Heavy metal pollution status in surface sediments of the coastal Bohai Bay

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Abstract

Bohai Bay, the second largest bay of Bohai Sea, largely due to the huge amount of pollutants discharged into it annually and its geohydrologic condition, is considered to be one of the most polluted marine areas in China. To slow down, halt and finally reverse the environmental deterioration of Bohai Sea, some researchers have proposed to connect it with Jiaozhou Bay in the western coast of Southern Yellow Sea by digging an interbasin canal through Shandong Peninsula. In order to assess the heavy metal pollution and provide background information for such a large geoengineering scheme, surface sediments from 42 stations covering both riverine and marine regions of the northwestern coast of Bohai Bay were analyzed for heavy metal content and fractionation (Cd, Cr, Cu, Ni, Pb and Zn). Three empirically derived sediment quality guidelines were used to assess the pollution extent of these metals. The studied metals had low mobility except for Cd at all stations and Zn at some riverine stations. Although a high mobility of Cd was observed, it could hardly cause a bad effect on the environment owing to its low total concentrations. Anthropogenic influence on the accumulation of studied heavy metals in sediments of Bohai Bay was obvious, but their contents were relatively lower to date comparing with some other marine coastal areas that receive important anthropogenic inputs. Taking as a whole, surface sediments of northwestern Bohai Bay had a 21% probability of toxicity based on the mean effects range-median quotient.

1. Introduction

Heavy metal pollution is one of the environmental crises that accompany with the rapid economic development in many countries. Sediments in the coastal zone are normally dominated by terrigenous material through aeolian and alluvial processes (Libes, 2009), resulting in a large majority of land-derived contaminants accumulating in them (Bryan and Langston, 1992). For heavy metal pollutants, one of the largest problems associated with their threat to the ecosystem is the potential for bioaccumulation and biomagnification causing heavier exposure for some organisms than is present in the environment alone. So, the contents of many of them are often monitored to provide basic information for the judgment of environmental health risks (Long et al., 1995; SEPA, 2002).

The coastal region surrounding Bohai Sea is one of the three most densely populated and industrialized zones in China. As the second largest bay of Bohai Sea, Bohai Bay accounts for about one fifth of the total area of Bohai Sea. Bohai Bay receives
industrial and domestic wastewater discharges not only from the vicinity of Tianjin (the sixth largest city in China by urban population of about nine million) to which it connects but also from the second largest megacity in China — Beijing. Moreover, the western coast of Bohai Bay is the home to Tianjin Port, the fifth largest port in the world in cargo throughput. Bohai Bay is a shallow water basin with very mild-slope bottom and most of its sediments are composed of fine mud. The mean water depth of Bohai Bay is about 10 m. The width of tideland of Bohai Bay is 3–5 km and the average velocity of residual current is less than 0.1 m/s. The water exchange between Bohai Bay and Bohai Sea is weak and that makes the physical self-clean capacity of Bohai Bay very poor (Tao, 2006). The evidence of stable carbon and nitrogen isotopes indicated that particulate organic matter from anthropogenic sources is mainly trapped in riverine sediments in coastal Bohai Bay (Gao et al., in press). Many suggestions have been proposed to save the ecosystem of Bohai Sea, and of all the most ambitious one is to improve the water circulation of Bohai Sea by connecting it with the Southern Yellow Sea through an interbasin canal (Fig. 1; Wang, 2007).

The fact that sediments integrate the external environmental effects makes them an essential source for information acquisition in major marine monitoring programs. The main objectives of this study are to determine the contents and fractionations of six heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) that are usually used as environmental quality criteria in surface sediments of northwestern coast of Bohai Bay, estimate the anthropogenic influence, and assess the pollution status of this area. The northwestern coast of Bohai Bay was chosen because it is this area of Bohai Bay that faces the most serious threat from anthropogenic activities.

2. Materials and methods

2.1. Sampling

A total of 42 sediment samples collected from the northwestern coast of Bohai Bay in May 2008 were analyzed in this study (Fig. 1). The sampling stations were arranged along the major rivers of this area extending from the land to the sea and formed four transects. The surface sediments from the marine region were collected by a stainless steel grab sampler, and the surface sediments from rivers were collected using a plastic spatula. The samples were placed in acid-rinsed polyethylene bags and stored at ~4 °C in the dark until further analysis.

