Sources and geochemical background of potentially toxic metals in surface sediments from the Zhejiang coastal mud area of the East China Sea

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ABSTRACT

The geochemical background concentration (GBC) of potentially toxic metals in coastal surface sediments is a useful reference to assess the extent of sediment contamination caused by human activities. Using surface sediments collected from the Zhejiang coastal mud area of the East China Sea, a regional GBC function (GBCF) for potentially toxic metals in sediments was constructed based on statistical techniques. Principal component analysis (PCA) was utilized to identify potentially toxic metal sources. For potentially toxic metals of natural origin, the GBCF was developed by directly fitting concentration with Al_2O_3 in a linear regression model. For potentially toxic metals of anthropogenic origin, concentration data were normalized with Al_2O_3 to eliminate the influences of grain size and mineral, and cleaned by the cumulative distribution function before linear regression analyses. At each sampling station, the enrichment factor (EF) was modified by the corresponding GBC calculated from the GBCF, and was then applied to identify metal sources. The EF results were consistent with those of the PCA and correlation analyses, indicating that the GBCs of potentially toxic metals at each station were applicable. The approach used in this study will be useful for assessing potentially toxic metal pollution in sediment and managing sediment quality.

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1. Introduction

As one of our most important food sources, coastal ecosystems are significantly affected by human activities and often the ultimate receptacle of pollutants (Maanan et al., 2014; Magesh et al., 2011). With rapid industrialization and economic development in coastal regions, huge amounts of potentially toxic metals are discharged into coastal ecosystems every year via untreated industrial wastewater, municipal sewage, and surface run-off (Gao and Li, 2012). Enrichment of potentially toxic metals in coastal sediments can result from both anthropogenic activities and natural processes (Nriagu, 1989; Veena et al., 1997). High concentrations of potentially toxic metals from natural origins in sediments are often enriched by refractory minerals and do not exhibit potential toxicity to an ecosystem (Xu et al., 2009). Consequently, the clear identification of anthropogenic potentially toxic metals from natural sources is important for evaluating the extent of pollution, preventing further environmental damage, and planning remedial strategies.

The geo-accumulation index (Fu et al., 2013; Xu et al., 2014), pollution load index (Sun et al., 2010), enrichment factor (Magesh et al., 2011; Soltani et al., 2015), and potential ecological risk index (Yi et al., 2011; Liu et al., 2014) can quantitatively assess potentially toxic metal pollution, ecological risk, and pollution source in sediments, although reference levels of potentially toxic metals in sediments are firstly required. Average shale, upper crust, and preindustrial levels of potentially toxic metals have been used extensively as reference baseline concentrations (Zahra et al., 2014). However, regional background values of potentially toxic metals in sediments depend on local geological properties, which might differ from global reference levels (Jiang et al., 2013). Therefore, understanding the geochemical background concentrations (GBC) or baseline levels of potentially toxic metals in a studied area is essential for evaluating the extent of potentially toxic metal pollution and ecological risk.

There are three major methods for establishing GBC (Carballeira et al., 2000; Reimann and Caritat, 2000), which all require non-contaminated samples. The first approach relies on non-contaminated samples collected from pristine areas unaffected by human activities or by oceanic modification processes such as scavenging (Song et al., 2014; Xu et al., 2014). In the second approach, statistical methods are applied to

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infer GBC in surface sediments (Jiang et al., 2013; Wang et al., 2015; Karim et al., 2015). By making assumptions about the normal distribution of potentially toxic metals in non-contaminated samples, the GBC can be estimated by first removing data outliers, and then by applying several statistical techniques (Matschullat et al., 2000). The third method uses non-contaminated samples in core sediments, which can be defined by age in dated core sediments. This method is the most reliable for establishing GBC if post-depositional remobilization is negligible (Song et al., 2014). Although these three methods can establish a constant for GBC, using a single regional GBC alone has the disadvantage of excluding natural variability in potentially toxic metal concentrations (Loring, 1991; Daskalakis and O'Connor, 1995; Covelli and Fontolan, 1997). In particular, GBC may vary within a region and between regions due to the influences of sediment grain size as well as mineralogical and chemical composition (Reimann and Garrett, 2005; Singh et al., 2005; Jain et al., 2007).

Based on chemical sedimentation mechanisms, potentially toxic metal sources, and statistical techniques, we proposed a method to determine the GBC function (GBCF), and calculated the GBC of potentially toxic metals at each station along the Zhejiang coastal mud area of the East China Sea (ECS).

The ECS, which is adjacent to Zhejiang and Fujian provinces and the Yangtze River Delta (Fig. 1), is the largest agricultural production base in China (Wang et al., 2014). Its coastal zone includes many large and medium cities with dense human populations, such as Shanghai, Hangzhou, and Ningbo, as well as numerous concentrated industries. With the rapid economic development and intense industrialization in the area in recent decades, considerable amounts of anthropogenic potentially toxic metals and organochlorine pesticides have been delivered to the ECS by river conveyance (e.g., Yangtze and Qiantang rivers), and then transported via the Zhejiang-Fujian Coastal Current (ZFCC) (Lin et al., 2002; Zhou et al., 2013; Wang et al., 2014). Based on previous reports, water quality in the coastal areas around Hangzhou Bay and the Zhoushan islands is mostly below Grade I (Liu et al., 1991). Both organochlorine pesticide and potentially toxic metal pollution in the Yangtze River estuary and adjacent sea areas have been studied comprehensively (Chen et al., 2004; Yuan et al., 2004; Fang et al., 2009; Dong et al.,

2014.). However, reports related to the GBC of potentially toxic metals in the ECS are scarce.

2. Materials and methods

2.1. Study area

The study area is located along the inner shelf of the ECS (Fig. 1). The ECS is one of the largest marginal seas in the western North Pacific Ocean, and is noted for its tremendous river runoff, notably from the Yangtze River. Sediments on the ECS shelf consist of sand and mud. Muddy sediment occurs along the near-shore to inner shelf environments off the Yangtze River on the south coast of China (Saito et al., 1998). Sandy sediment occurs in the middle to outer shelf areas (Alexander et al., 1991), and is considered to be transgressive sediment deposited since the last glacial maximum ~20–18 ka BP (Bartek and Wellner, 1995).

The Yangtze River is the dominant contributor to the inner shelf mud wedge in the ECS. Of the 482 Mt/year of sediment load measured at Datong gauging station, channel aggradation and delta progradation trap about 70% of the sediment before it reaches the ECS, leaving ~150 Mt/year of sediment to be transported southward (Milliman et al., 1985). The southward dispersal of Yangtze River sediment occurs mainly along the inner shelf, especially landward of the 50 m isobath, though reaching to the 100 m isobath (Xu et al., 2009). This southward dispersal has created an elongated mud wedge, the inner shelf mud wedge, extending from the Yangtze River mouth to 1000 km into the Taiwan Strait.

Coastal oceanography in the study area is dominated by the southward flowing ZFCC, a relatively cold and brackish counter current (Fig. 1). This current intensifies in the winter, carrying the brackish water and sediment of the Yangtze southward along the inner shelf (Liu et al., 2006). Offshore is a northward flow of warm and saline water, known as the Taiwan Warm Current (TWC, Fig. 1), which intensifies in summer in response to the prevailing southeast monsoon and as the southward ZFCC weakens (Lee and Chao, 2003).

