Over One Hundred Years of Trace Metal Fluxes in the Sediments of the Pearl River Estuary, South China

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"Capsule": The combination of trace metal concentration, Pb isotopic composition, element normalisation and ²¹⁰Pb dating analysis can reveal the long-term accumulation of metals in estuarine sediments.

Abstract

The rapid economic development in the Pearl River Delta (PRD) region in south China in the last three decades has had a significant impact on the local environment. Estuarine sediment is a major sink for contaminants and nutrients in the surrounding ecosystem. The accumulation of trace metals in sediments may cause serious environmental problems in the aquatic system. Thirty sediment cores were collected in the Pearl River Estuary (PRE) in 2000 for a study on trace metal pollution in this region. Heavy metal concentrations and Pb isotopic compositions in the four ²¹⁰Pb-dated sediment cores were determined to assess the fluxes in metal deposits over the last one hundred years. The concentrations of Cu, Pb and Zn in the surface sediment layers were generally elevated when compared with the sub-surface layers. There has been a significant increase in inputs of Cu, Pb and Zn in the PRE since the 1970s. The results also showed that different sampling locations in the estuary received slightly different types of inputs. Pb isotopic composition data indicated that the increased Pb in the recent sediments was of anthropogenic origin. The

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results of trace metal influxes showed that about 30% of total Pb and 15% of total Zn in the sediments in the 1990s were from anthropogenic sources. The combination of trace metal analysis, Pb isotopic composition and ²¹⁰Pb dating in an estuary can provide vital information on the long-term accumulation of metals in sediments.

Keywords: sediment profiles; trace metals; fluxes; Pb isotopes; Pearl River Estuary

1. Introduction

The Pearl River Estuary (PRE) is created by inflows of freshwater to the South China Sea. The PRE and its upstream water network form the largest river system in southern China and is the region's major waterway. This water network covers an area of more than 8000 km². The PRE is a north-south bell-shaped area, with the distance from north to south averaging about 49 km, and from east to west varying from 4 to 58 km. The PRE has four major freshwater discharge outlets – the Humen, Jiaomen, Hongqimen and Hengmen. The annual flows from the Pearl River to the South China Sea are approximately 300-325 billion m³/yr (Neller and Lam, 1998). Large amounts of nutrients in this estuary support a wide variety of fish and invertebrates that are of significant ecological interest (Wong et al., 1995).

The rapid urbanisation and industrialisation in the Pearl River Delta (PRD) region since the 1970s has resulted in growing pressure on the local environment (Li et al., 1997). Increasing amounts of wastewater and other pollutants have discharged into the PRE without proper treatment, which has had a significant environmental impact on the aquatic environment (Wen and He, 1985; Wen et al., 1995; Huang, 1995).

Estuarine sediments are recognised as an important sink for a wide range of contaminants and nutrients. They can provide a record of the natural and anthropogenic inputs of contaminants into the aquatic environment. Heavy metals have a high affinity for fine-grained sediments and are the key contaminants in estuarine sediments. The accumulation of heavy metals in sediments can cause significant environmental problems in the surrounding areas. It is therefore important to understand the mechanisms of accumulation and the spatial distribution of metal contaminants in sediments. Pb isotope ratios have been widely used in many studies to distinguish and quantify Pb inputs between natural and anthropogenic sources (Rabinowitz, 1995; Farmer et al., 1996; Munksgaard et al., 1998; Li et al., 2001) because the Pb isotopic composition in sediments usually depends on the parent materials and external inputs from the environment. The ²¹⁰Pb dating method has been widely used to estimate the age of the sediments and sedimentation rates in modern sediments (Appleby et al., 1979; Towler and Smith, 2000). The historical inputs of pollutants and changes in the fluxes of pollutants over time are frequently estimated by combining the results of ²¹⁰Pb dating and the vertical variations in contaminant concentrations in sediment profiles (Kahkonen et al., 1998; Lee and Cundy, 2001; Yang et al., 2002).

The vertical distribution of heavy metals and organic contaminants in recent sediments of the PRE has been examined by a number of researchers (Zhang et al., 1999; Li et al., 2000; Zhang et al., 2002; Liu et al., 2003). However, there have been very few studies on metal fluxes to the estuary in the last few decades. In order to estimate the magnitude of heavy metal fluxes to the sediments of the PRE, the objectives of the present study were: (1) to assess the fluxes of trace metals (Zn, Pb, Cu, and Ni) in the PRE based on the metal concentrations in dated sediment cores, and (2) to evaluate the anthropogenic inputs of trace metals in sediments over time, particularly in the past 50 years in the PRE, using Pb isotope

analysis and the normalisation method by major elements (e.g. Fe). The findings will be useful in proposing measures for strategic environmental control in the PRD and other fastdeveloping coastal regions.

2. Materials and Methods

2.1. Sediment sampling

Thirty sediment cores were collected in the PRE in June 2000 with the assistance of the South China Sea Institute of Oceanology, Chinese Academy of Sciences. The sampling locations are shown in Fig. 1. The locations of the sediment cores were relatively evenly distributed across the estuary and most of the cores were located in areas undisturbed by channel-dredging activities. These core samples 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 corer was driven into the sediment by gravity and the sediment core was retained in the inside PVC tube. The cores collected at all sampling stations were stored in polyethylene bags at 4-6 °C immediately after collection and prior to laboratory analysis. Cores 3, 14, 25 and 30 were selected for more detailed analysis in the present study. For physical and chemical analysis 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. After slicing, the sub-samples were frozen and stored at -20°C prior to undergoing a freeze-dry process. The sediment core samples were freeze-dried at -45°C for three days. All of the sediment samples were then hand-ground in an agate grinder until fine particles (< 200 µm) were obtained.

