

Concentration distribution and assessment of several heavy metals in sediments of west-four Pearl River Estuary

Shanshan Wang · Zhimin Cao · Dongzhao Lan ·
Zhichang Zheng · Guihai Li

Received: 24 July 2007 / Accepted: 17 September 2007 / Published online: 18 October 2007
© Springer-Verlag 2007

Abstract Grain size parameters, trace metals (Co, Cu, Ni, Pb, Cr, Zn, Ba, Zr and Sr) and total organic matter (TOM) of 38 surficial sediments and a sediment core of west-four Pearl River Estuary region were analyzed. The spacial distribution and the transportation procession of the chemical element in surficial sediments were studied mainly. Multivariate statistics are used to analyses the interrelationship of metal elements, TOM and the grain size parameters. The results demonstrated that terrigenous sediment taken by the rivers are main sources of the trace metal elements and TOM, and the lithology of parent material is a dominating factor controlling the trace metal composition in the surficial sediment. In addition, the hydrodynamic condition and landform are the dominating factors controlling the large-scale distribution, while the anthropogenic input in the coastal area alters the regional distribution of heavy metal elements Co, Cu, Ni, Pb, Cr and Zn. The enrichment factor (EF) analysis was used for the differentiation of the metal source between anthropogenic and naturally occurring, and for the assessment of the anthropogenic influence, the deeper layer content of heavy

metals were calculated as the background values and Zr was chosen as the reference element for Co, Cu, Ni, Pb, Cr and Zn. The result indicate prevalent enrichment of Co, Cu, Ni, Pb and Cr, and the contamination of Pb is most obvious, further more, the peculiar high EF value sites of Zn and Pb probably suggest point source input.

Keywords West-four Pearl River Estuary ·
Surficial sediment · Heavy metals ·
Depositional environment · Enrichment factor (EF)

Introduction

Over the last few decades, a large number of studies have been made of the chemistry of estuary, coast and the shelf sediments in order to ascertain the origin of the various elements, especially heavy metals. Heavy metal concentration in estuarine or the coastal zone sediments are usually quite high due to significant anthropogenic metal loadings carried by tributary rivers (Zwolsman et al. 1996; Muniz et al. 2004; Guerra-García José and García-Gomez 2005), so the sediments especially the surficial sediment may serve as a metal pool that can release metals to the overlying water via natural or anthropogenic processes, causing potential adverse health effects to the ecosystems because of their serious toxicity and persistence (Lin and Liang 1995; Graham Evans et al. 2003; Howarth 2003; McCready et al. 2006).

The Pearl River estuary and the coastal are typical zones with strong continent–ocean interaction and process of human being. In the latest decades, because of the fast development of economics, the terrigenous drainage is much more serious, and the estuary and coastal region endure huge contaminational pressure, even the environmental

S. Wang (✉) · Z. Cao · D. Lan · G. Li
College of Marine Geosciences,
Ocean University of China,
Qingdao 266100, China
e-mail: shanshwang@gmail.com

Z. Cao
e-mail: zmcao@ouc.edu.cn

D. Lan
Third Institute of Oceanography,
SOA, Xiamen 361005, China

Z. Zheng
Guangzhou Marine Geological Survey,
Ministry of Land and Resources, Guangzhou 510760, China

quality of Pearl River and the estuary became one of the bottle-necks of the economic development (Hills et al. 1998).

The study of the heavy metal had been developed since 1980s and most of the research focused on the Ling Ding estuary for it being the biggest estuary of the Pearl River system, and many big cities setting at the sides of the estuary (Lin and Liang 1995; Li et al. 2000; Liu et al. 2003; Zhou et al. 2004). Most of the study about the west four estuaries of Pearl River system focus on the hydrodynamics and sedimentary environment for the complicated hydrodynamics and landform, and because of the difference and complexity between each estuary, the Jiti men, ModaoMen and the Huangmao Hai estuary were discussed separately (Ou et al. 1983; Yang 1993, 1994; Yang et al. 1997; Liang 2005; Wang et al. 2006). Nevertheless, less attention are paid for the concentration, distribution, source, and influence of trace metals elements, especially heavy metals elements. In order to understand the characteristic of heavy metals all-around, the study area cover Huangmao Hai estuary bay, four river gates and the region in shallow sea within inner continental shelf along the shore.

The main objectives of the study reported here were: (1) to determine the total concentration and spatial distribution of trace metal elements in the surficial sediments in the west-four Pearl river estuary region; (2) to evaluate the sedimentological and geochemical factors that control the distribution pattern and the source of trace elements; and (3) to explore the natural and anthropogenic input of heavy metals and to assess the pollution status on the area.

Materials and methods

Setting and sampling

The study area is in front of the drainage basin of Xijiang delta, to the west of Pearl River estuary including HuangMaohai estuary bay, the area in front and the low sea region in front of Jitimen estuary and Modaomen in south.

The HuangMaoHai estuary formed in post-glacial period from the drowned valley of peroe-pearl river is located in the southwest of the Pearl River Delta, and it is one of the main bell-mouthed estuary of Pearl river systems. The estuary is surrounded by many hills, and a series of islands are settled in the direction of NE–SW outside the estuary. Devonian sandstone, sand-conglomerate and shale, and Jurassic quartz sandstone, feldspar–quartz sandstone are two prevalent lithologies cropping out in the hills and islands (Yang 1993). Tan river and a branch of west river pour into the Huangmaohai through Yamen and

HutiaoMen, respectively, the suspended matter taken to the sea is 700×10^4 and $420 \times 10^4 \text{ ta}^{-1}$. Jiti Men is a bugle-shape estuary, it is the entrance of west river and north river, the suspended matter poured into the ocean is $550 \times 10^4 \text{ ta}^{-1}$; Modao Men is the main entrance of west river, the trunk stream of the west river pour into sea, and the suspended matter brought is $2470 \times 10^4 \text{ ta}^{-1}$ (Zhao 1983; Zhang et al. 1988). Beside the process of river discharge, there are also effect of tidal current, coastal current and shallow water wave.

The study area has been reconstructed significantly. The south part of east shore has been enclosed by a leading dam, and another long dam as long as 37.3 km starting at Yamen extends to the middle west shore (Chen 2000). In the 1990s, the foundation of the Gaolan Dam obstruct the interaction between Huangmao Hai and Jiti Men, and the same tidal dynamics status disappeared (Wang 2006). In the same way, the leading dam of Modao Men change the dynamic style from river-dominated estuary to river-wave estuary (Ou et al. 1983; Liang 2005; Wang et al. 2006).

Sampling was carried out in May 2005. HYPACK navigational fixing system was adopted. A sampling map is shown in Fig. 1. All of the 38 surface samples were collected with a grab sampler and the samples were stored in polyethylene bags at 4°C immediately after collected prior to analysis in a laboratory.

Analysis methods

Analyses of metal elements

The sediment samples were dried in an oven at 60°C, and then grounded to powder in an agate mortar before analyses.

Dry sediment ($\sim 0.125 \text{ g}$) samples were weighted and placed into 50 ml acid-washed Teflon lined digestion vessels. An acid mixture of HCl–HF–HNO₃–HClO₄ was added to the vessel to digested metals in sediments into solutions. Then, the solutions in the volumetric flasks were diluted to the 7% perchloric acid solution immediately and transferred to Teflon tubes prior to analysis. The concentrations of metal elements were measured by Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES, Perkin Elmer Optima USA, 4300 DC). For the analytical quality control, the reagent blank, standard reference materials (GBW-07313) were tested before analysis, the detective lines for Co, Cu, Ni, Pb, Cr, Sr, Zn, Zr are 0.0062, 0.0003, 0.0022, 0.0133, 0.0027, 0.0179, 0.0004 and $0.007 \mu\text{g g}^{-1}$. The recovery rates for Co, Cu, Ni, Pb, Cr, Sr, Zn and Zr are 102, 102, 94, 94, 106, 96, 94 and 103%. All analyses were carried on duplicate samples.

