Plutonium fluxes from the Rhône River to the Mediterranean Sea

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Abstract. Plutonium isotopes carried by the Rhône River mainly come from the catchment basin weathering affected by atmospheric fall-out and from the liquid effluent discharges from the fuel reprocessing plant located at Marcoule. Nowadays, while ^{238}Pu industrial inputs are still at least ten times higher than terrestrial inputs, $^{239+240}$Pu inputs from industrial and terrestrial source terms are of similar importance, i.e. 1 GBq y^{-1} each. An empirical relation between the $^{239+240}$ Pu activities in the river water downstream Marcoule and the Rhône flow rate is obtained from data collected over the 1987-1998 period. This relation underlines that the river bed sediments act as a delayed source of plutonium depending on the hydrological conditions of the river. During flood events this delayed source may contribute up to 40% of the plutonium activity at the lower course of the Rhône River. Furthermore over the 1987-1998 period the accumulated $^{239+240}$Pu and ^{238}Pu activities within the whole sedimentary compartment of the river or deposited on the terrestrial surroundings during flood events are 15 and 4 GBq respectively, thus representing about 10% of inputs. At present, this stock that can potentially be re-suspended, is an important $^{239+240}$Pu source term at the scale of the Rhône River catchment basin.

1. INTRODUCTION

Plutonium nuclides reach the Rhône River system through the weathering of surface soils contaminated by the global fallout from atmospheric nuclear tests, and through the liquid effluent discharges from the Marcoule nuclear fuel reprocessing plant.

The Rhône River catchment basin is 98845 km² large, and has a 52 $10^9 m^3$ annual liquid flow carrying from 2 to 20 10^6 tons of solid matters towards the Mediterranean Sea [1-5]. The Rhône River is 812 km long, among which 200 are in Switzerland. At its lower course and just upstream from the city of Arles it divides into two branches, the Grand Rhône and the Petit Rhône, which flow across a large Delta, the Camargue. The former branch drains 90% of the water discharge. The Rhône River is the most important river flowing to the Occidental Mediterranean Sea.

The whole set of radionuclides introduced into the Rhône River catchment basin will be partly exported to the Mediterranean Sea. Nevertheless the radionuclide transportation phenomena and residence time as well as fluxes and exportation kinetics within the river are only partially known [6]. $^{239+240}$Pu and ^{238}Pu activities in particulate phase were measured in the Grand Rhône at Arles between 1987 and 1998. The very last part of the river mixes all the radionuclides inputs received by the catchment basin. The analysis of these data allows then to qualify and to quantify the radionuclides exportation fluxes from the Rhône River to the Mediterranean Sea giving boundary conditions and parameters to their transfer models.

2. PU SAMPLING AND ANALYSES

From 1997 to 1998, water samplings were performed on the Grand Rhône, at the level of Arles (Figure 1). 100 to 250 l of non filtered and filtered (<450 nm) samples were analysed for ^{238}Pu and $^{239+240}$Pu content after co-precipitation with $Fe(OH)_3$ as described in [7] and using radiochemical procedures by solvent extraction and/or cation exchange. Upon radiochemical separation, plutonium

alpha sources were prepared by electrolytic plating onto stainless-steel discs. Two distinct tracers were required to quantify the recovery of plutonium isotopes extractions first by co-precipitation then by the radiochemical steps. The determination of Pu isotopes activities was achieved as described in [8].
The plutonium activities in the particulate phase, calculated by subtracting the activity measured in filtered samples from the activity found in unfiltered samples, are reported in table 1. The speciation of plutonium between the dissolved and particulate phases is discussed elsewhere [9, 10]. The SPM concentrations were measured by standard gravimetry. The Rhône River National Company recorded the Rhône River flow rates in Arles. Complementary data covering the 1987-1994 period were taken from the literature [11] (table 1).

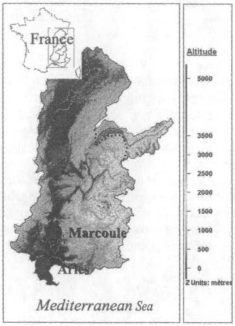

Figure 1: The Rhône river catchment basin.

Table 1: $^{239+240}$Pu and ^{238}Pu activities in the Rhône River, SPM at Arles between 1987 and 1998, flow rates at Arles and ^{238}Pu/ $^{239+240}$ Pu Activity Ratio (AR).

