Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China

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Abstract

In the present study, surface sediments and sediment cores were collected at the Pearl River Estuary (PRE) and its surrounding coastal area. The samples were analysed for total metal concentrations, metal concentrations in the five operationally defined chemical fractions, and Pb isotopic compositions. The concentrations of Co, Cr, Pb, and Zn of the sediments in the PRE were about twice of those at the adjacent coastal area, while the Cu concentrations of the PRE sediments were four times higher than the sediments at the coastal area. The distribution of Cu, Cr, Pb, and Zn demonstrated a typical diffusion pattern from the land to the direction of the sea. Two hotspots of trace metal contamination were located at the mixed zone between freshwater and marine waters. The distribution of trace metals in sediments showed that the major sources of metal contaminants were probably from the discharges of sewage and other outlets in the west bank of the estuary. The enrichment of metal in the sediments could be attributed to the deposition of the dissolved and particulate trace metals in the water column at the estuarine area. The similar Pb isotopic signatures of the sediments at the PRE and its surrounding coastal area offered strong evidence that the

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PRE was a major source of trace metals to the adjacent coastal area. Slightly lower $^{206}Pb/^{207}Pb$ ratios in the coastal sediments may indicate other inputs of Pb in addition to the PRE sources, including the inputs from Hong Kong and other parts of the region.

Keywords: Sediment; Heavy metals; Pb isotopes; Pearl River Estuary (PRE); South China Sea

"Capsule": *The distribution of Cu, Cr, Pb, and Zn in sediments demonstrated a typical diffusion pattern from the land to the direction of the sea, reflecting the contaminant sources from the estuary, and physical and chemical deposition processes.*

1. Introduction

Estuarine and coastal areas are complex and dynamic aquatic environment (Morris et al., 1995). Physical, chemical, and biological interactions between freshwater and saltwater systems can have profound influences on the transport and fate of trace metals. The distribution of trace metals through complex processes of material exchange within these aquatic environments can also be affected by anthropogenic inputs. Often, such an influence is more apparent in an estuarine and surrounding coastal area than in an open ocean due to intense human activities. The transport of trace metals from rivers to estuaries and then to the open ocean is dependent on the partitioning of trace metals between dissolved and particulate phases and other environmental conditions. Both estuaries and coastal areas are subject to the varying influences of riverine and atmospheric inputs, coastal and seafloor erosion, and biological activities. Nevertheless, physical and chemical transport and

biogeochemical interactions within these areas may be the key factors controlling land-derived natural and pollutant chemicals into the coastal areas.

Trace metals may be recycled via chemical and biological processes, within the sedimentary compartment and back to the water column (Förstner, 1984; Tessier and Campbell, 1987). The accumulation of metal contaminants in sediments can pose serious environmental problems to the surrounding areas. Trace metal contamination in sediment could affect the water quality and the bioassimilation and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implications on human health and ecosystem. It is therefore important to understand the mechanisms of accumulation and geochemical distribution of trace metals in sediments in order to develop pollution control strategies and approaches to water quality management in a coastal area. Human activities have greatly altered the geochemical cycle of trace metals, resulting in widespread environmental contamination (Nriagu and Pacyna, 1988). Trace metal contamination in a marine coastal environment is related to sources of pollution in the adjacent estuaries and rivers. Metals are mainly transported to the marine environment by rivers through estuaries. In most circumstances, the major contribution of anthropogenic metals in a marine coastal area is of terrestrial origin, i.e. from mining, industrial, and urban developments, and other human practices near rivers and estuaries (Morton and Blackmore, 2001). Grain size of sediment is one of the major controlling factors for the distribution of trace metals in coastal area. In general, coarse particles consist mainly of geological minerals, such as quartz and feldspars. A large proportion of trace metals in this fraction are in a crystalline solid state (usually in low concentration) and are environmentally immobile. On the other hand, fine particles, such as clay and colloidal materials, are generally surface-active and contain organic

matter and Fe/Mn oxide surface coatings, and they can play an important role in controlling in deposition of trace metals to sediments from an estuary to a coastal area. Some investigations have used Pb isotope compositions in sediments to distinguish and quantify Pb inputs between natural and anthropogenic sources (Farmer et al., 1996; Munksgaard et al., 1998; Li et al., 2001; Ip et al., 2004).

The Pearl River flows through large catchment areas into the PRE and finally reaches the South China Sea (SCS), which is the largest marginal sea on the western boundary of the Pacific Ocean. Various studies of trace metal contamination in the sediments of the PRE have recently been conducted (Li et al., 2000a, 2000b, 2001; Liu et al., 2003; Ip et al., 2004). The previous works showed that the enrichment of trace metals in the recently deposited sediments of the PRE was the result from rapid industrial development and urbanisation in the surrounding area in the last few decades. High concentrations of trace metals were also found in the aquatic organisms in the PRE (Ip et al., 2005). Therefore, more studies of the surrounding coastal area are needed to gain an understanding of the influences of anthropogenic trace metal inputs on the coastal area and the transport of trace metals from an estuarine environment to a marine coastal zone. A number of studies have demonstrated the geochemical cycling of some trace metals in dissolved and particulate phases between the estuaries and coastal areas (Morris et al., 1995; Guieu et al., 1998; Leermakers et al., 2001; Munksgaard and Parry, 2001). However, studies on the geochemistry of trace metals in the sediments between the estuary and the surrounding coastal areas are limited.

The present study aims to assess the trace metal contamination of the PRE and its surrounding coastal area. The objectives of this research project are (1) to examine trace metal concentrations in the sediments in the PRE and its surrounding SCS area,

(2) to investigate the relationship of trace metal contamination between the PRE and its surrounding coastal area, and (3) to evaluate the geochemical cycling process of trace metals in sediments between the PRE and its surrounding coastal area (e.g. physical and chemical transportation processes of trace metals in estuarine and coastal areas).

2. Material and Methods

Sediment sampling

Thirty-nine surface sediment samples and 12 sediment cores were collected in the study area in September 2002. A map of the sampling locations is shown in Fig. 1. The sampling locations were relatively evenly distributed across the PRE and its surrounding coastal area. The surface samples (to a depth of 10 cm) were taken with a grab sampler. The core samples were taken with a Kajak gravity corer[®]. The corer was driven into the sediment by gravity, and the sediment core was retained in a PVC tube. The diameter of the PVC coring tube was 70 mm. The sediment cores collected at all of the sampling locations were cut into sub-samples at 1-cm intervals on board the sampling ship. All of the sediment samples were stored in polyethylene bags at 4-6ºC immediately after collection and prior to undergoing analysis in a laboratory. The samples were freeze-dried (FTS System, Dura-Dry µP) at -45ºC for 3 days. Large debris and fragments of shells were removed before grounding. All of the sediment samples were then ground in an agate grinder until fine particles (<200 µm) were obtained.

Analyses of trace and major elements

The sediment samples were digested in concentrated nitric and perchloric acids to dissolve trace metals and major elements in solution (Li et al., 2001). About 0.250 g ground sediment samples was weighted and placed into acid-washed Pyrex test tubes. About 10.0 ml of nitric acid and 2.5 ml of perchloric acid was added to each tube. Each mixture was gently shaken using a vortex and then placed in an aluminium-heating block (FOSS TECATOR 2000). The heating program was as follows: 50°C for 5 hrs, 75°C for 1½ hrs, 100°C for 1½ hrs, 125°C for 2 hrs, 150°C for 6½ hrs, 175°C for 2 hrs, and 190°C until completely dry. After cooling, 10 ml of 5% nitric acid were added to the residue and heated at 70°C for 1 hr. The mixture was shaken gently, poured into polyethylene tubes, and centrifuged prior to undergoing metal concentration analyses. The trace and major element concentrations of the solutions were measured by inductively coupled plasma – atomic emission spectrometry (ICP-AES, Perkin Elmer Optima, 3300DV).