2.2. Analytical methods

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, oxidizable and residual. The detailed sequential extraction protocol used in this study has been described elsewhere (Gao et al., 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, HNO₃ and HClO₄ (5:2:1; Li et al., 2000) was used to digest all 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 five randomly selected samples was carried out 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 accounted for 87–113% of the values from 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

![Fig. 1 – Location of sampling sites in the coastal zone of Bohai Bay.](image-url)
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 were used to control the analytical quality. The results were consistent with the reference values, and the differences were all within 10%. All plastic and glassware were pre-cleaned by soaking in 10% HNO₃ (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-VCPH/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 3 groups of grain sizes were determined: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand).

The agglomerative hierarchical clustering analysis was conducted using the XLSTAT software to assess the interrelationships among the sampling stations.

3. Results and discussion

3.1. General characteristic of sediments

Grain size composition and TOC content were measured to get the general characteristics of sediment samples in this study. As shown in Fig. 2, the studied sediments were predominantly composed of silt, followed by clay. The sand content in most of the samples was <5%. The average percentage of silt and clay was 66.1% and 28.6% with the range of 57.0–78.7% and 11.6–40.6%, respectively. For the three sediments from Duliujian River, their fine fraction (clay + silt) contents decreased downriver, and the one from the station nearest to the sea had the lowest value among all the studied samples. The TOC contents varied between 0.9 and 7.2% of the dry sediment weight with an average of 2.3%. Their difference among the samples from the marine region was insignificant. The higher TOC contents (>2.5%) were all recorded at riverine sampling stations. At the Dou River-M transect, TOC contents showed a clear decreasing trend seaward from 5.9% to 1.1%.

3.2. Metals in total concentrations

As shown in Fig. 3, generally, the differences in metal concentrations in sediments from the marine region were not significant. Unlike the other three transects, the metal concentrations in sediments from the Duliujian River-T transect showed a trend of increase seaward, especially for Cr, Cu, Ni and Pb. The Cd, Pb and Zn concentrations in sediments from the Dou River-M transect, the concentrations of all the six studied metals in sediments from the Yongdingxin River-K transect, and the Cd, Cr and Zn concentrations in sediments from the Qingjinghuang and Ziyaxin Rivers-U transect showed a trend of decrease in the river-to-sea direction. The spatial distributions of Cr, Ni, Pb and Zn concentrations in sediments from the Yongdingxin River were uniform.

The highest concentration of Cd and Cr, which was 0.66 and 224.5 μg g⁻¹ respectively, was found in a sample from Ziyaxin River, and the concentration of Zn in this sediment was also much higher than in all the other samples except one of the three sediments from Dou River (Fig. 3). Sediment from Dou River with the highest concentration of Zn had a Pb concentration of 60.6 μg g⁻¹, which was just slightly lower than the highest value of 66.4 μg g⁻¹ recorded in one of the two sediments from Hai River. The apparently high concentration of Cu, ~63 μg g⁻¹, was recorded in the only one sample from Chaobai River and the one from Hai River with the highest Pb.
The spatial variations of studied heavy metals in total concentrations and their distributions in different geochemical phases of surface sediments from coastal Bohai Bay.
The summery of heavy metal contents in sediments collected from Bohai Bay. The average upper continental crust values and related values reported for surface sediments from some of the other coastal areas were also shown. Like that of their average concentrations in the upper continental crust, among the six studied metals, the mean concentration of Cd and Zn was the lowest and highest one, respectively. In surface sediments from the coastal Bohai Bay, the mean total contents of all the studied metals were clearly higher with respect to their corresponding average values in the UCC (Table 1). The average concentrations of all studied metals except Cr were within the range found in other coastal areas listed in Table 1. Among all the coastal areas chosen for comparison, the average concentration of Cr for coastal Bohai Bay was the highest one. Compared with the reports about sediments from Changjiang River Estuary and Pearl River Estuary, where their surrounding areas are the other two most heavily urbanized zones in China, the average concentrations of Cu, Ni, Pb and Zn were higher than those found in sediments of Changjiang River Estuary, whereas lower than those found in sediments of Pearl River Estuary. The average concentrations of Cd, Cu, Pb and Zn were significantly lower than those found in sediments of the Izmit Bay in Turkey and, to a lesser extent, lower than those found in sediments of the Masan Bay in Korea too. The average concentration of Pb recorded in this study was comparable to that in Jiaozhou Bay, and lower than those in Daya Bay, coast off southwestern Taiwan and western Xiamen Bay.

