Research Article

Spatial Distribution and Contamination Assessment of Heavy Metals in Surface Sediments of the Caofeidian Adjacent Sea after the Land Reclamation, Bohai Bay

He Zhu,^{1,2,3} Haijian Bing,¹ Huapeng Yi,² Yanhong Wu ¹ and Zhigao Sun ⁴

¹Key Laboratory of Mountain Surface Processes and Ecological Regulation, Institute of Mountain Hazards and Environment, Chinese Academy of Sciences, Chengdu 610041, China

²School of Resources and Environmental Engineering, Ludong University, Yantai 264025, China

³University of Chinese Academy of Sciences, Beijing 100049, China

⁴Key Laboratory of Humid Subtropical Eco-Geographical Process (Fujian Normal University), Ministry of Education, Fuzhou 350007, China

Correspondence should be addressed to Yanhong Wu; yanhong_wu@yeah.net and Zhigao Sun; zhigaosun@163.com

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Land reclamation can significantly influence spatial distribution of heavy metals in inshore sediments. In this study, the distribution and contamination of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in inshore sediments of Bohai Bay were investigated after the land reclamation of Caofeidian. The results showed that the concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the sediments were 0.20–0.65, 27.16–115.70, 11.14–39.00, 17.37–65.90, 15.08–24.06, and 41.64–139.56 mg/kg, respectively. These metal concentrations were generally higher in the area of Caofeidian than in other Chinese bays and estuaries. Spatially, the concentrations of Cd, Cr, Cu, Ni, and Zn were markedly lower in the sediments close to Caofeidian compared with other regions, whereas the concentrations of Pb showed an opposite case. Hydrodynamic conditions after the land reclamation were the major factor influencing the distribution of heavy metals in the sediments. Grain sizes dominated the distribution of Cu and Zn, and organic matters and Fe/Mn oxides/hydroxides also determined the distribution of the heavy metals. Multiple contamination indices showed that the inshore sediments were moderately to highly contaminated by Cd and slightly contaminated by other heavy metals. Similarly, Cd showed a high potential ecorisk in the sediments, and other metals were in the low level. Chromium contributed to higher exposure toxicity than other metals by the toxicity unit and toxic risk index. The results of this study indicate that after the land reclamation of Caofeidian the contamination and ecorisk of heavy metals in the sediments markedly decreased in the stronger hydrodynamic areas.

1. Introduction

Heavy metal contamination is a major issue in marine environment due to the toxicity, persistence, nonbiodegradability, and bioaccumulation [1–3]. After entering food chain, they can cause potential threat to human beings and other organisms [4]. In aquatic systems, sediments are the main sink of various contaminants discharged from industrial and agricultural processes [5–7], and they are regarded as an effective archive recording heavy metal contamination [2, 8, 9]. To date, a large number of studies have reported the accumulation of heavy metals in the sediments of aquatic

ecosystems [3, 10–13]. The main reason is that once the conditions of sedimentary environment change, heavy metals are apt to release into water from the sediments [14–16]. Therefore, it is necessary to understand the characteristics of heavy metals in aquatic sediments and assess their contamination states.

The coastal zone is one of the most frequent areas disturbed by human activities through plant and port construction, land reclamation, and tourism [1, 17–19]. Human activities, on the one hand, will increase the loadings of heavy metals in the aquatic system through direct industrial discharge, city sewage, domestic runoff, and so forth [20–22];

on the other hand, they can change pristine sedimentary environment which may contribute to the release of heavy metals from sediments. Among these human activities, land reclamation engineering is significant to influence aquatic environment [23–25]. It not only alters the hydrodynamic conditions surrounding the land but also may increase inputs of heavy metals through sewage discharge and shipping after the engineering. The distribution of heavy metals and their controlling factors in sediments of coastal zone still need to be explored under the land reclamation.

