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Distribution of heavy metals in sediments of the Pearl River Estuary, Southern China: Implications for sources and historical changes

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Abstract

The distribution of heavy metals (Pb, Zn, Cd and As) in sediments of the Pearl River Estuary was investigated. The spatial distribution of heavy metals displayed a decreasing pattern from the turbidity maxima to both upstream and downstream of the estuary, which suggested that suspended sediments played an important role in the trace metal distribution in the Pearl River Estuary. In addition, metal concentrations were higher in the west part of the estuary which received most of the pollutants from the Pearl River. In the sediment cores, fluxes of heavy metals were consistent with a predominant anthropogenic input in the period 1970–1990. From the mid-1990s to the 2000s, there was a significant decline in heavy metal pollution. The observed decline has shown the result of pollution control in the Pearl River Delta. However, it is noteworthy that the metal concentrations in the most recent sediment still remained considerably high. Taken together, the enrichment of heavy metals in sediments was largely controlled by anthropogenic pollution.

Key words: metal pollution; sediment; spatial distribution; historical change; the Pearl River Estuary

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Introduction

Heavy metals are one of the serious pollutants in the environment due to their toxicity, persistence and bioaccumulation problems. Arsenic (As), cadmium (Cd), and lead (Pb) are classified as priority pollutants, because these metals are not required for metabolic activity and can be toxic even at quite low concentrations (US EPA, 1999). Zinc (Zn) is biologically essential, but the identification of contamination sources of Zn and its behavior in the natural system are also necessary, since it has the potential to be toxic to biota above a certain threshold concentration (Vallee and Auld, 1990). Over the past century, heavy metals have been discharged into the aquatic systems as a result of the rapid industrial, agricultural and urban developments, thus, heavy metal contamination has become a serious problem in marine ecosystems throughout the world (Vallius and Leivuori, 1999; Cundy et al., 2003; Pekey, 2006). Previous studies have reported that marine sediments have a large capacity to retain heavy metals from various sources, and marine sediments often act as sinks for heavy metals (e.g., Calmano et al., 1993; Menon et al., 1998). Therefore, sediment can be adopted as an efficient indicator for monitoring heavy metal pollution in coastal areas.

During the past few decades, tremendous amounts of

heavy metals have been discharged into the Pearl River Estuary (PRE) due to the population increase and economic development in the Pearl River Delta (PRD). It is estimated that every year 3×10^3 tons of Pb, 15×10^3 tons of Zn, 0.3×10^3 tons of Cd and 1×10^3 tons of As flow down the Pearl River and into the sea, and most of them primarily come from industries and mines, ship maintenance, corrosion of metallic materials and agricultural sources (GGP, 1987; Li et al., 2006). High levels of heavy metals (mainly Pb, Cd and As) were observed in aquatic organisms in the estuary, and the contents of Cd and As in benthos like crustacea and mollusk during some cruises even exceeded the standard indexes of seafood (e.g., Wei et al., 2002; Ip et al., 2005). It is therefore important to investigate the spatial and temporal distribution of heavy metals in the PRE, and illustrate the potential sources and historical changes of trace metals in the estuary, and then provide pollution control strategies and approaches to water quality management in the PRE.

To date, there have been extensive studies on surface sediment pollution in the PRE (e.g., Tang, 1983; Wen et al., 1995), while studies on subsurface sediments (i.e. the sediments at depths greater than 5 cm) are limited (Liu et al., 2003; Ip et al., 2004), and almost nothing is known about the distribution of those higher bioaccumulation metals, such as Cd and As, in subsurface sediments. In addition, the amount of industrial effluent (including heavy

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metals) discharged into the estuarine system has decreased significantly over the past decade (Hu, 2004; Yuan et al., 2009; GDEPD, 2010). This was mainly due to the implementation of environmental protection policies and the improvement in wastewater treatment systems in the PRD, although domestic sewage characterized with heavy organic loads has still shown an increasing trend (Ho and Hui, 2001; Wong and Wong, 2004; Beyer, 2006). However, recovery of estuarine system due to such a reduction has received little attention despite such studies are important to assess the improvement after the implementation of measures taken to recover the water quality of the area.

In the present study, we examined the spatial distribution and temporal trends of heavy metals in sediments from the PRE. Special emphasis was placed on the effects of environmental regulations on sediment conditions since the mid-1990s. The study will provide useful information to understand current metal contamination in the estuary. Furthermore, obtained data may help to determine if current management practices are resulting in improved sediment quality.

1 Materials and methods

1.1 Study area

The Pearl River Estuary (PRE) is a subtropical estuary and the second largest in China in terms of discharge volume from the Pearl River (Zhao, 1990). Each year the Pearl River delivers $326 \times 10^9 \text{ m}^3/\text{yr}$ of fresh water and $89 \times 10^6 \text{ ton/yr}$ of sediment into the PRE via three major branches (Xijiang, West River; Beijiang, North River; and Dongjiang, East River). High discharge occurs for at least 3 months in the summer, and more than 80% of the total flow occurs between April and September, with the ratio between maximum and minimum discharge varying between three and six times. Tides in the estuary are mixed semi-diurnal with a tidal range of less than 2 m and current velocities range between 1 and 2 m/sec (Dong et al. 2006). A two-layer circulation in the vertical often occurs within the estuary, with a saltwater intrusion from the eastern side of the PRE via the East Channel and Lantau Channel, while the freshwater dominated the West Channel (Dong et al. 2006). This circulation, combined with tidal trapping and sediment resuspension and deposition processes, often lead to the formation of turbidity maxima in the estuary, which are located near or upstream of the salt-wedge intrusion (Wai et al., 2004).