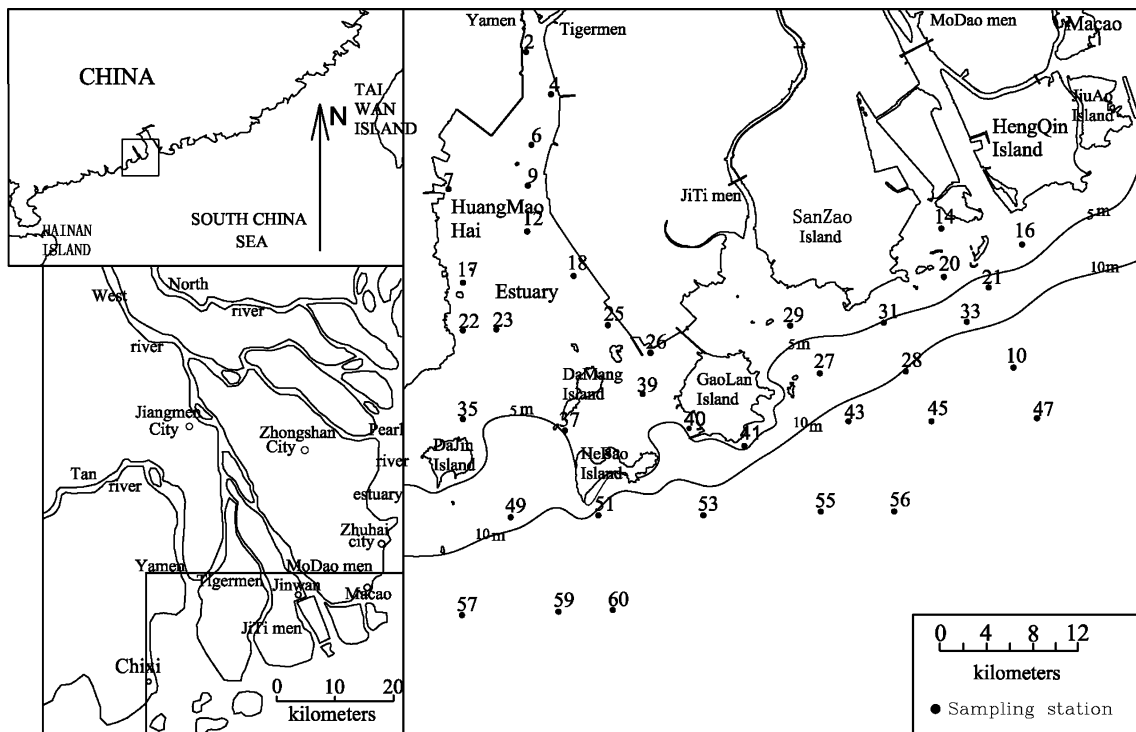


Fig. 1 Study area and sampling stations

Analyses of total organic matter

The total content of organic matter was determined by redox of potassium dichromate, re.GB/T17318.5-1998 China, the detail is below:

Certain (about 0.1–0.5 g) dried sample was placed into a glass-made test tube, 10 ml criterial concentrated sulfuric acid–potassium dichromate solution was added into the test tube. The organic carbon matter contained in the sediment sample was oxidate and transformed into carbon dioxide. The residual potassium dichromate was titrated by ferrous sulphate criterial reagent. The concentration of the organic matter was calculated by the formula below:

$$W_{org} = \frac{cFe^{2+}(V_1 - V_2) \times 0.0030}{M} \times 100\%$$

- W_{org} the concentration of total organic matter in dry sediment sample (%)
- cFe^{2+} the concentration of ferrous sulphate criterial reagent (mol/l)
- V_1 the volume of ferrous sulphate criterial reagent for blank (ml)
- V_2 the volume of ferrous sulphate criterial reagent for sediment sample (ml)
- M weight of dry sediment sample (g)

All reagents were of analytical grade or superpure quality and all analyses were carried on duplicate samples.

Analyses of grain size parameters

Sediment samples were washed several times using hydrogen peroxide to eliminate all organic matter before testing the grain size. Grain size analysis were performed by wet (fraction < 63 μm) and dry (fraction > 63μm) sieving. The sediment samples were separated into fractions on the basis of particle size: (1) >2 mm (2) 2–0.063 mm (3) 0.063–0.004 mm (4) <0.004 mm. The four fractions represent gravel, sand, silt and clay, respectively. Descriptive grain size parameters (mean grain size, sorting coefficient, skewness and kurtosis) were calculated using the formula of Folk and Ward (1957). All grain size in this paper will be given in Φ Udden Wentworth grade scale.

Statistical analyses

In present study, the pearson coefficients (PC) and the principle component analysis (PCA) were conducted using SPSS for Windows 12.0. in order to study the interrelationship among the chemical elements and the grain size parameters. The varimax method was chosen as the

rotation method for PCA. The distribution maps of all the elements are constructed using SUFFER 8.0. The interpolation method used was Kriging method.

Results

Grain size

The content of gravel, sand, silt and clay of all sites as well as mean grain size, sorting coefficient, Skewness and Kurtosis are shown in [Appendix 1](#). The content of the four fractions and other four grain size parameters vary significantly in the region. In the area near Yamen and Hutiao Men, the sediment were dominated by silt and clay, and were typified as silty clay, mean grain size was 7.85–9.97 ϕ ; in the region from the west shore of Huangmao Hai to the west of Dajin island, sediments were dominated by clay and silt, the contents of fine sediment (silt and clay) were above 99.5%, only silty clay can be observed here, mean grain size were 8.99–9.8 ϕ ; the east side of Huangmao Hai and the area arounded by Damang island and Gaolan island, the station 6 and 12 were typified as gravelly sand, the content of fine sediment were 22.05 and 2.25%, mean grain size were 2.39 and 1.26 ϕ , site 39 was typified as silty sand, stations 25 and 26 were typified as sand silt and clay, station 37 was typified as clayey silt, the sediment types in sites 9 and 18 were silty clay, the contents of fine sediment there were above 84%, and mean grain size were 8.02 and 7.94 ϕ ; the contents of sand were >92% in the stations in the east of Modao men channel, the mean grain size were 2.89–4.53 ϕ ; except site 20 (mean grain size 5.37 ϕ , silty sand), the stations near the coast 10 m water depth contour inside from the west of Modao men to the south of Dajin island were dominated by fine sediment (>92%), and were typified as silty clay and clayey silt, mean grain size were 7.86–9.22 ϕ ; except site 47 (sand–silt–clay, mean grain size 7.06 ϕ), the stations far from the coast outside the 10 m water depth contour were dominated by fine sand(89–98.3%), mean grain size were 7.91–9.14 ϕ , and clayey silt and silty clay were dominating types.

Metal elements and organic matter

The contents of metal elements and TOM are listed in [Table 1](#), sediment criteria of Hongkong and the content of shale are shown in [Table 1](#) as well. The spatial distribution maps of metal elements and TOM are shown in [Fig. 2](#).