Sampling date	Flow rate ($m^3 s^{-1}$)	SPM ($mg l^{-1}$)	^{238}Pu ($mBq g^{-1}$)	$^{239+240}$Pu ($mBq g^{-1}$)	RA
02/07/1987 [11]	2989	11,7	2,68	9,42	0,29
03/07/1987 [11]	3005	43,0	2,56	9,87	0,26
04/07/1987 [11]	2636	124,0	1,22	4,22	0,29
05/07/1987[11]	2352	715,0	0,18	0,78	0,23
10/03/1991 [11]	4554	1777,0	0,07	0,36	0,19
12/03/1991 [11]	2985	112,0	0,34	1,4	0,24
18/03/1991 [11]	1718	28,6	0,46	2,19	0,21
11/05/1994 [11]	1925	38,1	0,06	0,18	0,33
07/06/1994 [11]	1873	37,2	0,04	0,23	0,17
09/08/1994 [11]	1016	12,6	0,62	1,67	0,37
02/11/1994 [11]	1700	17,0	0,75	2,07	0,36
06/11/1994 [11]	8865	3600	0,03	0,17	0,18
13/05/1997 [9]	1800	31,2	0,57	1,40	0,41
14/09/1997 [9]	1230	16,9	0,65	1,84	0,35
18/11/1998	1872	35,9	0,12	0,41	0,29
19/11/1998	1846	39,5	0,11	0,33	0,33
23/11/1998	1203	15,0	0,15	0,48	0,31

3. RESULTS & DISCUSSION

Before 1992, the $^{239+240}Pu$ and ^{238}Pu source term within the Rhône River was mainly liquid effluents from the Marcoule complex as $^{239+240}Pu$ and ^{238}Pu annual inputs of industrial origin were 50 and 500 times higher than terrigenous ones, respectively (Figure 2). At present, while the major ^{238}Pu source term is still linked to the liquid effluents from the Marcoule facility, $^{239+240}Pu$ annual inputs related to the Marcoule installation and to the weathering of the catchment basin are of the same order of magnitude, i.e. of about 1 GBq y^{-1}. In 1990 a change in the liquid effluent treatment process within the Marcoule reprocessing plant led to reduce on a 3-year period by more than a factor 10 the ^{238}Pu and $^{239+240}Pu$ annual releases. Furthermore, in December 1997, the Marcoule fuel reprocessing plant was shut down and is now being dismantled. Nevertheless, the end of reprocessing operations does not have reduced the plutonium isotopes discharged activities yet as washing effluents are produced and released.

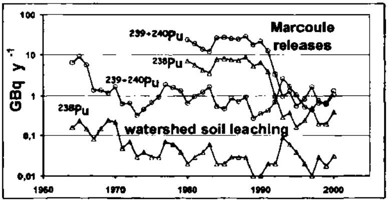

Figure 2: Historical account of ^{238}Pu and $^{239+240}Pu$ inputs by industrial [12] and terrigenous [13,14] source terms in the Rhône River, given in GBq y^{-1}. For industrial releases, ^{238}Pu activities are calculated from $^{239+240}Pu$ activities and a theoretical AR of 0.3.

$^{239+240}Pu$ activities measured in the particulate phase of the Rhône River fresh waters at Arles between 1987 and 1998 are reported on the Figure 3a and 3b. In an aquatic continental environment, plutonium shows a great affinity for particles and especially for particulate organic compounds and iron hydroxides and in the Rhône River it is mainly transferred in the particulate phase [9, 13]. From 1987 to 1998, activities observed in the particulate phase were reduced by a factor 50 i.e. a factor similar to the one found for the releases from the Marcoule complex over the same period of time, excepted for the Rhône River flood periods.

The Rhône river floods induce an increase in $^{239+240}Pu$ activities in the River fresh waters. As a matter of fact during the 1994 large flood episodes, $^{239+240}Pu$ activities in particulate phase were multiplied by a factor 20 compared to the activities observed the previous days when the river flow conditions were almost those of the mean annual flow, 1700 $m^3\ s^{-1}$. Thus during the 1994 great floods, $^{239+240}Pu$ concentrations reached the same levels that could be observed at the end of the eighties, before the decrease in Marcoule discharges.

