Journal of Environmental Radioactivity 101 (2010) 622–629

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Characterization of plutonium in deep-sea sediments of the Sulu and South China Seas

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ARTICLE INFO

Article history:
Received 27 October 2009
Received in revised form
15 March 2010
Accepted 23 March 2010
Available online 18 April 2010

Keywords:
Plutonium isotopes
Sediments
$^{240}Pu/^{239}Pu$ atom ratio
SF-ICP-MS
South China Sea
Sulu Sea

ABSTRACT

Anthropogenic Pu isotopes are important geochemical tracers for sediment studies. Their distributions and sources in the water columns as well as the sediments of the North Pacific have been intensively studied; however, information about Pu in the Southeast Asian seas is limited. To study the isotopic composition of Pu, and thus to identify its sources, we collected sediment core samples in the South China Sea and the Sulu Sea during the KH-96-5 Cruise of the R/V Hakuho Maru. We analysed the activities of $^{239+240}Pu$ and the atom ratios of $^{240}Pu/^{239}Pu$ using isotope dilution sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS). The $^{240}Pu/^{239}Pu$ atom ratios in the sediments of both areas (inventory weighted mean: 0.251 for the South China Sea and 0.280 for the Sulu Sea) were higher than the global fallout value (0.178 ± 0.019), suggesting the existence of Pu from the Pacific Proving Grounds in the North Pacific. Low inventories of $^{239+240}Pu$ in sediments were observed in the South China Sea (3.75 Bq/m^2) and the Sulu Sea (1.38 Bq/m^2). Most of the Pu input is still present in the water column. Scavenging and benthic mixing processes were considered to be the main processes controlling the distribution of Pu in the deep-sea sediments of both study areas.

1. Introduction

Anthropogenic radionuclides have entered the oceans as global or local fallout due to atmospheric nuclear weapons testing, as dumped radioactive wastes of liquid or solid forms, and as run off via rivers from the land. Although some radionuclides (typically, ^{137}Cs) are present as dissolved forms and remain in the water column, others are able to associate with marine particles and finally deposit in the seabed sediments over time. Plutonium, a man-made radionuclide, was distributed globally as a result of the atmospheric nuclear weapons tests in the last century. Additionally, there have also been releases of Pu to the environment from nuclear reprocessing facilities, and from satellite and reactor accidents.

According to Aarkrog (2003), total global fallout released $^{239+240}Pu$ was 10.87 PBq, and about 60% of that amount (6.6 PBq) has entered the world's oceans. Besides global fallout Pu, the second main source of Pu contamination in the North Pacific was from nuclear weapons tests conducted in the Pacific Proving Grounds (PPG) from 1946 to 1958 (42.2 Mt fission yield). Highly localized inputs were made from the nuclear weapons tests conducted over various coral islands or over shallow water. The contaminated particles deposited in lagoons, and on surrounding slopes and sediments from which they have been released and transported by water in solution form (partly in particles), especially with the North Equatorial Current (NEC) to the Northwest Pacific (Buesseler, 1997; Hamilton et al., 1996; Lee et al., 2005; Kim et al., 2004) as far as the East China Sea (Wang and Yamada, 2005), Yellow Sea (Nagaya and Nakamura, 1992) and the Japanese coast (Zheng and Yamada, 2004).

The first ocean-wide study of Pu in the Pacific Ocean originated with the GEOSECS sampling program in the early 1970s, some 10–15 years after the major input of fallout Pu (Bowen et al., 1980). Since then, Pu activities and their behaviours in water columns and sediments of the Pacific have been intensively studied. Generally, studies on the distributions of Pu isotopes in the western North Pacific and its marginal seas have revealed higher surpluses of total inventories in seawater than those derived from global fallout (Hirose and Aoyama, 2003; Hirose et al., 1999; Nagaya and Nakamura, 1992; Pettersson et al., 1999), which was not well understood, but commonly explained as the current migration of close-in fallout PPG-derived Pu to the western North Pacific. The vertical profile of $^{239+240}Pu$ in deep-seawater columns showed

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doi:10.1016/j.jenvrad.2010.03.011

a surface minimum, a subsurface maximum and a gradual decrease with increasing depth, followed by a slight increase near bottom due to re-dissolution of adsorbed Pu and/or re-suspension of surface sediments (Hirose, 2009; Hirose and Aoyama, 2003; Hirose et al., 1999; Hong et al., 2004; Povinec et al., 2003, 2004).

