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Heavy metal in surface sediments of the Liaodong Bay, Bohai Sea: distribution, contamination, and sources

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Abstract In an effort to assess the potential contamination and determine the environmental risks associated with heavy metals, the surface sediments in Liaodong Bay, northeast China, were systematically sampled and analyzed for the concentrations of Cu, Pb, Zn, Cr, Ni, As, and Hg. The metal enrichment factor (EF) and geoaccumulation index (I_{geo}) were calculated to assess the anthropogenic contamination in the region. Results showed that heavy metal concentrations in the sediments generally met the criteria of China Marine Sediment Quality (GB18668-2002); however, both EF and I_{geo} values suggested the elevation of Pb concentration in the region. Based on the effect-range classification (TEL-PEL SQGs), Cu, Pb, Ni, and As were likely to pose environment risks, and the toxic units decreased in the order: Ni>Pb>Cr>Zn>As>Cu>Hg. The spatial distribution of ecotoxicological index (mean-ERM-quotient) suggested that most of the surface sediments were "low–medium" priority zone. Multivariate analysis indicated that the sources of Cr, Ni, Zn, Cu, and Hg resulted primarily from parent rocks, and Pb or As were mainly attributed to anthropogenic sources. The results of this study would provide a useful aid for sustainable marine management in the region.

Keywords Heavy metals · Sediment contamination · Environmental assessment · Sediment quality guidelines · Liaodong Bay

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Introduction

In the past decades, a rapid industrialization and economic development in China, especially in the coastal areas, has resulted in severe environmental pollutions. Toxic chemicals such as heavy metals that were released to aquatic ecosystems and marine environment have been identified as a threat to human health, wildlife habitats, and ecosystems (Pan and Wang 2012). As a natural sink of environmental pollutants, marine sediments are vulnerable and sensitive to environmental pollution, which can be used as an indicator for potential environmental contamination (Adams et al. 1992). Heavy metal pollution in aquatic environment has recently attracted much public concerns, due to their toxicity, persistence, and bioaccumulation in ecosystems

(Pekey 2006; Sundaray et al. 2011; Tessier et al. 2011; Varol 2011; Liu et al. 2011a, b; Wu et al. 2012; Gao and Chen 2012; Feng et al. 2011).

Liaodong Bay located in the northwest of Bohai Sea, northeast China, is an outlet of several large rivers in the region, including Daliao, Liao, Shuangtaizi, Daling, Luan, and Daqing Rivers (Fig. 1). It was estimated that a total of 6.9×10^4 tons of toxic chemicals in 2009 had been discharged into the Liaodong Bay from Daliao, Shuangtaizi, and Daling Rivers, which had accounted for about 56 % of the annual Pb flux to the Bohai Sea alone (Zhang 2001). Although previous studies indicated that there was an elevation of heavy metals in Liaodong Bay in last 20 years (Liu et al. 2011a, b; Xu et al. 2009), the data were only available in the river outlets and/or estuary areas and thus lack spatial resolution (Hu et al. 2010; Luo et al. 2010; Wang et al. 2010a, b; Wu et al. 2012; Zheng et al. 2008; Meng et al. 2008; Li et al. 2012), which would limit our understanding of the transport or fate of such contaminants and their potential adverse environmental impacts.

This field study is to address the identified research gaps that would provide valuable information of the spatial distribution of the selected heavy metals in Liaodong Bay. Objectives were to: (1) examine the spatial variations of heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg) in the surface sediments of Liaodong Bay; (2) assess the metal contaminations using the enrichment factor (EF) and geoaccumulation index (I_{geo}); (3) evaluate the potential adverse biological impacts by Sediment Quality Guidelines (SQGs); and (4) identify the possible sources of the heavy metals with multivariate analyses.

Materials and methods

Study area and sample collection

The study area, Liaodong Bay, is one of the three bays forming Bohai Sea in northeast China (Fig. 1), which is the outlet of Daliao, Daling, Xiaoling, Shuantaizhi, Daqing, Liugu, and Gou Rivers. The watershed is located within the heavily industrial region in northeast China, which includes mining, metal smelting, petroleum refinery, and chemical industries. The wastewaters generated by the industries were directly discharged into the rivers and flowed into Liaodong Bay (Xu et al. 2009).

A total of 128 samples were systematically collected from the surface sediments (0–2 cm depth) in the bay area following a grid indicated in Fig. 1 and using a grab sampler during a survey cruise in 2009. Each sample was divided into four subsamples and then frozen on board prior to analyses.

Analytical methods

Prior to particle size analyses, the fresh subsamples were pre-treated with 10 % H_2O_2 and 1 N HCl for 24 h to remove organic matter and biogenic carbonate. The particle size analyses were performed using a Mastersizer-2000 laser particle size analyzer, with a size range of 0.02 to 2,000 μm at a resolution of 0.01 φ.

About 20 g of the subsamples were oven-dried at 45 °C for 24 h, then ground to pass a 0.25-mm sieve and stored in clean plastic bags at room temperature prior to analyses. An X-ray fluorescence spectrometer (XRF, Axios PW4400) was used for determining Al, Fe, Mn, Cu, Pb, and Zn, inductively coupled plasma mass spectrometry (ICP-MS, Thermo X series) for Cr and Ni, and atomic fluorescence spectrometer (AFS-920) for As and Hg. Total organic carbon (TOC) was measured by an elemental analyzer (Vario EL-III). Blanks and China Stream Sediment Reference Materials (GBW07345, GSD9, and GSD4) were included in the analyses for data QA/QC (Table 1). Replicated samples were measured with a variation of <10 %.