Surficial sediments were found to contain a wide range and complicated distributions of trace metal concentrations as for [Table 1](#) and [Fig. 2](#). In general, high content stations Co, Cu, Ni, Cr, Pb, Zn, Zr and Ba mainly distributed in the west coast of Huang Mao Hai estuary and shallow water area

near San zao island and Gao lan island, and parallel distribution pattern outside the Huang mao Hai estuary was observed. In detail, besides inner of estuary, one high content region of Co, Cu, Ni, Cr, Zr and Ba extended from site 7 in the end of Huangmao Hai estuary to the area around Dajin island; the other high content region covered low water area from the west of Modao Men to the south of Hebao islands. The maximum values of Co, Ni and Zr, 32.5, 52.3, 177 $\mu\text{g g}^{-1}$, respectively, were founded in site 7 located in the west coast of Huang mao Hai; the maximum values of Cr and Ba, 102, 461 $\mu\text{g g}^{-1}$, respectively were founded in site 17 located in the west coast of Huang mao Hai as well; whereas, the maximum value of Cu 77 $\mu\text{g g}^{-1}$ was at site 14 in the west of Hodao Men. Though the distribution of high contents region of Pb and Zn are the same with above, three “hot spots” appearing in site 14, 17 and 40 made them different, the concentrations of Pb (62.4 $\mu\text{g g}^{-1}$ for 14; 53.2 $\mu\text{g g}^{-1}$ for 17; 54 $\mu\text{g g}^{-1}$ for 40) and Zn (199 $\mu\text{g g}^{-1}$ for 14; 63 $\mu\text{g g}^{-1}$ for 17; 182 $\mu\text{g g}^{-1}$ for 40) in the three stations are much higher than the contents of stations neighbouring. Besides, Zn has a peculiar “hotspot” in site 9 (157 $\mu\text{g g}^{-1}$) in the east coast of the estuary. Sites 33 and 10 looked special for the obviously high contents of Co, Cu, Ni, Pb, Cr, Zn and Zr.

The distribution of Sr showed quite different pattern, the maximum value (209 $\mu\text{g g}^{-1}$) appeared at site 6 in the east shore of Huangmao Hai; in addition, parallel distribution pattern outside the Huang mao Hai estuary was not observed, and in the south the content is much higher than that observed in the near shore.

The content of TOM has the same distribution with Zn near the shore, with “hotspots” in the southeast of Sanzao island (3.3%) and the east shore of the estuary (4.1%), but didn't have parallel variation in the open sea.

Mean concentration of Cu, Ni, Pb, Cr and Zn exceed target value of Hong Kong obviously, and the mean concentration of Ni and Cr exceed trigger value of Hong Kong, furthermore, the aggregation of Cr seems more apparent for all 38 values exceeding the trigger value obviously. While comparing with Shale, elements of Cu, Pb, Zn and Cr are aggregate in more than half stations. It seems that most area of this region has been contaminated by Cu, Ni, Pb, Cr and Zn comparing with target value and the contamination of Cu, Ni, Cr is much more obvious by contrast with trigger value of Hong Kong.

Discussion

Grain size factors

As discussed above, more or less similarity is observed from the distribution pattern of elements and grain size

Table 1 Concentration of metal elements and TOM in surficial sediments

Site	Co ^a	Cu	Ni	Cr	Pb	Zn	Sr	Zr	Ba	TOM ^b
2	23.3	59.1	45.6	98.8	49.6	116	89	137	363	1.96
4	30.8	68.9	51.5	102	32.1	95.2	101	169	414	1.70
6	8.73	23.3	20.3	83.9	22.7	31.8	209	63.9	165	0.60
7	32.5	73.4	54.3	100	36.1	78.4	110	177	416	1.86
9	20.9	29.1	37.7	78.6	29.3	157	113	111	398	4.07
10	24.8	44.1	42.6	83.3	42.7	121	113	137	408	1.66
12	6.33	9.13	11.6	72.7	22.5	19.4	27	28	133	0.09
14	28.2	77	52.8	95.5	62.4	199	117	153	442	3.27
16	17	22.1	20.3	60	20.1	37.1	56.4	81.8	272	0.06
17	28.9	66.2	51.9	102	53.2	163	103	167	461	2.28
18	28.6	52.8	44.3	89.6	35.5	70.6	106	165	397	1.66
20	23.5	39.2	33.7	75.9	37.9	113	87	146	341	1.38
21	16.7	21.2	21.3	67.3	16.1	38.4	50.4	87.8	225	0.04
22	26.6	57.6	49.9	88.4	53.8	146	97.2	152	454	1.90
23	29.7	63.7	51.9	102	51.2	106	104	164	413	2.41
25	24	37.3	33.6	70.6	29.8	105	106	124	324	1.12
26	25.8	47.8	42.5	79.5	32	83.3	98.6	144	374	1.38
27	26	53.1	46.3	87.1	48	98.4	101	143	397	1.50
28	26.5	52.2	44.7	83.5	35.8	81.5	103	150	387	1.59
29	27.5	52.9	53.8	83	32.4	74.2	110	154	367	1.24
31	26.2	53.9	47.2	86.7	45.7	102	101	147	405	1.62
33	30.6	66.2	50.5	97.9	44.6	98.7	109	171	403	1.94
35	28.2	58.9	51.9	101	36	86.6	99.9	151	432	1.87
37	24.8	38.1	34.4	81.2	28.8	68	97.3	148	336	0.82
39	18.4	23.7	24.5	65.1	21.2	49.9	88.3	124	280	0.49
40	27.4	61.2	52.1	99.1	54	182	119	149	430	2.05
41	27.2	54.6	45.6	94.9	47.3	125	105	148	409	1.72
43	26.8	53.8	45.5	93.1	31.9	129	101	151	370	1.61
45	26.8	51.8	46.5	88.3	44.4	94.4	110	148	423	2.08
47	20.3	31.2	33.9	67.6	30.3	55.1	111	107	365	1.09
49	28	53	44.8	87.9	45.5	112	114	158	378	1.74
51	27.2	51.7	46.6	89.3	42.8	84.7	109	152	402	1.62
53	26.7	49.2	41.3	85.5	37.9	94	107	145	367	1.42
55	27	53.1	44.1	84.3	45.3	112	107	158	414	1.71
56	24.7	44.8	42.9	83.2	41.9	81.4	124	130	393	1.82
57	24.3	46.6	41.3	80.7	40	93.1	110	131	373	1.70
59	22.6	34.4	34.3	69.4	30.1	68	118	125	375	1.08
60	25.1	41.8	36	80	26.6	64.7	102	136	373	1.21
Mean ^c	24.70	47.85	41.42	85.23	37.83	95.66	103.53	137.72	370.5	1.56
Range	6.33–32.5	9.13–77.0	11.6–54.3	60.0–102.0	16.1–62.4	19.4–199.0	27.0–209.0	28.0–177.0	133.0–461.0	0.04–4.07
Target ^d		20	20	25	35	75				
Trigger ^e		55	35	50	65	150				
Shale ^f	19	45	68	90	20	95	300	160	580	

^a The concentration of trace metals in $\mu\text{g g}^{-1}$

^b Total organic matter in percentage

^c Arithmetic mean concentration in $\mu\text{g g}^{-1}$

^d Sediment quality criteria in Hong Kong, indicates the desired quality for fairly clean sediment that is close to background levels (Lau et al. 1993)

^e Sediment quality criteria in Hong Kong, indicates that the sediment is moderately contaminated (Lau et al. 1993)

^f The world average concentration of shale (Turekian and Wedepohl 1961)