2.2. Collection of surface sediment samples

In the summer of 2013, 350 surface sediment samples were collected along the Zhejiang coastal mud area of the ECS (Fig. 2). Sub-samples were taken from the top 2 cm of the box center. Each bulk sediment
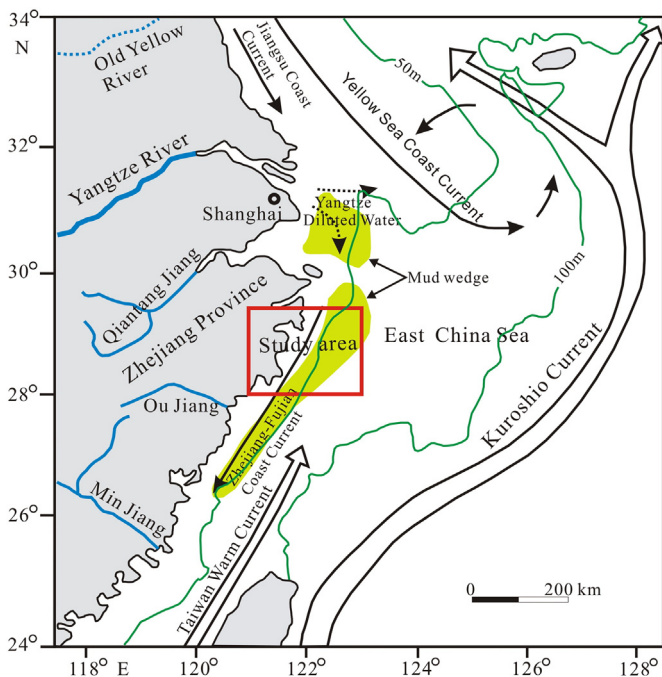

Fig. 1. Location of study area and current circulations in the East China Sea (ECS) (circulation systems are modified according to Zheng et al., 2010).
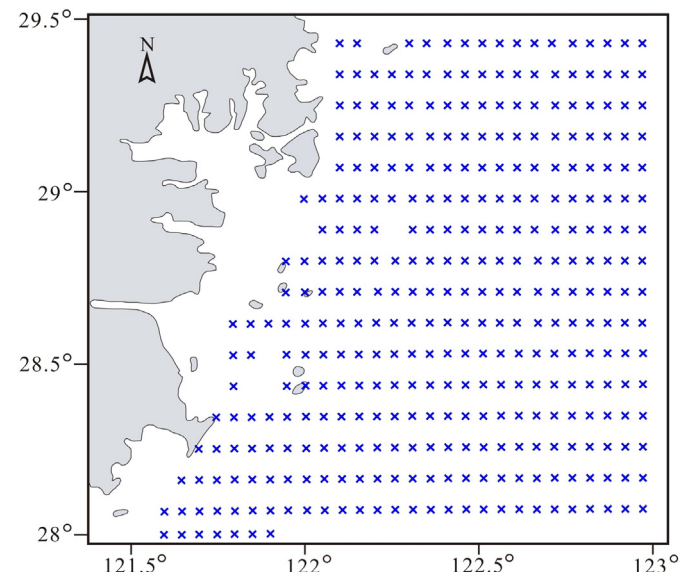

Fig. 2. Sampling stations of surface sediments in the Zhejiang coastal mud area of ECS.

Table 1

Analytical results of certified and obtained values of elements in national standard reference materials of GBW07343, GBW07314, and GBW07334.

Elements	Certified value	Measured value							Mean	Error (%)	References
Al_2O_3	11.87	11.71	11.72	11.72	11.73	11.74	11.74	11.71	11.72	−1.23	
K_2O	2.29	2.28	2.28	2.28	2.29	2.29	2.29	2.28	2.28	−0.25	
Na_2O	2.39	2.45	2.45	2.45	2.45	2.44	2.46	2.47	2.45	2.63	
MnO	0.076	0.076	0.077	0.076	0.077	0.077	0.077	0.076	0.077	0.75	
TFe_2O_3	4.21	4.18	4.17	4.18	4.12	4.12	4.12	4.18	4.15	−1.36	GBW07343
CaO	6.57	6.53	6.52	6.52	6.57	6.58	6.58	6.53	6.55	−0.35	
P_2O_5	0.142	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	−1.41	
Cu	22.5	22.8	22.3	22.5	22.4	22.4	22.4	22.8	22.5	0.1	
Pb	19.2	19.1	19.4	19.3	19.2	19	19	19.1	19.2	−0.2	
Zn	63	62.6	63.5	62.8	63.7	63.7	63.7	63.6	63.4	0.6	
TOC	0.5	0.52	0.51	0.48	0.48	0.49	0.51	0.52	0.50	0.29	GBW07314
Cr	60	58	57.6	57.9	57.3	58.4	57.4	58.2	57.8	−3.6	GBW07334
Cd	0.25	0.28	0.28	0.27	0.27	0.25	0.26	0.26	0.27	6.86	

sample was divided into two parts for determination of elements and grain size analysis, respectively.

2.3. Grain size analysis

Sediment samples were pretreated with 10% H_2O_2 to digest the organic matter. Excessive H_2O_2 solution was removed by heating and evaporation, and then 0.5% sodium hexameta-phosphate was added to disperse the sample completely. The mixture was analyzed with a Mastersize-2000 laser particle size analyzer at the Qingdao Institute of Marine Geology, China Geological Survey. Grain-size parameters were calculated following the formula of Folk and Ward (1957).

2.4. Chemical analysis and quality control

Element geochemistry of the samples was analyzed at the Testing Center in the Qingdao Institute of Marine Geology. Major elements (Al, Fe, K, Ca, Na, Mn, and P) and some trace elements (Cu, Pb, and Zn) were determined with an X-ray fluorescence spectrometer (model Philips PW4400), following Xia et al. (2008). Trace elements of Cd and Cr were measured by inductively coupled plasma mass spectrometry (ICP-MS) according to Dai et al. (2007). Total organic carbon (TOC) was determined with a Carlo-Erba™ elemental analyzer, as per Xu et al. (2015).

Quality control of element analyses was assessed using replicated analyses of certified national standard reference materials (GBW07343, GBW07314, and GBW07334). The results are shown in Table 1, in which the analytical errors ranged from −3.6% (for Cr) to 6.86% (for Cd).

3. Results

3.1. Physicochemical parameters

The calculated Mz of surface sediments varied from 2.9 to 7.5 Φ, with an average of 6.8 ± 0.9 Φ in the study area, indicating that sediments

were mainly composed of silt-sized particles. In addition, TOC concentrations (%) ranged from 0.78 to 17 (average 0.52 ± 0.12).

As shown in Fig. 3a, Mz values were larger than 6.5 Φ in the nearshore area, but were generally lower than 5 Φ in the eastern corners. The mean grain-size of sediments showed a general coarsening trend from west to east in the study area. In the western area, surface sediments were mainly composed of silt- and clay-sized material (Mz > 6.5 Φ), which were similar to the dominant silt- and clay-sized material discharged by the Yangtze River (Liu et al., 2006). In winter, monsoon-driven coastal currents flow southward and cause downwelling in nearshore areas, while the northward TWC causes upwelling in the eastern corner of the study area (Liu et al., 2007). The southward dispersal of the Yangtze fine-grain material occurs mainly along the inner shelf, especially landward of the 50 m isobath, due to downwelling, thereby forming a clinoform primarily comprised of silt- and clay-sized sediments (Xu et al., 2009). Since fine-grain matter cross-shelf transport is constrained by upwelling, fine-grain sediments cannot accumulate and cover the relic sand sediments formed during the transgressive period in the eastern corner area, as shown in Fig. 3b (Liu et al., 2007). Therefore, coarse-grain sediments were mainly located in the eastern study areas.

3.2. Major element concentrations

The concentrations of major elements in surface sediments from the Zhejiang coastal mud area are listed in Table 2. The ranges and average concentrations were 9.43 to 17.24% (average 15.66 ± 1.56%) for Al_2O_3, 3.95 to 7.33% (average 6.42 ± 0.70%) for TFe_2O_3, 2.26 to 3.34% (average 3.05 ± 0.22%) for K_2O, 3.42 to 9.49% (average 4.49 ± 0.93%) for CaO, 0.10 to 0.19% (average 0.16 ± 0.02%) for P_2O_5, 0.06 to 0.14% (average 0.10 ± 0.02%) for MnO and 1.35 to 7.02% (average 2.68 ± 0.61%) for Na_2O, respectively.

Coefficients of variation (CV) for K_2O, Al_2O_3, Tfe_2O_3, and P_2O_5 were as low as 10%, while CV values for MnO, CaO, and Na_2O were relatively high and close to 20%. According to Han et al. (2006), CV values of
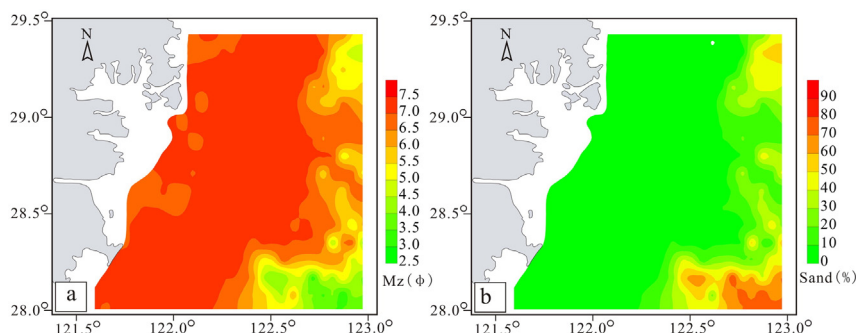
Fig. 3. Spatial distributions of mean grain size (Φ) and sand-sized component of surface sediments in the Zhejiang coastal mud area.