For the analytical quality control, reagent blanks, standard reference materials (NIST 1646a), and sample replicates were randomly inserted in the analysis. There was no sign of contamination in the analysis (metal concentrations in the blanks < 1% of the sediment samples), and all of the relative standard deviations of the replicate samples were <10% (1 σ). The recovery rates for most of the trace metals in NIST 1646a were higher than 80%, except for Pb (around 65%) due to the low Pb concentration (11.7 mg/kg) of NIST 1646a.

Selected sediment samples were also analysed for chemical partitioning, using a five-step sequential extraction method (Tessier et al., 1979; Li et al., 1995). The same quality control scheme was adopted in the sequential extraction. The concentrations of

the five fractions of Co, Cu, Fe, Mn, Pb, and Zn compared with the independent total metal concentrations ranged between 80% and 115%.

Analyses of Pb isotopic composition

The selected samples were analysed for Pb isotopic composition using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS, *Perkin-Elmer ELAN 6100 DRC^{plus}*). Optimisation of plasma and mass spectrometer was performed daily as recommended by Perkin Elmer SCIEX. The sensitivity of Pb should be optimised higher than 20,000 cps/ 1 ppb. The nebulizer gas flow rate was adjusted so that the CeO/Ce ratio was less than 3 %. If the sensitivity of ICP-MS was not satisfactory, the whole optimisation process would be repeated until satisfactory results were obtained. An international standard reference material (NIST SRM 981, common lead) was used for sample calibration and analytical control. All of the analytical solutions were diluted to about 30 μg/kg Pb by using 5% high-purity nitric acid. The instrumental parameters of the ICP-MS were set to 250 sweeps per reading and 10 readings per sample. The relative standard deviation of each sample measurement was < 0.5% (2 σ). The average measured $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$, and $^{208}Pb/^{207}Pb$ ratios of SRM 981 were 0.0645 ± 0.0001, 1.0935 ± 0.0014, and 2.3678 ± 0.0049, respectively. These values were very close to the certified standard values (0.0646, 1.0933, and 2.3704, respectively). In this study, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of sediment were used for data interpretation.

Particle size analysis of sediments

The particle sizes of the sediment samples at the surrounding coastal regions outside the PRE were obtained using wet sieving method, and were separated into fractions on the basis of particle size: (1) greater than 200 μm, (2) 40 ~ 200 μm, (3) 2 ~ 40 μm, and (4) less than 2 μm. The four fractions with particles sized greater than 200 μm, 40 ~ 200 μm, 2 ~ 40 μm, and less than 2 μm, represent coarse sand, fine sand, silt, and clay, respectively (Nanjing Institute of Soil Science, 1978).

Statistical analysis

In the present study, both a Pearson Correlation (PC) and Principal Component Analysis (PCA) were conducted using SPSS® for Windows Release 12.0. In order to study the general characteristics of the sediments at the PRE and its surrounding coastal zone, the concentrations of trace metals and major elements as well as the fine clay content of the surface sediments were used as the input data in both the PC and PCA. The sediments that showed a close correlation were identified and grouped to undergo a further spatial pattern analysis.

Geochemical mapping

The concentrations of trace metals in the surface sediments were used as input data for grid-based contour mapping to study the spatial distribution of metals in the PRE and its surrounding coastal zone. The software used for the geochemical mapping was SURFER6.0®. A geo-statistical method called Kriging was adopted for the interpolation of the geochemical data of the study area.

3. Results and Discussion

Trace metal concentrations in the Pearl River Estuary (PRE) and its surrounding coastal area

The mean, standard derivation, median, and range of the concentrations of trace metals in the sediment cores at the PRE and its surrounding coastal area are summarised in Table 1, and the concentrations of major elements in the sediments are shown in Table 2. The elemental concentrations of the sediments at the coastal area presented in these two tables were calculated from the 12 sediment cores at the surrounding coastal area of the PRE (sediments in the PRE were not included). In order to assess trace metal contamination in this region, the trace metal concentrations were compared with the sediment quality criteria – Target (A) in Hong Kong (see Table 3) as the reference site values for this coastal region. The Target (A) sediment quality criteria refer to the desired quality for fairly clean sediment that is close to background levels. The mean concentrations of some trace metals (Cu and Zn) of the sediments in the coastal area were similar to the reference site values, while the concentrations of other trace metals (Cr, Ni and Pb) were slightly elevated in comparison with the reference values.

As shown in Table 1, the concentrations of Co, Cr, Cu, Pb, and Zn of the sediments in the PRE were significantly higher than those at the coastal area. In general, the mean concentrations of Co, Cr, Pb, and Zn in the PRE were about twice of those at the coastal area. The elevation of the Cu concentrations of the PRE sediments was particularly evident when compared with those of the coastal area. The mean Cu concentration of the PRE sediments was four times higher than that at the

coastal area. The elevated concentration of Cu in the PRE was probably due to the discharge of municipal and industrial wastewaters (e.g. printed circuit board industries), and agricultural runoff (e.g. Cu containing herbicides) in the Pearl River Delta region. However, the concentrations of the major elements and Ni were similar in both areas (see Table 2). These results imply that the sediments in the PRE received comparatively higher inputs of anthropogenic trace metals in the estuary than its surrounding coastal area, possibly because of the wide use of trace metals in industry and their presence in emissions from urban centres in the PRD region (Hills et al., 1998; Li et al., 2000b).

Distribution of trace metals in the sediments of the PRE and the coastal zone

Fig. 2 shows the geochemical maps of some major elements (Al, Ca, and Fe) and the clay content of the sediments in the PRE and its surrounding coastal area. The water depth varies within the PRE and increases as the distance increases southward from the PRE to the surrounding coastal region (from 7 m at A1 to 85 m at C10). The geochemical maps of Cu, Ni, Pb, and Zn in the sediments of the PRE and its surrounding coastal area are shown in Fig. 3. The distribution of Cu, Pb, and Zn in the PRE and its surrounding coastal area displayed large spatial variations. The concentrations of Ni and major elements in the coastal area displayed a typical concentration gradient similar to the distribution of the clay content.

The dispersal of trace metals in sediments is related to the transport and deposition processes from sources to sinks in the coastal area. Trace metals can be deposited and incorporated into sediment after entering aquatic system. Cu, Pb, and Zn showed a similar spatial distribution in the study area. Two hotspots of these metals were

10

identified at the mouth of the PRE and the northwest part of the coastal zone (see Figures 3a, 3c, and 3d). As shown in Table 1, the Cu concentrations in the sediments of the coastal area ranged between 2.7 and 49 mg/kg. The Cu concentrations of these two hotspots were close to the Trigger (B) Level of Cu (55 mg/kg) of the sediment quality criteria in Hong Kong. As shown in Table 1, a sixteen-fold difference between the highest and lowest concentrations of Pb was recorded in these sediments, while the Zn concentrations varied from 32.2 to 161 mg/kg (see Table 1). The Pb and Zn concentrations in the hotspots were also higher than the Trigger (B) Level (65 mg/kg for Pb and 150 mg/kg for Zn) of the sediment quality criteria in Hong Kong. The trace metal concentrations (Co, Cr, Cu, Ni, Pb, and Zn) in the sediments in the present study were in a comparable range with those reported for the other coastal areas, where urban and industrial development have also occurred, in China (e.g. Yangtze River coastal region) and Europe (e.g. River Danube, Black Sea) (Zhang, 1999; Lin et al., 2002; Secrieru and Secrieru, 2002; Woitke et al., 2003; Feng et al., 2004). This reflects the strong influences of anthropogenic activities in urban centres and of industrial development.

