Historical Changes in ^{239}Pu and ^{240}Pu Sources in Sedimentary Records in the East China Sea: Implications for provenance and transportation

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Abstract:

Concentrations and isotopic composition of plutonium (Pu) are widely used for its source identification and to determine transport processes of Pu-associated particulate matter and water. We investigated the concentrations of ^{239}Pu and ^{240}Pu and their ratios in a number of sediment samples from the East China Sea (ECS) collected in summer (August 6-28) in 2013. The $^{239+240}\text{Pu}$ activity concentrations in surface sediment samples were found to range between 0.048 and 0.492 Bq kg⁻¹ and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios showed a similar trend as that of the $^{239, 240}\text{Pu}$ activities; the Pu atom ratios ranged from 0.158 to 0.297 and were mostly higher than the mean global fallout value of 0.18. The $^{239, 240}\text{Pu}$ inventories in the ECS varied widely, from 2 to 807 Bq m⁻², with the highest values commonly found in the coastal areas. In the Yangtze Estuary, the mean $^{239+240}\text{Pu}$ activity concentration is close to the estimated value in the suspended material from the Yangtze River catchment (0.18 Bq kg⁻¹), and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio was found to be ~ 0.18, which indicates that the Yangtze River input is the dominant source of Pu for this area. The total annual Yangtze River input of $^{239+240}\text{Pu}$ was estimated to be 2.4×10^{10} Bq, which is small compared to the total amount of $^{239+240}\text{Pu}$ buried, 3.1×10^{13} Bq in the whole ECS. The Pacific Proving Ground input appears to be the dominant source of Pu to the ECS, accounting for 45%-52% of the total inventory. The fractional amount of $^{239+240}\text{Pu}$ scavenged from the total $^{239+240}\text{Pu}$ transported by the Kuroshio Current (KC) and Taiwan Warm Current (TWC) into ECS sediments is estimated to be ~10%. Our study shows that the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio is useful not only to obtain a better insight of the biogeochemistry influenced by the KC, but also to trace the long-range transport of other particle-reactive species. Besides, the sedimentation rates obtained based on the penetration depths of $^{239+240}\text{Pu}$ and vertical profiles of excess ^{210}Pb agreed quite well (within uncertainties), which suggests that $^{239+240}\text{Pu}$ can potentially be used as a chronostratigraphic time marker in marine environment.

Key words: East China Sea; plutonium; isotopic ratio; sediment; transportation; mass balance

1. Introduction

^{239}Pu (half-life of 2.41×10^4 yr) and ^{240}Pu (half-life of 6.56×10^3 yr) in the environment are derived from thermonuclear bomb testing (e.g., MIKE in 1952 and BRAVO in 1954), which resulted in a large amount of global fallout (Donaldson et al., 1997), nuclear accidents (e.g., Chernobyl) (Clark and Smith, 1988) and nuclear reprocessing facilities and nuclear power plants (Peirson et al., 1982). Among the transuranic elements, concentrations of plutonium isotopes (^{239}Pu , ^{240}Pu) and their ratios have been most widely used as tracers and chronometers in aqueous and terrestrial environments. Vertical profiles of Pu isotopes in coastal and lacustrine sediments provide chronology for the past 60-65 years which is useful for the reconstruction of the temporal nutrient supply variations, organic and inorganic pollution history and biological productivity (Santschi et al., 1980; Olsen et al., 1989; Ravichandran et al., 1995; Baskaran et al., 1996). A comparison of the direct atmospheric fallout record of Pu (as determined from the atmospheric fallout record of ^{90}Sr) with that preserved in sediment cores is useful to infer the effects of sediment resuspension and/or mixing due to physical and/or biological processes. Moreover, the vertical distribution of Pu in sediment cores in conjunction with excess ^{210}Pb is used to delineate sediment mixing rate from sediment accumulation rates (e.g., Buffoni et al., 1992; Ravichandran et al., 1995; Su and Huh, 2002).

The $^{240}\text{Pu}/^{239}\text{Pu}$ ratios in the marginal seas of the Pacific Ocean vary depending on the sources of plutonium; an average $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of global fallout is 0.176 ± 0.014 (Krey et al, 1976; Kelley et al., 1999), which is distinctly different from ratios of 0.33 - 0.36 in the Pacific Proving Grounds (PPG) in the Marshall Islands (mainly Bikini and Enewetak Atolls) (Buesseler, 1997). In the North Pacific Ocean, the principal source of Pu is close-in (tropospheric) fallout from nuclear weapons testing at the PPG in the Marshall Islands and global (stratospheric) fallout, and the local regional fallout of ^{239}Pu and ^{240}Pu was estimated to be 2.4 PBq and 2.7 PBq (Hamilton, 2005), respectively. Pu from the Marshall Islands has been reported to have spread widely into the North Pacific Ocean, especially the Northwest Pacific, due to the westward flowing North Equatorial Current (NEC) (Povinec et al., 2003). The velocity of surface water-associated radionuclides transported by the NEC is approximately $13\text{-}18 \text{ km day}^{-1}$ (Donaldson et al., 1997). Therefore, Pu from the PPG can be transported long distances into the adjacent marginal seas of the western Pacific Ocean in less than one year and can subsequently reach the East China Sea (ECS) via the Kuroshio Current (Wang and Yamada, 2005; Liu et al., 2011). Thus the

characteristic $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio makes it an important tool to track the sources of Pu in the ECS.

ECS is one of the world's typical river-dominated ocean margin systems with large river input and complex current system. The Yangtze River is the largest river on the Eurasian continent, discharging a large amount of water (mean: $9.05 \times 10^{11} \text{ m}^3 \text{ yr}^{-1}$) and sediment into ECS, though sediment discharge has been reduced by 75% since 2000 (with the mean value from $4.3 \times 10^8 \text{ ton yr}^{-1}$ during 1950 and 2000 to $1.3 \times 10^8 \text{ ton yr}^{-1}$ in 2013), due to the construction of impoundments (Dai et al., 2013; 2014). It has been estimated that 40-50% of the river-derived sedimentary particles are deposited near the estuary and a fraction of which is subsequently transported offshore, mostly southward along the coasts of Zhejiang and Fujian Provinces (McKee, et al., 1983). The large riverine sediment discharge and complex current system result in ECS having high concentration of suspended particles, which makes ECS act as one of most important "sinks" for Pu originated in the PPG, compared to other adjacent marginal seas of the western Pacific Ocean. On a broader context, the estimation of Pu mass balance as well as the sediment inventory of Pu is relevant to the long-range transport of other particle-reactive radionuclides as well as the sediment focusing of radionuclides ^{210}Pb , ^{230}Th and ^{231}Pa .

