

Distribution and risk assessment of trace metals in sediments from Yangtze River estuary and Hangzhou Bay, China

Feipeng Li¹ · Lingchen Mao¹ · Yubao Jia¹ · Zhujun Gu¹ · Weiling Shi² · Ling Chen^{2,3} · Hua Ye¹

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Abstract The Yangtze River estuary (YRE) and Hangzhou Bay (HZB) is of environmental significance because of the negative impact from industrial activities and rapid development of aquaculture on the south bank of HZB (SHZB) in recent years. This study investigated the distribution and risk assessments of trace metals (Cr, Cu, Zn, Hg, Pb, and Cd) accumulated in surface sediments by sampling in YRE, outer and south HZB. Copper and Zn concentration (avg. 35.4 and 98.7 mg kg⁻¹, respectively) in surface sediments were generally higher than the background suggesting a widespread of Cu and Zn in the coastal area of Yangtze River Delta. High concentrations of Cu (~ 42 mg kg⁻¹), Zn (~ 111 mg kg⁻¹), Cd (~ 0.27 mg kg⁻¹), and Hg (~ 0.047 mg kg⁻¹) were found in inner estuary of YRE and decreased offshore as a result of terrestrial input and dilution effect of total metal contents by “cleaner” sediments from the adjacent sea. In outer HZB, accumulation of terrestrial derived metal has taken place near the Zhoushan Islands. Increase in sediment metal concentration from the west (inner) to the east (outer) of SHZB gave rise to the input of fine-grained sediments contaminated with metals

from outer bay. According the results from geoaccumulation index, nearly 75% of samples from YRE were moderately polluted ($1.0 < I_{geo} < 2.0$) by Cd. Cadmium and Hg contributed for 80~90% to the potential ecological risk index in the YRE and HZB, with ~ 72% sites in HZB under moderate risk ($150 \leq RI < 300$) especially near Zhoushan Islands.

Keywords Coastal sediments · Trace metal contamination · Spatial distribution · Yangtze River estuary · South Hangzhou Bay

Introduction

The Yangtze River delta is one of the most developed areas in China with a variety of industries and highly intense population, which inevitably leads to various environmental contamination in the offshore waters. Being as the watershed of substances into the sea, the Yangtze River estuary (YRE) was strongly affected by human activities as terrestrial pollutants were carried by river and inputted into the estuary. The China Marine Environment Bulletin (2013) reported that 486 million tons of sediments carrying 15,455 tons of toxic trace metals were discharged to the East China Sea (ECS) by the Yangtze River, besides the portion discharged by sewage outlets. In addition, the Huangpu River flowing through Shanghai discharges large amounts of pollutants from industrial activities such as wharf (Shidongkou, Bailonggang), petrochemical plants, sewage treatment plants, and landfill (e.g., Laogang landfill) to the inner estuary. Researchers have been putting more and more efforts in investigating the risk from trace metals to estuary environment, as they are not degradable by chemical or biological processes. Accumulation of metals in sediments leads to adverse effects on benthic community (Pan and Wang 2012), degradation of ecosystem (Fung et al. 2004),

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✉ Lingchen Mao
lingchen_mao@163.com

¹ School of Environment and Architecture, University of Shanghai for Science and Technology, Shanghai 200093, China

² College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

³ State Key Laboratory of Pollution Control and Resource Reuse, Shanghai 200092, China

and possible poisoning of human via food chain (Bryan et al. 1979). Sediment as carrier of trace metals could be a potential source of pollutants when natural and anthropogenic disturbance took place (Comans and van Dijk 1988; Man et al. 2004). In particular, trace metals in coastal sediments were more likely to take part in various physical, chemical, and biological processes and deposit in the estuarine and bottom of adjacent waters.

Terrestrial runoff, atmospheric deposition, and industrial waste disposal were notable sources of trace metals in estuarine environment (Kennish 1996; Pan and Wang 2012). Moderate to high environmental risk of trace metals in sediments from YRE was suggested by several recent studies (e.g., Wang et al. 2014; Wang and Liu 2003). Adsorbed to suspended particles in the inner YRE (Zhao et al. 2009), metals may be delivered to the outer and south bank of HZB and being dominant (Zhang et al. 2009; Wang et al. 2013a). This process however is complicated as it is controlled by various factors including sediment/water properties (Lin et al. 2002; Zhao et al. 2013), river flow, and ocean current (Hu et al. 2012) leading to an uncertain situation of both the outer and the south bank of HZB. Because of the dramatic increase of industrial and aquaculture activities in south HZB and Zhoushan Islands (out of the HZB), it is crucial to confirm the source of trace metals and to assess the potential ecological risk they bring to the area. Therefore, in this study, we looked into the distribution of six trace metals (Hg, Cd, Pb, Zn, Cu, and Cr) in surface sediment of YRE, outer and south bank of HZB and attempted to investigate the contribution of metal contamination from the river estuary to the area. The potential risk from the metals was also assessed to provide scientific information for local decision maker for proper environmental management.

Materials and methods

The study area and sediment sampling

The YRE and HZB are both typical funnel-shaped. Sediment discharged from the Yangtze River ($4.8 \times 10^8 \text{ m}^3 \text{ a}^{-1}$) gives a tremendous impact to the HZB and has been considered as one of the main sources of sediments in the bay (Milliman et al. 1984; Su and Wang 1989). The southern area of HZB (SHZB), however, receives a mix of sediments originated from the Yangtze River, Qiantang River, and ESC (Wang et al. 2013a). The SHZB has experienced rapid industrial and aquacultural development, especially for whiteleg shrimp (*Penaeus vannamei*), oysters, blue crab, etc., during the past several years (Wang et al. 2012). As a result of land reclamation and sedimentation, the tidal flat area on the south bank has been doubled from 2009 to 2013 (Cheng et al. 2015). The

conflict between human activities and the ecosystem in the area has therefore been intensified.

