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Vertical distributions and source identification of the radionuclides ^{239}Pu and ^{240}Pu in the sediments of the Liao River estuary, China

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ABSTRACT

Activity concentration of plutonium (Pu) and its isotopic compositions are extensively used for measuring transport processes of Pu and identifying its source. We investigated the spatial distribution characteristics of $^{239+240}$Pu activity concentrations and ^{240}Pu/^{239}Pu atom ratio in several sediment cores collected from the Liao River coastal zone. Additionally, we calculated the $^{239+240}$Pu inventories and based on the ^{240}Pu/^{239}Pu atom ratio to trace Pu source. The activity concentrations of $^{239+240}$Pu in surface sediments of the Liao River estuary ranged between 0.103 ± 0.008 and 0.978 ± 0.035 mBq/g, with an average of 0.294 ± 0.024 mBq/g. The ^{240}Pu/^{239}Pu atom ratios, ranging from 0.173 ± 0.047 to 0.215 ± 0.061 (mean: 0.188 ± 0.049 (1σ)), were consistent with global fallout value, which indicates the global atmospheric fallout is the main source of Pu in sediment cores from the both sides of Liao River estuary. As for the tidal flat core LT-2, the mean ^{240}Pu/^{239}Pu atom ratio, slightly higher than that of the global fallout value, was 0.217 ± 0.050. Such pattern of Pu isotopic compositions indicated that Pu on the tidal flat in the Liao River estuary is sourced from a combination of global fallout and close-in fallout from the PPG by ocean currents transporting. And by using a two end-member mixing model, the results indicate the relative contribution of the PPG close-in fallout to core LT-2 is round 27% and 73% can be attributed to global fallout and river input. Therefore, these results clearly indicate that the direct global fallout is the main source of Pu in the Liao River estuary.

1. Introduction

Anthropogenic radionuclides play important roles as tracers for various physical and biogeochemical ocean processes (Livingston and Povinec, 2002; Lindahl et al., 2010) and can be used for reconstruction of the historical environmental information (Wang et al., 2017). Therefore, in the past several decades, anthropogenic radionuclides in sediments and waters in the marginal seas, coastal areas, tidal flats, rivers, estuaries and lakes of the world have been extensively investigated in order to analyze the artificial radionuclide's inputs and redistributions, to elucidate their source terms, to rebuild the historical pollution events, to evaluate the various marine processes, and to assess their environmental behavior and impacts (Huh and Su, 1999; Lind et al., 2006; Zheng and Yamada, 2004, 2008; Tims et al., 2010; Hancock et al., 2011; Liu et al., 2011, 2013; Pan et al., 2011; Liao et al., 2014; Wu et al., 2014; Wang et al., 2017). Furthermore, the distribution of artificial radionuclides can be modeled to derive rates of ocean transport on timescales not attainable by direct measurement. Since the input histories of anthropogenic radionuclides to the environment are well known, it enables us to trace large-scale (circulation, sedimentation and biological productivity) and small-scale (near shore) oceanic processes and predict future climate change processes and their impact on the marine environment (Lindahl et al., 2010).

As anthropogenic radionuclides, $^{239+240}$Pu have been introduced into the environment since the nuclear era in the early 1940s through a variety of human activities (such as above ground nuclear weapons testing) (Harley, 1980; Sholkovitz, 1983), reprocessing plants of nuclear materials (Kershaw et al., 1995; Dai et al., 2002) and nuclear accidents releases (Hirose and Sugimura, 1990; Zheng et al., 2012). ^{239}Pu and ^{240}Pu have high toxicity and internal radiation threat and long-half-lives isotopes (half-lives 2.4×10^4 and 6.5×10^3 years) when released into the environment. In addition, the relative

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abundances of Pu isotopes, typically ^{240}Pu and ^{239}Pu, can be used to trace the specific Pu source because Pu isotopic ratios vary with reactor type, weapon type, neutron flux and energy, nuclear fuel burn-up time, and fallout from nuclear detonations (Dai et al., 2001). The mean ^{240}Pu/^{239}Pu atom ratio of global fallout is 0.18 ± 0.02 (Krey et al., 1976; Kelley et al., 1999). Weapons-grade Pu has a lower ^{240}Pu/^{239}Pu atom ratio (0.01–0.07) (Lindahl et al., 2011), while reactor-grade Pu has ^{240}Pu/^{239}Pu atom ratios ranging from 0.2 to 1.0 depending on the fuel burn-up (Warneke et al., 2002). The ^{240}Pu/^{239}Pu atom ratio of close-in fallout from the Pacific Proving Grounds (PPG) in the Marshall Islands is higher (0.30–0.36) than that of global fallout (Koide et al., 1985; Buesseler, 1997; Muramatsu et al., 2001). It has been indicated that Pu from the PPG can be transported long distances in the western Pacific Ocean and into its adjacent marginal seas by the North Equatorial Current and the Kuroshio current, thus impacting the northwestern Pacific Ocean (Lee et al., 2004; Zheng and Yamada, 2004, 2006b; Yamada et al., 2006), the East China Sea (Wang and Yamada, 2005; Liu et al., 2011; Wang et al., 2017), the South China Sea (Wu et al., 2014) and the Yellow Sea (Nagaya and Nakamura, 1992). Nagaya and Nakamura (1992) observed excess Pu in an amount higher than the fallout input in the estuary, and they attributed the lateral distribution to the supply of Pu by the Yangtze River. Tims et al. (2010) implied that much of the Pu was scavenged from seawater by particulates after they entered the estuary and before they were deposited. However, previous studies also suggested that much of the ^{137}Cs in the estuary was from riverine transport, and ^{137}Cs and Pu had different scavenging properties in the estuary (Nagaya and Nakamura, 1992; Huh and Su, 1999). The scavenging rate of Pu in the marine environment depends on the amount of particulate matter, the settling rate of particles, mixing processes and biogeochemical processes (Lindahl et al., 2010). It is reasonable to expect that the riverine source and PPG source of Pu have a complex exchange process which may be controlled by water and sedimentation dynamics in the estuary (Olsen et al., 1989). Therefore, the Pu transport processes and the source of Pu in the estuary are still a controversial issue. It is necessary to evaluate the relative contributions of the PPG and riverine source of Pu in the sediments in this area. However, the spatial distribution characteristics, migration path, the relative contributions of the PPG source and riverine source of Pu to the total budget in the sediments of the Liao River estuary have not been completely clear.