In recent years, several investigations have been carried out to determine $^{239+240}\text{Pu}$ in the ECS (Nagaya and Nakamura, 1992; Su and Huh, 1999; 2002; Wang and Yamada, 2005; Liu et al., 2011). However, ^{239}Pu and ^{240}Pu data in the Yangtze River catchment are very limited prior to 2008 (Liao et al, 2008), which limits a relatively accurate estimation of the contribution from the Yangtze River input, and determination of a reliable Pu mass balance for the ECS. The objective of this work is to determine the concentrations and isotopic ratios of ^{239}Pu and ^{240}Pu in surface sediments and sediment cores in the ECS and to investigate the sources and mass balance of Pu evaluated from the inventories of ^{239}Pu and ^{240}Pu and their atomic ratios. It is expected that this study will provide insights on the processes and mechanisms that control the transport and fate of Pu and other species that behave similarly to Pu using a simple mass balance of Pu for the ECS.

2. Materials and Methods:

2.1 Study area

The ECS is a marginal sea and has a very wide and flat continental shelf, with total area of $7.7 \times 10^5 \text{ km}^2$, a maximum width of 640 km, and a mean water depth of 72 m. The major current system in the ECS is very complicated, as was described in

Su (2001) (Fig. 1). The freshwater from the Yangtze River flows into the estuary and subsequently flows towards the south in winter and turns to the northeast in summer. In the southern part, there are two northward currents of which one is the warm and salty Kuroshio Current (KC) along the continental shelf break of the ECS, with a branch turning into the Yellow Sea known as the Yellow Sea Warm Current (YSWC), and the other is the Taiwan Warm Current (TWC) moving northward from the Taiwan strait. Along the coast, the southeastern North Jiangsu Coastal Current (NJCC) flows to the north of the Yangtze River mouth and the southwestern Zhejiang-Fujian Coastal Current (ZFCC) flows to the south of the Yangtze River mouth. In summer, the northward TWC intensifies and the southward ZFCC weakens under the prevailing southeast monsoon. The Yellow Sea Coastal Current (YSCC) is parallel to the NJCC in the middle of the Yellow Sea and intersects with the YSWC and the TWC to form a counterclockwise circulation.

2.2. Sampling and analysis

Sediment samples, including 23 surface sediments (0-2 cm) and 6 sediment cores (Fig. 1), were collected during the R/V “Dongfanghong 2” Cruise in August of 2013 using a box corer. The sediment cores were collected with 10-cm diameter Plexiglas core tubes and were sliced in 1-cm interval using a stainless steel knife and were stored in resealable plastic bags at 4 °C until laboratory analysis. Visual observations of the cores were also recorded.

An aliquot of 2 g dry sediment equivalent was used for the measurement of grain size using a laser particle analyzer (LS100Q, Beckman, USA). An aliquot of 60-120 g dry sample was homogeneously pulverized and sealed in a plastic container (70 mm diameter × 70 mm height) for at least three weeks to establish a secular equilibrium between ^{226}Ra and daughter products of ^{222}Rn before measurement. The activity concentrations of $^{210}\text{Pb}_{\text{ex}}$ and ^{137}Cs in sediment samples were measured following the method described by Du et al. (2010). The activities of ^{137}Cs , ^{226}Ra and ^{210}Pb were measured using HPGe γ -ray spectrometry (Canberra Be3830) with 35% relative counting efficiency and had an energy resolution of 1.8 keV (at 1332 keV). The activity of $^{210}\text{Pb}_{\text{ex}}$ was calculated from the measured total ^{210}Pb (46.5 keV, branching ratio: 4.25%) minus the parent-supported ^{210}Pb activity which is assumed to be the same as the ^{226}Ra activity. ^{226}Ra was determined using the gamma line at 351.9 keV (37.6%) for ^{214}Pb and 609.3 keV (46.1%) for ^{214}Bi . The activity of ^{137}Cs was determined from the gamma ray peak at 661.6 keV (85%). The efficiency calibration of the detector system was conducted using both the Laboratory Sourceless

Calibration Software (LabSOCS) and sediment standard prepared by diluting (GBW04127 was homogeneously mixed with natural marine sediment ($< 63 \mu\text{m}$)); the activities of the radionuclides were inter-calibrated by a number of laboratories (e.g., Dai et al., 2011; Wang et al., 2016; 2017).

The separation method of Pu was modified from Xu et al. (2014). Briefly, 5-20 g dried sediment samples were first ashed at 550°C overnight. After spiking with 6-10 mBq ^{242}Pu (NIST-SRM-4334G), the residue was leached with 50-200 mL aqua regia at 200°C for 2 h. The solution was filtered, and the leachate containing Pu was coprecipitated with iron hydroxides by adding $\text{NH}_3\cdot\text{H}_2\text{O}$. The precipitate was separated by centrifugation. The precipitate was washed with 2 mol L^{-1} NaOH and then was dissolved with $\sim 3 \text{ mL}$ of concentrated HCl. To this solution, $\sim 650 \text{ mg}$ of $\text{K}_2\text{S}_2\text{O}_5$ was added to reduce the overall Pu to Pu(III). The pH of the resulting solution was adjusted to ~ 9 -10 by adding ammonium hydroxide. The formed precipitate was separated by centrifugation and then dissolved with $\sim 4 \text{ mL}$ of concentrated HCl and 3 mL of concentrated HNO_3 for the oxidation of Pu(III)–Pu(IV) by NO_2^- in the HNO_3 solution. The solution was gently evaporated to near dryness and 5 mL of 8 mol L^{-1} HNO_3 was added to dissolve the residue. The solution was loaded on to a preconditioned AG 1-X4 anion-exchange column (1.0 cm in diameter and 20-cm height, 50-100 mesh, Cl^- form). After rinsing the column with 8 mol L^{-1} HNO_3 and 9 mol L^{-1} HCl to remove most uranium, thorium and other matrix elements, Pu was eluted with 70 mL of 0.5 mol L^{-1} HCl. Pu in the eluate was co-precipitated with $\text{Fe}(\text{OH})_3$ after adding 100 mg of Fe^{3+} (FeCl_3), then the redox pair of $\text{K}_2\text{S}_2\text{O}_5$ -conc. HNO_3 was used to adjust overall Pu to Pu(IV). The final sample solution prepared in 1 mol L^{-1} HNO_3 was loaded to a TEVA column (2 mL , 200 mesh). After rinsing with 60 mL of 1 mol L^{-1} HNO_3 and 60 mL of 6 mol L^{-1} HCl, Pu was finally eluted with 40 mL of 0.1 mol L^{-1} $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 2 mol L^{-1} HCl. The elute was evaporated to dryness on a hot-plate followed by adding 7-10 mL of concentrated nitric acid and heating at 200°C to decompose the hydroxylamine hydrochloride. The residue was finally dissolved in 0.5 mol L^{-1} HNO_3 and In (III) (as InCl_3) was added as an internal standard for measurement of ^{239}Pu and ^{240}Pu by the ICP-MS (X Series II, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs-skimmer cone and an ultrasonic nebulizer (U5000AT+, CETAC, USA) under hot plasma conditions. The separation of Pu using anion exchange chromatography followed by extraction chromatography (TEVA column) ensures sufficient removal of uranium, which interferes the measurement of ^{239}Pu by tailing and $^1\text{H}^{238}\text{U}$ ion. Uranium remained in

the separated sample was monitored by measurement of ^{238}U to be less than 0.02 ppb (for detailed information, Qiao et al., 2014 and Xu et al., 2014). A certified reference material (IAEA-376, marine sediment) was analyzed with the samples, and the analytical results of ^{239}Pu and ^{240}Pu agree well with the certified value.