The sampling area covered the mouth of Yangtze River, outer Hangzhou Bay, and south bank of Hangzhou Bay (SHZB) in the range of $121^\circ\text{E}\sim 123^\circ\text{E}$, $30^\circ\text{N}\sim 31.5^\circ\text{N}$ (Fig. 1). The study was carried out in three transects, Yangtze River estuary (A1–A11), Hangzhou Bay (B1–B18), and the south Hangzhou Bay (C1–C10), in order to (1) study the effect from industrial and domestic influence from the city of Shanghai which is located on southeast of the YRE; (2) make comparison between marine sediments from HZB, located in the south of YRE and linked with the ECS by water channel, and coastal sediments on its south bank. The surface marine sediment samples (0–10 cm in depth) in Yangtze River estuary and Hangzhou Bay were collected using a grab sampler in August 2011 and samples in the south Hangzhou Bay were collected using a spade in July 2014. They were taken back to laboratory and stored at -20°C before further treatment. All samples were freeze-dried for 48 h and ground to sieve (0.15 mm) for Cd, Pb, Zn, Cu, Cr, and Hg concentration analysis.

Analysis of metal concentration in sediments

For analysis of total Cd, Pb, Zn, Cu, and Cr concentration, sediment samples ($\sim 0.20 \text{ g}$) were digested with a mixture of $\text{HCl-HNO}_3\text{-HF}$ (7.5 mL HCl, 2.5 mL HNO_3 , and 5 mL HF of Guaranteed Reagent, Sinopharm Chemical Reagent Co, Ltd., China) performed in open Teflon vessel systems (DigiBlock S16). Perchloric acid ($\sim 5 \text{ mL}$) was added to remove HF and the digest was kept in 5% HNO_3 with Milli-Q water (Yang et al. 2014). For quality assurance, standard reference material (SRM 1646a, from National Institute of Standards and Technology) and reagent blanks were digested with each batch of 16 samples synchronously. The recoveries of metals in SRM 1646a varied from 83 to 109%. Reagent blanks were conducted through analysis process to correct the results. About 20% of the samples in each batch were digested in triplicates to assess the accuracy of methods and the relative standard deviation (RSD) was $< 10\%$. The concentrations of Pb, Zn, Cu, and Cr in digest were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Agilent 720ES) and that of Cd was analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700). Total concentration of Hg in sediment solid was measured by Direct Mercury Analyzer (MDA-80, Milestone Srl.) without digestion. The Hg concentration in instrument blank and sample blank was controlled to be $< 0.1 \text{ mg kg}^{-1}$ before measurement to avoid lab contamination. The standard reference material of Hg (ESS-3, GSBZ50013-88), from the China National Environmental Monitoring Centre, was analyzed and the recovery was in the range of 84.9–96.4%. Duplicates were made for all Hg analysis with $\text{RSD} < 7.76\%$.

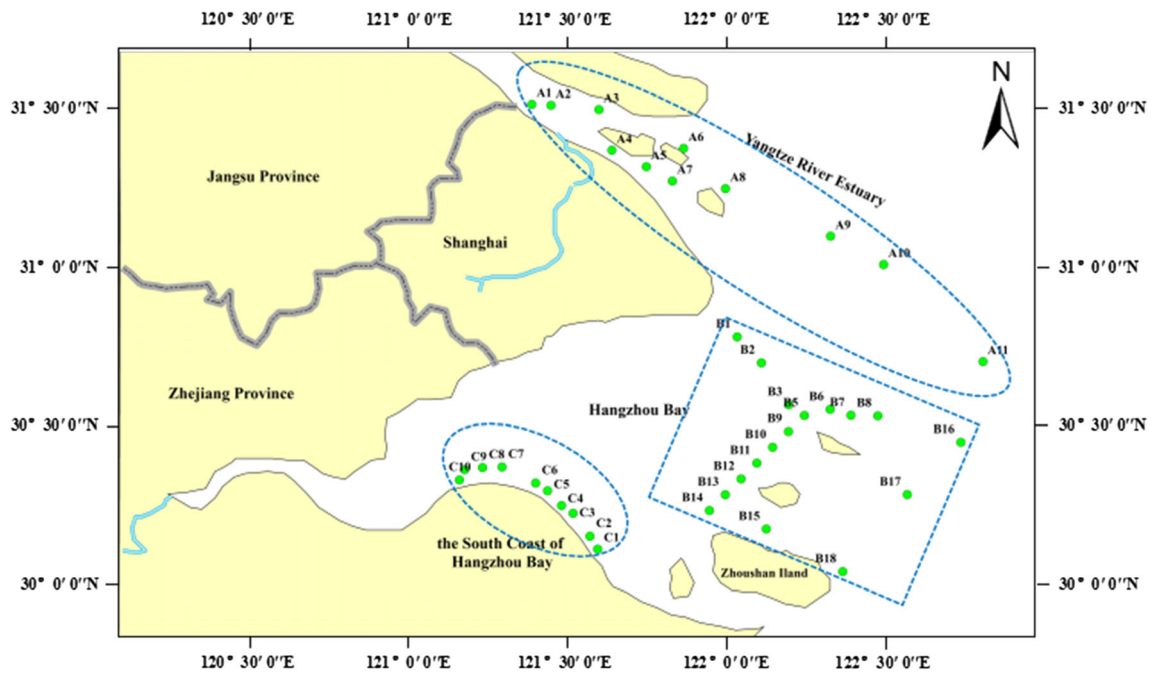


Fig. 1 Map of the study area and sampling sites, A1 to A11 (YRE) and B1 to B18 (HZB) collected in August 2011; C1 to C10 (SHZB) collected in July 2014

Risk assessment methods

Both geoaccumulation index (I_{geo}) and potential ecological risk index (RI) were used to assess the risk of toxic trace metals in sediment samples collected.

Introduced by Müller (1969), geoaccumulation index (I_{geo}) is a commonly used assessment model indicating trace metal pollution in sediments using the following equation:

$$I_{geo} = \log_2(C_n / (1.5B_n)) \tag{1}$$

where C_n is the concentration of measured metal “ n ” in the samples, B_n is the background concentration of the metal “ n ” employing the background concentrations for Cu (15 mg kg⁻¹), Pb (20 mg kg⁻¹), Zn (65 mg kg⁻¹), Cd (0.065 mg kg⁻¹), Hg (0.025 mg kg⁻¹), and Cr (61 mg kg⁻¹) in sediments from East China Sea (Zhao and Yan 1993). The constant of 1.5 is introduced to minimize the variation of background values. The values of I_{geo} were classified as unpolluted (< 0), unpolluted to moderately polluted (0–1), moderately polluted (1–2), moderately to strongly polluted (2–3), strongly polluted (> 3), strongly to extremely polluted (3–4), and extremely polluted (> 4) (Müller 1969).