The research report related to the source of Pu in the Liao River estuary has not come about yet. In the present paper, the Pu isotopes in seven sediment cores collected from the Liao River coastal zone were subjected to analyze the distribution characteristics of $^{239+240}$Pu activity concentrations and ^{240}Pu/^{239}Pu atom ratio. We also calculated the $^{239+240}$Pu inventories and based on the ^{240}Pu/^{239}Pu atom ratios to trace Pu source. The work fills in a gap of artificial radionuclides which has hitherto existed in the major river systems of China.

2. Materials and methods

2.1. Study area

Liao River (121°33′-122°36′E, 40°26′-41°27′N) is the principal river located in the northern Liaodong Bay of the Bohai sea and is one of the seven major river systems in mainland China (Fig. 1). The river is also popularly known as the “mother river” in Northeast China. Coursing 1396 km long, Liao River system drains a catchment basin of over 2.19×10^5 km^2, but its mean discharge is only about 500 m^3/s. The Liao River originates as two stems in the west: the Laoha River in southeastern Inner Mongolia, the Xinkai River (dry in its upper reaches except after thunderstorms) furthers north and the Hulin River (which almost never reaches the main stem of the river) in the extreme northwest of Liaoning. The eastern branch of the river is known as the Dongliao River and rises in low mountains in central Liaoning. The two stems of the river meet near the junction of Liaoning, Jilin and Inner Mongolia and flow across a vast plain to the Bohai Gulf. Two major tributaries of the river, the Hun River and the Taizi River, which flow down from the Qianshan, used to flow into the Liao River shortly before it flows into the sea. The Liao River has an exceedingly high sediment load because many parts of it flow through powdery loess. Along with the increasing activities of human beings, the sedimentary environments have been changing all the time, posing serious problems at present in the aspects of ecology and economy in the Liao River estuary.

2.2. Sample collection

The sample collection stations are shown in Fig. 1. The sampling sites in this paper revolve around the main vegetation (*Suaeda heteroptera Kitag* and *Phragmites*) on both sides of the Liao River. Six sediment samples were collected using a box corer from the two sides of the Liao River and a sediment core was collected from the tidal flat in the Liao River estuary in October 2012 and April 2015, respectively. Longitudes, latitudes, sampling date, sample depths and the main vegetation at the stations are presented in Table 1. The sediment cores are subsampled at 2–5 cm intervals. The bulk of the samples were then dried at 80 °C and ground in an amber mortar in preparation for Pu isotopic analysis. All the sediment samples are taken to the Ministry of Education Key laboratory of Coastal and Island Development in Nanjing University for Pu isotopic analysis.

2.3. Analysis of Pu isotopes in samples

Details about sample pretreatment, chemical separation and purification for Pu isotopes determination were described elsewhere (Zheng and Yamada, 2006b; Bu et al., 2014). The sediment samples were dried at 110 °C for at least 4 h. Approximately 2–5 g (depending on the activity concentrations level of plutonium deduced from the case of ^{137}Cs) were weighed out, and spiked with ^{242}Pu (ca. 1 mBq) as a chemical yield tracer. The extraction of Pu from the sediment samples was performed using 8M HNO_3 on a hot plate (180–200 °C) for at least 4 h. Then a two stage anion-exchange chromatography method using AG 1X8 and AG MP-1 M resins was used for the separation of Pu from the sample matrix and the further purification of Pu. The residue was finally dissolved and diluted to 2 ml using 0.5 mol/L HNO_3 media for the determination of Pu isotopes. The measurement of Pu isotopes (^{239}Pu, ^{240}Pu, ^{242}Pu) was performed at Soochow University by a section field ICP-MS (SF-ICP-MS) (Element 2, Thermo Scientific, Bremen, Germany). The SF-ICP-MS was equipped with an APEX-Q high efficiency sample introduction system (Elemental Scientific Inc, Omaha, NE, USA) combined with a membrane desolvation unit (ACM) and a conical concentric nebulizer (Zheng and Yamada, 2006a). All the measurements were made in the self-aspiration mode with an uptake rate of ~0.2 ml/min to reduce the risk of contamination from the peristaltic pump tubing. 0.1 ng/ml U standard solution was used for the optimization of SF-ICP-MS before the samples were measured each time. The detection limit for the determination of Pu was as low as 0.14 fg/ml.

3. Results and discussion

3.1. Spatial distribution of Pu in the surface sediments in the Liao River estuary

As for the surface sediment samples (0–5 cm) from the Liao River estuary, the activity concentrations of $^{239+240}$Pu and the ^{240}Pu/^{239}Pu atom ratios are given in Fig. 2. The activity concentrations of $^{239+240}$Pu in surface sediments of the investigated area ranged from 0.103 ± 0.008 to 0.978 ± 0.035 mBq/g (mean: 0.294 ± 0.024 mBq/g (1σ)) (Fig. 2a). The lowest $^{239+240}$Pu activity concentration (0.103 ± 0.008 mBq/g) was found at the sediment core LT-2, while the highest (0.978 ± 0.035 mBq/g) was observed at the sediment core