



Heavy metals of surface sediments in the Changjiang (Yangtze River) Estuary: Distribution, speciation and environmental risks

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ABSTRACT

Terrigenous sediment in estuarine environments serves as a major sink for heavy metals sourced from land, and thus has been widely used for the investigation of anthropogenic pollution and environmental risk. This study presents the concentrations and chemical speciation of eight heavy metals (Zn, Cu, Ni, Pb, Cr, Hg, As, Cd) in 34 surface sediment samples collected from the Changjiang (Yangtze River) estuarine area, which aims to investigate the potential sources and environmental risks of heavy metals. The concentrations of these metals in inner estuary are overall higher than those in coastal and offshore areas, with the highest values occurring in the South Branch, South Channel, and North Hangzhou Bay. Although the Changjiang river input is the dominant source of these heavy metals, the local contamination and variations in sediment characters especially the grain size and particulate organic matter account for the heterogeneous compositions of these heavy metals in these estuarine sediments. The sequential extraction results suggest that most of these heavy metals, except Cd, are bound in the geochemically inert residual fractions, and primarily determined by the Changjiang input from natural weathering sources. The results of geoaccumulation index (I_{geo}) and enrichment factor (EF) suggest that these heavy metals do not show obvious enrichments and contamination in this region, while the higher bulk concentrations of Cd in the estuarine and offshore sediments are predominantly inherited from the Changjiang sediments, although the residual Cd in the crystal lattice of minerals reflects the average Cd content in the upper continental crust. The extra Cd adsorbed to the river sediments is strongly bound to exchangeable-, carbonate- and Fe-Mn oxides-associated phases, which may be chemically reactive during estuarine processes and thus has high environmental risks under enhancing human activities.

1. Introduction

Heavy metal pollution has been widely recognized as a serious threat to natural environment due to the complex sources, persistent and toxic behavior, and bio-accumulation properties (Salomons and Förstner, 1980; He et al., 2012; Luo et al., 2015; Janadeleh et al., 2016; Karbassi et al., 2016; Hoang et al., 2018; De Vivo et al., 2018). Once incorporated with organic species, heavy metals have the capacity to interfere on ecosystem and exert adverse effects on fishery industry (Ip et al., 2005; Keshavarzi et al., 2018). And these metals can significantly influence human health via exposure process or food chain enrichment (Järup, 2003).

As the important interface of land-sea interaction and the major transition zone of terrigenous matter into the sea and ocean, an estuary is of great significance for various earth surface processes and material cycling. The complex hydrodynamics in an estuary plays a key role in

the transportation, deposition and resuspension of suspended solids (Pourabadehei and Mulligan, 2016; Wang et al., 2016), ultimately influencing the spatial distribution, transformation and bioaccumulation of heavy metals in the estuary. Also, estuaries provide habitats for a large number of various organisms and support very high productivity and biodiversity. With the rapidly increasing human activities, the ecosystems and marine environments of estuaries have been under increasing threat and degrading over the last several decades, such as a great amount of heavy metals from the catchments discharging into estuaries.

Terrigenous sediment in estuarine environments serves as a major sink for various pollutants, and has become an environmental archive for the investigation of anthropogenic pollution in the present day and over the geological past (De Vivo et al., 2018). The estuarine sediments, especially the fine-grained ones, have a great potential to fix and accumulate most heavy metals from the river and estuarine water, mostly

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by scavenging effect (Yang et al., 2009; Feng et al., 2017). With changing physical and chemical conditions in estuarine environments, the heavy metals adsorbed in sediments may release back into the ambient water, causing the secondary pollution (Peng et al., 2009; Gillan et al., 2012; Zhang et al., 2014). Thus, the source-to-sink processes of heavy metals in estuarine environments are complex and essential for the ecosystem health, which deserves more investigations.

The Changjiang (Yangtze River) is one of the largest rivers in the world and featured by a large river-dominated delta and adjoining estuary. Shanghai City as the metropolis of Asia, is located on the southern branch of the Changjiang Estuary and northern bank of Hangzhou Bay. It fosters about 24 million people on a land area of 6340 km², which makes it one of the largest cities in the world and most developed economic hubs in China. The Changjiang catchment has a population of about 450 million, above 1/3 of China's total population living in a catchment area of 1.8×10^6 km². With the rapid population increase and booming industrial development in the large catchment, the Changjiang Estuary and adjoining coastal areas have been facing the emerging heavy metal pollution and environmental risks (Bianchi and Allison, 2009; An et al., 2010; Pang et al., 2015; Wang et al., 2015; Yin et al., 2015).

Over the last two decades, many studies investigated the spatial distribution of major heavy metals and total concentration-based risk assessment in the surface or core sediments from the Changjiang estuarine area. However, most of these previous studies focused on the bulk concentrations of heavy metals, and few studies reported the metal speciation (Zhang et al., 1990; Zhang et al., 2001, 2009; Dong et al., 2012; Li et al., 2012; Liu et al., 2016; Feng et al., 2017; Han et al., 2017). Obviously, the total concentrations of metals provide insufficient information of their bioavailability, mobility and toxicity (Vaezi et al., 2015), which undermined the reliability of ecological risk evaluation. With the applications of sequential extraction protocols (Rauret et al., 1999; Yang et al., 2009; Zimmerman and Weindorf, 2010), however, we can operationally define and separate different heavy metal speciation, which may provide more robust constraints on the sources, origins, chemical behaviors, bioavailability, migration and transformation of heavy metals, and further increase the reliability of pollution assessment (Yu et al., 2010; Zimmerman and Weindorf, 2010; Sundaray et al., 2011; Elkhatib and Moharem, 2015).

This study measured the bulk concentrations and different chemical phases of eight heavy metals (Zn, Cu, Ni, Pb, Cr, Hg, As, Cd) in 34 surface sediment samples collected from the Changjiang Estuary and surrounding coastal areas around Shanghai City. Together with the data of grain-size, total organic carbon and major elements, we aim to illustrate the spatial distributions of these heavy metals in the study area, and further to decipher their sources and assess the potential environmental risks by using various geostatistical approaches.

2. Samples and methods

2.1. Study area and sample sources

The Changjiang originates in the eastern Tibetan Plateau and discharges tremendous suspended sediment (ca. 368×10^6 t/yr, based on the hydrological observations of 1950–2015) and water (ca. 893.1×10^9 m³/yr) into the East China Sea via one of the largest estuaries in the world (Ministry of Water Resources of the People's Republic of China, 2017). About half of the Changjiang-derived sediments were trapped in its estuary, which finally developed a large delta in the river mouth since the middle Holocene.

In June of 2007, a total of 34 surface sediment samples were collected from the Changjiang Estuary and surrounding coastal areas, including the north and south branches and north Hangzhou Bay (Fig. 1). The samples were taken by box cores and the surface 2 cm sediment was sampled and kept in refrigerators for this study.

2.2. Analytical methods

For the measurements of elemental concentrations, the bulk samples were air dried, salt washed and processed with a 20 mesh sieve for removing the organic debris. In this study, we measured the bulk concentrations and chemical phases of eight heavy metals (Zn, Cu, Ni, Pb, Cr, Hg, As, Cd) in the sediment samples. For the bulk compositions of these heavy metals, the powdered dry samples were completely digested with concentrated HF–HNO₃–HClO₄ in an airtight Teflon container.