The correlation matrix for the parameters studied was shown in Table 2. Except the relationships between Ni and Cd and Ni and Zn, all the metals were significantly correlated, suggesting a major common origin in sediments. The wastewater discharge especially from industrial sources could be responsible for this (Liu et al., 2003; Wang and Wang, 2007). As observed through their correlations, the concentrations of Cd, Pb and Zn appeared to be more influenced by the amount of organic matter than by the sediment grain size composition, the concentration of Ni appeared to be more influenced by the sediment grain size composition than by the amount of organic matter, the concentration of Cu appeared to be influenced by both the sediment grain size composition and the amount of organic matter, and the concentration of Cr appeared to be influenced by neither the sediment grain size composition nor the amount of organic matter.

### Table 1 - The summery of heavy metal contents in sediments collected from Bohai Bay. The average upper continental crust values and related values reported for surface sediments from some of the other coastal areas were also shown for comparison purpose. Content unit is µg g⁻¹ for all elements.

<table>
<thead>
<tr>
<th>Location</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Coastal Bohai Bay, China</strong></td>
<td>Range</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Present study</td>
</tr>
<tr>
<td><strong>UCC</strong></td>
<td>0.12–0.66</td>
<td>0.22</td>
<td>60.1–224.5</td>
<td>38.5</td>
<td>40.7</td>
<td>34.7</td>
<td>131.1</td>
</tr>
<tr>
<td><strong>Daya Bay, China</strong></td>
<td>0.098</td>
<td>35</td>
<td>25</td>
<td>20</td>
<td>20</td>
<td>71</td>
<td>Taylor and McLennan, 1995</td>
</tr>
<tr>
<td><strong>Pearl River Estuary, China</strong></td>
<td>0.052</td>
<td>na⁵</td>
<td>20.8</td>
<td>31.2</td>
<td>45.7</td>
<td>113</td>
<td>Gao et al., 2010</td>
</tr>
<tr>
<td><strong>Changjiang Estuary, China</strong></td>
<td>na</td>
<td>88.97</td>
<td>46.15</td>
<td>41.73</td>
<td>59.26</td>
<td>150.06</td>
<td>Zhou et al., 2004</td>
</tr>
<tr>
<td><strong>Coast off southwestern Taiwan</strong></td>
<td>0.26</td>
<td>78.9</td>
<td>30.7</td>
<td>31.8</td>
<td>27.3</td>
<td>94.3</td>
<td>Zhang et al., 2009</td>
</tr>
<tr>
<td><strong>Jiaozhou Bay, China</strong></td>
<td>0.56</td>
<td>73</td>
<td>32</td>
<td>35</td>
<td>44</td>
<td>158</td>
<td>Chen and Selvaraj, 2008</td>
</tr>
<tr>
<td><strong>Western Xiamen Bay, China</strong></td>
<td>0.08</td>
<td>45.1</td>
<td>24.9</td>
<td>na</td>
<td>32.3</td>
<td>69.7</td>
<td>Chen et al., 2005</td>
</tr>
<tr>
<td><strong>Izmit Bay, Turkey</strong></td>
<td>0.33</td>
<td>75</td>
<td>44</td>
<td>37.4</td>
<td>50</td>
<td>139</td>
<td>Zhang et al., 2007</td>
</tr>
<tr>
<td><strong>Masan Bay, Korea</strong></td>
<td>4.9</td>
<td>74.3</td>
<td>67.6</td>
<td>na</td>
<td>102</td>
<td>930</td>
<td>Pekey, 2006</td>
</tr>
<tr>
<td><strong>Pearl River Estuary, China</strong></td>
<td>1.24</td>
<td>67.1</td>
<td>43.4</td>
<td>28.8</td>
<td>44.0</td>
<td>206.3</td>
<td>Hyun et al., 2007</td>
</tr>
</tbody>
</table>

a Average concentrations of the upper continental crust.

b na: not available.