The toxicity of heavy metals is the priority in aquatic ecosystems [26–28]. In order to control the contamination of marine sediments and protect marine biological resources, China, USA, Canada, and other countries have established the standard of marine sediment quality for heavy metals [29, 30]. Meanwhile, various methods have been applied to assess the contamination and ecorisk of heavy metals in sediments, including enrichment factor [31, 32], index of geoaccumulation [33, 34], toxic units and toxic risk index [35], and potential ecorisk index [22, 36]. However, each method has its limitation or specialization, and thus it is necessary to use multiple methods in order to accurately obtain the contamination and ecorisk states of heavy metals in sediments [11, 15].

Bohai Bay is located in the western Bohai Sea. Due to the weak exchange capacity of the water in Bohai Bay, the contaminants from surrounding industrial cities are not easy to spread. Recently, the Bohai Bay has been regarded as a main region of contaminant accumulation, especially in the sediments [37–39]. These studies investigated the distribution of heavy metals and assessed their contamination, and the results showed that human activities increased the accumulation of heavy metals in the sediments of Bohai Bay [25, 40]. However, most of the studies were conducted in the areas of Tianjin Port [41, 42], whereas there are very few reports about the distribution and contamination states of heavy metals in the sediments of northern Bohai Bay. This limits our understanding of heavy metal distribution in the entire area of Bohai Bay. More importantly, the large-scale reclamation project has been finished in Caofeidian for few years. This engineering certainly influences the environment conditions of inshore and adjacent marine area. Whether the land reclamation causes significant difference of the distribution and contamination of heavy metals in the sediments around Caofeidian deserves to be explored.

In this study, the surface sediments in the coastal areas of Caofeidian were collected to analyze the concentrations of heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn). The main objectives are (1) to investigate distribution characteristics of these heavy metals in the sediments, (2) to explore the possible controlling factors for their spatial distributions, and (3) to assess the contamination and potential ecological risk of the heavy metals. This is the first time to reveal the distribution of heavy metal contamination in the surface sediments of Caofeidian after the land reclamation project.

2. Materials and Methods

2.1. Study Area. Caofeidian is located in the northern Bohai Bay (38°58′52″–38°54′42″N, 118°33′36″–118°30′03″E,

Figure 1). It is surrounded by Hebei province and Tianjin City on the north and west, respectively. Hai River, Luan River, Yongding River, and other small rivers discharge water into the inshore and adjacent areas of Caofeidian. Laolonggou, located in the eastern Caofeidian, is the ancient Luanhe River with previous tidal channel [43]. The study area has complex geomorphic types with a large number of sandbanks distributed in this area. The average water depth around the Caofeidian is approximately 30 m (Figure 1), and the deepest site (B20) reaches approximately 36 m due to the strong hydrodynamic conditions. Due to the presence of sandbanks and deep water depth, a large-scale reclamation project has been implemented in Caofeidian in 2003, and the project is basically finished in 2011. Now it becomes one of the busiest ports in the Bohai Sea with a cargo throughput of >5 billion tons in 2014 [28].

2.2. Sample Collection. The sampling was carried out in August 2014. Twenty-two sampling sites in the inshore and adjacent areas of Caofeidian were selected to collect the surface sediments (Figure 1). At each site, the sediment samples were collected using a gravity sampler, and then the surface sediments (0–5 cm) were sliced by a plastic spatula in the field. The samples were put in polyethylene bags and stored at –20°C for further analysis. In laboratory, the sediment samples were freeze-dried. The samples for the grain size analysis passed through 2 mm sieves, and those for the analysis of total organic carbon (TOC) and elements passed through 100-mesh Nylon screen.