Ecological risk assessment approaches

Enrichment factor

The metal enrichment factor (EF) is commonly used to estimate the metal sources and contamination level in river, estuarine, and coastal environments. For data normalization purpose, the sample metal concentrations were initially normalized by conservative elements such as Al, Fe, Co, Sc, etc. in order to alleviate the constituent variability produced by granulometric divergence. In this study, we defined the EF as the sample metal (Me) to aluminum (Al) ratio divided by the baseline metal/Al ratio, and expressed as:

$$EF = \frac{\left(\frac{Me}{Al}\right)_{sample}}{\left(\frac{Me}{Al}\right)_{baseline}} \qquad (1)$$

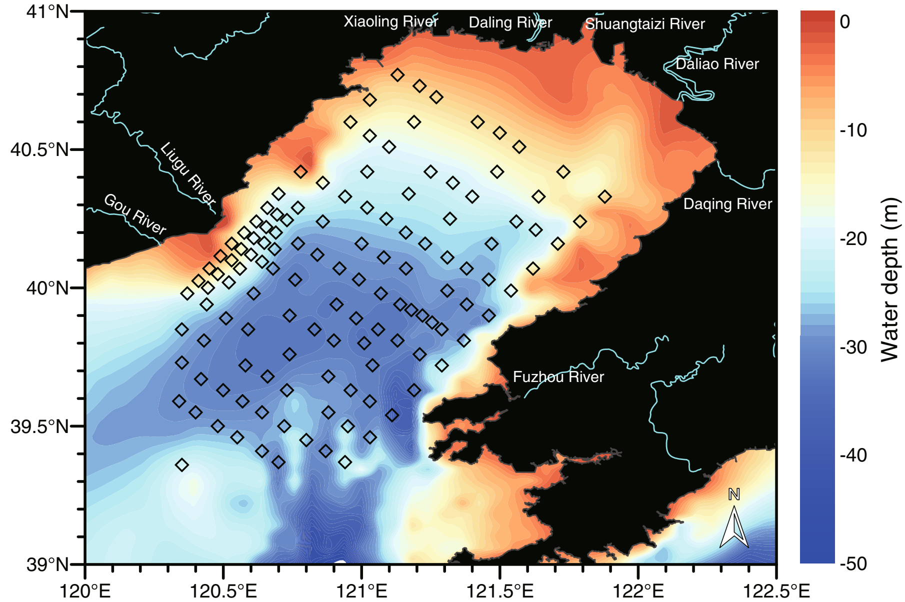

Fig. 1 Geographic location of the study area and the sampling sites.

The background metal values can be estimated based on the average crustal abundance data (Taylor 1972; Taylor and McLennan 1995) or the average shale values (Turekian and Wedepohl 1961). However, Rubio et al (2000) and Christophoridis et al. (2009) suggested that the regional background values might be more appropriate. In this study, the crustal average metal concentrations in eastern China (Gao et al. 1998) were used as the background metal values shown in (Table 2).

Geoaccumulation index

The geoaccumulation index that was originally introduced by Müller (1979) is another parameter to assess the potential of metal contamination. The I_{geo} values are defined by the formula below:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \quad (2)$$

where C_n is the concentration of metal (n) and B_n is the geochemical background concentration of metal (n). The factor of 1.5 is a background matrix correction factor that includes possible variations of the background values due to lithogenic effects (Müller 1979). The background values are the same to those used in the enrichment factor. The geoaccumulation index ranges from class 0 ($I_{geo} \leq 0$, unpolluted) to class 6 ($I_{geo} > 5$, extremely polluted, at least 100-fold enrichment above background) as defined by Müller (1981).

Table 1 Results (mean±standard deviation) obtained from certified reference materials analysis

	Certified value (mg/kg)	Measured value (mg/kg)	Reference materials
Cu	15±3.8	15.9±0.3	GWB07345 (*n*=6)
Pb	28±6.3	32.7±0.7	
Zn	45±9.4	45.8±1.9	
Cr	85±15.8	82.5±2.6	GSD-9 (*n*=10)
Ni	32±7.0	31.0±0.3	
As	19.7±4.7	19.5±1.1	GSD-4 (*n*=6)
Hg	0.044±0.013	0.047±0.001	

Sediment quality guidelines

Numerous sediment quality guidelines have been established to evaluate the contaminant toxicity or risks to aquatic ecosystems (Macdonald et al. 1996; MacDonald et al. 2000; Long et al. 2006). The most widely used SQGs for marine assessment were established by the National Oceanic and Atmospheric Administration (NOAA) (Long et al. 1995). Two sets of sediment quality guidelines such as threshold effects level (TEL) and probable effects level (PEL), or effects range low (ERL) and effects range medium (ERM) were proposed to determine whether the metals

Table 2 Summary of heavy metal concentrations in surface sediments of the Liaodong Bay (unit: $mg kg^{-1}$)