### 3.3. Metal fractionation

Metal fractionation is of critical importance to their potential toxicity and mobility (Maiz et al., 2000). It is no doubt that metal measurement in total concentration is the most fundamental way for sediment quality assessment. Yet, other approaches need to be applied for the understanding of potential mobility, bioavailability and toxicity of metals in sediments, because the properties of metals in sediments...
Pearson correlation matrix for the sediment components.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
<th>%Clay</th>
<th>%Silt</th>
<th>%Sand</th>
<th>%TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.761</td>
<td>0.609</td>
<td>0.273</td>
<td>0.703</td>
<td>0.801</td>
<td>0.046</td>
<td>-0.192</td>
<td>0.107</td>
<td>0.559</td>
</tr>
<tr>
<td>Cr</td>
<td>0.657</td>
<td>0.604</td>
<td>0.508</td>
<td>0.634</td>
<td>0.303</td>
<td>0.192</td>
<td>-0.192</td>
<td>-0.154</td>
<td>0.230</td>
</tr>
<tr>
<td>Cu</td>
<td>0.758</td>
<td>0.703</td>
<td>0.388</td>
<td>0.461</td>
<td>0.461</td>
<td>0.174</td>
<td>-0.174</td>
<td>-0.327</td>
<td>0.437</td>
</tr>
<tr>
<td>Ni</td>
<td>0.434</td>
<td>0.228</td>
<td>0.749</td>
<td>0.141</td>
<td>0.749</td>
<td>0.121</td>
<td>-0.121</td>
<td>-0.660</td>
<td>0.068</td>
</tr>
<tr>
<td>Pb</td>
<td>0.745</td>
<td>0.077</td>
<td>0.094</td>
<td>0.749</td>
<td>0.174</td>
<td>0.174</td>
<td>-0.174</td>
<td>-0.091</td>
<td>0.815</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.077</td>
<td>-0.074</td>
<td>0.137</td>
<td>0.643</td>
<td>0.643</td>
<td>0.643</td>
<td>0.643</td>
<td>0.643</td>
<td></td>
</tr>
</tbody>
</table>

a P < 0.001.
b 0.001 < P < 0.01.
c 0.01 < P < 0.05.

Fig. 4 – Hierarchical dendrogram in terms of the sampling stations based on the data of metals in total concentrations.

depend on the physicochemical form in which they occur besides their total contents (Gleyzes et al., 2002). The sequential extraction technique is proposed for this purpose to provide information about the strength and ways of metal associating with sediments (Tessier et al., 1979).

The percentages of heavy metal concentrations that were extracted in each step of the sequential extraction procedure used in this study were presented in Fig. 3.

The metals in acid soluble fraction are considered to be the weakest bonded metals in sediments which may equilibrate with the aqueous phase and thus become more easily bioavailable (Pardo et al., 1990). The more proportion of metals in this fraction, the more mobile they are, and the higher risk they could pose to the environment. Except for Cd at all stations and Zn at a few riverine stations, the relative proportions of metals in the acid soluble fraction were generally very low, especially for Cr. The mean proportions of acid soluble Cr, Cu, Ni and Pb were 0.3%, 2.3%, 3.5% and 2.2% respectively indicating that they had low mobility. The contents of acid soluble Cd on average were higher than other Cd fractions. The highest percentage of this fraction, up to 60.3%, was observed for Cd with the mean of 48%. The high proportion of Cd in this fraction may be owing to the fact that it is a typical anthropogenic element and mostly enters the aquatic environment through the discharge of industrial effluents. For Zn, although its mean proportion in the acid soluble fraction was only 8.2%, it presented a clear spatial variation with a range of 0.6–44.0%. On average, the percentage of Zn in the acid soluble fraction for sediments from the riverine region was higher than those from the marine region.

The spatial variations of the percentages of Cd, Cu and Zn in reducible fraction were more significant than the other three metals. Overall, reducible fraction was the most abundant non-residual fraction for Cu, Pb and Zn. The proportion of Pb in reducible fraction was much higher than that of other metals in this fraction. 51.5% of Pb was measured in this fraction with the range of 35.2–65.3%. The average proportion of Cr in this fraction was the lowest among the studied metals, and its value was 3.4%.

The mean percentage of metal in oxidizable fraction from low to high was 2.4% for Zn, 4.9% for Cu, 5.2% for Pb, 5.8% for Cd, 8.2% for Cr and 12.1% for Ni. At 10 sampling stations, the proportion of Zn in oxidizable fraction could be ignored and accounted for <1% of its total concentration in sediment.

Cr occurred mostly in the residual fraction of sediment at most sampling stations. Its average percentage in this fraction was 88% with the range of 36.5–94.2%, and its percentage in this fraction for sediments from the marine region was >90%. Only ~5–10% of Cr in total concentration was associated with oxidizable fraction, and more or less none was associated with acid soluble fraction. High proportions of this fraction were also observed for Cu, Ni and Zn. These facts indicated the mineralogical origin of these metals in sediments of the coastal Bohai Bay and their relatively low bioavailability and toxicity.