2.2. Determination of trace and major element concentrations in sediments

The sediment samples were digested using the nitric and perchloric acid decomposition method for 'total' concentrations (Li et al., 2001). Aliquots (~0.250g) of the ground sediment samples were weighed and placed into Pyrex test tubes. Samples were digested with 6 ml of nitric acid and 1.5 ml of perchloric acid by heating in an aluminium block (FOSS TECATOR 2000) at 50°C for 3 hrs, 100°C for 1 hr, 125°C for 1 hr, 150 °C for 3 hrs, 175°C for 2 hrs and 190°C until completely dry. After cooling, 10 ml of a 5% HNO₃ solution were added to the residue and heated at 70°C for 1 hr. The solutions were stored in polyethylene tubes prior to the determination of trace and major element concentrations by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin Elmer Optima, 3300DV) (Li et al., 2001).

Reagent blanks, a standard reference material (estuarine sediment - NIST 1646a) and sample replicates were used to assess the accuracy and precision of the analysis. The results showed that there was no sign of contamination, and the relative standard deviation of the replicate sample analysis was generally <10% of the mean concentration for each element. The recovery rates of the trace metals and major elements from the standard reference material were around 80% - 105%.

2.3. Pb isotopic analyses

Solutions from the digested sediment samples were analysed for Pb isotopic composition using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Perkin Elmer ELAN 6100 DRC^{plus}). The solutions were diluted to 30 Pb μ g/L or below by using a 5% high purity nitric acid solution. One hundred and fifty sweeps were used in the analysis. Ten replicates of each sample were measured, and the relative standard deviation (RSD) was < 0.5%. A standard reference material (NIST SRM 981), used for bias correction and analytical

quality control, was analysed at the beginning of the run, between every five samples, and at the end of the run. The average measured ratios of 204 Pb/ 207 Pb, 206 Pb/ 207 Pb, and 208 Pb/ 207 Pb of the standard reference materials were 0.0646 ± 0.0020, 1.0936 ± 0.0019, and 2.3711 ± 0.0034, respectively. These values were in good agreement with the certified standard values (0.0646, 1.0933, and 2.3704, respectively).

2.4. ²¹⁰Pb dating

The sediment cores were dated using the ²¹⁰Pb radiometric technique. The ²¹⁰Pb activities in sediment samples were measured via determination of the α radioactivity of its decay product ²¹⁰Po, on the assumption that the two are in equilibrium. The Po was extracted, purified, and self-plated onto silver disks at 70-80°C in 0.5M HCl, with ²⁰⁹Po used as the yield monitor and tracer in quantification. Counting was conducted by computerised multi-channel α spectrometry with gold-silicon surface barrier detectors. Supported ²¹⁰Pb was obtained by indirectly determining the α activity of the supporting parent, ²²⁶Ra, which was carried by co-precipitated BaSO₄. A constant rate of ²¹⁰Pb supply (CRS) model was applied to date the sediment cores to obtain sediment flux over time (McCall et al., 1984).

2.5. Statistical Analysis

The student *t* test was used to determine whether there were any significant differences between the trace metal flux inputs in different decades (from the 1950s to the 1990s). The *t* test was generated using SPSS[®] for Window Release 10.1. The normalised influxes of trace metals were used as the input data, and a paired sample *t* test was employed to examine if there were any significant differences between the different flux inputs.

3. Results and discussion

3.1.²¹⁰Pb Dating and Sedimentation Rates

Dated sediment cores are commonly used to reconstruct historical records of contaminant inputs in an aquatic system. Fig. 2 depicts unsupported ²¹⁰Pb activities of the four cores measured by ²¹⁰Pb analysis. The non-linear profiles showed independent evidence of accelerating sediment accumulation (Appleby and Oldfield, 1992), as changing accumulation rates may result in variations in initial ²¹⁰Pb activities. In order to construct a reliable ²¹⁰Pb chronology, a suitable model should be applied to process the ²¹⁰Pb accumulation data. In the constant initial ²¹⁰Pb concentration (CIC) model, the sediment core is dated by an average sedimentation rate and an average sedimentation flux (McCall et al., 1984; Zhang et al., 1999). The constant rate of ²¹⁰Pb supply (CRS) model assumes that over the time of the sedimentation there has been a constant flux of unsupported ²¹⁰Pb (derived from ²²²Rn in the atmosphere and rapidly decaying to ²¹⁰Pb) to the sediments and the specific activity of ²¹⁰Pb in the sediments varies exponentially with the cumulative dry-mass of the sediment (McCall et al., 1984; Oldfield and Appleby, 1984; Towler and Smith, 2000). The CRS model is suitable for a system where the transfer of ²¹⁰Pb to sediments is very efficient, such as large water bodies with long hydraulic retention times or for a system where the ²¹⁰Pb supply comes directly from atmospheric deposition (Appleby et al., 1979; McCall et al., 1984; Ugur and Yener, 2001). The CIC model, on the other hand, is appropriate for a system where the ²¹⁰Pb supply is directly proportional to erosive inputs (e.g. erosion of surface materials) (McCall et al., 1984; Appleby and Oldfield, 1992). Dramatic environmental changes have taken place over the past 50 years in the PRD region. Li et al. (2000, 2001) showed that

atmospheric deposition in the PRE is probably the main source of anthropogenic Pb in recent sediments. According to the previous studies on environmental conditions in the PRE (Zhang et al., 1999; Zhang et al., 2002), the profile of ²¹⁰Pb activity showed that changes had taken place in sedimentation rates. The CRS model, which displayed a general change in the sedimentation rates of the cores, was applied to date the four sediment cores in this study.

The sediment fluxes of the four cores measured by ²¹⁰Pb dating analysis are presented in Fig. 3. The average sediment fluxes of Cores 3, 14, 25, and 30 were 458 ± 123 mg/cm²/year, 1346 ± 439 mg/cm²/year, 426 ± 99 mg/cm²/year, and 927 ± 254 mg/cm²/year, respectively. The data showed that the deposition of sediments varied both among the selected sampling sites and over time. The highest sediment flux was recorded at Core 14, which was located in the West Channel, and estimated as about 2200 mg/cm²/yr around 1990. When the sediment flux is converted into sedimentation rate, the estimated value is about 2.5 cm/yr. This value was consistent with previous studies in the same area (Ke, 1991; Zhang et al., 2002).