Locations		Cr	Cu	Ni	Pb	Zn	As	Hg	References
Liaodong Bay, China	Range	8.00–75.8	5.7–37.1	7.0–40.5	18.9–61.2	14.5–145.0	3.1–20.3	0.00–0.40	This study
	Mean	46.4	19.4	22.5	31.8	71.7	8.3	0.04	
Jinzhou Bay, China		na	74.1	43.5	124.0	689.4	na	na	Li et al. 2012
Western Bohai Bay, China		53.1	27.9	31.4	20.5	83.6	na	na	Feng et al. 2011
Intertidal Bohai Bay, China		68.6	24.0	28.0	25.6	73.0	na	na	Gao and Li 2012
Coastal Bohai Bay, China		101.0	38.5	40.7	34.7	131.1	na	na	Gao and Chen 2012
Pearl River Estuary, China		89.0	46.2	41.7	59.3	150.1	na	na	Zhou et al. 2004
Changjiang Estuary, China		78.9	30.7	31.8	27.3	94.3	no	no	Zhang et al. 2009
West Xiamen Bay, China		75.0	44.0	37.4	50.0	139.0	na	na	Zhang et al. 2007
Izmit Bay, Turkey		74.3	67.6	na	102.0	930.0	22.1	na	Pekey 2006
Bremen Bay, Germany		131.0	87.0	60.0	122.0	790.0	na	na	Hamer and Karius 2002
Masan Bay, Korea		67.1	43.4	28.8	44.0	206.3	na	na	Hyun et al., 2007
Average crustal of East China		99	27	37	15	66	7	0.1	Gao et al. 1998
MSQ-1		80	35	na	60	150	20	0.2	CSBTS 2002
MSQ-2		150	100	na	130	350	65	0.5	CSBTS 2002
MSQ-3		270	200	na	250	600	93	1.0	CSBTS 2002

[a] MSQ-1, MSQ-2, and MSQ-3 are the Marine Sediment Quality standard criteria (GB 18668-2002) issued by the China State Bureau of Quality and Technical Supervision (CSBTS)

in sediments pose a threat to aquatic ecosystems (Long et al. 1995; Macdonald et al. 1996; MacDonald et al. 2000). In this study, we applied SQGs to assess the potential adverse biological effects by both sets above.

According to Long and MacDonald (1998), the mean-ERM-quotient (m-ERM-Q) takes into account both the number of pollutants showing concentrations higher than the respective SQGs values and the degree to which metals concentration exceed the SQGs. The m-ERM-Q can be used to assess the effects of multiple anthropogenic contaminations, as calculated below:

$$m - ERM - Q = \frac{\sum_{i=1}^{n} \left(\frac{C_i}{ERM_i}\right)}{n} \quad (3)$$

where C_i is the concentration of measured metal (i), ERM_i is the ERM values of metal (i), and n is the number of metal (i). Several classes of toxicity probability for biota were defined as: m-ERM-Q <0.1, 9 % probability of toxicity; 0.11–0.5, 21 % probability of toxicity; 0.51–1.5, 49 % probability of toxicity; and >1.51, 76 % probability of toxicity (Long and MacDonald 1998).

Statistical analysis

In order to decipher the interrelationship among heavy metals and to identify the possible sources, principal component analysis (PCA), hierarchical cluster analysis (HCA), and Pearson's correlation matrix (CM) were performed with a statistical software (SPSS 19.0 for Windows) (Gotelli and Ellison 2004). PCA is a widely used method in environmental studies, whereby a complex data set is simplified by creating several new variables or factors, each representing a cluster of interrelated variables within the dataset. Before performing PCA, Kaiser–Meyer–Olkin (KMO), and Bartlett's sphericity tests were used to examine the validity of PCA. HCA is a data classification technique and is the widely used in Earth sciences. HCA was performed on the standardized data sets (Z-cores) using

Ward's method with Euclidean distances as a measure of similarity. The classification of the samples into clusters is based on a visual observation of the dendrogram. Pearson's product CM was used to identify the relationship among the metals and confirm the results of multivariate analysis.

Kriging interpolation has been applied widely to elucidate spatial variation and distribution of many environmental parameters. It is based on the assumption that the value of unsampled location can be interpolated from a random field based on the measured values of the random field at nearby locations. Considering the evenly distribution of our sample sites, Kriging interpolation was selected to elucidate spatial variations of heavy metal concentrations and the mean ERM quotient using Surfer 10 (Golden Software, Colorado).

Results and discussion

Sediment characterization

The median grain size (Mz) of the sediments varied from 0.01 to 7.4 φ, with an average of 4.9±1.4φ. Total organic carbon had a range from 0 to 1.64 %, with an average of 0.37±0.21 %. It is well known that Mz and TOC are important factors controlling the abundance of trace metals in natural environment. Fine grain sediments tend to have relatively high metal contents, due to large specific surface area that would favor the surface adsorption and ionic attraction. Mz was found to be significantly correlated with Al or Fe concentration (Fig. 2a and b), suggesting that the Al and Fe concentrations were mainly controlled by the grain size as a result of natural weathering. A positive relationship between TOC and Mz indicated that the grain size did also affect TOC concentration (Fig. 2c).