There were some other notable points from the fractionation results. For example, the sediments with high concentration of total Zn (one sample from each of the four transects only) also contained higher contents of acid soluble Zn; the station ZYX-2 showed relatively high contents of oxidizable Cr and acid soluble Zn.

3.4. Metal enrichment and potential risk

Numerous sediment quality guidelines (SQGs) have been developed to deal with environmental concerns, and three of
them were chosen to assess the contamination extent of individual metals in surface sediments of the coastal Bohai Bay (Table 3).

The National Standard of China (NSC) GB18668-2002 (SEPA, 2002) has defined three grades of marine sediments, in which the contents of Cd, Cr, Cu, Pb and Zn are regarded as parameters used to classify marine sediment quality. According to this criterion, the first class quality is suitable for mariculture, nature reserve, endangered species reserve, and leisure activities such as swimming; the second class quality can be used for industry and tourism site; and the third class can just be used for harbor. All metals at all the sites were below the threshold values for Class I sediment except for Cr at sites ZYX-2 and QH-2 and Zn at sites DH-3 and ZYX-2. The Cd, Cr, Cu, Pb and Zn contents at 98%, 12%, 40%, 95% and 86% of sites were within the range for Class I sediment identification. Only sediments from five sites were clean enough to be classified as Class I grade when the contents of all the five metals were considered, and the other sites were at least contaminated by Cr.

In Hong Kong, a stricter criterion has been used to distinguish sediment quality (Lau et al., 1993). The contents of Cd, Pb and Zn in sediments from 93%, 55% and 7% of stations respectively were lower than 'target' values and showed no signs of contamination. The contents of Cd at 7% of stations, Cu at 95% of stations, Ni at 21% of stations, Pb at 43% of stations and Zn at 78% of stations were, to some extent, higher than the values which are regarded as the upper limit of the desired quality for fairly clean sediments, but lower than the threshold values which are used to indicate moderately contaminated sediments. Sediments from 12%, 5%, 17%, 2% and 5% of sites were moderately contaminated by Cr, Cu, Ni, Pb and Zn respectively, and sediments from 88%, 62% and 10% of sites were heavily polluted by Cr, Ni, and Zn respectively.

Our data suggested that no sites exceeded the Effects Range-Low (ERL) guideline (Long et al., 1995) for Cd. In the case of other metals, 14% of sites were below the ERL guideline for Cr, 33% of sites were below the ERL guideline for Cu, 86% of sites were below the ERL guideline for Zn, and 95% of sites were below the ERL guideline for Pb; whereas Ni at all sites exceeded the ERL guideline and its value at one site was even slightly higher than the Effects Range-Median (ERM) guideline (Long et al., 1995), which indicated a potential harm for benthic organisms. The Zn value at one site also exceeded the ERM guideline.

All the SQGs used above were achieved through assessing individual chemicals by comparing the chemical concentrations with their corresponding limit concentrations. Based on the fact that heavy metals always occur in sediments as complex mixtures, the mean ERM 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 (Carr et al., 1996):

$$\text{mean ERM quotient} = \frac{\sum(C_x/\text{ERM}_x)}{n}$$

where $C_x$ is the sediment concentration of component $x$, $\text{ERM}_x$ is the ERM 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 ERM quotients of $<0.1$ have a 9% probability of being toxic, the mean ERM quotients of $0.11–0.5$ have a 21% probability of being toxic, the mean ERM quotients of $0.51–1.5$ have a 49% probability of being toxic, and the mean ERM quotients of $>1.50$ have a 76% probability of being toxic (Long et al., 2000). As shown in Fig. 5, in surface sediments of the coastal Bohai Bay, the mean ERM quotients varied within the range of 0.16–0.47 indicating that the combination of the six studied metals might have a 21% probability of being toxic.

The total concentrations of metals in coastal sediments depend mainly on their quantities naturally present, the quantities added by human activities and the capacity of sediments for picking up the metals that are introduced into the system (Mecray and Buchholz ten Brink, 2000). In order to get a better understanding of distribution tendencies, different contribution sources or anthropogenic enrichments of metals in sediments, it is necessary to eliminate the effects of other factors such as the mineralogy and grain size variations.