Physical transportation of trace metals

The physical properties (e.g. grain size) of sediments can affect the concentration of trace metals in estuaries and coastal areas. Within the PRE, the clay content of the sediments increases southward to the direction of the sea. On the other hand, at the coastal area, the clay content of the sediments decreases southward along the direction of the ocean (see Figure 2d). This pattern reflects a typical sediment transport mechanism in river delta regions (Lin et al., 2002; DeMora et al., 2004). As shown in Figure 2d, the fine-grained sediments were concentrated at the mouth of the estuary

and near the shore of the coastal area, where the hotspots of trace metals are situated. On the other hand, the locations of hotspots were in good agreement with the locations of turbidity maximum identified by Wai et al. (2004). These results indicated that fine particles might be a major carrier for transporting trace metals from the upstream source area to the coastal zone.

The grain size of sediments is a reflection of the hydrodynamic processes and the deposition conditions in a coastal region. The distribution of fine grain sediments reflects the physical transportation of sediments and associated trace metals. As shown in Figure 2d, the coarse grained sediments are concentrated at the upstream estuary and the outer part of the coastal zone. This pattern is in agreement with the numerical modelling of the transport of sediments by tidal currents in the PRE (Chen et al., 1999). The sediment transported into the PRE is mainly accumulated from the four river outlets (Hu Men, Jiao Men, Hongqi Men, and Heng Men). The distribution of grain size is controlled by the physical transportation of sediment, including sediment aggregation and deposition, gravitational circulation, tidal pumping, and tidal trapping (Grabemann et al., 1997; Mitchell et al., 1998; Wai et al., 2004). Sediment aggregation and deposition are influenced by current velocity, salinity, and suspended particulate matter in the water column. The suspended particulate matter, arising from the weathering of geological formations, land surface runoff, and atmospheric inputs, were transported to the estuary and then to the open ocean through the river. The upstream estuary is mainly characterised by inputs of fresh water and is subject to daily tidal action. Therefore, the easily deposited particles, e.g. most of the coarse grain particles, tend to be deposited at the floor in the upstream area of the estuary due to the sudden change in the velocity of the water currents in this area (Chen et al., 1999). The fine particulates carried by rivers end up farther

away in the estuary or in bays where the rivers discharge their loads, or are perhaps carried offshore onto the coastal area and beyond. In general, the fine particulates tend to accumulate in places where waves and currents are absent or weak. However, these particulates might be re-suspended and transported down the estuary during ebb tides. Within a tidal cycle, materials will be re-suspended and exchanged between different depositional regions. The re-suspension will continue until the limited stockpile of easily eroded particles is depleted (Grabemann et al., 1997). The ebb tidal flow generally spreads south-west from the upstream area to the mouth of the PRE (Chau and Jiang, 2001). One explanation for the relatively low concentrations of trace metals in the sediments at the upstream area of the estuary is the mixing of the strong river flow and the estuarine tide. In addition, a strong tidal current is not suitable for the deposition of fine particles. The physical characteristics of the sediments at the PRE and the coastal area showed distinct patterns in relation to the distribution of some major elements (Al and Fe). Since clay minerals contain Al and Fe in their crystal structure, those elements mainly originated from terrestrial rock-forming materials. The distribution of particle size generally agreed with the spatial distribution of Al and Fe (see Figures 2a, 2b, and 2d). These results suggested that the estuary and the offshore area of the coastal zone are mainly under the influence of terrestrial materials (Guieu et al., 1998).

Some statistical analyses of the surface sediments in the PRE and its surrounding coastal area were performed to further evaluate the relationship between sediment characteristics and trace metal concentrations. Table 4 presents the Pearson Correlation (PC) coefficients matrices between trace and major elements and fine fractions of particles in the surface sediments. The trace and major elements and fine particles were significantly correlated with each other. In order to evaluate the

13

patterns of trace metal contamination with the particle size, a multivariate statistical analysis of trace metals and particle size in the sediment samples from the study area was also performed. The rotated component matrixes of the PCA of trace metals, major elements, and particle size < 2 μm are presented in Table 5. The loading plot of the first two principal components (PCs) of the surface samples is depicted in Figure 4. PCA is one of the analytical tools used to assess metal behaviour in the aquatic system (Shine et al., 1995; Liu et al., 2003). In the analysis, the first two principal components accounted for nearly 90% of the total variance. Ca and Mg formed a distinct group (PC2) away from other elements. The fine particle was also isolated from other elements, but it was still dominated by the first component (PC1).

The results of PC and PCA showed good agreement with each other. The fine clay particles were an important carrier of riverborne trace metals to the coastal area. Although most of the trace metals showed a significant correlation with the fine particles in the PC, the PC coefficients between fine particles and Co, Cu, Mn, Pb, and Zn were lower than that between fine particles and Al, Fe, Cr, Ni, and V. The results of PCA also showed a strong association among Co, Cu, Mn, Pb, and Zn, and a rather weak association with the fine clay content. The results of the PC showed the closest correlation of Al with the fine clay content in sediments. A cluster of elements (Al, Co, Cr, Cu, Fe, Mn, Ni, V, Pb, and Zn) was associated in the same principal component with the fine-grained material and can be considered as closely related with each other. The disparate association of Ca and Mg with other elements in both statistical analyses possibly suggested that these two elements were influenced by marine water and sedimentation processes (Li et al., 2000b).

14

Chemical transportation of trace metals

Elevated trace metal concentrations were mainly associated with the sediments with high clay content. As shown in Table 4, although the correlation coefficients between the contents of fine clay and Co, Cu, Mn, Pb, and Zn were significantly correlated, the correlation was generally weaker than with other elements in the sediments. Al, Fe, Cr, Ni, and V showed higher correlations with the fine clay contents than the trace metals (Co, Cu, Pb, and Zn). This implies that the concentration of trace metals in sediments cannot be interpreted simply by a change in grain size. Therefore, physical transportation is not the only way to control the pattern of trace metals in the estuary and coastal mixing zone. The most important factors controlling the spatial variations of the trace metals in sediments included grain size, the chemical condition (e.g. sorption-adsorption of trace metals, flocculation etc.) of the sedimentary environment, and anthropogenic pollution (Willams et al., 1994). The distribution of trace metals between solution and particulate materials is strongly affected by the changes in the chemical property of particles in estuaries and their surrounding coastal area. This activity is strongly related to the distribution of trace metals in sediments. The results of statistical analyses, both of the PC and PCA, may indicate that these trace metals in the sediments had distinct geochemical behaviours, and possibly originated from major anthropogenic sources through inputs of water and air.

In the coastal area, a decrease in the concentrations of Cu, Pb, and Zn in sediments was observed in the offshore direction. This pattern can be related to the concentration gradient from sources to sinks. In addition, it also demonstrated that dissolved trace metals could be retained in the coastal area by the circulation regime of the surface water. The trace metals dissolved in the coastal water can be scavenged to particles,

15

and deposited into bottom sediments via chemical processes. As a result, the trace metals (Cu, Pb, and Zn) were accumulated in the sediment at the freshwater-saltwater interface. Some studies have found that the suspended solids near the mouth of an estuary generally have higher concentrations of trace metal than in the turbidity zones of the middle estuary (Elbaz-Poulichet et al., 1984; Grabemann et al., 1997; Guieu et al., 1998). The elevated concentrations of trace metals in the mouth of an estuary may be attributed to the mixing of river suspension and marine suspension, and a large proportion of particulate matter could be trapped in the mixing zone (Elbaz-Poulichet et al., 1984; Guieu et al., 1998; Chester, 2000; DeFalco et al., 2003).