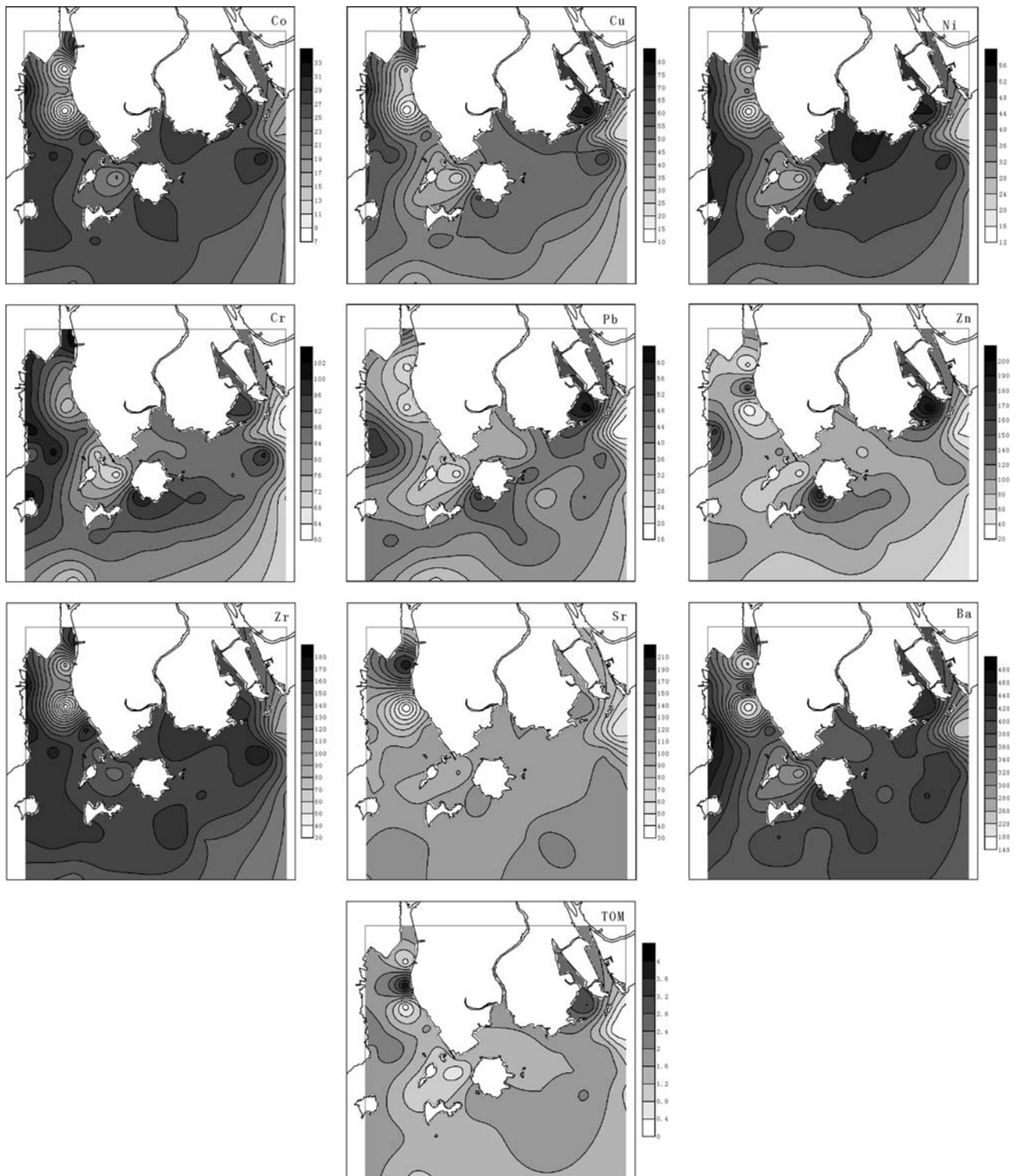


Fig. 2 Spatial distributions of metal elements and TOM

parameters in surficial sediments: Most of the stations with high trace metals contents are dominated by fine fraction, while, the sites with coarse fractions were always lack of trace metals. In order to make more clear the relationship between elements and grain size in this region, pearson

coefficient analysis was adopted, and the Pearson coefficient matrix is shown in Table 2.

The correlation coefficients between Cu, Ni, Cr, Pb, Zn, Ba, TOM and clay are 0.438~0.805, and are bigger than that between silt, indicates the enrichment of these metal

Table 2 Pearson coefficient matrix of chemical elements with grain size parameters in surficial sediments

	Co	Cu	Ni	Cr	Pb	Zn	Zr	Sr	Ba	TOM
Sand	-0.830	-0.790	-0.875	-0.690	-0.679	-0.588	-0.820	-0.417	-0.870	-0.676
Silt	0.725	0.567	0.649	0.323	0.473	0.420	0.745	0.286	0.679	0.418
Clay	0.662	0.686	0.788	0.721	0.557	0.438	0.546	-0.205	0.805	0.570
^a Fine sediment including silt and clay	FP ^a	0.855	0.794	0.882	0.670	0.678	0.596	0.838	0.361	0.893
^b Mean grain size	Mz ^b	0.894	0.819	0.911	0.683	0.681	0.613	0.857	0.280	0.941
^c Sorting coefficient	σ^c	0.267	0.294	0.373	0.314	0.317	0.258	0.343	0.712	0.322
^d Skewness	Ski ^d	0.012	-0.128	-0.176	-0.308	-0.304	-0.242	0.125	0.173	-0.192
^e Kurtosis	Kg ^e	-0.561	-0.544	-0.607	-0.482	-0.501	-0.340	-0.453	-0.037	-0.591

elements in clay fraction; while Co, Zr have bigger correlation coefficients with silt (0.725, 0.745) than with clay (0.662, 0.546), implies the much more obvious enrichment in silt fraction of Co and Zr. As a whole, obvious correlation between Co, Cu, Ni, Cr, Pb, Zn Zr, Ba and TOM with fine sediment and with mean grain size can be seen as Table 2, for the correlation coefficients above 0.6. This suggests that the concentration and distribution of Co, Cu, Ni, Cr, Pb, Zn Zr, Ba and TOM are controlled by the grain size in this region.

Hydrodynamics factors

Researchers have found that Hydrodynamic condition and landform can affect the physical properties of sediments, furthermore affect the concentration and the spatial distribution of trace metal associated (Grabemann et al. 1997; Mitchell et al. 1998; Peng et al. 2004). The distribution patterns of metal elements and grain size parameters inside Huangmao Hai and in the coastal area are quite different from Ling Ding Yang Estuary (Lin et al. 2002) and other estuary (DeMora et al. 2004). Local special hydrodynamics and landforms are main influencing factors.

First of all, the fine fraction area in the end of the estuary near Yamen and Hutiaomen is riched in most of the metal elements. In this area, the hydrodynamic power decreased abruptly for sudden change of the water surface, and some suspended fine particle sediment from Tan river and West river deposited and metal elements included aggregated as well.

In the inner of Huang mao Hai estuary, because of the effect of west leading dam, the strong descending runoffs from Yamen and Hutiao men lean to the east shore, wash and erode the bottom sediment and resuspend fine particle sediment to seawater, and the coarse sediments were leave behind in the east water channel. The resuspended matter was taken by a branch of water current from Yamen to the west shore and some flocculated there with seamud taken by flood tide. Because of the ebb-tidal current descending

along the westcoast, a large amount of suspended matter was take to the south, and settled around the mouth of Huang mao Hai for the obstruction of Dajin Island and Hebao Island (Yang 1993; Yang and Wang 1994). As tidal dominated estuary, the obstruction for ebb-tide of sediment barrier around the gate is dominating factor for the deposition of clay and metal elements associated in sites 22 and 23.