However, the inventories and the vertical profile of $^{239+240}$Pu in the sediment depended on the sampling stations and local oceanographic conditions. Inventories of $^{239+240}$Pu and ^{137}Cs in the sediment were found to be inversely related to water depth and linearly correlated with sediment accumulation rates (Hong et al., 1999, 2002). Therefore, inventories of radionuclides in sediments in the shallow water marginal seas and areas which have a relatively small volume of seawater above or have a high sediment accumulation rate were general higher than those of the deep-seas (Duran et al., 2004; Hirose, 2009; Moon et al., 2003; WOMARS, 2005). The distributions of Pu isotopes in sediments of marginal seas of the western North Pacific have been intensively studied in the late half of the last century (Hirose et al., 1999; Hong et al., 2002; Ito et al., 2007; Kim et al., 2002, 2004; Lee et al., 2003; Nagaya and Nakamura, 1987, 1992; Wang and Yamada, 2005; Yamada et al., 1996). Many studies have also demonstrated that the ^{240}Pu/^{239}Pu atom ratio is a powerful tool to verify the sources of Pu contamination in the marine environment. Buesseler (1997) reported ^{240}Pu/^{239}Pu atom ratios in deep-sea sediments higher than the global fallout value of 0.178 due to the contamination of the PPG-derived Pu. Similar results were published later focusing on the Yellow Sea (Kim et al., 2002; Moon et al., 2003), the Japan Sea (Zheng and Yamada, 2005), the East China Sea (Lee et al., 2004, 2005; Wang and Yamada, 2005) and Sagami Bay, Japan (Zheng and Yamada, 2004).

However, investigations on anthropogenic radionuclides in the waters and sediments of the Southeast Asian seas have been limited. Nozaki et al. (1999) had reported the distributions of dissolved rare earth elements and hydrography in the Sulu Sea (SS). Duran et al. (2001) assessed anthropogenic and natural radionuclides in marine sediment, biota and seawater in Philippine coastal waters. Yamada et al. (2006a) used the same SS sampling site of the Sulu Sea and reported an extremely high total ^{137}Cs inventory (3200 Bq/m^3) in the water columns compared with that of the South China Sea (SCS) (1900 Bq/m^3). Okubo et al. (2007) investigated the scavenging process of ^{230}Th, also at the same SS sampling sites.

To be the best of our knowledge, no systematic studies of Pu isotopes in the sediments of the SS and the SCS have been reported. Besides that, it is also of note that no direct observations on the anthropogenic radionuclides in the Southeast Asian seas have been reported till now, leading to a missing link in the hypothesized pathway of transport PPG-derived Pu to the western North Pacific Ocean. For the purpose of studying the isotopic composition of Pu in the oceans, and thus to identify the sources of radioactive contamination and realize a complete picture of PPG-derived anthropogenic radionuclide transport, we investigated $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in deep-sea sediments collected during late 1996 and early 1997 in the SS and SCS. We employed a two-stage anion-exchange chromatographic method for the separation and purification of Pu isotopes. The activities of $^{239+240}$Pu and the atom ratios of ^{240}Pu/^{239}Pu were determined using sector-field inductively coupled mass spectrometry (SF-ICP-MS) combined with a high-efficiency sample introduction system (APEX-Q) (Zheng and Yamada, 2006a). We discuss possible sources and characterizations of Pu isotopes in the SS and SCS.

2. Study area

2.1. South China Sea

The SCS (as shown in Figs. 1 and 2) is the largest marginal sea (3.5×10^6 km^2) in Southeast Asia with a maximum depth reaching 5000 m. It extends from the equator to 23°N and from 99°E to 121°E. On its eastern side, the Philippines and Palawan separate the SCS from the Pacific Ocean. The continental slope is steep and there is practically no continental shelf on the eastern side of the basin. There are three openings along the eastern boundary: the widest and the deepest is the Luzon Strait with a sill depth of 2000 m and there are two narrow, shallow passages north and south of Palawan Island which connect the SCS to the SS (Shaw and Chao, 1994). Bottom waters are derived from intermediate and deep waters of the Pacific Ocean which flow through the deep Basin Channel in the Luzon Strait (Broecker et al., 1986), located between Taiwan and Luzon (Van Riel, 1943). As a result, the SCS bottom waters have a psychrospheric temperature of approximate 2.4 °C and oxygen level of over 1.75 ml/l in the deeper portions of the basin (Rathburn et al., 1996).

2.2. Sulu Sea

On the other hand, the SS (as shown in Figs. 1 and 2) is a semi-isolated and roughly rectangular basin (2.5×10^5 km^2) with 5000 m depth, surrounding Borneo (Sabah), the Philippines, Palawan Island and the Sulu Archipelago, which places it in the humid tropical region of Southeast Asia. Typically sill depths are shallower than 100 m, inhibiting deep-sea flow in and out of the basin (Kuehl et al., 1993). A 420 m deep channel (Mindoro Strait) connecting the SS to the SCS is the only means by which replenishment of the SS deep water occurs (Van Riel, 1943). Surface waters flow into the SS during summer and flow out during the late winter in response to the monsoons. Because the South China Sea Intermediate Water flows opposite to surface currents, a semi-annual reversal is also observed in the subsurface flow, allowing replenishment of the SS deep water to occur during only half of the year (Van Riel, 1943; Linsley et al., 1985). A small extent of water exchange between the SS and SCS coupled with the tropical climate contributes to the formation of the warm, oxygen-deficient nature of the SS deep water. In contrast, the SCS deep water is well oxygenated as a result of replenishment by Western North Pacific Intermediate Water (NPIW).

