CHEMICAL PARTIONING OF PLUTONIUM AND AMERICIUM IN SEDIMENTS FROM THE PALOMARES MARINE ECOSYSTEM

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The marine environment adjacent to the coastal village of Palomares (Southeastern Spain) became a suitable area to investigate the behavior of the transuranics that reached the Mediterranean Sea after the partial land-to-sea transfer of the contamination dispersed as a consequence of the non-nuclear explosion of two thermonuclear bombs accidentally released during a plane crash in 1966 (GASCÓ *et al.*, 1992 and ROMERO *et al.*, 1992). To determine the potential post-depositional remineralization of these transuranics, their bioavailability to bottom feeding biota, along with the effect of their source term on their distribution within the major sedimentary phases, the geochemical association of these longlived radionuclides has been evaluated.

In this study, two sections from Station 13 (50 m depth, 37°11.21 N 1°47.1 W) were selected: PASD13(01) corresponds to the first centimeter of the core; PASD13(09) is a deeper layer, and it corresponds to the 8-9 cm section. Station 13 is located south of the Almanzora river mouth in an area of the continental shelf where enhanced concentrations of transuranics have been previously found (GASCÓ *et al.*, 1992).

Chemical partioning of Pu and Am was performed by applying the following sequential leaching procedure: 12 g subsamples were stirred for 18 h with the appropriate amount of extractant, as shown in Table 1. The supernatant was filtered through a Whatman GF/C filter paper. Spikes of ^{242}Pu and ^{243} Am were added to determine the radiochemical yield of the procedure (COOK *et al.*, 1984).

Fraction	Reagant	Volume(ml/g)
Readily available	$CaCl_2$ 0.05 M	20
Exchangeable	CH_3-COOH 0.05 M	20
Organically bound	$Na_4P_2O_7$ 0.1 M	100
Oxide bound	$(NH_4CO_2)_2$0.175 M/$C_2O_4H_2$ 0.1 M	75
Residual	HNO_3/HF/HCl conc.	75

Table 1. Scheme of the leaching procedure for marine sediments

The results of chemical partitioning for Station 13 are summarized in Tables 2 and 3. The order of association of Pu in PASD13(01) is (Table 2): organic > oxide > residual > exchangeable > readily available. The fractions considered most mobile (readily available/exchangeable) contain less than 3% of the plutonium. The majority is associated with insoluble organic chelated complexes (66%).

The order of association of Am in PASD13(01) is (Table 2): exchangeable > organic > residual > oxide > readily available. Almost 50% of the Am is linked to the exchangeable phase, known as a "soluble" phase. Am also appears to be less associated with the sesquioxides (Al,Fe,Mn) than plutonium.

The isotopic ratios ^{238}Pu/^{239}Pu=0.04±0.01 and Am/Pu=0.3±0.1 indicate global fallout as the source term of these transuranics.

Fraction	^{239}Pu activ. Bq/kg d.w.	* ^{239}Pu content	^{241}Am activ. Bq/kg d.w.	% ^{241}Am content
Read. avail.	BDL	-----	BDL	-----
Exchangeable	0.06 ± 0.01	2.5 ± 0.4	0.24 ± 0.02	40. ± 6.1
Organ. bound	1.53 ± 0.10	66. ± 2.3	0.2 ± 0.01	33.3 ± 3.7
Oxide bound	0.51 ± 0.04	22. ± 1.7	0.05 ± 0.02	8.3 ± 4.1
Residual	0.22 ± 0.05	9.4 ± 2.0	0.10 ± 0.04	16.6 ± 7.9
Σ activity	2.3 ± 0.12		0.6 ± 0.05	

Table 2. Sequential leaching of PASD13(01). Uncertainties are given in ± 1σ.

Fraction	^{239}Pu activ. Bq/kg d.w.	* ^{239}Pu content	^{241}Am activ. Bq/kg d.w.	% ^{241}Am content
Read. avail.	0.01 ± 0.005	0.09 ± 0.05	BDL	-----
Exchangeable	0.15 ± 0.02	1.36 ± 0.21	0.51 ± 0.06	17.3 ± 0.04
Organ. bound	0.91 ± 0.06	8.23 ± 0.85	0.46 ± 0.10	15.6 ± 0.03
Oxide bound	0.80 ± 0.05	7.23 ± 0.71	0.05 ± 0.03	1.7 ± 0.003
Residual	9.19 ± 0.92	83.1 ± 1.52	1.93 ± 0.18	65.4 ± 0.14
Σ activity	11.06 ± 0.92		2.95 ± 0.22	

Table 3. Sequential leaching of PASD13(09). Uncertainties are given in ± 1σ.

The order of association for Pu is (Table 3): residual > organic > oxide > exchangeable > readily available. Most of the Pu appears in the residual fraction (88%), suggesting that the Pu is very refractory, like Pu in the aerosol dispersed during the accident in 1966. The order of association for Am is (Table 3): residual > exchangeable > organic > oxide > readily available. Most of the Am also appears in the residual fraction, however, almost 20% is in the exchangeable phase.