The high sediment fluxes in Cores 3, 14 and 25 of the inner PRE occurred after the 1970s. The increasing sedimentation in recent decades may be due to the rapid urbanisation and industrial development of the surrounding PRD areas since the early 1970s. At the beginning of rapid economic development, a large amount of land was converted from agricultural to urban and industrial uses in the PRD region (Roberts and Chan, 1997). This would trigger greater amounts of surface run-off to the PRE, resulting in a higher sedimentation rate during the 1970s and 1980s. At Core 30, located outside of PRE, the highest sediment flux was recorded in the late 1950s and declined gradually afterwards. Due to the setting of this core, there was relatively less surface run-off directly from the Pearl River, but with more direct influences from Hong Kong. Therefore, the sedimentation in this

location might be affected by the reclamation and construction activities in Hong Kong peaking in the 1950s and 1960s.

3.2. Temporal Distribution of Trace Metals

The vertical profiles of trace metal concentrations in sediments can mirror changes over time. The concentrations of Pb, Zn, Cu, Ni and Fe in the sediment profiles of Cores 3, 14, 25 and 30 are presented in Figs. 4a-e. The sedimentation ages calculated by the CRS model from ²¹⁰Pb dating results are also presented in these figures.

A significant increase in Zn and Pb in the surface sediments of the PRE was reported in previous studies (Li et al., 2000; Zhang and Wang, 2001). In the present study, it is interesting to note that the elevated concentrations of Pb and Zn in these cores all appeared in the most recent period (from the 1970s to 1990s). This increase could be attributed to the increased natural weathering of soil materials and inputs from rapid industrial development and urbanisation in the last few decades. Usually, the increase in natural weathering in the watershed area can be reflected by the accumulation of rock-forming elements, such as Fe and Al, in sediments. However, no significant increase in Fe or Al in the sediment profiles was found for the last three decades (see Fig. 4e for example). This result suggests that the increase in trace metals in the PRE sediments since the 1970s may mainly come from anthropogenic sources of rapid urbanisation and intensive industrial activities in the surrounding areas. The peak concentrations of Pb, Zn and Cu appeared in the early 1990s, which may reflect the rapid growth of industrial operations and the relocation of Hong Kong's light industry to the PRD region (Li et al., 1997). In general, except in Core 3, Cu and Ni showed a relatively uniform distribution pattern along the profiles, which was similar to the major elements in the profiles (see Figs. 4c-e). These results indicated that these two elements were mainly of natural origin in these sediments.

3.3. Lead isotopic composition

All materials of natural origin, such as sediment, soil, and water, should have background Pb isotopic signature (Ault et al., 1970). The natural Pb isotopic composition of sediments depends on the natural inputs (e.g., bedrock, soil runoff). Before the 1950s, the PRD was mainly an agricultural region with very few industrial activities. At that time, the PRE mainly received inputs from the natural environment. The Pb isotopic ratios of the sediments before the 1950s can be considered as the natural background. The ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb ratios of the sediments in surface and subsurface layers are shown in Fig. 5. In this figure, the surface sediments were defined as the sediments dating from the 1990s, while the sub-surface sediments were from the layers dated prior to the 1950s. Most of the subsurface sediments (circled in Fig. 5) had a clearly different ²⁰⁸Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁷Pb signature from the surface sediments, particularly with ${}^{206}Pb/{}^{207}Pb > 1.20$. The clear differentiation between the surface and sub-surface sediments indicates the influence of anthropogenic inputs of Pb in recent sediments of the PRE. By averaging the Pb isotopic ratios of the sub-surface sediments of the four dated sediment cores, the average background 206 Pb/ 207 Pb and 208 Pb/ 207 Pb ratios of the sediments in the PRE (n = 21) are 1.20 ± 0.004 and 2.49 ± 0.006 , respectively. The values are very close to the results of a previous study (Li et al., 2001). Therefore, the pre-industrial background levels of Pb isotopic composition in the PRE sediments can be generally characterised as ${}^{206}\text{Pb}/{}^{207}\text{Pb} > 1.20$ and ${}^{208}\text{Pb}/{}^{207}\text{Pb} > 2.48$.

Elevated Pb concentrations were found in the sediments deposited after the 1970s in the four sediment cores. In order to gain a further understanding of potential Pb sources, the Pb isotopic composition of these samples was studied in the sediment profiles. In general, a lower ²⁰⁶Pb/²⁰⁷Pb ratio in the sediments indicates that the sediments may be affected by anthropogenic inputs (Sugden et al., 1993; Farmer et al., 1996). The ²⁰⁶Pb/²⁰⁷Pb ratios in the four ²¹⁰Pb-dated sediment cores are shown in Fig. 6. Relatively lower ²⁰⁶Pb/²⁰⁷Pb ratios in the surface layers were observed in all of these cores, suggesting that the increase in the amount of Pb in the surface sediments in the last few decades, particularly in the 1980s and 1990s, may come from anthropogenic sources. Core 3, located near the outlet of Humen, had relatively lower ²⁰⁶Pb/²⁰⁷Pb ratios starting from the 1950s. The low Pb isotopic ratio may be due to the fact that the sediments in the upper shoal near the mouth of the river receive more anthropogenic inputs from the discharges of the river than the sediments of other cores. The trends of total Pb concentrations and ²⁰⁶Pb/²⁰⁷Pb ratios were inversely related in the profiles (Fig. 4a and Fig. 6). These results indicated that anthropogenic inputs were among the major sources of increased Pb in recent sediments of the PRE, particularly during the 1980s and 1990s.