Because of the leading dams along the two sides of the Modaomen water channel, fresh water with a large quality of sand flow straight to the South China Sea. The runoff diffuse horizontally immediately outside the estuary and excursion to the west due to the strong impact of coastal current to the southwest, and fine sediment associated deposit near San zao island as well.

The special characteristics of sites 16 and 21 (extremely small sorting coefficients, high kurtosis, low metal contents) came from special dynamics in this area. In spite of large quantity of sand taken by Xijiang, runoff, wave and coastal current rushed and eroded the landform here, a lot of fine sediment would be resuspended, and the coarse sediment would be left.

In flood season, the sea-orient discharging in the surface layer together with the compensatory land-orientation water mass in deep in the 5–10 m water depth in shore inner continental shelf area always compose a double deck circumfluence (Ou et al. 1983; Lin and Liang 1995), and the fine sediment deposited in the bottom will be raised again to the overlying water above. The high content of fine sediment in site 33, 10 probably come from the deposition of resuspended sediment.

As discussed above, a large fine sediment region extended from the west of Modao men to the south of Dajin Island in the direction of southwest. The coastal current from Lingding Yang is the main transportation, and resuspended upriver matter from Modaomen sea area and Jitimen estuary are main sources.

Above all, except for peculiar sites, the area with weak hydrodynamics is always dominated by fine fraction and the aggregation of trace metal elements are obvious.

Chemical factors and source identification

Depending on the discussion above, the dynamics affects the general spatial distribution of fine grain sand, and further more, effects the concentration and distribution of metal elements associated. Whereas, the particular distribution characteristics of different elements and different correlations between chemical elements and grain size parameters implies that the concentration and distribution of trace metals in sediments cannot be interpreted simply by the hydrodynamic transportation in this study area. The existing station, sedimentational mode (e.g. physical sedimentation, chemical or biochemical sedimentation), the chemical characteristics (e.g. sorption–adsorption capacity of trace metals, flocculation, etc.), the chemical and biochemical condition of the sedimentary environment, and anthropogenic pollution are also important influence factors (Willams et al. 1994).

In order to make clear the other factors effecting the concentration and distribution of heavy metals here, Multivariate statistics (Pearson coefficient analysis and principle component analysis) were adopted and the result are shown in Tables 3 and 4, respectively. Principle component analysis is one of the analytical tools used to assess metal behaviour in the aquatic system (Shine et al. 1995; Ruiz 2001; Liu et al. 2003; Zhou et al. 2004), and it is applied to detect the “hidden” structure of the data set, trying to explain the influence of latent factors on the data distribution (Einax and Soldt 1999; Simeonov et al. 2000). In the analysis, the first three principal components accounted for nearly 88.5% of the total variance, and the variances of F1, F2 and F3 is 50.26, 28.46 and 9.77%, respectively. Apparently, the result of PCA is well corresponded with coefficient correlation matrix. The first group includes chemical elements of Co, Cu, Ni, Cr, Zr and Ba, and grain size parameters. The scores of F1 for these elements are much higher than the other two factors, and Relativity coefficient between this group of parameters exceed 0.85. Elements of Co, Ni and Cr belong to siderophile element, and are main rock-forming elements. It is easy for them entering into iron–magnesium silicate mineral for isomorphism with Fe and Mg; in natural environment, Cu and Zr always disperses in rock-forming minerals besides existing as independent minerals; in shallow sea environment, Ba usually exists in detrital silicate minerals (Zhao and Yan 1994). This association represents lithological input in the area, i.e. the elements in the group main come from the terrigenous detrital matter taken by the runoff, and the lithological characteristics of drainage area control the combination and concentration, and then, the succedent mechanical transportation accomplish the distribution pattern as discussed above.

F2 scores of Pb, Zn and TOM exceeds 0.75, beyond the other elements; the scores of Cu, Ni, Cr and Ba exceed 0.45 but less than 0.5. From coefficient matrix of Table 3, Zn has much higher correlation with TOM and Pb (0.811, 0.794) than with other parameters. As to the geochemical characteristics, for the weak transport capacity, only little soluble Pb can be transported into the ocean, absorbed by organic matter and deposited in deoxidize condition; Zn has quite similar geochemical character with Pb, and always accretes with it; the Zn in waters can also be absorbed by organic matter during the migration. From Fig. 2, the distribution pattern of Zn is quite different from that of the first group elements, it seems caused by point contamination. The trace metal elements of Cr, Co, Ni and Ba always migrate in colloid form in aquatic environment and deposit to the bottom sediment while encountering clay or organic matter or sudden physical–chemical change of waters. Therefore, the association of F2 is mainly related to local anthropogenic inputs and reflects the complexing nature of the organic matter.

The remain element of Sr is one of the important components of marine biota, and quite different from the other elements, so it is related to the marine sedimentation processes and mainly originate from marine calcic biota (Barcellos et al. 1997; Rubio et al. 2000).

Anthropogenic contribution and assessment of heavy metals

Because of the natural origin of metal elements, the gross concentrations of metal elements don't show the anthropogenic contribution specifically. The assessment of heavy metals from anthropogenic contribution must be made clear. Because the natural occurrence of heavy metals complicates assessments of potentially contaminated estuarine sediments, measurable quantities of metals do not automatically infer anthropogenic enrichment in the estuary.

Enrichment factor is a good tool to differentiate the metal source between anthropogenic and naturally occurring (Morillo et al. 2004; Selvaraj et al. 2004; Adamo et al. 2005; Vald'es et al. 2005; Chen et al. 2007), and is used as the main index for assessing the extent of the contamination (Chen et al. 2007).

The definition of F :

$$F = \frac{[\omega(M)/\omega(M_r)]_s}{[\omega(M)/\omega(M_r)]_b}$$

$\omega(M)$	the content of contamination elements
$\omega(M_r)$	the content of reference elements
s	study sample
b	background

Table 3 The Pearson coefficient matrix of metal elements and total organic matter in surficial sediments

	Cu	Ni	Cr	Pb	Zn	Zr	Sr	Ba	TOM
Co	0.890	0.918	0.666	0.623	0.561	0.973	0.148	0.904	0.573
Cu	1	0.947	0.870	0.782	0.650	0.875	0.246	0.826	0.635
Ni		1	0.812	0.764	0.664	0.893	0.279	0.907	0.700
Cr			1	0.697	0.567	0.669	0.296	0.619	0.608
Pb				1	0.794	0.620	0.220	0.742	0.674
Zn					1	0.549	0.195	0.712	0.811
Zr						1	0.212	0.868	0.543
Sr							1	0.208	0.318
Ba								1	0.742

Table 4 Rotated principal components matrix

Elements	F1	F2	F3
Co	0.944	0.271	-0.005
Cu	0.810	0.469	0.097
Ni	0.850	0.463	0.134
Pb	0.465	0.772	0.062
Cr	0.610	0.496	0.211
Sr	0.112	0.118	0.978
Zn	0.305	0.901	0.031
Zr	0.928	0.248	0.058
Ba	0.809	0.497	0.048
TOM	0.369	0.801	0.214
FP ^a	0.824	0.375	0.251
Mz ^b	0.860	0.385	0.158

^a Fine fraction sediment including silt and clay

^b Mean grain size

To assess the enrichment or depletion of trace elements in a sediment sample, the trace element concentrations can be normalized to an element which is conservative with respect to chemical weathering and which has no significant anthropogenic source. Zr belongs to oxyphilic elements, and always in form of oxide and silicate in nature; for the more, it has high chemo-stability during hypergenesis, so, most of them aggregate in placer deposits, a small quantity of them take part in sedimentation circulation; and are absorbed by clay.

