Distribution of Plutonium-237 between Sediment and Sea Water

by

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Abstract

Labora ory sorption experiments have been carried out with the short-lived gamma-ray emitting ^{237}Pu isotope and Mediterranean sediments. Under anoxic and oxic conditions, plutonium adsorbs with a distribution coefficient of about 1.5×10^4 independent of its valence III, IV or VI.

Résumé

Des expériences d'adsorption ont été menées en laboratoire avec l'isotope ^{237}Pu, émetteur de rayons gamma et de courte période, et avec du sédiment méditerranéen. Que ce soit dans un milieu aérobique ou anaérobique, le plutonium s'adsorbe selon un coefficient de distribution d'environ 1.5×10^4, indépendamment de sa valence III, IV ou VI.

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Previous determinations [DUURSMA & EISMA, 1973] of the distribution coefficient of plutonium on marine sediments indicated that plutonium was bound to sediments to a degree intermediate between that of ^{90}Sr and ^{137}Cs, i.e. having a distribution coefficient between 10^2 and 10^3. Using ^{237}Pu as a tracer, we conducted a series of experiments to determine the distribution coefficient of plutonium onto sediments both under oxic and anoxic conditions where the plutonium was added to sea water in three different valence states III, IV and VI. The chemical form of the plutonium was adjusted as follows (MURRAY, *personal communication*) :

a. Pu (III) : An aliquot of stock ^{237}Pu solution (likely to be in Pu-IV in $O.1N$ HCl) was evaporated to dryness with 2 ml of NH_2OH :HCl solution (50 mg NH_2OH :HCl/2ml H_2O) and the residue was taken up in 3 ml of $1.5N$ HCl.

b. Pu (IV) : An aliquot of the ^{237}Pu stock solution was evaporated to dryness with 2 ml of $16N$ HNO_3 in which solid sodium nitrite was dissolved and the residue was taken up in 3 ml of $1.5N$ HCl.

c. Pu (VI) : An aliquot of the ^{237}Pu stock solution was evaporated to dryness with 2 ml of concentrated $HClO_4$ and the residue was taken up in 3 ml of $1.5N$ HCl.

Two methods were used to determine the distribution coefficient of the various plutonium valence states onto sediments. These methods have been described in detail by DUURSMA & BOSCH [1970]. Briefly, in the water column method, aliquots of sediment were allowed to sink each day through a column of sea water, the decrease in the activity of the ^{237}Pu in the water column was measured and the sorption by the sediment calculated. In the thin layer method, a thin layer of 10mg of sediment, supported on a millipore filter, was placed in an active sea water media and the increase of the plutonium on the sediment was measured each day.

The measured distribution coefficients of the different plutonium valence states for a local Mediterranean sediment are presented in Table 1 along with the sorption " hall-time " values obtained by the thin layer method.

Table 1. : Plutonium-237 sorption by Mediterranean sediment

| | Oxic conditions pH = 7.8 - 8.0 | | | | Anoxic conditions pH = 7.8 - 8.0 | | | |
| | Sedimentation | | Thin layer | | Sedimentation | | Thin layer | |
Valence	K	R	K	$T\frac{1}{2}$	K	R	K	$T\frac{1}{2}$
III	1.6×10^4	10 %	2.1×10^4	3	1.9×10^4	2.5 %	—	
IV	1.8×10^4	9 %	1.9×10^4	1	1.3×10^4	3.0 %	$> 9.4 \times 10^4$	2.4
			1.5×10^4	1				
VI	1.3×10^4	11 %	5.7×10^4	4	2.2×10^4	9.0 %	—	—

K = distribution coefficient; R = % reduction in water/day without sediment in a plastic tube. $T\frac{1}{2}$ = half uptake time to apparent equilibrium in days.

All three valence states showed comparatively large distribution coefficients, i.e. 10^4. These values exceed those previously measured for ^{90}Sr and ^{137}Cs, but are smaller than those evidenced for [106]Ru, [95]Zr-Nb and [144]Ce.

For both exic and anoxic conditions, the distribution coefficients appear similar for all three plutonium valence states. It was not possible to determine whether reduction of Pu (VI) occurred in the reducing anoxic experiment. Plutonium in sea water containing no sediment generally showed a loss of plutonium from the sea water to the vessel walls or by precipitation. This decrease ranged between 8-10 % per day; Pu (III) under anoxic conditions showed a slower rate loss of some 2.5 % per day.

Half-time values measured by the thin layer method ranged between 1-4 days. Rapid uptake of nuclides by sediments suggests that some form of active reaction is occurring in the system (e.g. [137]Cs $T\frac{1}{2} = 0.7 \pm 0.4$ days). Precipitation reactions are normally slow (e.g. [59]Fe $T\frac{1}{2} = 18 \pm 6.5$ days). Thus, Pu (IV), $T\frac{1}{2} = 1$ day may be actively reacting with the sediment matrix; Pu (III) and Pu (VI) may be partly precipitating in addition to participating in active reactions with the sediment.

These data suggest, when applicable to [239]Pu and [240]Pu in contaminated areas, that the plutonium will be relatively strongly adsorbed by many marine sediments. Extrapolation to other sediments is reasonable, considering the identical results for various marine sediments and other radioactive waste isotopes [DUURSMA & EISMA, 1973].

The question whether plutonium, once bound by the sediment cannot be released at the long run is difficult to answer. Therefore, the long-term chemistry of sorbed plutonium needs further investigation, as was made for other radionuclides by ROS VICENT et al. [in press]. The problem is that this has to be done with another plutonium isotope, since [237]Pu has a too short half-life for such studies.

Conclusions as to its long-term fate in sediments are unwarranted at this time.

References

DUURSMA (E.K.) & BOSCH (C.J.), 1970. — Theoretical, experimental and field studies concerning diffusion of radioisotopes in sediments and suspended solid particles of the sea. Part B. Methods and experiments. *Neth. J. Sea Res.*, 4, pp. 395-469.

DUURSMA (E.K.) & EISMA (D.), 1973. — Theoretical, experimental and field studies concerning reactions of radioisotopes with sediments and suspended particles of the sea. Part C : Applications to field studies. *Neth. J. Sea Res.*, 6, pp. 265-324.

ROS VICENT (J.), COSTA YANGUE (F.), PARSI (P.), STATHAM (G.) & DUURSMA (E.K.) (in press). — The case of release of some trace metals and radionuclides being sorbed for prolonged periods by marine sediments. *Bul. Inst. Esp. Oceanogr.*