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Distribution and Risk Assessment of Heavy Metals in Sediment from Bohai Bay, China

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Abstract: Sediment core and porewater samples from the Western coastal tidal flat in Bohai Bay, China, were collected for meals and physical-chemical properties analysis. The vertical distribution characteristics of eight metals along the core was investigated based on ^{137}Cs and ^{210}Pb radionuclide dating. The chemical fractions of six metals (Cu, Pb, Zn, Ni, Mn and Cd) were also measured based on the modified European Community Bureau of Reference (BCR) sequential extraction procedures to better understand the mobility and bioavailability of these metals in the sediment. In addition, geoaccumulation index (I_{geo}) and risk assessment code (RAC) are used to assess risk status of these metals in the environment. ^{210}Pb measurement indicates a sedimentation rate of about -1.87 cm·year^{-1}. The metals Cu, Zn, Pb and Ni show similar vertical distributions throughout the core, while Mn and Cd show different distribution patterns. Ni, Cu, Pb and Zn are strongly associated with the residual fraction while Mn and Cd are dominant in the acid-soluble fraction. According to the estimated diffusive fluxes, the Zn ions were the most mobilized, followed by Cu, Ni, Pb, and to a lesser extent Cd. The result of I_{geo} shows that Ni in sediments does not reflect any pollution, and Cu, Pb and Zn are in a level from unpolluted to modest polluted throughout the core. Mn and Cd have obvious anthropogenic sources. Based on the RAC, Cd and Mn pose a high to very high risk to the local environment, respectively, due to the significant percentage of exchangeable fraction. Clay content is significantly positively correlated with Ni, Cu, Al and Fe, and Cu, Pb, Zn and Ni might originate from the same sources or be influenced by similar geochemical processes. River runoff and atmospheric deposition are important sources for heavy metals, and since 1998, domestic sewage discharge might have had an important influence on the source of heavy metals (except for Cd and Mn).

Keywords: heavy metal; distribution; fractions; risk assessment; sediment; Bohai Bay

1. Introduction

Large quantities of different kinds of elements and compounds are discharged into coastal seas each year by anthropogenic activities [1]. The coastal sediment is an important sink for many pollutants [2]. Of the pollutants in sediments, heavy metals are classified as the most persistent since they are relatively stable and cannot be degraded in natural conditions [3,4]. Therefore, they could be used as an identifier of environmental change and reflect anthropogenic impacts [5–7].

Fine-grained sediments are often used as a good indicator of trace metal contamination due to their large adsorption capabilities for metals [2,8]. Vertical profiles of trace metals in sediment cores could well reflect the pollution history based on the dating of the core [9,10]. A number of studies have used sediment profiles to describe the contamination history of trace metals in different environments [11–15]. In marine sediment, many approaches (e.g., the geoaccumulation index, potential ecological risk index, sediment quality guidelines, and enrichment factor) have been widely used around the world to assess the contamination of heavy metals based on the total concentration of metals in sediments [5,16–19]. In addition, the fractions of metals are often used to assess the mobility, toxicities and ecological risk of metals in the sediment based on sequential extraction procedures [5–7,20–22].

As a semi-closed interior sea located in northeast China, the Bohai Sea is an important region with an area of 77,000 km^2 and accounts for 1.63% of the marine belt areas in China [23]. This area is one of the most highly developed and densely populated regions in China and accounts for one quarter of the Chinese Gross Domestic Product (GDP) [24]. Bohai Bay, located in the west of the Bohai Sea and near the city of Tianjin, is a typical semi-enclosed coastal bay, with a mean depth of 12.5 m [25]. The Bohai Bay has weak water exchange with the ocean which makes the physical self-cleaning capacity of the Bay very poor [23,26]. Tianjin Port, as the fifth largest port in the world in terms of cargo throughput, is located in the western coast of Bohai Bay [27]. A large amount of organic pollutants and trace metals originated from industrial and domestic waste discharge from two megacities (Beijing and Tianjin) in China are transported into this region through direct discharges and/or loading from adjacent tributaries [28].

In recent years, investigations of the distribution, pollution status and toxicity of heavy metals in the coastal or estuarine surface sediment in the Bohai Bay have been carried out [23,27,29,30]. Some studies have also focused on metals' forms and mobility in the surface sediments of Bohai Bay [31]. Other studies have assessed the toxicity of metals in surface sediments from Bohai Sea based on acid-volatile sulfide (AVS)/simultaneously extracted metals (SEM) methods [32,33].