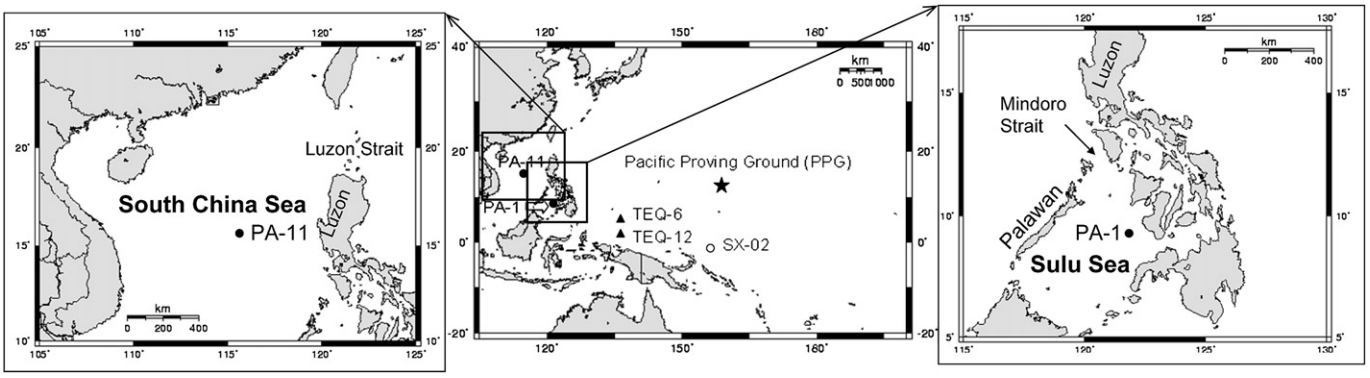

Fig. 1. Map showing the **s**ampling stations of the R/V Hakuho Maru in the Sulu Sea and the South China Sea. Samples were analyzed in this study for stations indicated by the solid circles. Data were cited from Moon et al. (2003) and our previous study (Dong et al., in press) for the stations indicated by the solid triangles and the open circles, respectively.