Speciation of heavy metals is essentially a function of mineralogy and chemistry of the sediment or soil samples examined. Quantification is typically done using different chemical solutions, but specific, strengths and reactivity to release metals from the different fractions of the examined samples. Over the last four decades, a large number of sequential extraction procedures (SEP) have been developed to define various fractions of heavy metals in the bulk samples, although there may exist large uncertainties in different SEPs (Zimmerman and Weindorf, 2010). Although the procedure proposed by Tessier et al. (1979) and then the BCR (Ryan et al., 2008) are generally accepted as the most commonly used protocols, they are still plagued by limitations (Zimmerman and Weindorf, 2010). Nevertheless, the wide variety of published extraction methods makes it impossible to compare the results unless the same extraction conditions and reagents were used (Hao et al., 2011). In order to unify and compare the speciation characteristics of heavy metals in sediments of estuary and soils of river basin, the speciation analytic method proposed by China Geological Survey was adopted in this study. We separated seven chemical phases of major heavy metals by following the geochemical analytic protocol of “Specification of Multi-Purpose Regional Geochemical Survey (1:250 000) (DZ/T 0258-2014)” and “Specification of Regional Biogeochemical Assessment (DZ/T 0289-2015)” issued by the China Geological Survey. This procedure has been widely used by the China Geological Survey for the quantification of heavy and trace metal contamination in soil and river sediments in China (Hao et al., 2011; Dai et al., 2013; Cui et al., 2015). The several chemical phases include water-soluble fraction (WS), ion exchangeable fraction (EXC), humic acid-bounded fraction (HUM), carbonate-associated fraction (CAR), Fe-Mn oxides-bounded fraction (FeMn), organic matter-bounded fraction (OM), and residual fraction (RES). Please refer to Table 2 for the detailed operating conditions for SEP. The concentrations of heavy metals were measured by using inductive coupled plasma mass spectrometry (ICP-MS) for Cd, Pb, Zn, Cr, Cu, and Ni. Concentrations of As and Hg in the bulk samples as well as different fractions were analyzed using Atomic Fluorescence Spectrometer. The measurements of these heavy metals were carried out in Hefei Mineral Resources Supervision and Test Center, Ministry of Land Resources, China. The detection limits and relative errors for geostandards of these methods were shown in Appendix Tables 1 & 2. The determined and certified values of national geostandards were generally required to be < 15%. The analytic precisions of the geostandards (GSF-2 and GSF-3) range from 1% to 15% (Table 1).

For the comparison, the bulk concentrations of major oxides of CaO, SiO₂, MgO, Al₂O₃ and Fe₂O₃ were measured by wavelength dispersive X-ray Fluorescence Spectrometry (XRF). Total carbon (TC) in the bulk samples was measured by Combustion-IR Absorption Spectroscopy. For the measurement of total organic carbon (TOC), the bulk samples were digested using potassium dichromate and analyzed through ammonium ferrous sulfate titration method. For the detailed instrument methods and detection limits of the major oxides, please refer to Appendix Table 1. The analytic precisions (relative errors) of the geostandards (GSS-01 and GSS-03) range from 2% to 9%. The analyses of TC, TOC and all the major oxides were carried out in Nanjing Mineral Resources Supervision and Test Center, Ministry of Land Resources, China.

For the measurement of grain size composition, the bulk sediment samples were analyzed by the laser size analyzer (Coulter LS13320,

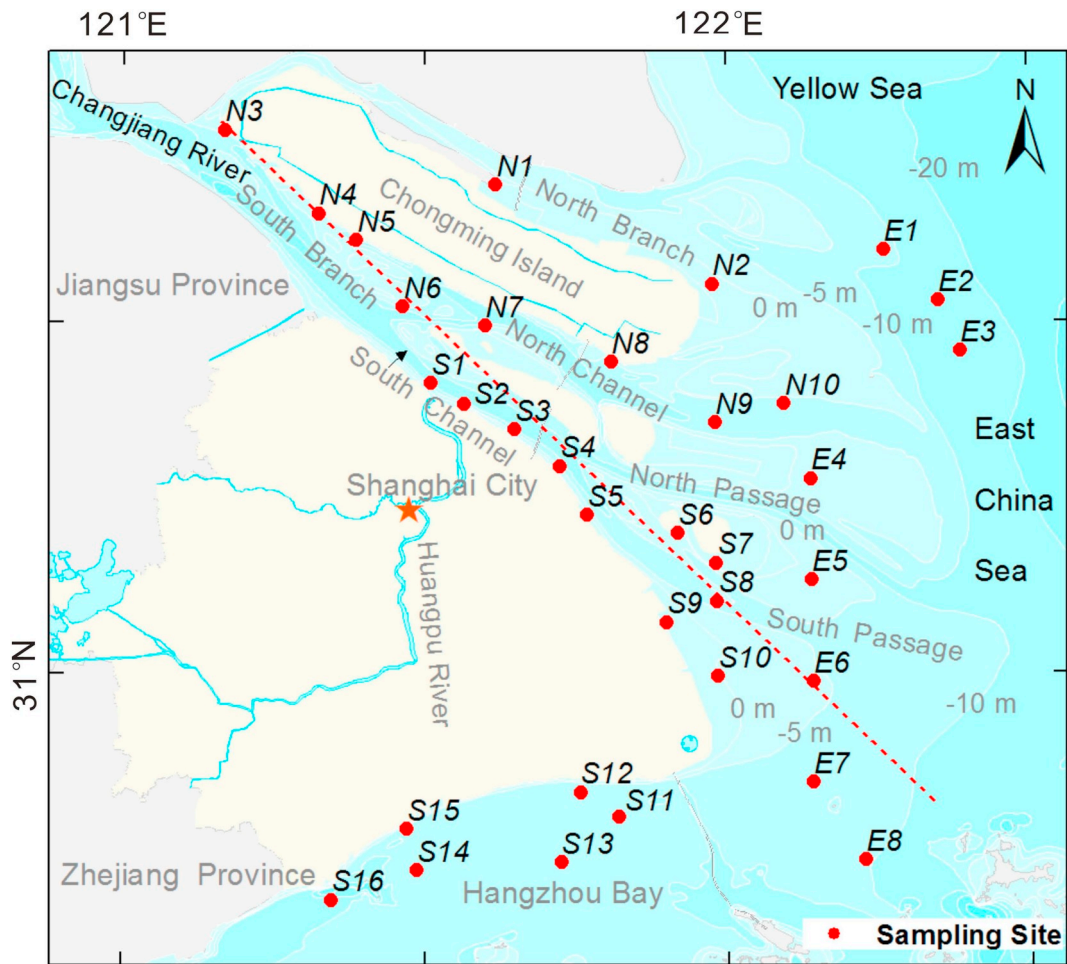


Fig. 1. Map showing the locations of 34 surface sediment samples in the Changjiang Estuary and surrounding coastal areas.

USA), after processing ca. 5 g sample with 10 mL 10% H₂O₂ and 10 mL 10% HCl to remove organic matter and carbonate, respectively. The measurement error is ≤ 1%. The grain size analyses were carried out in the State Key Laboratory of Estuarine and Coastal Research at East China Normal University.