The normalization is a means of compensating for the effect of these factors and it allows us to detect and quantify the anthropogenic metal contributions (Loring, 1991). Technically, the parameter suitable for normalization needs to be the textural characteristic or component of sediments to compensate for variations in both grain size and composition. 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 a normalization technique widely used to separate the metals of natural variability from the metal fraction that is associated with sediments due to modern activities. The EF for each element was calculated to evaluate anthropogenic influences on heavy metals in sediments using the following formula (Selvaraj et al., 2004):

$$\text{EF} = \frac{C_{x}/C_{Al}}{C_{x}/C_{Al}} \times 100$$

where $C_{x}$ is the metal fraction that is associated with sediments due to modern activities and $C_{x}/C_{Al}$ is the normalization ratio for metal $x$. The Enrichment Factor range of metals and the classification are important parameters for evaluating heavy metal contamination in coastal sediments.
EF = \left( \frac{C_x}{C_{Al}} \right)_{S} / \left( \frac{C_x}{C_{Al}} \right)_{UCC}

where \( C_x \) and \( C_{Al} \) denote the concentrations of elements \( x \) and \( Al \) in the samples of interest (S) and the upper continental crust (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).

The spatial distributions of calculated EFs for each of the studied metals were displayed in Fig. 6. Taking as a whole, the

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**Fig. 5** – The spatial distribution of mean ERM quotient values in surface sediments of coastal Bohai Bay.

**Fig. 6** – The spatial distributions of EF values for heavy metals in surface sediments of coastal Bohai Bay. The horizontal lines represent EF value of 1.5.
mean EF values of all the studied metals suggested their enrichments in surface sediments of Bohai Bay coast. The mean EF value of 2.91 made Cr the most contaminated metal of all, followed by Cd, Ni, Zn, Pb and Cu in sequence, the mean values of which were 2.23, 2.04, 1.89, 1.76 and 1.54 respectively. According to the work of Hakanson (1980), metals in surface sediments of this study could be classified into the following 2 groups based on the pollution potential: (1) negligible to low contamination ($EF < 2$), which was the case of Cu, Pb and Zn; (2) moderate contamination ($2 < EF < 4$), which was the case of Cd, Cr and Ni. Specifically, apparently higher EF values for Cd, Cu, Pb and Zn were mainly recorded at five sampling stations, namely DH-3, DH-2, CB-1, HH-1 and ZYX-2. These five riverine stations also relatively contained higher TOC contents, more acid soluble Zn, more non-residual Cd and higher reducible Pb (Figs. 2 and 3). These suggested that riverine sediments in these stations were likely to be contaminated with these heavy metals. Further, sediments of all other stations, especially from the marine region were not or slightly contaminated with most of the metals studied.

Given that the metals in residual fraction are an indication of lithogenic input, while those in non-residual fractions can mainly be explained by anthropogenic inputs. As shown in Fig. 7, for all the six metals studied, there was a significant correlation between metals in non-residual fraction and their corresponding EF values. This indicated that anthropogenic inputs were probably the major contributor for their enrichment in the surface sediments of coastal Bohai Bay. For Cu, Ni and Pb, the contribution of lithogenic input was as important as that of anthropogenic inputs.

4. Conclusions

Except for a few riverine samples, Cd, Pb and Zn contents in the coastal Bohai Bay sediments were characteristics of unpolluted levels. Besides, on average, more than 50% of Cr, Cu, Ni and Zn were associated with the residual fraction. The metals associated with this fraction could not be remobilized under the conditions normally present in nature. Although on average 48% of Cd was found in acid soluble fraction of sediments, which made it the one with the highest mobility among all the six studied metals, it could hardly cause a bad effect on the environment owing to its low total concentration. Taking as a whole, surface sediments of the coastal Bohai Bay had a 21% probability of toxicity based on the mean effects range-median quotient.

The results of this project revealed that the behaviors of heavy metal partitioning onto sediments were generally uniform in marine sediments of the coastal Bohai Bay. Anthropogenic influences might be responsible for the obvious spatial variation of metal fractionation patterns in riverine sediments. Heavy metal enrichment in sediments of the coastal Bohai Bay was widespread. Non-point source inputs from both fluvial transport and atmospheric deposition were important ways for the sediment contamination in this area. The exceptionally elevated concentrations at some riverine spots could be related to land-based point source discharges.

This study also suggested that the metal contamination could not be simply evaluated by examining metal concentrations alone. The fractionation should be considered in order to provide a more accurate appraisal of the risk of these metals to the environment.

Considering that this study was carried out in the area of Bohai Bay receiving most anthropogenic influence, a greater extent of contamination by these metals in surface sediments of other parts of Bohai Bay is not expected, except for some harbor areas which are usually severely polluted by heavy metals. Altogether, the Bohai Bay could not be considered as one of the highly polluted marine areas of China at least in terms of these heavy metals.
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