Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary

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“Capsule”: *Multivariate statistical analysis identified the heavy metal accumulation layers of sediment profiles and showed the various sources of metals in the estuary.*

Abstract

The concentrations and chemical partitioning of heavy metals in the sediment cores of the Pearl River Estuary were studied. Based on Pearson correlation coefficients and principal component analysis results, Al was selected as the concentration normalizer for Pb, while Fe was used as the normalizing element for Co, Cu, Ni and Zn. In each profile, sections with metal concentrations exceeding the upper 95% prediction interval of the linear regression model were regarded as metal enrichment layers. The heavy metal accumulation mainly occurred at sites in the western shallow water areas and east channel, which reflected the hydraulic conditions and influence from riparian anthropogenic activities. Heavy metals in the enrichment sections were evaluated by a sequential extraction method for possible chemical forms in sediments. Since the residual, Fe/Mn oxides and organic/sulfide fractions were dominant geochemical phases in the enriched sections, the bioavailability of heavy metals in sediments was generally low. The ²⁰⁶Pb/²⁰⁷Pb ratios in the metal-enriched sediment sections also revealed the influence of anthropogenic sources. The spatial distribution of cumulative heavy metals in the sediments suggested that the Zn and Cu mainly originated from point sources, while the Pb probably came from non-point sources in the estuary. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Estuaries are complex and dynamic environments, which receive large amounts of anthropogenic contaminants from nearby urban areas and industrial sites. Among the various contaminants, heavy metals are of particular concern due to their environmental persistence and biogeochemical recycling and ecological risks. The high total concentrations of heavy metals in sediments may not necessarily indicate anthropogenic contamination, because of different background levels in parent materials and sediment properties. The natural occurrence and chemical speciation of metals can also complicate the evaluation of potentially polluted aquatic sediments (Schiff and Weisberg, 1999).

Numerous efforts have been made to normalize the dilution effect invoked by coarse particles on metal contaminant concentrations in sediments, in order to understand the potential factors influencing the distribution of metals among different locations in a specific study area. The corresponding methods can be classified as the physical separation of different fractions in sediments and the mathematical normalization of the chemical data by a suitable sediment property (i.e. a reference element or constituent). The latter, containing ratio calculation and regression analysis, may be preferable, due to the difficulties associated with the efficiency and feasibility of mechanical separation presented in many cases. The reference element, a fundamental or conservative tracer of the natural metal-bound phases, is assumed to have a uniform flux from the coastal bedrock. Therefore, the anthropogenic inputs of trace metals can be identified by alterations of the relationships between trace metals and the reference

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element (Luoma, 1990). However, there is no uniform protocol on the appropriate sediment constituent for metal concentration normalization. The common normalizers for heavy metal concentrations mainly include Al, Fe, total organic carbon (TOC) and Li. However, the accuracy or reliability of either Al or Fe may be not suitable if the contaminant source introduces large quantities of these two elements (Tam and Yao, 1998). TOC, without a geochemical basis, is also subject to considerable influence by human activities, and is often a pollutant by itself. Relationships between Li and trace metals in fine-grain sediments are usually similar to those of Al (Daskalakis and O'Connor, 1995).

The estuary sediments are usually derived from different mineralogical sources (e.g. of fluvial origin, marine provenance and mixtures). It is often impossible to find a single representative reference site for spatial comparison to detect and quantify anthropogenic pollution. Alternatively, the background variability of metal concentrations in sediments can be estimated or corrected by a baseline model of linear regression (Daskalakis and O'Connor, 1995; Chapman and Wang, 2001). This method fully considers the background concentrations of naturally occurring substances and provides important insight into the origins of contamination.

It is generally regarded that the bioavailability of heavy metals is closely related to their chemical forms, rather than the total concentration in sediments (Förstner, 1993). Heavy metals in sediments occur in different geochemical forms, which have distinct mobility, biological toxicity and chemical behaviors. It is essential to distinguish and quantify the various forms of metals to yield a better understanding of the potential and actual environmental impacts of contaminated sediments. However, direct determination of specific chemical forms is generally impractical due to various binding phases of metals and their structural properties. Alternatively, sequential extraction procedures, which define the metal activity by the analytical schemes, become preferred (Gonzalez et al., 2000). In addition, the isotopic composition of Pb has been utilized as an indication of pollution sources (Monna et al., 1999; Weiss et al., 1999), since the stable Pb isotope ratios in sediments usually depend on the parent materials and anthropogenic sources.

