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Distribution of plutonium isotopes in sediments of Melanesian Basin, Central Pacific

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Abstract The anthropogenic plutonium isotopes are important geochemical tracers for environmental studies. The distributions and sources of the Pu isotopes in water column or sediments of the North Pacific have been intensively studied. However, knowledge on the distribution of Pu isotopes in sediments of the Central Pacific, when available, is limited. To study the composition of Pu isotopes in the ocean, thus to identify the sources of radioactive pollution, sediment core samples were collected in the Central Pacific by R/V Hakuho Maru in the KH-04-5 cruise. The activity concentrations of $^{239+240}$Pu and the ^{240}Pu/^{239}Pu atom ratio were determined using a sector-field inductively coupled mass spectrometry (SF-ICP-MS) combined with a high efficiency sample introduction system (APEX-Q). Possible sources and sedimentation behavior of Pu isotopes are discussed.

Keywords Plutonium · Global fallout · Close-in fallout · Sediments · $^{239+240}$Pu activity concentrations · ^{240}Pu/^{239}Pu atom ratios · Pu inventory · Melanesian Basin · Central Pacific

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Introduction

Plutonium, a man-made artificial radionuclide used or produced in the nuclear weapons, was distributed globally as a result of the atmospheric nuclear weapons tests. The tests during 1945–1951 produced mainly tropospheric fallout which deposited around the latitude band of the test sites. After that, U.S. (United States) and FSU (Former Soviet Union) tested their thermonuclear weapons in 1952 and 1953, respectively, which was the beginning of worldwide distribution of Plutonium. In the following 30 years, about 500 atmospheric nuclear weapons tests were carried out around the world [1], and it was estimated that between 3 and 6 tons of Pu isotopes have subsequently entered the environment [2]. Additionally, there have also been releases of Pu into the environment from nuclear reprocessing facilities, and from satellite and reactor accidents [3].

Pacific is the largest ocean in the world. Many studies have addressed to the distribution and marine environmental behavior of Pu isotopes in the Pacific due to the relatively high input of Pu, and the unique current systems in Pacific Ocean. In temperate regions and the equatorial parts of the Pacific Ocean, the major source of Pu caused by nuclear weapons tests was the Pacific Proving Grounds (PPG) at the Marshall Island from 1946 to 1958 (42.2 Mt fission yield). In contrast to the large scale tests that were conducted primarily in the atmosphere, the majority of the tests at these sites were conducted at or just above the earth's surface. Surface bursts conducted over coral islands or over shallow water produced highly localized input. Therefore, these surface-based tests will produce significant quantities of close-in or called tropospheric fallout, which is rapidly moved or deposited in the vicinities of the test sites. Subsequently, the contaminated particles deposited in lagoon, surrounding slopes and/or sediments will be

released and moved with water transport in solution form (partly in particles), forming new sink or sources for radionuclides contamination. The mean residence times for Enewetak and Bikini lagoon water vary from 30 to 140 days [4].

The distribution and sources of Pu isotopes in water columns or sediments of the North Pacific Ocean (especially in the Northwest Pacific), have been intensively studied because it serves as a powerful geochemical tracer to study fundamental issues in marine environment, such as the removal scavenging process in the water columns and the sediment mixing rates in the bottom of the ocean [5–11]. Most recently, Zheng and Yamada [12] and Okubo et al. [13] investigated the scavenging process of Pu in settling particles in the western Northwest Pacific. However, to the best of our knowledge, studies on the distribution of Pu isotopes in sediments of the central Pacific Ocean, when available, is limited, especially for $^{240}Pu/^{239}Pu$ atom ratio, which was of important value for distinguishing different Pu sources.

To study the composition of Pu isotopes in the ocean, thus to identify the sources of radioactive pollution, sediment core samples were collected from 2004 to 2005 in the Pacific Ocean. The concentration of $^{240+239}Pu$ and the atom ratio of $^{240}Pu/^{239}Pu$ were determined using a sector-field inductively coupled mass spectrometry (SF-ICP-MS) combined with a high efficiency sample introduction system (APEX-Q). Possible sources of Pu isotopes will be searched and discussed.