Table 2
Descriptive statistics of major element concentrations in surface sediments from the Zhejiang coastal mud area of the East China Sea (ECS).

	Al_2O_3 (%)	TFe_2O_3 (%)	K_2O (%)	CaO (%)	P_2O_5 (%)	MnO (%)	Na_2O (%)
Range	9.43–17.24	3.95–7.33	2.26–3.34	3.42–9.49	0.10–0.19	0.06–0.14	1.35–7.02
Mean	15.66 ± 1.56	6.42 ± 0.70	3.05 ± 0.22	4.49 ± 0.93	0.16 ± 0.02	0.10 ± 0.02	2.68 ± 0.61
Median	16.19	6.65	3.11	4.17	0.16	0.10	2.66
CV	10.0%	10.9%	7.2%	20.7%	12.5%	20%	22.8%
Y R[a]	13.38	6.11	2.48	4.48	No data	0.13	1.23
Y R[b]	18.30	7.71	No data	4.23	No data	0.12	0.88
Mud area of ECS[c]	12.46–16.91	4.94–6.70	2.46–3.29	2.53–8.94	No data	No data	1.75–2.30
	15.19 ± 0.79	5.95 ± 0.31	2.96 ± 0.13	3.48 ± 0.79	No data	No data	2.00 ± 0.11
Mud area of ECS[d]	14.12–19.45	5.79–7.81	2.67–3.71	0.95–2.41	No data	0.057–0.1	0.84–1.73
	17.66 ± 0.7	7.05 ± 0.29	3.41 ± 0.13	1.35 ± 0.28	No data	0.08 ± 0.01	1.2 ± 0.12

[a] Yangtze River sediments (Yang et al., 2004).
[b] Suspended particles from the Yangtze River (Li et al., 1984).
[c] Mud area of East China Sea (Liu et al., 2013).
[d] Mud area of East China Sea (Xiao et al., 2009).

elements dominated by natural sources are relatively low, while CV values of elements influenced by non-natural sources (biological and anthropogenic) are relatively high (Guo et al., 2012). In the current study, the CV values indicate that K_2O, Al_2O_3, TFe_2O_3, and P_2O_5 were probably from naturally weathered material, whereas MnO, CaO, and Na_2O were probably influenced by human activities and/or of biological origin.

The median concentrations of Al_2O_3 and TFe_2O_3 in the study area were close to those of suspended particles in the Yangtze River, further suggesting that Al_2O_3 and TFe_2O_3 were mainly sourced from the Yangtze River and differences in their concentrations were primarily due to grain size. Normally, the enrichment of elements in fine-grain material must be higher than that in coarse-grain materials. In contrast, however, the median concentrations of MnO, CaO, and Na_2O were higher than those in the Yangtze River suspended particles, indicating that these elements might be partially from non-natural sources.

3.3. Concentrations of potentially toxic metals

Descriptive statistics of potentially toxic metal concentrations in surface sediments from the Zhejiang coastal mud area are given in Table 3. Total metal concentrations ($mg\,kg^{-1}$) varied from 11.4 to 49.3 (average 33.3 ± 9.2) for Cu, 19.8 to 56.5 (average 33.5 ± 5.0) for Pb, 58.6 to 148.0 (average 117.3 ± 17.6) for Zn, 49.9 to 99.5 (average 85.9 ± 11.0) for Cr, and 30 to 150 $\mu g\,kg^{-1}$ (average 90 ± 30 $\mu g\,kg^{-1}$) for Cd, respectively.

Although the materials in the study area were mainly from the Yangtze River, the Yangtze estuary is characterized by tremendous runoff and "unpolluted" coarse-grain sediments, constituting a unique diluted setting (Chen et al., 2004). As a result, the potentially toxic metal concentrations in the Yangtze estuary sediments were lower than those in the study area. In addition, the mean concentrations of all potentially toxic metals in the present study were higher than those in the

sediments of the ECS. The research area was mainly located in the coastal mud area of the ECS, where sediment grain sizes were generally fine. However, Yu et al. (2013) studied the outer shelf of the ECS, where sediments were mainly composed of sand-sized components.

Marine Sediment Quality Standards (GB 18668-2002) were promulgated by the China State Bureau of Quality and Technical Supervision (CSBTS) to prevent and control marine sediment pollution, protect marine organisms and resources, utilize marine resources sustainably, maintain ecological equilibria, and protect human health. In Table 3, the mean concentrations of all potentially toxic metals, except for Cr, were lower than the levels of the Marine Sediment Quality Standards (CSBTS, 2002), indicating that sediment quality was generally good in the study area. Comparatively, the mean concentrations of potentially toxic metals were all higher than the upper crust concentrations, suggesting that the potentially toxic metals were enriched in this region, probably by human activities. It is possible, however, that such an inference might be inaccurate because the upper crust concentrations of potentially toxic metals are global reference levels, which might not represent actual regional geochemical baseline concentrations. Therefore, accurate determination of real background levels of potentially toxic metals in the research area is crucial and necessary for future study.

4. Discussion

4.1. Correlation analyses

Variation in potentially toxic metal concentration in sediment is primarily influenced by the mineralogical and chemical composition of sediment, human activities, organism enrichment, and various physicochemical processes (Singh et al., 2005; Jain et al., 2007). Relationships among metals in regards to common origins, uniform distributions,

Table 3
Descriptive statistics of potentially toxic metal concentrations in surface sediments from the Zhejiang coastal mud area of ECS.

	Cu ($mg\,kg^{-1}$)	Pb ($mg\,kg^{-1}$)	Zn ($mg\,kg^{-1}$)	Cr ($mg\,kg^{-1}$)	Cd ($\mu g\,kg^{-1}$)
Range	11.4–49.3	19.8–56.5	58.6–148.0	49.9–99.5	30–150
Mean	33.3 ± 9.2	33.5 ± 5.0	117.3 ± 17.6	85.9 ± 11.0	90 ± 30
YRE[a]	23.9	23.4	78.1	80.9	200
ECS[f]	23.7	24.6	83.8	71.4	200
MSQ I[b]	35.00	60.00	150.00	80.00	500
MSQ II[c]	100.00	130.00	350.00	150.00	1500
UCC[d]	32	15	69	69	61
UCC[e]	27	20	75	73	60

[a] Yangtze River Estuary sediment (Wang et al., 2014).
[b] Marine Sediment Quality I (CSBTS, 2002).
[c] Marine Sediment Quality II (CSBTS, 2002).
[d] Upper crustal concentrations of trace elements (Gao et al., 1998).
[e] Updated Upper crustal concentrations of trace elements (Hu and Gao, 2008).
[f] East China Sea sediment (Yu et al., 2013).

similar behaviors, and various associations can be revealed by correlation analysis (Diop et al., 2015). To explore the influencing factors of potentially toxic metal concentrations in this study, Pearson's correlation analyses using SPSS were conducted for major elements, potentially toxic metals, TOC, and Mz of surface sediments (Table 4).

The strong positive correlations of Mz with Al, Fe, K, Zn, and Cr ($r > 0.9$, $p < 0.0001$), and strong correlations of Mz with Cu and Pb ($r > 0.83$, $p < 0.0001$) showed that these metals were primarily controlled by sediment grain size, and Al, K, and Fe (especially Al) could be used as grain-size proxies. In addition, these results also suggest that the elements generally had a uniform spatial distribution pattern with Mz.

The strong positive correlations among Al, Fe, and K indicated that these elements were mainly from terrigenous sources. Al, K, and Fe are major constituents of common silicate minerals. In particular, Al is extremely resistant in the marine environment and is usually maintained in aluminosilicate minerals and regarded as a typical lithogenic element (Price et al., 1999; Qi et al., 2010). Therefore, the strong positive correlations between the potentially toxic metals of Zn and Cr and the lithogenic elements of Al, Fe, and K suggest that the potentially toxic metal concentrations were controlled by the mineralogical and chemical composition of the sediments. The strong positive correlations between the potentially toxic metals of Pb and Cu and the lithogenic elements of Al, Fe, and K suggest that the potentially toxic metal concentrations were generally controlled by the mineralogical and chemical composition of the sediments, but may also be affected by nonnatural sources to a certain extent. The moderate positive correlations between Cd and the lithogenic elements of Al, Fe, and K indicate that Cd concentration was probably controlled by the mineralogical and chemical composition of the sediments, but also influenced by human activities.