The potential ecological risk index (RI) was developed to assess ecological risks from the metals in sediments (Hakanson 1980). The methodology is based on the assumption that the sensitivity of an aquatic system depends on its productivity. It was built to assess the degree of pollution in

sediments according to the metal toxicity and the response from the environment could be calculated by Eq. 2:

$$C_f^i = C_n^i / C_0^i \tag{2a}$$

$$E_r^i = T_r^i \times C_f^i \tag{2b}$$

$$RI = \sum_{i=1}^n E_r^i \tag{2c}$$

where C_f^i is the contamination factor and C_n^i is the metal concentration in sediment. C_0^i is the background value which is used in the I_{geo} calculation aforementioned. T_r^i is the toxic response factor for a given substance that accounts for the toxic requirement and the sensitivity requirement (i.e., Hg = 40, Cd = 30, Cu = Pb = 5, Cr = 2, Zn = 1) (Hakanson 1980). E_r^i is the minimal potential ecological risk factor; RI is calculated as the sum of contribution from all assessed trace metals in sediments. Table 1 listed the classification of E_r^i and RI index and the corresponding potential ecological risk levels.

Results and discussion

Trace metals concentration in sediments

Trace metal concentration in surface sediments collected from the study area was summarized in Table 2 along with the results from other researches in the area. For all metals, the

Table 1 Classification of potential ecological risk value for E_r^i (for metal i) and RI index

E_r^i value	Level	RI value	Level
$E_r^i < 40$	Low	$RI < 150$	Low
$40 \leq E_r^i < 80$	Moderate	$150 \leq RI < 300$	Moderate
$80 \leq E_r^i < 160$	Considerable	$300 \leq RI < 600$	Considerable
$160 \leq E_r^i < 320$	High	$RI \geq 600$	Very high
$E_r^i \geq 320$	Extremely high		

concentration in samples from SHZB was significantly lower than those from YRE and HZB analyzed in this study as well as in others. Coefficient of variance (CV) of metal concentrations in sediments from all three areas was relatively low, within the range of 15.6–29.3%, except for Hg in YRE (39.43%) which implies the presence of potential point source (Yin et al. 2013). Total Cr, Cu, Pb, and Zn concentration was generally close between samples from YRE and HZB with the average Cr concentration lower than the background (61 mg kg⁻¹). In SHZB however, the Cr concentration was all lower than the background with a relatively small variance (CV = 19.6%). Average Pb concentration in sediments from all samples was close to the background. In contrast, Cu and Zn concentration was generally higher than the background and the results from previous studies suggesting a widespread of Cu and Zn contamination in the coastal area of Yangtze River Delta. Human activities in surrounding cities and sediment discharge from Yangtze River may both contribute to Cu and Zn contamination in the area (Fang et al. 2013). Relatively high concentrations of Cu ($7.47 \pm 10.40 \mu\text{g L}^{-1}$) and Zn

($10.42 \pm 9.07 \mu\text{g L}^{-1}$) in surface water collected from the Yangtze River mouth in 2006 and 2010 respectively were reported by Su et al. (2015) and An et al. (2010) indicating potential anthropogenic sources, e.g., anti-(bio)fouling paints from ships and offshore engineering (Su et al. 2015; Pan and Wang 2012), industrial wastewater, etc. that give rise to the elevated metal contents in the estuarine area and Hangzhou Bay (Turner 2010). Discharge of metal-contaminated sediments from the Yangtze River was reported in several studies as more than 80% of sedimentation fluxes with Zn (1.08×10^5 ton year⁻¹) and Cu (4.32×10^4 ton year⁻¹) were deposited in the inner shelf and the YRE (Pan and Wang 2012; Fang et al. 2009). Cadmium and Hg in most samples collected were beyond the background concentrations, with individuals from YRE were more than 3–5 times higher (e.g., Cd = 0.364 mg kg⁻¹ in A2; Hg = 0.0764 mg kg⁻¹ in A5). Compared with Cd concentration in sediments from west of Zhoushan Islands in ECS, Cd in both YRE and HZB was generally higher indicating anthropogenic impact to the area.

Compared with marine sediment quality (GB 18668-2002) of China (Marine Sediment Quality 2002, Table 2), for all sediments in the study area, the concentrations of Cr, Zn, Pb, Cd, and Hg were below the criteria except for Cr in two samples from HZB (B7 and B8) and Zn in B14. For Cu, however, more than 68% of the samples from YRE and HZB were higher than the criterion of 35 mg kg⁻¹. The risk to marine life from Cu in this area should be therefore better evaluated, as the factor of bioaccumulation of Cu in marine bivalves—as important seafood species, especially in oysters (Pan and Wang 2009), may bring negative effects to marine ecosystem as well as human health through food chain.

Table 2 Summary of Cr, Cu, Pb, Zn, Cd, and Hg concentration (mg kg⁻¹) of sediments in the Yangtze River estuary (YRE), Hangzhou Bay (HZB), and south Hangzhou Bay (SHZB), together with the background concentration and class 1 values of the national standard

Study area	Cr	Cu	Pb	Zn	Cd	Hg	Reference
YRE	37.4–69.9 53.7 (22.6%)*	23.0–51.8 38.8 (22.4%)	13.9–29.5 22.5 (22.0%)	70.0–127 107 (15.6%)	0.138–0.364 0.242 (24.9%)	0.029–0.076 0.043 (39.3%)	This study
HZB	38.1–83.4 56.9 (25.8%)	24.3–66.5 42.3 (27.9%)	15.2–31.7 22.6 (20.8%)	71.0–152 109 (22.5%)	0.072–0.293 0.169 (29.3%)	0.023–0.060 0.039 (22.9%)	
SHZB	47.4–61.2 54.8 (19.6%)	21.9–36.1 28.5 (28.1%)	13.9–24.6 19.3 (28.6%)	71.6–109 87.9 (21.1%)	0.041–0.081 0.061 (21.5%)	0.036–0.052 0.040 (18.1%)	
Intertidal zone of YRE	36.9–173 78.9 ± 19.7	6.87–49.7 30.7 ± 9.7	18.3–44.1 27.3 ± 5.6	47.6–154 94.3 ± 23.9	0.119–0.750 0.261 ± 0.125	–	Zhang et al. (2009)
West Zhoushan Islands	56.5–96.0 83.3 ± 8.4	13.2–41.6 31.1 ± 6.8	17.9–35.1 27.9 ± 3.7	66.9–124.0 102.3 ± 12.9	0.048–0.160 0.100 ± 0.02	–	Xu et al. (2015a)
HZB	47.79–150.91 79.76	4.71–50.71 31.11	1.73–62.38 23.04	49.12–230.83 97.54	–	–	Liu et al. (2012)
Background value	61	15	20	65	0.065	0.025	Zhao and Yan (1993)
Class 1*	80	35	60	150	0.5	0.2	Marine Sediment Quality (2002)