In order to underline the evolution of $^{239+240}Pu$ activities into the Rhône River waters with regards to the hydraulic flow, the $^{239+240}Pu$ activities measured from 1987 to 1998 have been normalised with respect to the annual discharges from the Marcoule plant to take into account the source term temporal diminution. The results evince an exponential relationship between the $^{239+240}Pu$ activity in particulate phase at Arles and the river hydraulic flow.

For a given year, the $^{239+240}Pu$ activity in particulate phase (C_y, in mBq m^{-3}) at Arles, can be represented by the mathematical relation [1].

$$C_y = 0{,}006\, M_y\, e^{0{,}0004\, Q} \qquad (n=17,\ r^2=0{,}61) \qquad \{1\}$$

With M_y, $^{239+240}Pu$ annual releases from Marcoule given in MBq y^{-1} and Q, the River hydraulic flow given in $m^3\ s^{-1}$.

Relation {1} could also allow understanding the impact of a plutonium accidental liquid release on the radiological quality of the river. The extrapolation to other artificial radionuclides is yet limited since the transfer of an element through the particulate phase depends on its own affinity with the suspended solid matters.

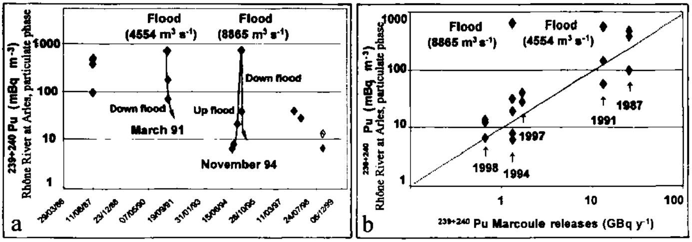

Figure 3: **a**- $^{239+240}Pu$ activities in particulate phase in the Rhône river at Arles between 1987 and 1998 (in mBq.m^{-3}). **b**- $^{239+240}Pu$ activities in particulate phase in the Rhône River at Arles between 1987 and 1998 (in mBq m^{-3}) normalised to $^{239+240}Pu$ (in GBq y^{-1}) quantities released by the Marcoule reprocessing plant during the year of sampling. 1987: dm = 2746 ± 310 $m^3\ s^{-1}$; 1991: dm = 2350 ± 900 $m^3\ s^{-1}$; 1994: dm = 1630 ± 420 $m^3\ s^{-1}$; 1997: dm = 1520 ± 400 $m^3\ s^{-1}$; 1998: dm = 1640 ± 380 $m^3\ s^{-1}$; with dm = average flow associated to data (except flood periods).

The plutonium activity increase under flood conditions is linked to a solid matters input originating either from the weathering of the catchment basin or from the re-suspension of some of the river sediments.

^{238}Pu and $^{239+240}Pu$ atmospheric fall-out have led to depositions characterized by $^{238}Pu/^{239+240}Pu$ Activity Ratio (AR) bordering 0.03. Constant theoretical AR of 0.3 characterizes the liquid effluents discharged by the Marcoule installation. AR evolution when in the particulate phase measured in relation to Q in the Rhône River waters at Arles, allows estimating the contribution of these two sources. The dilution of the Marcoule releases with the waters from the Rhône River catchment basin leads to obtain the theoretical dilution curve (Figure 4). AR varies from 0.37± 0,12 to 0,17 ± 0,05 for flows varying respectively from 1000 to 9000 $m^3\ s^{-1}$ and in a general way is greater than the theoretical activity ratios. These results demonstrate the action of a delayed secondary source labelled by the releases from Marcoule and dependent upon the River hydraulic flow. This delayed source is to be put in relation with the re-suspension of sedimentary stocks accumulated within the Rhône River, downstream the Marcoule complex in quiet hydrodynamic areas and/or periods.

The dispersion of the dots (Figure 4) is partly linked to the origin of data. As a matter of fact the data have been acquired on a relatively long time scale during which activity of the sedimentary stocks were not constant since the liquid effluents from the Marcoule complex have changed with time.

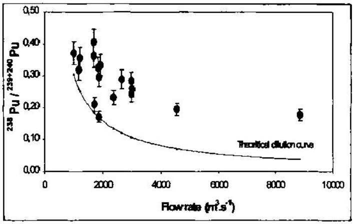

Figure 4: $^{238}Pu/^{239+240}Pu$ activity ratio measured in the Rhône river at Arles in terms of the Rhône River hydraulic flow. Equation of the theoretical dilution curve: $A = 232\ Q^{-0.96}$.