Organic carbon plays an important role in controlling the uptake of potentially toxic metals by sediments, suggesting a relative binding capacity of these potentially toxic metals with TOC (Singh et al., 2002). However, the concentrations of potentially toxic metals were not controlled by TOC in the current study. Although, TOC was well correlated with Pb, Zn, and Cr, the correlations were mainly due to their lithogenic origins (Um et al., 2013).

Ca is a biogenic element, and its geochemical properties are easily affected by biological processes. Therefore, Ca is considered a promising index for reconstructing paleoproductivity (Dymond et al., 1997). In the present study, CaO was well correlated with lithogenic elements, indicating that Ca was primarily from natural sources and might be influenced by biogenic processes. CaO also had good correlations with Cu, Pb, Zn, and Cr, which were principally due to their lithogenic origins. Similarly, Cd was also somewhat influenced by biogenic sources.

Table 5
Rotated component matrix for data of elements and Eigenvalues, percentage of variances, and eigenvectors for the three principal components.

Elements	PC1	PC2	PC3
K_2O	0.974	0.092	0.091
Al_2O_3	0.926	0.302	0.004
TFe_2O_3	0.916	0.385	0.031
Zn	0.933	0.328	−0.006
Cr	0.894	0.418	0.069
Pb	0.860	0.383	−0.087
Cu	0.679	0.683	−0.155
Cd	0.475	0.769	−0.237
MnO	0.383	0.868	−0.109
P_2O_5	0.119	0.675	0.555
Na_2O	0.015	−0.152	0.893
Eigenvalues	5.90	2.97	1.22
Total variance	53.64%	26.96%	11.08%
Cumulative variance	53.64%	80.60%	91.68%

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in four iterations.

The correlation analyses indicated that potentially toxic metal concentrations were primarily controlled by mean grain size and mineral and chemical composition of the sediment, and were probably affected by human activities and occasionally by biogenic sources and TOC.

4.2. Source analyses using PCA

Currently, source identification of potentially toxic metals is mostly conducted by calculating the enrichment factor to classify natural and anthropogenic origins (Xu et al., 2014; Luo et al., 2015), or by means of multivariate analysis to group natural and key anthropogenic input types (Yuan et al., 2004; Mamat et al., 2014; Luo et al., 2015; Soltani et al., 2015).

We used principal component analysis (PCA) with varimax normalized rotation, an effective statistical tool for potentially toxic metal source identification (Bhuiyan et al., 2010; Anju and Banerjee, 2012), to identify the factors influencing each other and to obtain more reliable information about the relationships among metals. PCA yielded three principal components (PCs) with eigenvalues >1 in the study area, which described 91.68% of total variance of data. The elements assembled around each factor with significant loadings, and formed three major elemental groups, indicative of three diverse sources (Table 5 and Fig. 4).

The first principal component (PC1) accounted for 53.46% of total variance and was primarily loaded with lithogenic elements, e.g. K_2O, Al_2O_3, and TFe_2O_3 (Table 5 and Fig. 4). Since the dominant loadings on Al, K, and Fe generally represent detrital components, PC1 was assigned

Table 4
Results of Pearson's correlation analyses for elements, TOC, and Mz ($n = 350$).

	Al_2O_3	TFe_2O_3	K_2O	TOC	CaO	P_2O_5	MnO	Na_2O	Cu	Pb	Zn	Cr	Cd	Mz
Al_2O_3	1													
TFe_2O_3	0.97[a]	1												
K_2O	0.96[a]	0.94[a]	1											
TOC	0.68[a]	0.67[a]	0.78[a]	1										
CaO	−0.70[a]	−0.74[a]	−0.70[a]	−0.36[a]	1									
P_2O_5	0.38[a]	0.39[a]	0.29[a]	0.32[a]	−0.31[a]	1								
MnO	0.60[a]	0.68[a]	0.43[a]	0.12[b]	−0.59[a]	0.49[a]	1							
Na_2O	−0.09	−0.03	0.02	0.39[a]	0.05	0.20[a]	−0.16[a]	1						
Cu	0.81[a]	0.87[a]	0.69[a]	0.31[a]	−0.71[a]	0.39[a]	0.88[a]	−0.17[a]	1					
Pb	0.87[a]	0.91[a]	0.83[a]	0.54[a]	−0.69[a]	0.28[a]	0.67[a]	−0.08	0.88[a]	1				
Zn	0.95[a]	0.98[a]	0.93[a]	0.65[a]	−0.73[a]	0.34[a]	0.64[a]	−0.05	0.86[a]	0.93[a]	1			
Cr	0.94[a]	0.99[a]	0.91[a]	0.66[a]	−0.74[a]	0.43[a]	0.70[a]	0.01	0.88[a]	0.90[a]	0.97[a]	1		
Cd	0.64[a]	0.72[a]	0.48[a]	0.11[b]	−0.57[a]	0.34[a]	0.86[a]	−0.22[a]	0.91[a]	0.73[a]	0.68[a]	0.73[a]	1	
Mz	0.96[a]	0.95[a]	0.909[a]	0.67[a]	−0.68[a]	0.42[a]	0.63[a]	0.02	0.83[a]	0.86[a]	0.94[a]	0.96[a]	0.68[a]	1

[a] Correlation is significant at the 0.01 level (two-tailed).
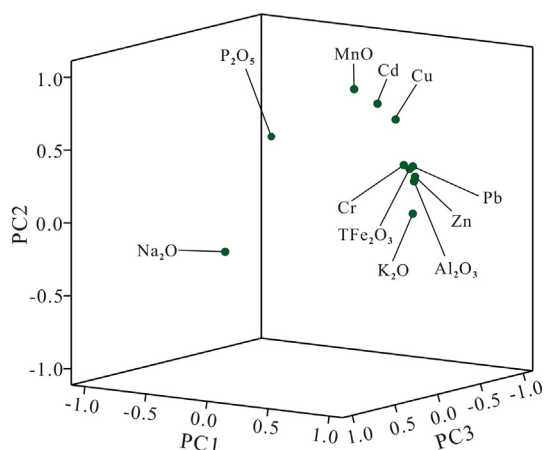[b] Correlation is significant at the 0.05 level (two-tailed).

Fig. 4. Plot of PC loadings on elements in surface sediments from the Zhejiang coastal mud area.

as being of detrital source. It was also characterized with higher loadings on Zn, Cr, and Pb, implying dominant terrigenous sources. This inference was consistent with the significant correlation of these potentially toxic metals with Al_2O_3 (Table 4). In addition, the lithogenic elements of K, Al, and Fe were proportional to most anthropogenic elements (Qi et al., 2010), as shown by their moderate positive correlations (Table 4). PC1 had some moderate loadings on Cu and Cd (Table 5), denoting that these metals were partially derived from lithogenic sources bound in aluminosilicate minerals.

PC2, which explained 26.96% of total variance, had high loadings on MnO, Cu, Cd, and P_2O_5, and constituted another element group as shown in Fig. 4 and Table 5. In general, these elements were considered as anthropogenic contaminants principally related to the discharge of agricultural wastewater (Fig. 4). Based on the characteristics of MnO concentration, the MnO in the collected samples might be from anthropogenic origins, such as trace element fertilizers, paints, and varnish desiccants (Zahra et al., 2014). Element P in sediment is also influenced by fertilizer-derived P (Machado et al., 2008). In addition, previous studies (Xia et al., 2011; Xu et al., 2014) have shown that the distribution of Cd is closely associated with intense phosphate fertilizer usage, in which significant amounts of metals (particularly Cd and As impurities) are found. Therefore, the dominant loadings of PC2 on these elements (e.g. MnO, Cu, Cd, and P_2O_5) are probably a reflection of anthropogenic sources.

PC3, which explained 11.08% of total variance, showed relatively higher loadings on two elements, including a loading of 0.893 on Na_2O (Table 5). Na_2O was not correlated with lithogenic or anthropogenic elements (Table 4), thereby indicating a marine, rather than terrigenous or anthropogenic, source. In marine sediments Na easily migrates, and is often enriched in bottom fine-grain sediment via adsorption and cation exchange (Zhao and Yan, 1994). Therefore, PC3 might represent marine chemical deposition.

