
Post-depositional reactivity of the plutonium in different sediment facies from the English Channel – an experimental approach

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Abstract. The post-depositional reactivity of the plutonium was investigated in bottom sediments collected in the central English Channel using an experimental approach. Medium to coarse grained surficial sediments and fine-grained undisturbed sediment cores were spiked with ²³⁸Pu. After a one-month incubation, pore waters were extracted under strictly anoxic conditions and dissolved plutonium was analysed by liquid scintillation techniques. Kd values ranged from 10² to 10⁵ in surficial sediments undergoing oxic diagenesis, and were shown to be grain-size dependant. In fine-grained sediments undergoing anoxic diagenesis, Kd values ranged between 10³ and 10⁵. Kd profile suggests an active recycling of the plutonium in the topmost sediment layers, and subsequent efficient uptake process at depth, tentatively acido-volatile sulphide (AVS) precipitation. This hypothesis was further confirmed by a correlation between the AVS content and the loosely bound plutonium extracted using an oxidising/complexing solution from sediment subsamples. In surficial sediments, by contrast, loosely bound plutonium was likely to be associated with the carbonate phase as surface complexes.

1. INTRODUCTION

The plutonium inputs in the English Channel mainly originate from the fallout of atmospheric weapon tests (through direct fallout on the area, Atlantic inflow and adjacent drainage basins) and of industrial releases from the nuclear reprocessing plant located at Cap La Hague [1]. The sediment inventory due to both atmospheric fallout and industrial discharges is roughly of the same order of magnitude as the total plutonium- α activity released by the reprocessing plant, about 5 TBq (Tab. 1).

The average velocity of the bed load transport is extremely low (some km.a⁻¹; [1]). As a consequence, most of the deposited plutonium is expected to remain in the bottom sediments of the English Channel for a long time. Furthermore, as the average penetration depth of the plutonium signal is ca 10 cm, most of the sediment plutonium inventory is available for a potential release to the water column and transfer in the food chain.

Table 1. Total sediment inventory of α -emitting plutonium isotopes in the English Channel and source contribution [1].

	Total sediment inventory (Bq)	Source contribution	
		Direct fallout + Atlantic input	Reprocessing plant at Cap La Hague
²³⁸ Pu	1,05 x 10 ¹²	13%	87%
^{239, 240} Pu	4,64 x 10 ¹²	64%	36%

Little is known about the processes by which the plutonium can be released from medium to coarse-grained sediments, by diffusion or resuspension. No data are available on the post-depositional reactivity of this element in fine-grained sediments of the English Channel. No direct evidence of the potentially involved processes due their transient character and to the weakness of dissolved plutonium concentrations induced, is possible. Only some of them are liable to be investigated by an experimental approach.

2. MATERIALS AND METHODS

During the DIAMAN cruise (April 2003), on board the French research vessel Thalia (IFREMER), sediment samples were collected using Shipeck grab and Flucha box-corer. They were carefully preserved and brought back to the laboratory for further experiments and analyses. Among them, 15 were selected to cover a wide variety of sediment facies: 12 medium to coarse-grained surficial sediments (uppermost 5 cm) and 3 sub-cores (25 cm long) for fine-grained sediments (Fig. 1).

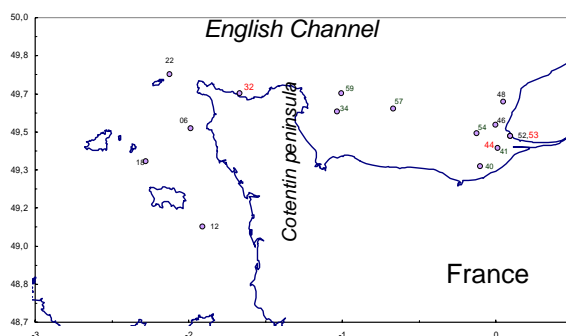


Figure 1. Location of sampling stations in the Central Channel; 32, 44 and 53 refer to box-cores.

The surficial sediment samples were set into plastic syringes and spiked with a 10 μL injection of ^{238}Pu through the interface (8×10^3 Bq). The undisturbed sub-cores were spiked the same way through predrilled holes in Plexiglas tubes and stopped with Silicone (Fig. 2). To prevent desiccation, a volume of 10 mL of seawater was maintained above the sediment samples (surficial and sub-cores) during a 1 month incubation (at 12°C, in the dark). In order to estimate the loss of plutonium through the sediment-seawater interface, the plutonium activity was periodically measured in the overlying seawater, which was renewed (7 times). No significant release of plutonium (less than 1% of the injected activity) was observed even in coarse-grained surficial sediments.