The Pearl River is the largest river system in Southern China, with an average water flow of 11,070 m³/s. With fast economic growth and an increasing population in the area, the annual discharges of industrial wastewater and sewage water have risen to as much as 200 million and 40 million tons respectively (Wong et al., 1995). Consequently, the inputs of pollutants, particularly heavy metals, to the local aquatic environment are greatly increased. The objectives of the present study are: (1) to evaluate heavy metal enrichment in sediment

profiles using the appropriate reference element ascertained by statistical correlation and principal component analysis, and (2) to examine the accumulation and bioavailability of heavy metals in sediments by the baseline model of linear regression, chemical partitioning, and Pb isotope composition analysis.

2. Materials and methods

2.1. Sampling and sample preparation

Sediment cores were collected in the estuary area (see Fig. 1) using a gravity corer equipped with an automatic clutch and reverse catcher. Each core was then sliced into sections at 10-cm intervals from 0 to 1 m and at 20-cm intervals from 1 to 2 m in depth (Li et al., 2000a). The physicochemical properties including organic matter (loss on ignition at 450 °C for 6 h) and particle size distribution were determined according to the methods described by Mudrich et al. (1996).

2.2. Chemical analysis

Sediment samples (0.1 g), dried at 105 °C and ground to pass through a 74-μm sieve, were digested with a mixture of concentrated HNO₃ (2 ml), HClO₄ (1 ml) and HF (5 ml) at 90–190 °C for 16 h in a heating block (Foss Tecator 2040 Digester). Afterwards, trace and major elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkin-Elmer Optima 3300DV). The details of the total metal concentration measurements can be found elsewhere (Li et al., 2000a).

Five operationally defined fractions can be obtained by sequential extraction procedures (Tessier et al., 1979; Li et al., 1995): the exchangeable form (1.0 M MgCl₂, pH 7.0, for 20 min), the carbonate bound form (1.0 M NaOAc, pH 5.0, for 6 h), the Fe/Mn oxide bound form (reducible phase; 0.04 M NH₂OH·HCl in 25% HOAc at 96°C for 6 h), the organic matter/sulfides bound form (oxidized phase; 30% H₂O₂ at 85°C for 3 h) and the residual form (total digestion with a concentrated mixture of HNO₃ and HClO₄). After each step, the separation of solid and solution was implemented by centrifuging at 2000 rpm for 15 min. The supernatant was then removed by pipette, and the residual sediment was rinsed by de-ionized water and centrifuged again. The washing water was discarded. Metal concentrations in solutions were acidified with HNO₃ and measured using ICP-AES (ICP-AES, Perkin-Elmer Optima 3300DV; Li et al., 2000b, 2001).

For Pb stable isotope analysis, 1 ml concentrated HNO₃ and 4 ml concentrated HClO₄ were applied to each sample (0.1 g) in a boron silicate tube. All the tubes were heated at 150 °C for 1 h, then at 180 °C for 5 h

Fig. 1. A sketch map of sampling sites in the Pearl River Estuary.

(Munksgaard et al., 1998). After cooling, 2.5 ml concentrated nitric acid was added into each tube and cooked at 120 °C for 30 min. DIW (20 ml) was then added, and the tubes were heated at 100 °C for 30 min. At room temperature, the digesting solution was filtered through a Whatman 40 membrane into a 50-ml volumetric flask and diluted to the total volume.

The Pb stable isotopes ^{206}Pb and ^{207}Pb were analyzed by inductively coupled plasma–mass spectrometry

(ICP–MS, Perkin-Elmer ELAN 6000), and calibrated by a standard reference material (RSM 981, NIST). The measured $^{206}\text{Pb}/^{207}\text{Pb}$ ratio for RSM 981 was 1.0925 ± 0.0019 ($n=8$), compared to the reference value of 1.0933. The average deviation of $^{206}\text{Pb}/^{207}\text{Pb}$ for duplicates was $0.24 \pm 0.34\%$ ($n=18$).

In this study, standard reference materials were used to verify the accuracy of metal analysis in total concentration and the sequential extraction procedure.

The recovery rates of heavy metals in the standard reference material were around 85–110%. In addition, the cumulative concentrations of metals in sequential extraction sediments were comparable to the independent total concentrations, with recovery rates of 82–104%. Reagent blanks were also employed for background correction and random error calculation. At least one duplicate was run for every six samples to confirm the precision of the sequential extraction method. The precision and bias were less than 10% in all analyses.