3. Results and discussions

3.1. The spatial distribution of Pu isotopes in the surface sediments of the ECS

The activity concentrations of Pu isotopes along with grain size are given in the supplemental file. The spatial distribution (Fig. 2) of radionuclides activities were produced by the Surfer mapping software package using Kriging interpolation based on a digital elevation model (DEM) with $6\text{ km} \times 6\text{ km}$ grid resolution. The $^{239+240}\text{Pu}$ activity concentrations in surface sediments (Table 2A) ranged between 0.048 ± 0.004 and $0.492 \pm 0.035\text{ Bq kg}^{-1}$ (mean: $0.188 \pm 0.119\text{ Bq kg}^{-1}$). The lowest $^{239+240}\text{Pu}$ concentrations were observed near the Yangtze Estuary and Hangzhou Bay, with a range of 0.048 ± 0.004 to $0.186 \pm 0.014\text{ Bq kg}^{-1}$. Earlier studies have shown that the sedimentation rates in these regions showed higher values of $> 1.5\text{ cm y}^{-1}$ (e.g., Huh and Su, 1999; Deng et al., 2006), so the low $^{239+240}\text{Pu}$ activity is likely related to dilution of massive influx of Pu-depleted river-borne sediments. The Pu concentrations in sediments north of the ECS region were also low. A decreasing trend of $^{239+240}\text{Pu}$ concentrations in sediments from the offshore towards the northwest was also observed, which is similar to the direction of the YSWC. The measured ^{239}Pu and ^{240}Pu concentrations in surface sediment in this work are comparable to the reported values in the ECS and other marginal seas of the Pacific Ocean such as the Yellow Sea ($0.13 - 0.35\text{ Bq kg}^{-1}$, mean: 0.23 Bq kg^{-1}) (Nagaya and Nakamura, 1992) and the South China Sea ($0.16 - 0.79\text{ Bq kg}^{-1}$, mean: 0.50 Bq kg^{-1}) (Wu et al., 2014) but are much lower than the values observed in the Okinawa Trough ($1.4 - 2.5\text{ Bq kg}^{-1}$, mean: 1.8 Bq kg^{-1}) (Wang and Yamada, 2005) and the northwest Pacific Ocean ($0.15 - 5.4\text{ Bq kg}^{-1}$, mean: 2.4 Bq kg^{-1}) (Moon et al., 2003).

3.2 Distribution of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios and sources term of Pu in the ECS

The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment cores from the ECS (Fig. 2d) ranged from 0.158 ± 0.022 to 0.297 ± 0.042 (mean: 0.238 ± 0.036), which falls in between the global fallout value of 0.18 ± 0.02 (Krey et al., 1976) and PPG close-in fallout value of $0.33-0.36$ (Buesseler, 1997). The major inputs of Pu to this study area are likely derived from: 1) atmospheric fallout from global weapons testing, 2) the close-in fallout (tropospheric) in PPG, 3) riverine input from the erosion and leaching of soils, 4) emission from the nuclear reprocessing plants, 5) nuclear accidents (e.g. Chernobyl

and Fukushima accidents) and 6) transport of effluents from adjacent sea area (e.g., Yellow Sea).

3.2.1 The close-in fallout and emission from the nuclear power plants

From Figure 3, the distribution of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios were ~ 0.18 in Chinese (Zheng et al., 2009; Dong et al., 2010; Liu et al., 2013; Bu et al., 2014) and Japanese soils profiles (Muramatsu et al., 1999, 2003), which implies that the direct input from the close-in fallout from Semipalatinsk, Lop Nur nuclear tests and Chernobyl accidents did not result in any significant contribution to the source of Pu in these areas, due to their distinctive $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of 0.03-0.05 (Beasley et al., 1998), < 0.1 (Wu et al., 2010) and 0.31-0.40 (Boulyga et al., 1997), respectively. Considering fact that the the location of the ECS is far away from the any nuclear weapons tests sites, and the catchment of the rivers flowing into the ECS is also far from the Chinese weapons testing site, Pu contribution from the close-in fallout of the Chinese weapons testing appears to be negligible. There were 14 nuclear power reactors (as of August 2013) operating along the Chinese coast in the ECS. However, all Pu produced in the reactors are confined within the fuel elements, and there is no report on the leakage of nuclear fuel from any of these NPPs, and hence the contribution from the Chinese NPPs would be negligible.

3.2.2 Riverine input from the erosion and leaching of soils

The Yangtze River and the Yellow River discharge huge amounts of sediments to China's marginal seas and are the potential riverine sources of $^{239,240}\text{Pu}$ to the ECS. It has been reported that the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in both of these river catchments are 0.18 (Zheng et al., 2009; Dong et al., 2010; Bu et al., 2014) and that the riverine Pu contribution eventually originates from the global atmospheric fallout. Moreover, there are several small rivers that flow into the ECS from the Zhe-Min coast but the contributions from these rivers are likely negligible considering the relatively small amount of sediment discharge ($< 7 \times 10^6 \text{ ton yr}^{-1}$) and catchment area (e.g., the largest catchment of all smaller rivers, streams and tributaries is Min River catchment with an area of $61,000 \text{ km}^2$, CWRC, 2013). Because of very limited published Pu data in the Yangtze watershed, the reported river-borne input of $^{239+240}\text{Pu}$ has high uncertainty. Recently, some investigations of Pu isotopes in soils and sediments of the Yangtze River catchment (Liao et al, 2008; Dong et al., 2010; Bu et al., 2014) have been conducted, which enables us to obtain a better estimation of the river input of Pu. Smith et al. (1987) and Dominik et al. (1987) investigated several catchments and estimated the watershed residence time of Pu to be 800-3,000 yr. The Yangtze