However, research reflecting the vertical distribution, toxicity assessment and sources of heavy metals combined with a chronology in the sediments of the Bohai Sea is still lacking, especially in the last five decades. The aims of this study are to (1) examine the vertical variation of heavy metals in the sediments of Bohai Bay based on radionuclide dating, (2) assess the level of sediment contamination and toxicity, and identify the possible sources of heavy metals.

2. Materials and Methods

2.1. Sampling and Analysis

A total of three parallel sediment cores (32 cm long) were collected using PVC (polyvinyl chloride) tubes from the North–Western coastal zone of Bohai Bay in July 2014 (Figure 1) for the metal and physical-chemical properties analysis of the sediment cores. Of the three cores collected, the first core was used for the extraction of porewater, and the second core used for physical-chemical properties analysis, and the third one used for meals analysis. All these cores were sliced into subsamples immediately at 1 cm intervals between 0–10 cm, and 2 cm intervals below 10 cm, respectively, with a plastic knife and placed into acid-rinsed polyethylene bags. Porewater samples were taken from sediment core samples, which were centrifuged at 4390 g for 10 min to separate the porewater. After filtering through a membrane filter (0.45 μm), aqueous samples were stored in polyethylene bottles and acidificated by HNO_3 until reaching pH 1–2. In addition, a long core (64 cm long) was sampled at the same site for ^{210}Pb and ^{137}Cs dating analysis and sliced at 4 cm intervals. All sediment samples were stored at 4 °C in the refrigerator until analysis. For the metal and physical-chemical characteristic analyses of the sediment samples, the detailed pretreatment procedures were laid out in [34].

The metals Al, Fe and Mn concentrations in sediments were analyzed by X-ray fluorescence spectrometer (AB-104L, PW2404). Trace metals of Cu, Pb, Zn, Ni and Cd in sediment and porewater were analyzed by ICP-MS (ELEMENT XR) at the Analytical Laboratory of the Institute of Geophysical and Geochemical Exploration in the Chinese Academy of Geological Sciences (Langfang, China). The quality of the solid phases analysis was monitored by Chinese standard reference material GSD3a, GSD4a and GSD5a. The results showed good recovery rates (92–112%) and a relative standard deviation of less than 10%. Sediment grain size was determined using a laser size analyzer (Malvern

Mastersizer 2000, Malvern Panalytical Ltd., Malvern, UK). The total organic carbon (TOC) content of the sediments was determined using a TOC analyzer (Vario TOC Cube, Elementar, Langenselbold, Germany). Total inorganic carbon (TIC) was calculated as the difference between TC and TOC (i.e., HCl treated). The cold diffusion method was adopted to extract AVS in this study [35,36]. Water content was determined according to weight loss after the drying of sediment samples at 100 °C for 24 h. The porosity of sediment was calculated assuming a sediment density of 2.65 g·cm^{-3} and a water density of 1.027 g·cm^{-3}.

