Concentration and fractionation of trace metals in surface sediments of intertidal Bohai Bay, China

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ABSTRACT

Surface sediments from intertidal Bohai Bay were sampled for the geochemical and environmental assessment of six trace metals (Cd, Cr, Cu, Ni, Pb and Zn). Results indicate that sediment grain size plays an important role in controlling the distribution and fractionation of them. Metal concentrations in clayey silt sediments are all clearly higher than in sand and silty sand ones. Cd and Pb in clayey silt sediments are more mobile than in sand and silty sand ones. Two sediment quality guidelines and two geochemical normalization methods (index of geoaccumulation and enrichment factor) were used to judge the potential risk and accumulation of metals. According to the mean probable effects level quotient, the combination of studied metals may have a 21% probability of being toxic. The sediments with high fraction of clay and silt have been contaminated by trace metals to various degrees, among which Cr contributes the most to contamination.

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The ubiquitous use of metals in human society has significantly changed their original distribution patterns in natural environments. Trace metals are recognized as an important indicator of the degradation of aquatic environments (e.g. MacDonald et al., 1996; Allen Burton, 2002). Huge amounts of trace metals are entering the coastal environment each year as contaminants from anthropogenic-related processes by the ways of untreated industrial wastewater, municipal sewage effluent, surface run-off and so on. In aquatic environments, many trace metals are transported predominantly in association with particulate matter, which makes coastal sediments the most important repository for metal pollutants that enter the seas (Ridgway and Shimmield, 2002). Sediments have been used frequently in the initial phase of environmental assessment to locate areas of possible concern and trace historical changes because they give an integrated picture of contaminants over time.

Contamination of trace metals in the environment is of major concern because of their potential toxicity and threat to ecosystems (Purves, 1985). Trace metals interact with sediment matrix through different binding mechanisms, including adsorbed to mineral surfaces, associated with carbonates, Fe/Mn oxyhydroxides, organic matter, sulfides and the lattice of refractory crystalline minerals, such as silicates (Das et al., 1995; Tack and Verloo, 1995; Gleyzes et al., 2002; Sahuquillo et al., 2003). The mobility

of trace metals in sediments is environmentally dependent on and controlled by several factors: the sediment type on the basis of the parameters that affect metal interaction, basically pH, cationic exchange capacity, nutrient status, carbonates and organic matter contents, redox potential and texture; the nature of the contamination in terms of origin and characteristics of deposition and composition; the environmental conditions that may lead to weathering, such as acidification, redox processes, temperature and water regime (Sahuquillo et al., 2003). Therefore, besides measuring their total concentrations, determining the geochemical fractionation of trace metals in sediments is equally important in assessing their potential toxicity and threat to ecosystems (Das et al., 1995; Quevauviller, 1998; Sahuquillo et al., 2003).

Bohai Bay is the second largest bay of the Bohai Sea. Two megacities of China, namely Beijing and Tianjin, are located near the northwestern coast of Bohai Bay. With the economic boom in its surrounding areas, the ecosystem of Bohai Bay, especially in its coastal environment, has become one of the most degraded in China (SOA, 2010). An investigation focusing on the surface sediment quality was carried out in the northwestern coastal Bohai Bay in May 2008 covering its intertidal and sublittoral zones and the major rivers it connects with, and a series of papers have been published based on the results of this investigation (Wang et al., 2011; Gao and Chen, 2012; Gao et al., 2012). In this paper, the concentrations and fractionations of six trace metals (Cd, Cr, Cu, Ni, Pb and Zn) in the surface sediments of intertidal Bohai Bay are presented as a part of our investigation and assessment of the

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sediment contamination from anthropogenic sources in this area. Cd, Cr, Cu, Ni, Pb and Zn were studied because they are usually used as environmental quality criteria.

A total of 15 sediment samples collected from five locations in Bohai Bay intertidal zone in May 2008 were used in this study (Fig. 1). At each location, sampling started at the time when the tide was at its lowest in the daytime of that day; beginning from the vicinity of low tide line, three samples were collected at the lower intertidal zone, middle intertidal zone and upper intertidal zone, respectively. Undisturbed top 5–10 cm sediments were sampled and placed in acid-rinsed polyethylene zipper bags using a plastic spatula. The samples from lower intertidal zone were labeled with A1, B1, C1, D1, F1, the samples from middle intertidal zone were labeled with A2, B2, C2, D2, F2 and the samples from upper intertidal zone were labeled with A3, B3, C3, D3, F3. All samples were stored at ~4 °C in the dark until further analysis.

The sequential extraction procedure reported by Rauret et al. (1999) was used to obtain the information about the fractionations of metals. This scheme partitions elements into four operationally-defined geochemical fractions including: acid soluble, reducible, oxidisable and residual. The detailed sequential extraction protocol used in this study has been described elsewhere (Gao et al., 2008, 2010).