The metal concentrations were element dependent, with a range as 4.16–7.98 % for Al, 0.91–4.7 % for Fe, 263–2,735 mg/kg for Mn, 5.7–37.1 mg/kg for Cu, 18.9–61.2 mg/kg for Pb, 14.5–145 mg/kg for Zn, 8.0–75.8 mg/kg for Cr, 7.04–40.5 mg/kg for Ni, 3.1–20.3 mg/kg for As, and 0–0.4 mg/kg for Hg (Table 2). Means of heavy metal concentrations of Liaodong Bay were comparable to or lower than those in other regions, such as Bohai and other estuary areas in China as listed in Table 2. In addition, the metal concentrations in Liaodong Bay were much lower than those found in sediments of the Izmit Bay in Turkey (Pekey 2006) and the Bremen Bay in Germany (Hamer and Karius 2002), and lower than that of Masan Bay in Korea (Hyun et al. 2007).

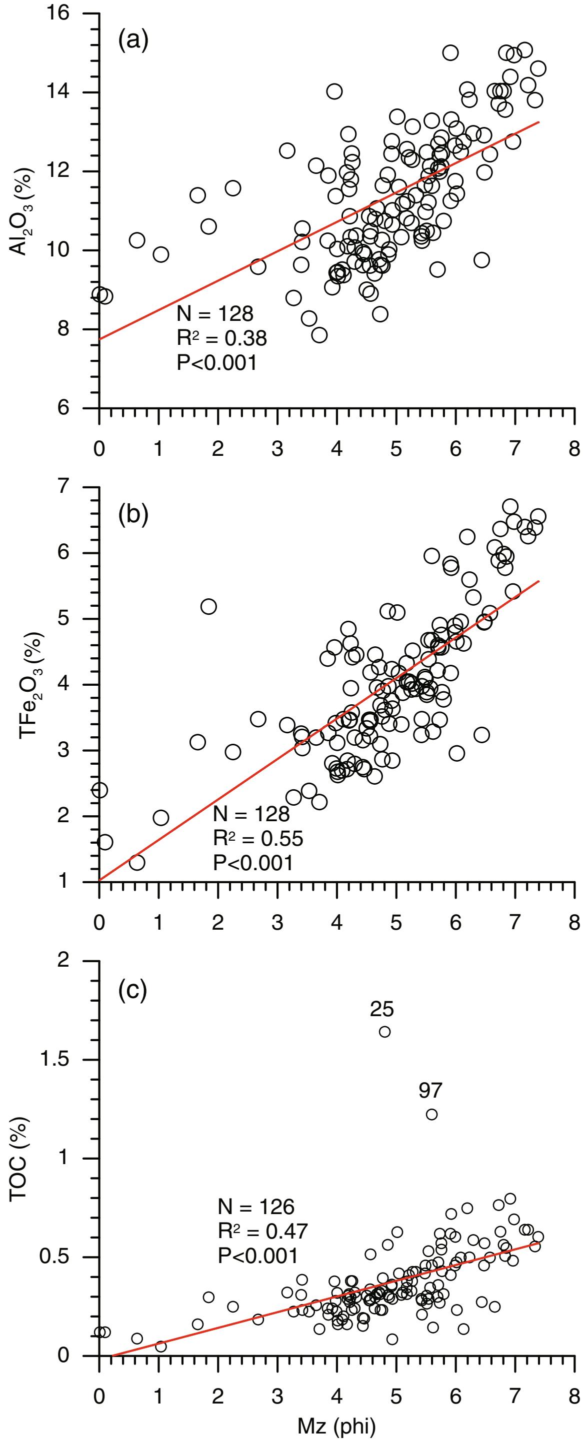

Fig. 2 Correlations of Al, Fe, and TOC with mean grain size (Mz)

Spatial distribution patterns of heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg) and TOC shown in Fig. 3 illustrated the distinctly variable concentrations zones in the Liaodong Bay. Copper, Zn, Ni, Cr, and TOC displayed a similar spatial distribution pattern in the Liaodong Bay, with higher concentration zones located in the northern and southwest areas. Significantly positive correlations between Mz and Cu, Zn, Ni, and Cr suggested that grain size is a primary factor controlling the spatial variability of Cu, Zn, Ni, and Cr. By contrast, As and Pb were higher in the offshore area of Jinzhou Bay and central area of Liaodong Bay, suggesting a different source and/or sediment behavior. Furthermore, a higher Hg concentration at the offshore area of Jinzhou Bay indicated a nearby pollution source from Jinzhou Bay (Li et al. 2012). The correlations between heavy metals and other parameters will be discussed in detail later.

Marine Sediment Quality (GB 18668-2002), established by China State Bureau of Quality and Technical Supervision (CSBTS, 2002), contains three standard criteria for marine sediments, with the primary criteria (MSQ-1) for metal toxicity to wildlife and human; the secondary criteria (MSQ-2) for general industry and coastal tourism; and the tertiary criteria (MSQ-3) for harbors and ocean exploration. When the metal concentrations were compared with Marine Sediment Quality (GB 18668-2002), the average of each metal concentration of the sediments was below or close to the primary criteria (Table 2). However, the metal concentrations at several sampling sites exceeded the MSQ-1. For example, three sites in northwest Liaodong Bay had Hg concentrations exceeding the primary criteria, but below the secondary criteria. Among the 128 sampling sites, there were only two sites exceeding the primary criteria for Cu, one for Pb and As, and three for Hg. In general, the surface sediments quality of Liaodong Bay was in compliance with the GB 18668-2002.