Materials and methods

Sediment core samples were collected in the Pacific Ocean by R/V Hakuho Maru in the KH-04-5 cruise. The sampling location (Fig. 1) and date were 0°39.72′S, 157°30.87′E, Melanesian Basin, and December 6, 2004, respectively. The water depth in the sampling site (namely SX-02) was 2,080 m and the sediment core length was 27 cm, with the calcareous ooze as the main character of the sediments.

For the analysis of Pu isotopes, the dried and weighed sediments (about 2.5 g) were spiked with yield monitor of ^{242}Pu (1 pg), leaching in a covered beaker with about 50 mL 8 M HNO_3 on a hotplate at 180–200 °C for at least 4 h. An anion-exchange chromatographic method described by Liao et al. [14] was employed for the separation and purification of Pu. The chemical recovery of this method was about 50–70%, calculated using ^{242}Pu tracer. For samples with low $^{239+240}Pu$ activity, lower chemical recovery was obtained due to the increase of sample size for analysis.

The measurements of Pu isotopes using SF-ICP-MS in Nakaminato Laboratory for Marine Radioecology (NIRS, Japan) were described in details in previous work [15].

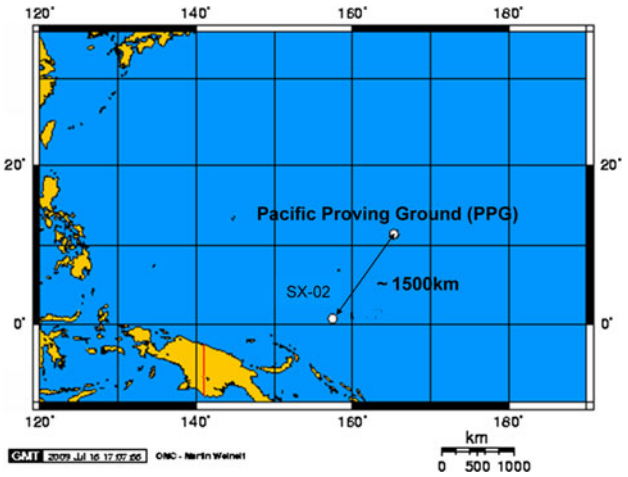

Fig. 1 Map of sampling site (SX-02) and Pacific Proving Ground (PPG)

Zheng and Yamada [12] reported a high sensitive SF-ICP-MS analytical method with a low detection limit of 0.14 fg mL^{-1} for Pu isotopes in marine settling particles and seawaters. Most recently, Liao et al. [14] reported determination of Pu isotopes in the freshwater lake sediments using SF-ICP-MS combined with a two-stage anion-exchange chromatography. In this work, we employed SF-ICP-MS to analyze Pu isotopes in low level deep-sea sediments.

Results and discussion

$^{239+240}Pu$ activity concentrations and inventory

The inputs of Pu isotopes from global fallout to the South Pacific were estimated to be half or even less than those of the North Pacific. Sediment core sample (SX-02) was collected in the latitude band 0–30°N and analysed for its $^{239+240}Pu$ activities and $^{240}Pu/^{239}Pu$ atom ratios by SF-ICP-MS. The results are summarized in Table 1.

In the sediment of SX-02, the $^{239+240}Pu$ activity in the top layer was 0.226 ± 0.007 Bq kg^{-1} ($\pm 1\sigma$). Moon et al. [10] and Lee et al. [16] reported Pu activity in the sediment of deep sea in the North Pacific Ocean: high activity up to 15 Bq kg^{-1} was observed, which was attributed to global fallout with a contribution from local fallout (Bikini Island). However, at the St. TEQ 6 and St. TEQ 12, the maximum activity was observed as 0.22 and 0.23 Bq kg^{-1}, which agreed well with our result of SX-02 in the same latitude band (0–30°N). $^{239+240}Pu$ decreased exponentially with depth and no subsurface maximum was observed at this site (Fig. 2).