catchment is one of the largest river catchments in the world and contains many dams (e.g., The Three Gorges Dam); therefore, we used the largest value of the range (3,000 yr) as the watershed residence time of Pu and the corresponding fractional erosional input of 0.023% ($= 100/(\ln 2 * 3,000 \text{ yr})$) of the total Pu in the drainage catchment eroded each year. The Yangtze River input of $^{239+240}\text{Pu}$ was calculated following the equation (modified from previous studies: Ravichandran et al., 1995; Baskaran et al., 1997):

$$I_{Pu} = A_d * I_f * f_e \quad (1)$$

where A_d is the area of the catchment ($1.8 \times 10^{12} \text{ m}^2$), I_f is the inventory of $^{239+240}\text{Pu}$ (Bq m^{-2}) and f_e is the fraction of the inventory of $^{239+240}\text{Pu}$ eroded each year (0.023%). The inventories of $^{239+240}\text{Pu}$ in soils of the Yangtze catchment listed in Table 1 range from 19.0 ± 1.6 to $114 \pm 6 \text{ Bq m}^{-2}$ (arithmetic mean: $59 \pm 35 \text{ Bq m}^{-2}$). The mean Pu input derived from the Yangtze River was calculated to be $(0.79 \pm 0.07) \times 10^{10}$ – $(4.7 \pm 0.2) \times 10^{10} \text{ Bq y}^{-1}$ (mean: $(2.4 \pm 1.4) \times 10^{10} \text{ Bq y}^{-1}$). The Yangtze River delivers approximately $1.3 \times 10^8 \text{ tons yr}^{-1}$ of terrestrial sediment to the ECS (CWRC, 2013). Therefore, the mean $^{239+240}\text{Pu}$ activity concentration in the suspended materials eroded from the drainage area was calculated to be 0.06 ± 0.01 – $0.36 \pm 0.02 \text{ Bq kg}^{-1}$ (mean: $0.18 \pm 0.10 \text{ Bq kg}^{-1}$). The mean value was close to the values of surface sediments near the Yangtze Estuary and Hangzhou Bay (Fig. 2). Considering the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios are ~ 0.18 in this area, we suggest that the Yangtze River input is the main source of Pu isotopes for the estuarine area in the ECS. Liu et al. (2011) also suggested that the dilution of riverine input played an important role in the distribution of Pu isotopes near the Yangtze Estuary. The magnetic minerals and particulate heavy metals in this area have also been reported to be from the Yangtze River input (Che et al., 2003; Liu et al., 2010). This is because $\sim 50\%$ of the Yangtze River-derived fine sediments were deposited near the Yangtze Estuary and Hangzhou Bay under cumulative action of delivery by the CDW and the barrier effect from the northward flowing TWC (Che et al., 2003; Liu et al., 2006). All these observations support that soil erosion in the Yangtze River catchment contributes the major fraction of Pu to the estuarine sediment.

3.2.3 Long-range transport from the PPG

Fukushima accident has been reported to have released a very small amount of Pu to marine environment (Zheng et al., 2012) and thus, the contribution from the long distance transport from Fukushima coastal waters to the ECS is assumed to be negligible. However, the Pu derived from the PPG transport has been suggested to be

an important source of $^{239+240}\text{Pu}$ (Lee et al., 2004; Zheng and Yamada, 2004; Wang and Yamada, 2005; Liu et al., 2011). The distribution of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in surface sediments (including sediment cores) and seawater (Fig. 3) around the NEC and KC pathway showed a similar variation pattern with a mean atom ratio of ~ 0.24 (e.g., Kim et al., 2004; Zheng and Yamada, 2004; Yamada et al., 2006). A strong signature of the PPG Pu was recorded in a natural coral of Guam site with a mean atom ratio of 0.31 (Lindahl et al., 2011). The spatial distribution of the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio coincided with the water mass distribution in the ECS, which apparently shows the influence of Pu transported from PPG by the KC and the TWC. These observations further support that Pu could be transported from the PPG into the ECS. As a particle-reactive nuclide in marine environment, some of the dissolved Pu in ECS can be removed from the water column into sediments by particle scavenging, after the advective lateral transport from the open ocean to the ocean margin (e.g., Scott et al., 1985; Zheng and Yamada, 2006).

The riverine input and global fallout $^{239+240}\text{Pu}$ can be regarded as one end-member considering their same $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios. The other end member is the Pu signature from PPG. A simple two end-member mixing model described by Krey et al. (1976) can be used to estimate the relative contribution of plutonium isotopes from global fallout and PPG in the ECS:

$$\frac{(Pu)_P}{(Pu)_G} = \frac{(R_G - R_E)(1 + 3.68R_P)}{(R_E - R_P)(1 + 3.68R_G)} \quad (2)$$

where (Pu) and R represent the $^{239+240}\text{Pu}$ activity concentration and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio, respectively. The subscripts P, G and E refer to the PPG, global fallout, and the ECS, respectively. The constant 3.68 is their ratio of their decay constant of $^{240}\text{Pu}/^{239}\text{Pu}$ which is used to convert the activity ratio to the atomic ratio. The value of R_G and R_P are 0.18 and 0.33-0.36, respectively (Krey et al. 1976; Buesseler, 1997). The calculated results showed that the contributions of Pu from the PPG to surface sediment of the ECS ranged from $< 1\%$ to $72\% \pm 7\%$ (mean: $41\% \pm 6\%$) if R_P is taken to be 0.36 and from $< 1\%$ to $82\% \pm 8\%$ (mean: $47\% \pm 7\%$) if $R_P = 0.33$. Apparently, the PPG input had a great influence on the sedimentary Pu in the ECS and is found to be the main source of Pu to the ECS.