2.3. Chemical Analysis. The grain sizes of the surface sediments were measured by a Mastersizer-2000 laser particle size analyzer (Malvern, UK) after removal of organic matters with 30% H₂O₂ with the dispersion of sodium hexametaphosphate. Three classes of grain sizes were divided into clay (<4 μm), silt (4–63 μm), and sand (>63 μm). The concentrations of TOC in the sediments were measured 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 concentrations of metals in the sediments were measured according to the method of Gao and Chen [23]. Briefly, approximately 0.1 g samples were digested in Teflon Vessel with the mixed concentrated acids of HF-HNO₃-HClO₄ (5:2:1) and then heated (140–150°C) to dryness. The residue was digested with HNO₃ again. At the end, the extraction was diluted to 50 mL volume. The concentrations of Fe and Mn were measured by an inductively coupled plasma atomic emission spectrometer (ICP-AES), and those of Cd, Cr, Cu, Ni, Pb, and Zn were detected by an inductively coupled plasma mass spectroscopy (ICP-MS). Quality assurance and control were evaluated using duplicates, blanks, and standard reference materials (GBW 07401) from the National Research Center for Standards in China. According to the measurement of the repeated samples and reference materials, the relative standard deviation was below 3% for ICP-AES and below 5% for ICP-MS, respectively. The recovery of the reference materials was 95.3%–107.3%.

FIGURE 1: The location of the study area and the sampling sites in the Bohai Bay.

2.4. Calculation of Contamination and Ecorisk Indices

2.4.1. Enrichment Factors (EFs). The EFs of heavy metals in the sediments are calculated as follows [11]:

$$EF = \frac{(Me/Fe)_{\text{sample}}}{(Me/Fe)_{\text{background}}}, \quad (1)$$

where $(Me/Fe)_{\text{sample}}$ is the concentration ratio of a metal to Fe in a sample and $(Me/Fe)_{\text{background}}$ is the corresponding ratio in the background.

2.4.2. Geoaccumulation Index. The geoaccumulation index (I_{geo}) is another indicator used to assess the contamination of heavy metals in sediments [33]:

$$I_{\text{geo}} = \log_2 \left(\frac{C_n}{k \times B_n} \right), \quad (2)$$

where C_n is the concentration of a metal measured in a sample, B_n is the geochemical background of the metal, and k is a background matrix correction factor (1.5) due to lithogenic effects [31]. The contamination classes of I_{geo} are classified as $I_{\text{geo}} \leq 0$, uncontaminated; $0 < I_{\text{geo}} \leq 1$, uncontaminated to moderately contaminated; $1 < I_{\text{geo}} \leq 2$, moderately contaminated; $2 < I_{\text{geo}} \leq 3$, moderately to heavily contaminated; $3 < I_{\text{geo}} \leq 4$, heavily contaminated; $4 < I_{\text{geo}} \leq 5$, heavily to extremely contaminated; $I_{\text{geo}} > 5$, extremely contaminated [33].

2.4.3. Potential Ecorisk Index (E_r^i). The potential ecorisk index is commonly used to assess the ecorisk of heavy metals in sediments [36]:

$$E_r^i = T_r^i * \frac{C_o^i}{C_n^i}, \quad (3)$$

$$RI = \sum_{i=1}^n E_r^i,$$

where E_r^i is the potential ecorisk index, T_r^i is the toxic response coefficient of a given metal, C_o^i is the concentration of a metal measured in a sample, and C_n^i is its geochemical background. The toxic response coefficient of Cd, Cr, Cu, Ni, Pb, and Zn is 30, 2, 5, 2, 5, and 1, respectively. The potential ecorisk level of heavy metals in sediments is classified as $E_r^i \leq 40$, low; $40 < E_r^i \leq 80$, moderate; $80 < E_r^i \leq 160$, high; $160 < E_r^i \leq 320$, very high; $E_r^i > 320$, extremely high. The risk classes of RI are classified as <150 , low risk; $150-300$, moderate risk; $300-600$, considerable risk; ≥ 600 , disastrous risk [39].

2.4.4. The Toxic Units (TUs) and Toxic Risk Index (TRI). The TU defined by Pedersen et al. [48] is the ratio of a metal concentration to the probable effects level (PEL). $\sum TUs$ is the sum of the ratio of six heavy metals to PEL. These indices can assess heavy metal toxicity relative to the standard. $\sum TUs < 4$ represents nontoxicity and $\sum TUs > 6$ represents acute toxicity:

TABLE 1: The concentrations of heavy metals and physiochemical properties in the sediments.