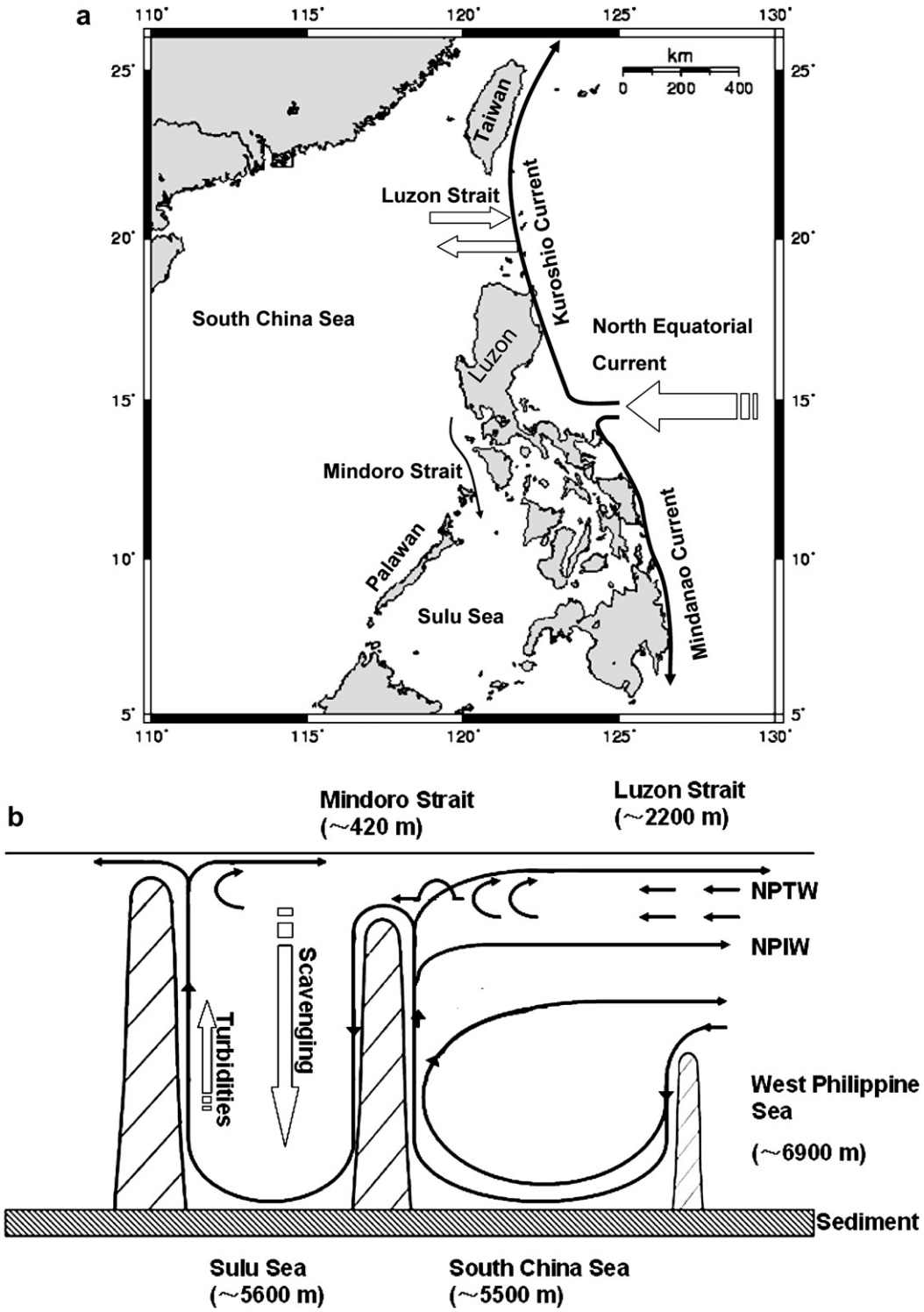

Fig. 2. a) Schematic representation of the mean Kuroshio pathway (upper solid thick line) along the North Pacific western boundary. The arrows south of Taiwan denote the free water exchange in the Luzon Strait. b) Schematic flow in the West Philippine Sea, SCS and SS, and the water change pathways of North Pacific Intermediate Water (NPIW), and North Pacific Tropical Water (NPTW) (redrawn from Chen et al., 2006).

3. Materials and methods

Sediment core samples were collected in the SCS (PA-11; 15°26′N, 115°20′E; 4234 m water depth) and the SS (PA-1; 8°50′N, 121°48′E; 4988 m water depth), during the Piscis Austrinus Expedition (KH-96-5 Cruise) from December 19, 1996 to February 18, 1997 by the R/V Hakuho Maru. The sediment core samples were cut into 1 cm segments and stored in an on-board refrigerator until brought back to the land-based laboratory for further treatments. The oceanographic data, such as the salinity and potential temperature of seawater in the overlying water column of PA-11 and PA-1 were described in a previous study (Yamada et al., 2006a).

For the analysis of Pu isotopes, details for sample preparation have been described elsewhere (Zheng et al., 2004). In brief, the dried and weighed sediment (~2.5 g) was spiked with yield monitor of ^{242}Pu (1 pg), leaching in a covered beaker with 50 ml 8 M HNO_3 on a hotplate at 180–200 °C for at least 4 h. A two-stage anion-exchange chromatographic method described by Liao et al. (2008) was employed for the separation and purification of Pu. The total recovery of this method

was about 50–75%, calculated using ^{242}Pu tracer. For samples with low $^{239+240}$Pu activity, a lower chemical recovery was obtained due to the necessary increase of sample size for analysis.

The measurements of Pu isotopes using SF-ICP-MS (Element 2) were conducted in the Nakaminato Laboratory for Marine Radioecology (NIRS, Japan). An APEX-Q high-efficiency sample introduction system (Elemental Scientific Inc., Omaha, NE, USA) with membrane desolvation unit (ACM) and a conical concentric nebulizer were used as sample introduction systems. Additionally, the normal skimmer cone was replaced by a high-efficiency cone (X-cone, Thermo Finnigan) to further increase sensitivity of SF-ICP-MS. All the measurements were made in the self-aspirating mode to reduce the risk of contamination by the peristaltic pump tubing. Details on the instrument optimization and determination of Pu isotopes have been described previously (Zheng and Yamada, 2006a).

4. Results and discussion

4.1. Distribution of $^{239+240}$Pu in sediments

Analytical results of Pu isotopes are given in Table 1 together with the mass depth. The $^{239+240}$Pu activities of the sediments in PA-1 (SS) and PA-11 (SCS) ranged from 0.002 to 0.508 mBq/g and 0.002 to 0.157 mBq/g, respectively.

The $^{239+240}$Pu activity in surface sediment of the SCS (0.157 mBq/g) was similar to that of the Yellow Sea (0.107 mBq/g) but lower than the East China Sea (0.47 mBq/g), which was explained by the transportation of large amounts of water and suspended sediments containing Pu from the mouth of the Yangtze River (Nagaya and Nakamura, 1992). This result was also comparable but slightly lower than the results for adjacent open oceans of the Pacific Ocean such as the West Caroline Basin (0.22–0.58 mBq/g, stations TEQ-6 and TEQ-12, in Fig. 1) and the Melanesian Basin (0.226 mBq/g, station SX-02 in Fig. 1) reported, respectively, by Moon et al. (2003) and Dong et al. (in press) (as shown in Table 2). The $^{239+240}$Pu activity in the surface sediment of the SS (PA-1) (0.508 mBq/g) was similar to that of the North Pacific Ocean, although hardly any $^{239+240}$Pu activity was observed in the sub-layers.