2.3. Geochemical proxies (EF and Igeo) for the evaluation of heavy metal enrichment

The enrichment factor (EF) is a widely used proxy for the estimation of geochemical anomaly and the anthropogenic impact on sediment chemistry, which refers to the enrichment degree of metal concentrations in sediments investigated relative to uncontaminated background levels (baseline) (Ip et al., 2007). EF is expressed as:

$$EF = \frac{(C/X)_{sample}}{(C/X)_{baseline}}$$

where C denotes specific heavy metal investigated, and X is the reference element that is predominantly bound in silicate minerals, geochemically conservative and resistant to chemical alteration during earth surface processes. Elements including Al, Fe, Li, Co, Sc, Ti and Cs have often been used as the reference elements. In this study, Al is used as the reference element for the calculation of EF. Generally, an EF value of 0.5–1.5 suggests that a given metal may be entirely sourced from crustal materials by natural weathering process, while EF value higher than 2.0 (EF > 1.5) suggests that this metal may be partly or mostly derived from non-crustal materials including from anthropogenic contamination (Sutherland, 2000; Shumilin et al., 2002). As for the selection of baseline for the calculation of EF, the previously published data of major and trace elements in the core sediments (pre-

Table 1
Operating conditions for the modified extraction procedure using 2.5 g of air dry sample.

Chemical speciation	Extractants and conditions	
Water soluble (WS)	2.5 g sample + 25 mL Milli-Q water, shake for 2 h, centrifuge and filter	(1)
Exchangeable (EXC)	Wash sample from (1) + 25 mL 1 M MgCl ₂ , shake for 2 h, centrifuge and filter	(2)
Bound to carbonates (CAR)	Wash sample from (2) + 25 mL 1 M NaOAc, shake for 2 h, centrifuge and filter	(3)
Weakly bound to organic matter (HUM)	Wash sample from (3) + 50 mL 0.1 M Na ₄ PO ₇ , shake for 2 h, centrifuge and filter	(4)
Bound to Fe-Mn oxides (FeMn)	Wash sample from (4) + 50 mL 0.25 M NH ₂ OH·HCl, shake for 2 h, centrifuge and filter	(5)
Strongly bound to organic matter (OM)	Wash sample from (5) + 3 mL 0.02 M HNO ₃ , 5 mL 30% H ₂ O ₂ , heat for 1.5 h at 85 °C, + 3 mL 0.02 M H ₂ O ₂ + 2.5 mL 3.2 M NH ₄ OAc in 0.02 M HNO ₃ , centrifuge and filter	(6)
Residual (RES)	Wash sample from (6), digest with 20 mL 16 M HNO ₃ + 10 mL HF	

industrial deposition) from the Changjiang Delta area are considered in this study (Chen et al., 2008), i.e. As = 9.29 mg/kg, Cd = 0.09 mg/kg, Cr = 72.4 mg/kg, Cu = 22.5 mg/kg, Hg = 0.04 mg/kg, Ni = 30.0 mg/kg, Pb = 24.3 mg/kg, Zn = 68.0 mg/kg, Al_2O_3 = 13.8%.

Geoaccumulation index (I_{geo}) is another often used proxy for the evaluation of heavy metal enrichment in sediments and soils (Müller, 1969), which assesses the degree of metal pollution in terms of seven classes based on the increasing values. The I_{geo} is expressed as:

$$I_{\text{geo}} = \log_2 \frac{C_i}{1.5b_i}$$

where C_i is the measured concentration of the examined metal i , and b_i is the background concentration of metal i , and factor 1.5 refers to the possible variation in background values due to lithogenic effect and weathering. As a qualitative scale of pollution intensity, I_{geo} is classified as unpolluted ($I_{\text{geo}} < 0$), unpolluted to moderately polluted ($0 < I_{\text{geo}} < 1$), moderately polluted ($1 < I_{\text{geo}} < 2$), moderate to strongly polluted ($2 < I_{\text{geo}} < 3$), strongly polluted ($3 < I_{\text{geo}} < 4$), strongly to extremely polluted ($4 < I_{\text{geo}} < 5$), and extremely polluted ($I_{\text{geo}} > 5$) (Farkas et al., 2007). Similar as the calculation of proxy EF, Al is used as the reference element for the calculation of I_{geo} (Müller, 1981; Zhao et al., 2017) and the baseline values of heavy metals investigated are also the same for EF and I_{geo} .

3. Results

3.1. Sample properties and major elements

The compositions of grain size, TC, TOC and major oxides in the samples examined are summarized in Table 2 and Fig. 2. Please refer to Table S1 for the original dataset. The surface sediments in this region mainly consist of clayey silt (silt > 60%, clay < 30% in proportion) and silty sand (sand > 60% and silt > 10%). The median grain size (Md) ranges from 4.1 μm to 238 μm . Overall, the fine-grained samples are distributed in the inner estuary and in the north Hangzhou Bay, while several sandy samples with Md ranging from 209.2 μm to 241.3 μm were located in the offshore sites, to the east of Changjiang Estuary (Fig. 2a). In particular, the sediment samples in the North Channel of South Branch are generally coarser than those in North Branch and the South Channel of South Branch, suggesting a stronger hydrodynamic condition in this channel (Chen et al., 1979).

The TC and TOC contents were 0.27–2.42 and 0.12–1.80%, with mean values of 1.26% and 0.58%, respectively. The compositions of major oxides in these samples are generally stable. The concentrations of SiO_2 , Al_2O_3 , Fe_2O_3 and K_2O in the surface samples were 51.8–68.3%,

Table 2

The data of mean grain size and elemental concentrations in the 34 sediment samples from the Changjiang Estuary and surrounding coastal areas.

	Unit	Minimum	Maximum	Mean	Standard deviation	Baseline*
Md	μm	4.1	238.6	55.9	70.4	n.d.
Clay	%	1.1	31.9	14.8	9.4	n.d.
TC	%	0.27	2.42	1.26	0.45	n.d.
TOC	%	0.12	1.80	0.58	0.42	0.42
SiO_2	%	51.80	68.3	60.7	4.28	n.d.
Al_2O_3	%	9.17	17.8	12.6	2.58	13.8
Fe_2O_3	%	3.37	12.6	5.82	1.70	n.d.
K_2O	%	1.50	3.26	2.40	0.44	n.d.
Zn	$\mu\text{g/g}$	46.8	330.3	89.5	49.7	68.0
Cr	$\mu\text{g/g}$	42.5	230.8	84.7	43.5	72.4
Cu	$\mu\text{g/g}$	5.89	85.8	24.3	17.6	22.5
Ni	$\mu\text{g/g}$	21.4	56.2	33.5	9.20	30.0
Pb	$\mu\text{g/g}$	11.0	37.7	21.0	7.40	24.3
As	$\mu\text{g/g}$	4.89	19.9	10.3	4.05	9.29
Cd	$\mu\text{g/g}$	0.05	0.63	0.25	0.15	0.09
Hg	$\mu\text{g/g}$	0.02	0.19	0.06	0.04	0.04

Note: Md denotes median grain size; TC and TOC indicate total carbon and total organic carbon respectively. n.d. indicates no determination. *The baseline data refers to Chen et al. (2008).