3.3. Temporal Variations of Pu in the sediment cores in the ECS

The concentration of $^{239,240}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio in vertical profiles of Pu isotopes are given in supplemental file (Table A4). Strictly speaking, sedimentation rates estimated from gradients of $^{210}\text{Pb}_{\text{ex}}$ are valid only if the sedimentary deposition

did not change drastically within the hundred years, there was no change in the concentration of $^{210}\text{Pb}_{\text{ex}}$ depositional flux and there was no post-depositional mobility of ^{210}Pb . The sedimentary particles deposition in the ECS is indeed influenced by complex dynamic conditions, especially in a short time-scale, but over longer time scale (~60 yr), the sediment deposition could be assumed to be at steady state in this area (except in the Yangtze Estuary). The vertical profiles of five sediment cores (except for C1) generally showed exponential decrease with depth throughout the length of the cores (Table A3). Generally, the mass depth (g cm^{-2}) is plotted against $\ln(^{210}\text{Pb}_{\text{ex}})$ for each sediment core to calculate the mass accumulation rate ($\text{g cm}^{-2} \text{ y}^{-1}$), rather than the linear depth (cm) to overcome the effect of sediment compaction in a vertical sedimentary column. Since earlier results were published in linear sedimentation rate (cm y^{-1}), here we also have calculated the linear sedimentation rates, which are estimated to be: 0.77 ± 0.10 , 0.32 ± 0.03 , 0.38 ± 0.07 , 0.13 ± 0.01 and $0.13 \pm 0.02 \text{ cm y}^{-1}$ at E1, M7, B6, C12 and F8 sites, respectively (Fig. 4). C1 is located near the river mouth, where there is considerable reworking of mobile mud and surface sediments commonly undergoes erosion (Yang et al., 2011; Wang et al., 2016). Thus, the estimated sedimentation rate of the C1 core by $^{210}\text{Pb}_{\text{ex}}$ is less reliable and significantly lower than the reported value of 3.0 cm y^{-1} (Deng et al, 2006). However, the good linear correlation ($r > 0.84$) in the other five sediment cores suggests that those estimated sedimentation rates are relatively feasible though the resolutions of $^{210}\text{Pb}_{\text{ex}}$ profiles are not so high.

The depth corresponding to maximum $^{239+240}\text{Pu}$ activity concentration varied in these cores due to variable sedimentation rates. The relatively low sampling resolution of Pu in sediment cores prevented us from identifying the exact depth layer corresponding to 1963 Pu peak which would have resulted in getting better mean sedimentation rate. The penetration depths of Pu corresponding to 1952, when Pu fallout started from many high yield nuclear weapons tests starting from 1951 can be used as a chronological marker to determine independent sedimentation rates. The lowest $^{239+240}\text{Pu}$ concentrations measured in the bottom layers of cores E1, M7, B7, C12 and F8 (Fig. 5) are at levels comparable to the detection limits of $^{239+240}\text{Pu}$ (0.01 Bq kg^{-1}). As it has discussed above, Pu from the PPG can be transported into the ECS in less than one year (Wang and Yamada, 2005). Considering the uncertainty (1.5 cm) from sedimentary particle compaction during sub-sectioning and the transport time (1.0 yr) from the PPG to the ECS sediment, the mean sedimentation rates were estimated to be 0.78 ± 0.03 , 0.38 ± 0.03 , 0.35 ± 0.03 , 0.20 ± 0.03 and $0.14 \pm 0.02 \text{ cm y}^{-1}$ at

E1, M7, B6, C12 and F8, respectively. The atomic ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in deep layers of cores were found to be higher, especially in E1, B6 and F8 where it varied between 0.269 and 0.314 and decreased upward from the bottom. This tendency suggests that the PPG released Pu was diluted by the global fallout after 1960s and stronger signal from Pu fallout in the sediment cores supports $^{239+240}\text{Pu}$ -based sedimentation rates. However, $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in C12 (located in the north Okinawa Trough) were relatively lower. A previous study also reported the similar lower values in the upper layer of a sediment core in the same area (SST1, 0.21-0.26, Wang and Yamada, 2005), which may be attributed to another input source of Pu with lower $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio (e.g., terrestrial input) for C12. Previous studies have suggested that these fine sedimentary particles in the north Okinawa Trough were mostly derived from terrestrial input, including Yangtze input and finer particles from Taiwan (e.g., Oguri et al., 2003; Dou et al., 2010; Li et al., 2015). As discussed above, these terrestrial particles had a lower $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.18 and hence the lower $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio was also observed in the north Okinawa Trough.

The discernible concentration peak for ^{137}Cs corresponding to 1963 was not observed in six cores (Fig. 4). Utilizing the penetration depths of ^{137}Cs in C12 (4.5-6.5 cm) and F8 (4.5-6.5 cm), we estimate the sedimentation rates to be $0.09\pm0.05\text{ cm y}^{-1}$ at these two cores, which were much lower (>38%) than those based on $^{239+240}\text{Pu}$ and $^{210}\text{Pb}_{\text{ex}}$ in core C12 and F8. This is likely related to the longer residence time of ^{137}Cs in ocean water (Lee et al., 2004) and high mobility of ^{137}Cs in porewater. This very low value is less reliable due to the higher post-depositional mobility of ^{137}Cs related to its low K_d (< 500) in marine systems (Cochran et al., 1995; Delfanti et al., 2003; Wang et al., 2016). A number of studies have suggested that the post-depositional mobilization of ^{137}Cs results in a vertical movement of ^{137}Cs in marine sediment, which makes the ^{137}Cs penetration-based sedimentation rate problematic (e.g., Evans et al., 1983; Huh and Su, 1999; Foster et al., 2006). Considering the high sedimentation rate and short length of core C1 (42 cm), it is not possible to evaluate the sedimentation rate of C1 by $^{239+240}\text{Pu}$ or ^{137}Cs . There is a very good correlation ($r=0.98$, $p<0.01$) between $^{239+240}\text{Pu}$ -based and $^{210}\text{Pb}_{\text{ex}}$ -based sedimentation rates in the other five cores. The differences in the sedimentation rates obtained by these two methods differ generally by less than $\pm 16\%$ (within uncertainties), except in C12 ($35\%\pm 20\%$) which is attributed its low resolution of $^{239+240}\text{Pu}$ profile. But considering the high uncertainty, two methods also agrees well in core C12. Besides, the sedimentation rates estimated in this work using Pu isotopes are comparable to the

data published in literature (0.5 - 0.8 cm y⁻¹ for E1, 0.3 - 0.5 cm y⁻¹ for M7 and B6, 0.1 - 0.2 cm y⁻¹ for C12 and F8, Deng et al., 2006). In summary, ²³⁹⁺²⁴⁰Pu is a better time marker compared to ¹³⁷Cs to validate the ²¹⁰Pb_{ex} chronology in marine environment.