Zr have been used widely in geochemical studies of mineral weathering as a “conservative” lithogenic element to indicate enrichment or depletion of more reactive heavy metals in sediments in past studies (Shotyk 1996; Blaser et al. 2000; Rubio et al. 2000; Zhang 2006; Roussiez et al. 2006), and to reduce the scattering of data and to allow an accurate statement of background value as normalizer (Cobelo-García and Prego 2003). In this study, Pearson coefficient correlation analysis, Zr show obvious correlation with all the heavy metal elements Cu, Co, Ni, Pb, Cr

and Zn, so Zr are also chosen as the reference elements of the heavy metals in this study.

The sediment core located in the high deposition velocity zone, the average deposition velocity is about 1.4 cm a^{-1} from the ^{210}Pb data and the contrast of the historical chart (Chen and Luo 1991; Chen 1995), so the sediment layers below 200 cm can represent the sedimentary status of pre-industrial China (1860 AD). The average concentration of heavy metals in the sediment layers below 200 cm was calculated as the background in this study. The result is shown in Table 5, and the enrichment factors calculated of Co, Cu, Ni, Pb, Cr and Zn in surficial sediments are shown in Table 5 as well.

The EF values are interpreted as suggested by Blaser et al. (2000) and Zhang and Liu (2002): the $\text{EF} < 1$ indicates depletion, $\text{EF} > 1$ indicates enrichment and $\text{EF} > 1.5$ is considered to indicate that an important proportion of trace metals is delivered from non-crustal materials or non-natural weathering processes, instead from biota and /or point and non-point pollution sources (Zhang and Liu 2002), $\text{EF} > 2$ means the significantly enrichment.

From Table 6, almost all the EF values of Co, Cu, Ni, Pb and Cr exceed 1, and 17 stations are enriched in Zn. But while comparing with the distributions of all the heavy metals in Fig. 2, the distributions of EF values of Co, Cu, Ni, Pb, Cr and Zn showed quite different patterns. In detail, the concentrations of Cr, Co, Cu, Ni, Pb and Zn in station 6, 12, 16 and 21 are much lower than the background values in Table 5; whereas, the most EF values of Co Cu, Ni, Pb and Cr in station 6, 12, 16 and 21 show enrichment even significant enrichment as in Table 6.

The dynamics in 6, 12, 16 and 21 are powerful, the bottom sediment can easily be washed and corroded by runoff, coastal current and tidal current, and left relict sediment. The mean grain size of 6, 12, 16 and 21 are small, and the concentration of fine particle sediment are much lower than the other stations as in Appendix 1. Because Zr-mineral can hardly enrich in the coarse sediment with grain size above, So, the concentrations of Zr in the four stations are 63.9, 28, 81.8 and 87.8 $\mu\text{g/g}$, much lower than the background value, and also lower than the other stations, and the EF values are much higher than the other stations. In addition, because of the tiny content of Co, Cu, Ni, Pb, Cr and Zn, mild anthropogenic influence will significantly alter the composition and concentration of trace heavy metal elements in sediment, so, the high EF values in these stations cannot reflect the influencing degree of human being properly.

Except the four stations, 17 stations of EF values for Pb exceed 1.5, these stations distribute not only in near-shore area of the main land or the islands (17, 14, 22, 23, 40 and 41), but in the open sea area (45, 47, 55, 56 and 49) far from the land. The distribution implied the obvious anthropogenic

Table 5 Back ground and enrichment factors of heavy metals in surficial sediments

Site	Co	Cu	Ni	Pb	Cr	Zn	Site	Co	Cu	Ni	Pb	Cr	Zn
2	1.15	1.70	1.48	1.98	1.68	1.28	29	1.20	1.35	1.55	1.15	1.26	0.73
4	1.23	1.60	1.35	1.04	1.41	0.85	31	1.20	1.44	1.42	1.70	1.38	1.05
6	0.92	1.44	1.41	1.94	3.06	0.75	33	1.21	1.52	1.31	1.42	1.34	0.87
7	1.24	1.63	1.36	1.11	1.32	0.67	35	1.26	1.54	1.52	1.30	1.56	0.87
9	1.27	1.03	1.51	1.44	1.65	2.14	37	1.13	1.01	1.03	1.06	1.28	0.70
10	1.22	1.27	1.38	1.70	1.42	1.34	39	1.00	0.75	0.88	0.93	1.23	0.61
12	1.52	1.28	1.84	4.39	6.06	1.05	40	1.24	1.62	1.55	1.98	1.55	1.85
14	1.24	1.98	1.53	2.23	1.46	1.97	41	1.24	1.45	1.37	1.75	1.50	1.28
16	1.40	1.06	1.10	1.34	1.71	0.69	43	1.20	1.40	1.34	1.15	1.44	1.29
17	1.17	1.56	1.38	1.74	1.43	1.48	45	1.22	1.38	1.39	1.64	1.39	0.97
18	1.17	1.26	1.19	1.18	1.27	0.65	47	1.28	1.15	1.41	1.55	1.47	0.78
20	1.09	1.06	1.02	1.42	1.21	1.17	49	1.20	1.32	1.26	1.57	1.30	1.07
21	1.28	0.95	1.08	1.00	1.79	0.66	51	1.21	1.34	1.36	1.54	1.37	0.84
22	1.18	1.49	1.46	1.93	1.36	1.46	53	1.24	1.34	1.26	1.43	1.38	0.98
23	1.22	1.53	1.40	1.71	1.45	0.98	55	1.15	1.32	1.24	1.57	1.25	1.07
25	1.31	1.18	1.20	1.31	1.33	1.28	56	1.28	1.36	1.46	1.76	1.49	0.95
26	1.21	1.31	1.31	1.21	1.29	0.88	57	1.25	1.40	1.40	1.67	1.44	1.08
27	1.23	1.46	1.44	1.83	1.42	1.04	59	1.22	1.08	1.22	1.32	1.30	0.82
28	1.19	1.37	1.32	1.30	1.30	0.82	60	1.24	1.21	1.17	1.07	1.37	0.72
elements	Co	Cu	Ni	Pb	Cr	Zn	Zr						
BG ^a	22.47	38.48	34.15	27.73	64.92	99.98	151.5						

BG background values in $\mu\text{g g}^{-1}$

influence in the near shore area and the deep sea area as well, the atmospheric sedimentation may be a major reason for the far-land pollution (Lee et al. 2007). The maximum EF values 2.23 in station 14 indicated a point source pollution from JinWan city. In contrast, the EF values of Co are all above 1 and below 1.5, indicating mild contamination. The variation of EF for Zn is significant, i.e. EF values of 9, 14 and 40 are 2.14, 1.97 and 1.85, respectively, and 16 stations have EF values below 1. Element of Zn can easily separate out of sediment to the water for the active chemical activity as well as the semi-tropical climate, so some stations of EF values are below 1 indicating the depletion of Zn, while high EF values in station 9, 25, 17, 40, 41 and 14 indicated the human drainage to the coast from mainland and island; the peculiar maximum EF value 2.14 for Zn in station 9 indicates high probability of sewage drainage of Zn in the west of the Huangmao Hai estuary. The maximum EF values for Cu (1.98) appeared in 14, reflecting the industrial pollution from Jin wan city neighbouring, and similarly the high value in station 40 reflected the input from Gaolan island, differently, the higher EF values in 2, 4, 7, 17, 23 and 35 indicate the Cu-contaminated matter input from West river and Tan river. Most of the EF values for Ni and Cr are close to 1.5, only several EF values are slightly higher than 1.5, the distribution and concentration of Ni and Cr indicated that though the contamination of Ni and Cr in study area is not as

obvious as Pb, it has been influenced more or less at large by anthropogenic input, and the upriver drainage and coastal industrial input are main sources.