The correlation between the ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios of the sediments, atmospheric deposition and soils as well as some natural and anthropogenic sources in the surrounding area is depicted in Fig. 7. The Pb isotopic ratios of the air deposits and soils exhibited a wider range than those of the PRE sediments, indicating that the air deposits and soils were affected by various types of Pb sources (Wong et al., 2002; 2003). The PRE sediments showed less variation in Pb isotope ratios compared with the two potential sources in the PRD. The ²⁰⁶Pb/²⁰⁷Pb ratios were in a range of 1.161 to 1.177 for atmospheric deposition, and 1.173 to 1.204 for agricultural soils in the surrounding PRD region. The ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb ratios in the sediments showed similar patterns as uncontaminated soils and geological materials in the PRD region. However, The ²⁰⁶Pb/²⁰⁷Pb ratios of the surface sediments showed the shifting towards to vehicle sources,

industrial emissions and recent air depositions in the PRD and Hong Kong (Fig. 7), indicating the influences the anthropogenic inputs in the last few decades.

3.5. Influx of Trace Metals over Time

The calculated influx of trace metals represents the integrated trace metal inputs to sediments and provides a more reliable assessment of contamination trends (Lee and Cundy, 2001). Some studies have reported that the major chemical patterns of geochemical systems are not affected by temporal variations in the natural environment. The extra inputs of trace metals can be estimated by the metal influxes to an aquatic system (Ridgway et al., 2003).

To identify the influence of anthropogenic inputs on trace elements in the PRE sediments, the influxes of trace metals in the last five decades (the 1950s to 1990s) were calculated. The influxes of trace elements for decade j in sediment core i were calculated by the following equation (Yang et al., 2002):

Influx of trace elements = $\sum A_i \rho_{it} D_{it} C_{it}$ (1)

Where A_i = area of the sediment core (m²)

 ρ_{it} = sediment dry density for interval t (e.g. decade) (kg/m^3)

 D_{it} = thickness of sediment for interval t within decade j in core i (m)

 C_{it} = metal concentration for sediment interval t (mg/kg)

The calculated influxes of trace metals, Fe and total sediment of the four cores in the last five decades are presented in Table 1. The relative changes of the influxes in the last four decades to the 1950s are also shown in Table 1. A gradual increase of influxes of trace metals was observed in the Cores 3, 14 and 25 of the inner PRE from the 1970s to 2000, reflecting the influences of the rapid economic development of the surrounding PRD region in the last

few decades. In the outside location of the PRE (*e.g.* Core 30), the peak metal flux occurred in the 1960s and decreased from the 1970s.

Trace metal influxes would be affected by the sedimentation rates, granulometric and mineralogical variability of the sediments and/or the variability of anthropogenic contamination over time (Shine et al., 1995; Tam and Yao, 1998; Aloupi and Angelidis, 2001, Liu et al., 2003). From Table 1, the influxes of Fe and sediment fluxes showed significant variations in the last few decades. These results indicated that the influxes of trace metals could not only be affected by the sedimentation rates in the estuary, but also be influenced by the granulometric and mineralogical variability of sediments.

Some studies showed that geochemical normalisation could compensate for the effect of the granulometric and mineralogical variability of sediments (Tam and Yao, 1998; Aloupi and Angelidis, 2001; Liu et al., 2003). The differences in sediment properties should be minimised in the comparison of trace metal fluxes over time and among various locations. On the other hand, diagenesis of sediments may also affect trace metal fluxes in sediments (Lee and Cundy, 2001; Deflandre et al., 2002). Many studies showed that diagenetically formed Fe-Mn oxyhydroxides play a pivotal role in regulating concentrations of trace metal accumulation, speciation, and distribution along sediment profiles in some estuaries (Lion et al., 1982; Belzile et al., 1989; Buckley, 1989; Belzile and Tessier, 1990; Hamilton-Taylor et al., 1996). However, Douglas and Adeney (2000) found that the diagenetic processes in sediments do not substantially influence the trace metal/Fe ratios. In order to eliminate the effects of diagenetic, granulometric and mineralogical variability of the sediments on trace metal influxes, normalisation to Fe was adopted in the current study. Iron is one of the major elements present in the earth crust. Although Fe is a redox-active element in some surface environments, most of the Fe is mainly introduced naturally through the weathering of soil parent materials to the estuary sediments, and is mainly associated with residual fractions in the rock-forming minerals in the PRE (Li et al., 2001). The normalised influxes of trace metals in the sediments of the PRE and the percentage change in every decade relative to the 1950s are presented in Table 2 and Fig. 8).

The period before the 1950s in the PRE can be considered as the pre-industrial stage, with natural background levels. The increased normalised fluxes of trace metals in comparison with the 1950s could be regarded as the estimation of the anthropogenic metal inputs accumulated in each decade. In Fig. 8a, relatively higher influxes of Cu, Ni, Pb and Zn were recorded in Core 3 after the 1970s. The increment of normalised influx of Pb from the 1950s and 1990s was <8%, while the increment for Ni and Zn was about 15%, and nearly 50% for Cu (see Table 2). Increases in the Pb influx in the 1990s and in the Zn influx in the 1970s and 1980s were found at Core 14, while there were no significant changes in the normalised influxes of Ni and Cu (Fig. 8b). The 206 Pb/ 207 Pb ratios of Core 14 decreased dramatically from the 1990s to the present (Fig. 5b), which was in good agreement with the results of the normalised influx of Pb for this core.

A gradual increase in the normalised influxes of Pb and Zn from the 1970s to the 1990s was found in Core 25 (Fig. 8c). The increased percentages of normalised influxes of Pb and Zn from the 1950s to the 1990s were more than 50% and 25%, respectively (Table 2). The influxes of Cu and Ni were relatively stable. The results indicated no significant Cu and Ni contamination at this location. The ²⁰⁶Pb/²⁰⁷Pb ratios showed a gradually decreasing trend from the 1970s to the 1990s, which was consistent with the normalised influx of Pb in this core. Similar patterns of the influxes of trace metals were observed in Core 30 (Fig. 8d). The normalised influx of Pb and Zn increased steadily and there was no significant change for Ni and Cu. As presented in Table 2, the increments of Pb and Zn influxes from the 1950s to the 1990s were about 50% and 10%, respectively. The ²⁰⁶Pb/²⁰⁷Pb ratios from the 1970s to the

1990s were also in good agreement with the influx of Pb in this core. In addition, a gradual increase was observed in the normalised influx of Cu between the 1970s and 1990s. The increased percentage from the 1950s to the 1990s was >70%.