3.4. Inventory of Pu in the ECS sediment cores

The inventories of Pu (= ²³⁹Pu inventory + ²⁴⁰Pu inventory) and ²¹⁰Pb_{ex} were obtained from the activities in the measured layers and the interpolated activity for those layers where the radionuclides were not measured (inventory for a layer = activity in that layer (or interpolated activity for that layer) × mass depth of that layer). The total inventory in a sedimentary core is the summation of inventories in all of the individual layers in that core. The inventories of ²³⁹⁺²⁴⁰Pu and ²¹⁰Pb_{ex} were estimated to be 35.6±2.5, 118±5.0, 65.4±2.5, 58.3±4.6, 33.9±0.7, 1.9±0.1 Bq m⁻² for ^{239,240}Pu and 12.3±1.5, 14.9±2.1, 6.7±5.4, 13.1±1.2, 29.2±1.6, 3.2±0.9 kBq m⁻² for ²¹⁰Pb_{ex} at core C1, E1, M7, B6, C12 and F8, respectively. Combined with the previously reported data (Table 1), the ²³⁹⁺²⁴⁰Pu inventory in the ECS varied widely range from 1.90±0.06 to 807±7 Bq m⁻². Higher inventories, with two peak values in the Yangtze Estuary and the south Hangzhou Bay (Fig. 6), have been observed and are apparently higher than those expected from direct atmospheric deposition (36 - 42 Bq m⁻²) at 20 °N - 40 °N (Kelley et al. 1999); this is likely due to intense scavenging of particle-reactive radionuclides resulting from higher particle fluxes and likely due to sediment focusing in these two areas (Che et al., 2003; Huang et al., 2013). Both ²³⁹⁺²⁴⁰Pu and ²¹⁰Pb_{ex} inventories in core E1 were lower than the reported values in the same area during 1998 (Fig. 1, 420 Bq m⁻² and 21 kBq m⁻² for ²³⁹⁺²⁴⁰Pu and ²¹⁰Pb_{ex}, respectively; Su and Huh, 2002). There is steady sediment supply to the Zhe-Min coast carried by ZFCC each year, thus, the inventory reduction in the Zhe-Min coast was not likely caused by sediment erosion; instead, the notable sediment focusing indicated by the ²³⁴Th in this region may result in this reduction (Wang et al., 2016) in some areas and increased inventories in other areas, depending on the bottom water currents. However, the reduction of Yangtze sediment discharge has been suggested to lead to the erosion occurring in the Yangtze Estuary during past decade (Yang et al., 2011). In Yangtze Estuary, the erosion is likely one of the important reasons for the reduction in the sedimentary ²³⁹⁺²⁴⁰Pu inventory, from 807 Bq m⁻² obtained in 1997 (BC16, Su and Huh, 2002) to ~400 Bq m⁻² obtained in 2006 (station 18 and SC07, Liu et al., 2011; Pan et al., 2011).

3.5 The mass balance of Pu in the ECS sediments

The sources of Pu buried in the ECS potentially include Yangtze River input,

global fallout in ECS, PPG input and the Pu derived from land areas adjoining the ECS watersheds. A simple mass balance was used to estimate the contribution of Pu from different sources. The total surface area of ECS corresponding to the $^{239+240}\text{Pu}$ inventories was estimated by Google Earth to be $3.28 \times 10^{11} \text{ m}^2$. The inventory of $^{239+240}\text{Pu}$ from global fallout was reported to be 36 Bq m^{-2} between 20°N and 30°N and 42 Bq m^{-2} between 30°N and 40°N (UNSCEAR, 2000); here we used the mean value ($39 \pm 4 \text{ Bq m}^{-2}$) and estimated the total global Pu (direct atmospheric deposition) in the ECS to be $(1.3 \pm 0.1) \times 10^{13} \text{ Bq}$. Using the arithmetic mean value of the $^{239+240}\text{Pu}$ inventory in four segments of the ECS (details are shown in supplemental file), the total buried Pu was estimated to be $(3.1 \pm 1.4) \times 10^{13} \text{ Bq}$. In order to estimate the PPG contribution Pu to sediment column of the ECS, the mean value of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment cores were calculated by: the total inventory of $^{239+240}\text{Pu}$ multiplied the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in each layer and divided by the sum of $^{239+240}\text{Pu}$ inventory in each layer (Zheng and Yamada, 2004). The mean atom ratios range from 0.223 ± 0.016 to 0.302 ± 0.012 (geometric mean: 0.247 ± 0.021) (Table 2). Then the Pu contribution from the PPG input was estimated to be $45\% \pm 4\%$ ($R_p=0.36$) - $52\% \pm 4\%$ ($R_p=0.33$) based on the geometric value (0.247 ± 0.021) of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio. The PPG input was estimated to be $(1.4 \pm 0.7) \times 10^{13}$ - $(1.6 \pm 0.7) \times 10^{13} \text{ Bq}$ by total Pu $\times$ Pu fraction of Pu derived from PPG. Moreover, the total inventory of the Yangtze input of $^{239+240}\text{Pu}$ during 61 years (1952-2013) was estimated to be $(0.15 \pm 0.08) \times 10^{13} \text{ Bq}$ based on the annual input rate from Yangtze River of $(2.4 \pm 1.4) \times 10^{10} \text{ Bq}$. Besides, we can observe that there was other source of Pu in the ECS with value of $(0.06 \pm 1.4) \times 10^{13}$ - $(0.28 \pm 1.4) \times 10^{13} \text{ Bq}$, characterized by the global fallout $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio. Previous studies (Liu et al., 2003) had suggested that the finer part of sedimentary material of the Yellow River could be transported southward into the ECS, especially influenced by the strong southward coastal current during winter. Dai et al. (2011) reported that a small portion of sediment in the North Jiangsu coast could be transported into the north branch of the Yangtze River driven by the NJCC and then entered the ECS. Meanwhile, the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in Lanzhou (the Yellow River catchment) and the North Jiangsu tidal flats were also reported to be ~ 0.18 (Zheng et al., 2009; Liu et al., 2013). The errors associated with these estimates are high and hence we will not be able to assess if there is another small source/sink of Pu from Yellow Sea to the study area. Even if there is some small input from Yellow Sea, it is that the input will vary spatially within the ECS. Finally, we attempted to construct a mass balance (Fig. 7) of sedimentary $^{239+240}\text{Pu}$ for sediment in

the ECS. Although the Yangtze River input is the important Pu source for the estuary area of the Yangtze River, it is relatively small compared to the entire inventory of Pu in the ECS, and the dominant contribution of $^{239+240}\text{Pu}$ to the ECS remains from the PPG by the KC.

The TWC and the KC bring abundant high-salinity water to the ECS, with water volume of $7.9 \times 10^{14} \text{ m}^3 \text{ y}^{-1}$ and $4.1 \times 10^{13} \text{ m}^3 \text{ y}^{-1}$, respectively (Kagimoto and Yamagata, 1997; Su, 2001). The mean $^{239,240}\text{Pu}$ activity in the upper 200 m of sea water in the northeast of the Taiwan Island and near the KC was reported to be $3.3 \pm 2.7 \text{ mBq m}^{-3}$ (CB-11; 25.24°N , 124.52°E ; Nagaya and Nakamura, 1992), a value that is comparable to the mean value over two decades of surface water in the western Pacific Ocean ($2.4 - 3.6 \text{ mBq m}^{-3}$, Povinec et al., 2005). Using the mean $^{239,240}\text{Pu}$ activity (3.3 mBq m^{-3}) and multiplying the total flow of the KC and TWC for 61 years (1952-2013), we can roughly estimate that $(1.6 \pm 1.3) \times 10^{14} \text{ Bq } ^{239+240}\text{Pu}$ passed through the ECS by the KC and TWC during the past six decades. Therefore, the buried $^{239+240}\text{Pu}$ in sediments of ECS accounted for $8.8\% \pm 8.3\% - 10.0\% \pm 9.2\%$ of the total $^{239+240}\text{Pu}$ transported by the KC and TWC into the ECS. It should be noted that $^{239+240}\text{Pu}$ concentration in the KC seawater might be much higher in 1950's than the present value; and these reported values in the seawater column might not include the particle associated Pu, so the estimation reported here might be an upper limit.

