Short communication

Mercury profiles in sediments of the Pearl River Estuary and the surrounding coastal area of South China

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ABSTRACT

The spatial and temporal variations of mercury (Hg) in sediments of the Pearl River Estuary (PRE) and the surrounding coastal area (South China Sea) were studied. In surface sediments, the concentrations of Hg ranged from 1.5 to 201 ng/g, with an average of 54.4 ng/g, displaying a decreasing trend with the distance from the estuary to the open sea. This pattern indicates that the anthropogenic emissions from the Pearl River Delta (PRD) region are probably the main sources of Hg in this coastal region. Using the ²¹⁰Pb dating technique, the historical changes in the concentrations and influxes of Hg in the last 100 years were also investigated. The variations in Hg influxes in sediment cores obviously correlate with the economic development and urbanization that has occurred the PRD region, especially in the last three decades.

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1. Introduction

The biogeochemistry of mercury (Hg) in coastal and estuarial environments has been widely studied because of the high toxicity and biomagnification of this chemical element in the aquatic system (Mason et al., 1996; Horvat et al., 1999; Hines et al., 2000; Conaway et al., 2003; García-Rico et al., 2006). However, the biogeochemical cycles of Hg in different estuaries are variable and complicated due to the diverse input, physical, chemical, and hydrological conditions of Hg. As a result, the behavior of Hg may differ from one estuary to another (Horvat et al., 1999; Conaway et al., 2003).

China plays an important role in global anthropogenic Hg emissions. Hg emissions in China were estimated to total approximately 696 tons in 2003, with an average rate of increase of 2.9% per year during the period 1995–2003 (Wu et al., 2006). A large amount of the Hg emissions obviously correlates with the rapid economic development that has taken place in the region during the last three decades. The increase in emissions of Hg has also caused the air, water, and soil in China to become seriously polluted (Feng, 2005; Jiang et al., 2006).

The Pearl River Estuary (PRE), located in south China, is created by the inflows of fresh water to the South China Sea. The estuary covers an area of 8000 km², with the distance from north to south averaging about 49 km, and from east to west varying from 4 to 58 km (Zhang et al., 2003; Ip et al., 2004). The PRE has been found to be contaminated by a number of metal and organic pollutants, a result of the rapid urbanization and industrialization that has been occurring in the Pearl River Delta (PRD) region during the last a few decades (Hong et al., 1999; Fu et al., 2003; Ip et al., 2005; Liu et al., 2005; Mai et al., 2005; Chen et al., 2006). The PRD region, consisting of part of Guangdong Province as well as China's two special administrative regions of Hong Kong and Macao, is known as one of the most industrialized and urbanized regions in China. A large number of factories have been set up in the PRD region to produce a wide range of goods, including electronic products, medicines, cars, toys, clothing, and others. In 2002, exports from the PRD accounted for 35% of China's total exports (Streets et al., 2006). Without effective treatment, the pollutants from the PRD would enter the PRE through direct discharge or with the run-off of river water. Several studies have demonstrated that PRE is the main reservoir of persistent organic pollutants, such as OCPs, PAHs, PCBs, and PBDEs (Chen et al., 2006; Guan et al., 2007, 2009). An estimated 23 metric tons of PBDEs have been discharged into the PRE in the

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last 20 years (Guan et al., 2007). Meanwhile, high concentrations of trace metals have also been found in the sediments and aquatic organisms of the PRE (Ip et al., 2005, 2006). However, Hg has largely been ignored in most studies of pollutants in the region, and thus the extent to which the PRE is contaminated with Hg is still unknown. Our previous investigation in Victoria Harbour, a part of the PRE, showed that the total Hg concentrations in surface sediments ranged from 47 to 855 ng/g (dry wt.), indicating the possible contamination of Hg in this area (Shi et al., 2007).

The aim of the present work was to study the spatial and temporal distribution of Hg in sediments of the PRE and its surrounding coastal area. Using the ^{210}Pb dating technique, the historical changes in the concentrations and influxes of Hg in the last 100 years were also investigated.

