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Baseline

Heavy metals in surface sediments of the intertidal Laizhou Bay, Bohai Sea, China: Distributions, sources and contamination assessment

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ABSTRACT

Surface sediments from the intertidal zone of the southwestern Laizhou Bay were analyzed for heavy metals to seek their concentrations, distributions, pollution status, potential ecological risks and possible sources. The concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn were in the ranges of 4.65–9.65, 0.11–0.28, 25.85–42.75, 7.57–21.29, 0.022–0.054, 12.85–25.35, 9.65–17.65 and 38.22–73.81 $\mu g\,g^{-1}$ dry sediment weight, respectively. Cd and Hg presented a status of no pollution to moderate pollution and moderate to considerable potential ecological risks; they were enriched to some extent at some sampling stations, while the other studied metals were not. The combined effects of the studied metals in the sediments made them have a 21% probability of being toxic to biota. The results indicated that As, Cr, Cu, Zn, Ni and Pb were mainly from natural contribution, while a significant portion of Cd and Hg was likely from anthropogenic discharges in addition to natural inputs.

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It is well-known that heavy metals are toxic when their concentrations are over certain thresholds, and have received worldwide concern due to their significant adverse impact on both environment and human health. They are resistant to biodegradation and have the potential for bioaccumulation and biomagnification, which make them pose potential long-term risks for human health and ecosystem. Sediments are not only the effective sink for heavy metals in marine and coastal ecosystems, but also act as a source of metals for aquatic organisms (Chapman et al., 1998; Breslin and Sañudo-Wilhelmy, 1999; Dural et al., 2007; Li and Gao, 2014). Many studies have shown that heavy metals in sediments could significantly impact the health of aquatic ecosystem (Snodgrass et al., 2008; Zheng et al., 2008; Besser et al., 2009). It is therefore important to monitor heavy metals in sediments for the purpose of assessing environmental health risks and developing pollution control strategies and approaches to environmental quality management in a coastal area (Long et al., 1995; SEPA, 2002). With the rapid socio-economic development, the marine ecosystem of China has been facing severe environmental problems such as pollution especially in recent two decades, and the environmental

conditions and ecological risks of heavy metals in sediments of different marine areas attract lots of researchers to study (e.g. Feng et al., 2011; Pan and Wang, 2011; Gao and Chen, 2012; Gao and Li, 2012; Yuan et al., 2012; Gao et al., 2013, 2014, 2015a,b; Yu et al., 2013; Li et al., 2014; Wu et al., 2014).

The intertidal zones are complex and dynamic aquatic environment, where physical, chemical, and biological interactions between continents and marine systems have profound influence on the transport and fate of heavy metals (Lau and Chu, 2000; Spencer, 2002). Therefore intertidal sediment is identified as one of the major reservoirs of heavy metals from both natural and anthropogenic sources, and it also plays an important role in the biogeochemical cycling of metals (Duran et al., 2008; Ding et al., 2009). Compared with that of other marine areas, the distribution of heavy metals in estuaries and their surrounding tidal areas is generally affected more by various influences of intense human activities, riverine and atmospheric inputs, coastal and seafloor erosions, and biological activities.

The Laizhou Bay is one of the three major bays of the Bohai Sea, making up ~10% of its total area. There are almost ten rivers flowing into the Laizhou Bay from its southwestern coast, most of which are small and seasonal. Around the Bay, industrialization and urbanization are booming in the past decades. Due to the abundant seawater and underground brine resources, hundreds of chemical enterprises are established along the southwestern

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coast of the Laizhou Bay. Although previous studies showed that heavy metal pollution on the whole could not be a key threat to the ecological system of the Laizhou Bay, some evidence indicated that the concentrations and potential mobility of some heavy metals in the surface sediments from some spots in the lowermost reaches of the rivers in the southwestern coast of the Bay may have negative influence on biota (Zhuang and Gao, 2013, 2014a,b; Gao et al., 2015b). Yet, no information can be found about the heavy metals in the intertidal sediments of this area, so the condition remains unknown up to now. In order to have more information about the environmental conditions of heavy metals in this area, an investigation was carried out in the intertidal zone of this area. The main objectives of this study were: (1) to determine the concentrations of heavy metals including As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in the surface sediments of the intertidal zone in the southwestern Laizhou Bay (SWLZB); (2) to evaluate the pollution status and identify the possible sources of these metals; and (3) to assess their potential ecological risks.

The sediment samples used in this study were collected from 18 stations in the intertidal zone of the SWLZB during 17–24 July, 2013. Fifteen sampling stations were arranged along the bank of the major estuaries of this area extending from the high tide mark to the low tide mark and formed five transects. Sites A1 to A3, B1 to B3, C1 to C3, E1 to E3 and F1 to F3 were in the tidal flats off the Xiaoqinghe River mouth, Bailanghe River mouth, Yuhe River mouth, Weihe River mouth and Jiaolaihe River mouth; stations D1 to D3 were located at a non-estuarine tidal flat area (Fig. 1). At each transect, three sampling stations were arranged landwards

at the areas near to the low tide mark, the middle tide mark and the high tide mark. All materials that were utilized for sampling, treatment and storage were carefully chosen and properly treated to minimize external anthropogenic contamination of the samples. At each sampling station, the top 0–5 cm sediment was collected with a plastic spatula and packed in a new polyethylene zipper bag, and a total of 18 samples were obtained. After the collection, the samples were stored and transported to the laboratory in a cooler box with ice packs and transferred to a ~4 °C fridge for further analyses.

