MAN-MADE PLUTONIUM IN FRESHWATER AND MARINE ENVIRONMENTS

S. Krishnaswami

(*Physical Research Laboratory, Ahmedabad* 380009)

Abstract

Significant concentrations of plutonium isotopes are found in lake and coastal marine sediments accumulating at rates of 1–5 mm/yr. The activity levels of $^{239, 240}$Pu range between 0·7–3·3 dpm/g for post 1960 sediments. The measured and the calculated integrated activities of ^{239}Pu in the lake sediments are in agreement. This suggests that plutonium is chemically reactive in freshwater environments and it is removed to sediments from the water column shortly after its injection.

A delay of about three years has been observed between the peak of plutonium fallout and its incorporation in the varved sediment from Santa Barbara basin. Based on this observation the mean size of particles transporting plutonium to the basin sediments is estimated to be about three microns.

The usefulness of plutonium isotopes as a tracer nuclide for estimating sedimentation rates for the last two decades have been evaluated.

1. Introduction

The world-wide dissemination of man-made radionuclides in the atmosphere by nuclear detonations has two important implications (i) use of these isotopes as neclear tracers in geophysical studies such as sedimentation rates, water movements, particle settling rates, etc., and (ii) hazardous radiations of these pollutants which could produce adverse effects on ecosystems. The nature of distribution of the potentially hazardous man-made nuclides, *e.g.*, ^{90}Sr, ^{55}Fe have been studied in detail (Jennings, 1968; Volchok *et al.*, 1971). However, the isotopes of plutonium, $^{238, 239, 240}$Pu, have until recently received only very little attention compared to ^{90}Sr, ^{55}Fe and ^{14}C. Plutonium is toxic because of its high specific alpha activity and long biological half life. On the basis of the earlier studies of its distribution in sea water (Pillai *et al.*, 1963), it was believed that its chemical behaviour is similar to Sr or Cs in the hydrosphere, *i.e.*, it is relatively chemically passive. However the results

of Miyake and Sugimura (1968) and Bowen *et al.* (1971) who observed a reduced $^{239}Pu : {}^{90}Sr$ ratio in surface ocean waters compared to atmospheric aerosol values suggested that ^{239}Pu is chemically more reactive than ^{90}Sr in the marine environment. Additionally the recent discovery by Noshkin and Bowen (1973) of plutonium isotopes in coastal and open ocean sediments confirm that the plutonium isotopes are more reactive and are removed from the water column faster than the ' typical soluble ' fallout nuclides by particulate materials. To understand the role of particulate materials and sediments in the removal of plutonium from the water column we have studied in detail the depth distribution of plutonium isotopes in lake and in varved coastal marine sediments. The results have proved to be significant in understanding both the chemical behaviour of plutonium in aquatic reservoirs and its importance as a tracer nuclide for studying sedimentation.

2. MATERIALS AND METHODS

The relevant details of cores studied are given in Table I. The lake cores were collected during the years 1969–70 and were 9 cm in diameter. The 20 cm box core from Santa Barbara Basin was collected during September

TABLE I

Relevant details of cores analysed for Pu isotopes

Core (Location)	Water depth (m)	*in situ** density (g/cc)	Nature of sediment	Mean annual rainfall (cm)
EM-5 (Lake Pavin, France)	92	0·1	Laminated siliceous clay	170
MONT-1 (Lake Montcynere, France)	17	0·14	Diatomaceous clay containing organic matter	170
LGV-1 (Lake Lagodivelle, France)	43	0·18	Siliceous clay	170
TAC-2 (Lake Tansa, Bombay) Dredge sample	8–10	0·3	Brownish black clay	250
SBB-262-4 (Santa Barbara Basin; 34° 12·5′ N; 120° 00′ W)	592	0·18	Varved silty clay with 10% $CaCO_3$	42

* Average of the top 5–10 cm of the core.

1971. All the cores used were previously radiometrically dated using ^{210}Pb and ^{55}Fe methods (Krishnaswami *et al.*, 1973).

The procedure for the extraction and purification of Pu isotopes from sediments is similar to that of Wong (1971). Briefly, 2–5 g dry sediment samples were leached twice with boiling $12N$ nitric acid in presence of ^{236}Pu tracer and 2–5 ml of hydrogen perioxide. The leachates were combined and the Pu isotopes were purified using anion exchange techniques (Wong, 1971). The purified Pu isotopes were electroplated on platinum planchets from $2N$ NH_4Cl medium at pH $= 2$ (Mitchell, 1960).