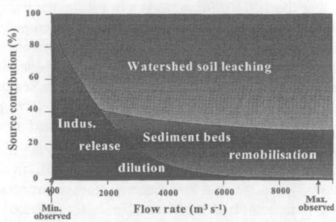

Figure 5: Schematic representation of Plutonium isotopes inputs into the Rhône river downstream the Marcoule releases, in terms of the hydraulic flow.

These observations allow schematising the contribution of the various source terms involved in the Rhône River catchment basin in relation to the hydraulic flow of the river (Figure 5). During the River flood periods, the major source terms are the catchment basin weathering and the re-suspension of the River sedimentary stocks, the latter representing up to 40% of the exported radioactivity.

In order to estimate both the plutonium isotopes fluxes and exportation status performed by the Rhône River, the empirical relation [1] was applied for the years 1987 to 1998. The results obtained underline a 73% exportation representing 82.5 GBq of $^{239+240}Pu$ in the particulate phase. If we consider that 20% of the plutonium are present in dissolved phase then the overall quantity (dissolved+particular) of $^{239+240}Pu$ transferred at Arles can be assumed to be 99 GBq. Furthermore the Petit Rhône River located upstream Arles derives approximately 10% of the fluxes. Thus on the studied time scale, the overall quantity of $^{239+240}Pu$ exported towards the sea by the Rhône River system is about 109 GBq. The calculated quantity for ^{238}Pu is 30 GBq.

From 1987 to 1998, the Marcoule $^{239+240}Pu$ and ^{238}Pu inputs represent 113 and 34 GBq, respectively. During the same period, the catchment basin contribution in $^{239+240}Pu$ and ^{238}Pu is estimated to a 10.5 and 0.3 GBq, respectively. Thus the $^{239+240}Pu$ and ^{238}Pu source term made up of both the liquid effluents from the Marcoule complex and the catchment basin weathering is 123.5 and 34.3 GBq, respectively.

The quantities accumulated from 1987 to 1998 in the global Rhône River sedimentary compartment or deposited on the ground during flood periods would then reach about 15 GBq for $^{239+240}Pu$ and 4 GBq for ^{238}Pu. These estimated stocks represent more than 10% of the global inputs on the studied period. Sedimentary stocks depend on the flood events chronicle and then on the time scale.

These sedimentary stocks represent around 10 times the annual quantities of plutonium isotopes discharged now by the Marcoule plant.

4. CONCLUSION

$^{239+240}Pu$ and ^{238}Pu carried by the Rhône River originate in both the weathering of the catchment basin affected by atmospheric fall-out and the controlled liquid effluents discharged by the Marcoule complex set up in the Rhône River valley. Before 1992 industrial wastes represented the major $^{239+240}Pu$ source term in the Rhône River. At present, annual $^{239+240}Pu$ inputs related to liquid effluents from the Marcoule complex and from the erosion weathering of the catchment basin are of the same order of magnitude (1 GBq y^{-1}). As to ^{238}Pu, its main source term is still linked to the Marcoule fuel reprocessing plant discharges. However the difference between industrial and terrigenous inputs has been reduced by a factor 50.

Over the 1987-1998 periods, our results have shown that the decrease in $^{239+240}$Pu and ^{238}Pu activities at the lower course of the Rhône River has been proportional to the decrease in Marcoule liquid releases, apart from flood conditions. Flood events generate an increase in plutonium activities partly due to the remobilisation of sediment beds. This delayed secondary source of plutonium may contribute up to 40% in the plutonium exported to the Mediterranean Sea during floods events.

Mass balances estimated over the 1987-1998 period show that the accumulated activities in the overall Rhône River sedimentary compartment or deposited on the ground during floods are about 15 GBq for $^{239+240}$Pu and 4 GBq for ^{238}Pu. At the moment, this stock would represent the main $^{239+240}$Pu source term in the Rhône River catchment basin, in so far as terrigenous and industrial inputs are of about 1 GBq.y^{-1} each. Such a sedimentary storage process probably applies to all the radionuclides or to any other contaminant that shows an affinity for particles carried by the River.

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