Freeze-dried aliquots were ground and homogenized using an agate mortar and pestle. Then, ~0.05 g of each sample was digested in closed Teflon digestion vessel with 8 ml mixed acid solution (HNO_3:$HClO_4$:HF = 2:1:5), the mixture was heated in an electric heating thermostat at 170 °C for 48 h and then unclosed and heated on an electric heating plate at 100 °C until it evaporated to semi-dryness. After cooling, the digested samples were brought to a final volume of 40 ml using a solution of 2% nitric acid. The concentration of Al was determined by inductively coupled plasma optical emission spectrometry (PerkinElmer Optima 7000 DV) for the purpose of calculating enrichment factors of each element. Heavy metals (Cr, Cd, Cu, Ni, Pb and Zn) were measured with inductively coupled plasma mass spectrometry (PerkinElmer Elan DRC II). As and Hg were measured by hydride generation atomic fluorescence spectrometry (Beijing Haiguang Instrument Co. AFS-2202).

The granularity of each sample was measured with a Malvern Mastersizer 2000 laser diffractometer to calculate the percentages
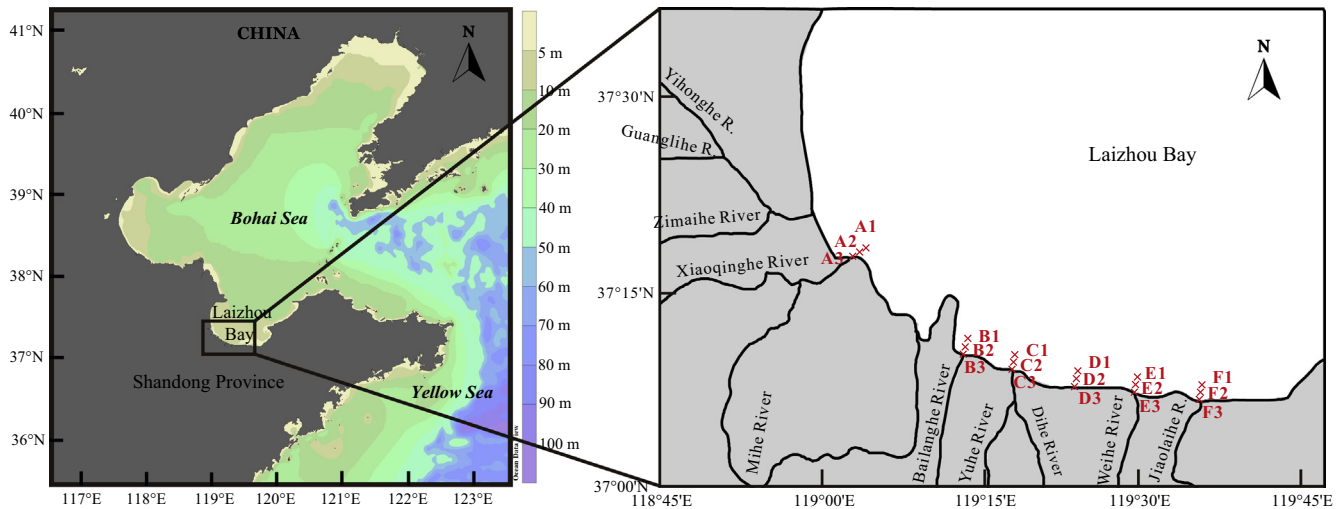

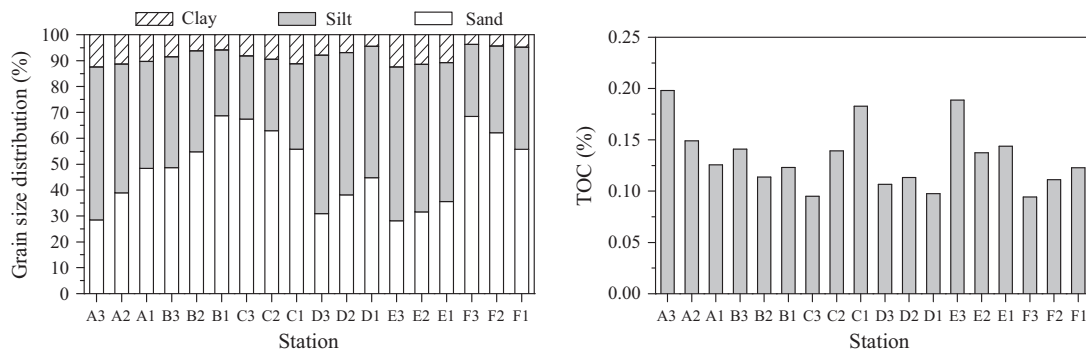**Fig. 1.** Location of sampling stations in the intertidal zone of the SWLZB.

Fig. 2. Grain size (left) and TOC (right) distributions in the surface intertidal sediments of the SWLZB.