It has been reported that sample drying could alter the solid phase distribution of trace elements (Rapin et al., 1986; Hjorth, 2004). Furthermore, the elemental concentrations in sediments are highly dependent on the grain size (Horowitz and Elrick, 1988; Howari and Banat, 2001); a triturating treatment could potentially alter the extractability of elements (e.g. Gilliam and Richter, 1988). So, wet and unground sediments were used for the sequential extraction procedure in this study to reduce errors.

The mixture of concentrated HF, HNO_3 and $HClO_4$ (5:2:1; Li et al., 2000) was used to digest all the remaining metals in the residues instead of the so-called pseudototal digestion with aqua regia used by Rauret et al. (1999). The total digestion of three randomly selected samples was performed by the same method used to get the metal contents in the residual fraction. The total contents of metals in sediments were estimated by summing up the results of the four fractions, and they account for 89–107% of the values in the total digestion experiment.

Inductively coupled plasma-mass spectrometry (Thermo X Series II) was applied in this work for the determination of Cd, Cr, Cu, Pb, Ni and Zn. In addition, the concentration of Al was analyzed by inductively coupled plasma-atomic emission spectrometry (Thermo IRIS Intrepid II) to calculate the enrichment factor for each element. The Chinese national geostandard samples of GSS-1 and GSS-8 from National Research Center for Certified Reference Materials, China were used to control the analytical quality. The results were consistent with the reference values, and the differences were all within 10%. All plasticware and glassware were precleaned by soaking in 10% HNO_3 (v/v) for at least 2 days, followed by soaking and rinsing with de-ionized water. All chemicals used in the experiment were guaranteed reagent grade. Blank determinations were carried out for each set of analysis using the same reagents. All data were corrected for dry weight of the sample.

The water content of sediments was determined gravimetrically by comparing the weight difference before and after heating an aliquot at 105 °C until constant weight. The percentages of water were used to convert substance content of sediment from wet to dry weight base. The total organic carbon (TOC) in sediments was obtained by subtracting the inorganic carbon from the total carbon, which was determined by a Shimadzu TOC-V_{CPH}/SSM-5000A and Elementar vario MACRO cube CHNS analyzer, respectively. The precision of the measurements was within 5% based on replicate sediment analyses. The sample granulometry was analyzed using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 µm. The percentages of the following three groups of grain sizes were determined: <4 µm (clay), 4–63 µm (silt), and >63 µm (sand).

Grain size distribution and TOC content are two important factors that greatly influence the geochemical behaviors of trace metals in sediments.

The ternary diagram in Fig. 2 categorizes the sediments of intertidal Bohai Bay according to the classification of Shepard (1954). It shows that the sediment texture of intertidal Bohai Bay has a very clear spatial distribution pattern. The sediments from the northern two sampling locations are dominated by clayey silt. Except for the two samples from the upper intertidal zone of sites A and B, namely samples A3 and B3, the sediments from the southern three sampling locations are dominated by sand and silty sand; samples A3 and B3 are silt and sandy silt, respectively. Considering that the geochemical behavior of metals in sample A3 is similar to that in clayey silt sediments and their behavior in sample B3 is similar to that in sand and silty sand sediments, which will be discussed in detail below, clayey silt sediments refer to the samples from the northern two sampling locations and B3, and sand and silty sand sediments refer to the rest of samples hereafter to keep it simple in this study. The average clay, silt and sand contents in
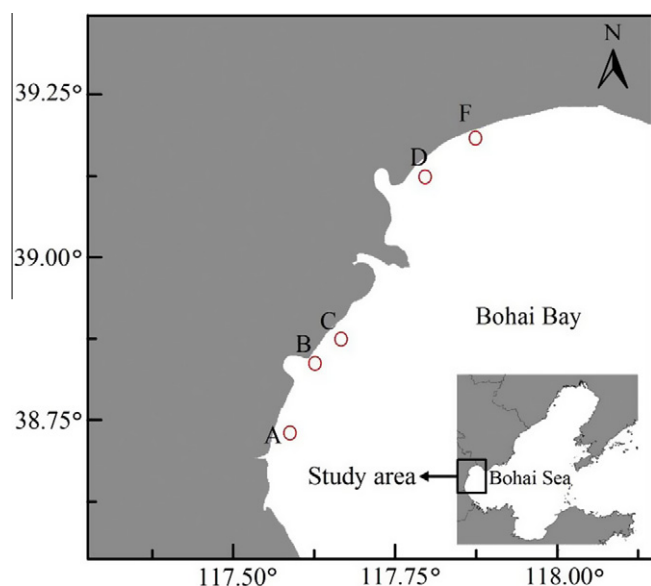