1.2 Sampling

Surface sediment samples (0–5 cm) were collected from 20 stations in the estuary using a grab sampler in October 2009 (Fig. 1). Surface sediments consist of brown sandy mud, except the samples taken in the mouth of the estuary which were black muddy sand. Three sediment cores were collected with a gravity core sampler during a summer cruise in 2009 (Fig. 1). These sampling sites were located in the areas considered to be less affected by the continuous dredging activity and dumped material. The sediment cores

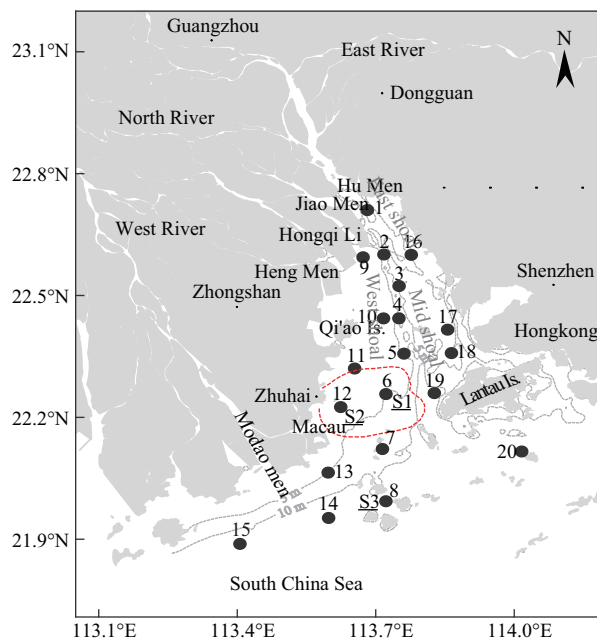


Fig. 1 Map of study area and sampling sites. 1–20: surface sediments; S1–S3: sediment cores; bold dashed line: the location of hypoxic zone ($\text{DO} < 3 \text{ mg/L}$) in July 1999 (Pan et al., 1999; Yin et al., 2004).

were carefully subsectioned into 2 cm intervals and stored frozen (-20°C) until chemical analysis. In laboratory, all sediment samples were oven dried at 60°C to a constant weight, homogenized and powdered using an agate mortar. Each ground sample was then stored in clean plastic bags prior to analyses.

1.3 Trace metal analyses

For trace metal determination, the $\text{HNO}_3\text{-HClO}_4$ acid digestion was performed, following the procedure recommended by AOAC (1990). Approximate 1 g of sample was placed in a 250-mL volumetric flask and 10 mL of concentrated HNO_3 was added. The mixture was boiled until it was nearly dried. After cooling, 5 mL of concentrated HClO_4 was added and the mixture was boiled gently until dense white fumes appeared. After cooling, 20 mL of distilled water was added and the mixture was boiled further to release any fumes. The solution was cooled, transferred quantitatively to a glass tube and diluted to 25 mL with distilled water. The metal concentrations were determined using an atomic absorption spectrometry (AAS) (Varian SpectrAA 220, Varian Inc., USA; Pb, Cd and As by graphite furnace, and Zn by flame). Together with the samples, certified reference standard from the State Oceanic Administration of China (GBW 07334) was digested and run, to test the analytical and instrument accuracy of the method. The recoveries were between 90% and 99% for all the metals, with a precision of 10%.

1.4 Chronology and accumulation rates

Sedimentation rates and sediment chronologies were estimated using ^{210}Pb dating techniques using an EG&G Ortec Gamma Spectrometry at the Nanjing Institute of Geography and Limnology, China. ^{210}Pb radioisotope activities were measured for selected sectioned samples of all three cores. The constant initial concentration model

(CIC model) was applied to give sedimentation rates for sediment cores (Goldberg, 1963). Mass accumulation rates (MAR) ($\text{g}/(\text{cm}^2\cdot\text{yr})$) were calculated according to Bruns and Hass (1999):

$$\text{MAR} = \text{DBD} \times \text{SR} \quad (1)$$

where, DBD (g/cm^3) is the dry bulk density, and SR (cm/yr) is the linear accumulation rate. The measured wet weight, water content and sediment volume were used to compute the dry bulk density.