Table 1

The summary of heavy metal mean concentrations in the surface sediments collected from the intertidal zone of southwestern Laizhou Bay. The related values reported for surface intertidal sediments from some other coastal areas in and out of China, the metal guideline values of the criteria used to distinguish marine sediment quality and the element background values in soil of Shandong Province were also shown for the comparison purpose. Content unit is $\mu g\ g^{-1}$ for all elements.

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	References
Laizhou Bay, China	Range	4.65–9.65	0.11–0.28	25.85–42.75	7.57–21.29	0.022–0.054	12.85–25.35	9.65–17.65	38.22–73.81	Present study
	Mean	7.1	0.19	32.69	10.99	0.039	17.38	13.37	50.63	
Beihai coast, China	Range	0.68–34.1	0.06–0.82	na[a]	4.0–32.8	0.014–0.22	na	1.9–72.9	35.0–118.4	Xia et al. (2008)
	Mean	9.1	0.22	na	12.7	0.07	na	16.6	69.8	
Bohai Bay, China	Range	na	0.05–0.19	36.7–110	7.9–46.7	na	14.1–47.9	18.8–39.1	34.0–123	Gao and Li (2012)
	Mean	na	0.12	68.6	24	na	28	25.6	73	
Yangtze Estuary, China	Range	na	0.12–0.75	36.9–173	6.9–49.7	na	17.6–48.0	18.3–44.1	47.6–154	Zhang et al. (2009)
	Mean	na	0.261	78.9	30.7	na	31.8	27.3	94.3	
Quanzhou Bay, China	Range	17.7–30.2	0.28–0.89	51.1–121.7	24.8–119.7	0.17–0.74	16.1–45.7	34.3–100.9	105.5–241.9	Yu et al. (2008)
	Mean	21.7	0.59	82	71.4	0.4	33.4	67.7	179.6	
San Simón Bay, Spain	Range	2.5–17.0	na	19.9–94.1	0.01–19.2	na	2.19–10.6	29.6–1988	27.4–112.6	Paula et al. (2007)
	Mean	9.0	na	42.46	6.53	na	5.45	566.28	54.45	
California Bight, USA		5.1	0.33	39	15	0.05	na	10.9	59	Schiff and Weisberg (1999)
Class I upper limit[b]		20	0.5	80	35	0.2	na	60	150	SEPA (2002)
Class II upper limit[c]		65	1.5	150	100	0.5	na	130	350	SEPA (2002)
Class III upper limit[d]		93	5	270	200	1	na	250	600	SEPA (2002)
TEL guideline[e]		7.3	0.68	52.3	18.7	0.13	15.9	30.2	124	MacDonald et al. (1996)
PEL guideline[f]		41.6	4.2	160	108	0.7	42.8	112	271	MacDonald et al. (1996)
Background value in soil of the Shandong Province		9.3	0.084	66.0	24.0	0.019	25.8	25.8	63.5	CNEMC (1990)

[a] na: not available.

[b] Class I upper limit: a marine area where sediment with metal concentrations lower than these guidelines is suitable for mariculture, nature reserve, endangered species reserve, and leisure activities such as swimming.

[c] Class II upper limit: a marine area where sediment with metal concentrations lower than these guidelines is suitable for industry and tourism sites.

[d] Class III upper limit: a marine area where sediment with metal concentrations lower than these guidelines is suitable for harbors.

[e] TEL guideline: metal concentrations in marine sediments below which adverse effects on biota are rarely observed.