Contamination assessment

In order to better understand the current environmental status and assess the metal contamination in Liaodong Bay, both enrichment factor (EF) and geoaccumulation index (I_{geo}) were used. The EF can be utilized to differentiate the metals sources (anthropogenic source vs. natural origin) and evaluate the degree of anthropogenic impacts. The EF value of 0.5–1.5 suggests that the metals may be entirely originated from crustal materials or natural weathering processes, whereas the EF value of >1.5 indicates a significant portion from non-crustal materials or anthropogenic sources (Zhang and Liu, 2002). As shown in Fig. 4a, the EF value of Cu ranged from 0.24 to 1.4; EF (Pb), 1.7 to 5.2; EF (Zn), 0.3 to 2.6; EF (Cr), 0.1 to 0.7; EF (Ni), 0.3 to 1.1; EF (As), 0.63 to 4.1; and EF (Hg), 0.0 to 4.9 (Fig. 4a). The average of the EF value for Cu (0.81±0.2), Zn (1.05±0.3), Cr (0.53±0.12), Ni (0.69 ±0.17), As (1.48±0.63), and Hg (0.41±0.59) suggested that the metal contaminations were not of environmental concern although a few sites had moderate to significant enrichment for specific metals. For example, a moderate enrichment of Zn, Hg, and As was found in the northwest Liaodong Bay (offshore areas of the Jinzhou Bay), which suggested the contributions of local riverine inputs and was consistent with previous studies (Zheng et al. 2007; Wang et al. 2010a, b; Li et al. 2012). In contrast, the average enrichment factors of Pb (2.45±0.51) indicated a moderate to significant contamination of Pb present in Liaodong Bay.

Similar to the EF, geoaccumulation index can be also used to estimate the degree of metal pollution. As shown in Fig 4b, the calculated I_{geo} values in the sediments were −0.13 to −2.83 for Cu, −0.25 to 1.44 for Pb, −2.77 to 0.55 for Zn, −4.21 to −0.97 for Cr, −2.98 to −0.45 for Ni, −1.65 to 1.06 for As, and −7.16 to 1.49 for Hg. According to the Müller scale (Müller 1981), all averages of the I_{geo} value for Cu (−1.15± 0.51), Cr (−1.76±0.52), and Ni (−1.39±0.53) were below zero, suggesting no pollution in the region. Although the I_{geo} values for Zn (−0.78±0.56), As (−0.33±0.52), and Hg (−2.80±1.50) were less than zero, there were a few specific sites having the values large than zero, illustrating a moderate metal pollution. The Pb I_{geo} values (0.47±0.28) implied that Liaodong Bay might be moderately polluted with Pb.

Adverse biological effects and sediment toxicity

To determine the potential toxicity of the sediments to aquatic ecosystems, two sets of the sediment quality guidelines were applied. Low values of the TEL and ERL shows a minimal adverse biological impact while the PEL and ERM represent a frequent adverse biological effect (Long and MacDonald 1998; MacDonald et al. 2000). The comparisons of SQGs and their potential impacts in context of metal concentration were presented