It was found that $^{239+240}Pu$ penetrated to the top 10 cm in SX-02 site. As a particle-reactive nuclide, particle

Table 1 Water depth, mass depth, results of $^{240+239}$Pu concentration, ^{240}Pu/^{239}Pu atom ratio, and calculated inventory of SX-02

Depth in core (cm)	Mass depth (g/cm^2)	$^{239+240}$Pu activity (Bq/kg)	Inventory (Bq/m^2)	^{240}Pu/^{239}Pu
0–1	0.381	0.226 ± 0.007	0.861 ± 0.025	0.189 ± 0.012
1–2	1.162	0.113 ± 0.006	0.881 ± 0.044	0.199 ± 0.017
2–3	1.846	0.074 ± 0.004	0.508 ± 0.027	0.193 ± 0.016
3–4	2.498	0.036 ± 0.003	0.233 ± 0.020	0.232 ± 0.033
4–5	3.147	0.031 ± 0.003	0.201 ± 0.018	0.210 ± 0.030
5–6	3.829	0.032 ± 0.003	0.221 ± 0.018	0.186 ± 0.020
6–7	4.59	0.024 ± 0.003	0.181 ± 0.020	0.196 ± 0.027
7–8	5.254	0.026 ± 0.003	0.171 ± 0.020	0.206 ± 0.027
8–9	5.976	0.023 ± 0.002	0.168 ± 0.018	0.238 ± 0.030
9–10	6.641	0.006 ± 0.003	0.041 ± 0.017	–
10–11	7.321	0.005 ± 0.002	0.033 ± 0.013	–
11–12	8.094	0.003 ± 0.001	0.022 ± 0.010	–
12–13	8.813	0.001 ± 0.002	0.008 ± 0.012	–
13–14	9.504	0.002 ± 0.001	0.017 ± 0.007	–
14–15	10.292	0.002 ± 0.001	0.015 ± 0.007	–

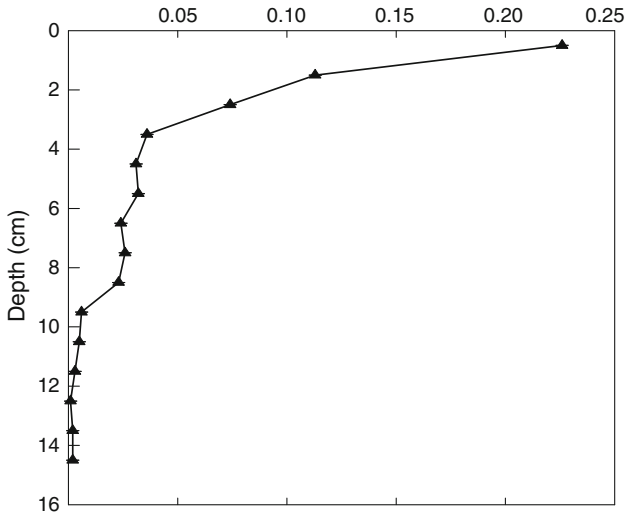

Fig. 2 The depth profile of $^{239+240}$Pu activity concentrations in SX-02 (Bq kg^{-1})

scavenging is the main process for the removal and deposition of Pu isotopes in the ocean. The sedimentation rates in the deep sea ranged from 0.12 to 1.8 cm kyr^{-1} using U–Th dating method [10]. A depth of 10-cm sediments may represent a sedimentation of thousands or tens of thousands years. The release of Pu isotopes into the environment, however, began in ca. 60 years ago. Pu isotopes detected in this sediment core were not solely resulted from the sedimentation process, but also, and more importantly from the post-deposition processes, such as physical mixing of bottom currents and the bioturbation effect. The plutonium may be associated with surface derived large particles, of which food values are high, so that they are segregated and transported by benthic organisms to deeper depths in the sediment column.