[f] PEL guideline: metal concentrations in marine sediments above which adverse effects on biota are frequently observed.
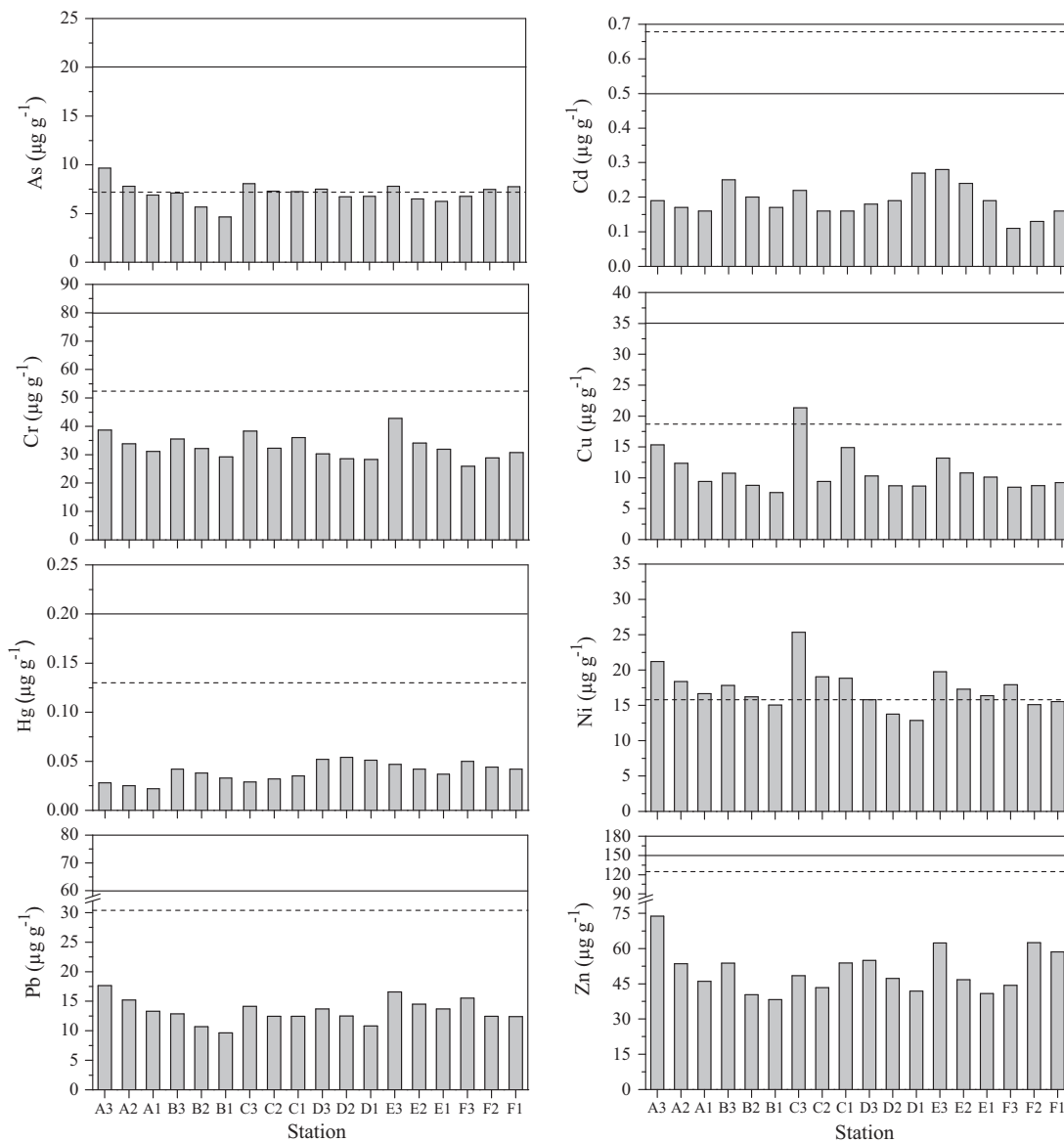
Fig. 3. Spatial distributions of the studied heavy metals in the surface intertidal sediments of the SWLZB. The dash and solid lines represent their corresponding TEL concentrations and the higher boundary values of the Class I sediment category of China, respectively.

of its clay (<4 μm), silt (4–63 μm) and sand (>63 μm) fractions. The TOC in sediments was obtained by determining the total carbon with an Elementar vario MACRO cube CHNS analyzer after the inorganic carbon was removed with 1 M HCl.

The quality assurance and quality control were done by method blanks and standard reference materials. Blank samples were also performed throughout all the analyses. To explicitly guarantee the analytical precision, all samples were determined in triplicate. Precision, expressed as relative standard deviation, was better than 10%. Accuracy of the total analysis and analytical quality was assured using the standard reference materials GBW-07333 and GBW-07314. The recoveries ranged from 90% to 110% and the differences were all within 8%.

In the intertidal surface sediments of the SWLZB, the clay, silt and sand fractions ranged from 2.8% to 12.5%, 14.4% to 61.2% and 28.5% to 82.4%, with an average of 7.2%, 40.4% and 52.4%, respectively. Therefore, the sediments in this area were mainly composed of slit and sand (Fig. 2), which was consistent with the other researchers' results in the southwestern coastal areas of the Laizhou Bay (Qiao et al., 2010; Hu et al., 2011; Zhuang and Gao,

2013). In this research, the sediments from the high tide mark were generally finer than those from the lower tide mark except for those at the C-transect and the F-transect (Fig. 2). The previously reported spatial variation pattern of surface sediment texture in the southwestern coastal areas of the Laizhou Bay (Zhuang and Gao, 2013) indicated a similar feature to this.

The TOC contents in the sediments varied from 0.09% to 0.20% with an average of 0.13% (Fig. 2). Although the TOC contents fluctuated among the sediment samples with no regular distribution patterns (Fig. 2), all of them displayed a typical concentration gradient similar to the distribution of the clay content. Generally, the concentrations of TOC were higher in the western part of the sampling areas. The TOC contents were the lowest at the non-estuary stations (D-transect; Fig. 2), indicating that the input from the rivers was an important source of TOC in the surface sediments of the studied area.