*Marine sediment quality of China includes three classes and Class 1 is applied to protecting the habitats for marine life including natural, rare, and endangered species as well as the areas for human recreation and sports. Concentration values were the upper limits for the grades

**Values in the brackets were coefficient of variance (%)

Trace metal distributions

Figure 2 displayed the distributions of all measured metals in surface sediments from YRE and HZB. The concentrations

of Cu, Zn, Cd and Hg were high in inner estuary of YRE and decreased offshore. In comparison, studies of sediment metals in adjacent ECS reported much lower levels of contaminations. For example, Zhao et al. (2008) reported a

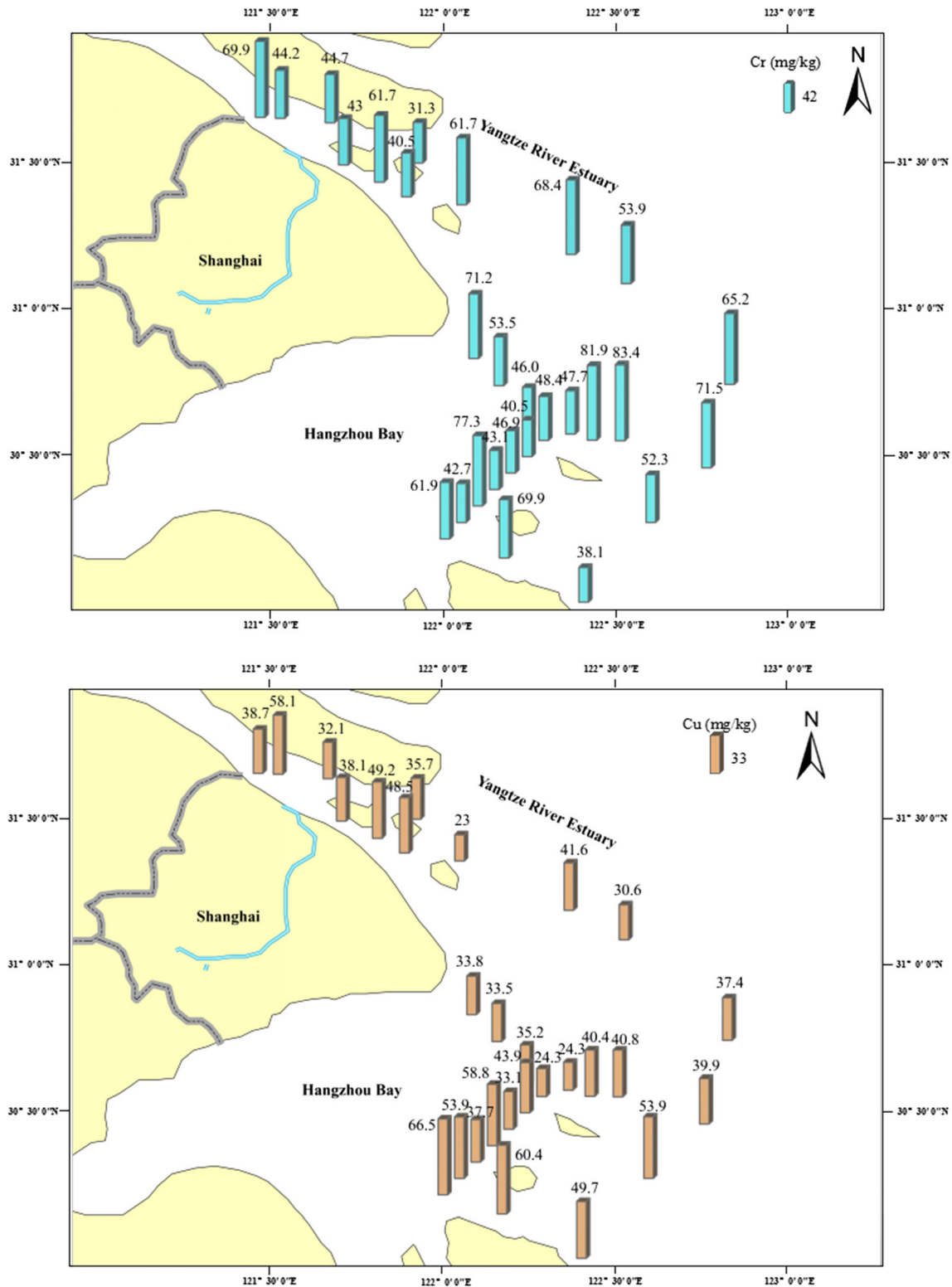


Fig. 2 Distribution of Cr, Cu, Zn, Cd, Pb, and Hg in surface sediments in the Yangtze River estuary (YRE) and outer Hangzhou Bay (HZB)