As shown in Table 1, calculated inventory of $^{239+240}$Pu for SX-02 was 3.56 ± 0.28 Bq m^{-2} ($\pm 1\sigma$). Cohran et al. reported the $^{239+240}$Pu activity in the core top 0–2 cm section to be 0.3–0.5 Bq kg^{-1}, and its inventory ranged from 2.67 to >8.50 Bq m^{-2} in the east equatorial Pacific (1–12°N, 140–90°W) [17]. Detailed comparisons of sedimentary Pu inventory in the Pacific Ocean are summarized in Table 2 [10, 18–24]. The inventories at each latitude band and ocean area showed large differences in times, even in orders of magnitude. In the middle latitude of North Pacific, the inventory changed depending on the sampling sites and could be different even in the same zone, for instance, the sediment samples from Northern-Central Basin. There are three main possibilities to interpret this phenomenon: (1) Close-in fallouts around sampling sites are predominantly higher than global fallout; (2) Strong ocean currents passed through the known sinks or sources of Pu in the Pacific Ocean and the sampling sites which bring Pu from coral reefs redissolved in water and from lagoon water to the open ocean; (3) Various topography in the bottom of the ocean leads to different deposition of Pu isotopes.

Nagaya and Nakamura [23] studied the Pu inventory in sediments and corresponding water columns in the Yellow Sea of China, found that >90% of the Pu have entered the sediments due to the relatively shallow (<10 m) water above the bottom and high frequency biota turbulence on the shelf. However, considering the extremely large water volume above the bottom sediment in the deep sea, most of the Pu isotopes, therefore, may exist in the seawater till

Table 2 Comparison of Pu concentration and inventory in deep sea sediments in the Pacific Ocean

Location	Water depth (m)	Concentration (mBq/g)	Inventory (Bq/m^2)	References
48°N 163°E	5,500	0.12–0.26	–	[18]
44°N 145°E	1,214–3,053	0.04–3.61	81–271	[19]
35°N 140°E	2,519	0.006–1.24	192 ± 120	[20, 21]
35°N 146°E	5,924	0.03–1.85	28.6	[10]
35°N 135°E	16–26	0.74–4.78	214 ± 14	[22]
26°N 125°E	2,170	0.011–0.107	8.9 ± 0.3	[23]
22°N 153°E	5,600	0.02–0.23	2.8	[10]
16°N 160°E	5,390	0.06–5.38	71.8	[10]
12°N 165°E	4,530	0.02–15.1	130	[24]
5°N 137°E	4,629	0.04–0.22	6.82	[10]
2°N 137°E	4,157	0.03–0.23	8.95	[10]
0.5°S 158°E	2,080	0.001–0.226	3.56 ± 0.28	This study

now. Recently, <1% of Pu in sediments was observed by Ito et al. [25] comparing to the majority Pu in seawater in the Japan sea (3,013 m) because of the long vertical distance and unobvious biota movements in the deep ocean which have weakened scavenging mechanism.

Therefore, we may conclude that: the inventory of the sediments in the deep sea of equatorial Pacific Ocean are lower than that of North Pacific as well as the expected value from global fallout, partly due to the relatively low fallout, mainly because of the water maintenance of Pu and slow scavenging process in the central Pacific Ocean.

^{240}Pu/^{239}Pu atom ratios and sources of Pu in sediments of Central Pacific

Generally, it is known that ^{240}Pu/^{239}Pu atom ratio is a good indicator to identify Pu sources in the environment, since the ratio depends upon the specific weapon design and test yields. High ratios can be expected with higher neutron fluxes associated with an increase in the yield of a nuclear detonation.

The results of ^{240}Pu/^{239}Pu atom ratio are presented in Fig. 3, which ranged from 0.186 to 0.238 in the Melanesian Basin of SX-02 with a mean value of 0.205, which is typically higher than that of global fallout (0.174 ± 0.014). It is reasonable to suggest that the global fallout is not the solely Pu source in this area.