The results of normalised influxes of trace elements showed significant differences among the sediment cores. The anthropogenic inputs to sediments may be estimated from the increased normalised influx. The elevated trace metal concentrations in the sediments of the estuary probably come from various types of anthropogenic sources. Metal concentrations at the early pre-industrial stage were usually low and stable, with relatively high ²⁰⁶Pb/²⁰⁷Pb ratios in comparison with the periods of intensive industrial activities (Kahkonen et al., 1998; Schuster et al., 2002). Based on the consistent trends of Pb isotopic composition and on the normalised influxes of trace metals in the sediments, it was evident that the elevated influx of Pb was mainly due to the anthropogenic inputs from the rapid economic development in the PRD in the last few decades.

A paired samples t test was conducted in order to examine the significance of the differences between normalised trace metal influxes in the PRE sediments. The factors of the paired samples t test for Cu, Ni, Pb and Zn fluxes in the sediments during the 1960s, 1970s, 1980s, and 1990s compared with the 1950s are presented in Table 3. The critical value of t one-tailed is 2.353 and 1.638 for confidence intervals of 95% and 90%, respectively. The differences in the normalised influxes of Pb and Zn between the 1950s and the periods after the 1970s were all above the 90% confidence interval in the t test. As shown in Tables 2 and 3, Pb and Zn exhibited statistically significant differences among the different periods, and influxes of these metals tend to be higher in more recent decades. Pb contamination was particularly significant in this case. The four cores also showed more anthropogenic Pb accumulation in the sediments in the 1990s. By averaging the percentage of anthropogenic

inputs among the sediment cores, it was found that about 30% of the Pb in the PRE was from anthropogenic inputs in the 1990s. The anthropogenic Pb probably comes from non-point sources, such as atmospheric deposition and wastewater discharges (Li et al., 2000 & 2001; Liu et al., 2003). The influx of Zn also increased with time, with a significant proportion of Zn coming from anthropogenic sources. About 15% of Zn inputs were estimated to have come from anthropogenic sources in the 1990s. In general, no significant increase in the influxes of Cu and Ni was found in the overall estuary, although Cores 3 and 30 showed some increase in the normalised influx of Cu.

4. Conclusions

Relatively higher sedimentation rates were recorded in the PRE from the 1970s, reflecting the increase in surface runoff into the estuary resulting from the rapid economic development of the PRD region. The Pb isotopic composition indicated that sediments in the PRE mainly started to receive anthropogenic inputs of trace metals since the 1970s. In addition, the synchronous temporal changes in the concentration of Pb, in ²⁰⁶Pb/²⁰⁷Pb ratio and in the normalised influx of Pb in the PRE sediments showed clearly that the increase in Pb in the recent sediments was caused by anthropogenic activities in the PRD in recent decades. In the 1990s, about 30% of Pb and 15% of Zn inputs were anthropogenic in nature.

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Table 1

The influx of heavy metals (Cu, Ni, Pb, Zn, and Fe) and sediment in Cores 3, 14, 25, and 30 of the PRE and % changes in the last four decades relative to the 1950s

		Influx of metals per area (mg/cm ² /decade)					% change with the 1950s (%)						
		Cu	Ni	Pb	Zn	Fe	Sediment	Cu	Ni	Pb	Zn	Fe	Sediment
							flux						flux
Core 3	1950 – 1959	0.174	0.175	0.205	0.568	127.2	3717	-	-	-	-	-	-
	1960 – 1969	0.141	0.147	0.160	0.464	107.0	4177	-19	-16	-22	-18	-16	12
	1970 – 1979	0.194	0.184	0.233	0.658	131.3	5367	11	5	14	16	3	44
	1980 – 1989	0.444	0.402	0.474	1.310	269.5	5952	155	129	132	131	112	60
	1990 - 1999	0.405	0.317	0.350	1.028	201.6	3689	133	81	71	81	59	-1
Core 14	1950 – 1959	0.330	0.318	0.214	0.773	261.6	11514	-	-	-	-	-	-
	1960 – 1969	0.394	0.386	0.276	0.961	317.1	11133	19	21	29	24	21	-3
	1970 – 1979	0.538	0.512	0.372	1.331	426.2	12836	63	61	74	72	63	11
	1980 – 1989	0.590	0.514	0.359	1.332	434.7	14255	79	62	68	72	66	24
	1990 – 1999	1.140	1.028	0.820	2.809	841.2	18234	246	223	283	263	222	58
Corro 25	1050 1050	0.162	0 150	0.005	0 222	126.0	4052						
Core 25	1950 - 1959	0.162	0.150	0.085	0.333	126.0	4952	-	-	-	-	-	-
	1960 - 1969	0.195	0.185	0.108	0.397	155.4	5110	21	23	27	19	23	3
	1970 – 1979	0.482	0.450	0.287	1.025	378.7	5044	199	199	238	208	201	2
	1980 - 1989	0.264	0.251	0.185	0.629	220.3	3509	64	67	117	89	75	-29
	1990 – 1999	0.119	0.106	0.101	0.317	94.0	2766	-26	-29	18	-5	-25	-44
Core 30	1950 - 1959	0.177	0.599	0.369	1.434	509.2	12723	-	_	_	_	_	_
Core 50	1960 - 1969	0.216	0.735	0.455	1.732	623.9	112723	22	23	23	21	23	-11
	1970 - 1979	0.139	0.755	0.433	0.840	282.5	9680	-21	-41	-33	-41	-45	-24
	1980 - 1989	0.139	0.311	0.243	0.726	242.1	7977	-38	-48	-42	-49	-53	-37
	1990 - 1999	0.072	0.150	0.213	0.373	120.1	5038	-59	-75	-64	-74	-76	-60
	1770 - 1777	0.072	0.150	0.151	0.575	120.1	5050	-57	-15	-04	-/+	-70	-00