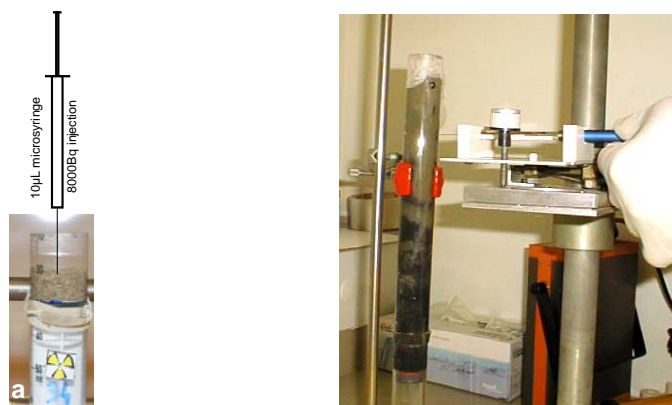


Figure 2. Plutonium spiking of surficial sediments (a) and of undisturbed sub-cores (b).

After the one month incubation, surficial sediments were recovered and sub-cores were extruded and divided into 1 cm thick slices, under strictly anoxic conditions (N₂-flushed glove-box). Dissolved plutonium concentrations were measured in interstitial water recovered by centrifugation under nitrogen. In sediment subsamples, the less than 50 µm fraction abundance was determined by wet sieving and carbonate content was measured by volumetric calcimetry. The acido-volatile sulphide (AVS) and chromium reducible sulphide (CRS) concentrations were measured after release as H₂S by acid digestion (HCl 6M at room temperature for 90 minutes) and Cr²⁺ reduction (at 90°C for 120 minutes), respectively [2].

Subsequently, leaching experiments were carried out. Sediment subsamples were stirred under oxic conditions in a complexing solution, hereafter referred to as R0 reagent (Na citrate 0.175M, pH 8, 1 g of wet sediment in 50 mL of solution for 1 hour). This extraction has been demonstrated (i) to be able to remove exchangeable plutonium, weak plutonium surface complexes and reactive sulphides [3]; (ii) to have no effect, neither on the carbonate lattice, nor on the Fe-Mn oxides; (iii) to efficiently prevent any resorption of the extracted plutonium.

After adequate acidification (interstitial waters and R0 extraction supernatants) or acid digestion (sediments), plutonium concentrations were determined by standard liquid scintillation techniques (Packard 2700 TR) with a detection limit of 0.007 Bq.

3. RESULTS AND DISCUSSION

3.1 Sediment characterization

As expected from visual selection, the less than 50 µm fraction covers a wide range in surficial samples. Figure 3 displays the less than 50 µm fraction profiles in the fine-grained subcores: no significant downcore trend is observed. The core collected in the roads of Cherbourg (DIAM32) is more silty (70% of <50 µm fraction) than those collected in Le Havre harbour (DIAM53) and the eastern Bay of Seine (DIAM44): 88% and 90% of <50 µm fraction, respectively. The carbonate contents range between 15 and 70% in surficial samples, and display very homogenous profiles (30-40%) in all cores (Fig. 3).