9.2–17.8%, 3.4–12.6% and 1.5–3.3%, with standard deviations of 4.3, 2.6, 1.7 and 0.4, respectively (Table 2). The spatial distributions of major oxides are closely related to the types of sediment samples. The high contents of SiO_2 are mainly distributed in the sandy area of the estuary, while the high Al_2O_3 and Fe_2O_3 contents occur mainly in the clayey and silty areas. A maximum Fe_2O_3 value was observed in the east of the South Branch.

3.2. Bulk concentrations and speciation analysis of heavy metals

The concentrations of eight heavy metals were given in Tables S1 and S2 and summarized in Table 2, with the mean values following the order: Zn > Cr > Ni > Cu > Pb > As > Cd > Hg. The compositional percentages of different chemical phases of these heavy metals from all the samples are shown in Fig. 3. Overall, these seven fractions including RES, OM, FeMn, HUM, CAR, EXC, and WS in the surface samples in this study area display the following orders in percentages:

Zn: RES > FeMn > OM > HUM \approx CAR > WS \approx EXC
 Cr: RES > HUM \approx FeMn \approx OM > CAR > EXC \approx WS
 Cu: RES > FeMn > HUM > CAR > OM > WS \approx EXC
 Ni: RES > FeMn > OM > CAR > HUM > WS \approx EXC
 Pb: RES > FeMn > CAR > HUM > OM > EXC > WS

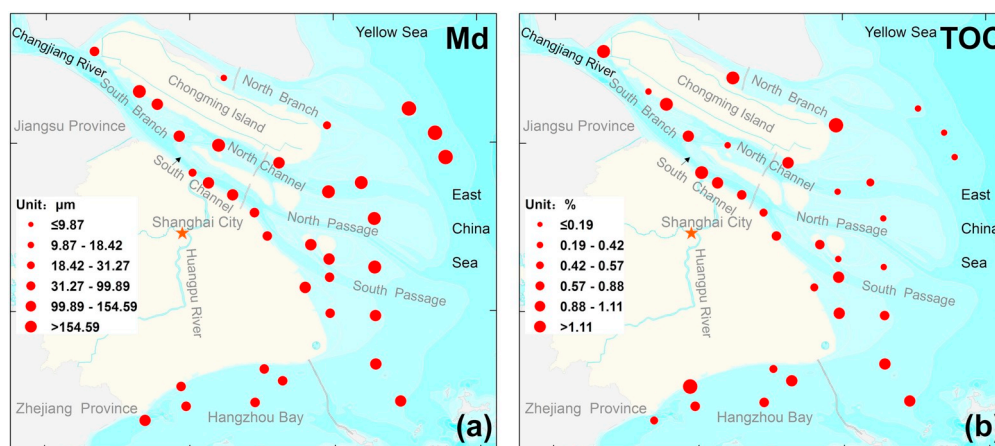


Fig. 2. Distributions of medium grain size (a) and concentrations of total of organic carbon (TOC, b) in the 34 sediment samples.

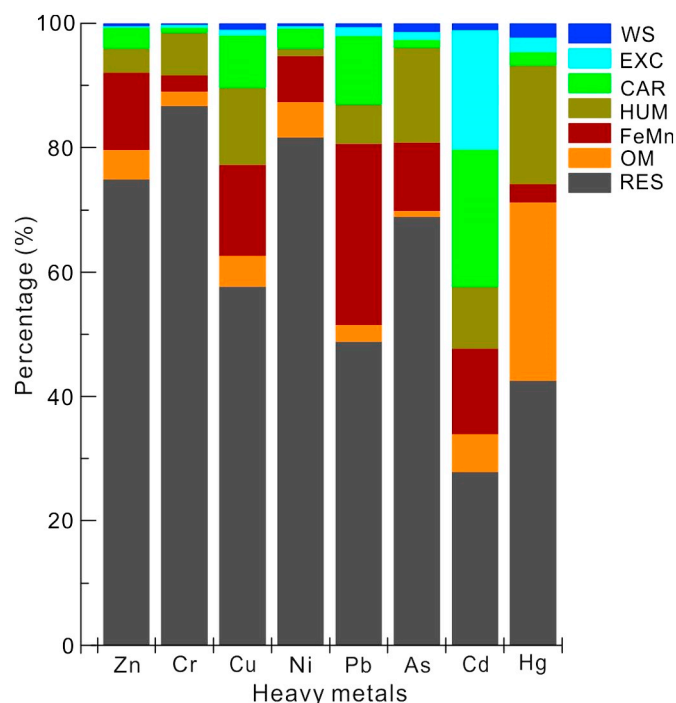


Fig. 3. Percentages of seven chemical fractions of heavy metals in the sediments. RES, residual fraction; OM, organic matter bounded fraction; FeMn, Fe-Mn oxides bounded fraction; HUM, humic acid bounded fraction; CAR, carbonate-associated fraction; EXC, exchangeable fraction; WS, water-soluble fraction.

As: RES > HUM > FeMn > WS ≈ CAR ≈ EXC > OM
 Cd: RES > CAR > EXC > FeMn > HUM > OM > WS
 Hg: RES > OM > HUM > FeMn > WS ≈ EXC ≈ CAR

Obviously, the residual fraction (RES) accounts for the highest proportions in all these chemical phases of all the sediment samples, albeit with different percentages for different heavy metals. Previous study also reported the dominance of residual fraction of Ni, Cu and Pb in the Changjiang sediment (Zhang et al., 1990), although a five-step sequential extraction procedure was adopted in their study. Overall, Cr, Ni, Zn, As and Cu have the RES percentages above 50%: 86.5% of Cr, 81.8% of Ni, 74.7% of Zn, 69.1% of As and 56.5% of Cu. However, Cd has the lowest percentage of RES in the heavy metals examined, with only 28.4% on average. Besides the RES fraction, FeMn, HUM and CAR fractions have also large proportions in the bulk compositions for most heavy metals (FeMn: 12.4% of Zn, 2.7% of Cr, 15.2% of Cu, 7.2% of Ni, 28.2% of Pb, 10.8% of As, 13.6% of Cd, 2.9% of Hg; HUM: 4.1% of Zn, 7.0% of Cr, 12.6% of Cu, 1.5% of Ni, 6.2% of Pb, 15.3% of As, 10.0% of Cd, 19.2% of Hg; CAR: 3.4% of Zn, 0.9% of Cr, 8.9% of Cu, 3.2% of Ni, 11.2% of Pb, 1.3% of As, 21.8% of Cd, and 2.2% of Hg). Overall, the WS fractions are very low for most heavy metals in this study, generally < 2% except for Hg. Interesting to note that Cd has the highest proportion of CAR fraction (21.8% on average) and Hg has the highest proportion of OM fraction (28.4% on average). Positive correlations occur between the total contents of eight heavy metals with their residual fractions, suggesting the dominance of residual fractions in the bulk compositions.

The spatial patterns of eight heavy metals are presented in Fig. 4. The localities with high As contents mainly distribute in the sandy area offshore the North Branch, i.e. northeast part of the Changjiang Estuary. High total concentrations of Zn, Cu, Cd and Hg are observed in the inner Changjiang Estuary with silty deposition, while the much lower concentrations of these metals mostly occur in the outer estuary and offshore sites of E1 to E8 with dominantly sandy deposition. The high contents of Cr are mostly located in the North Channel (Figs. 1, 2).