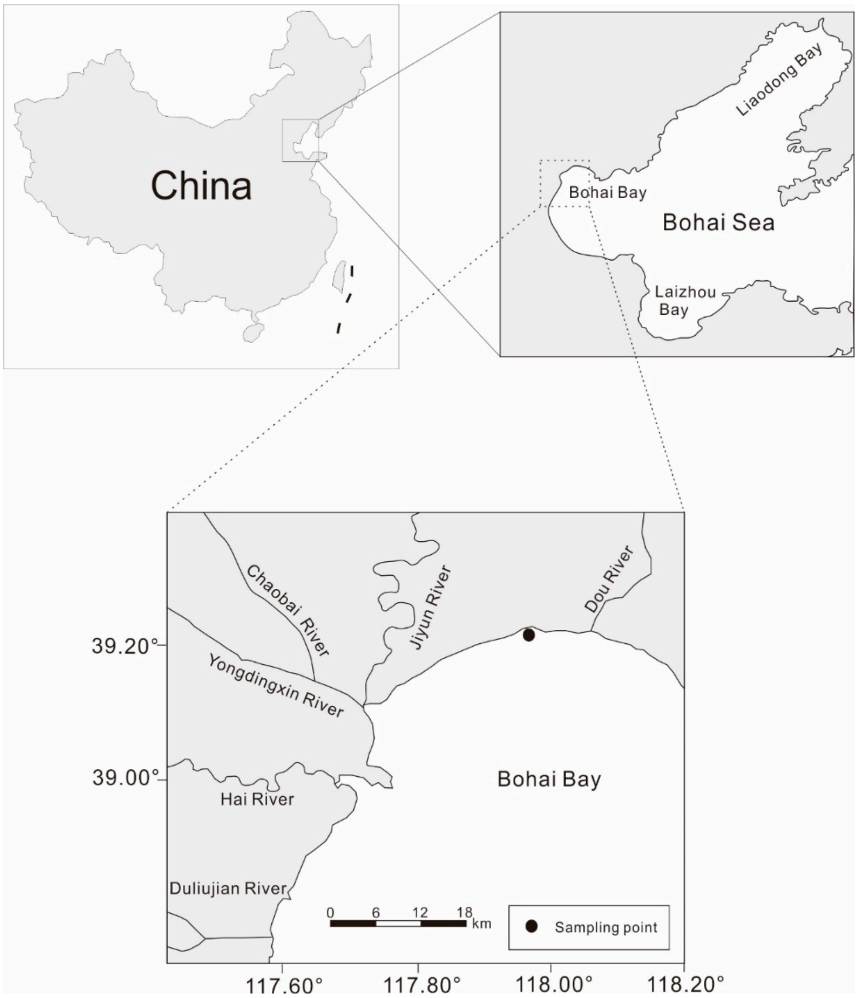

Figure 1. Geographic map showing the study area and sampling location map.

The geochemical speciation of metals was determined by a modified BCR sequential extraction procedure proposed by [37], which divided the fractions of metals into four speciations based on four sequential extraction steps (F1: acid-soluble fraction; F2: reducible fraction; F3: oxidizable fraction; F4: residual fraction). The Chinese national standard sediment sample GBW07436 was used (*N* = 3) to check the accuracy of the sequential extraction procedure. Comparing the sum of the four steps average values from the sequential extraction with the total metal content measured by HR-ICP-MS, good recovery percentages were observed for the metals, thus indicating the high reliability of data presented in this work. The average recovery value for all metals ranged from 70% to 93%.

Both ^{137}Cs and ^{210}Pb radionuclide records were measured to identify the sedimentation rate. Activities of ^{137}Cs, total ^{210}Pb and ^{226}Ra were determined by a γ-ray spectrometer gamma-spectrometer. The excess ^{210}Pb activity is calculated from the following equation:

$$^{210}\mathrm{Pb}_{\mathrm{excess}} = {}^{210}\mathrm{Pb}_{\mathrm{total}} - {}^{210}\mathrm{Pb}_{\mathrm{supported}}, \quad (1)$$

where the activity of the supported ^{210}Pb activities is equal to the ^{226}Ra background activity and is estimated from the average activities of ^{226}Ra measured in deeper sections of the core. Sediment cores were dated at the Nanjing Institute of Geography and Limnology, Chinese Academy of Science (Nanjing, China).

2.2. Flux Calculations

The profiles of dissolved heavy metals in the pore water could suggest the possible diffusion of heavy metals ions along the concentration gradient generated by the maximum concentration peaks.

The magnitude of this diffusive flux was estimated by Fick's first law. The diffusion flux of heavy metals (J_d, mg·m^{-2}·a^{-1}) in sediment could be calculated according to the following equation [38]:

$$J_d = -\varphi D s \Delta C / \Delta z \tag{2}$$

where J_d represents the diffusive flux of metals (mg·m^{-2}·a^{-1}) with negative values showing an upward flux from the sediment, φ is the porosity, $\Delta C/\Delta z$ is the concentration gradient (mg·m^{-4}) in dissolved metal concentrations between depth intervals, C is the concentration of dissolved metal measured in the deeper layer (mg·L^{-1}), and D_s is the molecular diffusion coefficient (m^2·year^{-1}), which is assumed to be equal to D_0/θ^2, where θ is the tortuosity and D_0 is the diffusion coefficient in water at 18 °C [39]. The value of θ^2 is assumed to be equal to $1 - \left[\ln\left(\varphi^2\right)\right]$ [40]. The steepest gradients in the interstitial waters' profiles after a five-point moving average are used to calculate the upward and downward dissolved metal fluxes. The concentration gradient (mg·m^{-4}) at the sediment–water interface is used to calculate the outward flux from the sediment.