Table 2

The normalised influxes of heavy metals (Cu, Ni, Pb Zn) in different decades and % changes relative to the 1950s in Cores 3, 14, 25, and 30 of the PRE

		Normalised influx of metals $(x10^4)$				% change with the 1950s (%)				
		Cu/Fe	· ·	Pb/Fe	Zn/Fe	Cu/Fe	(Pb/Fe	Zn/Fe	
Core 3	1950 - 1959	13.7	13.8	16.1	44.7	-	-	-	-	
	1960 – 1969	13.2	13.7	14.9	43.4	-3.3	-0.4	-7.2	-2.8	
	1970 – 1979	14.7	14.0	17.8	50.1	7.9	1.8	10	12	
	1980 - 1989	16.5	14.9	17.6	48.6	21	8.4	9.2	8.9	
	1990 – 1999	20.1	15.7	17.3	51.0	47	14	7.7	14	
Core 14	1950 – 1959	12.6	12.2	8.19	29.5	-	-	-	-	
	1960 – 1969	12.4	12.2	8.69	30.3	-1.5	0.2	6.1	2.6	
	1970 – 1979	12.6	12.0	8.72	31.2	0.1	-1.2	6.5	5.7	
	1980 - 1989	13.6	11.8	8.27	30.6	7.7	-2.7	1.0	3.7	
	1990 – 1999	13.6	12.2	9.75	33.4	7.5	0.5	19	13	
Core 25	1950 – 1959	12.8	11.9	6.75	26.4	-	-	-	-	
	1960 – 1969	12.5	11.9	6.95	25.5	-2.3	-0.4	3.0	-3.4	
	1970 - 1979	12.7	11.9	7.59	27.1	-0.7	-0.4	12	2.5	
	1980 - 1989	12.0	11.4	8.40	28.6	-6.4	-4.4	24	8.1	
	1990 – 1999	12.7	11.3	10.7	33.7	-0.9	-5.2	59	28	
Core 30	1950 – 1959	3.5	11.8	7.24	28.2	-	-	-	-	
	1960 – 1969	3.5	11.8	7.29	27.8	-0.5	0.1	0.6	-1.4	
	1970 – 1979	4.9	12.6	8.78	29.8	42	7.1	21	5.6	
	1980 - 1989	4.6	12.8	8.78	30.0	32	9.3	21	6.5	
	1990 – 1999	6.0	12.5	10.9	31.0	73	6.0	50	10	

Table 3

The results of a paired sample t test of normalised trace metal fluxes in different decades (1960s, 1970s, 1980s, and 1990s) compared with those during the 1950s

	1960s	1970s	1980s	1990s
Cu	2.402**	-1.552	-1.394	-1.725*
Ni	1.000	-0.926	-0.691	-0.931
Pb	-0.022	-2.501**	-1.686*	-3.715**
Zn	0.988	-2.257*	-3.781**	-4.874**

Notes: ^{**} The trace metal fluxes at the above periods were significantly different from those in the 1950s at 95% confidence intervals (p<0.05).

^{*}The trace metal fluxes at the above periods were significantly different from those in the 1950s at 90% confidence intervals (p<0.10).

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Fig. 8. The relative influxes of Pb, Ni, Cu and Zn normalised by Fe in every decade in a) Core 3, b) Core 14, c) Core 25, and d) Core 30 of the PRE.

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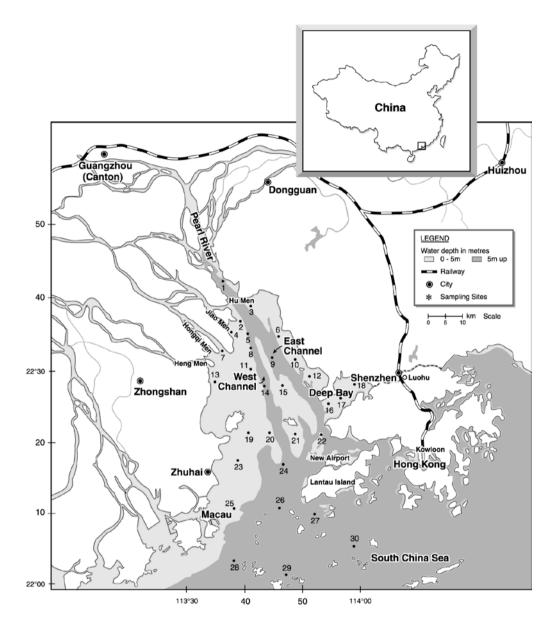


Fig. 1. The location of the sampling site in the Pearl River Estuary

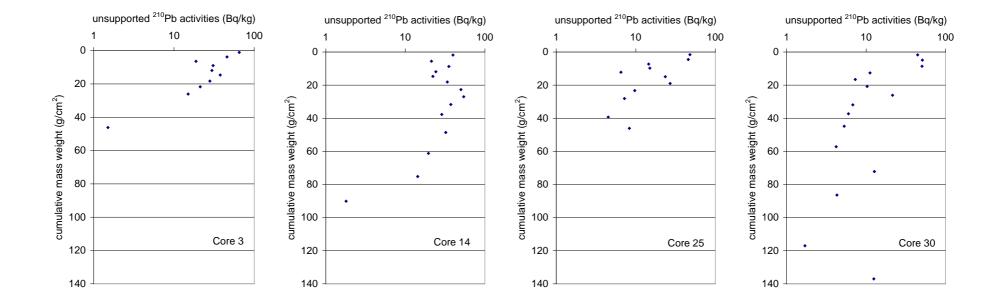


Fig. 2. The unsupported ²¹⁰Pb activities in Cores 3, 14, 25, and 30.