4. Discussions

4.1. Factors control the distribution patterns of heavy metals

It is widely known that the bulk concentrations of heavy metals in the terrigenous sediments are primarily determined by sediment source, chemical weathering, hydrodynamic sorting during sediment transport and depositional processes, and post-depositional diagenetic alteration. Human activity is another major factor that can greatly enrich heavy metals in recently deposited sediments. The prerequisite for evaluation of heavy metal contamination in the samples investigated is to identify and discriminate the natural sources and anthropogenic contributions of heavy metals. Here, we apply the statistic analyses for revealing the sources and origins of these heavy metals examined.

Table 3 displays the Pearson correlation coefficient matrix for the heavy metals, major oxides, clay content and TOC in the samples. Overall, Zn, Ni, Cu, Pb and Hg yield highly positive correlations ($P < 0.01$, $r > 0.45$) between each other and with TOC, major oxides and clay contents, and they also show similar spatial patterns shown in Fig. 4. The observation of high contents of Zn, Cu, Ni and Pb corresponding with high clay and TOC contents in the North and South Branches apparently suggests that clay and organic matter can greatly incorporate the heavy metals and/or increase the adsorption of pollutants from water environment (Anbuselvan et al., 2018). This observation also suggests that these heavy metals may be derived from same sources and/or have similar geochemical behaviors during sedimentary processes, such as their enrichments in fine-grained sediments.

Element As yields high correlations with Ni, Pb and K_2O , and weak or no correlations with other metals, TOC and major oxides. Element Cr yields a significant correlation with Fe_2O_3 , showing higher contents Cr in the North Channel, and weak or no correlations with other metals and parameters. This observation may imply the locally-derived sources of Cr and Fe_2O_3 , especially from the Baosteel Group Corporation (one of the largest steelmaking companies in China) (Dai et al., 2015; Wang et al., 2018). The irregular distribution of high Pb contents in the study area may also indicate the local contamination sources (Wang et al., 2018). The high contents of As distributed in the sandy sediments offshore the North Branch may be caused by the local contamination and/or natural background (relict sand formed in low stand of sea level but subject to diagenetic alteration). Nevertheless, it deserves more in-depth investigation on the origins and sources of particulate As in the Changjiang estuarine area. All the heavy metals display negative correlations with SiO_2 , suggesting the dilution effect of detrital quartz on elemental compositions.

The principal component analysis (PCA) is a multivariate technique that processes the several inter-correlated quantitative dependent variables in a data table, and can extract the important information from the data set. It thus provides more constraints on the quantification of heavy metal compositions in sediment and their controlling factors. In this study, four principal components (PC1 to PC4) can be recognized, and they explain 88% of the total variance, suggesting these PCs can represent the whole variance of the variables measured. The loading plots of these four principal components are shown in Fig. 5. Based on the loadings (coefficients of correlation) of these variables and components, we suggest that PC1 predominantly accounts for the grain size effect, showing obviously different loadings of SiO_2 , median size and chemical elements. PC2 is featured by high loadings of most heavy metals, except for Cr, Ni and As, probably suggesting the similar dominant sources of these heavy metals. PC3 is characterized by extremely high loading of As, suggesting the unique distribution of this heavy metal in the Changjiang Estuary. Highly positive loadings of Cr and Fe_2O_3 in PC4 imply that Cr may be tightly bound in Fe-oxides, suggesting the local contamination sources. Overall, both the Pearson correlation analysis and PCA suggest that most of these heavy metals bear similar geochemical distribution patterns in the samples examined, and sediment grain size may exert an important control on their bulk

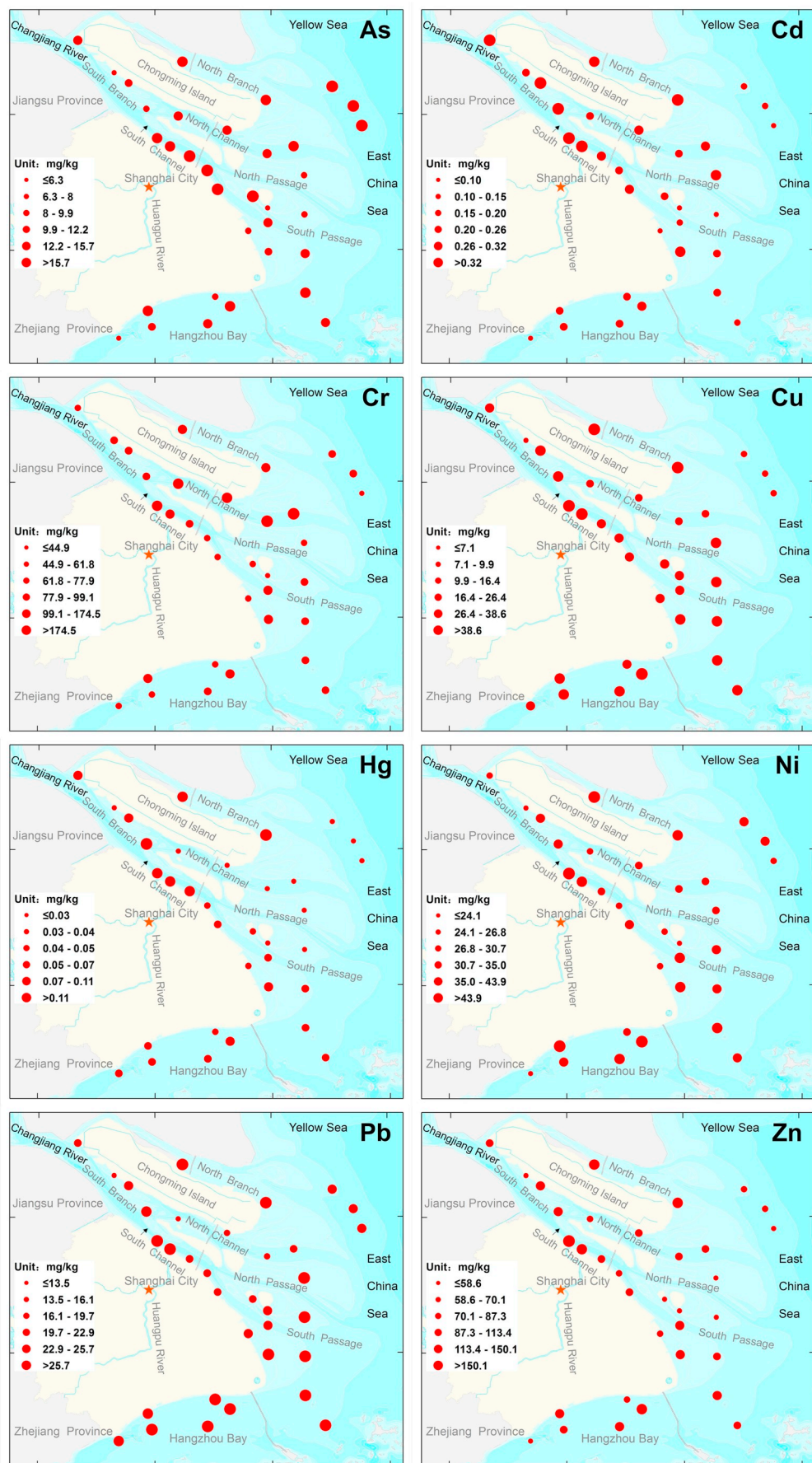


Fig. 4. Total concentrations of heavy metals in all the sampling sites of this study.