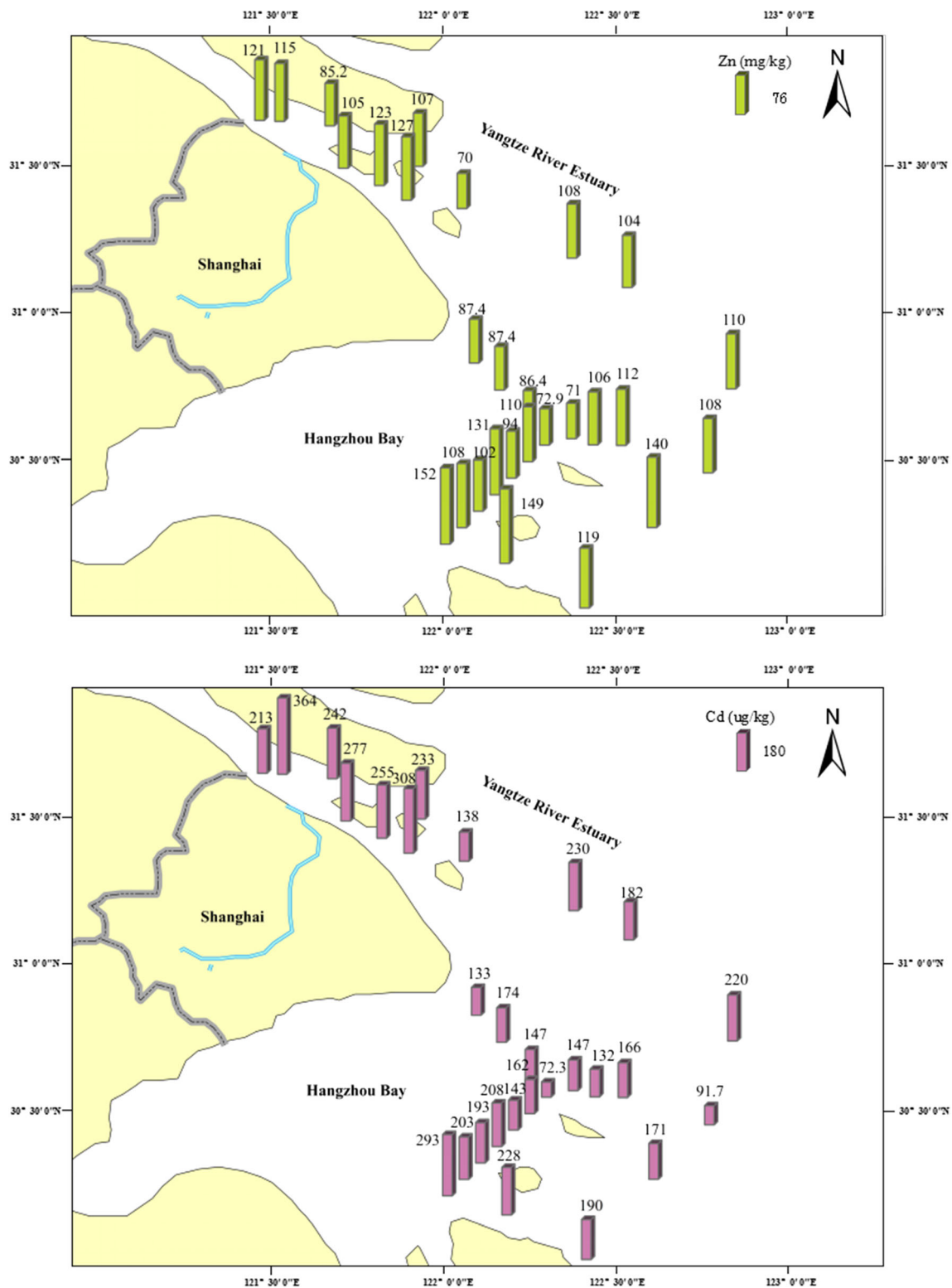


Fig. 2 (continued)

range of 2–36 mg kg⁻¹ of Cu and 24–105 mg kg⁻¹ of Zn in sediments; Fang et al. (2009) demonstrated a clear distribution of decreasing Fe, Cu, Mn, Ni, Pb, and Zn concentration in sediments away from the seashore of Zhejiang and Fujian

provinces to the offshore. Higher contamination level was commonly found close to the estuarine coast as a result of more intense human activities (e.g., atmospheric deposition, waste water treatment plants). Rubio et al. (2000) presented

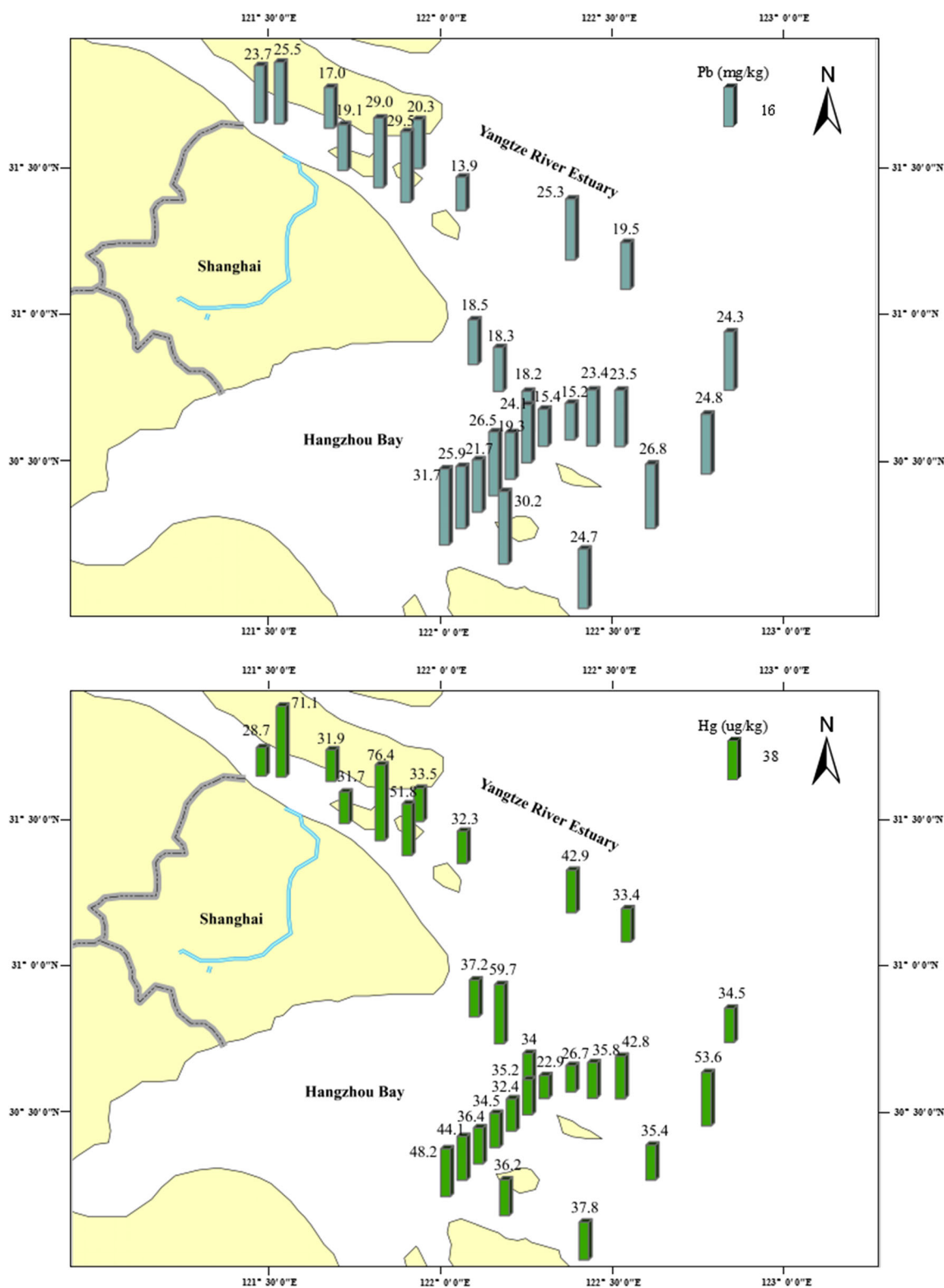


Fig. 2 (continued)