Fig. 1. Location of sampling sites in the intertidal zone of Bohai Bay.
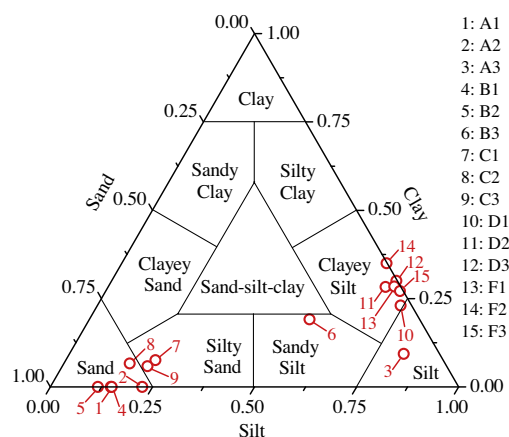

Fig. 2. The ternary diagram showing the Shepard's classification and the sediment deposition patterns.

sand and silty sand samples are 4.9%, 22.1% and 73.0%, respectively; the average percentages of clay, silt and sand components in clayey silt samples are 25.9%, 71.5% and 2.6%, respectively. Except for samples A3 and B3, the grain size distribution is very similar among clayey silt sediments or among sand and silty sand sediments (Fig. 2), and this can also be reflected by their very similar values of median particle size (D50; Fig. 3).

As shown in Fig. 3, TOC contents in sediments with coarser components are notably lower. TOC contents in sand and silty sand sediments vary between 0.25% and 0.75% of the dry sediment weight with an average of 0.41%; TOC contents in clayey silt sediments vary between 0.85% and 1.60% of the dry sediment weight with an average of 1.22%. For the three samples collected at each site, the highest TOC contents are recorded at the upper intertidal zone for sites A and B, and they are recorded at the middle intertidal zone for the other three sites.

The range and mean concentrations of metals studied in surface sediments of intertidal Bohai Bay were summarized in Table 1. The average upper continental crust (UCC) values and related values reported for surface sediments from some of the other coastal areas of China were also shown for comparison. The intertidal Bohai Bay falls in the low end of the mean concentrations of the six trace metals studied in surface sediments of the coastal areas of China that were listed in Table 1. Except for Cr, the mean concentration of which is apparently higher than that in UCC, the mean concentrations of the other elements in surface sediments of intertidal Bohai Bay are comparable to their corresponding values in UCC. As shown in Fig. 4, for all the metals studied, their total concentrations in sand and silty sand sediments are much lower than in clayey silt sediments. On average, their total concentrations in sand and silty sand sediments are 0.08, 43.6, 9.7, 15.3, 19.9 and 39.5 $\mu g\,g^{-1}$ for Cd, Cr, Cu, Ni, Pb and Zn, respectively, and the corresponding values in clayey silt sediments are 0.17, 97.3, 40.5, 42.5, 32.2 and 111 $\mu g\,g^{-1}$, respectively. For each metal except Cd, its total concentrations in clayey silt sediments or in sand and silty sand sediments are very similar, and its coefficient of variation is usually <10%.

The correlation matrix for trace metals, grain sizes and TOC is shown in Table 2. The balance between waste discharge and current dispersal of fine sediments is a critical determinant of pollution (Owen and Sandhu, 2000). The data in Table 2 show that, with no exception, all metals are significantly correlated, which suggests a major common origin in sediments from non-point sources. The results also show that the concentrations of metals are positively and highly correlated with silt and clay contents while they are negatively correlated with sand contents.

Organic matter has long been found playing an important role in controlling the physicochemical behaviors of metals at solid–water interface (e.g. Davis, 1984; Stumm, 1992; Schmitt et al., 2002), and then has a significant influence on the bioavailability, reactivity and mobility of metals in sediments. In this study, the

percentage of metals in the oxidizable fraction, which represents the metals bound to organic matter and sulfides in sediment, is small referring to Fig. 4, so although TOC shows a significant correlation with all the metals studied (Table 2), it might not be a major factor affecting the spatial distribution of metals in surface sediments of intertidal Bohai Bay. It is more likely that the distribution of TOC in surface sediments of this area itself is governed by sediment grain size based on the significant correlation between it and the three grain size components, i.e. clay, silt and sand ($P < 0.001$; not shown).