2.3. Statistical analysis

All statistical calculations, including Pearson correlation coefficients, principal component analysis (PCA) and linear regression, were conducted using Statistica for Windows Ver. 4.5 (StatSoft Inc., USA).

3. Results and discussion

3.1. Metal concentrations in the profiles

The average and range of metal concentrations in the sediment cores, as well as some regional background values and sediment quality guidelines, are listed in Table 1. In comparison, the concentrations of Cu, Ni, Pb and Zn were generally elevated in the sediment cores. In addition, the average concentrations of these metals had increased in the last 20 years relative to the previous monitoring results (Wong et al., 1995). These results showed the influences of the increasing discharges of contaminants from local industrial, agricultural and urban activities.

The average metal concentrations in the surface or subsurface sections were generally higher than in the deeper layers, although the differences were small, and there were distinguish patterns among the individual profiles. The vertical distribution of metal concentrations is commonly affected by many factors, such as sediment properties, hydrodynamic conditions (surface waves, turbulence and tidal currents) and dredging activities. On the whole, three distribution patterns can be categorized for the individual cores in this study. The first is the mixed-up pattern at the top and bottom sections located in the river mouth area (close to the river channels), possibly due to annual dredging operations, effluent input and natural hydrodynamic conditions. The second is the enriched trend at the top layers of the profiles in the western coastal zones, which indicates the accumulation of metal pollutants from adjacent land sources under relatively stable and normal sedimentation processes, particularly in recent years. The last is the uniform pattern in the inter-tidal area, where strong mixing is caused by tidal currents, and the high

salinity of the marine water facilitates the element diffusion through the profiles (Li et al., 2000a).

3.2. Selection of normalizer elements

In most sedimentary environments, there is a linear relationship between inert element (normalizer) concentrations and the fine particle-size fractions (silt + clay) of the samples, which allows the use of normalizer concentrations as a substitute for the granulometric variability of the sediments. Therefore, geochemical normalization by a normalizer can compensate for both granulometric and mineralogical variability of metal concentrations in sediments (Aloupi and Angelidis, 2001). Reference elements as the metal concentration normalizer can be determined by statistical analyses. The Pearson correlation coefficients of trace and major elements and sediment properties in the cores are summarized in Table 2. The related results of PCA applied to the entire data set are listed in Table 3.

From Table 2, there were strong associations between Co, Cu, Ni, and Fe, whereas Pb displays a different behavior from these metals. Principal component analysis (PCA), a multivariate statistical technique, is generally employed to reduce the dimensionality of a data set while attempting to preserve the relationships present in the original data. In this study, three principal components (PC) can be extracted; they account for about 84% of the total variance. Based on the loading distribution of the metal variables in PCA (see Table 3), Co, Cu, Ni, Zn and Fe constitute a firmly related group (PC 1), while another group is composed of Pb and Al (PC 2). These results are in agreement with the Pearson correlation coefficient matrix, which may indicate the different origins or controlling factors of the heavy metals in sediments, e.g. the lithogenous component (Rubio et al., 2000). As for Mg and Ca (PC 3), both are usually affiliated to the marine water and sedimentation processes (Li et al., 2000a), and show apparent distinct patterns from other elements in the PCA.

Considering the significance of the correlation coefficient and principal component loading, Fe was better for Co, Cu, Ni and Zn normalization in these sediments than Al, organic matter and fine fractions of grain-size ($> 63 \mu\text{m}$, silt + clay), whereas aluminum was the most appropriate normalizer for Pb in the study area.

3.3. Metal enrichment by the linear baseline model

The naturally occurring metals should have a relatively uniform distribution with depth in all cores, since their concentrations in the sediments are not affected by the discharges from anthropogenic sources. To identify and evaluate the intensity of anthropogenic metals in the cores, natural variability has to be considered by normalizing data to a reference element. The relationships

Table 1
Heavy metal concentrations and particle size distribution in different sediment sections of the profile