that trace metal contamination were serious in the surrounding of the harbor because of runoff and flocculation processes. Brady et al. (2014) founded that the sites were influenced by anthropogenic activities (e.g., boat building,

industrial process) and had higher contents of trace metal. The phenomenon of decrease in metal concentration in sediments away from the seashore can be a combination of two factors: (1) metals input from surrounding cities had a

deposition process in the estuary before they reach the sea (Chen et al. 2001; Zhao et al. 2009); (2) a dilution of total metal contents by “cleaner” sediments from the outer sea (Lin et al. 2002). The effect from the later has been proven to be significant in the area by other researches investigating the nature of sediments from particle size distribution (Chai et al. 2015). This trend, however, was less significant for Pb and Cr distribution in YRE. Xu et al. (2015b) demonstrated the distribution of sediment Pb and Cd from YRE to seashore of ECS and found that Pb in the area was more evenly distributed than Cd suggesting a potential source of atmospheric deposition.

For HZB samples, metal concentrations were relatively high in samples close to the Zhoushan Islands (B8–B14 from HZB). This may be explained by the accumulation of terrestrial-derived contaminated sediments in the area. Many researches had been programmed about the boundary of the Yangtze River sediment spreading to continental shelf, and it was generally agreed that the boundary is within 123°E (Yun et al. 1981; Wang et al. 2013b). The sediment was unable to spread out as a result of the prevention of coastal current and settled down near Zhoushan Island due to currents and block of Zhoushan Island (Chen et al. 2009). Therefore, those contaminated riverine sediments, deposited on the edge of near shore shelf of ECS, became a source of trace metals into the Hangzhou Bay (Milliman et al. 1984). Moreover, fine-grained sediments from the Yangtze River, as a better carrier of metal contaminants than sand, were dominant in inner shelf and contribute to high metal

contents in the area. In contrast, metal cations were less likely to accumulate in sandy sediment in the east of Zhoushan Islands (Xu et al. 2015a). Che et al. (2003) founded that the transfer of sediments in YRE and HZB may be demonstrated by the distribution of Cu, as high Cu level was found near 123°E. This pattern of metal distribution in sediments was also found in more recent studies by Xu et al. (2015b) for Pb (42.0 mg kg^{-1}); Sheng et al. (2008) for Pb ($44.0\text{--}48.0 \text{ mg kg}^{-1}$), Cu (49.0 mg kg^{-1}), As (13 mg kg^{-1}), Cd (0.23 mg kg^{-1}); Chai et al. (2015) for Pb (32.0 mg kg^{-1}), Zn ($85\text{--}90 \text{ mg kg}^{-1}$) collected from the range of 122.35E~123.0E and 30.0N~31.0N. The boundary, however, varies in response to natural alternation of dry/wet season (Huang et al. 2011) as well as anthropogenic hydrological change of the river channel (Feng et al. 2014).

A decrease in concentration for all metals from the east to the west was found in sediments from SHZB (Fig. 3). The sediments in west mainly from Qiantang River were coarser (41.7% clay, 56.5% silt, and 1.8% sand from C10) than the east (56.3% clay and 43.7% sand from C1) from outer Hangzhou Bay (Shi 2017). Fine-grained sediments were the main carrier of trace metals which can explain the reason of higher contents in the east (Che et al. 2003; Duan et al. 2015; Xu et al. 2015b). This trend of metal distribution in sediments in the SHZB, together with the fact that relatively small variation of metal contents (avg. CV% = 22.8%) may also imply that the sediments were mainly from the Yangtze River estuary with similar sources of trace metals.