Conclusions

The concentration and spatial distribution of trace metals Co, Cu, Ni, Pb, Cr, Zn, Ba, Zr Sr has been observed at a number of sites in west-four Pearl river area including Huangmao Hai, JitiMen and Modao Men. Trace metals of Co, Cu, Ni, Pb, Cr, Zn, Ba and Zr main come from the terrigenous matter, the special hydrodynamic power and landform are the dominating factors controlling the large-scale distribution; while the anthropogenic input in the coastal area alters the regional distribution of heavy metal elements Co, Cu, Ni, Pb, Cr and Zn.

From enrichment factor analysis, the study area is prevalently enriched in Co, Cu, Ni, Pb and Cr, and the aggregation of Pb is the most obvious. The peculiar high EF value sites of Zn and Pb suggest that point source input of some specific metal contaminant may has caused significant sediment contamination in the local area. With the further industrialization and economic development in the region, greater attention should be paid to point source contamination around the area.

The disagreement of EF analysis result of element contents in four stations implied the limitation of EF analyse. The difference of grain size may cause quite exceptional result and cannot explain the anthropogenic influence properly. So the EF analysis must be used restrainedly.

The EF analysis results show that the calculated pre-industrial content of heavy metals can be used as the regional background values effectively.

Acknowledgments We thank Professor Zhigang Guo and Professor Dejian Fan of ocean University for their precious advice in editing the paper. This work was founded by the Research project: Envolvement, Sediment Record and Sutainable Development of Main Delta of China (908-02-02-05)and Six Framework Program, Sustainable Option for People, Catchment and Aquatic Resources (INCO-CT-2004-510706).

Appendix

Table 6.

Table 6 Content (%) of each fraction and grain size parameters of all sites

Site	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Mz (Φ)	Si (Φ)	Ski (Φ)	Kg (Φ)	Sediment type
2		16.6	31.3	50.48	7.86	4.26	-0.19	1.23	Silty clay
4		1.15	42	56.82	8.97	2.56	0.25	0.96	Silty clay
6	14.55	63.4	7.88	14.17	2.39	4.36	0.53	1.78	Gravelly sand
7		0.5	36.4	63.11	9.4	2.62	0.21	0.91	Silty clay
9		15.6	30.6	53.8	8.02	3.45	-0.22	1.17	Silty clay
10		5.15	41.2	53.68	8.69	2.88	0	0.98	Silty clay
12	5.06	92.69	2.25	0	1.26	1.24	-0.18	0.92	Gravelly sand
14		2.8	46.9	50.26	8.43	2.75	0.16	0.9	Silty clay
16		95.47	4.53	0	3	0.33	0.14	1.79	Sand
17		0.2	41.9	57.91	9.25	2.66	0.32	0.92	Silty clay
18		13.4	41.5	45.09	7.94	3.6	0.25	0.83	Silty clay
20		42.95	40.2	16.84	5.39	2.5	0.72	1.68	Silty sand
21		97.09	2.89	0	3.23	0.29	0.28	1.46	sand
22		0.15	36.9	62.98	9.27	2.48	0.04	0.92	Silty clay
23		3.25	41.6	55.18	8.99	3.14	0.24	0.95	Silty clay
25		36.15	40	23.88	6.4	3.42	0.68	1.07	Sand-silt-clay
26		45.25	31.9	22.85	6.01	3.11	0.76	1.1	Sand-silt-clay
27		4.05	46	50	8.41	2.93	0.19	0.92	Silty clay
28		3	57	39.97	7.86	3.01	0.3	0.88	Clayey silt
29		4.9	56.5	38.55	8.09	3.38	0.39	1.03	Clayey silt
31		2.9	43	54.09	9.12	3.28	0.3	0.93	Silty clay
33		1.4	38.2	60.43	9.09	2.68	0.16	0.94	Silty clay
35		0.35	25.2	74.49	9.8	2.4	0	0.98	Silty clay
37		11.55	55.9	32.57	7.15	3.55	0.56	1.06	Clayey silt
39		61.7	26.8	10.67	4.48	2.19	0.68	2.01	Silty sand
40		7.75	33.5	58.77	8.7	2.89	-0.02	1.03	silty clay
41		2.85	40.3	56.84	8.72	3.07	0.05	0.89	silty clay
43		1.7	45.7	52.61	8.91	3.19	0.31	0.94	silty clay
45		2.8	39.4	57.77	9.14	2.89	0.17	0.99	silty clay
47		29.2	35.8	35.04	7.06	3.86	0.22	0.82	Sand-silt-clay
49		6.1	49	44.88	8.33	3.34	0.2	0.86	Clayey silt
51		2.35	37.4	60.31	9.22	2.96	0.17	0.94	silty clay
53		3.25	53.3	43.5	8.2	3.1	0.34	0.93	Clayey silt
55		9.56	47.9	42.53	8.26	3.69	0.34	0.94	Clayey silt
56		7.5	42.5	50.05	8.24	2.86	0.02	0.94	silty clay
57		10.05	47.4	42.57	7.91	3.3	0.21	0.85	Clayey silt
59		5	50.2	44.84	8.42	3.34	0.28	0.93	Clayey silt
60		3.65	46.3	50.06	8.46	2.93	0.21	0.92	silty clay