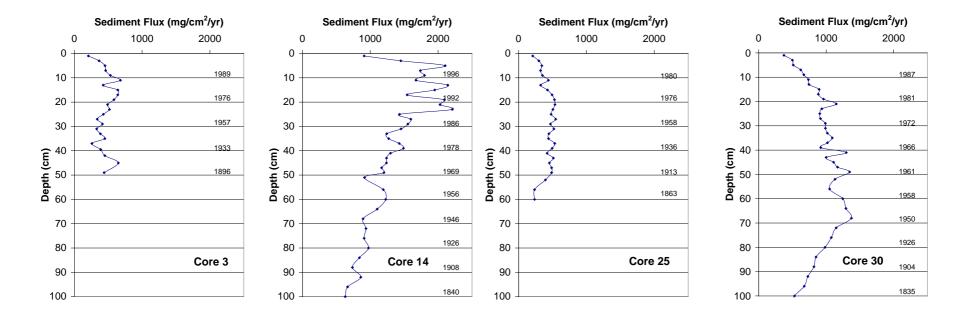


Fig. 3. The sediment flux of Cores 3, 14, 25, and 30 using CRS model.

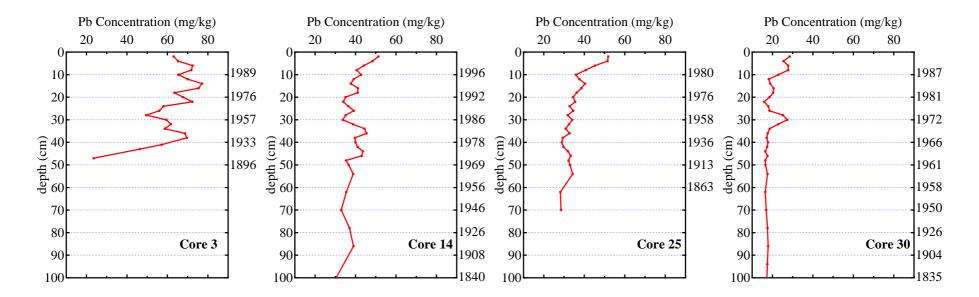


Fig. 4a. The profile of Pb concentration over time in Cores 3, 14, 25, and 30.

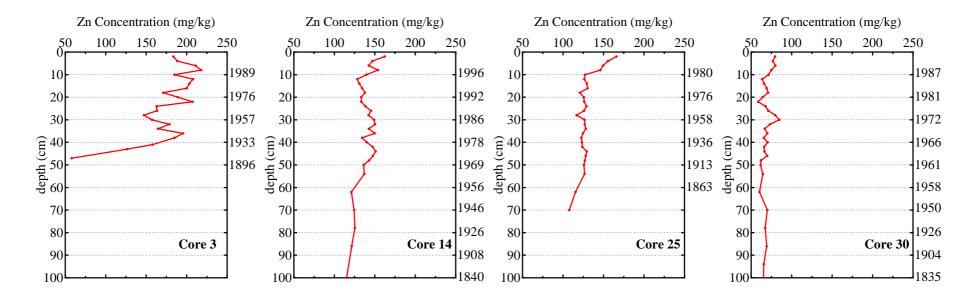


Fig. 4b. The profile of Zn concentration over time in Cores 3, 14, 25, and 30.

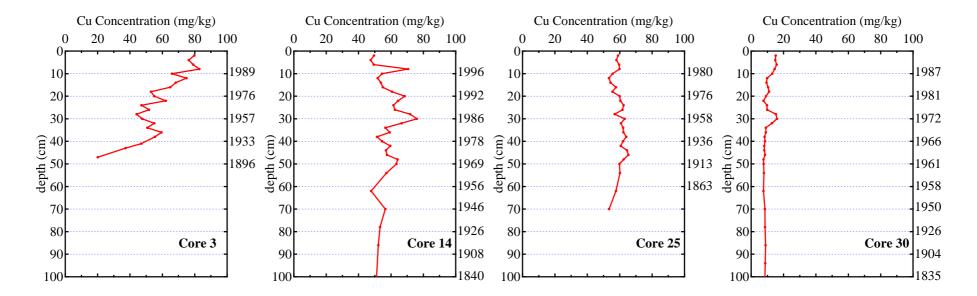


Fig. 4c. The profile of Cu concentration over time in Cores 3, 14, 25, and 30.

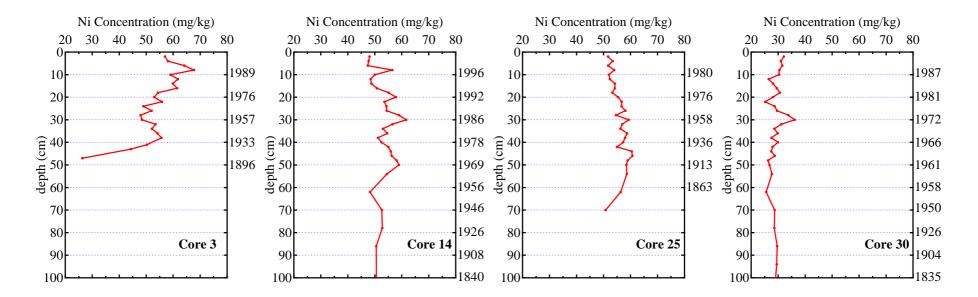


Fig. 4d. The profile of Ni concentration over time in Cores 3, 14, 25, and 30.