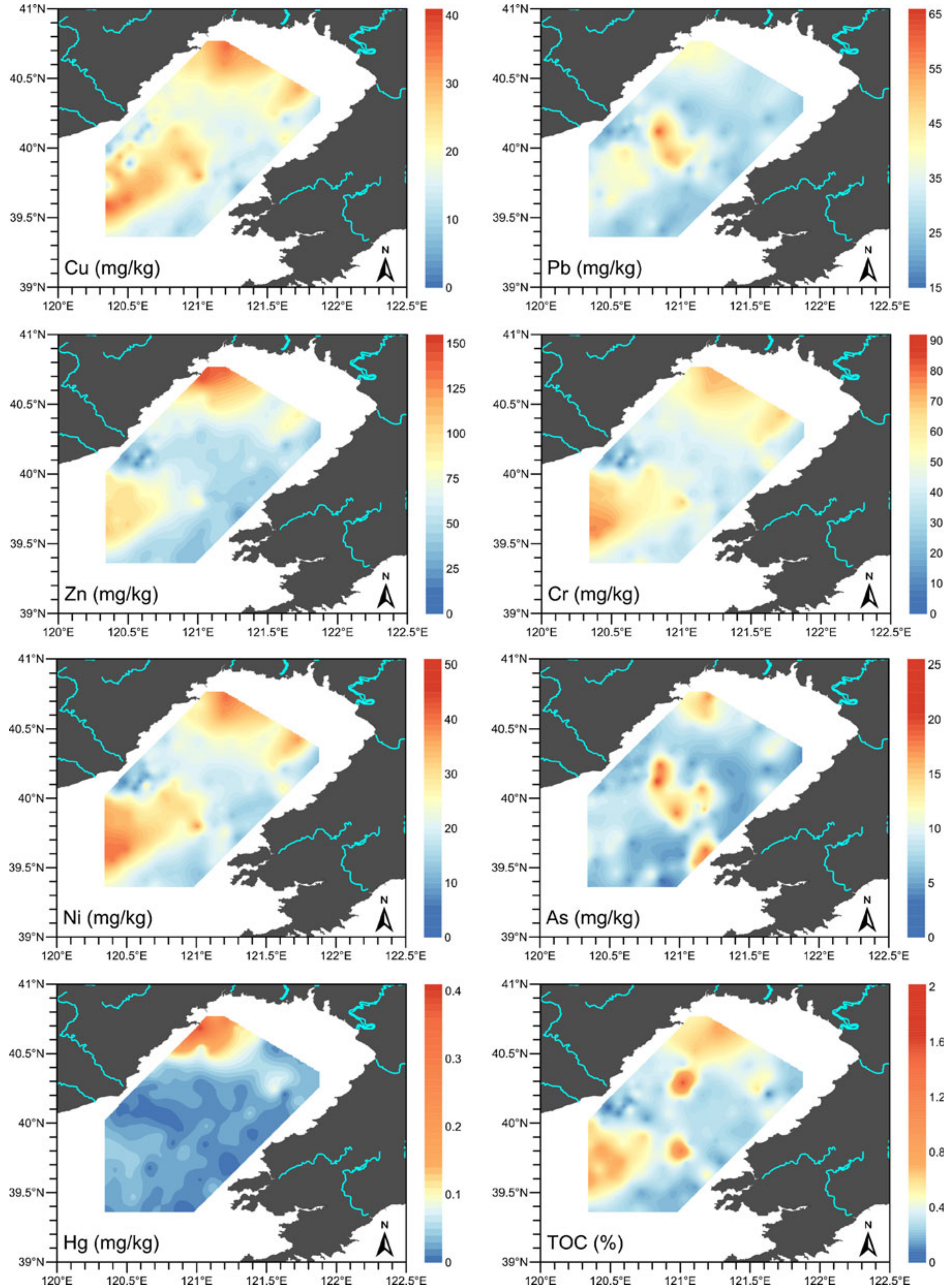

Fig. 3 Spatial distribution of heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg) and TOC in the study area

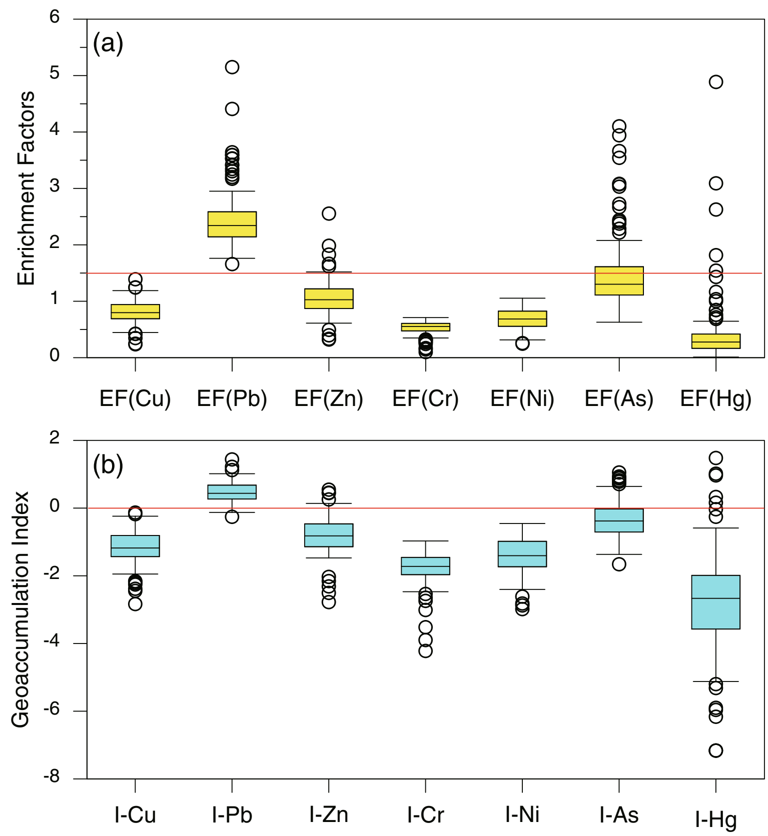

Fig. 4 The metal enrichment factors (*EF*) (**a**) and geoaccumulation indexes (I_{geo}) (**b**) of heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg) in the surface sediments

in Tables 3 and 4, respectively. When compared to the TEL–PEL SQGs, the percentage of the samples having the concentrations of Cu, Pb, Zn, Cr, Ni, As, and Hg below TEL were 55, 48, 98, 71, 20, 45, and 97 %, respectively, and the remaining samples all fell in the range between the TEL and PEL. However, when compared with the ERL–ERM SQGs, most of the metals (Cu, Pb, Zn, Cr, and Hg) were below the ERL. With respect to Ni and As, 50 % and 41 % of samples fell in the range between ERL and ERM, respectively.

In order to combine metal-specific SQG values and then to determine the possible biological effect of combined metals, the mean-ERM-quotients (m-ERM-Q) for the seven measured heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg) were calculated (Long et al. 1998). The spatial distribution of multi-metal toxicity risk potential of the Liaodong Bay presented in Fig. 5 showed that almost all of the m-ERM-Q were higher than 0.1, with the highest ecotoxicological potential zones located in the northwest and southwest parts of Liaodong Bay.