The activities of Pu isotopes were assayed using a 400 mm^2 area nuclear diode solid state detector coupled to a 128 channel pulse height analyser. The detector had a background of less than a count per day in the ^{239}Pu region (5·0–5·2 MeV). A typical Pu spectrum is shown in Fig. 1.
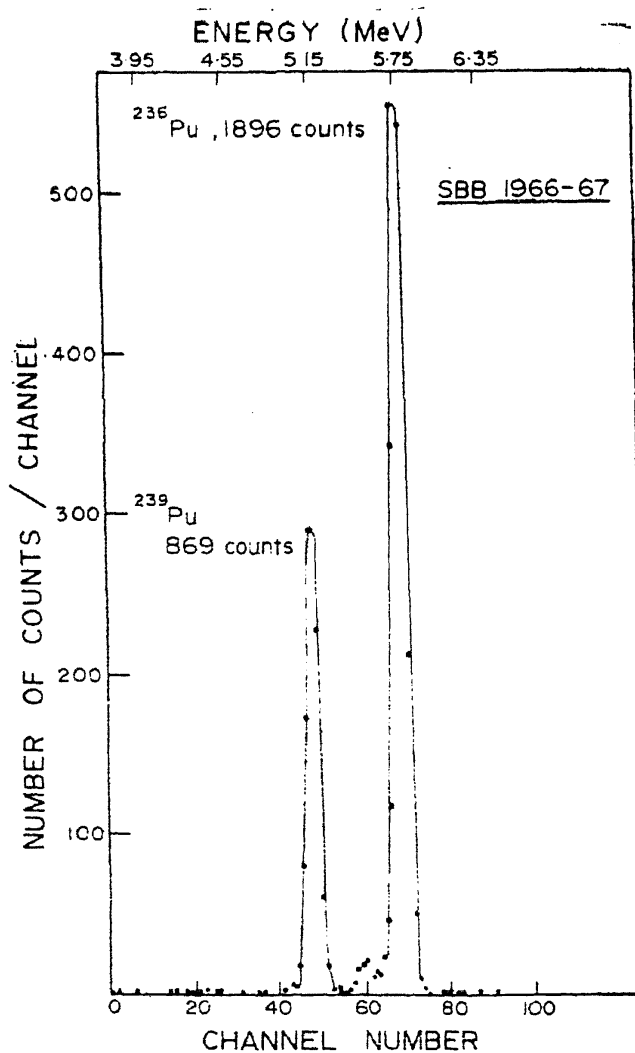

FIG. 1. Alpha spectrum of plutonium isotopes extracted from Santa Barbara sediment, The sample was counted approximately for a day,

3. RESULTS AND DISCUSSION

The measured concentration of [239]Pu and [240]Pu in the lake sediments and the core SBB 262-4 are given in Tables II and III and Fig. 2. The isotopes [239]Pu and [240]Pu are reported as [239]Pu, since they cannot be resolved by alpha spectrometry. The uncertainties in the calibration of detector efficiency and tracer concentrations are expected to be less than 10%.

TABLE II

[239]Pu concentration of lake sediments

Core (Lake)	Sampling depth (cm)	[239]Pu* (dpm/g)	Core (Lake)	Sampling depth (cm)	[239]Pu* (dpm/g)
EM-5 (Pavin)	0–1·6	3·3 ±0·2	MONT-1 (Montcynere)	0–1	2· 1±0·1
	1·6–3·4	1· 6±0·1		1–2	2· 7±0·1
	3·4–6·8	0·06±0·02		2–3	1· 5±0·09
				4–5	0·24±0·05
LGV-1 (Lagovivelle)	0–4	1· 0±0·04	TAC-2 (Tansa)	Dredge† (0–10)	0·19±0·04
	4–5	0·12±0·02			

* Errors quoted are one standard deviation due to counting statistics.

† Assumed value.

The concentration level of [239]Pu in the top sections of cores range between 0·7–3·3 dpm/g, one to two orders of magnitude higher than those previously reported in shallow water and open ocean sediments (Wong *et al.*, 1970; Wong, 1971; Noshkin and Bowen, 1973). The observed high concentrations of [239]Pu in the samples studied can be attributed to a cumulative effect of (i) shallow sampling locations which leads to a faster removal of plutonium to the sediments, unlike in open ocean areas where most of [239]pu injected is still in the water column above the sediments due to larger water depths of the basin, (ii) faster deposition of sediments, 1–5 mm/yr (Krishnaswami *et al.*, 1971, 1973). This allows sampling the recent past, *i.e.*, last 1–2 decades, without dilution from materials deposited prior to the nuclear weapon testing era, a problem which would be encountered while working with deep sea sediments where the rate of sedimentation is generally less than 1 cm/10^3 yr.