As shown in Table 1, the concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in the surface sediments of intertidal SWLZB were in the ranges of 4.65–9.65, 0.11–0.28, 25.85–42.75, 7.57–21.29, 0.022–0.054, 12.85–25.35, 9.65–17.65 and 38.22–73.81 μg g^{-1}, with the

Table 2
Pearson correlation matrix for the sediment components.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	%Clay	%Silt	%Sand	%TOC
As	1.000	0.039	0.523[c]	0.606[b]	−0.172	0.557[c]	0.727[a]	0.840[a]	0.386	0.288	−0.366	0.519[c]
Cd		1.000	0.538[c]	0.261	0.203	0.097	0.067	0.091	0.317	0.494[c]	−0.503[c]	0.536[c]
Cr			1.000	0.757[a]	−0.358	0.737[a]	0.542[c]	0.514[c]	0.764[a]	0.249	−0.379	0.733[a]
Cu				1.000	−0.399	0.885[a]	0.495[c]	0.595[c]	0.524[c]	−0.033	−0.074	0.435[c]
Hg					1.000	−0.512[c]	−0.121	−0.031	0.485[c]	0.304	−0.169	0.417[c]
Ni						1.000	0.592[b]	0.326	0.513[c]	−0.214	0.085	0.355
Pb							1.000	0.625[b]	0.589[c]	0.435	−0.506[c]	0.623[c]
Zn								1.000	0.324	0.362	−0.389	0.762[b]

[a] $P < 0.001$.
[b] $0.001 < P < 0.01$.
[c] $0.01 < P < 0.05$.

averages of 7.10, 0.19, 32.69, 10.99, 0.039, 17.38, 13.37 and 50.63 $\mu g\,g^{-1}$, respectively, all of which were lower than their corresponding upper limits of Class I sediment category according to the marine sediment quality classification in the National Standard of China GB18668-2002 (Table 1; SEPA, 2002), indicating that the whole studied area is suitable for mariculture, nature reserves, endangered species reserves and leisure activities in view of sediment quality. Except for As, Cu and Ni, the concentrations of the other studied metals, namely Cd, Cr, Hg, Pb and Zn, at all the sampling stations were below their corresponding values of threshold effects level (TEL) (Table 1; Fig. 3), which indicated that they were in a relatively uncontaminated state and might pose limited risks of toxicity.The spatial patterns of the studied heavy metals were generally similar to TOC and clay (Figs. 2 and 3). They generally showed a decreasing trend in the seaward direction except at the F-transect. Unlike those at the other transects, the metal concentrations of the sediments from the F-transect showed an increasing trend in the seaward direction, especially for As, Cd, Cr, Hg and Zn. Among the studied heavy metals, As and Pb showed less variability than the others. The maximum concentrations of Cu and Ni, which were apparently higher than their corresponding values at the rest of sampling stations, were found in a sample from the high tide mark station at C-transect (Fig. 3).

Among the intertidal areas in China that were listed in Table 1, except for the mean concentration of Cd in the present study which was higher than that found in the intertidal Bohai Bay, the mean concentrations of the other seven studied metals for the intertidal sediments from the SWLZB were the lowest, while the highest values for the eight studied metals were found in sediments of the intertidal Quanzhou Bay. The average concentrations of Pb and As were higher than those found in sediments of the intertidal California Bight in USA, and the mean Cu and Ni concentrations were higher than those found in sediments from the intertidal San Simón Bay in Spain (Table 1). The average concentrations of As, Cd, Cu, Hg, Pb and Zn recorded in this study were comparable to those in the intertidal Beihai coast, and lower than those in the intertidal Bohai Bay, intertidal Yangtze Estuary and intertidal Quanzhou Bay (Table 1).

The correlation matrix for the parameters studied was shown in Table 2. Except the relationships between Cd and the other metals and between Hg and the other metals, generally most of the studied metals were significantly correlated with each other, suggesting a major common origin for sediments. The special conditions of Cd and Hg in the sediments indicated they probably had different origins from the other studied metals. Except for As, Cd and Zn, the concentrations of other studied heavy metals and the clay contents were significantly correlated with each other, and except for Ni, the concentrations of other studied heavy metals and TOC contents were significantly correlated with each other too. These findings were similar to the previous study by Gao and Chen (2012), the results of which indicated that the concentrations of Cd and

Zn appeared to be more influenced by the amount of organic matter than by the sediment grain size composition and the concentration of Ni appeared to be more influenced by the sediment grain size composition than by the amount of organic matter.

The distribution of heavy metals in sediments was related to the deposition and transportation processes from sources to sinks in the intertidal zone. The heavy metals and their transportation in the intertidal sediments could be influenced by physical, chemical and biological processes of the intertidal system. Through these processes heavy metals deposited and incorporated into sediments.

The grain size and sediment components can affect the concentrations of heavy metals in the intertidal area, since the increasing specific surface of fine sediments favored adsorption processes. Correlation analysis indicated that the heavy metals and the clay contents were significantly correlated with each other (Table 2). Such a phenomenon suggested that the fine particles contained more heavy metals and might be a major carrier of them. Accordingly, the distribution of fine-grained sediment could reflect the physical transportation of heavy metals in the sediments. In this research, corresponding to the clay distribution, metal concentrations of the sediments from the high tide mark were generally higher than the sediments from the low tide mark (Fig. 3).