Vertical distributions of $^{239+240}$Pu activity in the SCS and SS are shown in Fig. 3. The $^{239+240}$Pu activity was only found in the surface layer (0–3 cm) for PA-1 sediment core in SS, while for PA-11 in SCS, Pu isotopes were detected at depths down to 13 cm, and the $^{239+240}$Pu activity decreased nearly exponentially with depth. Generally, the activity distributions are related to sedimentation rates, water depth, grain sizes, and organic content as well as the biogeochemical processes in the water columns. Kuehl et al. (1993) investigated high-resolution seabed profiles of ^{14}C and ^{210}Pb, revealing that sedimentation rates for the SS (6.0–12.3 cm/ky) are 2–3 times higher than that of the SCS (2.7–3.0 cm/ky) at any given water depth. The lack of a subsurface $^{239+240}$Pu peak in bottom sediments in these areas may be due to poor time resolution resulting from low sedimentation rates, and that the horizon of 1963 is constrained within the upmost sampling layer. Sometimes, subsurface peaks appear in some deep-sea sediment samples and they are generated mostly by biological activity (Yang et al., 1986).

On the other hand, the above results also suggested that the sedimentation process is not a key factor controlling the vertical distribution of Pu depositing into sediments in both the SCS and SS, although scavenging is known as the main mechanism for Pu removal from water. Biological mixing in surface sediment columns, nevertheless, largely controls the $^{239+240}$Pu penetration depth as well as the $^{239+240}$Pu activity profiles in the sediment. Benthic mixing rates determined using ^{210}Pb generally are much lower in the SS (0.004–0.254 cm^2/y) as compared with the SCS (0.17–1.57 cm^2/y) due to the low dissolved oxygen concentration in bottom water and shallow penetration of O_2 into pore water (Rutgers van der Loeff, 1990). If we assumed that ca. 45 years had passed since 1952 (the sediments were sampled in 1996–1997), the roughly estimated diffusion distance (penetration depth) in the SCS and the SS, i.e. the square root of the mixing coefficient and the time elapsed (DeMaster et al., 1985), would be 2.8–8.4 cm and 0.4–3.4 cm, respectively, which was slightly lower than the observed value (around 10 cm) in the SCS and completely consistent with the result in the SS (around 3 cm). Similarly, Kuehl et al. (1993) observed that for the Sulu Sea, particularly for the 3000 m and 4000 m sites, the penetration depths of excess ^{210}Pb were less than 3 cm. These findings suggested that in the SS, "diffusion-type" mixing governs the vertical transport of Pu in the sediment columns, agreeing with the low bio-activity in the deep-sea environment of the SS. In the SCS, Pu may have been transported preferentially by organisms to great depths through burrows as well as by "diffusion-type" mixing, causing the deeper penetrated depth than the calculated value. It is not clear why the $^{239+240}$Pu activities from 2 to 6 cm were almost constant for PA-11, but it might be explained as homogeneous mixing (Lee et al., 2003).

Plutonium inventories in sediment columns are an important parameter for geochemical study of Pu because they are less affected by local topography and the mixing process, compared to $^{239+240}$Pu concentrations. The inventories of $^{239+240}$Pu in the sediments of PA-11 (3.75 ± 0.29 Bq/m^2) and PA-1 (1.38 ± 0.06 Bq/m^2)

Table 1
Massic activities of $^{239+240}$Pu and atom ratios of ^{240}Pu/^{239}Pu in sediment cores of PA-1 and PA-11.

Station	Sampling date	Depth (cm)	Mass depth (g/cm^2)	$^{239+240}$Pu Activity (mBq/g)	^{240}Pu/^{239}Pu atom ratio
PA-1 (Sulu Sea)	12/24/96	0–1	0.5909	0.508 ± 0.010	0.281 ± 0.012
	12/24/96	1–2	1.0313	0.015 ± 0.002	0.257 ± 0.053
	12/24/96	2–3	1.5494	0.013 ± 0.003	–
	12/24/96	3–4	2.0542	0.002 ± 0.001	–
	12/24/96	4–5	2.6280	0.002 ± 0.001	–
	12/24/96	5–6	3.1808	0.002 ± 0.001	–
PA-11 (South China Sea)	2/11/97	1–2	1.0502	0.157 ± 0.010	0.228 ± 0.035
	2/11/97	2–3	1.4976	0.099 ± 0.004	0.243 ± 0.019
	2/11/97	3–4	1.9621	0.101 ± 0.007	0.252 ± 0.030
	2/11/97	4–5	2.4660	0.102 ± 0.011	0.245 ± 0.040
	2/11/97	5–6	2.9990	0.098 ± 0.005	0.241 ± 0.023
	2/11/97	6–7	3.4857	0.056 ± 0.005	0.264 ± 0.033
	2/11/97	7–8	3.9622	0.047 ± 0.004	0.255 ± 0.037
	2/11/97	8–9	4.4581	0.040 ± 0.003	0.262 ± 0.032
	2/11/97	9–10	5.0414	0.027 ± 0.004	0.300 ± 0.056
	2/11/97	10–11	5.5861	0.033 ± 0.003	0.294 ± 0.047
	2/11/97	11–12	6.0389	0.027 ± 0.003	0.271 ± 0.041
	2/11/97	12–13	6.4675	0.019 ± 0.002	0.227 ± 0.058
	2/11/97	13–14	7.0075	0.002 ± 0.001	–

Table 2
Range of massic activities of $^{239+240}$Pu and ^{240}Pu/^{239}Pu atom ratios of the deep-sea sediments in Fig. 1.