The observed values for the integrated deposition of [239]Pu (dpm/cm^2) in the sediments are given in Table IV along with the expected overhead fall-

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TABLE III

239Pu concentrations in Santa Barbara basin core SBB 262 4

Year of deposition*	In situ depth interval (cm)	239Pu† (dpm/g)	Year of deposition*	In situ depth interval (cm)	239Pu† (dpm/g)
1970–71 Sept.	0–1·6	0·67 ⏐ 0·07	1962 63	5·5–6·4	0·55 ⏐ 0·06
1968–69	1·6–3·0	0·86 ⏐ 0·04	1960 61	6·4–7·1	0·30 ⏐ 0·03
1966–67	3·0–4·4	1·05 ⏐ 0·04	1958 59	7·1–7·8	0·23 ⏐ 0·03
1964–65	4·4–5·5	0·88 ⏐ 0·06	1936–37	13·8 14·3	0·06

* From varve data (Krishnaswami *et al.*, 1973).

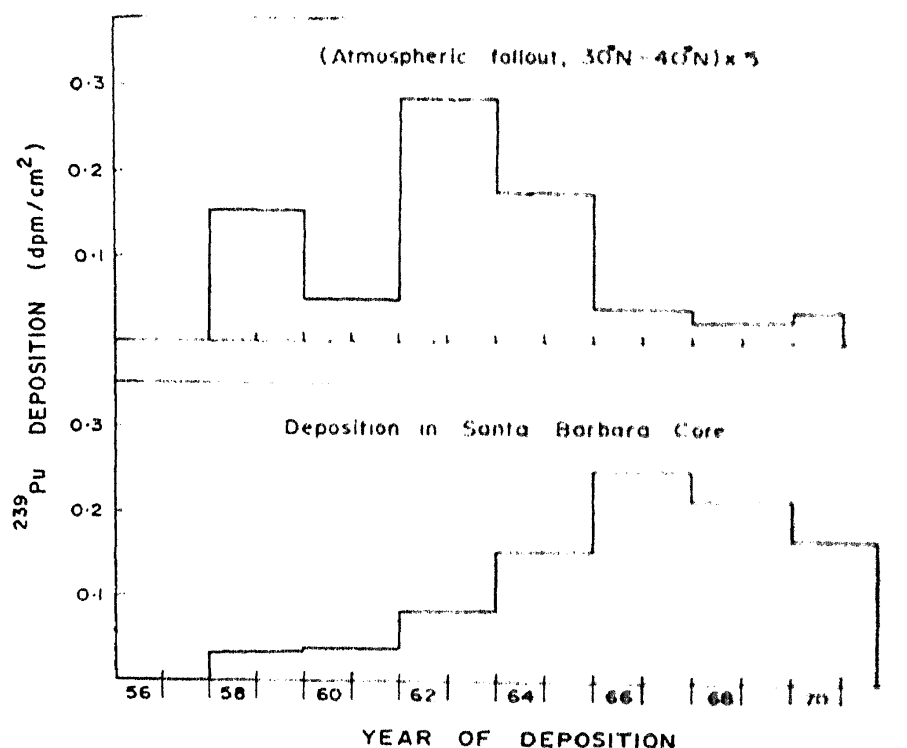† Errors quoted are one standard deviation due to counting statistics.

FIG. 2. Pattern of fallout of plutonium isotopes for the latitudinal belt 30 40 N and the observed in Santa Barbara sediment. The atmospheric fallout pattern is estimated from 90Sr data assuming 239Pu/90Sr = 0·028. The delay of about three years between the peaks in fallout evident.