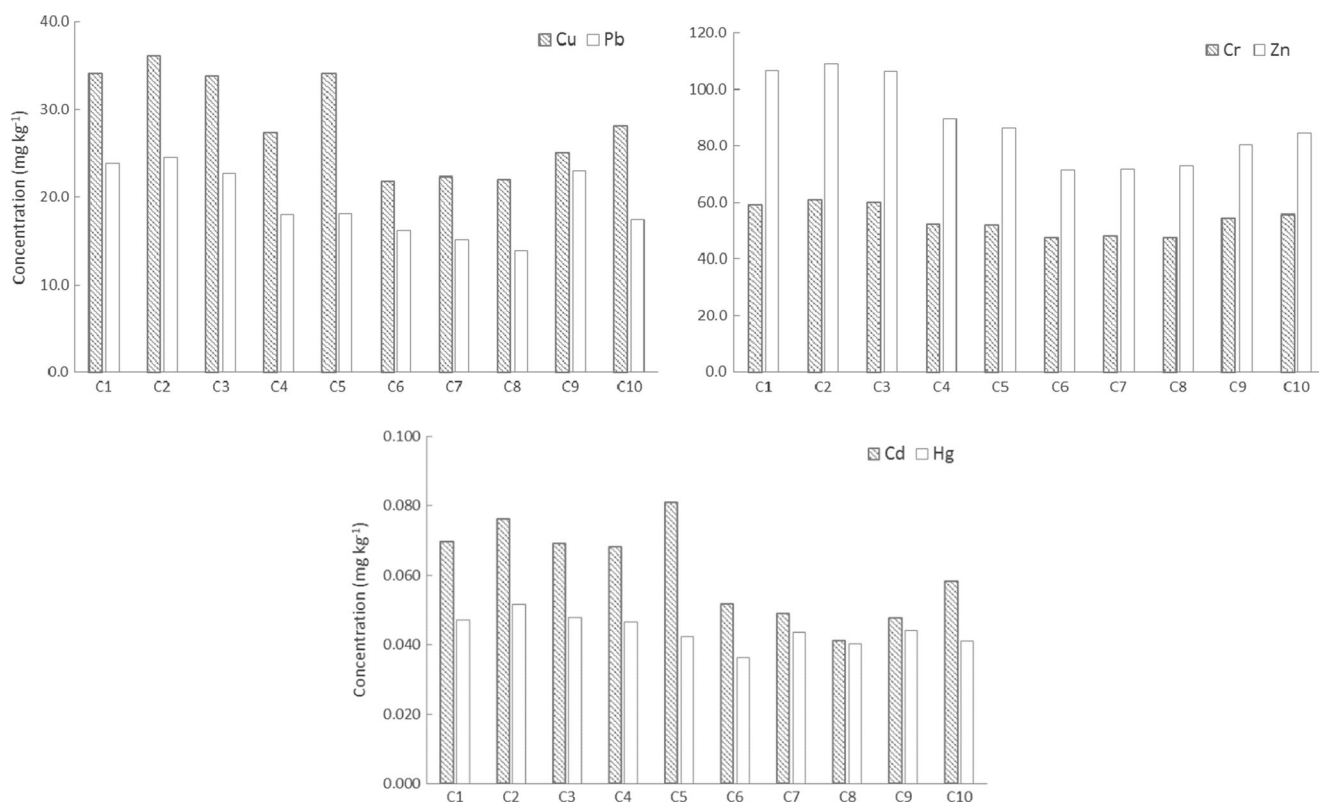


Fig. 3 Distribution of Cr, Cu, Zn, Cd, Pb, and Hg in south Hangzhou Bay (SHZB) from west (outer, C1) to east (inner, C10)

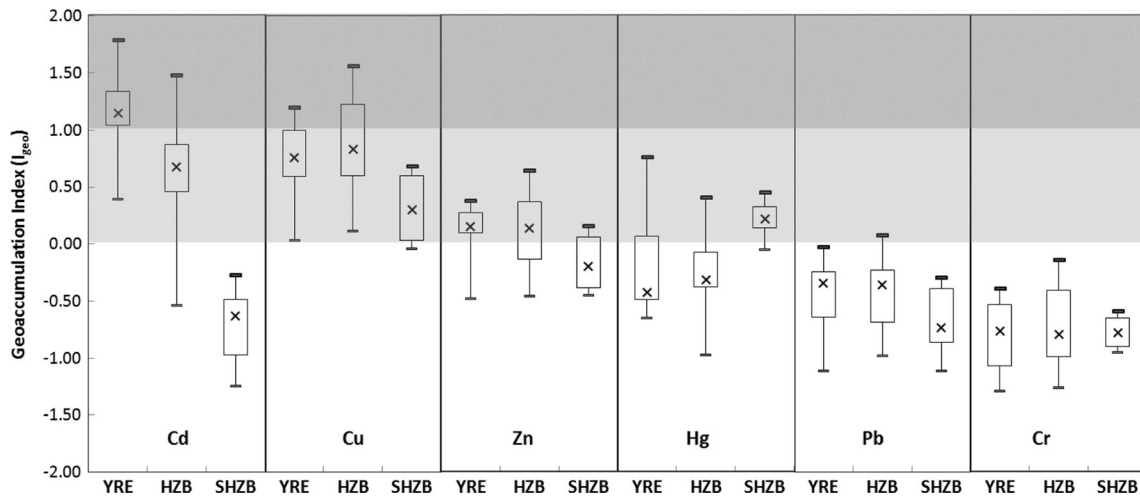


Fig. 4 Values of I_{geo} for trace metals in sediment from Yangtze River estuary (YRE), Hangzhou Bay (HZB), and south bank of Hangzhou Bay (SHZB)

Numerous researchers have investigated the sediment concentrations and distributions in YRE and HZB. Most of these studies concluded that the trace metal pollution has been dramatically increased in the last few decades, ascribed to the growing anthropogenic impacts (An et al. 2010; Liu et al. 2012; Fang et al. 2016). The SHZB has also experienced metal accumulation in sediments, reported in regional studies (Pang et al. 2015; Jin et al. 2017). Therefore, it is important to study the spatial distribution and sources of trace metals and cover the two major aquaculture areas (outer and south Hangzhou Bay). Previous studies on the whole Hangzhou Bay suggested that the

sediments and the trace metals therein mainly originated from the Yangtze River and the Qiantang River (Fang et al. 2016; Liu et al. 2012). In this study, based on the results from all three transections, it is reasonable to conclude that the surface sediments from the outer HZB and coastal sediment from the SHZB were mainly originated from the YRE, while the ECS and the Qiantang River may pose minor influence on metal concentration. Due to important aquaculture areas in the studies area, the government should intensify sediment quality monitoring in the outer HZB and establish more proper environmental protection regulation for the local environment and ecological system.