Information on the chemical partitioning of trace metals can provide further evidence of the potential interactions of trace metals between an estuary and a coastal area. The chemical partitionings of trace metals (Cu, Pb, and Zn) of selected sediment samples are presented in Fig. 5. The means and ranges of Cu, Pb, and Zn in different geochemical fractions of the sediment samples in the PRE (Li et al., 2000a, 2001; Liu et al., 2003) and the surrounding coastal areas (in the present study) are summarised in Table 6. Significantly elevated concentrations of trace metals in the five operationally defined geochemical fractions were found in the PRE in comparison with the surrounding coastal area. As mentioned in the previous section, salinity is a factor affecting the aggregation and deposition of sediment. An increase in salinity from a freshwater zone to a marine zone favours the adsorption of trace metals on particulates, induces flocculation, and further encourages the aggregation and deposition of sediment. This factor can contribute to different concentrations of trace metals in various geochemical fractions between the PRE and the surrounding coastal area. In Figures 5a and 5c, the geochemical partitioning of Cu and Zn showed a significant differentiation between the sediments in the PRE and the coastal area. A

higher percentage of trace metals binding to the non-residual fractions was found in the sediments in the PRE than that in the surrounding coastal area. The higher percentage of trace metals binding to the non-residual fractions suggested that the trace metals might simply be affected by sorption-adsorption processes (Tessier et al., 1979). This result implied that a larger fraction of sediment in the estuary was freshly deposited and formed by the adsorption of trace metals. The saturation of mineral cations in the freshwater-saltwater interface may lead to a reaction between metal ions and mineral cations and form precipitation (Song and Müller, 1999). In addition, the upstream estuary areas are close to intensive industrial operations. Industrial discharges may lead to a large input of metals to the estuary. Flocculation affects both organic and inorganic components, such as fluvial clay mineral suspension, colloidal species of Fe, and dissolved organics. The aggregation of particles into larger sizes may take place via biological mediation (Chester, 2000). The resulting materials may be temporarily deposited at the mouth of estuary and associate with the non-residual fraction in sediments.

In the present study, the fraction of Fe/ Mn oxides was a dominant non-residual fraction among three other non-residual fractions. Fine grain-sized particles consist of larger surface-active fractions and Fe/Mn oxide surface coatings. These fine particles can bind more strongly with metal ions than coarse particles. Freshly formed Fe/Mn oxides are very efficient scavengers for metals. In addition, due to some biogeochemical mechanism between the estuarine and coastal areas, the dissolved trace metals can form coagulations of colloidal materials under higher salinity conditions with more efficient scavenging capability. Therefore, both the adsorption and coagulation of dissolved trace metals were induced, followed by deposition to the bottom sediment in this freshwater and marine water interface. With the increase in

salinity, the amount of dissolved trace metals in the water column available for the process of coagulation decreases; hence, the concentrations of trace metals in the non-residual fraction of the sediment is decreased in the coastal area (Nriagu, 1979). Fig. 6 shows a schematic representation of the transportation of trace metals from estuary to open ocean. Figure 6a shows the physical transportation of trace metals from estuary to open ocean, while Figure 6b shows the chemical transportation of these trace metals. Overall, the distribution patterns of different metals in sediments may arise from the different locations of their terrestrial sources, solid speciation, and the response to an increase in salinity, and/or the differential bioavailability and particle scavenging of metals in water columns. Therefore, a variety of hydrodynamic, physical, chemical, and biological processes between the estuary and coastal mixing zone plays an important role in the transport and deposition processes of trace metals in the study area.

Possible Pb sources in sediments

Pb contamination of the coastal area was relatively significant compared with that of other trace metals in terms of total metal concentrations in sediments. In order to assess Pb contamination and identify potential Pb sources of sediment, the Pb isotopic compositions of the total concentrations of Pb in selected samples of sediment were analysed. Table 7 presents the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of these sediments.

Estuaries and coastal areas receive a variety of inputs of trace metals from natural and anthropogenic sources. The Pb isotopic compositions of some natural and anthropogenic sources in the region have previously been studied (Zhu, 1995; Zhu et al., 1998 & 2001; Duzgoren-Aydin et al., 2004). The Pb isotopic composition of the

surface and sub-surface sediments showed clear differentiation (Ip et al., 2004). This makes it possible to differentiate between the recent anthropogenic inputs and the natural geological Pb of the sediments in the adjacent coastal area. The average $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the total Pb in the coastal sediments were 1.188 ± 0.0027, and 2.484 ± 0.0047 respectively. As shown in Table 8, the range of Pb isotopic compositions varied significantly among different environmental media. Geochemical background Pb generally has relatively high $^{206}Pb/^{207}Pb$ ratios (~ 1.200), while low $^{206}Pb/^{207}Pb$ ratios (< 1.190) may indicate recent anthropogenic inputs. The results of the present study showed that the Pb ratios of sediments were relatively low compared with the geological materials, suggesting the influence of anthropogenic inputs in the coastal area.

The correlation between the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios of the sediments within the PRE and at the coastal area is presented in Fig. 7. The Pb isotopic signatures of air depositions and soils as well as other known natural and anthropogenic sources in the region are also presented in this figure. The linear correlation of the Pb isotope ratios in the sediments at the coastal area was insignificant (R^2 = 0.186), indicating that the Pb in the sediments did not fit a binary mixing model, and that there may be more than two possible sources. Sediments could receive Pb from multiple sources, including atmospheric depositions, wastewater discharge, soil erosions, and biogenetic particulates in the marine environment. The sediments in the coastal area had a similar range of Pb isotopic ratios as the surface sediments within the PRE. The $^{206}Pb/^{207}Pb$ ratios were in the range of 1.181 to 1.192 for the sediments in the coastal area, and 1.187 to 1.198 for the sediments of the PRE. The spatial distribution of Pb (see Figure 3c) indicated that the Pb concentrations of the sediments generally decreased as distance from the PRE

to the coastal area increased. Increasing Pb isotopic ratios in sediments were found from the land to sea direction, indicating the diffusion pattern of anthropogenic Pb in the coastal area. On the other hand, the similar Pb isotopic signatures of the sediments between the estuary and the mouth of the estuary suggested that the Pb in the coastal area came mainly from the PRE and the tributaries. In general, only a rather small proportion of the sediment is transported beyond the shelf edge and reaches the bottom of the deep sea. However, the $^{206}Pb/^{207}Pb$ ratios of the sediments in the coastal area generally were lower than those in the PRE, suggesting that the sediments in the coastal area were not only affected by the PRE sediments, but also by other anthropogenic sources, including the Pb signature in Hong Kong and/or some long-range air deposition in the region (Wong and Li, 2004; Duzgoren-Aydin et al., 2004).

4. **Conclusions**

The present study showed clear anthropogenic inputs of trace metals mainly from the PRE and West River to the surrounding coastal area of the South China Sea. The results indicated the potential pathways of trace metals via the transport of sediment from the PRE to the coastal area. Trace metal associated with coarse particles mainly deposited on the upstream area of the PRE, while dissolved trace metals and trace metals associated with fine particulates could be transported downstream or even to its surrounding coastal area by physical transportation. Dissolved trace metals and trace metals associated with fine particles tended to be deposited at the interface between freshwater and marine water zones due to the processes of adsorption and coagulation of dissolved trace metals with particulates as well as aggregation of particulates. Cu, Pb, and Zn showed different spatial distribution and chemical partitioning patterns from other elements, reflecting their anthropogenic origins in the

estuarine areas. The Pb isotopic compositions of coastal sediments suggested that the anthropogenic origin of Pb in the sediments was mainly from sources in the PRE, with additional inputs from Hong Kong and other regions. The synchronous signatures of Pb isotopic compositions, metal partitioning and elemental concentration of coastal sediments showed the diffusion gradient from land to sea indicating anthropogenic origin of trace metals from the PRE. The trace metals associated with the sediment in the upstream area were mainly controlled by the physical process, while those deposited in the interface zone between freshwater and marine water were dominated by the chemical process.

Acknowledgements

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Table 1.