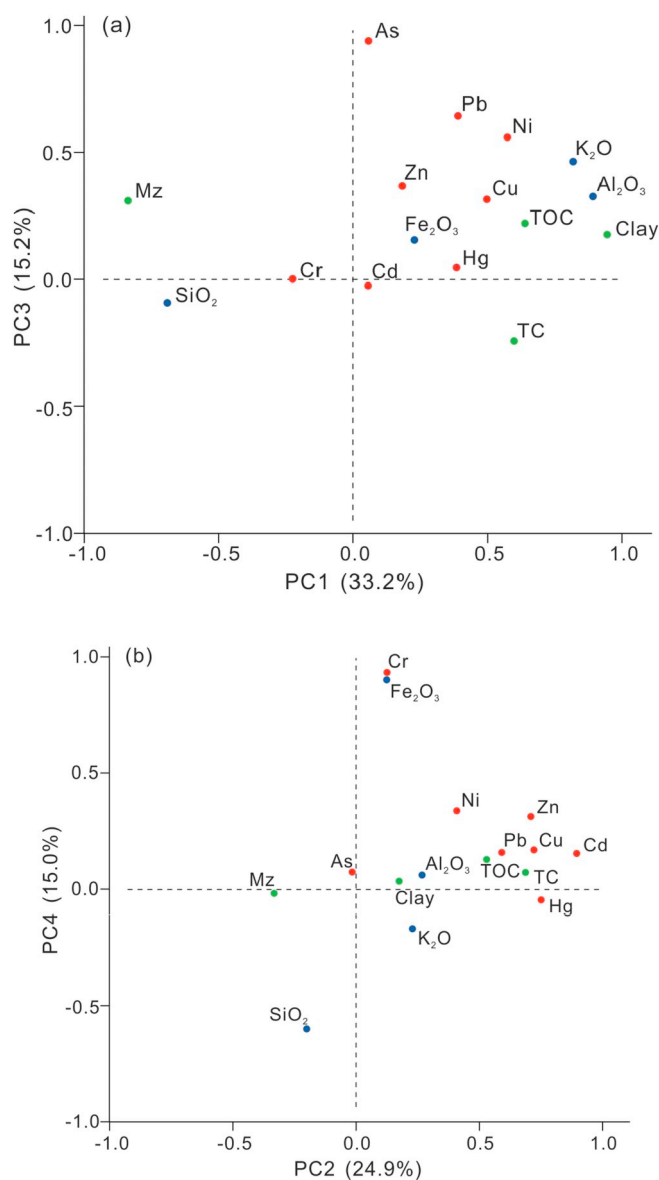
Table 3

Pearson correlation coefficient matrix of heavy metals, major elements, clay content and TOC in the surface sediments.

	Zn	Cu	Ni	Pb	Cr	Hg	As	Cd	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Clay	TOC
Zn	1													
Cu		1												
Ni			1											
Pb				1										
Cr					1									
Hg						1								
As							1							
Cd								1						
SiO ₂									1					
Al ₂ O ₃										1				
Fe ₂ O ₃											1			
K ₂ O												1		
Clay													1	
TOC														1

* Correlation is significant at 0.05 level (two-tailed).

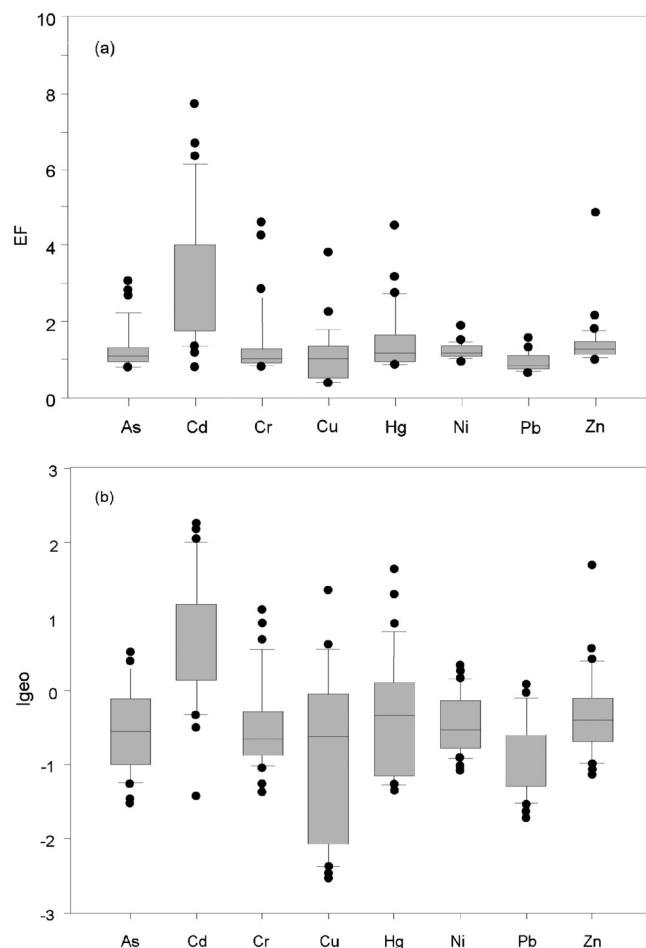
** Correlation is significant at 0.01 level (two-tailed).

**Fig. 5.** The loading plot of principal component analysis (PCA) of sedimentary texture parameters, TC, TOC, major oxides and heavy metals in the surface sediments from the Changjiang estuarine and surrounding areas.

concentrations. Among these heavy metals, As displays somewhat different geochemical behavior.

4.2. Enrichments of heavy metals in the Changjiang Estuary

The mean values of enrichment factor (EF) mostly vary around 1, showing the decreasing order of Cd > Hg > Zn > Cr > As > Ni > Cu > Pb (Fig. 6a). Except for Cd, the mean EF values of these heavy metals are all below 1.5, suggesting primary natural sources of these

**Fig. 6.** Geochemical proxies of EFs (a) and Igeo (b) of heavy metals in the surface sediments of the Changjiang estuarine and surrounding areas.

metals. Nevertheless, some samples do have higher EF values (> 3.0) for As, Cr, Cu, Hg and Zn, implying weak enrichments of these heavy metals in some sites although no obvious heavy metal enrichments are observed in the large Changjiang estuarine and surrounding areas. Element Cd has the highest mean EF value (3.0) among all the heavy metals investigated, indicating that Cd may be mostly derived from non-crustal sources, possibly obvious Cd contamination in the Changjiang catchment and study area (Dai et al., 2015).

The Igeo values of these heavy metals in the samples investigated range from -2.52 to 2.22 , with the mean values mostly varying between 0 and -1 . Again, Cd is the exceptional, and yields a mean Igeo value of 0.66 . Based on the classification of Igeo (Müller, 1969), most of the samples were unpolluted in terms of the relatively low Igeo values (< 0), while some samples have higher Igeo values (> 0) for As, Cr, Cu, Hg and Zn, suggesting weak enrichments of these heavy metals in some localities of the study area. In addition, Cd has the highest mean Igeo value among all the heavy metals examined, indicating the slight to moderate pollution degrees in most of the study sites. Overall, the similar results of both the EF and Igeo indices suggest that most of the investigated samples do not exhibit obvious enrichments and weak pollution risks of these heavy metals investigated, and only Cd yields moderate enrichments in the Changjiang estuarine region (Dai et al., 2015). Previous studies also reported the dominance of natural weathering detrital sources of heavy metals in the lower mainstream and estuarine sediments of the Changjiang (Zhang et al., 1990), but the local enrichments of Cd, Hg, Cu, Zn and Pb may indicate the anthropogenic activities (Liu et al., 2016; Han et al., 2017; Dai et al., 2015; Wang et al., 2018) or atmospheric input to river and estuarine environment (Zhang et al., 1990; Dai et al., 2015).