The transportation and deposition of heavy metals were controlled by material sources, transportation media, transportation modes and the sedimentary environment. The sediment transportation and distribution were strongly affected by hydrodynamic processes and the deposition conditions. As mentioned above, in the intertidal zone of the SWLZB, the sediments from the high tide mark were finer than the sediments from the low tide mark (Fig. 2). This distribution pattern could be the consequence of joint effects of tidal currents, residual currents, coastal currents, continental diluted currents, the anti-clockwise circulation of the Laizhou Bay and the sudden change in the velocity of water currents. These hydrodynamic processes caused the re-suspension of fine surface sediments near the estuaries in the Bohai Sea (Jiang et al., 2000; Qiao et al., 2010). The sediments transported into the intertidal zone of this region could be mainly from the rivers (i.e. the Xiaoqinghe River, the Bailanghe River, the Yuhe River, the Weihe River and the Jiaolaihe River). When sediments were transported from rivers into intertidal zone, the coarse grained sediments deposited quickly, while the fine parts of sediments could be more easily retained in seawaters, moved and sorted by the above-mentioned hydrodynamic processes.

Organic matter is an important component of fine-grained marine sediments, and heavy metals often deposit in sediments combining with organic matter. The TOC contents in the intertidal zone of the SWLZB surface sediments were 0.09–0.20% with an average of 0.13% (Fig. 2). The TOC contents in the high tide mark were higher than in the low tide mark (Fig. 2). This research found that concentrations of most studied heavy metals and TOC

contents had significant correlations except for Ni (Table 2), indicating that these metals and organic matter may have common origin and were probably introduced to the system with organic matters. The dead phytoplankton, byproduct of the zooplankton, benthos metabolic activities and bacterial degradation would accelerate the organic matter accumulation and release (Dellwig et al., 2007). So, the organism biomass and the associated growth of bacteria were the controlling factors of the organic matter and coupled metals.

An essential task of geochemical research is to distinguish elements originating from anthropogenic activities and those from natural crustal contribution. Normalization is a widely applied technique, that is metal concentrations are normalized to a textural or compositional characteristic of sediments. Al is a commonly used normalizing element to compensate for fluctuations in both grain size and composition, since it represents the quantity of aluminosilicates, which is the predominant carrier phase for adsorbed elements in coastal sediments (Chatterjee et al., 2007). This method is also an effective tool for the regional comparison of trace metal concentration in sediments and can also be applied to determine enrichment factors (EFs). It is defined as the concentration ratio of a considered element to a reference element in a given sample, divided by the same ratio of their background concentrations, that is:

$$EF = \frac{(C_x/C_{Al})_{Sample}}{(C_x/C_{Al})_{Background}}$$

where C_x and C_{Al} denote the concentrations of elements "x" and Al in the samples of interest (Sample) and their background concentrations (Background) (Table 1). According to the recently published literature of Xu et al. (2015), sediment in the Laizhou Bay was primarily from the material discharged by rivers along its western and southern coasts. So, the element background concentrations in soil of Shandong Province were adopted to calculate the EF values in this research as that of Xu et al. (2015) did. It is generally accepted that it may be entirely from crustal materials or natural weathering processes if the EF value of a metal in solid geochemical samples such as marine sediments or suspended particulate matter is between 0.5 and 1.5, and a significant portion of it is from other sources rather than natural origins if its EF value is greater than 1.5 (Zhang and Liu, 2002; Feng et al., 2004).

In order to get information about the potential sources of heavy metals in the intertidal sediments of the SWLZB, the EF value of each element at each station was calculated. The results showed that the EF values of the eight studied heavy metals followed the sequence Cd > Hg > Zn > As > Ni > Pb > Cr > Cu (Fig. 4). The mean
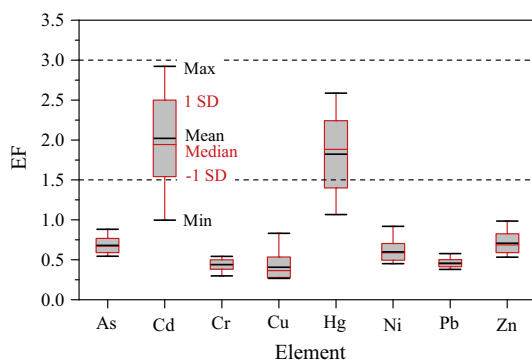
EF values of Cd and Hg were higher than 1.5, while those of the other studied metals fell in the range of natural variability. Therefore, Cd and Hg were the most anthropogenically influenced among the studied elements in the surface sediments of the intertidal SWLZB based on the results of EF analysis. With a mean value of 2.02, the EF values of Cd varied greatly across the studied area, and they were over 1.5 but less than 3 at all stations except stations F3 and F2, indicating a minor enrichment status. The EF values of Hg at all sampling stations were over 1 with a mean value of 1.82, and 14 of them exceeding 1.5 but less than 3, suggesting a minor enrichment status too. Except for Cd and Hg, the EF values of the other studied metals were lower than 1, suggesting that they were not enriched and might be mainly from the Earth's crust. Except for Hg, the EF values of the metals at the western sampling stations were generally higher than those at the eastern stations, indicating that the western sampling area was relatively more enriched by heavy metals than the eastern area. The spatial distribution pattern of EF_{Hg} suggested that the major sources of Hg in the sampling area might be different from that of the other studied metals; such a case was reassured by Pearson correlation analyses (Table 2), and Hg presented insignificant correlations with the other metals which differentiates it from the other seven metals. Generally speaking, the heavy metal pollution in the intertidal sediments of the SWLZB was not serious based on the results of EF analysis.