	Unit	Max	Min	Average
Cd	mg/kg	0.65	0.20	0.34
Cr	mg/kg	115.70	27.16	85.59
Cu	mg/kg	39.00	11.14	28.82
Ni	mg/kg	65.90	17.37	41.35
Pb	mg/kg	24.06	15.08	21.02
Zn	mg/kg	139.56	41.64	88.64
Fe	mg/g	50.02	20.72	37.09
Mn	mg/kg	868.15	302.49	571.33
Clay	%	17.91	7.67	13.05
Silt	%	80.52	37.71	63.42
Sand	%	54.62	3.29	23.53
TOC	%	0.95	0.26	0.72

$$\sum \text{TUs} = \sum_{i=1}^n \frac{C_s^i}{C_{\text{PEL}}^i}. \quad (4)$$

The TRI is used to assess the integrated toxic risk based on the threshold effect level (TEL) and PEL of heavy metals [26]:

$$\text{TRI} = \sqrt{\frac{(C_s^i/C_{\text{TEL}}^i)^2 + (C_s^i/C_{\text{PEL}}^i)^2}{2}}, \quad (5)$$

where C_s^i is the concentration of a metal measured in the sample, and C_{TEL}^i and C_{PEL}^i are the TEL and PEL of the metal, respectively. The TRI can be classified as no toxic risk ($\text{TRI} < 5$), low toxic risk ($5 \leq \text{TRI} < 10$), moderate toxic risk ($10 \leq \text{TRI} < 15$), considerable toxic risk ($15 \leq \text{TRI} < 20$), and very high toxic risk ($\text{TRI} \geq 20$).

2.5. Statistical Analysis. Pearson correlation analysis was applied to establish the relationships between heavy metals and sediment physiochemical properties by the software package SPSS 16.0 for Windows. The spatial distribution characteristics of heavy metals and physiochemical properties in the sediments were performed by the software ArcGIS 10.2 with the method of inverse distance weighted (IDW).

3. Results and Discussion

3.1. Sediment Physiochemical Properties. The composition of grain sizes showed the order of silt (37.71–80.41%, average: 63.42%) > sand (3.29–54.62%, 23.53%) > clay (7.39–17.91%, 13.05%) (Table 1). Spatially, clay and silt presented a similar distribution pattern (Figure 2). The lower contents of silt and clay were observed in the Laolonggou, compared with other regions, whereas the higher contents occurred in the western Caofeidian and the central Bohai Bay. The spatial distribution of sand generally showed the opposite case to that of clay and silt.

The concentrations of TOC varied between 0.26% and 0.95% with the average of 0.72% (Table 1). The concentrations of TOC were relatively lower in the eastern Caofeidian

than in other areas, and the highest was observed in the central Bohai Bay (Figure 2). The concentrations of Fe and Mn varied between 50.02 and 20.72 (average: 37.09, g/kg) and between 302.49 and 868.15 (average: 571.33, mg/kg), respectively (Table 1). The concentrations of Fe and Mn were lower in the eastern and western Caofeidian than in the central Bohai Bay (Figure 2).

3.2. The Concentrations of Heavy Metals in the Sediments. The concentrations of heavy metals in the sediments are presented in Table 1. Specifically, the concentrations (mg/kg) varied between 0.20 and 0.65 (average: 0.36) for Cd, between 27.16 and 115.70 (78.64) for Cr, between 11.14 and 39.00 (29.07) for Cu, between 17.37 and 65.90 (41.35) for Ni, between 15.08 and 24.06 (21.11) for Pb, and between 41.64 and 139.56 (89.60) for Zn. The concentrations of all the heavy metals in the sediments exceeded their background standards in the upper continental crust (Table 2). Compared with some bays and estuaries in China, the Cd concentrations in the inshore sediments of Caofeidian were higher except for the Liaodong Bay (Table 2). For other heavy metals, their concentrations in our study area were generally higher than those in other estuaries.