Previous study also observed the elevated levels of Cd and Cu in the sediments from the Changjiang Estuary, of Pb and Zn in the Minjiang River estuary, and of As in the Yellow River Estuary (Bi et al., 2017). Another large estuary, the Pearl River Estuary in South China, witnesses the slight to moderate Cd contamination in the surface sediments, and Pb, Cr, Cu, and Zn are associated with both natural and anthropogenic sources (Zhao et al., 2017). The Liaohe Estuary in North China is featured by the contamination of Cd and Hg in the surface sediments (Li et al., 2017). The heavy metal enrichments were also widely observed in the other estuaries and coastal areas in the world, e.g. high Cd and Pb contamination in the Amazon Estuary and Coromandel Coast of Bay of Bengal in India (Nascimento et al., 2006; Anbuselvan et al., 2018).

4.3. Origin of Cd enrichment and its environmental risk in the Changjiang Estuary

Cadmium (Cd) is a toxic metal present in soil, air, water, food, tobacco smoke and other media, and its high levels in the environment may cause adverse health effects on human bodies through inhalation, ingestion and dermal contact (ATSDR, 2012). Thus, Cd has become a health concern for the general public, and it is important to investigate the environmental contamination and health risks of Cd exposure. Naturally, Cd makes up about 0.1 ppm of Earth's upper continental crust (UCC) (Rudnick and Gao, 2003), and is widespread throughout the environment due to its industrial and agricultural uses. Rocks mined for phosphate fertilizers contain varying amounts of Cd, resulting in the concentration of Cd reaching 300 mg/kg and highly enriched in agricultural soils (Grant and Sheppard, 2008).

Previous studies revealed that sediments of the Changjiang have Cd concentrations several times higher than the background value, with the Cd anomalies along the river occurring from the economically undeveloped western region to the developed eastern basin (Xia et al., 2007). The investigation of sources and origin of Cd enrichment in the Changjiang Estuary is thus of great significance for reliable evaluation

of the environmental risk of Cd enrichment. As discussed above, Cd concentrations in the Changjiang estuarine sediments range between 0.05 and 0.63 $\mu\text{g/g}$ and average at 0.25 ± 0.15 $\mu\text{g/g}$, higher than the baseline value of 0.09 $\mu\text{g/g}$ (Chen et al., 2008). The analyses of EF and Igeo indices display obvious enrichments of Cd in most of the sediment samples from the Changjiang estuarine region, similar with previous result (Dai et al., 2015). Compared to the mean concentration of Cd (0.32 $\mu\text{g/g}$) in the lower Changjiang sediments sampled in 1984 (Zhang et al., 1990), this study presents the close mean content of Cd (0.25 $\mu\text{g/g}$). Similarly, the Chinese geostandard GSD-9 that was based on the sediment collected in the middle Changjiang mainstream in 1980s, yields the certified Cd content of 0.26 ± 0.04 $\mu\text{g/g}$ (Xie et al., 1989), almost the same mean Cd concentration as reported in this study. In addition, the Cd concentrations in different sediment grain size fractions yield irregular variations (Zhang et al., 1990), indicating the weak control of particle size effect. Consequently, our study suggests that the mean content of Cd in the Changjiang sediment overall remains small variability over the last two decades, although considerable temporal and spatial variations of sediment samples exist in these studies.

Nevertheless, the higher Cd concentrations as much as 0.63 $\mu\text{g/g}$ were measured in some sampling sites of the Changjiang estuarine region (Table 2, Fig. 4). The higher Cd concentrations of 0.75 – 1.2 $\mu\text{g/g}$ were also reported in the suspended sediments of the lower reaches near Nanjing (Xia et al., 2007). Recently, Li et al. (2013) reported much higher and variable concentrations of Cd (4.65 ± 4.25 $\mu\text{g/g}$) in the surface sediments of Dongting Lake and in the ambient $\text{PM}_{2.5}$ and PM_{10} in Wuhan where are located in the middle Changjiang valley. Based on the reflectance spectroscopy study, Xia et al. (2007) suggests that the total Cd concentration in the Changjiang sediments was exponentially related to the spectral proxies for organic matter, clay minerals, and Fe oxides, which indicates the dominant mineral and chemical phases of Cd in the bulk sediments. Xia et al. (2007) further applied three-step BCR sequential extraction procedure to constrain the binding forms of Cd in the sediment, which suggests that the exchangeable and reducible phases (non-residual fractions) comprise no $< 70\%$ of total Cd. This observation corresponds well with our results of sequential leaching experiment that Cd concentration in the residual fraction yields $< 30\%$ on average of the bulk composition (Fig. 7a), close to the average of 0.1 ppm in Earth's upper continental crust (Rudnick and Gao, 2003).

Among all the seven chemical phases, the exchangeable and carbonate-bound speciation accounts for large proportions of total Cd, and Fe-Mn oxides-associated speciation also plays a considerable role in the chemical phases. The humic acid bound fraction comprises unignored proportions in some samples, while the organic matter bound phase overall occupies small proportions of total Cd. As a whole, the chemical speciation of Cd does not display some regular changes from the river end-member to offshore areas, despite the relative increase of water soluble fractions (WS) in the most southeastward sites. Interesting to note that the ratios of bulk Cd/ Al_2O_3 and Cd/TOC display overall decreasing trends along the transect from landward to seaward, and yield some exceptionally high values in the sampling localities near the Chongming Island (Fig. 7b). Combining the observations of bulk compositions and sequential extraction analysis, we infer that the higher bulk concentrations of Cd in the Changjiang estuarine and offshore sediments are predominantly inherited from the higher Cd contents in the Changjiang sediments. The residual Cd in the crystal lattice of various minerals is ultimately sourced from natural source and reflects the average Cd content in the upper continental crust. The extra Cd adsorbed to the river sediments is strongly bound to exchangeable-, carbonate- and Fe-Mn oxides-associated phases. These chemically-reactive Cd phases can be highly enriched in some estuarine sediments as observed in Fig. 7b, apparently suggesting the potential contamination of Cd by industrial and agricultural uses.