Ocean-derived particulate matter containing Pu have been reported in the estuarine and coastal waters. For example, a significant fraction of Pu in estuarine bottom sediments of the Savannah estuary was attributed to oceanic sources rather than river-borne sources (Olsen et al., 1989). Peirson et al. (1982) observed an excess of $^{239,240}\text{Pu}$ in sediments along the British coast and attributed to have been derived from the Sellafield. In addition to the ECS, long-distance transport of oceanic input Pu also plays a vital role on the Pu mass balance in other marginal seas of Western Pacific, like the South China Sea, Yellow Sea, North Sea, Sagami Bay, etc (Kim et al., 2004; Zheng and Yamada, 2004; Yamada et al., 2006; Wu et al., 2014). If we establish a correlation between Pu isotopes (with specific $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios) and other particle-reactive radionuclides such as ^{210}Pb , ^{230}Th , ^{231}Pa , and other particle-reactive organic and inorganic species, the fraction of these species derived from long-transport can be estimated. For example, except the abnormal value in C12 (with very high $^{210}\text{Pb}_{\text{ex}}$ inventory of $29.2 \pm 1.6 \text{ kBq m}^{-2}$), the inventories (Bq m^{-2}) of $^{239+240}\text{Pu}$ and $^{210}\text{Pb}_{\text{ex}}$ in other five sediment cores of the ECS showed a linear relationship between them: $[^{210}\text{Pb}_{\text{ex}}] = (123 \pm 38) \times [^{239+240}\text{Pu}] + (4282 \pm 1852)$ ($r = 0.88$,

p=0.05). Using this equation and PPG input $^{239+240}\text{Pu}$, we can roughly estimate that the oceanic $^{210}\text{Pb}_{\text{ex}}$ input into the ECS from the same region to be $(1.7\pm 1.0) \times 10^{15} - (2.0\pm 1.1) \times 10^{15} \text{ Bq}$, which is close to the previous estimated result ($1.2 \times 10^{15} \text{ Bq}$, Su and Huh, 2002). Therefore, the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio can not only be used to obtain a better insight of the biogeochemistry influenced by the KC, but also used to trace the long-range transport of other particle-reactive radionuclides, organic and inorganic species in the aqueous system where the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios are distinct from the global fallout ratio (0.18).

5. Conclusion

The $^{239, 240}\text{Pu}$ activity concentrations in the ECS surface sediments ranged between 0.048 and 0.492 Bq kg^{-1} (mean: $0.188 \pm 0.007 \text{ Bq kg}^{-1}$). The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in the ECS, ranging from 0.158 to 0.297 (mean: 0.234 ± 0.024), were mostly higher than the global fallout value of 0.18 and were lower than the signature value (0.36) of the PPG, which indicates a finite fraction of Pu from PPG input to the ECS. The sedimentation rates estimated from the penetration depths of $^{239+240}\text{Pu}$ were similar to the values based on $^{210}\text{Pb}_{\text{ex}}$ at cores E1, M7, B6, C12 and F8. Considerable movement of ^{137}Cs in marine sediments has been widely documented and hence, $^{239+240}\text{Pu}$ can be used as a better chronostratigraphic time marker in marine environment.

The estimated $^{239+240}\text{Pu}$ concentration in the suspended material in the Yangtze River catchment (0.18 Bq kg^{-1}) is within the range of the values found in the Yangtze Estuary sediments, and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios are ~ 0.18 , which indicates that the Yangtze River input dominates as the source of Pu in the ECS estuary area. The estimated PPG input of $^{239+240}\text{Pu}$ is $(1.4-1.6)\times 10^{13} \text{ Bq}$ over a period of 6 decades, which accounts for 45%-52% of the total Pu estimated in the entire ECS and the scavenging ratio of the total $^{239+240}\text{Pu}$ transported by the KC and TWC into ECS sediments is estimated to be $\sim 10\%$. These Pu inputs were mainly deposited in coastal and shelf regions via scavenging process. $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio can not only be used to obtain a better insight of the biogeochemistry influenced by the KC, but also be potentially used to trace the long-range transport of other particle-reactive species.

Acknowledgements

This research was supported by the Ministry of Science and Technology of PR China (2011CB409801), the U.S. National Science Foundation (OCE-1237059), the China Scholarship Council (No. 201406140049) and the Fund of ECNU for Overseas Scholars. One of the authors, Mark Baskaran, is thankful for the support from the “High-end Foreign Experts Recruitment Program” sponsored by the State

Administration of Foreign Affairs (P. R. China). We also wish to thank Editor, Dr. Martin Frank and two anonymous reviewers for their constructive comments for improvement of the original manuscript.

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Figure Captions

Figure 1 Location of sites occupied during the August cruise tracts in 2013 (surface sediment in blue and sediment core in purple). Several sediment cores from literature are marked in red color (6, BC16, Su and Huh, 2002; 18, Liu et al., 2011; SC07, Pan et al., 2011). Bathymetry (m) of the ECS shelf is also shown by grey lines. The summer regional surface currents are modified after Su, 2001 and Hu et al., 2015: Changjiang diluted water (CDW); Zhejiang-Fujian Coast Current (ZFCC); North Jiangsu Coast Current (NJCC); Yellow Sea Coastal Current (YSCC); Yellow Sea Warm Current (YSWC); Taiwan Warm Current (TWC); Kuroshio Current (KC); North Equatorial Current (NEC); Mindanao Current (MC). Several rivers are also plotted, including a: Yellow River (5460 km), b: Yangtze River (6400 km), c: Qiantang River (459 km), d: Jiao River (198 km), e: Ou River (388 km), f: Min River (577 km).

Figure 2 Spatial distribution of the ^{239}Pu , ^{240}Pu , $^{239+240}\text{Pu}$ activities and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of surface sediment in August of 2013.