out *via* precipitation.   The overhead fallout of [239]Pu for the years 1954–70 has
been estimated from the reported [239]Pu inventory based on soil data   (Hardy
et al., 1972 ; Noshkin and Bowen, 1973). The delivery to the basin site was
estimated by multiplying the mean inventory for the latitudinal band (from
Noshkin and Bowen, 1973) by the ratio of the local to the mean rainfall in
the belt.   Thus the expected delivery over the French lakes is about two fold
higher than the mean for the latitudinal belt since the rainfall over the lakes
is about a factor of two more (Table I) compared to the mean rainfall in
the 40–50° N band.   The data in Table IV show that the expected fallout
via precipitation and the observed cumulative deposition of [239]Pu are in
agreement for the lake cores.   This agreement implies that in freshwater
environments [239]Pu gets removed to the sediments from the water column
in a short time after its injection.   The fast removal of plutonium could be
due to its adsorption on the suspended materials and their subsequent gravi-
tational settling.   This hypothesis is in agreement with the results of Mango
et al. (1970) who observed that considerable fraction of plutonium released
from the NFS processing plants gets adsorbed on suspended material and
settles rapidly.   Thus the residence time of [239]Pu in these water bodies must
be controlled mainly by the settling times of particulate matter present.   (It
must be mentioned here that there could be an additional input of [239]Pu
to the lakes *via* run-off from the catchment area.   The magnitude of this
contribution is difficult to estimate.   However, the agreement between the
expected and the observed fallout seems to indicate that the [239]Pu influx
via run-off is small.)

Table IV

Estimated sedimentation rates and integrated deposition of [239]Pu

Core	Depth of [239]Pu tail occurrence (cm)	Sedimentation rate (mm/yr) based on			Integrated [239]Pu deposition (dpm/cm²)	
		[239]Pu [a]	[55]Fe [b]	[210]Pb [b]	Observed	Expected
EM–5	3·4	2·1	2·0	1·3	0·8	1·0
MONT–1	5·0	3·1	1·5	1·5	1·0	1·0
LGV-1	5·0	3·1	..	0·7	0·74	1·0
SBB–262–4	7·8	4·6	6·0	3·6	0·95	0·18

(a) Calculated by assuming that the tail is due to the fallout in the year 1954.

b Data from Krishnaswami *et al.* (1971, 1973).

In the core SBB 262–4 the measured cumulative ^{239}Pu deposition is 0·95 dpm/cm^2 (Table IV). This is much in excess of the expected overhead fallout of 0·18 dpm/cm^2. (The expected delivery to the basin is about a factor of two lower compared to the mean in the latitudinal band since the rainfall over the basin is only half of that in the belt.) This situation is analogous to ^{55}Fe and ^{210}Pb (Krishnaswami *et al.*, 1973), the accumulation is 5–10 times more than the expected fallout for these nuclides. The measured excess deposition of ^{239}Pu could be due to (i) its transportation to the basin as adsorbed on particulate matter, (ii) preferential uptake of ^{239}Pu from the waters entering the basin by biogenic or inorganic particulates and their subsequent deposition to the sediments. Similar to ^{55}Fe and ^{210}Pb the origin of ^{239}Pu excess in the basin sediments is intriguing and warrants further investigation.

From the data in Table III and Fig. 2 it is seen that there is a delay of of about three years in the peak between atmospheric fallout of ^{239}Pu (in 1963) and its deposition in the SBB core (1966–67). The delay, if attributed to the settling time of particulate matter in the basin with which ^{239}Pu is associated, corresponds to a mean settling velocity of about 200 m/year for the " ^{239}Pu-labelled particles ". This in turn corresponds to a mean particle size of about 2·8 microns assuming Stokes law of settling to be valid in the present case.

Based on the depth distribution of ^{239}Pu in the cores their sedimentation rates for the last two decades have been estimated. The rates were calculated by correlating the lowest depth in the core where an unambiguous signal of ^{239}Pu was observed to the year 1954. The deduced sedimentation rates are given in Table IV along with the values obtained from ^{55}Fe and ^{210}Pb. The results show that the rates based on ^{55}Fe and ^{239}Pu are mutually consistent. However, the long term average accumulation rates obtained from ^{210}Pb data for the same cores are lower. This discrepancy could be due to compaction of sediments at lower depths resulting in lower sedimentation rates for long term averages.

The observed fast removal of plutonium isotopes from the water columns in both fresh and marine environments is beneficial towards minimising its radiation hazards. The results suggest that most of the plutonium injected in the freshwater basins would have been removed to the sediments. If similar processes are operative in the open ocean areas a " ^{239}Pu particulate front " would be expected around a water depth of 2000 m. This fast removal of plutonium isotopes from the water column decreases its hazards

n the euphotic zone of high organic productivity but increases its dose for he benthic organisms.

4. ACKNOWLEDGEMENTS

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