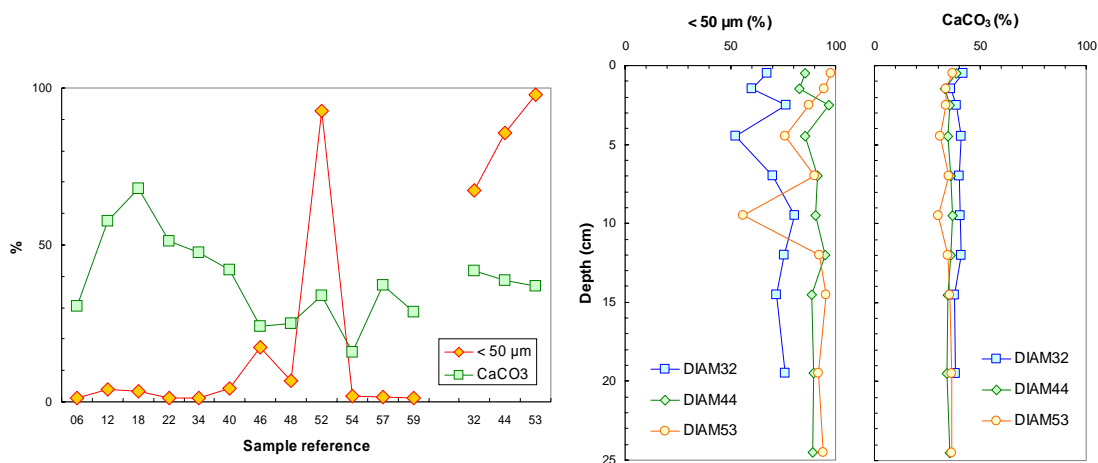


Figure 3. The less than 50 µm fraction abundance and carbonate content in surficial sediments 06 to 59 (including topmost layer of cores: 32, 44 and 53) and in sediment cores DIAM32, DIAM44 and DIAM53.

Very high amounts of AVS were found in the core DIAM32 (roads of Cherbourg): more standard values [4] were measured in other cores (20-200 mgS.kg^{-1} ; fig. 4). In surficial sandy sediments, AVS concentrations are very low ($<20 \text{ mgS.kg}^{-1}$) and are not expected to play a significant role in the plutonium solid partition. For surficial sediments as well as sediment cores, the CRS represent a less reactive but more abundant sulphide pool (such as pyrite). The CRS concentrations can reach 2000-4000 mgS.kg^{-1} at depth in sediment cores with a significant negative gradient upwards observed in cores DIAM32 and 44.

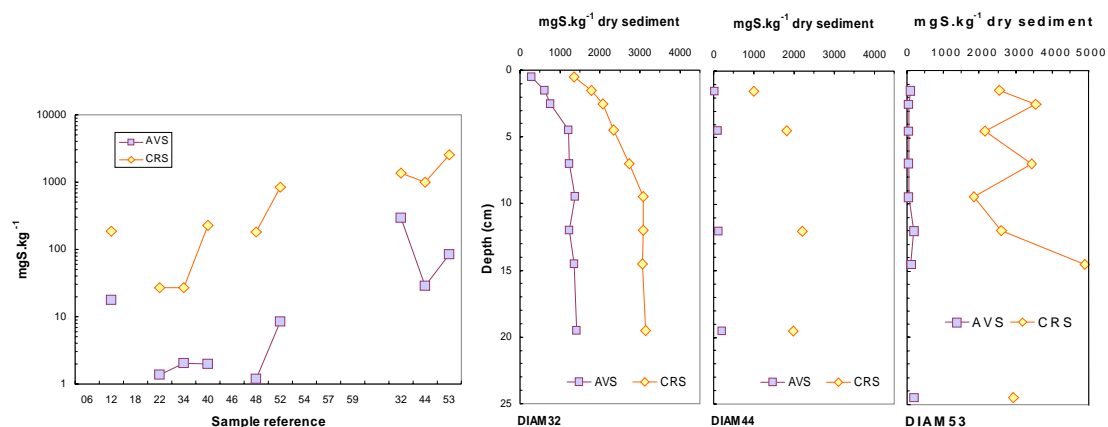


Figure 4. The acid volatile sulphides (AVS) and chromium reducible sulphides (CRS) in surficial sediments 06 to 59 (including topmost layer of cores: 32, 44 and 53) and in sediment cores DIAM32, DIAM44 and DIAM53.

3.2 Plutonium solid/liquid distribution

Experimental distribution coefficients of plutonium between solid and liquid phases were calculated for surficial sediments and the DIAM32 core. In cores DIAM44 and 53 and in surficial sediments 46 and 48, dissolved plutonium concentrations were lower than the detection limit. In surficial sediments, K_d values range between 10^2 and 10^5 . In the DIAM32 core, K_d values decrease from $ca 10^5$ for the uppermost layer to 4×10^3 at 10 cm depth (Fig. 5a). Deeper in the core, the K_d values were probably much higher, as plutonium concentrations in pore waters remained under the detection limit of our liquid scintillation detector. This suggests an active cycling of the plutonium in the upper 10 cm then an efficient uptake process, tentatively, AVS precipitation, at depth.