4.3. Determination of GBCF

Statistical methods have been widely used in previous studies to infer GBC in surface sediments. By making assumptions about the normal distribution of potentially toxic metals in non-contaminated sediments, the GBC can be established by removing data outliers and then applying several statistical techniques (Karim et al., 2015; Jiang et al., 2013; Wang et al., 2015). Cumulative distribution function (CDF) for potentially toxic metal concentration can be used to remove artificially-influenced potentially toxic metal concentration data points regardless of grain size, mineral influences, or potentially toxic metal sources (Karim et al., 2015; Jiang et al., 2013; Wang et al., 2015); however, this approach might delete naturally high values and cause unexpected errors.

In reality, some potentially toxic metals are obviously of natural origin, and CDF curve bends are not cut-off points but natural variations. Naturally deleting high concentrations based on CDF curvature can result in lower GBC values.

To avoid these issues, we applied the method proposed by Matschullat et al. (2000), with some modification, to infer GBC in surface sediments. The sources of potentially toxic metals were first identified, and apparent potentially toxic metal concentration outliers were then removed based on their descriptive statistics. If the potentially toxic metal was of natural origin, a linear regression model for potentially toxic metals and lithogenic and particle-size proxy elements was constructed, and data points outside the 95% confidence interval were removed. Linear regression analysis was then conducted for the remaining data points to obtain a final GBCF. If the potentially toxic metal was of mixed natural and anthropogenic origin, the potentially toxic metal data were normalized by lithogenic and particle-size proxy elements to exclude the influences of grain size and/or mineral, and the CDF of the normalized potentially toxic metal was then calculated to remove data points affected by human activities. Finally, linear regression was again conducted as per that performed for potentially toxic metals of natural origin. The corresponding GBC at each station was calculated according to the GBCF.

Both correlation analysis and PCA results suggested that the major element Al was a typical lithogenic element, which is extremely resistant in the marine environment and usually held in aluminosilicate minerals (Price et al., 1999; Qi et al., 2010). In addition, Al showed significant correlation with mean grain-size. Therefore, using Al_2O_3 as a normalizer could compensate for the influences of both grain-size and mineralogical variations in other elements, especially potentially toxic metals. The actual natural concentration of potentially toxic metals for each sample can be estimated by the linear regression function derived from the relationship between Al_2O_3 and potentially toxic metals ($r > 0.9$ and $p < 0.0001$). We used the approach described above to obtain the GBCF for each studied potentially toxic metal in the surface sediments from the Zhejiang coastal mud area of the ECS.

4.3.1. GBCF for Cr, Zn, and Pb

Summers et al. (1996) asserted that datasets used in normalization and linear regression analyses must be solely based on natural concentrations in order to obtain reliable statistical relationships between the metal and reference element. Based on source analyses for potentially toxic metals, the potentially toxic metals of Cr, Zn, and Pb were of terrigenous origin. Accordingly, 14, 11, and 9 data outliers of Cr, Zn, and Pb, respectively, were removed by drawing the distribution histograms of elemental concentrations. Linear regression analyses were conducted for Zn, Cr, and Pb with Al_2O_3, respectively, and their scatter plots are shown in Fig. 5a–c. Data points falling outside the 95% confidence limit were considered as potentially toxic metal to proxy element ratio outliers, and were removed. Data points falling inside the 95% confidence limit of potentially toxic metals versus Al_2O_3 were characterized as natural sediments (Jiang et al., 2013; Wang et al., 2015), and were applied to determine the GBCF to improve correlation coefficients (Fig. 5). The correlation coefficients increased from 0.96 to 0.992 for Zn, 0.87 to 0.904 for Pb, and 0.96 to 0.973 for Cr, which were all statistically significant at $p < 0.0001$. The final GBCFs for Zn, Pb, and Cr are shown in Fig. 5d–f.

4.3.2. GBCFs for Cu and Cd

Source identification of potentially toxic metals in our study suggested that Cu and Cd were of mixed terrigenous and anthropogenic origin. Accordingly, outliers and samples influenced by human activities were removed to produce a relatively clean dataset, and then normalized by lithogenic element Al to reduce the influence of grain size and mineral. The CDFs of the Cu/Al_2O_3 and Cd/Al_2O_3 ratios were drawn to identify the cut-off points that separated the dataset into natural and
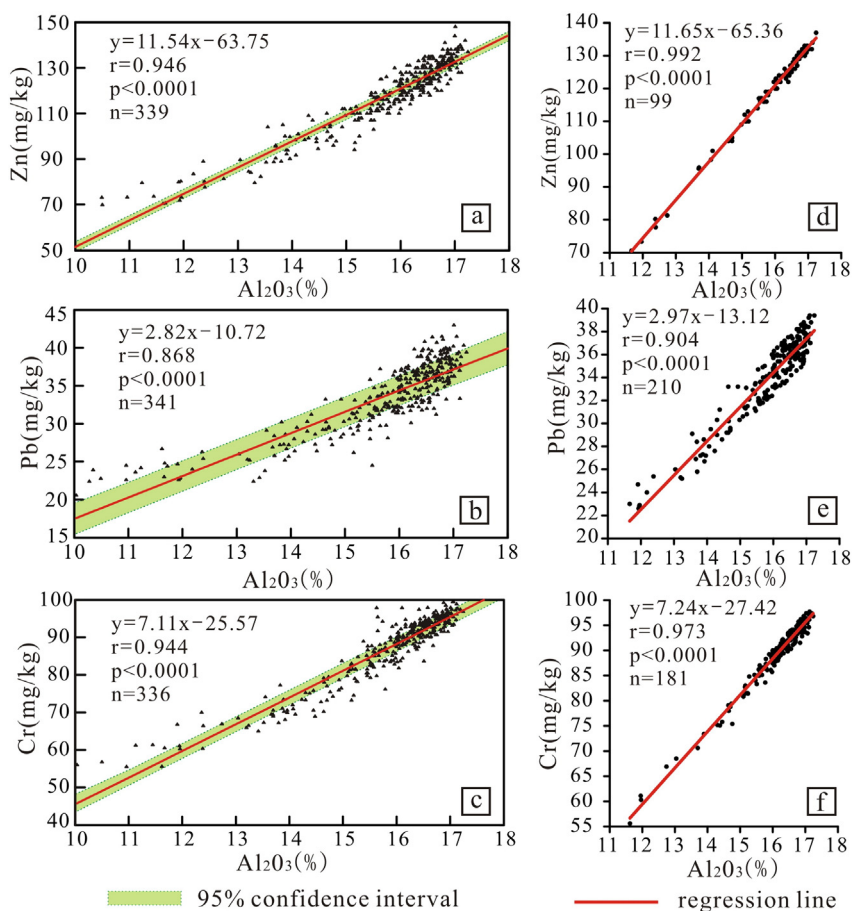
Fig. 5. Scatter plots of the liner regression models of Zn, Cr and Pb in surface sediments from the Zhejiang coastal mud area.

artificially-influenced concentration ratios based on the slope, as shown by the red curves in Fig. 6.

The natural frequency distribution of normalized potentially toxic metals should follow normal distribution, and correspondingly, the CDF curve slopes should increase at first to a maximum value and then decrease. If the frequency distribution of a potentially toxic metal shows two or more peaks, the first peak suggests terrigenous origin, but the second or more peaks suggest influence from human activities. This assumption was confirmed by the melioration of the correlation coefficients between Cu and Cd and Al_2O_3 when the noisy data points in curves with more than one peak were removed. For example, correlation coefficients increased from 0.81 to 0.94 for Cu and from 0.64 to 0.788 for Cd, respectively (Table 3 and Fig. 7a–b). Therefore, based on CDF, the ratios of Cu/Al_2O_3 and Cd/Al_2O_3 of terrigenous origin and the ratios influenced by human activities were separated by the first slope minimum. Based on the approach described above, the cut-off points were 2.04 for Cu/Al_2O_3 and 5.57 for Cd/Al_2O_3, as shown in Fig. 6. The data from stations affected by human activities (Cu/Al_2O_3 ratio > 2.04 and Cd/Al_2O_3 ratio > 5.57) were removed in the following procedure.