References

- Adamo P, Arienzo M, Imperato M, Naimo D, Nardi G, Stanzione D (2005) Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port. *Chemosphere* 61(6):800–809
- Barcellos C, de Lacerda LD, Ceradini S (1997) Sediment origin and budget in Sepetiba Bay (Brazil)—an approach based on multi-elemental analysis. *Environ Geol* 32(3):203–209
- Blaser P, Zimmermann S, Luster J, Shotyk W (2000) Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb and Zn in Swiss forest soils. *Sci Total Environ* 249:257–280
- Chen YT (1995) Sedimentation divisions of Pearl River Mouth. *Acta Scientiarum naturalium universitatis sunyatseni* 34(3):109–114
- Chen XH (2000) Allocation and variation of sediment for branching channels main river in the pearl delta—a case study of the west and north river delta. *Tropic Geogr* 20(1):22–26
- Chen YT, Luo ZR (1991) Modern sedimentary velocity and their reflected sedimentary characteristics in the Pearl River Mouth. *Tropic oceanol* 10(2):57–64
- Chen CW, Kao CM, Chen CF, Dong CD (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere* 66:1431–1440
- Cobelo-García A, Prego R (2003) Heavy metal sedimentary record in a Galician Ria (NW Spain): background values and recent contamination. *Mar Pollut Bull* 46:1253–1262
- DeMora S, Sheikholeslami MR, Wyse E, Azemard S, Cassi R (2004) An assessment of metal contamination in coastal sediments of the Caspian Sea. *Mar Pollut Bull* 48:61–77
- Einax JW, Soldt U (1999) Geostatistical and multivariate statistical methods for the assessment of polluted soils—merits and limitations. *Chemomet Intell Lab Syst* 46:79–91
- Grabemann I, Uncles RJ, Krause G, Stephens JA (1997) Behaviour of turbidity maxima in the tamar (U.K.) and Weser (F.R.G) estuaries. *Estuar Coast Shelf Sci* 45:235–246
- Graham E, Richard J Howarth, Nombela MA (2003) Metals in the sediments of Ensenada de San Simón (inner Ría de Vigo), Galicia, NW Spain. *Appl Geochem* 18:973–996
- Guerra-García José M, García-Gomez JC (2005). Assessing pollution levels in sediments of a harbour with two opposing entrances. Environmental implications. *J Environ Manage* 77(1):1–11
- Hills P, Zhang L, Liu JH (1998) Transboundary pollution between Guangdong Province and Hong Kong: threats to water quality in the Pearl River Estuary and their implications for environmental policy planning. *J Environ Plann Manage* 41:375–396
- Howarth RJ, Nombela MA (2003) Metals in the sediments of Ensenada de San Simon (inner Ria de Vigo), Galicia, NW Spain. *Appl Geochem* 18:973–996
- Lau MM, Rootham RC, Bradley GC (1993) A strategy for the management of contaminated dredged sediment in Hong Kong. *J Environ Manage* 38:99–114
- Lee CSL, Li XD, Zhang G, Li J, Ding AJ, Wang T (2007) Heavy metals and Pb isotopic composition of aerosols in urban and suburban areas of Hong Kong and Guangzhou, South China. Evidence of the long-range transport of air contaminants. *Atmos Environ* 41(2):432–447
- Li XD, Wai OWH, Li YS, Coles B, Eamsy MH, Thornton I (2000) Heavy metal contaminants in sediment profiles of the Pearl River Estuary. *Appl Geochem* 15:567–581
- Liang J (2005) Characteristics of the sediment and sedimentary environment in the Modaomen estuary. *Trop Geogr* 25(2):117–122
- Lin ZH, Liang SH (1995) Modern sedimentary environment and heavy metal content distribution in bottom load in Pearl Estuary. *Mar Sci Bull* 14(4):43–49
- Lin S, Hsieh IJ, Huang KM, Wang CH (2002) Influence of the Yangtze River and grain size on the spatial variations of heavy metals and organic carbon in the East China Sea continental shelf sediments. *Chem Geol* 182:377–394
- Liu WX, Li XD, Shen ZG, Wang DC, Wai OWH, Li YS (2003) Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environ Pollut* 121:377–388
- McCready S, Gavin F. Birch, Edward R. Long (2006) Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity—a chemical dataset for evaluating sediment quality guidelines. *Environ Int* 32:455–465
- Mitchell SB, West JR, Arundale AMW, Guymer I, Couperthwaite JS (1998). Dynamics of the turbidity maxima in the upper Humber estuary system, UK. *Mar Pollut Bull* 37:190–205
- Morillo J, Usero J, Gracia I (2004) Heavy metal distribution in marine sediments from the southwestcoast of Spain. *Chemosphere* 55:432–442
- Muniz P, Danulat E, Yannicelli B, Garcia-Alonso J, Medina G, Bicego MC (2004) Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). *Environ Int* 29:1019–1028
- Ou XJ, Zhao HT, Song CJ (1983) Hydrological and sedimentary characteristics of the Modaomen distributary mouth, Xijiang (west river). *Tropic oceanol* 2(4):278–288
- Peng XT, Zhou HY, Ye Y, Chen G Q (2004) Characteristics of sediment grain size and their implications for bottom hydrodynamic environment in the Pearl River estuary. *Acta Sedimentologica Sinica* 22(3):487–493
- Roussiez V, Ludwig W, Monaco A, Probst JL, Bouloubassi I, Buscail R, Saragoni G (2006) Sources and sinks of sediment-bound contaminants in the Gulf of Lions (NW Mediterranean Sea): a multi-tracer approach. *Continental Shelf Res* 26:1843–1857
- Ruiz F (2001) Trace metals in estuarine sediments from the southwestern Spanish coast. *Mar Pollut Bull* 42(6):482–489
- Rubio B, Nombela MA, Vilas F (2000) Geochemistry of major and trace elements in sediments of the Ria de Vigo(NW Spain): an assessment of metal pollution. *Mar Pollut Bull* 40:968–980
- Selvaraj K, Mohan VR, Szefer P (2004) Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: geochemical and statistical approaches. *Mar Pollut Bull* 49(33):174–185
- Shotyk W (1996) Peat bog archives of atmospheric metals deposition: geochemical assessment of peat profiles, natural variations in metal concentrations, and metals enrichment factors. *Environ Rev* 4(2):149–183
- Shine JP, Ika RV, Ford TE (1995) Multivariate statistical examination of spatial and temporal patterns of heavy metal contamination in New Bedford Harbour marine sediments. *Environ Sci Technol* 29:1781–1788
- Simeonov V, Massart DL, Andreev G, Tsakovski S (2000) Assessment of metal pollution based on multivariate statistical modeling of ‘hot spot’ sediments from the Black Sea. *Chemosphere* 41:1411–1417
- The Chinese national criteria GB/T17318.5–1998, specification for oceanographic survey-Marine geology and geophysics investigation
- Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth’s crust. *Geol Soc Am Bull* 72:175–192
- Vald’es J, Vargas G, Sifeddine A, Ortlieb L, Guinez M (2005) Distribution and enrichment evaluation of heavy metals in

- Mejillones Bay (23°S), Northern Chile: geochemical and statistical approach. *Mar Pollut Bull* 50:1558–1568
- Wang S (2006) Project design research of East Dam in the west shore of Jiti Men. *Guangdong Water resource and Hydropower* (in chinese)
- Wang SJ, Hu D, Li CC (2006) The recent evolution of Modaomen Estuary and its effect on flood drainage. *Mar Sci Bull* 25(2):21–26
- Willams TP, Bubb JM, Lester JN (1994). Metal accumulation within saltmarsh environments: a review. *Mar Pollut Bull* 28:277–290
- Yang XW (1993) Sediment load sources and transportation process in Huang mao Hai bay west of Pearl Estuary. *Mar Sci Bull* 12(6):53–62
- Yang XW, Wang WJ (1994) A statistical study on hydrodynamic sedimentation and sand movement Huangmaohai Estuary Bay. *Ocean Eng* 12(4):42–51
- Yang XW, Yu HB, Sun ZX, Liang TM (1997) The modern dynamic geomorphological system and erosion–depositional process analysis of HuangmaoHai Bay, west of Pearl River estuary. *Tropic oceanol* 16(1):49–59
- Yang L, Li CC, Tian XP (2006) Concentrations and content distribution of heavy metals in surface sediments in Modao Men distributary mouth of Pearl River estuary. *Ecol Environ* 15(3):490–494
- Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals in China-Weathering features, anthropogenic impact and chemical fluxes. *Estuar Coast Shelf Sci* 54:1051–1070
- Zhang GW, Ma DX, Xu MG, Zhou QW, Lan XH (1988) Sedimentary environments and structures of modern sediments in the mouth of Zhujiang river. *Mar Geol Quaternary Geol* 8(3):71–83
- Zhang XZ, Bao ZY, Tang JH (2006) Application of the enrichment factor in evaluation of heavy metals contamination in the environmental geochemistry. *Geol Sci Technol Information* 25(1):65–72
- Zhao HT (1983) Hydrological characteristics of the Zhujiang (pearl river) delta. *Tropic Oceanol* 2(2):108–117
- Zhao YY, Yan MC (1994) *Geochemistry of sediments of the China Shelf Sea* [M]. Science Press, Beijing
- Zhou HY, Peng XT, Pan JM (2004) Distribution, source and enrichment of some chemical elements in sediments of the Pearl River Estuary. *China Continental Shelf Res* 24:1857–1875
- Zwolsman JJG, van Eck GTM, Burger G (1996) Spatial and temporal distribution of trace metals in sediments from the Scheldt Estuary, South-west Netherlands. *Estuar Coast Shelf Sci* 43(1):55–79