Summary of trace metal concentrations in the sediment cores from the Pearl River Estuary (PRE) and its surrounding coastal zone

Metals	Concentration (mg/kg)	PRE (n=606)	Coastal zone (n=426)
Co	Mean ± SD[*]	14.6 ± 3.4	8.91 ± 1.61
	Median	14.7	9.02
	Range	7.4 ~ 24.0	4.49 ~ 15.9
Cr	Mean ± SD	87.6 ± 22.0	47.1 ± 10.5
	Median	88.4	47.4
	Range	33.8 ~ 135	20.3 ~ 84.5
Cu	Mean ± SD	46.8 ± 17.0	10.4 ± 6.0
	Median	49.5	9.90
	Range	6.2 ~ 100	2.71 ~ 49.1
Ni	Mean ± SD	34.8 ± 10.1	30.4 ± 5.6
	Median	35.5	30.4
	Range	10.6 ~ 54.1	13.9 ~ 48.5
Pb	Mean ± SD	47.9 ± 13.7	21.7 ± 7.7
	Median	47.6	23.3
	Range	16.0 ~ 96.3	4.6 ~ 73.8
Zn	Mean ± SD	140 ± 42	72.1 ± 17.0
	Median	142	72.2
	Range	55.1 ~ 268	32.2 ~ 161

[*] SD – standard derivation

Table 2.

Summary of concentrations of major elements in the sediment cores from the PRE and its surrounding coastal zone

Metals	Concentration (%)	PRE (n=606)	Coastal zone (n=426)
Al	Mean ± SD[*]	5.34 ± 1.31	4.69 ± 1.08
	Median	5.34	4.70
	Range	2.48 ~ 9.87	1.67 ~ 7.5
Ca	Mean ± SD	0.698 ± 0.514	2.06 ± 1.44
	Median	0.589	1.53
	Range	0.088 ~ 4.10	0.563 ~ 7.60
Fe	Mean ± SD	3.76 ± 0.67	2.60 ± 0.41
	Median	3.85	2.62
	Range	2.16 ~ 5.48	1.32 ~ 3.93
Mg	Mean ± SD	0.722 ± 0.133	1.00 ± 0.10
	Median	0.727	1.01
	Range	0.228 ~ 1.15	0.677 ~ 1.23
Mn	Mean ± SD	0.0673 ± 0.0209	0.0491 ± 0.0115
	Median	0.0659	0.0516
	Range	0.0204 ~ 0.139	0.0198 ~ 0.0910

[*] SD – standard derivation

Table 3.

Sediment quality criteria in Hong Kong (Lau et al., 1993)

Class	Cr	Cu	Ni	Pb	Zn
Target (A) [a]	25	20	20	35	75
Trigger (B) [b]	50	55	35	65	150
Action (C) [c]	80	65	40	75	200

Notes: [a] Target (A) – indicates the desired quality for fairly clean sediment that is close to background levels;

[b] Trigger (B) – indicates that the sediment is moderately contaminated;

[c] Action (C) – indicates heavily polluted sites.

Table 4.

Pearson Correlation (PC) coefficient matrix between the trace and major elements and fine fractions of sediments (n=38)

	Al	Fe	Ca	Co	Cr	Cu	Mg	Mn	Ni	Pb	V	Zn
Fe	0.925*	-										
Ca	-0.387	-0.459*	-									
Co	0.862*	0.971*	-0.566*	-								
Cr	0.890*	0.969*	-0.445*	0.947*	-							
Cu	0.740*	0.829*	0.489*	0.860*	0.890*	-						
Mg	0.667*	0.542*	0.228	0.382	0.468*	0.106	-					
Mn	0.632*	0.819*	-0.567*	0.871*	0.763*	0.671*	0.194	-				
Ni	0.930*	0.958*	-0.347	0.924*	0.970*	0.835*	0.585*	0.705*	-			
Pb	0.787*	0.880*	-0.627*	0.904*	0.869*	0.899*	0.185	0.808*	0.817*	-		
V	0.935*	0.922*	-0.413*	0.912*	0.936*	0.895*	0.475*	0.643*	0.954*	0.838*	-	
Zn	0.874*	0.948*	-0.508*	0.958*	0.970*	0.943*	0.339	0.793*	0.949*	0.929*	0.946*	-
FP[a]	0.806*	0.746*	-0.185	0.664*	0.706*	0.464*	0.766*	0.420*	0.780*	0.534*	0.726*	0.639*

* Correlation is significant at the 0.01 level (2-tailed)

[a] FP – fine fractions of sediments (< 2μm)

Table 5.

The rotated component matrixes of sediments of trace metals, major elements, and particle size < 2 μm in the PRE and surrounding coastal area

Element	PC1	PC2
Al	0.912	0.310
Ca	-0.554	0.607
Cd	0.982	0.013
Co	0.982	-0.041
Cr	0.974	0.088
Cu	0.899	-0.217
Fe	0.979	0.133
Mg	0.413	0.875
Mn	0.822	-0.240
Ni	0.955	0.239
Pb	0.931	-0.228
V	0.950	0.141
Zn	0.985	-0.046
ps0.002	0.702	0.567

Table 6.

Means and ranges of trace metal concentrations in various operationally defined geochemical fractions in the surface sediments from the PRE (Li et al., 2000a, 2001; Liu et al., 2003) and the surrounding coastal area (mg/kg)

		Cu		Pb		Zn	
		PRE	Coastal zone	PRE	Coastal zone	PRE	Coastal zone
Exchangeable	Mean	0.19	0.09	0.65	0.04	0.14	0.08
	Range	ND - 0.34	ND - 0.53	ND - 1.5	ND - 0.07	0.06 - 0.23	ND - 0.16
Carbonate	Mean	2.4	0.70	11	6.5	5.8	2.9
	Range	1.41 - 3.42	ND - 3.26	2.3 - 19.7	ND - 11.2	2.79 - 11.7	0.34 - 23.1
Fe-Mn oxide	Mean	5.0	1.3	42	8.1	36	18
	Range	1.89 - 8.48	ND - 4.23	20.2 - 203	1.74 - 19.9	16.0 - 89.1	8.38 – 50.0
Organic	Mean	8.8	3.0	17	2.3	6.8	5.0
	Range	0.68 - 14.7	0.47 - 11.6	9.3 - 27	0.54 - 5.33	2.48 - 18.4	2.17 - 13.2
Residual	Mean	30	10	40	6.3	71	48
	Range	4.75 - 41.6	3.00 - 30.1	19.5 - 60.9	1.81 - 12.7	16.4 - 95.6	24.7 - 77.7

Table 7.

Pb isotopic ratios of selected sediments samples at the coastal zone

Sample ID [*]	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
A2-01	1.187	2.486
A2-06	1.190	2.488
A2-10	1.191	2.489
C3-02	1.187	2.485
C3-20	1.182	2.477
C3-36	1.191	2.494
C4-01	1.181	2.481
C4-15	1.186	2.488
C4-27	1.190	2.487
C6-01	1.182	2.480
C6-11	1.188	2.489
C6-23	1.188	2.492
D1-01	1.189	2.490
D1-26	1.188	2.486
D1-49	1.190	2.488
D2-01	1.186	2.483
D2-25	1.188	2.484
D2-49	1.188	2.484
D3-01	1.186	2.484
D3-16	1.186	2.492
D3-41	1.186	2.482
E1-01	1.188	2.478
E1-18	1.189	2.480
E1-34	1.186	2.478
E2-01	1.187	2.483
E2-26	1.189	2.482
E2-49	1.188	2.484
E3-01	1.186	2.478
E3-21	1.185	2.478
E3-42	1.190	2.486
E6-01	1.192	2.480
E6-14	1.191	2.483
E6-27	1.191	2.477

[*] The prefixes of the sample IDs represent the locations of the samples shown in the sampling map, while the number after the prefixes correspond to the depths in the sediment profiles

Table 8.