Plotting the K_d values versus the less than $50 \mu\text{m}$ fraction in medium to coarse grained surficial sediments yields a significant positive correlation between these two parameters (Fig. 5b): in oxic conditions, the plutonium adsorption is a predominantly non-selective surface process. In other words, the amount of adsorbed plutonium depends on the specific surface area of the sediment. No such correlation is observed in the core DIAM32 (Fig. 5b): this suggests that reactive processes start being active soon after the burial of the plutonium carrier phases.

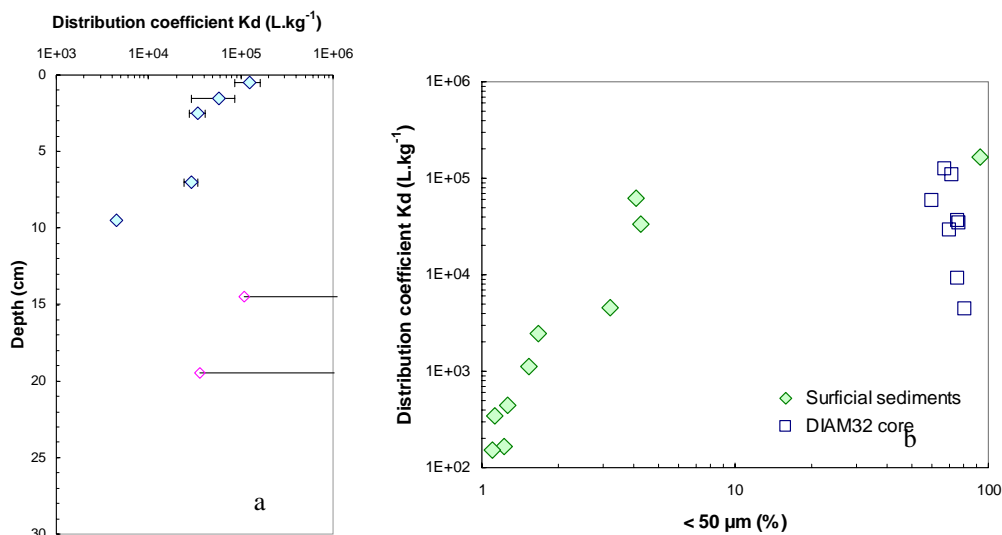


Figure 5. a: plutonium distribution coefficient profile in the DIAM32 sub-core; opened diamonds represent lower limits of K_d values; b: plot of K_d values versus the less than 50 μm fraction in surficial sediments and in the core DIAM32.

3.3 Plutonium solid partition

In oxic surficial sediments, the proportion of the plutonium removed by the R0 reagent ranges between 18 and 60% (Fig. 6a). No correlation is observed with the less than 50 μm fraction or with AVS concentrations. By contrast, correlation between carbonate content and plutonium amount in the R0 reagent suggests that this element is linked to the carbonate phase (Fig. 7a). As the R0 reagent has been demonstrated to have no effect on the dissolution of carbonates [3], we suggest that freshly injected plutonium is preferentially adsorbed onto carbonate particles as surface complexes.

In sediment cores undergoing anoxic diagenesis, 25 to 90% of the total plutonium were found to be removed by the R0 reagent. Moreover, a significant correlation was observed between the AVS (freshly precipitated sulphides) concentrations and the amount of plutonium extracted by the complexing and oxidizing solution (R0 reagent; fig. 7b). This reinforces the idea that AVS are an important sink phase for plutonium, as well as a very reactive carrier phase as reported by [5-6] from field studies in the eastern Irish Sea.

4. SUMMARY

The present work brings new insight into the post-depositional reactivity of the plutonium in marine sediments, from an experimental approach.

In medium to coarse grained sediments undergoing oxic diagenesis:

- experimental K_d values can be very low (10^2) especially in coarse grained sediments, to which little attention have been paid up to now;
- the plutonium adsorption is a predominantly non-selective surface process and, thus, depends on the specific surface area of the sediment, which dramatically increases as the average grain size decreases;
- the proportion of the loosely bound plutonium (removed by an oxidising/complexing reagent) ranges between 18 and 60% in the studied sediments;