2 Results and discussion

2.1 Spatial distribution of heavy metals and the implication for main sources

Spatial variations of heavy metals in surface sediments from the PRE are presented in Fig. 2. Generally, all the metals have similar distribution patterns, with a decreasing trend in concentrations from the northwest to the southeast in the study area. Hierarchical cluster analysis (HCA) was used to identify the similarity groups between the sampling sites. HCA rendered a dendrogram as shown in Fig. 3, grouping all 20 sampling sites into two statistically significant clusters. Cluster 1 was formed by most of the stations from the east shoal, deep channels and lower reach of the estuary. The most relevant in this study was Cluster 2, formed by most stations located in the west shoal of the PRE. These stations were characterized by their higher heavy metal concentrations, which might be related to the specific location of major tributaries of the Pearl River system and, consequently, are closer to sources of contamination, associated with the steering effect of the Coriolis force (Fig. 1).

The highest concentrations of heavy metals were found in sediments near Qi'ao Island (Station 5 and 10), which could be linked with the turbidity maximum zone in the PRE (Yang et al., 2005). Within the turbidity maximum zone, mineral particles and organic/inorganic colloids were abundant, and the predominant sizes of suspended sediment particles in the PRE ranged between 2 and 40 μm , hence provide favorable conditions for gradual adsorption, flocculation and subsequent deposition of heavy metals (Zheng, 1992; Xia et al., 2004). Consequently, estuarine

sediments are observed to have local distributions of high concentrations of heavy metals. Similar enrichment of finer-size fractions and contaminants were also observed in Chesapeake Bay and Hudson River Estuary (e.g., Nichols et al., 1982; Menon et al., 1998). Thus, adsorption by mineral particles or flocculation reactions was also a major factor in controlling the spatial variations of metals in the PRE sediments.

Compared with the sediment quality guideline values (i.e., the background levels in marine sediments from the South China Sea and soils from Guangdong Province), the surface sediments collected from the PRE were significantly contaminated by the four heavy metals to some extent (Table 1). As a whole, the concentrations of Pb, Zn, Cd and As in the present study were comparable to other studies reported in literature (Table 1). However, they were slightly higher than those in sediments from the Changjiang Estuary (Sheng et al., 2008) and the coastal areas of northern Bohai and Yellow Seas (Luo et al., 2010), but lower than those from the Gulf of Finland (Vallius and Leiuori, 1999) and Izmit Bay, Turkey (Pekey, 2006), both areas receive large amounts of heavy metal contaminants and have relatively long residence times (> 1 yr) of the water masses.

2.2 Sedimentary record of heavy metals

2.2.1 Dating and sedimentation rates

Over the last decades, the study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environments (e.g., Vallius and Leiuori, 1999; Cundy et al., 2003). Hence, three sediment cores were collected to assess environmental change over time by studying the change in anthropogenic metal concentrations (Fig. 1). The studied cores belong to different hydrodynamic environments and have diverse human interference with a variable degree of exposures to trace metal contamination. Sedimentation rates, as calculated by the CIC model, varied from 0.83 to 1.65 cm/yr (Table 2). The differences might be attributed to highly variable sedimentary and hydrodynamic conditions in the estuary (Zhao, 1990). Although cores are too short to examine the whole period of human development in this area, they do allow an analysis of the most recent decades of urbanization and

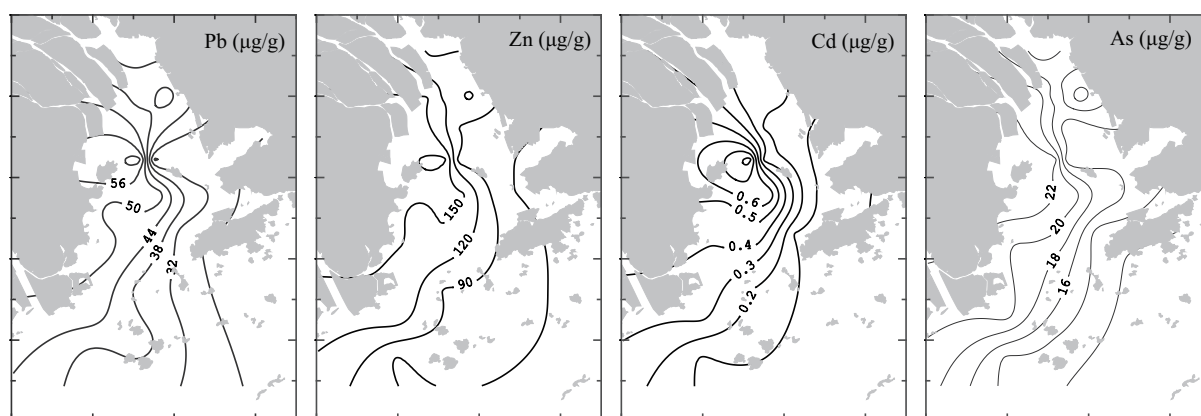


Fig. 2 Spatial distribution of analyzed metals in surface sediments from the Pearl River Estuary.