Table 3 Classification of sediment quality guidelines (SQGs) and its effects

SQGs		Effect	References
TEL and PEL guidelines	<TEL	Not associated with adverse biological effects	MacDonald et al. 2000
	≥TEL<PEL	May occasionally be associated with adverse biological effects	
	≥PEL	Frequently associated with adverse biological effects	
ERL and ERM guidelines	<ERL	Minimal effects range	Long et al. 1995
	≥ERL<ERM	Effects would occasionally occur	
	≥ERM	Effects would frequently occur	

Table 4 Comparison between heavy metals concentration (mg/kg) in Liaodong Bay and sediment quality guidelines (SQGs) with percentage of samples in each guidelines

Sediment Quality Guidelines	Metal concentration (mg/kg)						
	Cu	Pb	Zn	Cr	Ni	As	Hg
TEL	18.7	30.2	124	52.3	15.9	7.2	0.174
PEL	108.2	112.2	271	160.4	42.8	41.6	0.486
ERL	34	47	150	80	21	8.2	0.15
ERM	270	218	410	370	52	70	0.71
Compared with TEL and PEL		% of sample in each guideline					
<TEL	55 %	48 %	98 %	71 %	20 %	45 %	97 %
≥TEL<PEL	45 %	52 %	2 %	29 %	80 %	55 %	3 %
≥PEL	0 %	0 %	0 %	0 %	0 %	0 %	0 %
Compared with ERL and ERM							
<ERL	98 %	98 %	100 %	100 %	50 %	59 %	96 %
≥ERL<ERM	2 %	2 %	0 %	0 %	50 %	41 %	4 %
≥ERM	0 %	0 %	0 %	0 %	0 %	0 %	0 %

Referring to the initial classification, the SQG-based evaluation for the seven priority metal pollutant suggested that the sediments in Liaodong Bay were "medium–low" priority areas (m-ERM-Q values >0.1) or "low" priority areas (m-ERM-Q values <0.1). Accordingly, Fig. 5 clearly showed the ecological risk of Liaodong Bay may be considered as negligible, which was consistent with the results of comparison with sediment quality criteria (GB 18668-2002).

Multivariate statistical analyses

In order to obtain an overview of the heavy metals' behaviors and possible metal sources in the study area, multivariate statistical analyses (CM, PCA, and HCA) were carried out. Pearson's CM was applied to measure the degree of correlation among the heavy metals and to provide insight information regarding possible heavy metal sources and pathways (Table 5). PCA was

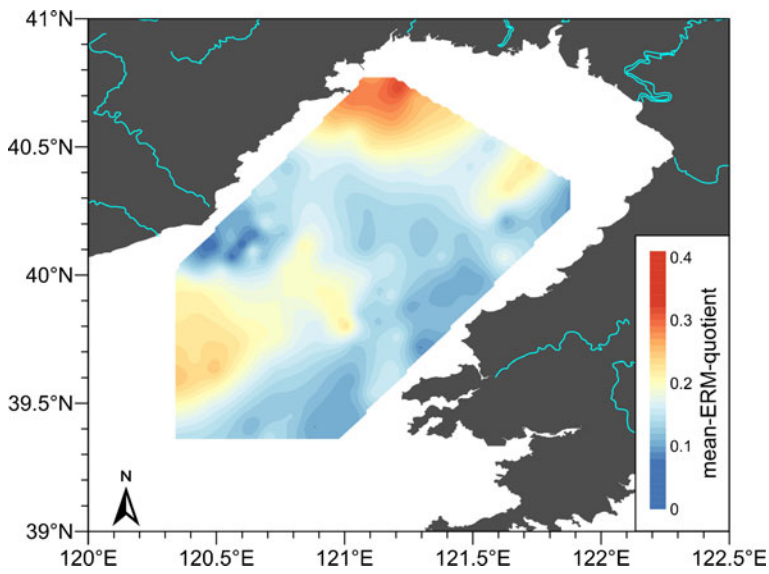

Fig. 5 Spatial distribution of mean-ERM-quotient values for the surface sediments

Table 5 Pearson's correlation matrix for the heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg) and major elements (Al, Fe, and Mn), TOC, and grain-size (Mz)

	Mz	Al	Fe	Mn	TOC	Cu	Pb	Zn	Cr	Ni	As
Al	**0.619****										
Fe	**0.743****	**0.823****									
Mn	0.070	0.170	0.335**								
TOC	**0.526****	**0.557****	**0.671****	0.150							
Cu	**0.623****	**0.659****	**0.812****	0.433**	**0.582****						
Pb	0.374**	0.409**	**0.588****	**0.651****	0.319**	**0.598****					
Zn	**0.733****	**0.777****	**0.885****	0.223*	**0.639****	**0.774****	**0.532****				
Cr	**0.843****	**0.725****	**0.915****	0.207*	**0.655****	**0.746****	0.448**	**0.862****			
Ni	**0.803****	**0.780****	**0.951****	0.374**	**0.686****	**0.825****	**0.558****	**0.877****	**0.956****		
As	0.272**	0.196*	0.489**	**0.554****	0.286**	0.450**	**0.646****	0.369**	0.330**	0.452**	
Hg	0.331**	0.302**	0.379**	0.010	0.305**	0.415**	0.304**	**0.695****	0.365**	0.376**	0.288**

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

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

performed on major elements (Al, Fe, and Mn), heavy metals (Cu, Pb, Zn, Cr, Ni, As, and Hg), mean grain size, and TOC concentrations with varimax rotation. KMO and Bartlett's results were 0.831 and 1,889.18 (df=66, $p<0.01$), indicating that PCA may be useful in dimensionality reductions. Generally, the component total of >0.71 is regarded as a major contributor while <0.32 as a minor contributor. The two principal components with eigenvalue >1 were estimated and together accounted for 74.4 % of total variance (Table 6), which indicated that the different sources or controlling factors for the heavy metals in the surface sediments of Liaodong Bay.