Depth (cm)	Content	Co (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	FP ^a (%)
0–5	Mean	16.3	40.9	33	59.5	114.5	79.5
	Range	5.8–18.8	7.1–63	7.5–48.5	27–72	32.3–210	14.6–99.2
10–15	Mean	13.6	40.4	32.6	57	111	79.7
	Range	5.5–18	6.4–60.9	7.5–45	19.5–82.5	28.2–204	11.2–99.1
20–25	Mean	13.4	37.8	31.2	51.6	103.4	77
	Range	4.8–19	5.4–63.7	7–46	19.5–81	26.6–187	0.9–99.7
30–35	Mean	13.3	37.5	31.4	52.3	113.4	74.2
	Range	6–19	6.6–67.6	9.5–47	22.5–91.5	35.9–332	17–99.8
40–45	Mean	13.8	38.8	34.6	50.3	110.4	79.9
	Range	6.8–20.3	6.8–68.3	10.5–91	27–79.5	41–229	17.1–99.9
50–55	Mean	13.8	39.1	32.3	50.4	102.2	78.4
	Range	8.3–20.5	7.9–74.3	11.5–47.5	30–76.5	41–167	16.5–99.7
60–65	Mean	13.4	37.2	31.7	50.9	115.1	81.9
	Range	8.5–20.3	8.9–68.3	11.5–49	31.5–99	47.8–239	22.3–99.6
70–75	Mean	13.4	37.5	32.1	48.4	101.2	80.2
	Range	7.8–19.5	8.5–66.7	12–48.5	30–88.5	45.3–175	25.6–99.7
80–85	Mean	13.5	38	32.5	49.2	101.9	82.9
	Range	7.5–19	8.4–66.8	11–46.5	30–88.5	40.5–183	23.1–99.9
90–95	Mean	13.4	36.1	31.6	50.7	98.4	81.1
	Range	6.8–20.3	7.4–64.1	10.5–49.5	28.5–75	37.7–154	27.5–99.8
100–105	Mean	13.7	37.2	32.8	49.6	99.9	85.5
	Range	8–20.3	9.2–65.1	13–47.5	30–90	48.3–144	26.1–99.9
120–125	Mean	13.5	36.9	32.6	48.2	98.9	85.9
	Range	7.5–19.3	8.8–62	12–46.5	28.5–82.5	42.9–126	18.4–99.6
140–145	Mean	13.6	38.7	33	49.2	100.9	86.5
	Range	8.5–19.5	9.4–66.1	12–50.5	33–90	46.7–172	25.9–99.6
160–165	Mean	13.2	36	31.7	47	94.8	83.1
	Range	7.3–19.8	10.9–67.9	13.5–50	28.5–78	44–125	31.0–99.8
180–185	Mean	12.9	33.9	31.4	49.7	95.4	84.5
	Range	8.5–19.3	9.8–61.5	13.0–47	30–87	45.5–122	30.6–99.3
Coast BK ^b	Average		30		25	80	
Marine BK ^c	Average		15	25	50	94	
Estuary BK ^d	Average		10	15	29	70	
HK BK ^e			7	10	19	40	
Target ^f			20	20	35	75	
Trigger ^g			55	35	65	150	
Action ^h			65	40	75	200	
ISQV ⁱ —Low			65	40	75	200	
ISQV ⁱ —High			270	ND ^j	218	410	

^a Fine fractions of particles (<63 µm, silt + clay).

^b Background values of Chinese coastal areas (Zheng et al., 1992).

^c Background values of the marine sediments in Hong Kong (Tanner et al., 2000).

^d Background values of the estuary sediments in Hong Kong (Tanner et al., 2000).

^e Local background levels in Hong Kong (Lau et al., 1993).

^f Desired quality for fairly clean sediment, slightly exceeding but close to the background levels (Lau et al., 1993).

^g Moderate pollution, equated to about 50% of the trigger levels (Lau et al., 1993).

^h Heavy pollution (Lau et al., 1993).

ⁱ Interim sediment quality values (ISQVs, Chapman et al., 1999).

^j No data.

between trace metals and reference elements in the baseline data set can show the range of naturally occurring concentrations of trace metals. The upper 95% prediction interval, derived from the linear regression model, can form a baseline range to segregate anthropogenic inputs from natural variations of metal concentrations in the bulk sediments (Sokal and Rohlf, 1995; Doherty et al., 2000). In this study, the upper 95%

prediction interval was utilized for identifying metal enrichment in the sediment sections. The linear regression results, as well as the upper 95% prediction intervals and the low levels of the ISQVs, are illustrated in Fig. 2.

All data-points which fall inside the 95% confidence band can be designated as natural sediments with no pollution disturbance, while points above this area can

Table 2

Pearson correlation matrix for the metal concentrations and sediment properties^a

Element	Fe	Al	OM ¹	FP ²	Co	Cu	Ni	Pb	Zn
Fe	1.000	0.770	0.766	0.795	0.885	0.900	0.905	0.426	0.714
Al		1.000	0.770	0.778	0.558	0.637	0.680	0.641	0.632
OM ^b			1.000	0.837	0.582	0.677	0.715	0.495	0.622
FP ^c				1.000	0.629	0.719	0.773	0.433	0.602
Co					1.000	0.954	0.924	0.213	0.685
Cu						1.000	0.945	0.271	0.753
Ni							1.000	0.276	0.701
Pb								1.000	0.553
Zn									1.000

^a All correlation is significant at $P < 0.05$ ($N = 267$).^b Organic matter (loss on ignition).^c Fine fractions of particles ($< 63 \mu\text{m}$, silt + clay).