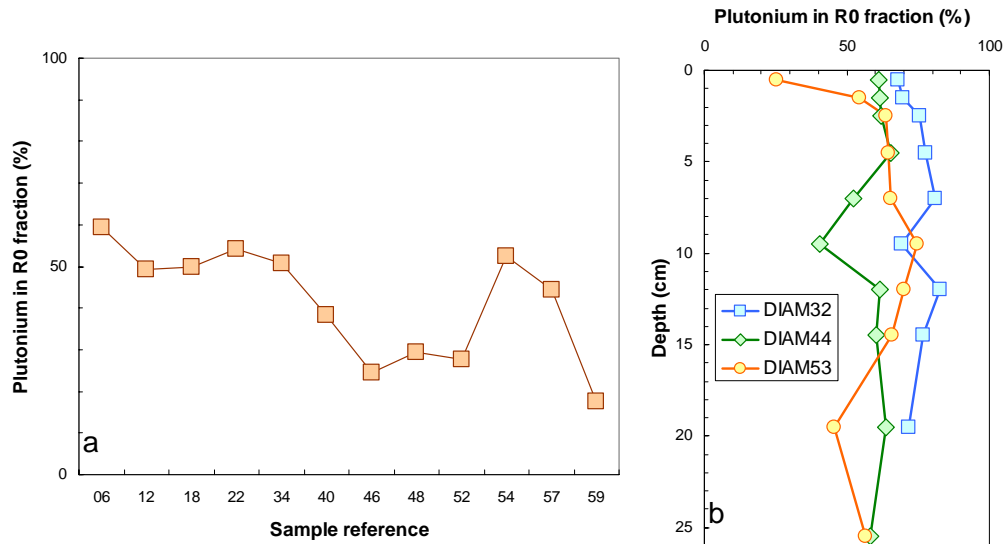


Figure 6. Proportion of the plutonium removed by the R0 reagent expressed as the ratio of plutonium extracted by a complexing/oxidizing solution (R0 reagent) to the total plutonium; a: in oxic medium to coarse grained surficial sediments; b: in anoxic fine-grained sediment cores.

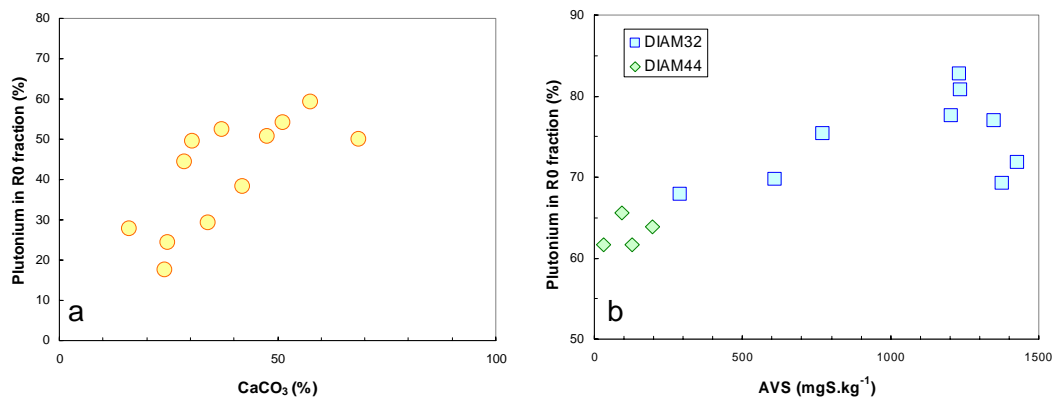


Figure 7. Plutonium in R0 reagent correlation with sedimentological parameters; a: versus the carbonate content in surficial coarse-grained sediments; b: versus AVS concentrations in two anoxic sub-cores, DIAM32 and 44.

- the correlation between carbonate content and loosely bound plutonium, together with the evidence of the absence of any dissolution of the carbonate phase, suggests that plutonium is linked to the carbonate phase as surface complexes.

In fine grained sediments undergoing anoxic diagenesis:

- experimental K_d values decrease downwards from 10⁵ to some 10³, in the topmost centimetres; deeper in the core, plutonium K_d values are probably very high; this suggests a progressive release of plutonium and its subsequent uptake at depth, tentatively, AVS precipitation.
- 25 to 90% of the total plutonium were found to be loosely bound to sediment particles (removed by an oxidising/complexing reagent);

- the significant correlation observed between the AVS (freshly precipitated sulphides) concentrations and the amount of extracted plutonium reinforces the idea that AVS are an important sink phase for plutonium, as well as a very reactive carrier phase.

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