The distribution of heavy metals in the sediments displayed significantly different spatial patterns (Figure 3). The concentrations of Cd in the sediments were generally lower in the surrounding areas of Caofeidian relative to the south-eastern and southwestern area. The similar distribution of Cr, Cu, Ni, and Zn was observed spatially, and their lower concentrations occurred in the eastern and western Caofeidian compared with other areas. The distribution of Pb in the sediments showed that its concentrations were markedly higher in the inshore areas of Caofeidian and the central Bohai Bay compared with the western study area.

3.3. Factors Controlling the Distribution of Heavy Metals. Hydrodynamic conditions are a main factor influencing the distribution of heavy metals in the sediments. The concentrations of heavy metals except for Pb were higher in the central Baohai Bay compared with those in the western and eastern Caofeidian (Figure 3). The oceanic current in the northern

FIGURE 2: The spatial distribution of grain sizes, TOC, Fe, and Mn in the sediments.

Bohai Bay has been observed flowing from east to west [49]. The land reclamation of Caofeidian blocks the oceanic current which should have passed through the Caofeidian area before the reclamation project. The channel of the oceanic current becomes narrow in the northern Bohai Bay, resulting in much erosion in the Laolonggou area (Figure 1), and then the current enters the cape of Caofeidian [24, 49]. The variation of the hydrodynamic conditions around the Caofeidian cape led to the fine particles washed out and hard to deposit in the eastern area and the cape of Caofeidian [43]. This was a major reason for the low distribution of heavy metals in the eastern area and the cape of Caofeidian. With the flow of the oceanic current forward, the hydrodynamic conditions became weakened which favored the sediment

deposition and then the heavy metal accumulation in the western Caofeidian.

The results of Pearson correlation analysis showed that Cu and Zn correlated significantly with clay and silt ($p < 0.05$, Table 3). The concentrations of heavy metals in sediments increase with decreasing particle size because the fine-grained sediments tend to adsorb much more heavy metals due to their high specific surface area [50, 51]. The fine particles were markedly observed in the western Caofeidian and the central Bohai Bay compared with the Laolonggou and the cape of Caofeidian (Figure 2). Lu et al. (2009) also reported that the grain sizes of the sediments in the study area decreased from the eastern to western Caofeidian [24]. The tidal current induced the runoff and sorting of the sediments

TABLE 2: The concentrations of heavy metals in the sediments of Caofeidian adjacent sea and other reports (Unit: mg/kg). The concentrations using to assess the contamination of heavy metals are also shown.

	Cd	Cr	Cu	Ni	Pb	Zn	
Caofeidian inshore	0.19–0.65	2716–115.70	11.14–39.01	1737–65.90	15.08–24.06	41.64–139.56	This study
Intertidal Bohai Bay	0.36	78.64	29.07	41.35	21.11	89.60	[10]
Laizhou Bay	0.12	68.6	24	28	25.1	73	[44]
Coastal Bohai bay	0.12	60	22	-	21.9	60.4	[22]
Liaodong Bay	0.22	101.4	38.5	40.7	34.7	131.1	[7]
Luan River Estuary	1.2	46.4	19.4	22.5	31.8	71.7	[28]
Yangtze River Estuary	0.09	41.14	17.17	15.6	30.98	44.63	[15]
Yangtze River Estuary	0.19	79.1	24.7	31.9	23.8	82.9	[45]
Background (UCC)	0.15	34.64	17.46	-	30.47	66.91	[46]
Class-1	0.10	35	25	20	20	71	[30]
Class-2	0.50	80	35	-	60	150	
Class-3	1.5	150	100	-	130	350	
TEL	5.00	280	200	-	250	600	
TEL	0.68	52.3	18.7	15.9	30.2	124	[47]
PEL	4.21	160	108	42.8	112	271	

UCC: upper continental crust; TEL (threshold effect level): guideline values indicate the metal concentrations below which adverse effects on biota are rarely observed; PEL (probable effects level): guideline values indicate the metal concentrations above which adverse effects on biota are probably observed.