The percentage of each metal in different extracted fractions is also shown in Fig. 4. The studied metals take on different fractionation patterns. On average, all the studied elements except Cd are dominated by residual fraction, the mean value of which is 31.5%, 92.3%, 69.5%, 74.6%, 56.7% and 77.6% of its mean total concentration for Cd, Cr, Cu, Ni, Pb and Zn, respectively. For Cd, acid soluble fraction is the most abundant form averagely accounting for 39.0% of its mean total concentration, and the percentages of it in reducible and oxidizable fractions are almost equal. The percentage of Cr in acid soluble fraction is negligible. Reducible fraction is the most abundant fraction of non-residual Cu, Pb and Zn. For Cr and Ni, oxidizable fraction is the dominant form of non-residual fractions; the average percentages of metals in this fraction follow the order of Cd (14.7%) > Ni (12.1%) > Cu (5.9%) > Zn (5.6%) > Cr (4.9%) > Pb (3.0%). It has been considered that the metals in extractable fractions, namely non-residual fractions, are more or less available to aquatic biota and may correlate with their concentrations in microorganisms (e.g. Batley, 1987; Bourgoin et al., 1991). The high proportion of Cr, Cu, Ni, Pb and Zn in residual fraction indicates that they have a minor potential threat to biota.

Fig. 4 also indicates that the fractionation pattern of most studied metals shows a significant spatial variation. For example, no acid soluble Cd and Ni is measured in the sample from the upper intertidal zone of sampling site B, namely sample B3, whereas this fraction of Cd and Ni is found in all the rest samples and up to 53.7% of Cd and 7.4% of Ni are in this fraction in sample B2, the one from the middle intertidal zone of the same sampling site like sample B3. It is notable that, except for Cr and Ni, the fractionation of metals in the two types of sediments shows different distribution characteristics (Fig. 4). The average percentage of Cu and Zn in acid soluble fraction is clearly higher in sand and silty sand sediments than in clayey silt sediments. The average percentages of Cd, Cu, Pb and Zn in reducible fraction are higher in clayey silt sediments than in sand and silty sand samples. Unlike that of Cr, Cu, Ni and Zn, the average percentage of which in residual fraction in the two types of sediments is very similar, the average percentage of residual Cd and Pb is more abundant in coarser sediments; in other words, these two metals in fine sediments are more mobile.

Metals are natural components of the Earth's crust and many of them serve as micronutrients that are essential for healthy organisms. Only when their contents exceed certain values could metals become contaminants to the environments. During the past decades, many sediment quality guidelines (SQGs) have been developed to deal with environmental concerns and in response to regulatory programs (Allen Burton, 2002). The most basic and widely used way to determine sediment contamination is by assessing the bulk chemical concentrations of individual compounds and comparing them with background or reference values (e.g. Van Veen and Stroetelder, 1988; Lau et al., 1993; Long et al., 1995, 1998; MacDonald et al., 1996).

All the studied metals except Ni in this research are indicators for marine sediment quality classification in the National Standard of China GB18668-2002 (Table 3; SEPA, 2002). This standard has defined three grades of marine sediments based on the concentrations of some metals, metalloids and organic compounds. The first class quality (Class I) of sediment is suitable for mariculture, nature
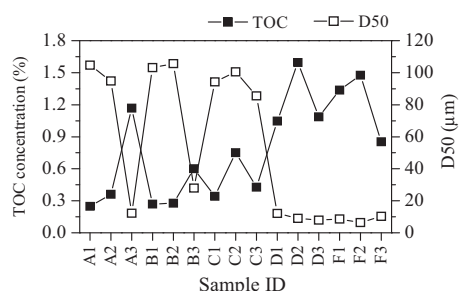

Fig. 3. The spatial distribution of TOC concentration in surface sediments of intertidal Bohai Bay.

Table 1
The summary of trace metal contents in surface sediments of intertidal Bohai Bay. The average upper continental crust values and related values reported for surface sediments from some of the other coastal areas of China were also shown for comparison purpose. Content unit is µg g^{-1} dry weight for all elements.

| Location		Cd	Cr	Cu	Ni	Pb	Zn	References
Intertidal Bohai Bay, China	Range	0.05–0.19	36.7–110	7.9–46.7	14.1–47.9	18.8–39.1	34.0–123	This study
	Mean	0.12	68.6	24.0	28.0	25.6	73.0	
Coastal Bohai Bay, China	Range	0.12–0.66	60.1–225	20.1–62.9	23.4–52.7	20.9–66.4	55.3–457	Gao and Chen (2012)
	Mean	0.22	101	38.5	40.7	34.7	131	
Coastal Liaodong Bay and north coast of northern Yellow Sea, China	Range	0.05–0.83	4.2–94	0.53–35	NA[a]	9.5–49	9.8–170	Luo et al. (2010)
	Mean	0.15	47	13	NA	25	60	
Intertidal Changjiang Estuary, China	Range	0.12–0.75	36.9–173	6.9–49.7	17.6–48.0	18.3–44.1	47.6–154	Zhang et al. (2009)
	Mean	0.26	78.9	30.7	31.8	27.3	94.3	
Coast off southwestern Taiwan	Range	0.22–1.20	56–96	14–57	26–40	21–53	85–244	Chen and Selvaraj (2008)
	Mean	0.56	73	32	35	44	158	
Daya Bay, China	Range	0.03–0.11	NA	15.7–28.2	27.7–35.5	35.4–54.6	95.6–140	Gao et al. (2010)
	Mean	0.05	NA	20.8	31.2	45.7	113	
Upper continental crust		0.098	35	25	20	20	71	Taylor and McLennan (1995)