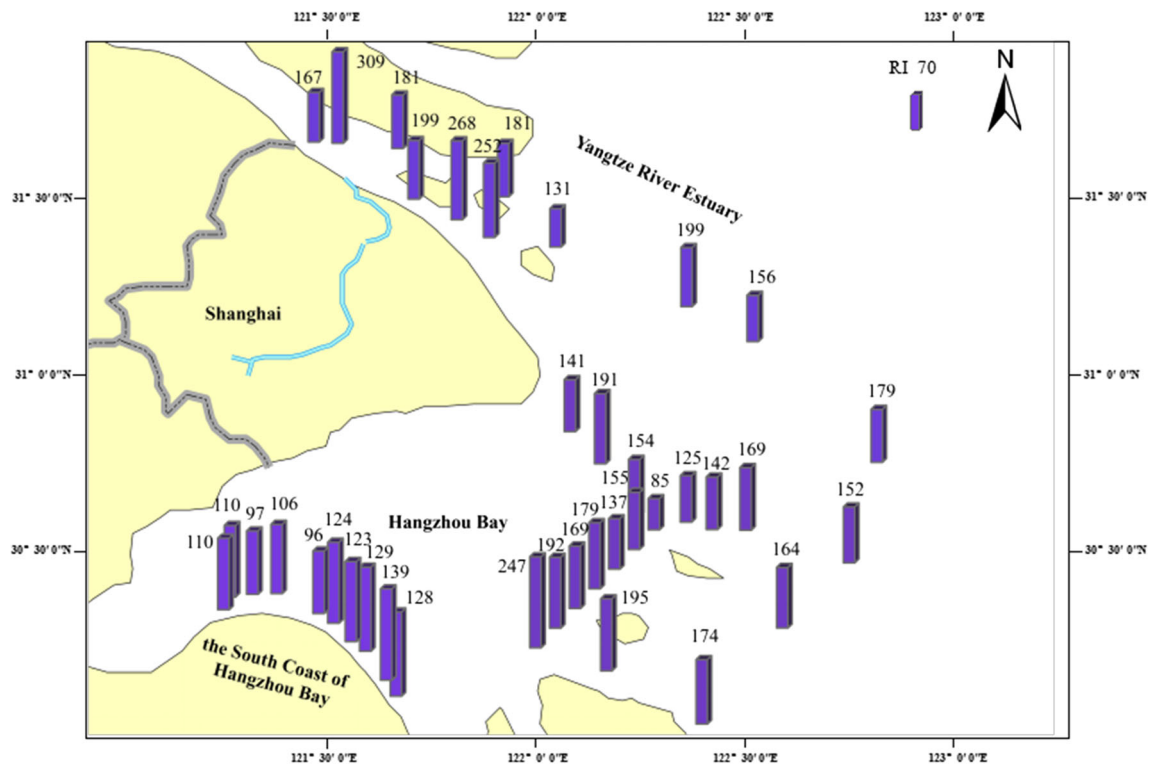


Fig. 5 Distribution of potential ecological risk index (RI) of trace metals in sampled sediments

Risk assessment

Geoaccumulation index (I_{geo}) and potential ecological risk index (RI) were used to assess the pollution level of the study area. The values of I_{geo} for trace metals in surface sediments of YRE, HZB, and SHZB were shown in Fig. 4. According to the I_{geo} values, the area studied was mainly polluted by Cd, Cu, and Zn, with individual sites contaminated by Hg. The sequence of pollution degree for each metal was Cd > Cu > Zn > Hg > Pb > Cr except for Cd in SHZB. The I_{geo} for Cd in nearly 75% of sites in YRE were between 1 and 2 suggesting the area was moderately polluted by Cd. For HZB, the situation was similar to that of YRE with more significant contamination by Cu and Cd than by other metals. Metal contamination in SHZB was less observed than in the other two, with individual sites slightly polluted by Cu and Zn, mainly in the east part of the bank. However, accumulation of Hg was generally found in SHZB.

Considering the toxicity of these trace metals to aquatic organisms, potential ecological risk index was used to estimate the risk from the sediments. Figure 5 shows the RI values of the sample sites. The inner part of YRE and Zhoushan Island had higher RI values while that of SHZB was relatively lower. The RI values for nine sites in YRE were in the range of 150 to 300 indicating that the integrated pollution degree was moderate, and for A2 site, it exceeded 300 suggesting considerable ecological risk to the ecosystem. About 72% of the sites in HZB were in moderate ecological risk with high values appeared in the range of Zhoushan Islands. In contrast, the RI values for SHZB were generally the lowest among the three transects. Accounted for about 80–90% of RI values, the E_r for Cd and Hg in both YRE and HZB suggested that these two metals were the main contributors to the ecological risk. Both metals can be highly accumulated in marine organisms and sediments (Kennish 1996) with strong toxicity and high bioavailability (Smolders et al. 1999). Table 3 listed the contribution from Cd and Hg based on the E_r values in all three transects. The results showed that Cd was the prior metal that caused considerable ecological risk in YRE and HZB but not in SHZB. Moderate ecological

risk from Hg was generally found in most samples from three transects. Above all, based on the I_{geo} values and RI values, Cu, Cd, and Hg were the primary contributor of risk from metal contamination in the sampling area.

Although the potential ecological risk index method can to some extent reflect metal contamination in sediments and have been used extensively in various studies (Cui et al. 2014; Zhang et al. 2016; Vetrimurugan et al. 2017), it should be noticed that there are substantial limitations when applying to high energy environments where turbulent and/or hydrodynamic movements are dominated (Hakanson 1980). Evaluation using total metal contents in sediments has also been controversial for not considering the bioavailability of the metals (Brady et al. 2016). Modified ecological risk index using weak acid extractable metals may provide a more realistic indication in complex environments as the ecological risk assessment may underestimate the risk for not taking geogenic metals into consideration (Duodu et al. 2016; Brady et al. 2015; Duodu et al. 2017). This implied that the situation in the studied area may even worse especially near Zhoushan Islands and SHZB where aquacultural activities are intense.

Conclusion

Trace metal distribution and pollution assessments were investigated in YRE, HZB, and SHZB in this study. It was found that Cu and Zn concentration in surface sediments was generally higher than the background from all three sampling areas suggesting a widespread of Cu and Zn contamination in the coastal area of Yangtze River Delta. The concentration of Cd and Hg in individual samples from YRE was 3–5 times higher than the background indicating the anthropogenic impact to the area.

Copper, Zn, Cd, and Hg concentration was high in inner estuary of YRE and decreased offshore as a result of metals input from surrounding cities and dilution effect of total metal contents by “cleaner” sediments from the adjacent sea. Higher metal concentrations were also found in samples close to the Zhoushan Islands which can be explained by accumulation of terrestrial-generated contaminated sediments in the area. The decrease in concentration for all metals from the east to the west was found in sediments from SHZB due to the input of fine-grained sediments contaminated with metals from the outer bay.

According to the results from geoaccumulation index as well as potential ecological risk assessment, nearly 75% of samples from YRE were moderately polluted by Cd. The values of E_r for Cd and Hg accounted for about 80–90% for RI values in YRE and HZB. Most of the sampled sediments in the outer and south bank of Hangzhou Bay were moderately polluted by Hg.

Table 3 Distributions of E_r^i values for Cd and Hg in the Yangtze River estuary (YRE), Hangzhou Bay (HZB), and south Hangzhou Bay (SHZB)

Level	E_r^i	YRE		HZB		SHZB	
		Cd	Hg	Cd	Hg	Cd	Hg
Low	$E_r^i < 40$	–	–	6%	6%	100%	–
Moderate	$40 \leq E_r^i < 80$	9%	73%	56%	83%	–	90%
Considerable	$80 \leq E_r^i < 160$	82%	27%	38%	11%	–	10%
Very high	$160 \leq E_r^i < 320$	9%	–	–	–	–	–

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