FIGURE 3: The spatial distribution of heavy metals in the sediments.

[52, 53]. As a result, the concentrations of Cu and Zn in the sediment showed the higher values in the western Caofeidian and the central Bohai Bay than in the Laolonggou and the cape of Caofeidian. However, other heavy metals did not show significant relationships with the fine particles, which indicated that other factors determined their distribution in the sediments.

Organic matters and Fe/Mn oxides/hydroxides were considered as the controlling factors in the spatial distribution of heavy metals in the sediments. Organic matters can regulate the geochemical behavior of heavy metals via adsorption, desorption, and complexation [54]. In our study, Cd, Cr, Cu,

Ni, and Zn in the sediments showed a significant positive correlation with TOC ($p < 0.05$, Table 3), which indicated that the adsorption and/or complexation of the organic matters might control the distribution of these metals in the sediments. However, there was a clear spatial difference of the distribution between TOC and heavy metals in the western Caofeidian. This indicated that organic matters were not the major controlling factor in the distribution of the heavy metals in this area. The Fe/Mn oxides/hydroxides coated on clay minerals or in individual minerals are important carriers of heavy metals. In this study, the heavy metals in the sediments correlated significantly with Fe and Mn ($p < 0.01$,

TABLE 3: Pearson correlation of heavy metals with physicochemical properties in the sediments.

	Mn	Fe	Cd	Cr	Cu	Ni	Pb	Zn	Clay	Slit	Sand	TOC
Mn	1											
Fe	0.80**	1										
Cd	0.52*	0.77**	1									
Cr	0.81**	0.82**	0.71**	1								
Cu	0.60**	0.86**	0.64**	0.68**	1							
Ni	0.77**	0.84**	0.71**	0.92**	0.86**	1						
Pb	0.61**	0.63**	0.45*	0.69**	0.47*	0.69**	1					
Zn	0.57**	0.89**	0.71**	0.68**	0.90**	0.81**	0.60**	1				
Clay	0.16	0.51*	0.32	0.21	0.70**	0.42	0.14	0.68**	1			
Slit	-0.09	0.35	0.27	-0.04	0.53*	0.17	0.02	0.58**	0.88**	1		
Sand	0.06	-0.38	-0.28	0.01	-0.56**	-0.21	-0.04	-0.61**	-0.91**	-1.00**	1	*
TOC	0.47*	0.80**	0.64**	0.50*	0.81**	0.61**	0.30	0.85**	0.76*	0.68**	-0.70**	1

**Correlation is significant at the 0.01 level (two-tailed); *Correlation is significant at the 0.05 level (two-tailed).

Table 3), and spatially the distribution of heavy metals was in agreement with that of Fe and Mn. This indicated that the Fe/Mn oxides/hydroxides played an important role in the distribution of heavy metals, especially in the western Caofeidian.

As shown in Figure 3, the distribution of Pb in the sediments was different from that of other heavy metals. Besides the factors of hydrodynamic conditions and Fe/Mn oxides/hydroxides, the accumulation of Pb in the sediments could be attributed to its sources. In the coastal area of Caofeidian, the ancient Luanhe River alluvium contains a high geological background of Pb [55]. Thus, the erosion of land materials may be a reason for the different distribution of Pb from other metals in the sediments. Moreover, the Luanhe River is the main input river to the Caofeidian areas, and the concentration of Pb in the sediments of Luanhe River was higher than that in other rivers surrounding Bohai Bay (Table 2). This is why the concentration of Pb was markedly higher in the sediments of eastern Caofeidian (Figure 3). In addition, a large number of steel and chemical plants and the Caofeidian Port were established after the land reclamation of Caofeidian. The industrial emissions from electroplating materials and paint coatings for corrosion protection as well as shipping contaminants further induced the complex distribution of Pb in the sediments [56].