Pb isotopic compositions of some natural background and anthropogenic sources in the PRD and Hong Kong (HK)

|	$^{204}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	Reference
Natural sources:				
Uncontaminated soils in the PRD	0.06400	1.1952	2.4815	Zhu et al., 2001
Bedrock of Tap Mun Island (HK)	0.0636	1.2206	2.5291	Duzgoren-Aydin et al., 2004
Natural geological sources (HK)	-	1.2265 ± 0.0228	2.5480 ± 0.0581	Present study
Granite in the eastern Cathaysia	0.06381	1.1834	2.4680	Zhu et al., 1998
Granite in the PRD	0.06375	1.1842	2.4824	Zhu et al., 1998
Volcanic rocks in Foshan	0.06375	1.1842	2.4824	Zhu et al., 1998
Upper continental crust	0.0636	1.229	2.484	Kramers and Tolstikhin, 1997
Pollutant sources:				
Tunnel ceiling dusts (HK)	0.0645	1.1254	2.4017	Duzgoren-Aydin et al., 2004
Automobile exhaust in the PRD	0.06420	1.1604	2.4228	Zhu et al., 2001
Fankou Pb-Zn deposit	0.06374	1.1716	2.4725	Zhu et al., 1998
Road dust in HK	0.0641	1.1558	2.4408	Duzgoren-Aydin et al., 2004
Gully sediments in HK	0.0642	1.1515	2.4322	Duzgoren-Aydin et al., 2004
Urban Soils in HK	0.0633 ~ 0.0648	1.126 ~ 1.225	2.405 ~ 2.534	Wong and Li. 2004; Li et al., 2004

List of Figure Captions

Fig. 1. The locations of the sampling sites at the Pearl River Estuary (PRE) and its surrounding coastal zone

Fig. 2. Spatial distribution of (a) Al, (b) Fe, (c) Ca, and (d) particle size < 2 μm (in percentage) in the sediments of the PRE and its surrounding coastal zone

Fig. 3. Spatial distribution of (a) Cu, (b) Ni, (c) Pb, and (d) Zn in the sediments of the PRE and its surrounding coastal zone

Figure 4. The principal component analysis loading plot of trace metals, major elements, and particle size < 2 μm in the sediments

Fig. 5. The chemical partitioning of (a) Cu, (b) Pb, and (c) Zn along the N-S transect of the surface sediments collected at the PRE (Li et al., 2000a; Li et al., 2001; Liu et al., 2003) and the surrounding coastal area (in the present study)

Fig. 6. Schematic representation of the transportation of trace metals from the estuary to the open ocean

Fig. 7. The relationship between $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ of the sediments at the coastal zone (this study) and the PRE (Ip et al., 2004), atmospheric deposition (Wong et al., 2003) and soils in the PRD region (Wong et al., 2002) and Hong Kong (Li et al., 2004), as well as natural geological sources and anthropogenic sources in the PRD (Zhu et al., 2001) and Hong Kong (Duzgoren-Aydin et al., 2004; this study)
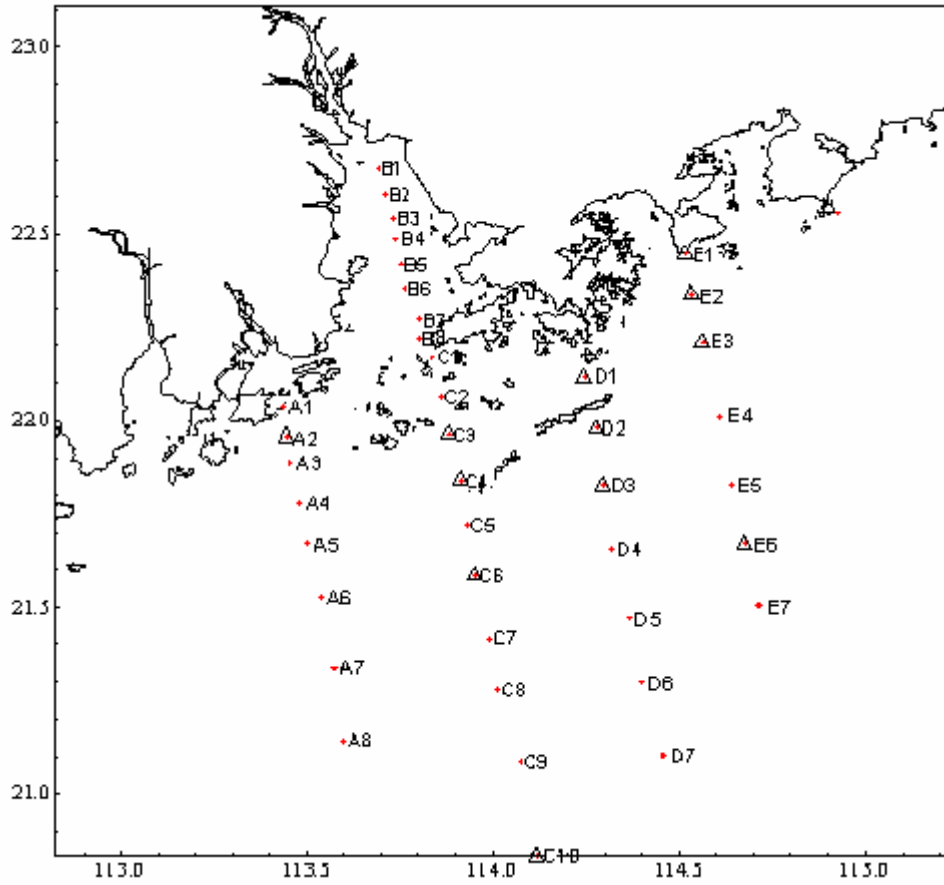
Fig. 1. The locations of the sampling sites at the Pearl River Estuary (PRE) and its surrounding coastal zone

Notes: + - The sampling locations for surface grab samples

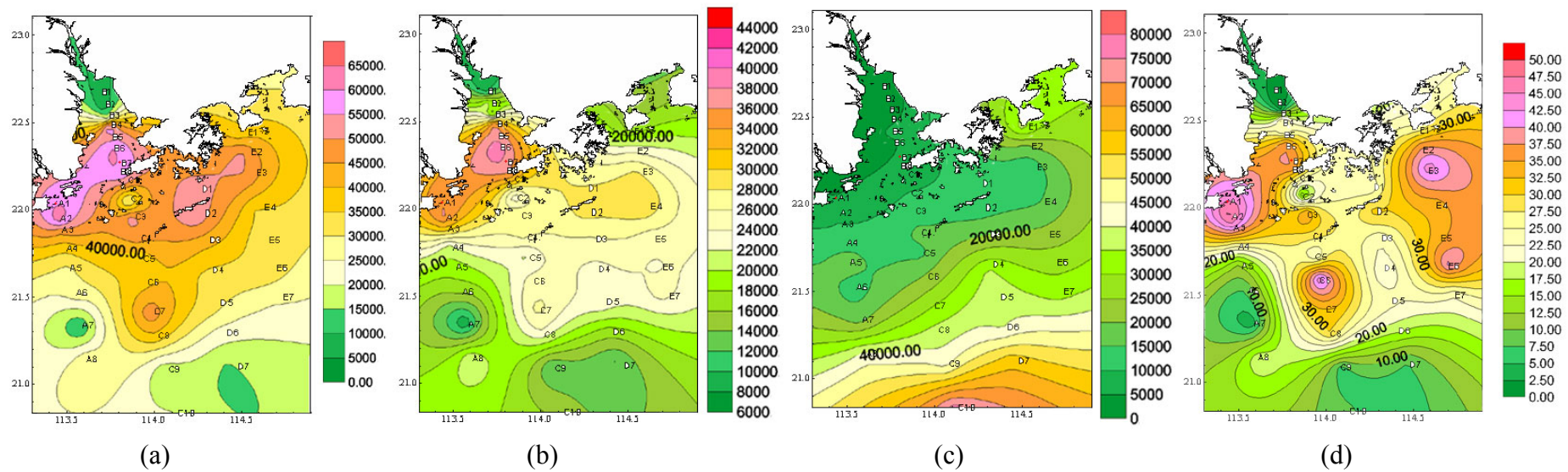Δ - The sampling locations for sediment cores