[a] NA: not available.
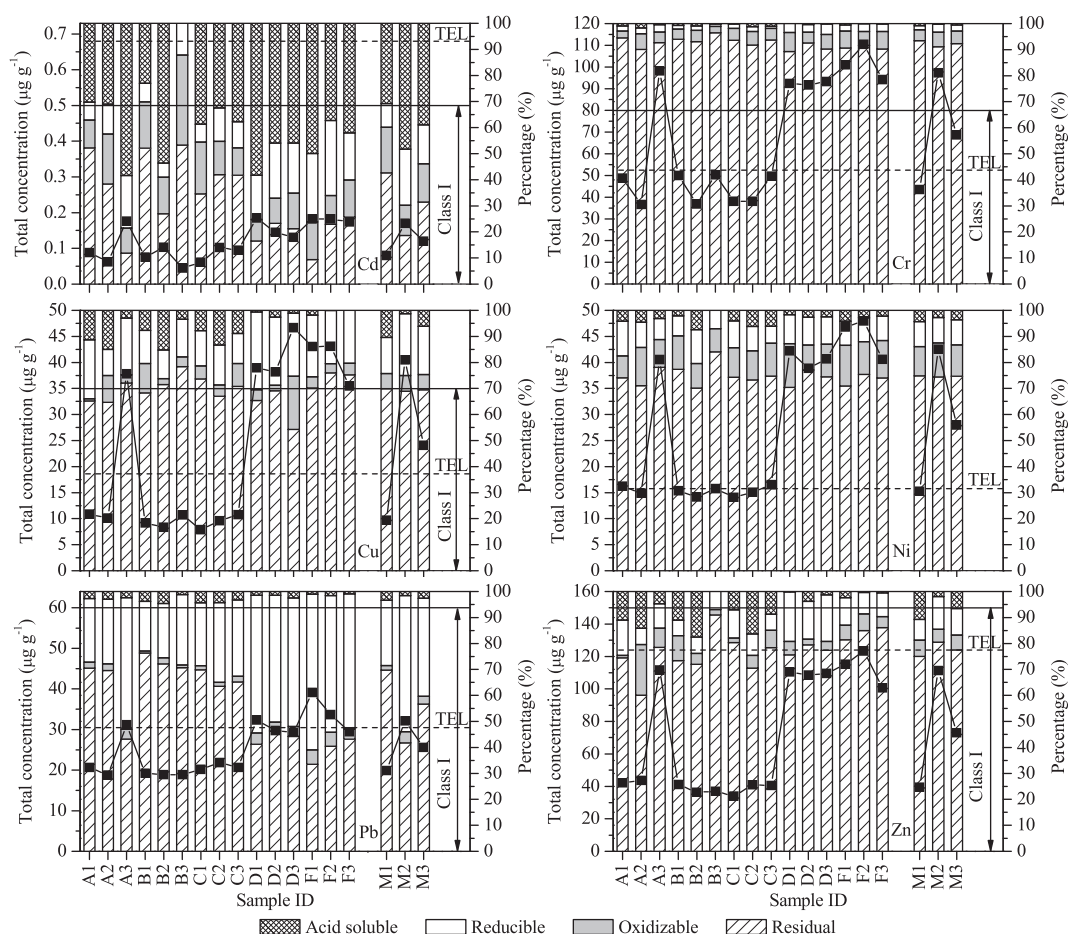
Fig. 4. The spatial variations of each studied trace metal in total concentrations and their distributions in different geochemical phases of surface sediments from intertidal Bohai Bay. M1, M2 and M3 represent the mean values calculated based on the data for sand and silty sand sediments (samples A1, A2, B1, B2, B3, C1, C2 and C3), clayey silt sediments (samples A3, D1, D2, D3, F1, F2 and F3) and all sediments, respectively. The horizontal dash and solid lines represent their corresponding TEL concentrations and the higher boundary values of Class I sediment category of China, respectively.

reserve, endangered species reserve, and leisure activities such as swimming; the second class quality (Class II) can be used for industry and tourism site; and the third class (Class III) can just be used for harbor. The results indicate that the concentrations of Cd, Pb and Zn fall into Class I sediment category for all samples (Fig. 4). For the sediment from upper intertidal zone of sampling location A (i.e. sample A3) and all the sediments from sampling location

D and F, the concentrations of Cr and Cu fall into Class II sediment category, while their concentrations fall into Class I sediment category for the other sediments (Fig. 4).