For the remaining data points of samples of terrigenous origin, linear regression analyses were similar to those of Cr, Zn, and Pb, as described above. The final GBCF for potentially toxic metals of Cu and Cd are shown in Fig. 7c–d. The GBCs of potentially toxic metals for each sample were calculated by the GBCF based on the corresponding lithogenic Al_2O_3 concentration. The calculated GBC of a potentially toxic metal represented the actual natural background characteristics, and was therefore more accurate in assessing potentially toxic metal pollution and identifying pollution sources in sediments than the constant GBC or global references cited in previous studies (Idris, 2008; Sun et al.,
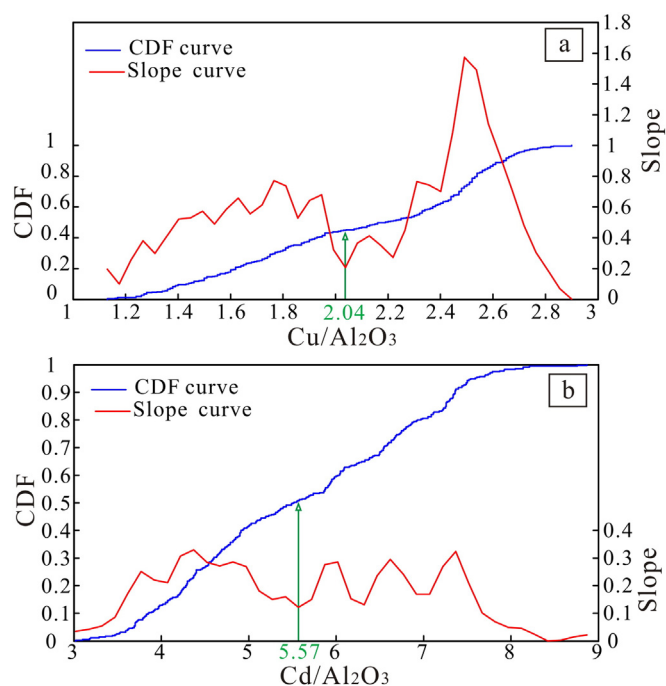

Fig. 6. Cumulative distribution functions (CDF) of Cu and Cd in surface sediments from the Zhejiang coastal mud area. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
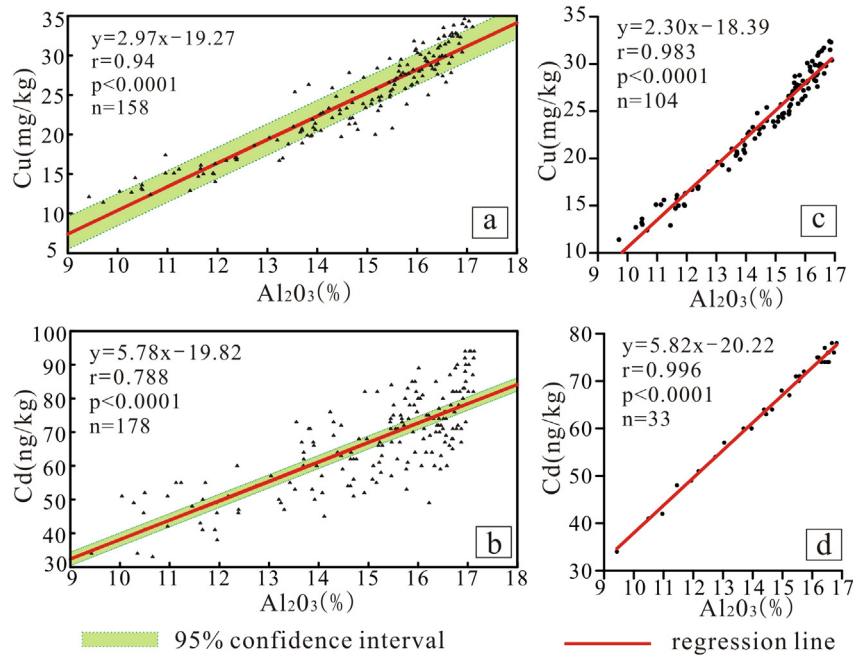
Fig. 7. Scatter plots of the liner regression models of Cu and Cd in surface sediments from the Zhejiang coastal mud area.

2010; Magesh et al., 2011; Fu et al., 2013; Xu et al., 2014; Soltani et al., 2015).

4.4. Enrichment factor

Enrichment factor (EF) is extensively used to estimate anthropogenic impact on potentially toxic metal concentrations in sediments. To identify possible anomalous potentially toxic metal concentrations, geochemical normalization of potentially toxic metal concentration to a conservative element is frequently employed (Shumilin et al., 2002; Shevchenko et al., 2003; Lee et al., 2009). In our study, the calculated potentially toxic metal concentration through the GBCF excluded the influences of grain size and mineral, and EF was defined as the ratio of metal concentration in a sample to metal GBC. Typically, an EF value between 0.5 and 1.5 indicates that a metal in sediment is entirely from crustal contribution (e.g., weathering product), while EF values >1.5 indicate an important proportion of non-crustal materials from either natural processes (e.g., biota contributions) and/or anthropogenic influences (Zhang and Liu, 2002; Xu et al., 2014).

In our study, EF values varied from 0.8 to 1.4 (average 1.0) for Zn, 0.9 to 1.2 (average 1.0) for Cr, 0.7 to 1.6 (average 1.0) for Pb, 0.8 to 1.6

(average 1.2) for Cu, and 0.7 to 1.9 (average 1.2) for Cd (Fig. 8). The fact that all average EF values were less than 1.5 indicates predominantly natural origins for the potentially toxic metals. However, one station for Pb, 57 stations for Cu, and 95 stations for Cd had values larger than or equal to 1.5, indicating that these stations might be affected by biota contributions and/or anthropogenic influences. Considering the inference from correlation analyses, potentially toxic metals at these stations might be affected by human activities. These artificially-influenced stations were also mostly located in near-shore areas (Fig. 9).

The EF results were consistent with those from PCA, indicating that the GBCs for each sample calculated by the GBCF were appropriate in the current research, and could be applied to effectively assess potentially toxic metal pollution, identify pollution sources, and prevent environmental contamination. The GBCF approach in our study might be a helpful reference for similar studies in other regions.

5. Conclusions

In this study, the GBCs of potentially toxic metals in surface sediments were estimated by the GBCF, which was developed by statistical techniques and geochemical sedimentation. Firstly, the potentially toxic metal source was identified by PCA, and potentially toxic metal concentration outliers were removed by analyzing metal distribution histograms. Secondly, the GBCF of the natural metal was determined by fitting potentially toxic metal concentrations to Al concentration in a linear regression model. With respect to anthropogenic potentially toxic metals, the CDF of normalized potentially toxic metals was analyzed to remove artificially-influenced samples, with the linear regression model then fitted for the remaining natural samples to obtain the final GBCF.

At each station, the EF modified by the corresponding GBC estimated by the GBCF was applied to identify potentially toxic metal sources in surface sediments from the Zhejiang coastal mud area of the ECS. Results suggested that Cu and Cd were of anthropogenic origin at many stations, whereas Zn, Cr, and Pb were generally of natural origin. The EF results were consistent with those from PCA, suggesting that the GBC for each sample calculated by the GBCF was applicable, at least for our study area. The calculated GBCs effectively assessed potentially toxic metal pollution and identified possible pollution sources. Since
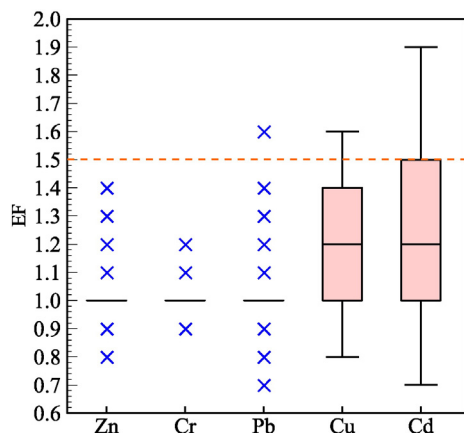

Fig. 8. Box-and-whisker plots for the enrichment factors (EFs) of potentially toxic metals in the surface sediments from the Zhejiang coastal mud area.
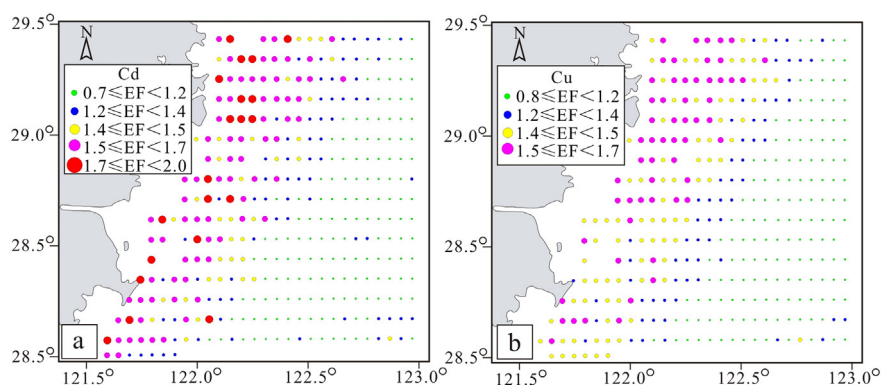
Fig. 9. Spatial distribution of the enrichment factor (EF) of Cd and Cu in surface sediments from the Zhejiang coastal mud area.

this approach was only used in a limited geographical area, further research in other regions is required in the future.