2. Materials and methods

2.1. Sample collection

The map of the study area and the locations of the sampling sites are shown in Fig. 1. A total of 39 surface sediment samples were collected in September 2002. The

sampling locations were distributed across the PRE and its surrounding coastal area. The surface sediments (top 10 cm) were taken with a stainless steel grab sampler. Three sediment cores were also collected in this area in June 2000. The core sediments were taken using a gravity corer with an automatic clutch and reverse catcher. The diameters of the outside steel corer and the inside sampling PVC coring tube were 56 and 46 mm, respectively. The sediment cores were sliced into 2 cm intervals from 0 to 50 cm and into 4 cm intervals from 50 cm to the end of the cores.

All of the samples were stored in polyethylene bags at $-45\text{ }^{\circ}\text{C}$ immediately after collection. In the laboratory, the sediments were freeze-dried at $-45\text{ }^{\circ}\text{C}$ for 3 days and then ground in an agate grinder until fine particles were obtained.

2.2. Determination of Hg in sediments

To analyze the total amount of Hg present in the samples, about 0.25 g of grounded sediment samples were digested with 5 mL of aqua regia in an AIM 500 Automated Block Digestion System (A.I. Scientific Pty Ltd, Australia) at $95\text{ }^{\circ}\text{C}$ for 2 h and shaken frequently. After cooling down, the solutions were diluted to 25 mL with Milli-Q water and then centrifuged at 3000 rpm for 15 min. The Hg concentrations were determined by the Flow Injection Mercury System (FIMS, Perkin Elmer) using SnCl_2 for the reduction step.

For the analytical quality control, reagent blanks, certified reference materials (CRMs), and sample replicates were randomly inserted in the analysis. The determined concentrations of Hg in two sediment CRMs ($36 \pm 2\text{ ng/g}$ in NIST 1646a and $282 \pm 8\text{ ng/g}$ in GBW07310, $n = 4$) were both in good agreement with their certified

Fig. 1. Map of the study area.

Fig. 2. The spatial distribution of Hg in surface sediments.

values (40 ng/g in NIST 1646a and 280 ± 40 in GBW07310), indicating the method was accurate and reliable.

2.3. ^{210}Pb dating

The ^{210}Pb radiometric technique was used to estimate the chronology of the sediment cores. A constant rate of the ^{210}Pb supply (CRS) model was applied to date the sediment cores, to obtain sediment influxes over time (McCall et al., 1984). The detailed method and results of ^{210}Pb dating have been described elsewhere (Ip et al., 2004).

2.4. Geochemical mapping

The concentrations of Hg were used as the input data for grid-based contour mapping, to study the spatial distribution of Hg in the PRE and its surrounding coastal area. The software used was ArcGIS 8.2, and the Inverse Distance Weighted (IDW) method was adopted for the interpolation of the geochemical data.

3. Results and discussion

3.1. Spatial distribution

The concentrations of Hg in surface sediments ranged from 1.5 to 201 ng/g. The average and median concentrations were 54.4 and 36.2 ng/g, respectively. The geochemical map of Hg in the study area is shown in Fig. 2. The spatial distribution of Hg was similar with those of Cu, Zn, and Pb (Ip et al., 2006), displaying a decreasing pattern with increasing distance from the estuary to the open sea. This indicates that anthropogenic emissions from the PRD are

probably the main sources of Hg in the sediments of the PRE and its surrounding coastal area. Although it had been thought that the outflow of the Pearl River is the most important source of Hg in the estuary, the concentrations of Hg in sediments near the end of the Pearl River were relatively low. By contrast, two hotspots were found at the mouth of the PRE and the northwest part of the coastal zone, a sign of the influence of the discharge of waste from the coastal cities, and the circulation currents in the estuary.

Table 1 shows the content of Hg in different marine sediments. Compared with the reported background total Hg levels in marine sediments (50–80 ng/g, (Fujii, 1976); 20–100 ng/g, (Lindqvist et al., 1984)), the sediments collected from the PRE were significantly

Table 1
Comparison of the concentrations of Hg in different marine sediments.