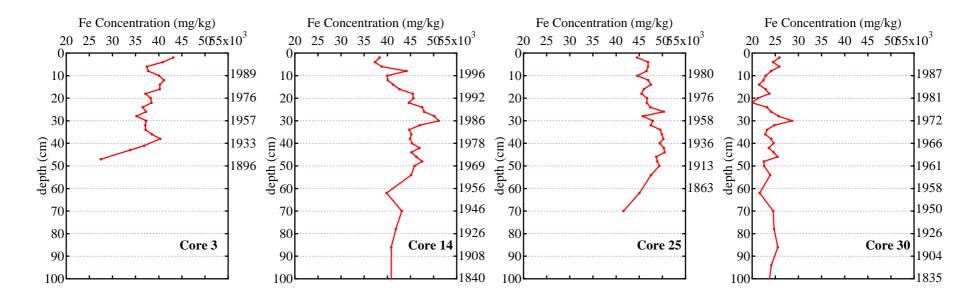


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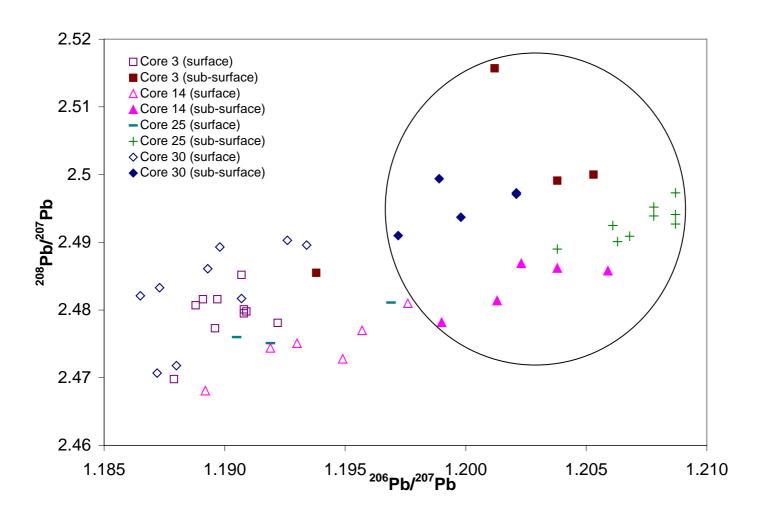


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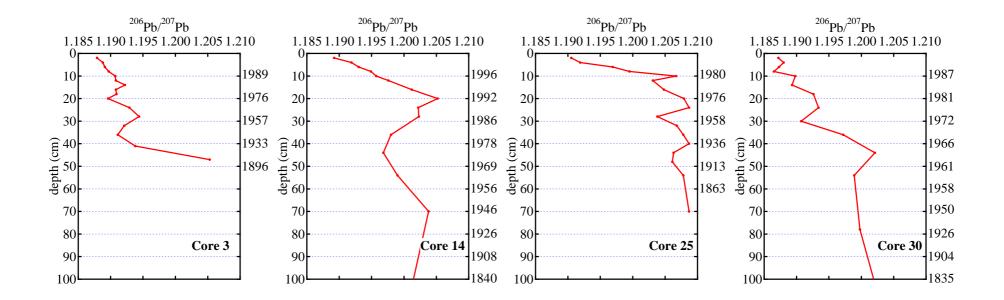


Fig. 6. The profile of 206 Pb/ 207 Pb over time in Cores 3, 14, 25, and 30.

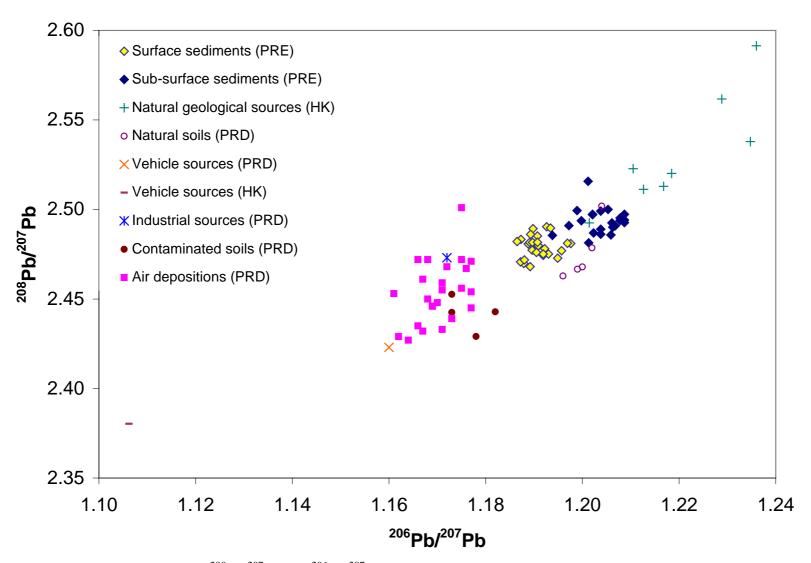
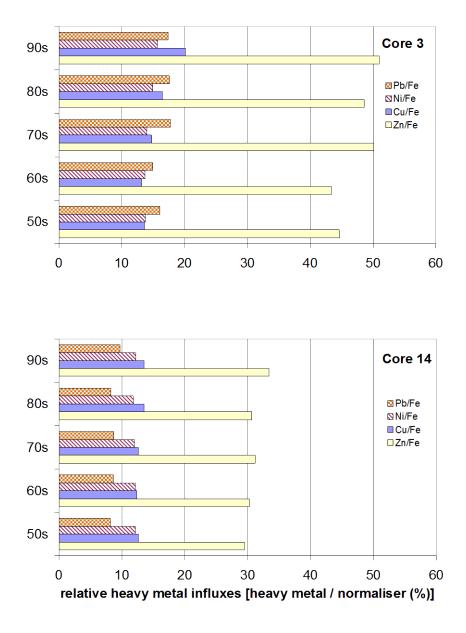


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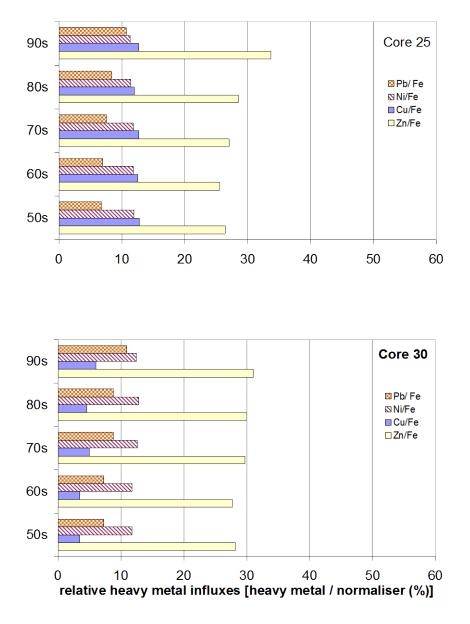


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