Threshold effects level (TEL) and probable effects level (PEL) concentrations for some substances with potential environmental risks were derived to aid in the interpretation of sediment chemistry data (MacDonald et al., 1996). Generally, the TELs have been

Table 2

Pearson correlation matrix for the sediment components. The total concentrations of metals were used in the data analysis. All values are significant at $P < 0.01$.

Variables	Cd	Cr	Cu	Ni	Pb	Zn	%Clay	%Silt	%Sand	%TOC
Cd	1.00	0.90	0.88	0.93	0.93	0.92	0.68	0.78	−0.77	0.80
Cr		1.00	0.97	0.99	0.94	0.98	0.85	0.92	−0.93	0.89
Cu			1.00	0.99	0.94	0.99	0.86	0.91	−0.93	0.90
Ni				1.00	0.97	0.99	0.86	0.91	−0.93	0.90
Pb					1.00	0.95	0.80	0.85	−0.86	0.89
Zn						1.00	0.83	0.91	−0.92	0.91

Table 3

The metal guideline values of some different criteria used to distinguish marine sediment quality ($\mu g\, g^{-1}$).

	Cd	Cr	Cu	Ni	Pb	Zn	References
Class I	0.5	80	35		60	150	SEPA (2002)
Class II	1.5	150	100		130	350	SEPA (2002)
Class III	5	270	200		250	600	SEPA (2002)
TEL[a]	0.68	52.3	18.7	15.9	30.2	124	MacDonald et al. (1996)
PEL[b]	4.21	160	108	42.8	112	271	MacDonald et al. (1996)

[a] TEL (Threshold Effect Level) guideline values indicate concentrations below which adverse effects on biota are rarely observed.
[b] PEL (Probable Effects Level) guideline values indicate concentrations above which adverse effects on biota are frequently observed.

used to identify relatively uncontaminated samples that pose a limited risk of toxicity; the PELs have been used to identify those samples in which chemical concentrations were sufficiently elevated to warrant further evaluation (Long et al., 1998).

According to this criterion, the concentrations of Cd in all samples and Cu, Pb and Zn in sand and silty sand sediments are far below their corresponding TEL values; the concentrations of Cr and Ni in sand and silty sand sediments and Pb and Zn in clayey silt sediments are close to their corresponding TEL values (Fig. 4 and Table 3). For Cr, Cu and Ni in clayey silt sediments, their concentrations are apparently higher than their corresponding TEL values but far below their corresponding PEL concentrations (Fig. 4 and Table 3). In other words, the concentrations of Cd and Zn in all sediments, Cr, Cu and Pb in all sand and silty sand sediments and Ni in six of the eight sand and silty sand sediments could be regarded as relatively uncontaminated samples that pose a limited risk of toxicity.

Although background/reference comparisons do give a base to evaluate SQGs and are important in environmental studies, they provide little insight into the potential ecological impact of contaminants.

Based on the fact that trace metals always occur in sediments as complex mixtures, the mean PEL quotient method has been applied to determine the possible biological effect of combined toxicant groups by calculating mean quotients for a large range of contaminants using the following formula (Long et al., 1998, 2000; Long and MacDonald, 1998; Hyland et al., 2003):

$$\text{mean PEL quotient} = \sum (C_X/PEL_X)/n$$

where C_x is the sediment concentration of component x, PEL_x is the PEL for compound x and n is the number of components. Based on the analyses of matching chemical and toxicity data from over 1000 sediment samples from the USA estuaries, the mean PEL quotients of <0.1 have a 8% probability of being toxic, the mean PEL quotients of 0.11–1.5 have a 21% probability of being toxic, the mean PEL quotients of 1.51–2.3 have a 49% probability of being toxic, and the mean PEL quotients of >2.3 have a 73% probability of being toxic (Long et al., 2000).

As shown in Fig. 5, in surface sediments of the intertidal Bohai Bay, the mean PEL quotients vary within the range of 0.16–0.50 (mean 0.31) indicating that the combination of the six studied metals may have a 21% probability of being toxic. Qualitatively, clayey silt sediments have distinctly higher mean PEL quotients,
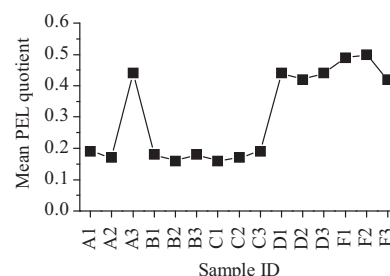

Fig. 5. The spatial distribution of mean PEL quotient values in surface sediments of intertidal Bohai Bay.

which on average is more than twice as that of sand and silty sand sediments.

The concentrations of elements in sediments should be explained by natural sources if there were no anthropogenic disturbances. However, composition of sediment could be modified by contributions from various anthropogenic sources. The degree of these modifications of sediment chemical compositions may be different from area to area due to different magnitudes of source contributions. Normalization is a technique frequently used to separate the metals of natural variability from the fraction that is associated with sediments due to human activities. A range of geochemical data normalization methods can be used to compensate for the influence of the natural variability in sediment mineralogical composition, and identify anomalous metal concentrations (e.g. Loring and Rantala, 1992; Kersten and Smedes, 2002).