Table 3

Principal component (PC) loading of heavy metals and sediment properties^a

Variable	PC 1 (62.96%)	PC 2 (11.61%)	PC 3 (9.40%)
Mg	0.29	0.16	0.92
Ca	−0.44	−0.52	0.56
Mn	0.78	0.20	−0.03
Fe	0.80	0.43	0.36
Al	0.44	0.81	0.12
OM ^b	0.49	0.70	0.27
FP ^c	0.56	0.66	0.27
Co	0.95	0.15	0.12
Cu	0.95	0.26	0.07
Ni	0.89	0.32	0.17
Pb	0.06	0.85	0.06
Zn	0.67	0.49	0.00

^a The percentage in brackets is the explained contribution of principal components to the total variance.^b Organic matter (loss on ignition).^c Fine fractions of particles ($< 63 \mu\text{m}$, silt + clay).

be considered as sediments with heavy metals accumulated from anthropogenic sources. In the regression plot between the total metal concentrations and the appropriate normalizers, the data points below the upper 95% prediction limit probably originated from natural sources. From Fig. 2, the strength of the linear relationships, in terms of correlation coefficient (r^2), partially confirms the applicability of Fe for Co, Cu, Ni and Zn, and Al for Pb as the concentration normalizers in this study. Based on the corresponding number of sediment sections (n_1 and n_2 in Fig. 2), heavy metals with total concentrations beyond the two threshold ranges mainly involve Pb, Zn and Cu. This result reflects, to a large extent, the constituent characteristics of metal contaminant sources in the river system, including industrial discharges and domestic sewage from riparian

areas, as well as marine traffic and runoff from upstream mining activities (Chen and Zhou, 1992).

For the spatial distribution, most metal-enriched sediment sections were located in the western coastal zone (e.g. Cores A, B, C and D) and the east channel of the estuary (such as Cores 6, 7 and 8). The patterns reflect that the hydraulic conditions (e.g. slow current) and high clay contents may facilitate the pollutant deposition in the western shallow water areas. The inputs from the main tributaries and marine traffic, and strong mixing effects can cause elevated heavy metal concentrations in the east channels (Li et al., 2000a).

3.4. Metal chemical forms in the enrichment sections

In general, the results of the background enrichment approach, based on a linear regression model, do not necessarily imply biological effects of the contaminants in sediments. However, metal enrichment identification can be utilized as a sifting tool to assist cost-effective use of sediment toxicity tests. Therefore, only those with metal concentrations exceeding the expected natural background levels will be further studied on toxicity (Chapman and Wang, 2001). Since mobility, biological availability and potential toxicity of heavy metals are generally dependent on their existing chemical forms (Förstner, 1993), it is important to identify the chemical species of heavy metals in the sediments of interest. Accordingly, the chemical partitioning of heavy metals in the enriched sections, identified by the linear regression model, is presented in Table 4. Because most enriched sections occurred in the range of 0–65 cm depth based on the linear baseline model, for simplicity, enriched sections deeper than 65 cm are not included.

From Table 4, the dominant binding phases for Cu, Pb and Zn were the residual, Fe/Mn oxides and organic matters/sulfide fractions, which are generally regarded as relatively stable or inert under normal conditions. Among the non-residual fractions, Pb was mainly associated

Fig. 2. Scatter plots of the linear regression models ($N = 267$): (a) Co; (b) Cu; (c) Ni; (d) Pb and (e) Zn. The solid line is the linear regression equation. The dotted and dashed lines indicate the upper 95% prediction interval based on the linear regression model and the low ISQV value of each metal, respectively. The incorporated equations represent the linear regression relationships. The n_1 and n_2 denote the number of sections with metal concentration above the upper 95% prediction interval and above the low ISQVs, respectively.

with the Fe/Mn oxide fraction. Besides the Fe/Mn oxide fraction, the organic/sulfide fraction was another dominant binding phase of Zn. For Cu, the organic/sulfide fraction was an important carrier. The contributions of active species, such as exchangeable and carbonate/specifically adsorbed fractions, are generally low in the sediments. However, the proportions of Pb in the carbonate/specifically adsorbed fraction were relatively high in some cores (see Table 4), which may indicate recent input from anthropogenic sources.