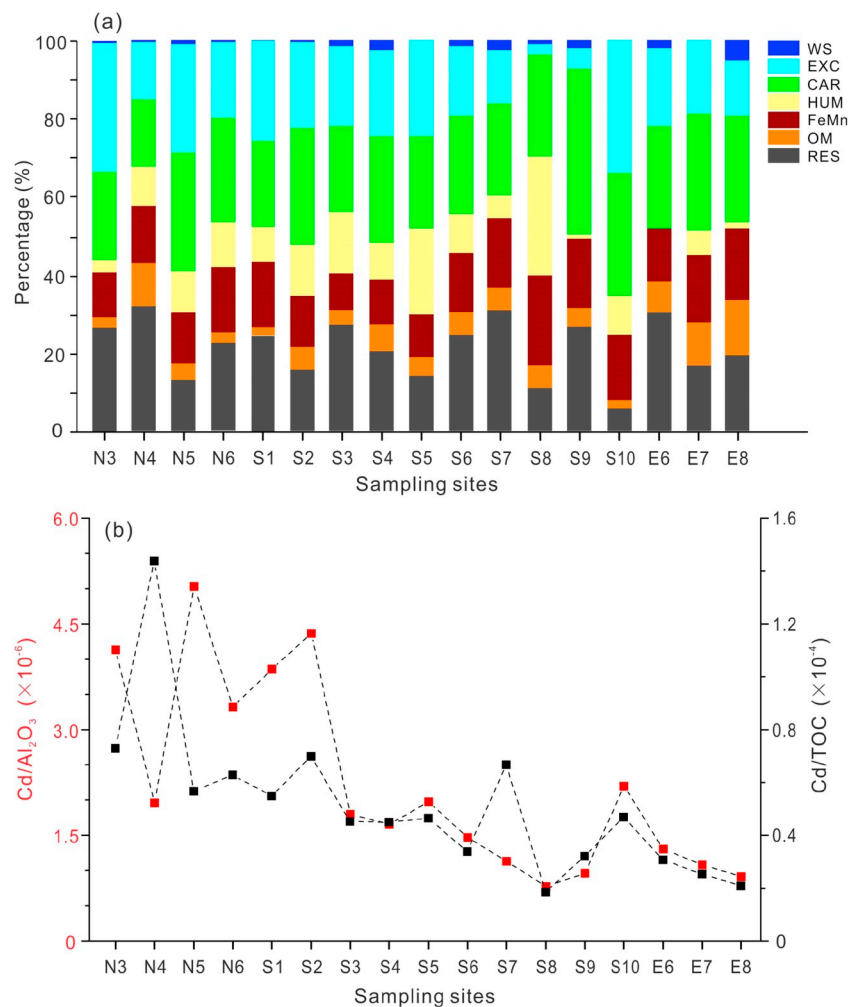


Fig. 7. (a) Chemical speciation of Cd in the sediment samples along the transect shown as red dashed line in Fig. 1; (b) the spatial changes of Cd/Al₂O₃ (red squares) and Cd/TOC (black squares) along the transect. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5. Conclusions

This study presents the bulk concentrations and chemical phases of major heavy metals (Zn, Cu, Ni, Pb, Cr, Hg, As, Cd) in the sediment samples collected from the Changjiang Estuary and surrounding coastal area, and aims to illustrate the sources, enrichments and potential environmental risks of these heavy metals. We obtain the major conclusion as follows:

- (1) The estuarine and offshore sediments are predominantly composed of clayey silt and silty sand. The mean bulk concentrations of these heavy metals follow the order of Zn > Cr > Ni > Cu > Pb > As > Cd > Hg, yielding irregular spatial distributions in the study area. Results of seven-step sequential extraction analyses suggest that Cr, Ni, Zn, As and Cu are dominated by residual fractions that account for above 50% of total concentrations, while Cd has the lowest percentage of residual fraction in the heavy metals examined. In addition, FeMn oxides-bound fraction is also dominant in the bulk compositions for most heavy metals, except for Cd and Hg.
- (2) The results of both the EF and Igeo indices suggest no obvious enrichments and environmental risks of these heavy metals in the Changjiang estuarine and surrounding region, and only Cd yields

moderate enrichments in some sites near the Chongming Island. The higher Cd concentrations in the Changjiang sediments basically determine the relative enrichments of Cd in the estuarine and offshore sediments. The residual Cd is ultimately sourced from natural rocks and represents the average Cd content in the upper continental crust, while the extra Cd adsorbed to the river and estuarine sediments is primarily bound to exchangeable-, carbonate- and Fe-Mn oxides-associated phases. These non-residual Cd fractions are overall less concentrated in the offshore regions, but they are chemically reactive and their environmental risks during complex estuarine processes and under increasing human activities deserve more in-depth investigations.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gexplo.2018.12.015>.

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Appendix Table 1

Major analytic methods for the major oxides and heavy metals reported in this study.

Elements	Analytic method	Detection limit	Unit	RE (%)
SiO ₂	XRF	0.05	%	2.0
Al ₂ O ₃	XRF	0.03	%	2.4
Fe ₂ O ₃	XRF	0.01	%	5.2
K ₂ O	XRF	0.004	%	2.3
Na ₂ O	XRF	0.004	%	3.6
CaO	XRF	0.001	%	4.5
MgO	XRF	0.005	%	8.9
TC	Non-aqueous titration of tubular furnace combustion	0.05	%	2.8
TOC	Ammonium ferrous sulfate volumetric method	0.01	%	5.2
As	AFS	0.5	µg/g	5.3
Cd	ICP-MS	0.03	µg/g	6.0
Cr	ICP-MS	3	µg/g	7.3
Cu	ICP-MS	1	µg/g	4.7
Hg	AFS	0.005	µg/g	4.3
Ni	ICP-MS	1.5	µg/g	2.4
Pb	ICP-MS	2	µg/g	1.5
Zn	ICP-MS	2	µg/g	3.0

Note: XRF denotes X-ray fluorescence; AFS is atomic fluorescence spectrometry; RSD indicates relative standard deviations. RE indicates the relative error.

Appendix Table 2

Detection limits and relative errors (RE) of heavy metal concentrations in difference chemical speciations.

	Detection limits/RE	WS	EXC	CAR	HUM	FeMn	OM	RES
As	Detection limit (µg/g)	0.05	0.1	0.1	0.1	0.1	0.1	1
	RE (%)	10.3	8.5	12.5	3.5	7.2	14.9	6.1
Cd	Detection limit (µg/g)	0.005	0.02	0.02	0.02	0.02	0.02	0.03
	RE (%)	6.4	2.7	4.7	5.4	10.6	6.3	9.6
Cr	Detection limit (µg/g)	0.1	0.5	0.5	1	0.5	0.5	5
	RE (%)	4.7	7.1	3.7	4.7	9.4	4.6	16.5
Cu	Detection limit (µg/g)	0.05	0.3	0.3	0.3	0.3	0.3	1
	RE (%)	14.8	19.9	2.4	4.6	8.7	1.3	10.4
Hg	Detection limit (µg/g)	0.001	0.002	0.002	0.002	0.002	0.002	0.005
	RE (%)	7.0	8.7	7.2	1.4	7.2	1.5	3.7
Ni	Detection limit (µg/g)	0.05	0.3	0.3	0.5	0.3	0.5	2
	RE (%)	10.7	7.4	5.5	4.9	3.4	5.0	5.8
Pb	Detection limit (µg/g)	0.1	0.5	0.5	0.5	0.5	0.5	2
	RE (%)	8.1	7.1	3.2	1.2	1.8	1.8	13.5
Zn	Detection limit (µg/g)	0.1	0.5	0.5	0.5	0.5	0.5	2
	RE (%)	2.2	7.4	4.7	3.4	6.4	3.8	10.6

Note: WS = water-soluble fraction, EXC = ion exchangeable fraction, HUM = humic acid bounded fraction, CAR = carbonate-associated fraction, FeMn = Fe-Mn oxides bounded fraction, OM = organic matter-bounded fraction, RES = residual fraction.

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