Table 6 Total variance explained using principle component analysis (two principal components are selected)

Element	Component matrix		Rotated component matrix	
	PC1	PC2	PC1	PC2
Cr	0.97	−0.07	0.93	0.18
Zn	0.96	−0.05	0.92	0.23
Ni	0.93	−0.18	0.90	0.35
Fe	0.92	−0.23	0.89	0.36
Mz	0.87	0.09	0.85	0.06
Al	0.80	−0.25	0.83	0.12
Cu	0.79	−0.30	0.75	0.45
TOC	0.71	−0.20	0.73	0.13
Hg	0.66	0.59	0.51	0.11
Mn	0.50	−0.12	0.02	0.89
Pb	0.40	0.80	0.35	0.81
As	0.53	0.64	0.21	0.81
Initial eigenvalue	7.24	1.69	6.24	2.69
% of total variance	60.31	14.12	52.00	22.42
% of cumulative variance	60.31	74.43	52.00	74.43

The first principal components (PC1), with high loadings of Cr, Zn, Ni, Fe, Al, Mz, Cu, TOC, and

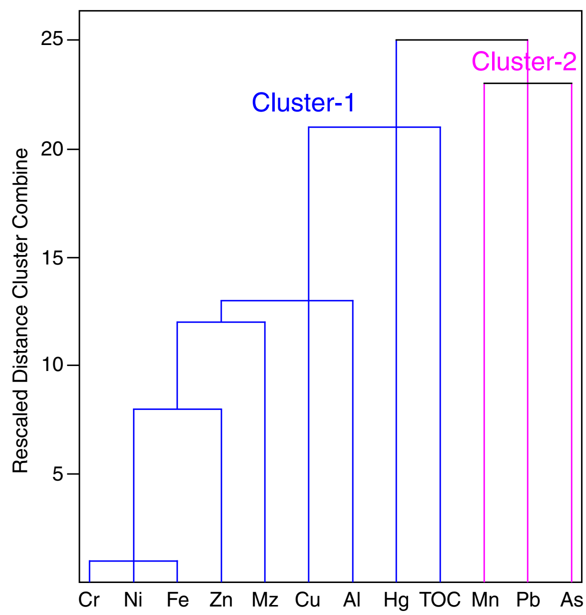

Fig. 6 Hierarchical clustering analysis among the measured parameters. Distance metrics are based on the Euclidean distance single linkage method (nearest neighbor)

medium loading of Hg, accounted for 52 % of total variance. Aluminum and iron are structural elements of the terrigenous aluminosilicates and are primary lithogenic component. Significantly positive correlations between Mz (Al and Fe) and Cr, Zn, Ni, or Cu found in Table 5 suggested that the four heavy metals were predominantly associated with fine terrigenous sediments (particularly clay minerals) through preferential exchange and/or adsorption (Bergaya et al. 2006; Ip et al. 2007; Larrose et al. 2010). Combined with the results of EF and I_{geo}, it was suggested that Cr, Zn, Ni, and Cu were mainly derived from parent rocks, and their distribution patterns may depend on local hydrodynamic conditions. However, mercury (Hg) was poorly correlated with other metals (except Zn), probably due to point source of pollutant in the northwest Liaodong Bay, implying that Hg could be from both natural and anthropogenic sources.

The second principal components (PC2) included that Mn, Pb, and As had accounted for 22.4 % of total variance. Manganese (Mn) is the most mobile elements during early diagenetic processes in marine sediments (Thomson et al. 1986). Under anoxic water conditions, dissolved Mn(II) can be converted into insoluble Mn (III) and Mn(IV) oxides/hydroxides. The lack of coherent variation patterns between Mn and both Al and Fe suggested that Mn occurred mostly as oxyhydroxides rather than being associated with lithogenous clay minerals (Karageorgis et al. 2005; Dill 2010). In the study area, Mn was positively correlated with As (0.55) and Pb (0.65) (Table 5), suggesting that As and Pb may be associated with Mn oxides/hydroxides via its scavenging heavy metals (Tessier et al. 1979). According to the results of EF and I_{geo}, PC2 can be regarded as an "anthropogenic factor".

Hierarchical cluster analysis was performed on the same data as PCA by with Ward's method, using Euclidean distances as a measure of similarity. As shown in Fig. 6, there were two distinct clusters revealed by the analysis. One includes Cr, Ni, Fe, Zn, Cu, Al, Mz, TOC, and Hg whereas the other includes Mn, Pb, and As, suggesting different origins of two metal groups. Results confirmed the findings from the PCA analysis.

Conclusion

This field study demonstrated that the sediment quality in Liaodong Bay generally met the primary sediment criteria of Chinese Marine Sediment Quality (GB 18668-2002). Both the metal enrichment factor and geoaccumulation index (I_{geo}) showed a moderate to significant Pb contamination in Liaodong Bay and a significant Hg pollution in the northwest areas. In compared with consensus-based SQGs, Cu, Pb, Ni, and As were likely to result in occasionally adverse biological effects on the aquatic ecosystems. The potential metal toxicity of the surface sediments indicated that the ecological risk may be negligible in Liaodong Bay. Results of PCA and CA identified that the loadings of Cr, Ni, Zn, Cu, and Hg were related to the natural origin, whereas Pb and As from the anthropogenic origin.

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