Sample no.	Areas	Locations	Water depth (m)	Specific activity (mBq/g)	Inventory (Bq/m^2)	^{240}Pu/^{239}Pu atom ratio	References
TEQ-6	West Caroline	5°N 137°E	4629	0.04–0.22	6.82	–	Moon et al., 2003
TEQ-12	West Caroline	2°N 137°E	4157	0.03–0.23	8.95	–	
SX-02	Melanesian Basin	0.5°S 157.5°E	2080	0.001–0.226	3.6	0.193–0.238	Dong et al., in press
PA-11	South China Sea	15.5°N 115.3°E	4234	0.002–0.157	3.75	0.227–0.300	This study
PA-1	Sulu Sea	8.9°N 121.5°E	4988	0.002–0.508	1.38	0.257–0.281	This study
Global fallout	22.2 Bq/m^2 (10–20°N)						UNSCEAR, 1982

were comparable to the results of the equatorial Pacific reported by Dong et al. (in press) (3.56 Bq/m^2) and Moon et al. (2003) (<10 Bq/m^2). These values were significantly lower than those of the most marginal seas: 16–80 Bq/m^2 in the East China Sea (Nagaya and Nakamura, 1992), 10–12 Bq/m^2 in the Yellow Sea (Hong et al., 2002) and 13–68 Bq/m^2 (Lee et al., 2003), 27–122 Bq/m^2 (Ito et al., 2007), 5.7–241 Bq/m^2 (Zheng and Yamada, 2005) in the Japan Sea/East Sea, and 0.6–74 Bq/m^2 (Zheng and Yamada, 2006b) in the Sea of Okhotsk. The above results agreed well with previous findings that the inventories of $^{239+240}$Pu in the sediment were inversely related to water depth and linearly correlated with sediment accumulation rates (Hong et al., 1999, 2002), which also meant the inventories of radionuclides in sediments in the shallow water marginal seas and areas which have a relatively small volume of seawater above or have a high sediment accumulation rate were general higher than those of the deep-seas. The inventories of $^{239+240}$Pu in the sediments of PA-11 and PA-1 were about 17% and 6.2% of that expected from the global fallout (22.2 Bq/m^2) at 10–20°N (UNSCEAR, 1982), suggesting deep water contained a significant amount of Pu.

4.2. ^{240}Pu/^{239}Pu atom ratios and the possible sources of Pu

Generally, the isotopic signature of Pu is characteristic of various Pu sources in the environment. Compared with the global fallout atom ratio (^{240}Pu/^{239}Pu = 0.178 ± 0.019, Kelley et al., 1999), weapons-grade Pu is characterized by a low ^{240}Pu isotope content, thus low ^{240}Pu/^{239}Pu atom ratios (typically ≤0.05) (Harley, 1980). Plutonium from the PPG source is known to have a high atom ratio of ^{240}Pu/^{239}Pu ranging from 0.30 to 0.36 (Muramatsu et al., 2001; Buesseler, 1997). Therefore, the ratio of ^{240}Pu/^{239}Pu offers a reliable method for distinguishing Pu from global fallout and local fallout, since high ^{240}Pu/^{239}Pu ratios can be expected for high-yield nuclear detonations associated with higher neutron fluxes.

The ^{240}Pu/^{239}Pu atom ratios ranged from 0.227 to 0.300 in the SCS with the inventory-weighted mean of 0.251, and from 0.257 to 0.281 in the SS with the inventory-weighted mean of 0.280. These ratios were significantly higher than that of global fallout, which meant mixing between the PPG Pu with higher ^{240}Pu/^{239}Pu atom ratio and the global fallout Pu had occurred. According to previous observations (Kim et al., 2002; Lee et al., 2005; Zheng and Yamada, 2004, 2005), ^{240}Pu/^{239}Pu atom ratios in the Yellow Sea and the Japan Sea/East Sea have shown higher values (0.22–0.30), and similar results were also obtained in seawater in the Northern Pacific Ocean (Buesseler, 1997; Kim et al., 2004; Lee et al., 2003; Yamada et al., 2006b), especially along the pathway of the NEC and its bifurcations, e.g. Kuroshio Current (Lee et al., 2004; Wang and Yamada, 2005). Although a variety of possibilities were suggested to explain the surplus $^{239+240}$Pu and high ^{240}Pu/^{239}Pu atom ratios in the Japan Sea/East Sea, it has been established that the excess $^{239+240}$Pu inventories found in the western North Pacific and marginal seas were due to transport from the PPG close-in fallout Pu (Kim et al., 2004; Livingston et al., 2001; Zheng and Yamada, 2004). Wang and Yamada (2005) observed higher ^{240}Pu/^{239}Pu atom ratios (0.295–0.336) in the deepest sediment samples of the Okinawa Trough and the East China Sea, which suggested that