A simple approach to normalize geochemical data is to compare the total metal concentration of target sediment with the corresponding natural background level as reference. The index of geoaccumulation (I_{geo}) proposed by Müller (1969), which has been widely applied to the assessment of soil and sediment contamination (e.g. Santos Bermejo et al., 2003; Loska et al., 2004), is representative of such normalization technique:

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

where C_n is the measured concentration of a given metal in sediment and B_n represents the geochemical background concentration of it. In this study, the concentrations of elements in UCC (Taylor and McLennan, 1995) were used as background values. The factor

Table 4
Geoaccumulation index in relation to pollution extent (Müller, 1969).

I_{geo} value	Pollution intensity
<0	Unpolluted
0–1	Unpolluted to moderately polluted
1–2	Moderately polluted
2–3	Moderately to strongly polluted
3–4	Strongly polluted
4–5	Strongly to very strongly polluted
>5	Very strongly polluted

1.5 is introduced to take into consideration possible differences in the background values due to lithological variation. The I_{geo} defines seven classes of sediment quality to assess the degree of metal pollution (Table 4). $I_{geo} < 0$ indicates an unpolluted state of sediment, and $I_{geo} > 5$ indicates a more than 50-fold enrichment above background value that corresponds to a very strongly polluted state.

The spatial distributions of I_{geo} values for trace metals in surface sediments of intertidal Bohai Bay are shown in Fig. 6. All the metals studied take on a clear and similar distribution pattern that clayey silt samples have notable higher I_{geo} values than those of sand and silty sand samples. The difference of I_{geo} values among clayey silt samples or sand/silty sand samples is insignificant except for Cd.

According to Müller's classification (Müller, 1969), the I_{geo} of studied metals in all samples from sites A, B and C except the one from the upper intertidal zone of site A (sample A3) present values falling into the unpolluted class, and the I_{geo} values of studied metals in the other samples fall into unpolluted to moderately polluted class. On average, the order of I_{geo} values in sand and silty sand samples is Cr (−0.29) > Pb (−0.60) > Cd (−0.95) > Ni (−0.98) > Zn (−1.44) > Cu (−1.96), and the order of I_{geo} values in clayey silt samples is Cr (0.89) > Ni (0.50) > Cd (0.18) > Cu (0.11) > Pb (0.09) > Zn (0.06), which shows that in all samples Cr is more accumulated than the other five studied metals.

Besides introducing a background value, some relative complex normalization approaches introduce a conservative element to compensate for the effect of sediment mineralogical variation. Technically, the parameter suitable for this purpose needs to be the textural characteristic or component of sediments. Among all the proxies used for normalization, Al is a more popular one than the others, since it represents the quantity of aluminosilicates which is generally the predominant carrier phase for metals in coastal sediments (Alexander et al., 1993). Enrichment factor (EF) is one of the normalization techniques of this kind most often used to separate the metals of natural variability from the metal fraction that is associated with anthropogenic activities. The EF for each metal studied in this research was calculated to evaluate
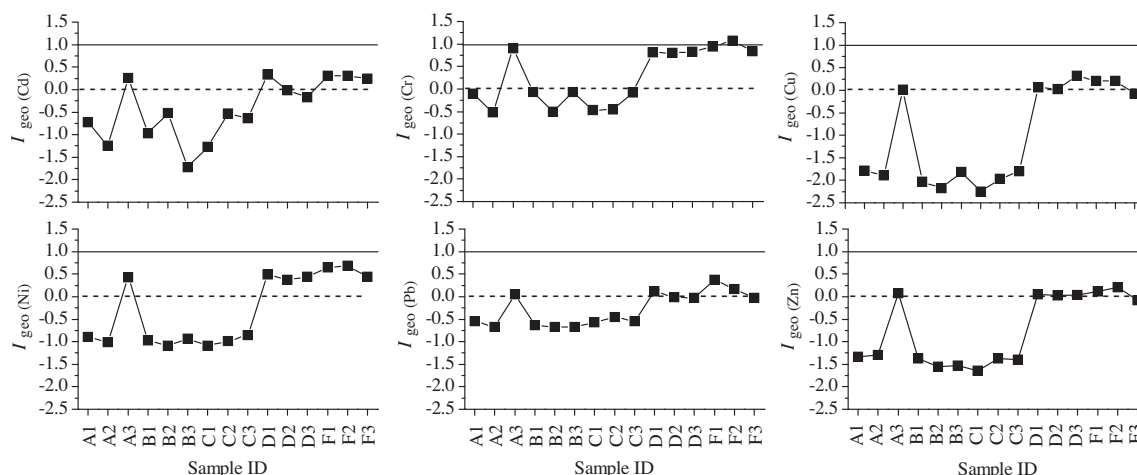

