrations in seawater throughout that time period.

CONCLUSIONS

(1) The Pu concentrations in surface sediments were about ten times higher on the Ligurian Sea continental shelf than in the river sediments which served as a source of particles to the shelf; this stands in contrast to published results on ^{137}Cs in the same location which showed no significant increases in concentration in the sea. The Pu concentrations generally increased with distance from the river mouth and showed a high correlation with sediment porosities.

(2) The well-preserved subsurface maximum in Pu concentrations in the core from Portovenere showed that the sediment mixing rates were low at this station. Because of this we were able to calculate a surface sedimentation rate (corrected for compaction in the core) of 0.52 ± 0.06 cm y^{-1}.

(3) The Pu inventory of 3.5 mCi km^{-2} in the Ligurian Sea is nearly twice the integrated fallout value at this latitude. We concur with the suggestion of Beasley et al. (1982) that particle populations are the important parameter in the removal of Pu to the sediments in coastal marine environments and we emphasize that the source of these particles may not be solely the input from land or production *in situ* but may also be from resuspension of bottom sediment in high energy environments. This process could help explain the differences in inventory among coastal sediments of the Mediterranean, Atlantic and Pacific.

ACKNOWLEDGEMENTS

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