3.5. Pb isotope compositions of the sediments

Analysis of Pb stable isotopes in the sediment column can help to identify various sources of Pb in an estuary

environment (Farmer et al., 1996; Munksgaard et al., 1998; Li et al., 2001). In general, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio can be used for assessing anthropogenic inputs of Pb in soils and sediments. In many cases, the geochemical background Pb generally has a high $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, while the Pb from recent industrial discharges or other anthropogenic inputs displays a relatively low ratio. The natural background of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios is 1.197–1.198 (mean value) in the Pearl River Estuary; a decrease in the ratio may suggest the occurrence of anthropogenic sources (Zhu et al., 2001). From the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in aerosols (1.151 ± 0.010) and in the fly ash of coal combustion (1.169 ± 0.021) collected in Hong Kong, the atmospheric input of Pb in the estuary is estimated to have an isotope ratio of 1.15–1.17 (Wong et al., 2002).

Table 4

Percentage of different chemical forms to total metal concentrations in the metal-enriched sections

Metal (Core No.)	Depth (cm)	Exchangeable	Carbonate	Fe/Mn oxide	Organic/sulfide	Residue
Pb (Core 2)	0–5	1.3	8.9	20.3	9.8	59.7
	10–15	1.3	4.5	27.1	9.3	57.8
Cu (Core 4)	0–5	0.0	15.3	25.8	7.3	51.6
	10–15	0.0	15.4	22.8	8.0	53.8
Zn (Core 5)	60–65	0.0	0.2	19.4	29.8	50.6
Pb (Core 6)	0–5	1.5	7.3	25.3	12.7	53.3
	10–15	1.1	6.0	21.0	14.4	57.4
	20–25	1.3	7.4	29.4	11.8	50.0
	30–35	0.9	6.3	20.2	11.7	60.9
	50–55	1.5	8.4	20.8	14.0	55.4
Zn (Core 6)	10–15	0.0	5.6	27.8	13.2	53.5
	30–35	0.4	4.5	18.1	50.2	26.8
	40–45	0.0	5.0	19.5	39.2	36.3
Pb (Core 7)	0–5	0.7	19.7	30.6	12.5	36.4
	10–15	0.5	17.3	32.1	15.8	34.2
	20–25	0.3	16.1	33.4	14.3	35.9
	30–35	0.5	18.8	29.4	16.0	35.3
	40–45	0.5	18.3	24.3	18.7	38.2
Zn (Core 7)	60–65	0.0	0.7	22.2	29.2	47.9
Zn (Core 8)	60–65	0.0	0.0	32.8	32.2	35.0
Cu (Core A)	10–15	0.7	6.8	10.5	18.2	63.8
	20–25	0.6	7.8	10.5	18.4	62.7
	30–35	0.5	8.0	8.2	15.6	67.7
	40–45	0.4	7.8	9.8	15.7	66.2
	50–55	0.4	8.6	9.2	15.3	66.5
	60–65	0.5	7.5	10.9	18.4	62.7
Pb (Core A)	0–5	0.0	13.9	34.4	21.1	30.6
	10–15	0.0	17.3	35.0	19.7	28.0
	60–65	0.0	14.7	33.0	21.3	31.0
Zn (Core A)	0–5	0.0	0.7	42.8	7.6	48.9
	10–15	0.0	0.9	41.3	8.4	49.4
	20–25	0.0	3.4	44.1	8.6	43.9
	60–65	0.0	3.6	42.1	9.7	44.5
Cu (Core B)	0–5	0.6	2.3	13.1	16.5	67.5
	10–15	0.2	1.6	9.7	14.4	74.1
	20–25	0.2	2.1	8.5	14.3	74.9
	40–45	0.2	1.2	11.7	16.2	70.7
	60–65	0.2	0.6	7.0	12.6	79.7
Pb (Core B)	0–5	0.1	2.3	49.2	27.0	21.5
	10–15	0.1	5.1	49.0	25.2	20.5
	20–25	0.1	4.9	49.2	26.3	19.5
Zn (Core B)	0–5	0.1	3.7	34.8	12.6	48.9
	10–15	0.1	3.7	30.2	11.3	54.8
	20–25	0.1	3.6	31.3	13.7	51.3
	30–35	0.1	3.9	33.0	12.1	50.9
	40–45	0.1	4.5	29.0	13.4	53.1
Cu (Core C)	0–5	0.2	1.4	12.8	19.5	66.2
	10–15	0.1	1.4	11.9	20.0	66.6
Zn (Core C)	0–5	0.0	3.1	36.4	6.9	53.6
Zn (Core D)	0–5	0.1	6.5	34.1	11.6	47.7

The excessive range of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the top sediments was close to that of fly ash, therefore coal burning by industries, such as power plants, and the subsequent atmospheric deposition may be one of the major sources of Pb in the sediments (Li et al., 2000a).