The I_{geo} was used to evaluate the levels of heavy metal contamination and possible sediment enrichment of metals. The formula used for the calculation of I_{geo} is:

$$I_{geo} = \log_2\left(\frac{C_x}{1.5B_x}\right)$$

where C_x is the measured concentration of element "x", and B_x is the geochemical background concentration of element "x". As in the EF calculation, the corresponding metal background concentration in soil of Shandong Province (Table 1) was adopted as B_x. The calculated I_{geo} values of the studied metals are shown in Fig. 5. The I_{geo} values of six studied metals (As, Cr, Cu, Ni, Pb and Zn) at all sampling stations were less than 1, suggesting that they were in an unpolluted status in the intertidal surface sediments of the SWLZB. Exactly like the descending order of the studied metals on EF values, the mean value of 0.56 meant that Cd was relatively the most contaminated metal of all based on the results of I_{geo} analysis, followed by Hg, Zn, As, Ni, Pb, Cd and Cu in sequence, the mean values of which were 0.41, −0.93, −0.99, −1.17, −1.55, −1.61 and −1.76, respectively. According to Müller (1969), metals in the surface sediments of this study could be classified into the following

Fig. 4. Enrichment factors of the studied heavy metals in the surface sediments in intertidal SWLZB using Al as normalizer. Values in the section below the bottom dot line (EF < 1.5) suggest that the elements may be entirely from crustal materials or natural weathering processes; values in the section between the two dot lines (1.5 < EF < 3) indicates that a portion of the elements may be from other sources rather than natural origins.
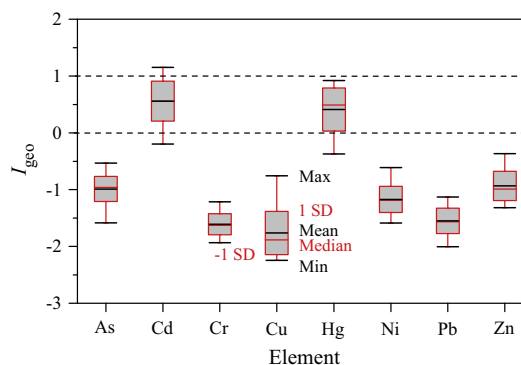

Fig. 5. Index of geoaccumulation of the studied heavy metals in the surface sediments in the intertidal SWLZB. Values in the section below the bottom dot line (I_{geo} < 0) indicate that the elements were at a practically unpolluted level; values in the section between the two dot lines ($0 \leqslant I_{geo} < 1$) indicate that the elements were at an unpolluted to moderately polluted level; values in the section above the top dot line ($1 \leqslant I_{geo} < 2$) indicate that the elements were at a moderately polluted level.

two groups based on the pollution potential: (1) practically unpol- luted ($I_{geo} < 0$), which was the case of As, Cr, Cu, Ni, Pb and Zn; (2) unpolluted to moderately polluted ($0 < I_{geo} < 1$), which was the case of Cd and Hg. The general information that the I_{geo} results of Cd, Cr, Cu, Ni, Pb and Zn indicated in this study was similar to the previous observation on the surface sediments in the inshore area of the SWLZB reported by Gao et al. (2015b).

The EF and I_{geo} were techniques through which individual met- als are assessed by normalization. But the fact is that heavy metals always occur in sediments as complex mixtures, and they form combined toxicant groups in sediments. In order to evaluate the possible biological effects of the coupled toxicity of the studied metals in the surface intertidal sediments of the SWLZB, the mean PEL quotient method introduced by Carr et al. (1996) was used and values were calculated using the following formula:

$$\text{mean PEL quotient} = \frac{\sum_{x=1}^{n} \frac{C_x}{PEL_x}}{n}$$

where C_x is the sediment concentration of metal "x", PEL_x is the PEL (probable effects level; Table 1) for metal "x", "n" is the number of the studied metals and is 8 in this study. It was reported that the mean PEL quotients of <0.1 have a 9% probability of being toxic, the mean PEL quotients of 0.11–0.5 have a 21% probability of being toxic, the mean PEL quotients of 0.51–1.5 have a 49% probability of being toxic, and the mean PEL quotients of >1.50 have a 76% prob- ability of being toxic (Long et al., 2000). It can be seen in Fig. 6 that the mean PEL quotients in the surface intertidal sediments of the SWLZB varied within the range of 0.13–0.20, indicating that the
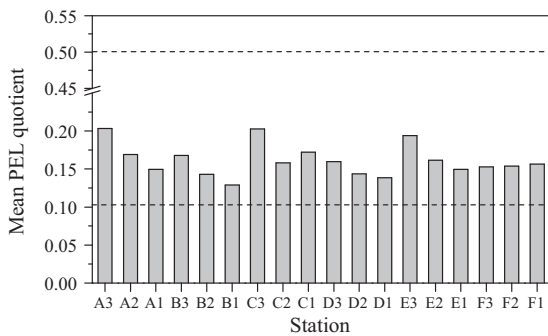
combined effects of the studied metals in the sediments may cause a 21% probability of being toxic to biota.