References

Alexander, C.R., DeMaster, D.J., Nittrouer, C.A., 1991. Sediment accumulation in a modern epicontinental-shelf setting: the Yellow Sea. Mar. Geol. 98, 51–72.
Anju, M., Banerjee, D.K., 2012. Multivariate statistical analysis of heavy metals in soils of a Pb-Zn mining area, India. Environ. Monit. Assess. 184, 4191–4206.
Bartek, L.R., Wellner, R.W., 1995. Do equilibrium conditions exist during sediment transport studies on continental margins? An example from the East China Sea. Geo-Mar. Lett. 15, 23–29.
Bhuiyan, M.A.H., Parvez, L., Islam, M.A., Dampare, S.B., Suzuki, S., 2010. Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. J. Hazard. Mater. 173, 384–392.
Covelli, S., Fontolan, G., 1997. Application of a normalization procedure in determining regional geochemical baselines. Environ. Geol. 30, 34–45.
Carballeira, A., Carral, E., Puente, X., Villares, R., 2000. Regional-scale monitoring of coastal contamination, nutrients and heavy metals in estuarine sediments and organisms on the coast of Calicia (northwest Spain). Int. J. Environ. Pollut. 13, 534–572.
CSBTS, 2002. Marine Sediment Quality. Standards Press of China, Beijing.
Chen, Z.Y., Saito, Y., Kanai, Y., Wei, T., Li, L.Q., Yao, H.H., Wang, Z.H., 2004. Low concentration of heavy metals in the Yangtze estuarine sediments, China: a diluting setting. Estuar. Coast. Shelf Sci. 60, 91–100.
Daskalakis, K.D., O'Connor, T.P., 1995. Normalization and elemental sediment contamination in the coastal United States. Environ. Sci. Technol. 29, 470–477.
Dymond, J., Collier, R., McManus, J., Honjo, S., Manganini, S., 1997. Can the aluminum and titanium contents of ocean sediments be used to determine the paleoproductivity of the oceans? Paleoceanography 12, 586–593.
Dai, J.C., Song, J.M., Li, X.G., Yuan, H.M., Li, N., Zheng, G.X., 2007. Environmental changes reflected by sedimentary geochemistry in recent hundred years of Jiaozhou Bay, North China. Environ. Pollut. 145, 656–667.
Dong, C.Y., Zhang, W.G., Ma, H.L., Feng, H., Lu, H., Dong, Y., Yu, L.Z., 2014. A magnetic record of heavy metal pollution in the Yangtze River subaqueous delta. Sci. Total Environ. 476–477, 368–377.
Diop, C., Dewaele, D., Cazier, F., Diouf, A., Ouddane, B., 2015. Assessment of trace metals contamination level, bioavailability and toxicity in sediments from Dakar coast and Saint Louis estuary in Senegal, West Africa. Chemosphere 138, 980–987.
Folk, R.L., Ward, W.C., 1957. Brazos river bar: a study in the significance of grain size parameters. J. Sediment. Petrol. 31, 514–519.
Fang, T.H., Li, J.Y., Feng, H.M., Chen, H.Y., 2009. Distribution and contamination of trace metals in surface sediments of the East China Sea. Mar. Environ. Res. 68, 178–187.
Fu, J., Hu, X., Tao, X.C., Yu, H.X., Zhang, X.W., 2013. Risk and toxicity assessments of heavy metals in sediments and fishes from the Yangtze River and Taihu Lake, China. Chemosphere 93, 1887–1895.
Gao, S., Luo, T.C., Zhang, B.B., Zhang, H.G., Han, Y.W., Zhao, Z.D., Hu, Y.K., 1998. Chemical composition of the continental crust as revealed by studies in East China. Geochim. Cosmochim. Acta 62, 1959–1975.

Gao, X.L., Li, P.M., 2012. Concentration and fractionation of trace metals in surface sediments of intertidal Bohai Bay, China. Mar. Pollut. Bull. 64, 1529–1536.
Guo, G., Wu, F., Xie, F., Zhang, R., 2012. Spatial distribution and pollution assessment of heavy metals in urban soils from southwest China. J. Environ. Sci. 24, 410–418.
Han, Y.M., Du, P.X., Cao, J.J., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, central China. Sci. Total Environ. 355, 176–186.
Hu, Z.C., Gao, S., 2008. Upper crustal abundances of trace elements: a revision and update. Chem. Geol. 253, 205–221.
Idris, A.M., 2008. Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. Microchem. J. 90, 159–163.
Jain, C.K., Malik, D.S., Yadav, R., 2007. Metal fractionation study on bed sediments of Lake Nainital, Uttaranchal, India. Environ. Monit. Assess. 130, 129–139.
Jiang, J.B., Wang, J., Liu, S.Q., Lin, C.Y., He, M.C., Liu, X.T., 2013. Background, baseline, normalization, and contamination of heavy metals in the Liaohe River watershed sediments of China. J. Asian Earth Sci. 73, 87–94.
Karim, Z., Qureshi, B.A., Mumtaz, M., 2015. Geochemical baseline determination and pollution assessment of heavy metals in urban soils of Karachi, Pakistan. Ecol. Indic. 48, 358–364.
Li, Y.H., Hisayuki, T., Yang, Z.S., Chen, J.S., 1984. The element composition of suspended particles from the Yellow and Yangtze rivers. Geochim. Cosmochim. Acta 48, 1561–1564.
Liu, P.Z., Yu, Y.Q., Liu, C.Y., 1991. Studies on the situation of pollution and countermeasures of control of the oceanic environmental in Zhoushan Fishing Ground - the largest fishing ground in China. Mar. Pollut. Bull. 23, 281–288.
Loring, D.H., 1991. Normalization of heavy metal data from estuarine and coastal sediments. ICES J. Mar. Sci. 48, 101–115.
Lin, S.W., Hsieh, I.J., Huang, K.M., Wang, C.H., 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.
Lee, H.J., Chao, S.Y., 2003. A climatological description of circulation in and around the East China Sea. Deep-Sea Res. II Top. Stud. Oceanogr. 50, 1065–1084.
Liu, J.P., Li, A.C., Xu, K.H., Velozzi, D.M., Yang, Z.S., Milliman, J.D., DeMaster, D.J., 2006. Sedimentary features of the Yangtze River-derived along-shelf clinoform deposit in the East China Sea. Cont. Shelf Res. 26, 2141–2156.
Liu, J.P., Xu, K.H., Li, A.C., Milliman, J.D., Velozzi, D.M., Xiao, S.B., Yang, Z.S., 2007. Flux and fate of Yangtze River sediment delivered to the East China Sea. Geomorphology 85, 208–224.
Lee, B., Zhu, L.M., Tang, J.W., Zhang, F.F., Zhang, Y., 2009. Seasonal variations in elemental composition of aerosols in Xiamen, China. Geochem. J. 43, 423–440.
Liu, S.F., Shi, X.F., Liu, Y.G., Wu, Y.H., Yang, G., Wang, X.C., 2013. Holocene paleoclimatic reconstruction based on mud deposits on the inner shelf of the East China Sea. J. Asian Earth Sci. 69, 113–120.
Liu, J.L., Wu, H., Feng, J.X., Li, Z.j., Lin, G.H., 2014. Heavy metal contamination and ecological risk assessment in the sediments and zoobenthos of selected mangrove ecosystems south China. Catena 119, 136–142.
Luo, X.S., Xue, Y., Wang, Y.L., Cang, L., Xu, B., Ding, J., 2015. Source identification and apportionment of heavy metals in urban soil profiles. Chemosphere 127, 152–157.
Milliman, J.D., Shen, H.T., Yang, Z.S., Mead, R.H., 1985. Transport and deposition of river sediment in the Changjiang estuary and adjacent continental shelf. Cont. Shelf Res. 4, 37–45.
Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background - can we calculate it? Environ. Geol. 39, 990–1000.
Machado, W., Luiz-Silva, W., Sanders, C.J., Patchineelam, S.R., 2008. Coupled anthropogenic anomalies of radionuclides and major elements in estuarine sediments. J. Environ. Radioact. 99, 1329–1334.
Magesh, N.S., Chandrasekar, N., Vetha Roy, D., 2011. Spatial analysis of trace element contamination in sediments of Tamiraparani estuary, southeast coast of India. Estuar. Coast. Shelf Sci. 92, 618–628.
Maanan, M., Saddik, M., Maanan, M., Chaibi, O.A., Zourarah, B., 2014. Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon, Morocco. Ecol. Indic. 48, 616–626.
Mamat, Z., Yimit, H., Ji, R.Z., Eziz, M., 2014. Source identification and hazardous risk delineation of heavy metal contamination in Yanqi Basin, northwest China. Sci. Total Environ. 493, 1098–1111.