Figure 3 The synthesis of $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in the areas surrounding the ECS: Chinese and Japanese soil (black color, Muramatsu et al., 1999, 2003; Zheng et al., 2009; Dong et al., 2010; Liu et al., 2013; Bu et al., 2014), sediment (red color, This study; Buesseler, 1997; Zheng and Yamada, 2004; Wang and Yamada, 2005; Liu et al., 2011; Wu et al., 2014), seawater (blue color, Kim et al., 2004; Yamada et al., 2006) and a natural coral (orange color, Lindahl et al., 2011).

Figure 4 Distribution of $\ln(^{210}\text{Pb}_{\text{ex}})$ and ^{137}Cs activities in sediment cores collected from the ECS at six stations: estuary (C1), South inshore (E1), North offshore (M7, B7), and Okinawa Trough (C12, F8).

Figure 5 $^{239+240}\text{Pu}$, and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment cores collected from the ECS at six stations.

Figure 6 Spatial distribution of $^{239+240}\text{Pu}$ inventories in sediment, including literature data (Nagaya and Nakamura, 1992; Su and Huh, 1999; 2002; Wang and Yamada, 2005; Pan et al., 2011; Liu et al., 2011).

Figure 7 The mass balance of $^{239+240}\text{Pu}$ in sediment in the ECS. The PPG input and additional source are estimated to be $(1.4 \pm 0.7) \times 10^{13}$ - $(1.6 \pm 0.7) \times 10^{13}$ Bq and $(0.06 \pm 1.4) \times 10^{13}$ - $(0.28 \pm 1.4) \times 10^{13}$ Bq, respectively, with mean values plotted in this figure. The errors associated with this additional source are high and hence we will not be able to assess if this additional source is a source or sink of Pu to the ECS.

Fig 1

Fig 2

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Fig 7

Table 1

Inventories of ^{239}Pu , ^{240}Pu , $^{239+240}\text{Pu}$ and the mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment cores from the Yangtze River catchment.

Sample	Longitude (E)	Latitude (N)	²³⁹⁺²⁴⁰ Pu (Bq m ⁻²)	²⁴⁰ Pu/ ²³⁹ Pu	²³⁹ Pu (Bq m ⁻²)	²⁴⁰ Pu (Bq m ⁻²)	References
Southwest China							
GY	106.67	26.66	63.0 ± 2.4	0.191 ± 0.010	37.0 ± 2.3	26.0 ± 2.3	Bu et al., 2014
WL	107.85	29.52	114 ± 6	0.185 ± 0.004	67.9 ± 5.8	46.1 ± 3.4	
ZX	107.85	30.53	19.0 ± 1.6	0.182 ± 0.008	11.4 ± 1.6	7.6 ± 1.0	
Central China							
DK	112.19	31.15	44.9 ± 5.9	0.183 ± 0.052	26.9 ± 5.0	18.0 ± 7.5	Dong et al., 2010
GLZ	111.42	32.24	54.6 ± 4.4	0.200 ± 0.013	31.5 ± 4.2	23.1 ± 3.4	
Atmospheric fall		20-30	36.0	0.180	21.7	14.3	Kelley et al. 1999; UNSCEAR, 2000
		30-40	42.0		25.3	16.7	

Table 2

Inventories of ^{239}Pu , ^{240}Pu , $^{239+240}\text{Pu}$ and the mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in sediment cores from the ECS.

Sample	Longitude (E)	Latitude (N)	Water depth (m)	²³⁹⁺²⁴⁰ Pu (Bq m ⁻²)			²⁴⁰ Pu/ ²³⁹ Pu			²³⁹ Pu (Bq m ⁻²)			²⁴⁰ Pu (Bq m ⁻²)			References
Estuary	122-124	30-32	23-58 (42)	48.5-807 (245)**												*Su and Huh, 2002
Inner shelf	120-124	26-30	26-84 (55)	81.7-420 (221) **												
Outer shelf	122-124.5	26-32	55-67 (61)	50.1-117 (83.3) **												
Slope	124.5-125	28.5-29.5	232-1053 (735)	16.7-93.3 (43.7) **												
CB-7-2	125.37	25.78	2170	8.9	±	0.3										*Nagaya and Nakamura, 1992
CB17	123.50	28.50	65	79.9	±	2.2				No data reported						
CB23	123.51	32.50	42	77.4	±	1.4										
CB34	123.50	33.00	37	53.8	±	1.3										
CB35	123.50	33.50	64	16.2	±	0.3										
G2	126.74	28.00	999	32.5	±	2.3	0.245	±	0.017	17.1	±	1.2	15.4	±	1.1	Wang and Yamada, 2005
PN3	127.35	28.10	1000	47.2	±	3.1	0.258	±	0.018	24.2	±	2.3	23.0	±	1.1	
SST1	127.38	28.38	1080	47.0	±	2.3	0.230	±	0.012	25.5	±	1.2	21.5	±	1.2	
PN5	126.43	28.80	127	101	±	5	0.263	±	0.014	51.2	±	3.2	49.5	±	2.1	
PN8	125.09	29.59	87	60.9	±	4.4	0.254	±	0.016	31.5	±	2.3	29.4	±	1.6	
PN12	123.08	31.20	50	81.5	±	3.6	0.242	±	0.010	43.2	±	2.1	38.3	±	1.5	This study
C1	122.35	30.90	13	35.6	±	2.5	0.223	±	0.016	19.6	±	2.0	16.0	±	1.6	
E1	121.80	28.21	22	118	±	5	0.280	±	0.013	58.3	±	3.3	59.6	±	3.7	
M7	124.03	33.23	66	65.4	±	2.5	0.225	±	0.010	35.8	±	1.7	29.5	±	1.8	
B6	125.77	31.03	62	58.3	±	4.6	0.236	±	0.018	30.7	±	2.6	27.7	±	3.7	
C12	127.07	28.12	998	33.9	±	0.7	0.243	±	0.012	18.2	±	0.4	15.7	±	0.6	
F8	122.60	25.53	619	1.90	±	0.06	0.302	±	0.012	0.91	±	0.04	1.00	±	0.04	
SC07	122.38	31.00	14	407	±	27	0.242	±	0.023	216	±	25	191	±	31	Pan et al., 2011
18	122.50	31.00	20	388	±	21	0.237	±	0.011	208	±	20	180	±	18	Liu et al., 2011

*: The Pu inventories ($^{239,240}\text{Pu}$) reported in these two preferences were calculated based on the combined activity of ^{239}Pu and ^{240}Pu , as alpha spectrometry method yields $^{239,240}\text{Pu}$ activity due to overlapping alpha energies of ^{239}Pu and ^{240}Pu .

** : A total of 32 inventory samples from Su and Huh (2002) in the ECS are included. For a complete inventory distribution in the ECS, see Table A5.