2.3. Statistical Analysis

Pearson correlation analysis has been used in this study to better understand the effects of sediment properties on metal concentration and identify the relationship between metals in the estuarine system by using Statistica (Version 10.0, StatSoft, Tulsa, OK, USA) for Windows.

3. Results

3.1. Sediment Core Dating

^{210}Pb is a reliable dating method for sediment deposited within the last 150 years and it is often used together with ^{137}Cs in dating to reduce uncertainty [41]. Dating by ^{210}Pb has been successfully applied in lake [42–44] and marine sediment [45]. In this study, the vertical variation of excess ^{210}Pb activities in the sediment core is shown in Figure 2. The excess ^{210}Pb activity below 6 cm decreases approximately exponentially as a function of sediment depth, making it possible to apply the constant initial concentration (CIC) model to calculate the sedimentation rates. The average sedimentation rate of the core is 1.87 cm·a^{-1}. In the case of ^{137}Cs, there is a distinct peak at 14 cm, and values decrease below detection limits at 30 cm depth (Figure 2). If we assume that the ^{137}Cs peak at 14 cm corresponds to the 1963 atmospheric maximum, the basal depth of the ^{137}Cs appearance at 30 cm should represent the widespread onset in 1954 of atmospheric nuclear testing. In addition, although the accident of nuclear reactor of Chernobyl released significant amount of ^{137}Cs into the environment in 1986, the peak of ^{137}Cs associated with this disaster was not identified in the sediment core. It was consistent with a study in the Liaodong Bay in the Bohai Sea [46]. Therefore, we obtain an average sedimentation rate of 2.2 cm·a^{-1} based on the ^{137}Cs profile, which is slightly higher than the sedimentation rate calculated from ^{210}Pb activities. However, relatively high specificity activity of ^{137}Cs and wide peak in the upper layers of sediment may show evidence of post-depositional redistribution [42] or catchment erosion, which disturbed the ^{137}Cs profile [43]. Thus, ^{137}Cs profile in the sediment was not suitable for the dating of sediment core. Therefore, we have assigned the core an average sedimentation rate of 1.87 cm·a^{-1} based on ^{210}Pb geochronology. The base of the core (64 cm) could be dated to approximately 1980.

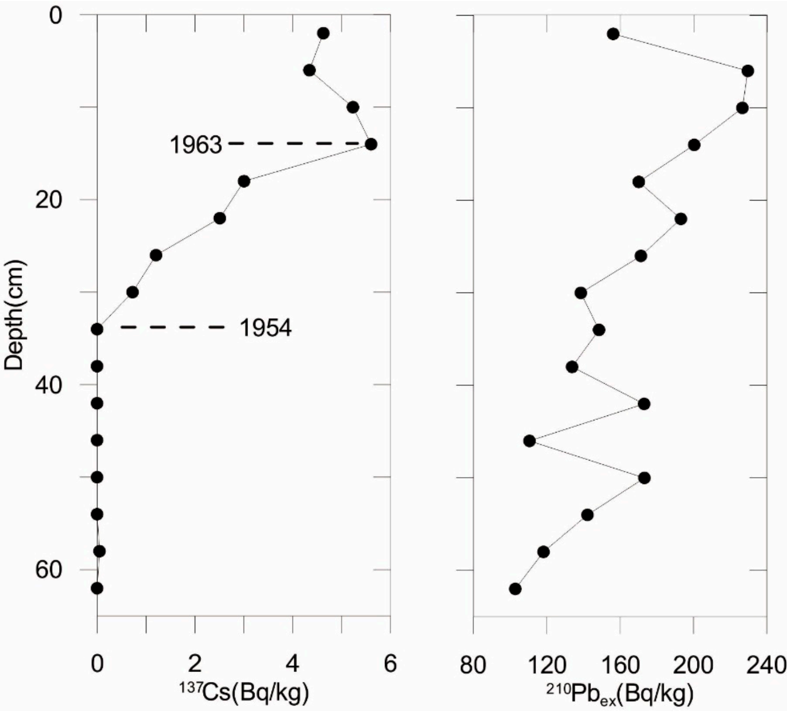

Figure 2. Depth profiles of ^{137}Cs and excess ^{210}Pb of core.

