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Spatial and temporal variations of plutonium isotopes (^{238}Pu and ^{239,240}Pu) in sediments off the Rhone River mouth (NW Mediterranean)

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Abstract

The dispersion and fate of the Rhone River inputs to the Gulf of Lions (Northwestern Mediterranean Sea) have been studied through the spatial and temporal distributions of plutonium isotopes in continental shelf sediments. Plutonium isotopes (^{238}Pu and ^{239,240}Pu) are appropriate tracers to follow the dispersion of particulate matter due both to their high affinity for particles and their long half-lives. In the Rhone River valley, plutonium isotopes originate from both the weathering of the catchment basin contaminated by global atmospheric fallout, and the liquid effluents released from the Marcoule reprocessing plant since 1961.

This work presents a first detailed study on ^{238}Pu and ^{239,240}Pu distributions in sediments from the Rhone prodelta to the adjacent continental shelf, since the decommissioning of Marcoule in 1997. The vertical distribution of Pu isotopes has been analysed in a 4.75 m long core sampled in 2001 at the Rhone mouth. Despite this length, plutonium is found at the last 10 cm, manifesting the high sedimentation rate of the prodeltaic area and its ability for trapping fine-grained sediments and associated contaminants. The highest ^{238}Pu and ^{239,240}Pu concentrations reached 1.26 and 5.97 Bq kg^{-1} respectively and were found within the layer 280–290 cm. The ^{238}Pu/^{239,240}Pu activity ratios (AR) demonstrated an efficient and huge trapping of the Pu isotopes derived from Marcoule. The fresh sediments, located on the top of the core, show lower plutonium activity concentrations and lower ^{238}Pu/^{239,240}Pu ratios. This decrease is in close relation with the shut down of the Marcoule reprocessing plant in 1997.

In 2001, plutonium isotopes were also analysed in 21 surface sediments located offshore and concentrations ranged from 0.03 to 0.17 Bq kg^{-1} for ^{238}Pu and from 0.33 to 1.72 Bq kg^{-1} for ^{239,240}Pu. The ^{238}Pu/^{239,240}Pu AR ranged from 0.24 close to the river mouth to 0.06 southwards, indicating the decreasing influence of the Marcoule releases (global fallout AR 0.03–0.05 and Marcoule AR 0.30). This is in good agreement with the main direction spread of the Rhone River plume and the bottom current. This dataset has been compared to those obtained in the same area in 1984 and 1990 in order to follow the time trend in Pu concentrations. This

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comparison highlights the decrease with time in plutonium concentrations close to the Rhone River mouth, but further away this reduction is not so evident.

Keywords: Plutonium; Marine sediment; Contaminant dispersion; Rhone River; Gulf of Lions; Mediterranean Sea

1. Introduction

Because of their high productivity, mainly due to riverine inputs of nutrients and organic particulate matter, estuarine and prodelta environments contribute substantially to the economic importance of coastal waters (Costanza et al., 1997). Coastal environments are also major repositories of sediment and associated contaminants, and one of the most important active sites of organic matter burial on the Earth's surface (Hedges and Keil, 1995). For these reasons, the dispersion and fate of riverine inputs on adjacent continental margins is a key issue since it can significantly influence many global biogeochemical cycles and continental margin processes.

In the Mediterranean Sea, the Gulf of Lions is the largest river-dominated ocean margin system (RiOMar, McKee et al., 2004), strongly influenced by the Rhone River inputs. Indeed, the Rhone River is the most important source of freshwater, nutrients and continental matter to the western Mediterranean. The mean flux of total suspended matter from the Rhone River to the Mediterranean was estimated as 9.9 ± 6.4 Mt y^{-1} (Sempéré et al., 2000). When entering the sea, the Rhone River discharges lead to the formation of a prodeltaic structure characterized by fine-grained deposits in the proximal area of the shelf (Roussiez et al., 2005). The Rhone prodelta is a large heterogeneous area with important bathymetric gradients between 10 and 60 m depth. On the Rhone prodelta, net sedimentation rates were estimated by the Chernobyl ^{137}Cs peak (Calmet and Fernandez, 1990) and by the $^{134}Cs/^{137}Cs$ ratio released by Marcoule (Charmasson et al., 1998). Net sedimentation rates range from 30 to 50 cm y^{-1} on the prodelta and they are the balance between sediment deposition and resuspension that occurred during flood and storm events respectively. Consequently, high values of net sedimentation rates would result from progradation of the top of the Rhone prodelta (Sabatier et al., 2006). Further offshore, sediment accumulations decrease exponentially with distance from the river mouth and are in the order of 0.1 cm y^{-1} on the continental shelf (Radakovitch et al., 1999; Miralles et al., 2005). Therefore, considering all of these factors, the prodeltaic area off the Rhone River mouth appears as an interesting zone to study the sequestration of riverborne substances such as heavy metals and artificial radionuclides.

In the Rhone valley, plutonium isotopes originate from both the weathering of the catchment basin contaminated by global atmospheric fallout, and the liquid effluents released by the Marcoule reprocessing plant. Since 1961, low-level radioactive liquid wastes were discharged into the Rhone River by the Marcoule reprocessing plant, located 120 km upstream from the river mouth. The plant was shut down in 1997 leading to a significant decrease in the discharge flux but releases have continued since washing effluents have been discharged up to 2000. Eyrolle et al. (2004) estimated that 92 ± 5 GBq of ^{238}Pu and 443 ± 72 GBq of $^{239,240}Pu$ were discharged by the Marcoule reprocessing plant into the Rhone River from 1961 to 2000. These inputs have contributed to more than 85% and 55% respectively of the total ^{238}Pu and $^{239,240}Pu$ introduced to the Rhone River basin. Over these years, a repository of artificial radionuclides (^{60}Co, ^{137}Cs, ^{238}Pu, $^{239,240}Pu$) has been built up both in the sediments of the river and near the Rhone River mouth (Martin and Thomas, 1990; Charmasson et al., 1998; Charmasson, 2003). However, Marcoule is being decommissioned since 1997 and no study was carried out to follow the decrease of artificial radionuclides in sediments off the Rhone mouth.

Due to their high affinity for particles (IAEA, 2004), the long-lived anthropogenic plutonium isotopes (^{238}Pu $T_{1/2}$: 87.8 y; ^{239}Pu $T_{1/2}$: 24 110 y; ^{240}Pu $T_{1/2}$: 6569 y), are not only good indicators of radioactive contamination but also useful tracers of particle behaviour within the aquatic environment (Baxter et al., 1995). In the Rhone River, Eyrolle and Charmasson (2004) have estimated that at least 85% of Pu is associated with the particulate matter. In addition, the use of $^{238}Pu/^{239,240}Pu$ activity ratios (AR) gives information on the source of Pu bound to particles (Thomas, 1997). In the Rhone valley, the two main sources of plutonium are characterized by different $^{238}Pu/^{239,240}Pu$ activity ratios. Today, atmospheric inputs demonstrate an AR in the range of 0.03–0.05 (Hardy et al., 1973; León Vintró et al., 1999; Gascó et al., 2002; Lee et al., 2003; MacKenzie et al., 2006), while Marcoule releases are characterised by a theoretically constant AR of 0.30 (characteristic value for reprocessing