In the sections with Pb enrichment assessed by the linear regression model, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios are either the lowest or among the lowest values in the sediment profiles (see Table 5). The ratio values derived from the upper sediment sections are generally lower than those of the deeper sections, indicating that the enrichment of heavy metals in sediments mainly results from local industrial operations and urbanization during recent decades.

3.6. Quantitative evaluation of metal enrichment

The Pearl River delta is the most rapidly developing region in China. Large amounts of untreated wastewater and sewage, especially from metal industries, have caused degeneration in the environmental quality of the Pearl River Estuary. To evaluate trace metal contamination, the regression calculation can be combined with PCA and other multivariate methods (Shine et al., 1995; Doherty et al., 2000). After normalization using Fe or Al, the correlation coefficients and the PCA analyses, performed on the metal/normalizer ratios in the entire profiles and at the top layers, are shown in Tables 6 and 7, respectively.

Based on the normalized concentrations, the correlation coefficients of Cu, Pb and Zn with Co decreased significantly compared with the total concentration results (see Table 2), and the correlation coefficients of Cu and Zn with Pb were changed from positive values to negative values. On the other hand, the strong association

between Cu and Ni persists to a large extent after normalization (see Table 2). In the PCA results, the first two principal axes retained 73.2 and 89.2% of the total variance for the data on the entire cores and the top layers, respectively. Further, two main clusters of metal variables could be classified with the normalized metal concentrations: one consisting of Co, Cu, Ni and Zn, and the other consisting of only Pb. Like the case of the Pearson correlation coefficients, notable variations were observed for Co and Pb on the principal component axes when using normalized concentrations of heavy metals (see Fig. 3). The change in the loading of Cu, Ni and perhaps Zn is, however, relatively small. Therefore, the normalization of metal concentrations with Fe or Al can further identify and clarify the relationships between different heavy metals, and their actual geochemical characteristics, such as Co and Pb in this study.

Table 6

Pearson correlation coefficients of the normalized metal concentrations in the sediment cores (upper panel, $N=267$) and in the top layers (lower panel, $N=18$)^a

Metal	Co	Cu	Ni	Pb	Zn
Co	1.000	0.190	0.250	0.184	0.087
Cu		1.000	0.814	-0.568	0.337
Ni			1.000	-0.628	0.288
Pb				1.000	-0.030
Zn					1.000
Co	1.000	0.316	0.261	0.114	0.558
Cu		1.000	0.943	-0.635	0.708
Ni			1.000	-0.817	0.585
Pb				1.000	-0.125
Zn					1.000

^a The bold values denote significance level at $P < 0.05$.

Table 5

Distribution of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the selected sediment cores^a

Depth (cm)	Core 2	Core 5	Core 6	Core 7	Core 9	Core 14	Core A	Core B
0–5	1.191	1.198	1.191	1.188	1.192	1.186	1.184	1.187
10–15	1.192	1.198	1.180	1.192	1.197	1.198	1.181	1.185
20–25	1.201	1.198	1.191	1.189	1.182	1.197	1.184	1.183
30–35	1.187	1.197	1.186	1.191	1.196	1.193	1.191	1.194
40–45	1.197	1.197	1.183	1.192	1.196	1.201	1.188	1.192
50–55	1.198	1.201	1.188	1.191	1.196	1.199	1.190	1.203
60–65	1.194	1.192	1.169	1.199	1.194	1.200	1.179	1.196
70–75	1.201	1.187	1.189	1.197	1.194	1.198	1.180	1.199
80–85	1.201	1.187	1.196	1.194	1.198	1.198	1.186	1.206
90–95	1.193	1.190	1.201	1.192	1.190	1.190	1.180	1.199
100–105	1.189	1.194	1.188	1.196	1.198	1.203	1.183	1.200
120–125	1.198	1.186	1.183	1.198	1.194	1.195	1.185	1.193
140–145	1.195	1.193	1.196	1.199	1.189	1.195	1.188	1.197
160–165	1.194	1.189	1.186	1.197	1.188	1.198		1.207
180–185	1.197	1.190	1.194	1.201	1.195	1.178		1.201

^a The bold values denote the sections with anthropogenically enriched Pb based on metal concentrations normalized by Al in the linear regression model.