3.2. Sediment Characteristics

The grain size, TOC and TIC in the sediments core samples are presented in Figure 3. The sediment is mainly composed of silt and clay. The content of silt ranges from 59.2–70.6%, with an average of 68.1%. The content of clay ranges from 13.3% to 32.1%, with an average 29.0%. The content of sand ranges from 0.46% to 27.5%, with an average of 2.92%. Vertically, the content of clay, silt and sand generally stays stable throughout the core except for reaching minimum values and maximum values at a 28 cm depth, respectively. TOC content decreases from 1.39% at the bottom of the core to 0.88% at a depth of 24 cm, and then keeps generally stable until the top. Low TIC content is observed at the bottom of the core, with a sharp increase from a 10 cm depth upward. AVS decreases from a maximum (2140 mg·kg^{-1}) at the bottom to a minimum (37 mg·kg^{-1}) at the surface sediment.

3.3. The Concentrations and Distribution of Metals in the Sediment Core and Pore Water

The concentrations of metals in the sediment core from the tidal flat in the Bohai Sea and some references are listed in Table 1. The concentration ranges of metals in the sediment core are as follows: Al, 7.0–8.3%, Fe, 3.8–5.0%, Mn, 0.12–0.22%, Ni, 37.6–51.3 mg·kg^{-1}, Cu, 31.4–44.4 mg·kg^{-1}, Zn, 91.8–121.5 mg·kg^{-1}, Cd, 0.16–0.24 mg·kg^{-1}, Pb, 27.4–34.9 mg·kg^{-1}, respectively. The mean concentrations of Fe, Mn and Ni are all higher than those of these metals in the Haihe River estuary [14], Yongding River estuary [14], and intertidal Changjiang estuary [47]. The concentration of Cu is higher than that in other areas in the Bohai Sea. The Pb concentration is comparable to that in other references, such as the Haihe River estuary [14], intertidal Changjiang estuary [47], and coast of the South Sea, Korea [48]. We also compared our metal concentrations with the Marine Sediment Quality (GB 18668-2002) proposed by the China State Bureau of Quality and Technical Supervision (Beijing, China) [49] (Table 1). Except for Cu, the overall mean concentrations of all of the selected metals in Bohai Bay sediments are below or close to the first-class standard, which is suitable for marine fisheries, nature reserve, and endangered species, suggesting that the concentrations of trace metals in the sediment generally meet the Marine Sediment Quality Grade I.

