PLUTONIUM AND AMERICIUM IN THE RHÔNE SEDIMENTS

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INTRODUCTION

^{238,239,240}Pu and ^{241}Am are measured in sediments from river ecosystems. These artificial radioisotopes are related to military and civilian activities. Small concentrations require an original radiochemical process, followed by alpha spectrometry. 104 analysis on sediment from the Rhône have been taken since 1989.

THE ORIGIN OF TRANSURANIC ELEMENTS IN THE RHÔNE

The transuranic elements present in sediment from the Rhône originate principally from the atmospheric nuclear tests carried out between 1945 and 1975, fallout from which spread some 1.2 x 10^{16} Bq of ^{239,240}Pu and 2.9 x 10^{13} Bq of ^{238}Pu into the atmosphere, 80% of which was in the Northern Hemisphere (1). Various accidents have also released transuranic elements into the environment. Such was the case with the SNAP-9A satellite, which burned up in April 1964 and released 5.1 x 10^{14} Bq of ^{238}Pu, 40% of that in the Northern Hemisphere (2). Fallout from the Chernobyl accident containing α emitters was negligible in France. Irradiated-fuel reprocessing plants (La Hague and Marcoule) are authorized to release α emitters in their liquid effluent. The Marcoule plant is authorized to release 150 GBq per year into the Rhône. In 1991, the Marcoule facility renovated its liquid effluent treatment station. The activities released diminished considerably, as is shown in the following table:

Years	$^{239+240}$Pu (MBq)	^{241}Am + ^{238}Pu (MBq)
1990	2.11 x 10^4	2.07 x 10^4
1991	1.26 x 10^4	1.36 x 10^4
1992	0.33 x 10^4	0.45 x 10^4
1993	9.54 x 10^2	2.18 x 10^3

Nuclear power generation stations are not authorized to release α emitters in their liquid effluent.

PLUTONIUM AND AMERICIUM DETERMINATION PROTOCOLS

The sediment sample is autoclaved at 110°C, then sifted at 2 mm. A 200-g sample is calcined at 550°C in order to destroy any organic material present. After cooling, the sample receives 20 mBq of ^{242}Pu and ^{243}Am respectively. These isotopes, not present in the sample, make it possible to determine the yield of the various radiochemical operations after the final counting by α spectrometry.

The sediment then undergoes a series of oxidizing acid attacks in order to render the transuranic elements soluble. The solution thus obtained is made up essentially of the stable major elements (Ca, K, Na, Fe) comprising the matrix and the radioisotopes of the artificial elements (Pu, Am, Cm) as ultra-traces. The problem of the analysis is to separate and purify the plutonium and americium using a protocol allowing progressive elimination of the totality of the stable major elements and all of the natural α-emitting radioisotopes. The proportioning protocol uses a radiochemical process whose successive stages make use of coprecipitation, ion-exchange chromatography, and extraction chromatography techniques. Through a first series of coprecipitation of plutonium and americium with calcium oxalate at pH=1.5, the alkalines are eliminated while the iron is maintained in solution through formation of complexes with the oxalate ion. The isolated and dried calcium oxalate precipitate is transformed into calcium carbonate through calcination. The latter is dissolved in a hydrochloric acid solution, diluted with distilled water, and brought to pH=8.00 in order to obtain precipitation of the last traces of iron in the form of ferric hydroxide. Quantitative coprecipitation of the plutonium with a few milligrams of iron makes it possible to eliminate almost all of the alkaline earths. The small volume of solution obtained after dissolving the precipitate in an 8M nitric medium is injected onto an AGIX8 anionic resin, which allows separation of the plutonium from the elements Th, U, Am, and Cm and the rare earths and other metals not eliminated during the coprecipitations. Separation of the americium from the elements Fe, Cu, Ni, and the rare earths requires two further extractions. The first consists of an extraction chromatography done on TRU-spec resin, and the second uses ion-exchange chromatography on AGIX4 resin.

Sequential separation of the elements Pu and Am is done through two electrodepositions, each carried out on a previously electropolished stainless-steel disk. Each electrolytic deposit is then counted in a chamber maintained under vacuum and equipped with an inserted passivated junction silicium detector having a useful surface equivalent to 280 mm^2. Duration of the count can be up to one week. The detection limit made possible both by equipment performance (a detection yield of between 0.25 and 0.30 - an electronic background noise level of < 2 cps/24 hours) and by that of the radiochemistry used (weight of the sample being processed, tracer purity, separation performance, peak resolution) varies between 1 and 10 mBq/kg for each radioisotope proportioned.

Pu AND Am CONCENTRATIONS IN SEDIMENTS

Distribution of transuranic elements in sediment is not uniform throughout the length of the Rhône. The river may be separated into three zones according to the potential source terms:

Sediments sampled upstream from Creys-Malville.

This part of the Rhône is not subject to the influence of any nuclear installation. The concentrations observed are, respectively: 0.017 to 0.086 Bq.kg $^{-1}$ dry for ^{239,240}Pu and < 0.001 to 0.0044 Bq.kg $^{-1}$ dry for ^{238}Pu. ^{241}Am was not measured.

The ^{238}Pu/ ^{239,240}Pu isotopic ratio of 0.043 ± 0.038 (3 significant values) is characteristic of fallout from atmospheric tests (values between 0.02 and 0.08) (3).

Sediments sampled from Creys-Malville to a point upstream from the Marcoule fuel reprocessing plant.