Buesseler [26] reported ^{240}Pu/^{239}Pu atom ratio in surface sediments and seawater collected during 1974–1982 in the North Pacific, and concluded that the Pacific Proving Ground (PPG) was a major source for the North Pacific, which was characterized by an elevated ^{240}Pu/^{239}Pu atom ratio (>0.2) relative to global stratospheric fallout (0.18–0.19). Norisuye et al. [27] observed high ^{240}Pu/^{239}Pu atom ratios (0.220–0.269) in seawaters in the NW Pacific. The range of contamination originated from Bikini and

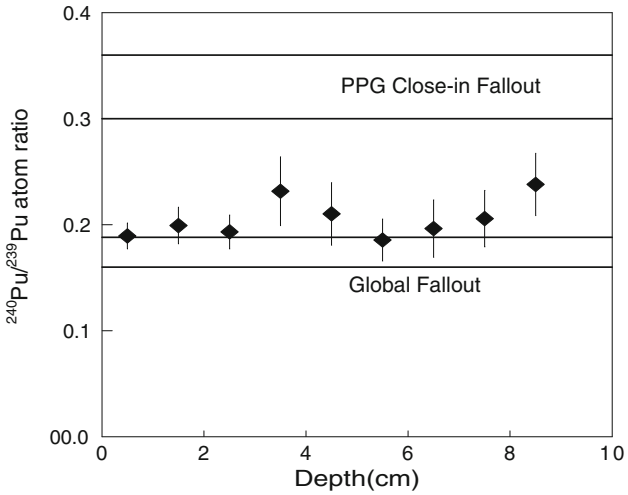

Fig. 3 The ^{240}Pu/^{239}Pu atom ratio of sediments in SX-02

Enewetak nuclear weapon tests in the 1950s was evaluated by Zheng and Yamada [20] and by Kim et al. [28], which was believed to be extended to Japanese Coast and the Coast of the Korean Peninsula by the transport of the North Equatorial Current. Our results of ^{240}Pu/^{239}Pu atom ratio in SX-02 (0.205, inventory-weighted mean) are comparable to above results. All these results also demonstrated the impact of local fallout from PPG to Melanesian Basin. Therefore, we are convinced that there are two Pu sources in Melanesian Basin: the global fallout and the close-in fallout derived from PPG. The direct fallout and oceanic current would be both plausible pathways for close-in fallout Pu in the Melanesian Basin. Generally, the prevailing winds transported the radioactive debris clouds toward the southwest. One exception, however, occurred during the Bravo event when unexpected change in the wind directions caused the cloud to travel toward the east over Bikini Island [29]. It is known that the North

equatorial Current is the main current corresponding to the transportation of PPG Pu, which is in the region above 10°N. Nevertheless, the main surface current across the Melanesian Basin is the south equatorial current which is in the region between 3°N and 20°S. Therefore, the mechanism that close-in fallout Pu was driven by the wind is more reasonable according to the above discussion. However, it needs to be verified by further study on Pu isotopes in soil/fallout materials.

Resolving global fallout and close-in fallout Pu isotopes

Since two isotopically distinctive Pu sources are identified, a simple two end-member mixing model was used, which is similar to the one described by Krey [30] to evaluate the relative contributions:

$$\frac{(\mathrm{Pu})_{\mathrm{P}}}{(\mathrm{Pu})_{\mathrm{G}}} = \frac{(R_{\mathrm{P}} - R)(1 + 3.66R_{\mathrm{P}})}{(R - R_{\mathrm{P}})(1 + 3.66R_{\mathrm{G}})} \quad (1)$$

where (Pu) is the activity of $^{239+240}$Pu; R is the ^{240}Pu/^{239}Pu atom ratio measured; R_{G} is the ^{240}Pu/^{239}Pu atom ratio of global fallout equal to 0.18; R_{P} is the PPG source ^{240}Pu/^{239}Pu atom ratio.

The results showed that Pu from PPG contributed 25 and 18% to the total fallout corresponding to the PPG atom ratio of 0.3 and 0.36, respectively. Due to different scavenging properties of global fallout and close-in fallout Pu (the close-in fallout Pu seems more particle-reactive), as well as the low inventory of Pu deposited in the deep-sea sediments, this close-in fallout Pu input did not produce significant increase of inventory in this deep sea sediment core sample.

Conclusions

The inventory of $^{239+240}$Pu is low in the Central Pacific because majority of Pu are still in the water column and the deposition of Pu in deep sea sediments is controlled and/or altered by complex physical, chemical and biological processes. The Pu contaminations from PPG have been observed in close-in territories of PPG probably due to the fallout driven by wind.

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