Fig. 6. The spatial distributions of I_{geo} values for trace metals in surface sediments of intertidal Bohai Bay. The horizontal dash and solid lines represent I_{geo} value of 0 and 1, respectively.
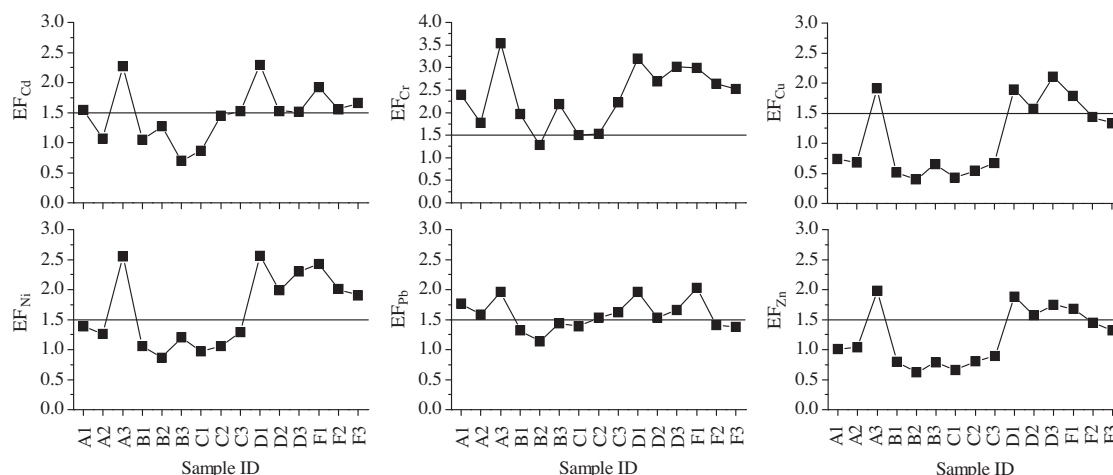

Fig. 7. The spatial distributions of EF values for trace metals in surface sediments of intertidal Bohai Bay. The horizontal lines represent EF value of 1.5.

anthropogenic influences on trace metals in sediments using the following formula (Selvaraj et al., 2004):

$$EF = (C_X/C_{Al})_S/(C_X/C_{Al})_{UCC}$$

where C_x and C_{Al} denote the concentration of element x and Al in the sample of interest (S) and the UCC (Taylor and McLennan, 1995).

Generally, an EF value of about 1 suggests that a given metal may be entirely from crustal materials or natural weathering processes (Zhang and Liu, 2002). Nevertheless, a slight positive deviation of EF value from unity may not arise from anthropogenic activities, for the natural difference in elemental composition between a pristine sediment and the reference Earth's crust used in EF calculation could also cause it. An EF value of >1.5 suggests that a significant portion of metal is delivered from non-crustal materials, or non-natural weathering processes, so anthropogenic sources may become an important contributor (Feng et al., 2004).

As shown in Fig. 7, like those of their total concentrations and I_{geo} values, the EF values of Cu, Ni and Zn show a similar spatial distribution pattern that they are obviously lower in sand and silty sand samples than in clayey silt samples. The EF of Cr in most samples is higher than 1.5, which is the threshold value for distinguishing the accumulation of anthropogenic inputs, with the highest value of 3.54 being recorded in sample A3. The EF values of Cd, Cu, Ni and Zn in most of sand and silty sand samples are <1.5 indicating the dominantly natural origin of these metals, and they vary within the range of ~1.5–2 in most of the rest samples indicating the minimal enrichment of these metals. The difference of EF values of Pb between the sediments with different granularity is not as apparent as that of the other metals. On average, the order of EF values in clayey silt sediments descends in the sequence of Cr (2.84) > Ni (2.20) > Cd (1.74) > Cu (1.69) > Pb (1.66) > Zn (1.61), and the order of EF values in sand and silty sand samples is Cr (2.04) > Pb (1.53) > Cd (1.30) > Ni (1.29) > Zn (0.96) > Cu (0.73). The EF values further strengthen the indication of I_{geo} that the surface sediments of intertidal Bohai Bay have anthropogenic inputs of Cr.

In summary, although the trace metal concentrations of Bohai Bay intertidal sediments presently are unlikely to have a significant impact on this ecosystem, with the rapid economic development and urbanization around Bohai Bay, coastal management and pollution control should focus on these potential contaminants. It is recommended that sediment assessment be carried out in this region on a regular basis to determine if the metal pollution situation is deteriorating. Sources of metal contaminants should be investigated by examining activities of local industries and possible pathways from such sources to the areas of identified contamination.

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