Fig. 2. Spatial distribution of (a) Al (mg/kg), (b) Fe(mg/kg), (c) Ca (mg/kg), and (d) particle size < 2 μm (in percentage) in the sediments of the PRE and its surrounding coastal zone
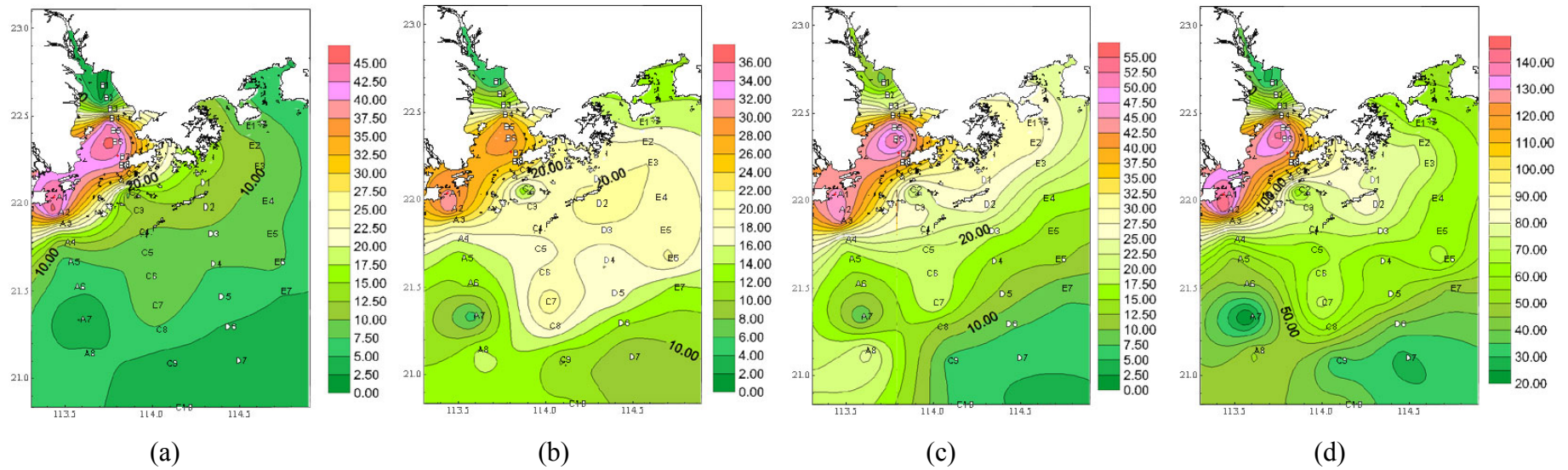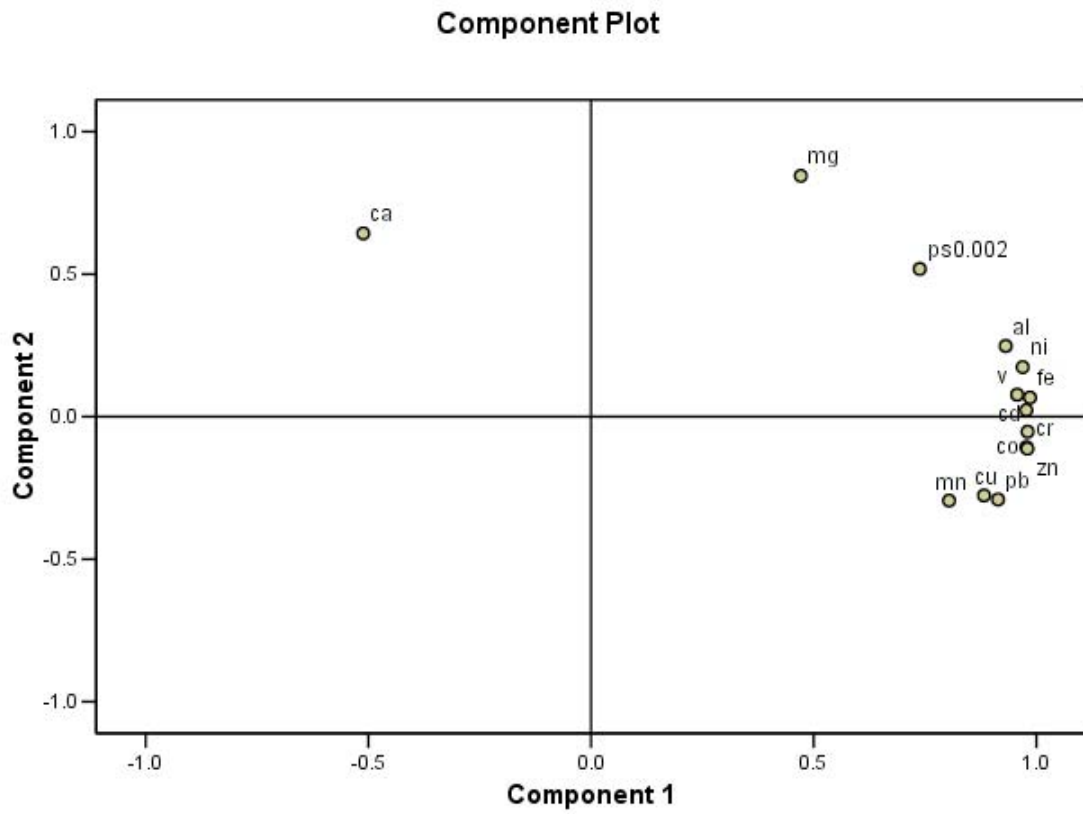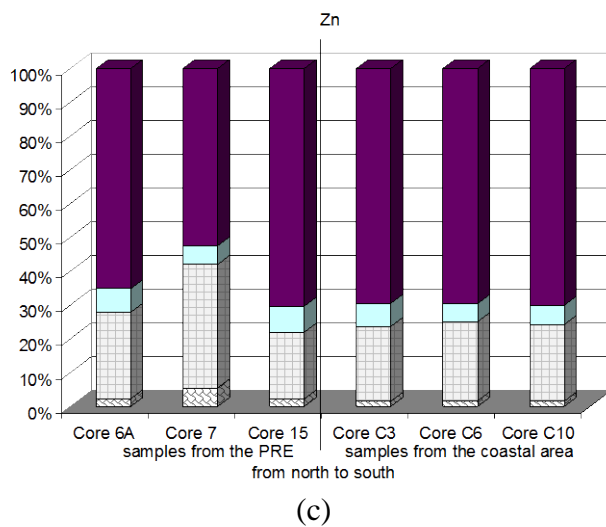
Fig. 3. Spatial distribution of (a) Cu (mg/kg), (b) Ni (mg/kg), (c) Pb (mg/kg), and (d) Zn (mg/kg) in the sediments of the PRE and its surrounding coastal zone