Table 1 Comparison of heavy metal concentrations in surface sediments collected from different estuaries and bays

Location	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	As ($\mu\text{g/g}$)	Reference
Pearl River Estuary	20.43–63.83 (40.51)	51.88–189.49 (109.09)	0.04–0.84 (0.29)	10.22–22.82 (17.42)	This study
Changjiang Estuary	25.01–54.79 (36.86)	28.00–209.93 (98.65)	0.11–0.25 (0.19)	7.19–17.29 (10.47)	Sheng et al., 2008
Northern Bohai and Yellow Seas	9.5–49 (25)	9.8–170 (60)	0.05–0.83 (0.15)	5.6–13 (8.5)	Luo et al., 2010
Gulf of Finland	26–88 (52)	77–513 (209)	0.28–2.19 (1.23)	6–28 (14)	Vallius and Leivuori, 1999
Izmit Bay, Turkey	55.2–172 (102)	440–1900 (930)	2.5–9.5 (4.9)	13.5–28.2 (21.8)	Pekey, 2006
Background of marine sediments in continental shelf of South China Sea	9.1–22.1 (15.6)	26.4–82.4 (54.4)	0.10–0.26 (0.18)	5.16–14.26 (9.71)	Zhang and Du, 2005
Background of soils in Guangdong Province	35.87	49.71	0.094	13.52	GPEMC, 1990

Data are expressed as minimum–maximum (arithmetic mean).

Table 2 Details of sediment cores collected from the Pearl River Estuary

Core	Latitude	Longitude	Water depth (m)	Core length (cm)	^{210}Pb rate (cm/yr)	Time period
S1	22 15.44°N	113 43.33°E	7.0	76	1.65	1963–2009
S2	22 13.52°N	113 37.45°E	4.5	80	0.95	1925–2009
S3	21 59.61°N	113 43.33°E	20.5	58	0.83	1939–2009

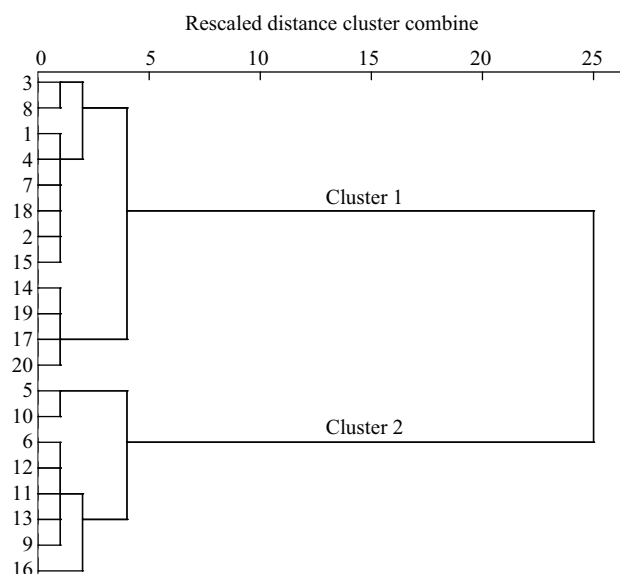


Fig. 3 Similarity dendrogram for sampling sites obtained using Ward's method. Two main groups of samples are identified. Dendrogram using ward method.

industrialization to be made.

Mass accumulation rates (MAR) of core S1, S2 and S3 ranged from 0.94 to 1.99 (mean 1.55), 0.47 to 1.03 (mean 0.84) and 0.38 to 1.06 (mean 0.79) $\text{g}/(\text{cm}^2\text{-yr})$, respectively (Fig. 4). The highest sediment flux was recorded at core S1, which was located near the West Channel, and estimated as about 1.99 $\text{g}/(\text{cm}^2\text{-yr})$ around 1991. The high sediment fluxes in core S1 and S2 occurred after the 1970s. The increase in sediment accumulation rates during recent decades might be linked to the enhanced continental erosion that associated with rapid population growth, intensity of land use and industrial development in the PRD areas began in the 1970s (Zhang et al., 2008 and references therein). Since the 1990s, sediment flux exhibited a decreasing trend, which might result from the dam constructions in the Pearl River Basin and subsequent decline in sediment discharge (Dai et al., 2008; Zhang et

al., 2008). The sedimentation rates obtained in this study are within the range of values (0.5–7.0 cm/yr) published earlier (Zhao, 1990; Lin et al., 1998), and are comparable with the value (0.41–1.67 cm/hr) for the Louisiana Bight and Chesapeake Bay, which receive large amounts of sediments from the drainage basin (Turner et al., 2004; Zimmerman and Canuel, 2000).

2.2.2 Sedimentary record of heavy metal pollution

Vertical profiles of Pb, Zn, Cd, and As concentrations for the three cores are shown in Fig. 5. Considering parts of heavy metals are normally derived from lithogenic source, ratios of metals to aluminum (Al), used as references to identify the extent of anthropogenic heavy metal pollution (e.g., Schropp et al., 1990; Qi et al., 2010), were also calculated. Generally, the sediments exhibit specific vertical variations in Pb, Zn, Cd, and As concentrations in each core. The minimum values, 11.8–18.4 $\mu\text{g/g}$ (Pb), 56.1–99.1 $\mu\text{g/g}$ (Zn), < 0.04–0.12 $\mu\text{g/g}$ (Cd), and 26.7–28.8 $\mu\text{g/g}$ (As), are typically found at the bottom of the cores. The maximum values, 22.3–47.1 $\mu\text{g/g}$ (Pb), 106.6–200.6 $\mu\text{g/g}$ (Zn), 0.06–0.69 $\mu\text{g/g}$ (Cd), and 35.8–76.5 $\mu\text{g/g}$ (As), are observed at the middle to upper parts of the cores. No significant differences are found between absolute and normalized metal concentrations in all three cores (Fig. 5).