Location	Hg (ng/g)	Reference
The Arctic Ocean Basin	10–116	(Gobeil et al., 1999)
South Florida Estuaries, USA	20 (1–219)	(Kannan et al., 1998)
The East China Sea, China	37 (<0.5–80)	(Shi et al., 2005)
Malaysian coast, Malaysia	61 (20–127)	(Kannan and Falandysz, 1998)
San Francisco Bay, USA	201 (20–702)	(Conaway et al., 2003)
Anadyr Estuary, Russia	339 (77–2100)	(Kannan and Falandysz, 1998)
Seine Estuary, France	460 (300–1000)	(Mikac et al., 1999)
The PRE and coastal area, South China	54.4 (1.5–201.3)	This work

Fig. 3. The vertical distribution of Hg in sediment cores.

contaminated with Hg. However, the concentrations of Hg in most sediments from the coastal area were still within the background range (<80 ng/g, see Fig. 2). As a whole, the concentrations of Hg in the study area were higher than those in sediments from the Arctic Ocean Basin, South Florida Estuaries (USA), and the East China Sea (China), but lower than those in the Malaysian coast (Malaysia), San Francisco Bay (USA), Anadyr Estuary (Russia), and Seine Estuary (France).

3.2. Temporal distribution

Three sediment cores were collected from the study area and dated using the ^{210}Pb technique. The vertical distributions of Hg in sediment cores and the year in which they are estimated to have become present are shown in Fig. 3. Cores 14 and 25 are located around the two zones with high concentrations of Hg. Core 30 is located in the South China Sea outside the PRE and close to Hong Kong. Therefore, the concentrations of Hg in cores 14 and 25 were significantly higher than those in core 30. In core 14, the concentrations of Hg were relatively higher in the upper 45 cm, corresponding to the period from 1972 to the present, and then

decreased with the depth in the rest of the core. The concentrations of Hg in core 25 decreased slightly with depth in the profile, but were significantly high in the top 10 cm of sediments (after 1980). In these two cores, the concentrations of Hg in the sediments of the PRE increased during the last century, especially in the last 2–3 decades. However, in core 30, the change in Hg concentrations with depth was not significant, except that the concentrations of Hg in 5–7 cm (1990–1993) and 27–31 cm (1970–1974) were slightly higher than in other layers.

3.3. Influx of Hg

In order to identify the influence of anthropogenic inputs, the influxes of Hg in the sediment cores were calculated. The influxes of Hg for decade j in sediment core i were calculated using the following equation (Yang et al., 2002):

$$\text{Influx} = \sum A_i \rho_{it} D_{it} C_{it}, \quad (1)$$

where A_i is the area of the sediment core (cm^2), ρ_{it} is the sediment dry density for interval t (e.g., decade) (g/cm^3), D_{it} is the thickness of

Fig. 4. The influxes of Hg in sediment profiles.

the sediment for interval t within decade j in core i (cm), and C_{it} is the concentration of Hg for interval t (ng/g). The changes of Hg influxes in sediment cores in the last 100 years are shown in Fig. 4. The influxes of Hg in core 14 increased gradually in the last century, but rapidly after the 1970s, especially in the 1990s. The influx of Hg in the 1990s was approximately 9 times that in the 1900s and 3 times that in the 1950s. In core 25, high influxes of Hg were also found after the 1970s, despite a small reduction in the 1980s and 1990s. The increase in influxes of Hg in cores 14 and 25 obviously correlates with the economic development and urbanization of the PRD region, especially in the last three decades. In core 30, which is located outside of the PRE, the influx of Hg increased from the 1950s and peaked in the 1960s. The influx of Hg in the 1990s was only 45% of that in the 1960s and even less than that in the 1950s. This showed that the Hg in this core probably came from discharges related to Hong Kong, because the development of Hong Kong's industry started in the 1950s and rapidly increased in the 1960s and 1970s. During this period, a large number of factories were established, which produced basic industrial chemicals, paints, electroplating, enamelware, batteries, and so forth. In the early 1980s, many factories were moved to mainland China, and industrial activities in the territory declined significantly in the last few decades. Meanwhile, since the 1980s, the Hong Kong government has made efforts to put in place some strict controls over the discharge of pollutants (Shi et al., 2007).

4. Conclusions

The concentrations of Hg in surface sediments of the PRE and the surrounding coastal area decreased with the increasing distance from the estuary to the open sea, indicating that the Hg contamination was mainly caused by anthropogenic emissions from the PRD region. By using the ^{210}Pb dating technique, the historical changes in the concentrations and influxes of Hg in sediment cores in the last 100 years were revealed. The influxes of Hg in sediments were found to significantly correlate with the economic development and urbanization that has taken place in the PRD region, especially in the last three decades.

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