Fig. 3. Comparison of the principal component loading of metal variables between the original concentrations and the normalized concentrations in the sediment cores. CoN, CuN, NiN, PbN and ZnN represent normalized concentrations of Co, Cu, Ni, Pb and Zn respectively.

Table 7

Principal component loading of PCA based on the normalized metal concentrations in the cores (upper panel, $N=267$) and in the top layers (lower panel, $N=18$)

Variable	PC 1 (49.55%)	PC 2 (23.68%)
Co	0.06	0.86
Cu	0.90	0.20
Ni	0.91	0.20
Pb	-0.82	0.42
Zn	0.34	0.48
Variable	PC 1 (61.89%)	PC 2 (27.32%)
Co	-0.03	0.89
Cu	0.85	0.45
Ni	0.95	0.30
Pb	-0.93	0.21
Zn	0.38	0.83

The percentage in parentheses is the contribution of the principal component to the total variance.

The element associations obtained by correlation coefficient and principal component score can indicate different origins of heavy metals in the sediments. The feature of point sources lies in that the inputs of heavy metals occur over a finite period of time and may have been effectively retained in the sediments near the sources, rather than re-suspended and distributed uniformly throughout the region. Distinct from point sources, metals from non-point sources are more uniformly distributed throughout the area (Shine et al., 1995).

Combined with the previous results (Li et al., 2000a), the sources of heavy metals in the sediments of the Pearl River Estuary differ for each element, but may include: (1) polluted tributaries as well as the weathering release of parent materials in the local bedrock, such as Cu and Ni; (2) terrestrial discharge of wastewater from the upstream area, accounting for the Zn; and (3) atmospheric transport and precipitation, exemplified by Pb (i.e. airborne Pb).

In view of the environmental significance of surficial sediments due to mass exchange with the overlying water and direct exposure to aquatic organisms (e.g. plankton and benthos), the principal component scores of the top layers (0–5 cm) and relevant loading of metal variables are depicted in Fig. 4. Four large groups of surface sediment samples can be approximately categorized according to a score plot showing the positions of samples in the coordinates of the principal component. They are (1) Cores A, B, C, D and 2, (2) Cores 7 and 8, (3) Cores 4 and 6, and (4) other sampling cores (see Fig. 4). In Fig. 4, it is clear that the spatial (or geographical) distributions of metal enrichment at shallower depths (above 65 cm) in the sediment cores are mainly in the western shallow water zone and in the east channel. The patterns confirm the results obtained from the linear regression models (see Table 4).

Furthermore, considering the principal component loading of metal variables (see Table 7 and Fig. 4), enrichment of Cu, Ni and Zn with both positive loading along the two principal component axes is evident in the

Fig. 4. Principal component scores of the surface sediment samples (0–5 cm) and principal component loading of metal variables using the normalized metal concentrations by Fe or Al. CoN, CuN, NiN, PbN and ZnN represent normalized concentrations of Co, Cu, Ni, Pb and Zn respectively.

western shallow water area of the estuary. This can be attributed to both the direct discharges from point sources, such as rivers and creeks carrying metal contaminants, and the relatively constant sedimentation conditions. On the other hand, Pb probably arises from non-point sources, for instance, atmospheric deposition. These features can be reinforced by other related studies (Li et al., 2000a, 2001).

4. Conclusions

The concentrations of Cu, Pb and Zn in the surface sediments of the Pearl River Estuary were elevated, especially in the western shallow region, reflecting the anthropogenic inputs from industrial development and urbanization in the last few decades. The normalization of heavy metal concentrations to suitable reference elements (Fe for Cu and Zn, and Al for Pb) could help to identify metal accumulation in sediment profiles. The residual, Fe/Mn oxide and organic/sulfide fractions were the dominant geochemical phases for heavy metals in these metal-enriched sediment layers. The Pb stable isotope composition also showed the anthropogenic sources of heavy metals in the sediments. In addition, multivariate statistical analysis indicated that Cu was derived from the weathering of parent materials and polluted streams. Elevated Zn mainly originated from the discharges of point sources along the coast, particularly from the main tributaries in the northwestern

estuary. Pb could have come from non-point sources, such as atmospheric deposition.

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