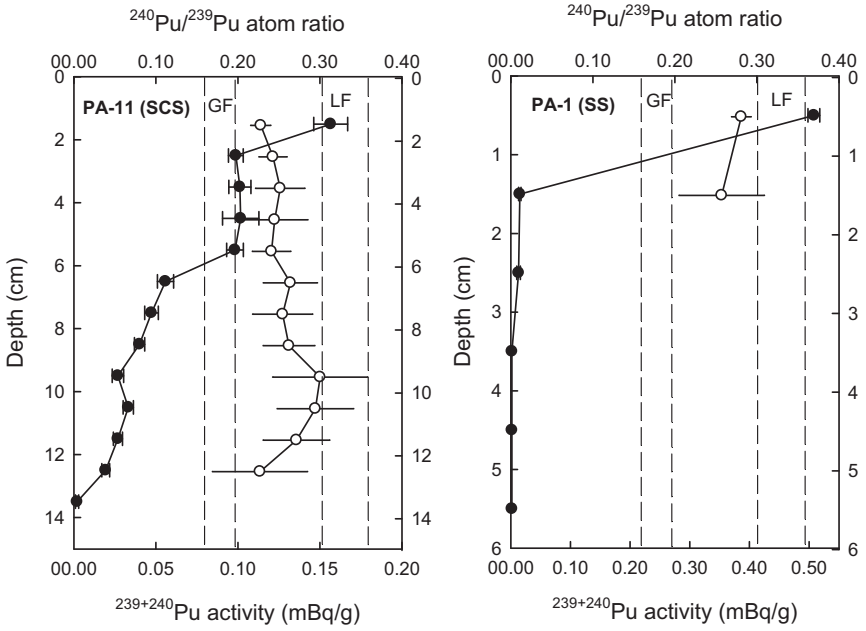

Fig. 3. Vertical profiles of $^{239+240}$Pu activity (solid circles) and ^{240}Pu/^{239}Pu atom ratio (open circles) at PA-11 and PA-1. The dashed lines represent the ^{240}Pu/^{239}Pu atom ratio ranges of global fallout (GF, 0.178 ± 0.019, 30–0°N) and PPG close-in local fallout (LF, 0.30–0.36). The errors are one standard deviation, indicating ICP-MS analytical uncertainty.

ocean surface input due to the early direct tropospheric fallout and continued releases and transport of the PPG-derived Pu by oceanic currents would deliver close-in fallout Pu with high $^{240}Pu/^{239}Pu$ atom ratios to the marginal sea areas. All these findings proposed that the movements of seawater transported some proportion of Pu from the PPG to the mid-latitude region of the western North Pacific and then to the SCS and the SS.

As Bikini (11.5°N, 165.5°E) and Enewetak Atolls (11.3°N, 162.3°E) are located in the pathway of the NEC (located between 10°N and 20°N), this current was recognized as the most probable pathway for transporting PPG Pu to the northwest Pacific Ocean. Nevissi and Schell (1975) estimated in the PPG area that continuous circulation of water in the lagoons and the exchanges of water with the open ocean have resulted in a removal rate of $^{239+240}Pu$ of 222 GBq/y into the NEC. Recent reports (Kim et al., 2004; Lee et al., 2003; Livingston et al., 2001; Zheng and Yamada, 2004) also suggested the lateral transport of the PPG close-in fallout Pu through the NEC. It is well-known that NEC carries water masses with very low biological productivity (Livingston et al., 2001), thus, less particle scavenging results in a long-term residence for the largest part of the delivered Pu in the water column on the transport pathway. To the best of our knowledge, the transporting process of Pu from the PPG to the SCS and SS could be described as follows: the NEC bifurcates east of the Philippines into the northward-flowing Kuroshio Current and the southward-flowing Mindanao Current, as shown in Fig. 2a. Subsequently, the Kuroshio Current flows northward passing the Philippine coast and encounters the Luzon Strait that connects the SCS with the open Pacific Ocean. The Luzon Strait has a width of 350 km and a depth of 2500 m in its deepest point, which allows part of the Kuroshio Current water with Pu that has a relatively rich and high $^{240}Pu/^{239}Pu$ atom ratio to be introduced into the SCS where a loop current is formed in the northern SCS, due to the prevailing north-east monsoons (Qiu, 2001). The range of influence of this bifurcation can reach as far as 117°E, blocked by only a shallow break. Centurioni et al. (2004) studied interactions of the Kuroshio Current with the SCS and observed incoming water from the Current to the SCS was characterized by a maximum volume transport value of 7.1 ± 1.7 Sv (1 Sv=10^6 m^3 s^{-1}) at 550 m depth. Those findings suggested that the PPG Pu probably has been transported into the SCS by the bifurcation of the NEC across the Luzon Strait, where it was then scavenged onto the sediments, resulting in relatively high $^{240}Pu/^{239}Pu$ atom ratios. Besides that, the surface and/or subsurface inflow of North Pacific Tropical Water (NPTW) as well as the free water exchange between the SCS and open ocean water above 2200 m depth without any hindrance by topography (Fig. 2b) could also contribute to addition of the PPG-derived Pu in the SCS, but in a limited way. Fig. 2a shows a schematic diagram of the current system indicating the possibilities of remobilisation of high-ratio Pu from the PPG to the SCS and SS.