Since mass accumulation rates varied significantly with time as well as among the sampling sites, "flux" might be a better parameter to assess temporal metal accumulation changes. The historical fluxes of Pb, Zn, Cd and As are present in Fig. 6. The influxes of all metals display basically similar patterns with their concentrations characterized by little change in the period before the 1970s and abrupt increase from 1970 to the mid of the 1990s. For the core S1, the average values of fluxes were 33.1, 147.4, 0.26, and 44.1 $\mu\text{g}/(\text{cm}^2\text{-yr})$ for Pb, Zn, Cd, and As respectively in the sediments before the 1970s, but these values increased to 60.3, 261.7, 0.73, and 40.3 $\mu\text{g}/(\text{cm}^2\text{-yr})$ from 1970 until around 1990. Since the mid-1990s, there is a significant decrease in the metal fluxes for all three cores.

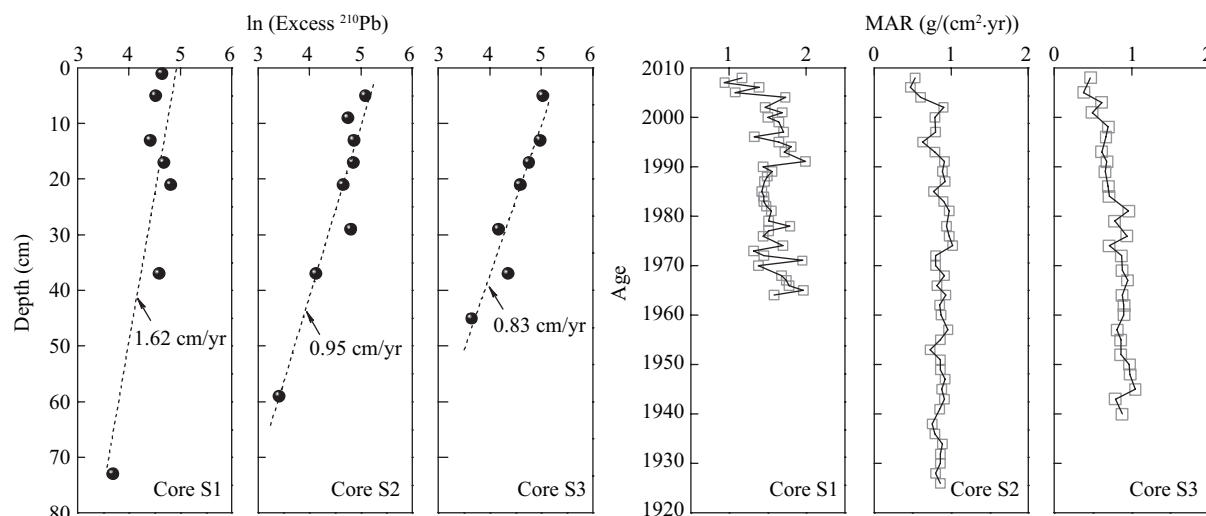


Fig. 4 CIC model ^{210}Pb -derived sedimentation and mass accumulation rates of core S1, S2 and S3. MAR: mass accumulation rates.

Cores S1 and S2 are located in the West Shoal, which is significantly influenced by freshwater flows and sediment loads from the Pearl River tributaries through river outlets on the west coast. Generally, the sediments of cores S1 and S2 exhibited non-steady increasing values of metal concentrations, particularly for Pb, Zn and Cd (Fig. 5), perhaps due to metal contributions from diffuse and point sources, or maybe related to the post-depositional migration and reprecipitation of metals as a consequence of sedimentary diagenesis (Elderfield and Hepworth, 1975; Cundy et al., 2003). If the vertical distribution of metals in both cores is mainly controlled by early-diagenetic remobilisation, it should be considered that the heavy metal profiles may resemble the organic carbon (OC) profiles to some extent, particularly in the surface layers (Cundy et al., 2003). However, this was not the case in the present study, which indicates that metals enrichments profiles in both cores cannot be explained by the early-diagenetic remobilization but mainly associated with contaminant input over the last several decades.

Actually, with an increase in the need for food and wood to meet the rapid population growth, vast extensions of land on the catchment area is cleared for agricultural purposes since the 1960s (Dai et al., 2008; Zhang et al., 2008). These practices are commonly related to widespread soil erosion and the export of eroded material, with its associated nutrient and metal content. In particular, phosphate fertilizer gradually came into use at the end of 1960s in China (Zhang et al., 2008). Rock phosphate fertilizers contain heavy metals, and the amount is dependent upon the source of the fertilizer, some of which could have significant amounts of metals (Mortvedt, 1996; Zhang and Shan, 2008). In addition, there has been a tremendous change in the economic basis since the late 1970s: with a slight decline in agriculture and a substantial increase in manufacturing; industrial effluents from hundreds of companies and municipal sewage with very little treatment have been discharged directly into the estuary (GGP, 1987; Wen et al., 1995; Wong and Wong, 2004). Meanwhile, the gross domestic product (GDP) of Guangdong has increased sharply from a low annual 6.4% growth between

1950 and 1978 to an annual average of 14.4% between 1979 and 1993, while the loss rate of cultivated land has increased from 0.5% in 1979 to 3.4% in 1993 (Fig. 7). Thus, an abrupt increase in sedimentary heavy metal concentrations was observed during this period, and the peak values of Pb, Zn and Cd appeared in the early 1990s correspondingly.