3.4. Contamination and Risk Assessment of Heavy Metals in the Sediments

3.4.1. Contamination Assessment of Heavy Metals. Sediment quality guidelines (SQGs) have been widely applied to assess the metal contamination levels in sediments. The contamination states of heavy metals in the study area were determined by comparing the metal levels in the sediments of the Chinese Marine Sediment Quality (GB 18668-2002) [30] and the TEL/PEL SQGs [53, 54] (Table 2). The results showed that the concentrations of Cd, Pb, and Zn in the sediments were blew Class 1 accounted for 100% of the total sampling sites. There were 54.5% and 31.8% sampling sites with the concentrations of Cr and Cu varying Class 1 and Class 2. According to the TEL and PEL, the adverse biological effect cannot occur when the concentrations of heavy metals are below the TEL, but it may emerge if the values reach the PEL [28, 57]. Our results showed that the concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the sediments below the TEL accounted for 100%, 18.2%, 4.6%, 0%, 100%, and 9.1% of the total sampling sites, respectively. There were 81.8%, 95.5%, 40.9%, and 90.9% of the sampling sites with the concentrations of Cr, Cu, Ni, and Zn varying between the TEL and PEL, suggesting occasional toxic to the ecosystem by these metals. In addition, 59.1% of the sampling sites showed the Ni concentrations exceeding the TEL (Table 4).

The $EF > 1.5$ commonly indicates a marked enrichment of heavy metals in the sediments [1, 28]. As shown in Table 4, the EF of Cd were higher than 2.5 with the average of 3.44 suggesting a clear contamination in the sediments, whereas the sediments were not contaminated by Cu with its EF of 0.75–1.46. The EF values of Cr and Ni were higher than 1.5 but lower than 3.0, which generally showed a low contamination

level. The EF values of Pb and Zn indicated that the sediments were slightly contaminated by Pb and Zn. Similar to the results of EF (Table 4), the I_{geo} values also showed that the Cd in the sediments of most of the study areas was in the moderate to heavy contamination level, Cr and Ni generally showed the uncontaminated to moderately contaminated level, and Cu, Pb, and Zn were in the uncontaminated level. Spatially, the distribution of heavy metal contamination in the sediments was in agreement with the distribution of their concentrations (Figure 3).

3.4.2. Risk Assessment of Heavy Metals. According to the Hakanson potential ecorisk index (Table 4), the potential ecorisk of Cd in the sediments was in a high level (65.45–212.75, average: 118.80). Other heavy metals in the sediments showed a very low ecorisk level (less than 10), suggesting their low potential ecorisk to marine biome. Moreover, the RI varied between 77.93 and 236.83 with the average of 137.29, and Cd accounted for 86.5% of the RI, suggesting Cd as the main metal for the sediment safety due to its high toxicity. Based on the RI, 36.4% of the sampling sites presented the moderate ecorisk level.

The index of $\sum TUs$ is used to assess the toxic effect of heavy metals in sediments, since it enables the comparison of the potential toxicity among various sediments based on chemical models [58]. In our study, $\sum TUs$ of heavy metals in the sediments were below 4.0 indicating no toxicity to the marine organisms. Spatially, $\sum TUs$ of the heavy metals in the sediments were higher in the central Bohai Bay than in the Caofeidian areas (Figure 4). The TU of an individual metal decreased in the order of Ni (0.97) > Cr (0.49) > Zn (0.33) > Cu (0.27) > Pb (0.19) > Cd (0.09), and the average contribution of each metal to the $\sum TUs$ was 41.4% for Ni, 21.1% for Cr, 14.2% for Zn, 11.5% for Cu, 8.1% for Pb, and 3.7% for Cd. Although the EF and I_{geo} of Cd in the sediments were the highest among the heavy metals, its contribution to the $\sum TUs$ was the least. This suggested that the high contamination of Cd must not induce toxicity to the marine biome, and the volumes or contents of Cd have to be considered, especially its bioavailable forms.