The $^{240}Pu/^{239}Pu$ atom ratio of sediments in the SS had a high value of 0.280, and the Pu activity was only found in the surface layers (0–3 cm). The SS neighbors the SCS as a semi-isolated basin surrounded by islands of the Philippines and Malaysia, preventing deep water of the SS from communicating with that of the open Pacific directly. Nozaki et al. (1999) suggested that water mass with low salinity observed at 700–1100 m depths is originating from the lateral transport of the SCS water into the Sulu Basin, across the ~420 m depth sill of the Mindoro Strait (Fig. 2). This also provides the only possible pathway for further transportation of the PPG-high $^{240}Pu/^{239}Pu$ atom ratio Pu from the SCS to SS. Moreover, Yamada et al. (2006a) observed higher ^{137}Cs inventory (3200 Bq/m^2) at the same station compared to that of the SCS (1900 Bq/m^2), indicating that significant amounts of ^{137}Cs-rich water were conveyed into the deep layers. High inventories of ^{137}Cs in the water column suggested occurrence of accumulation processes of anthropogenic radionuclides in the SS, due partly to the lateral input from the SCS and the unique semi-closed geo-condition of the SS which significantly weakens water exchange with open seas.

However, it is still unclear why the heavy input of anthropogenic radionuclides in the water column did not produce a significant increase of Pu inventory in the deep-sea sediments. Two possibilities are suggested herein: 1) most of the $^{239+240}Pu$ was maintained in the water column with more than 4000 m depth due to the weakened particle scavenging; and 2) the bottom turbidity currents enhanced re-suspension/re-dissolution of Pu in the bottom sediments and further altered the distribution of Pu in the water/sediment interface of the SS. Further investigations into the distributions of $^{240}Pu/^{239}Pu$ atom ratios in the water column and the water–sediment interface of the SS are needed to verify the above hypothesis.

Since two isotopically distinctive Pu sources were identified, we used a simple two end-member mixing model, which is similar to the one described by Krey et al. (1976) to evaluate the relative contributions:

$$\frac{(Pu)_P}{(Pu)_G} = \frac{(R_G - R)(1 + 3.66R_P)}{(R - R_P)(1 + 3.66R_G)} \quad (1)$$

where (Pu) is the activity of $^{239+240}Pu$ and subscripts P and G refer to the PPG close-in fallout and global fallout, respectively; R is the $^{240}Pu/^{239}Pu$ atom ratio we measured; R_G is the $^{240}Pu/^{239}Pu$ atom ratio of global fallout 0.18; and R_P is the PPG-derived $^{240}Pu/^{239}Pu$ atom ratio (ranging from 0.30 to 0.36, according to previous studies by Muramatsu et al. (2001) and Buesseler (1997)).

The results showed that $^{239+240}Pu$ from the PPG source contributed 48–65% (average 57%) in the SCS, and 70–86% (average 78%) in the SS to the total $^{239+240}Pu$ inventories in the sediments using R_P values of 0.30 and 0.36, respectively. The value of the SCS agreed well with previous estimations that up to of 60% of the Pu inventory in the North Pacific originated from a local source (Bowen et al., 1980; Livingston et al., 2001), and also was consistent with the range observed in East China Sea sediments (46–67%) (Wang and Yamada, 2005). In the SS deep-sea sediments, the PPG source Pu contributed significantly to the total $^{239+240}Pu$ inventory, suggesting that the PPG-derived $^{239+240}Pu$ may be preferentially transported to sediment compared with global fallout Pu.

5. Conclusions

Sediment cores collected from the deep basins of the Southeast Asian seas (the South China Sea (SCS) and the Sulu Sea (SS)) provide an ongoing and historical record of contamination by artificial radionuclides in the world's oceans. The inventory weighted mean $^{240}Pu/^{239}Pu$ atom ratios in the sediments of the SCS and the SS were 0.251 and 0.280, respectively, which are believed to be influenced by the Pu derived from the Pacific Proving Grounds in the North Pacific. The activities and inventories of $^{239+240}Pu$ in the sediments in the SCS were comparable to those of the equatorial Pacific Ocean, indicating similar input and behaviour of Pu in these study areas. The inventory of Pu in the sediment in the SS, however, was significantly low, probably due to the particular hydrography in the Sulu Basin. More data on the distribution of Pu in the water column in the SCS and SS will further illuminate the mechanisms and provide detailed knowledge about Pu behaviours in marine environments.

Acknowledgments

We express our deep appreciations to the captain, crew and research colleagues of the R/V Hakuho Maru for their assistance

during the sampling. The authors wish to acknowledge the helpful and constructive comments provided by Dr. S. Hisamatsu and two anonymous reviewers. This study was supported by the Mid-term Plan Project in the National Institute of Radiological Sciences, Japan.

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