Reductions in metal concentrations can be clearly seen in both cores from the mid-1990s to the 2000s, despite increases in population and economic activities. With the aim of protecting the natural environment and human health, many environmental laws and regulations were revised and/or issued in China in the 1990s, especially after the UN Conference on Environment and Development in 1992. These laws introduced stricter environmental regulation of water quality, air pollution, and industrial wastes, and provided a more severe punishment of polluters than did the previous version (Sinkule and Ortolano, 1995; Zhang and Wen, 2008). At the local level, some provinces (including Guangdong, Shandong and Jiangsu) even issued local laws with more details (Beyer, 2006). In addition, the central and local governments decided to transform its economic pattern toward technological innovation with reduced consumption of resources and costs of energy (Zhang and Wen, 2008; Yuan et al., 2009). Consequently, the amount of industrial effluent (as well as heavy metals) discharged into the estuarine system has decreased significantly over the past decade (Hu, 2004; GDEPD, 2010). It can therefore be concluded that the decline in heavy metal pollution in sediments was due to the implementation of environmental protection policies and improved waste treatment systems in the PRD region during this period (Wong and Wong, 2004; Yuan et al., 2009). Similar trends in contamination levels (including Cu, Pb, Zn, Cd and Hg) were also found in the water column (Yuan et al., 2009), aquatic organisms (Wei et al., 2002), and surface sediments (Table 3) collected in the PRE during the last decade. However, there were substantial increases in heavy metal concentrations in recent sediments, which might reflect the worsened heavy metal pollution since the industrial effluents increased again in recent years (GDEPD, 2010).