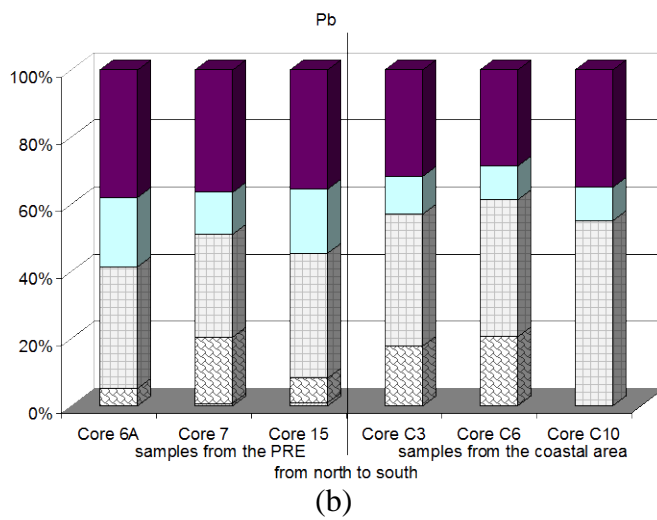Fig. 4. The principal component analysis loading plot of trace metals, major elements, and particle size < 2 μm in the sediments
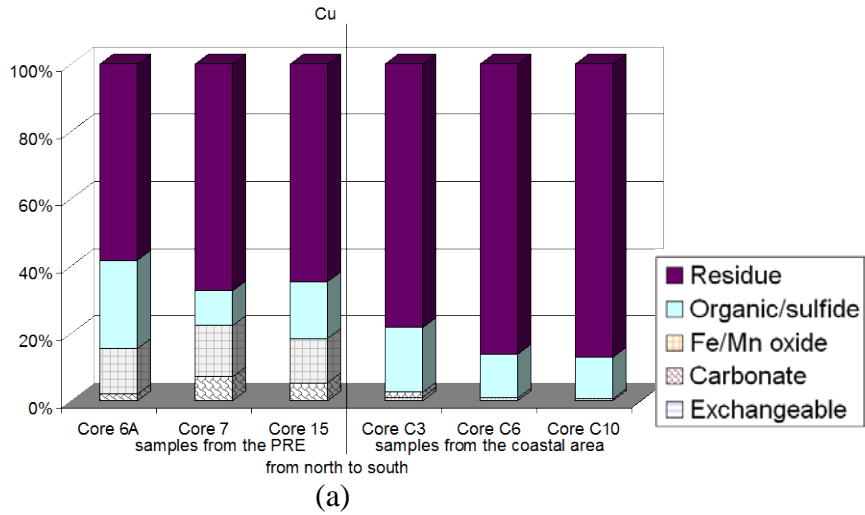
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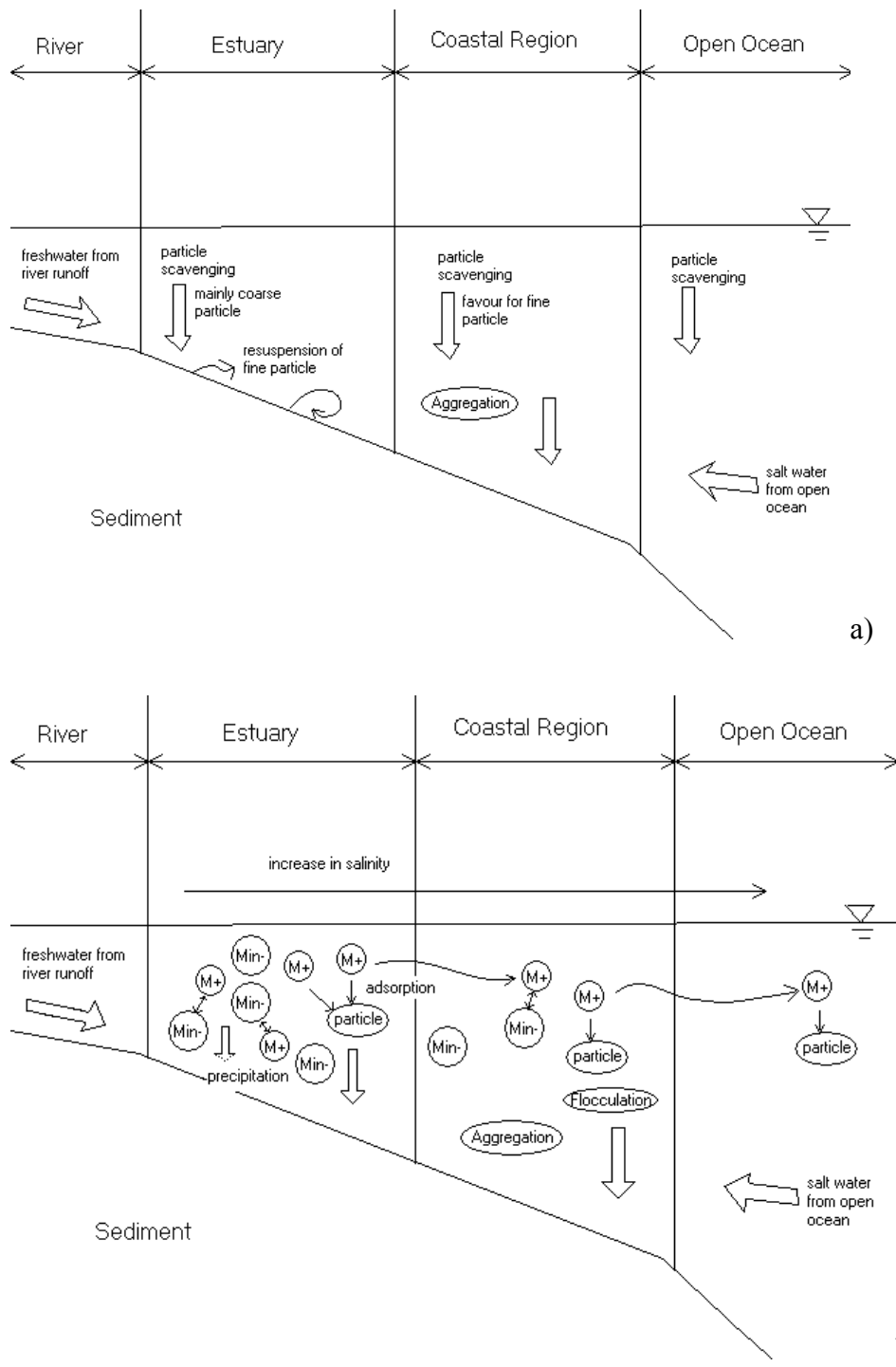
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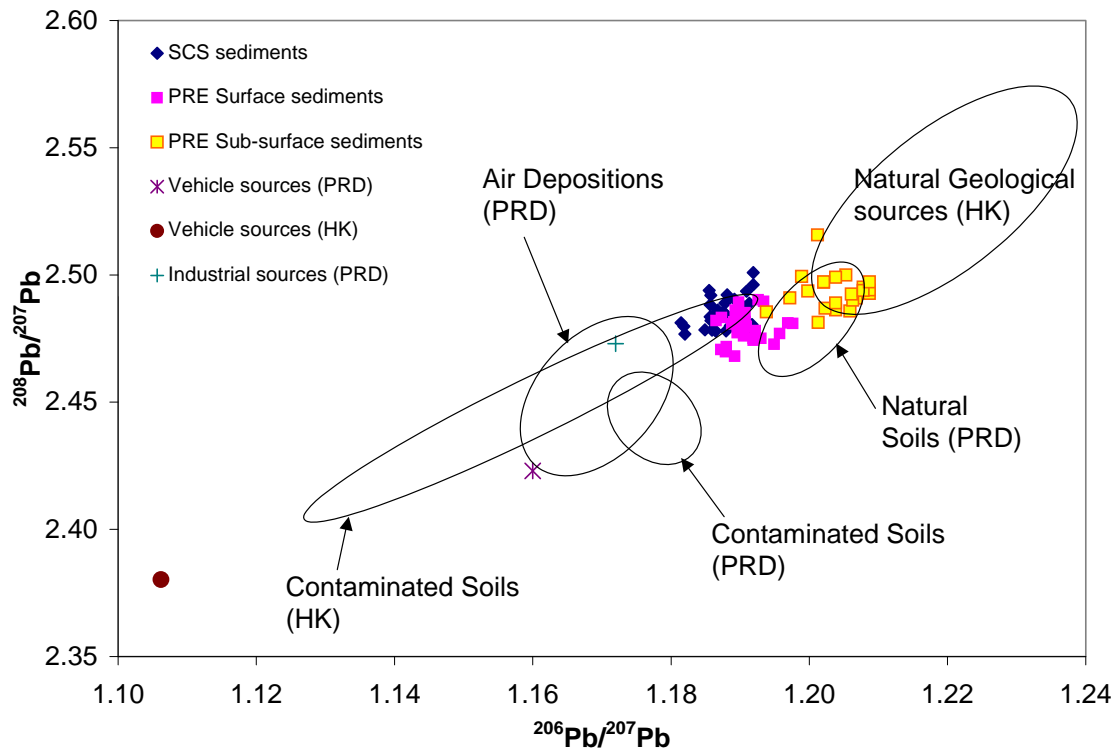
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