The TRI considering the TEL and PEL was applied to assess the toxic risk of heavy metals in the sediments to marine organisms (Figure 4). The results showed that the TRI of heavy metals in the sediments varied between 3.08 and 8.25 with the average of 5.6, and 31.8% of the sites in the Caofeidian area were in the nontoxic level and 68.2% of the sites in the central Bohai Bay were in the low toxic level. The average contribution of each metal to the TRI was 34.7% for Ni, 19.8% for Cr, 19.7% for Cu, 9.9% for Zn, 9.1% for Pb, and 6.7% for Cd, which revealed Ni as the main metal contributing to the sediment toxicity.

3.5. Implication of the Land Reclamation of Caofeidian for the Heavy Metal Contamination. Land reclamation for agriculture or harbor can cause a series of environmental issues. For example, Bai et al. found that the concentrations of heavy metals in the sediments of Pearl River Estuary increased with the reclamation time [59]. Rahman and Ishiga reported that marine sediments became significantly contaminated by

TABLE 4: Contamination and ecorisk indices of heavy metals in the sediments.

	Cd	Cr	Cu	Ni	Pb	Zn
<Class 1 (%)	100	45.5	68.2	-	100	100
Class 1 - Class 2 (%)	0	54.5	31.8	-	0	0
<TEL (%)	100	18.2	4.6	0	100	91
TEL - PEL (%)	0	81.8	95.5	40.9	0	90.9
>PEL (%)	0	0	0	59.1	0	0
EF	2.50-5.00	1.00-2.82	0.75-1.46	1.08-2.64	0.81-1.54	0.91-1.52
	3.44	2.11	1.09	1.92	1.03	1.19
I_{geo}	0.54-2.24	-0.95-1.14	-1.75-0.06	-0.79-1.14	-0.99-0.32	-1.35-0.39
	1.32	0.52	-0.42	0.38	-0.51	-0.30
Hakanson	65.45-212.75	1.55-6.61	2.23-7.80	1.73-6.59	3.77-6.01	0.57-1.97
	118.80	4.49	5.81	4.13	5.28	1.26

FIGURE 4: The spatial distribution of the TUs and TRI of heavy metals in the sediments.

heavy metals in the coastal region near the urban areas and harbors of Japan [60]. The study of Xiao et al. revealed the wetland reclamation elevated the accumulation of heavy metals in the soils of Cixi [61]. Zhang et al. found that the reclamation processes in coastal areas resulted in serious contamination of heavy metals to the aquatic ecosystem of Pearl River Estuary [62]. All the studies above showed the land reclamation had negative effects on the aquatic ecosystems. However, according to the spatial distribution of the concentrations, contamination, and ecorisk indices of heavy metals in the sediments of our study area (Figures 3 and 4), the reclamation project of Caofeidian did not induce the markedly high contamination and ecorisk of heavy metals in the sediments. In contrast, the low contamination level of heavy metals in the sediments of Laolonggou and the cape of Caofeidian was clearly observed. This was mainly related to the way of the project and its effect on the hydrodynamic conditions [24]. Whether the accumulation of heavy metals in the sediments increases after the land reclamation project of Caofeidian still needs to be explored in future.

4. Conclusions

The concentrations of heavy metals were generally higher in the sediments of Caofeidian area than of other Chinese bays and estuaries. The markedly lower concentrations of Cd, Cr, Cu, Ni, and Zn in the sediments existed surrounding the land of Caofeidian compared with other regions, whereas those of Pb was markedly higher in the inshore areas of Caofeidian and the central Bohai Bay. Hydrodynamic conditions were the major factors affecting the distribution of heavy metals. The composition of grain sizes determined the distribution of Cu and Zn in the sediments, and organic matters and Fe/Mn oxides/hydroxides also controlled the distribution of heavy metals. The inshore sediments were moderately contaminated by Cd, whereas they were uncontaminated or uncontaminated to moderately contaminated by other metals. Similarly, Cd showed a high potential risk in the sediments, and other metals were in the low risk level. Chromium was a main metal that contributed to the exposure toxicity.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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