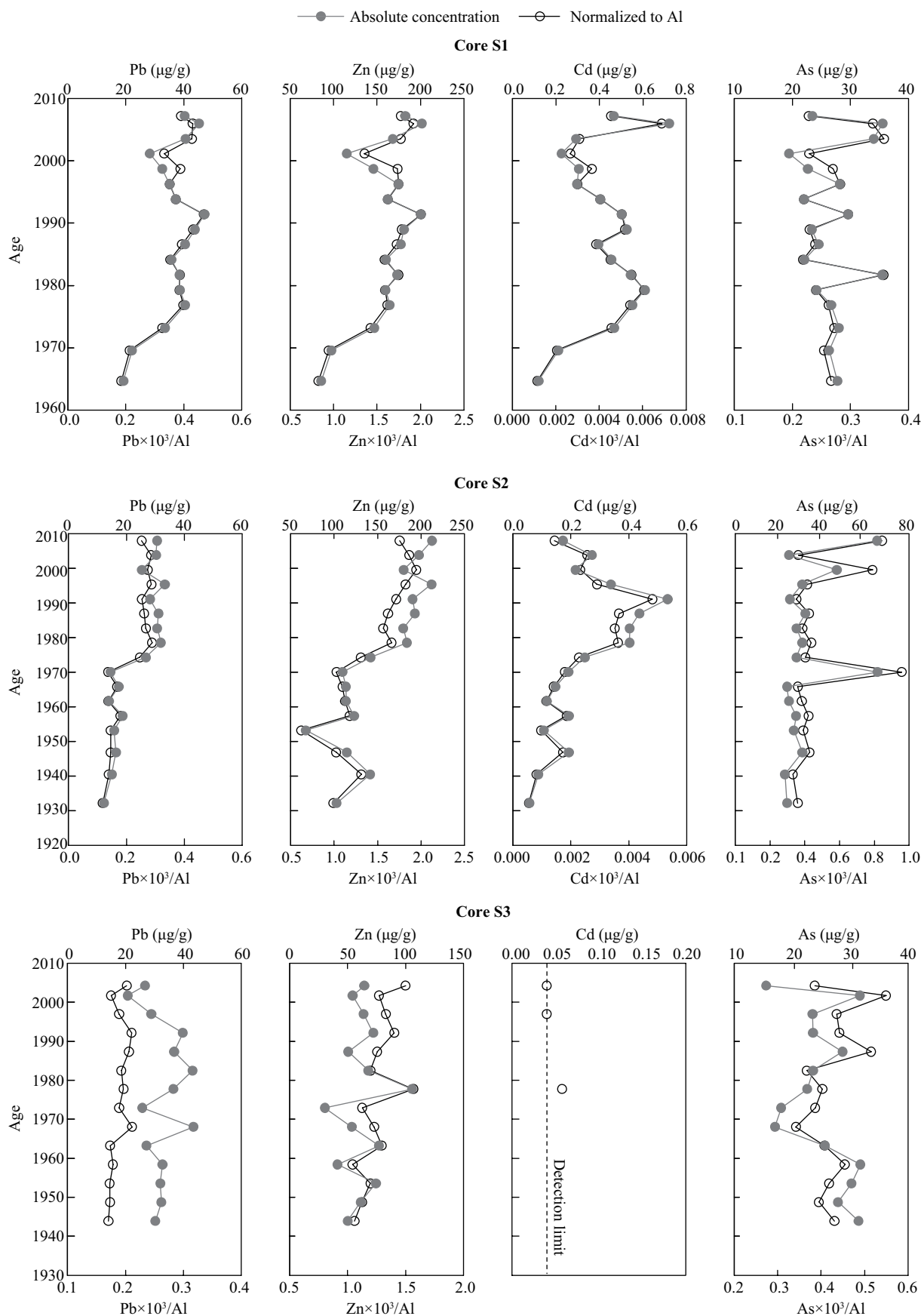


Fig. 5 Temporal distribution (absolute concentration and Al-normalized concentration) of Pb, Zn, Cd and As in core sediments, S1–S3, of the Pearl River Estuary.

At core S3, which is located near the mouth of the estuary and is influenced strongly by the oceanic water,

the concentrations of Pb, Zn, Cd and As are relatively low as compared to the inner zone cores. Metal contents

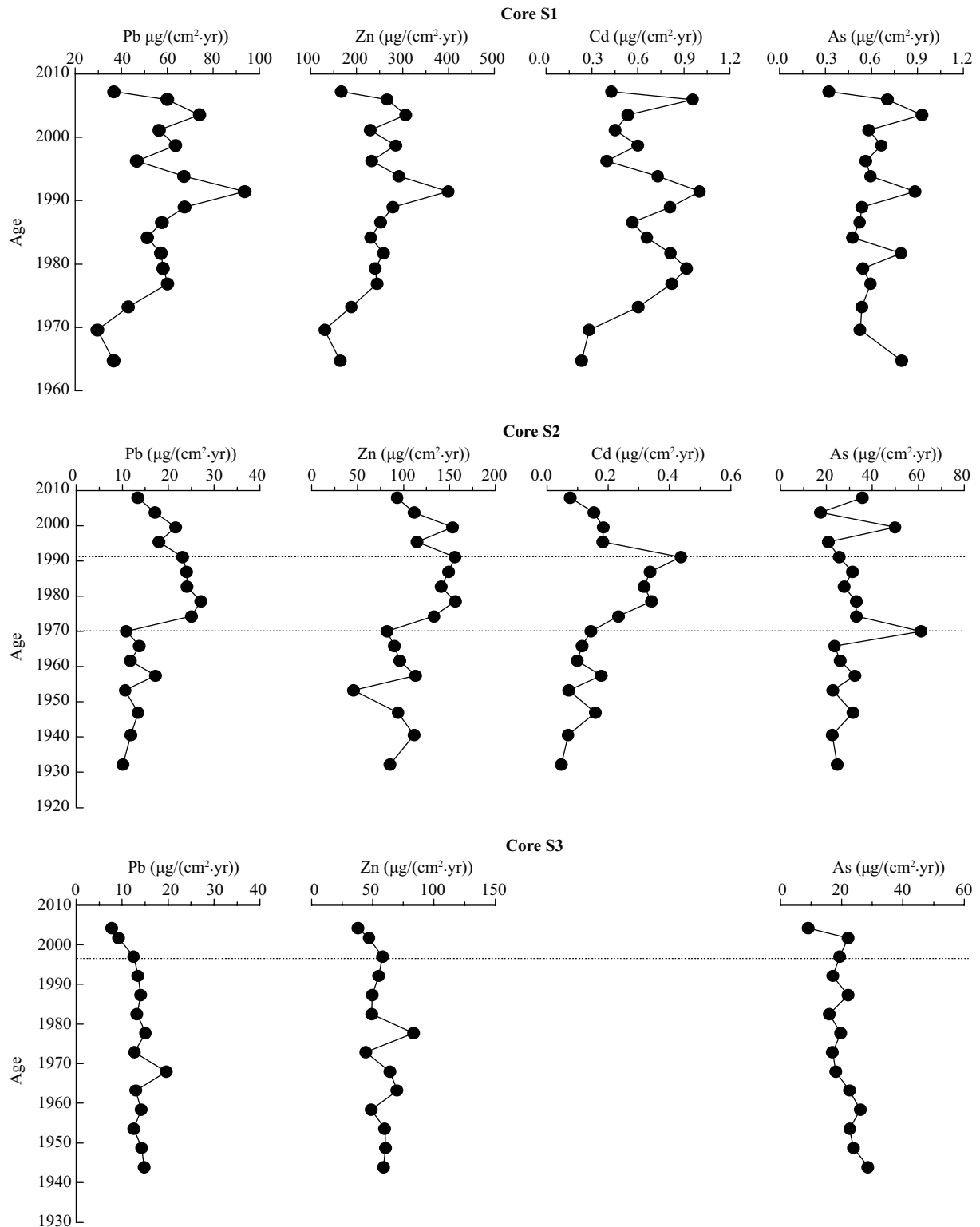


Fig. 6 Historical fluxes of Pb, Zn, Cd, and As in core sediments, S1–S3, of the Pearl River Estuary.

changed little throughout the whole core, and a high percentage (78.6%) of the samples had no detectable value for Cd ($<0.04 \mu\text{g/g}$) by AAS. The main reason for the low concentrations might be related to particle dispersion and dilution with uncontaminated sediment within the core.