For the purpose of evaluating the potential risk to the intertidal ecosystem posed by the heavy metals in the intertidal surface sed- iments of the SWLZB, ecological risk assessment was conducted in this research. The ecological risk index (RI), which was originally introduced by Håkanson (1980), was calculated as:

$$E_r^i = T_r^i \cdot C_f^i = T_r^i \cdot (C_o^i / C_n^i);$$

$$RI = \sum_{i=1}^{8} E_r^i = \sum_{i=1}^{8} T_r^i \cdot C_f^i$$

where E_r^i is the potential ecological risk factor of metal "i"; T_r^i and C_f^i are the toxic-response factor and the contamination factor of metal "i", respectively; C_o^i and C_n^i are the measured concentrations of metal "i" in the sample and its reference value, respectively. The T_r^i values of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn are 10, 30, 2, 5, 40, 5, 5 and 1, respectively (Håkanson, 1980; Wang et al., 2011). RI indi- cates the total potential ecological risk for a sampling region based on the sensitivity of the ecosystem to all the studied heavy metals. Like that of EF and I_{geo} calculation, the corresponding metal back- ground concentrations in soil of Shandong Province (Table 1) were adopted to calculate the E_r^i and RI values of the studied metals in this study. According to Håkanson (1980), the potential ecological risk of heavy metals in sediments can be divided into the following categories: Low risk: $E_r^i < 40$, RI < 150; Moderate risk: $40 \leqslant E_r^i < 80$, $150 \leqslant RI < 300$; Considerable risk: $80 \leqslant E_r^i < 160$, $300 \leqslant RI < 600$; High risk: $160 \leqslant E_r^i < 320$; Very high risk: $E_r^i \geqslant 320$, RI $\geqslant 600$.

Fig. 7 shows the calculated E_r^i values of each metal and RI of the eight studied metals in the intertidal surface sediments from the SWLZB. Overall, the ecological risk of studied metals in the inter- tidal surface sediments of the SWLZB was from low to consider- able, and the risks were mainly from Cd and Hg. It can be seen that Hg presented the highest ecological risk among the eight heavy metals, primarily due to its high toxic-response factor. E_r^i of Hg fluctuated greatly across the studied area compared to the other studied metals, with the range from 46.3 to 113.7 and a mean value of 82.2 which exceeded 80, indicating on the whole a consid- erable risk from Hg. E_r^i values of Cd ranged from 39.3 to 100, and its mean E_r^i value was 68.1, indicating that it had a moderate risk in general. E_r^i values of the other six studied elements, namely As, Ni, Cu, Pb, Cr and Zn, were all far below 40, indicating a low ecolog- ical risk from them. The RI values indicated that they were higher than 150 at 13 of the sampling stations showing that the surface sediments at these sampling stations were generally at a moderate

Fig. 6. The mean PEL quotients of the studied metals in each sampling station. Values in the section between the two dot lines (0.11 < mean PEL quotient < 0.5) indicate that the combined effect of the studied metals in the sediments has a 21% probability of toxicity to biota.
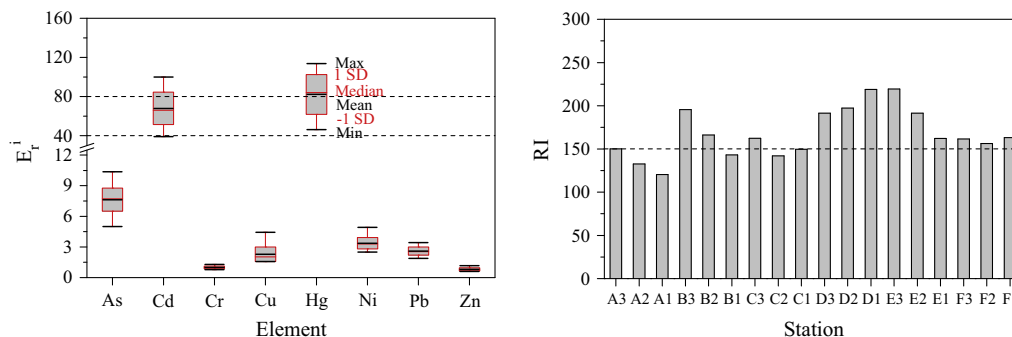

Fig. 7. E_r^i value of each metal in the studied area (left) and RI value of the studied metals for each station (right). For E_r^i values, these in the section below the bottom dot line ($E_r^i < 40$) indicate that the potential ecological risks of the studied elements in the sediments were at a low level, these in the section between the two dot lines ($40 \leqslant E_r^i < 80$) indicate that the potential ecological risks of the studied elements in the sediments were at a moderate level, and these in the section above the top dot line ($80 \leqslant E_r^i < 160$) indicate that the potential ecological risks of the studied elements in the sediments were at a considerable levels. For RI values, these in the section below the dot line (RI < 150) indicate that the combined potential ecological risk of the studied elements in the sediments was at a low level and these in the section above the dot line ($150 \leqslant RI < 300$) indicate that the combined potential ecological risk of the studied elements in the sediments was at a moderate level.

ecological risk level in terms of the combined effects of the studied heavy metals, while they were lower than 150 at stations A2, A1, B1, C2 and C1 showing that the combined effects of the studied heavy metals had a low ecological risk for the environment (Fig. 7).

Acknowledgments

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