The sediments show concentrations of 0.030 to 0.201 Bq.kg $^{-1}$ dry for ^{239,240}Pu, from <0.001 to 0.017 Bq.kg $^{-1}$ dry for ^{238}Pu, and from <0.005 to 0.076 Bq.kg $^{-1}$ dry for ^{241}Am.

The ^{238}Pu/^{239,240} Pu isotopic ratio is 0.046 ± 0.010 (15 significant values). As in the case of the previous zone, it shows that the plutonium measured is from atmospheric testing fallout. Higher plutonium concentrations were measured downstream from the Creys-Malville plant than upstream in Rhône sediments collected in 1991. But all the isotopic ratios are characteristic of atmospheric fallout. The differences observed are due only to granulometric differences (4). In fact, plutonium radioisotopes have a great affinity for finer particles.

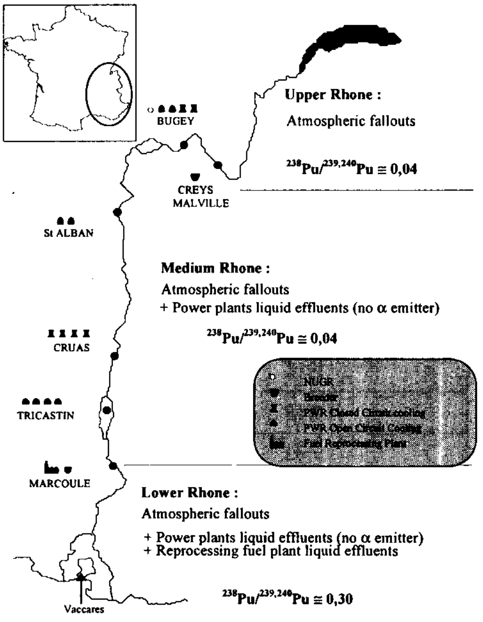

Figure 1. Source terms and Pu ratio in the Rhone river sediments

If the plutonium isotopic ratio departs from this value, this can be a sign that the plutonium is from another source. Thus in the Loire, Martin and Thomas (3) found a ratio of 0.15 to 0.40 downstream from the C.N.P.E. facility at St-Laurent-des-Eaux following an incident in 1982 that led to the melting of two fuel elements in reactor 2. The ratio was less than 0.04 in 1994 (5). Similarly, downstream from the C.N.P.E facility at Bugey, sediment collected in July 1989 had an isotopic ratio of 1.66 (6). This could be explained by an incident at the site's graphite-gas reactor. A second sediment sample collected in 1992 showed a ratio of 0.05, which is consistent with the characteristic value for atmospheric test fallout.

Sediments sampled downstream from the Marcoule fuel reprocessing plant.

In the sediments from this area, concentrations vary between 0.2 and 7.8 Bq.kg^{-1} dry for ^{239,240}Pu, between 0.17 and 2.1 Bq.kg^{-1} dry for ^{238}Pu, and between 0.4 and 5.3 Bq.kg^{-1} dry for ^{241}Am. The plutonium isotopic ratio is 0.280 ± 0.023 (56 significant values), thus greater than that found farther upstream (7). It is characteristic of the plant's liquid effluent (8). The startup of the liquid effluent treatment station in 1991 caused a decrease in the concentrations observed in sediments collected between Marcoule and the Camargue:

Dates	^{239,240}Pu (Bq.kg^{-1} dry)	^{238}Pu (Bq.kg^{-1} dry)	^{241}Am (Bq.kg^{-1} dry)
September 1990	0.77 to 5.49	0.54 to 1.82	< 0.48 to 4.46
September 1991	0.27 to 4.39	< 0.1 to 1.42	< 0.26 to 4.12
September 1992	0.26 to 2.58	0.06 to 0.72	0.13 to 4.14
1993 *	0.07 to 2.59	0.07 to 0.60	0.04 to 2.18

A sediment sample was taken in Lake Vaccarès (in the Camargue) in September 1992. The measurements resulted in the following values: 0.058 ± 0.006 Bq.kg^{-1} dry for ^{241}Am, 0.107 ± 0.010 Bq.kg^{-1} dry for ^{239,240}Pu, and 0.0038 ± 0.0010 Bq.kg^{-1} dry for ^{238}Pu (9). The ^{238}Pu/ ^{239,240}Pu isotopic ratio of 0.035 indicates that the point on the lake sampled is not influenced by the liquid effluent from the Marcoule plant.

CONCLUSION

Transuranic elements measured in sediments from the Rhône are in weak concentrations. In the entire part of the river not affected by effluent from Marcoule, the ^{238}Pu/^{239,240}Pu isotopic ratio is in the area of 0.04, which is characteristic of fallout from atmospheric testing.

Downstream of the Marcoule plant, the ratio is 0.3, which is characteristic of the liquid effluent from the irradiated fuel reprocessing plant. Since 1991, concentrations of transuranics in the sediments have decreased as a result of the startup of the liquid effluent treatment station.

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* The level of the Rhône rose greatly in October 1993 and January 1994, flooding a small part of the Camargue region. In the flooded areas, plutonium radioisotopes from sediments from the Rhône were found in the soil of the rice fields. Their isotopic ratio was 0.2, characteristic of Marcoule. Agricultural work reduced the plutonium concentrations by a factor of 3 (0.03 Bq.kg^{-1} for ^{238}Pu and 0.19 Bq.kg^{-1} for ^{239,240}Pu). No significant activity could be measured in the rice.