Regarding the historical metal fluxes in the sediments of the estuary, with the exception of anthropogenic inputs, the changes in sediment flux and redox conditions may also affect the fluxes of heavy metals (Calmano et al.,

1993; Qi et al., 2010). For example, the seasonal hypoxic zone (dissolved oxygen less than 3 mg/L) in the bottom waters, a symptom of degraded water quality resulting from anthropogenic activities (e.g., nutrient pollution and eutrophication), has been expanding during recent decades in the PRE (Fig. 1), while the seasonal occurrence of oxygen-depleted bottom waters can potentially alter chemical forms of redox-sensitive metals (e.g., Zn, Cd and Mn) in sediments and release them into the water column again

Table 3 Summary of heavy metal contents in surface sediments of the Pearl River Estuary

Sampling year	Pb ($\mu\text{g/g}$)	Zn ($\mu\text{g/g}$)	Cd ($\mu\text{g/g}$)	As ($\mu\text{g/g}$)	Reference
2005	15.1–76.9 (39.7)	26.8–240.9 (115.3)	n.a.	n.a.	Liu et al., 2010
2004	30.9–116.0 (53.3)	64.3–237.0 (130.4)	0.04–0.7 (0.20)	5.5–35.6 (21.1)	Huang et al., 2006
2002	28.1–85.3 (48.9)	68.5–255 (153.3)	0.02–4.10 (0.82)	n.a.	Wang et al., 2004
1999	49.3–78.9 (59.26)	28.4–237.16 (150.06)	n.a.	n.a.	Zhou et al., 2004
1997	27.0–76.5 (59.43)	32.3–210 (110.85)	0.096–1.099 (0.344)	1.0–9.0 (5.24)	Liu et al., 2002
1989–1992	5.0–74.9 (54.2)	78–213.5 (162.7)	0.9–2.3 (1.6)	n.a.	GIRGP, 1995
1988–1989	24–84 (50.8)	54–192 (145.2)	0.20–0.75 (0.51)	n.a.	Wen et al., 1995
Before 1982	30–40	80–100	0.2–1.0	n.a.	Tang, 1983
1980–1981	10–93 (40)	20–90 (51)	0.029–0.910 (0.360)	3.0–27.3 (16.7)	GGP, 1987
1976–1978	2.7–40.9 (23.7)	31.9–157.9 (89.7)	0.011–0.960 (0.207)	n.a.	Qiu, 1989

Data are expressed as minimum–maximum (arithmetic mean). n.a.: not available.

Sampling sites were widely distributed in the estuary in those literature, although the locations and total number might be different.

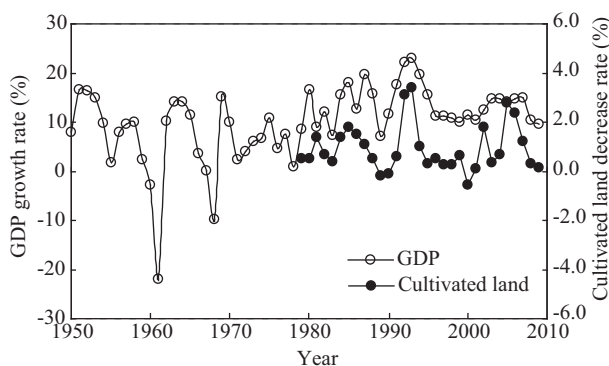


Fig. 7 Historical changes of GDP growth rate and cultivated land area decrease rate in Guangdong Province.

(Calvert and Pederson, 1993; Vallius and Leivuori, 1999; Lin et al., 2001).

Overall, the sharpest increases in concentrations (and fluxes) of heavy metals in cores S1 and S2 correspond to the period of rapid industrial, agricultural, and urban development in the PRD region, while the significant decrease during the past decade is most likely related to the pollution control that have taken place within the catchments from the mid-1990s to the present time. With regard to core S3, a core located in the lower reach of the PRE and less influenced by river discharge as well as anthropogenic activities, the burial influxes of all metals remained relatively constant, despite some fluctuations were observed.

3 Conclusions

The spatial distributions of heavy metals in surface sediments from the PRE were mainly influenced by the anthropogenic inputs of heavy metals from the PRD region and the hydrological conditions in basin. In addition, the turbidity maxima, which are most likely associated with the amount of fine suspended sediments, seem to play a crucial factor for the observed changes. The most contaminated site was found in the west part of the estuary, which is close to the sources of metal contamination. By

using the ^{210}Pb -dated sediment cores, the historical course of the concentrations and influxes of these metals in the last 80 years were revealed. Significant upward increases in heavy metal contents in the sediment cores were found to be correlated with the period of rapid industrial and agricultural development in the PRD region and consequent anthropogenic metal inputs. The obvious decline in metal pollution from the mid-1990s was due to the pollution control being enforced by the local government.

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