Nriagu, J.O., 1989. A global assessment of the natural sources of atmosphere trace metals. Nature 338, 47–49.

Price, N.B., Brand, T., Pates, J.M., Mowbray, S., Theocharis, A., Civitarese, G., Miserocchi, S., Heussner, S., Lindsay, F., 1999. Horizontal distributions of biogenic and lithogenic elements of suspended particulate matter in the Mediterranean Sea. Prog. Oceanogr. 44, 191–218.

Qi, S., Leipe, T., Rueckert, P., Di, Z., Harff, J., 2010. Geochemical sources, deposition and enrichment of heavy metals in short sediment cores from the Pearl River estuary, southern China. J. Mar. Syst. 82, 528–542.

Reimann, C., Caritat, P.D., 2000. Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. Environ. Sci. Technol. 34, 5084–5091.

Reimann, C., Garrett, R.G., 2005. Geochemical background — concept and reality. Sci. Total Environ. 350, 12–27.

Summers, J.K., Wade, T.L., Engle, V.D., Malaeb, Z.A., 1996. Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. Estuaries 19, 581–594.

Saito, Y., Katayama, H., Ikehara, K., Kato, Y., Matsumoto, E., Oguri, K., Oda, M., Yumoto, M., 1998. Transgressive and highstand systems tracts and post-glacial transgression, the East China Sea. Sediment. Geol. 122, 217–232.

Shumilin, E.N., Carriquiry, J.D., Camacho-Ibar, V.F., Sapozhnikov, D.S., Kalmykov, S., Sanchez, A., Aguniga-Garcia, S., Sapozhnikov, Y.A., 2002. Spatial and vertical distributions of elements in sediments of the Colorado River Delta and Upper Gulf of California. Mar. Chem. 79, 113–131.

Singh, M., Mulle, G., Singh, I.B., 2002. Heavy metals in freshly deposited stream sediments of rivers associated with urbanisation of the Ganga plain, India. Water Air Soil Pollut. 141, 35–54.

Shevchenko, V., Lisitzin, A., Vinogradova, A., Stein, R., 2003. Heavy metals in aerosols over the seas of the Russian Arctic. Sci. Total Environ. 306, 11–25.

Singh, K.P., Malik, A., Sinha, S., Singh, V.K., Murthy, R.C., 2005. Estimation of source of heavy metal contamination in sediments of Gomti River (India) using principal component analysis. Water Air Soil Pollut. 166, 321–341.

Sun, Y.B., Zhou, Q.X., Xie, X.K., Liu, R., 2010. Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. J. Hazard. Mater. 174, 455–462.

Song, Y., Choi, M.S., Lee, J.Y., Jang, D.J., 2014. Regional background concentrations of heavy metals (Cr, Co, Ni, Cu, Zn, Pb) in coastal sediments of the South Sea of Korea. Sci. Total Environ. 482–483, 80–91.

Soltani, N., Keshavarzi, B., Moore, F., Tavakol, T., Lahijanzadeh, A.R., Jaafarzadeh, N., Kermani, M., 2015. Ecological and human health hazards of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in road dust of Isfahan metropolis, Iran. Sci. Total Environ. 506, 712–723.

Um, I.K., Choi, M.S., Bahk, J.J., Song, Y.H., 2013. Discrimination of sediments provenance using rare earth elements in the Ulleung Basin, East/Japan Sea. Mar. Geol. 346, 208–219.

Veena, B., Radhakrishnan, C.K., Chacko, J., 1997. Heavy metal induced biochemical effects in an estuarine teleost. Indian J. Mar. Sci. 26, 74–78.

Wang, J.W., Liu, R.M., Zhang, P.P., Yu, W.W., Shen, Z.Y., Feng, C.H., 2014. Spatial variation, environmental assessment and source identification of heavy metals in sediments of the Yangtze River estuary. Mar. Pollut. Bull. 87, 364–373.

Wang, J., Liu, G.J., Lu, L.L., Zhang, J.M., Liu, H.Q., 2015. Geochemical normalization and assessment of heavy metals (Cu, Pb, Zn and Ni) in sediments from the Huaihe River, Anhui, China. Catena 129, 30–38.

Xia, N., Zhang, Q., Yao, D., Li, G.H., 2008. Geochemistry analysis of marine sediments using fused glass disc by X-ray fluorescence spectrometry. Chin. J. Oceanol. Limnol. 26, 475–479.

Xiao, S.B., Li, A.C., Liu, W.G., 2009. Sediment provenance analysis in the Min-Zhe mud area. Chin. J. Prog. Nat. Sci. 19, 185–191.

Xu, K.H., Milliman, J.D., Li, A.C., Liu, J.P., Kao, S.J., Wan, S.M., 2009. Yangtze- and Taiwan-derived sediments on the inner shelf of East China Sea. Cont. Shelf Res. 29, 2240–2256.

Xia, P., Meng, X.W., Yin, P., Cao, Z.M., Wang, X.Q., 2011. Eighty-year sedimentary record of heavy metal inputs in the intertidal sediments from the Nanliu River estuary, Beibu Gulf of South China Sea. Environ. Pollut. 159, 92–99.

Xu, G., Liu, J., Pei, S.F., Kong, X.H., Hu, G., 2014. Distribution and source of heavy metals in the surface sediments from the near-shore area, Jiangsu Province, China. Mar. Pollut. Bull. 83, 275–281.

Xu, G., Liu, J., Pei, S.F., Gao, M.S., Hu, G., Kong, X.H., 2015. Sediment properties and trace metal pollution assessment in surface assessment of the Laizhou Bay, China. Environ. Sci. Pollut. Res. 22, 11634–11647.

Yang, S.Y., Jung, H.S., Li, C.X., 2004. Two unique weathering regimes in the Changjiang and Huanghe drainage basins: geochemical evidence from river sediments. Sediment. Geol. 164, 19–34.

Yi, Y.J., Yang, Z.F., Zhang, S.H., 2011. Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in middle and lower reaches of the Yangtze River basin. Environ. Pollut. 159, 2575–2585.

Yuan, C., Shi, J., He, B., Liu, J., Liang, L., Jiang, G., 2004. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environ. Int. 30, 769–783.

Yu, Y., Song, J.M., Li, X.G., Yuan, H.M., Li, N., 2013. Fractionation, sources and budgets of potential harmful elements in surface sediments of the East China Sea. Mar. Pollut. Bull. Sci. 68, 157–167.

Zhao, Y.Y., Yan, M.C., 1994. Geochemistry of Sediments of the China Shelf Sea. Science Press, Beijing.

Zhang, J., Liu, C.L., 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.

Zheng, Y., Kissel, C., Zhenag, H.B., Laj, H.B., Wang, K., 2010. Sedimentation on the inner shelf of the East China Sea: magnetic properties, diagenesis and paleoclimate implications. Mar. Geol. 268, 34–42.

Zhou, S.S., Tong, L., Tang, Q.Z., Gu, X.Q., Xue, B., Liu, W.P., 2013. Residues, sources and tissue distributions of organochlorine pesticides in dog sharks (Mustelus griseus) from Zhoushan Fishing Ground, China. Mar. Pollut. Bull. 73, 374–380.

Zahra, A., Hashmi, M.Z., Malik, R.N., Ahmed, Z., 2014. Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah-feeding tributary of the Rawal Lake reservoir, Pakistan. Sci. Total Environ. 470–471, 925–933.