The isotopic ratios ^{238}Pu/^{239}Pu=0.02±0.005 and 241Am/239Pu=0.24±0.03 suggest weapon grade Pu ratios, indicating that the transuranics detected at this depth originate from the Palomares accident.

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CAESIUM INVENTORIES IN SEDIMENT CORES IN AREAS UNDER THE INFLUENCE OF THE PO RIVER (ITALY) AND THE RHONE RIVER (FRANCE)

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The Po and the Rhône are two of the major rivers flowing into the Mediterranean sea. They both drain large basins, have annual liquid flows among the highest in the Mediterranean region (respectively 1500 and 1750 $m^3.sec^{-1}$) and carry a comparable amount of suspended solids (in the order of 10^7t.year^{-1}).

The Rhône is the river with the highest number of nuclear facilities along its banks : 6 nuclear power plants (NPP) with 17 reactors of different types and one fuel reprocessing plant in Marcoule. All these facilities are authorized to discharge low level radioactive liquid effluents into the aquatic environment after processing and compliance with the legislation in force. The outflow of the Rhône is transported by the prevailing currents mainly to the west during calm periods, and southwestward under Mistral conditions.

Along the Po river are located two NPP that were shut down in 1986. In addition being very far from the sea, they do not produce significant inputs of radionuclides into the Adriatic Sea. Water and suspended matter entering the Adriatic sea are dispersed mainly southward by the prevailing currents. Mud represents about 77% of the total particulate material.

In 1989-90 sampling campaigns were carried out in the marine areas under the influence of the Po and the Rhône rivers. Sediment cores have been collected in the areas of deposition of fine grained sediments, by using two types of box-corer, both with a large collecting area (300 and 730 cm^2), that allowed sediment cores of 30-40 cm long to be taken up. The cores were sectioned on board in 1 cm thick layers. The samples were dried, weighed and blended in the laboratory; ^{134}Cs and ^{137}Cs were determined by direct gamma spectrometry. From the vertical profiles of the two radionuclides, the inventories were determined from the sum of the total activity in each layer divided by the surface of the core. The results are reported on Fig. 1.

In the area under the influence of the Po river the inventories of ^{137}Cs ranged from 1.9 to 3.7 kBq.m^{-2}. In this area the contribution of Chernobyl ^{137}Cs, calculated from ^{134}Cs, was usually lower than 30%. In the sample collected in the prodelta area, southward and close to the Po river mouth, both concentration and inventory (more than 21.5 kBq.m^{-2}) were one order of magnitude higher, in relation to enhanced sedimentation regimes in this small, well protected area. In the Gulf of Lions, the ^{137}Cs inventories ranged from 1.2 to 6.9 kBq.m^{-2}. Again, in the prodelta, the concentration and inventory of ^{137}Cs (more than 26 kBq.m^{-2}) were much higher than in the surrounding area. Due to high sedimentation rates occurring near the Rhône mouth, ^{137}Cs inventories appear to be linked rather to recent inputs from the nuclear facilities than to the influence of the Chernobyl fallout and run off.

The studies carried out in both regions confirm that the greater part of suspended matter and the associated pollutants transported by the two rivers into the Mediterranean Sea are temporarily trapped in a small prodelta area, where the sedimentation processes are governed by electro-chemical flocculation and by particle aggregation phenomena. Off the prodelta areas, the inventories reflect what is known about the areas of influence of these two rivers.

Although the supply of suspended solids from the two rivers is very similar, the ^{137}Cs inventories found near the Po river mouth are about 40 % of those calculated for the area under the influence of the Rhône. These differences are certainly due, to some extent, to the input of radionuclides from nuclear facilities along the Rhône river. But, on the other hand, it must be considered that the North-Adriatic Sea is a shallow area, having no more than 40 m water depth and therefore, under the action of the strong winter winds, fine-grained sediments can easily be re-suspended from the bottom and transported elsewhere by the prevailing currents.

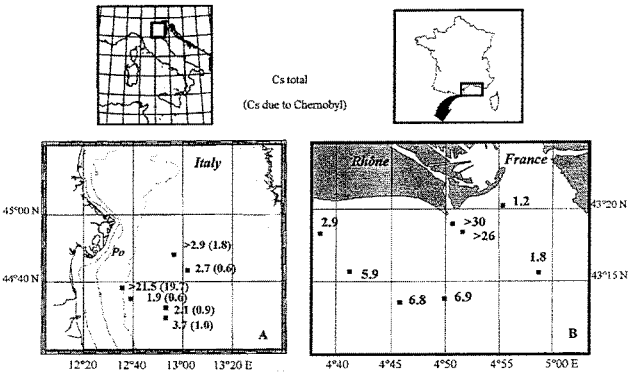

Figure 1: ^{137}Cs inventories (kBq.m^{-2}) in sediment near the mouth of the Po river (A) and the Rhône river (B). (> : core not sufficiently long to see termination of ^{137}Cs signal)

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