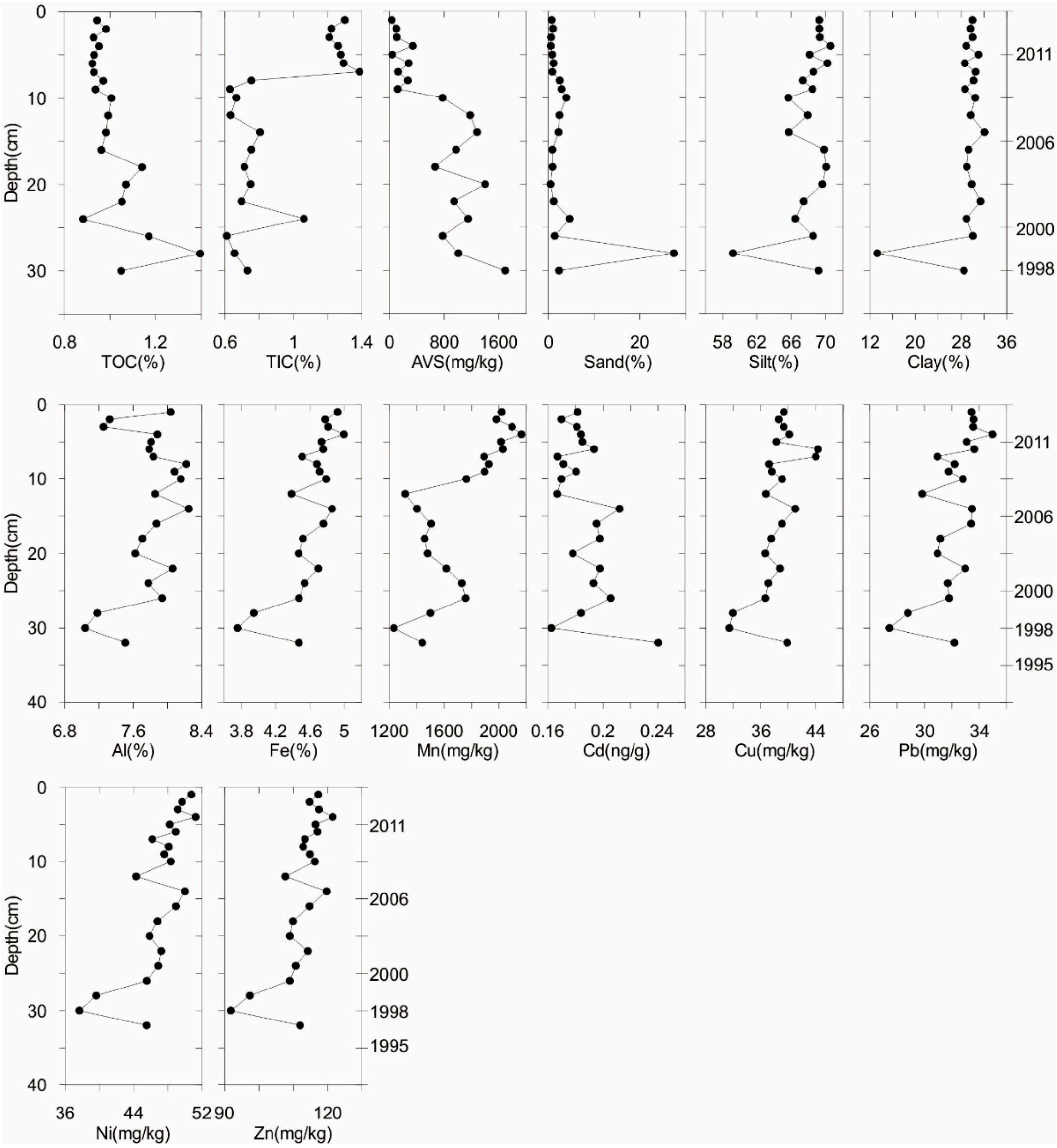

Figure 3. Vertical profiles of physical-chemical parameters and total metal concentrations in the solid phase.

The vertical distribution of total metal concentrations in the sediments is shown in Figure 3. The variations of concentrations of Fe, Al, Cu, Zn, Pb and Ni are very similar, showing an increasing trend since 1998. The variation of Cd is relatively stable between 2001 and 2012, except for a maximum value at the bottom of the core, approximately in 1997. The Mn concentration reaches two peak values at 25 and 5 cm in depth, corresponding to 2003 and 2012, respectively, with an obvious increase from 2008 to 2012.

Table 1. Comparison of concentrations of metals in the sediment from the Bohai Bay and some references (mg·kg^{-1}, except Al, Fe and Mn as %).

	Al	**Fe**	**Mn**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**	**References**
Sediment core from Bohai Bay									
Mean (21)	7.8	4.6	0.17	47.0	38.3	112.3	0.19	32.0	Present study
Minimum	7.03	3.75	0.12	37.6	31.4	91.8	0.16	27.4	
Maximum	8.25	5.0	0.21	51.3	44.4	121.5	0.24	34.9	
Standard Deviation	0.34	0.3	0.28	3.3	3.0	7.0	0.02	1.8	
Haihe River estuary, China		2.98		33.6	29.5	86.0	0.173	25.6	[14]
Yongding River estuary, China		3.19		31.2	31.4	92.9	0.124	20.4	[14]
Western Bohai Bay, Bohai Sea		3.74		31.4	27.9	83.6	0.129	20.5	[14]
Estuaries around Tianjin Bohai Bay					18.8	134.7	0.7	22.9	[23]
Intertidal Changjiang Estuary	6.5	3.3	0.077	31.8	30.7	94.3	0.26	27.3	[47]
Coast of the South Sea, Korea	8.8	4.0		29	21.9	109		31.6	[48]
Background value in the Bohai Sea and adjacent estuaries					19	57	0.069	11.5	[1]
Marine Sediment Quality Grade I					35	150	0.5	60	[49]
Marine Sediment Quality Grade II					100	350	1.5	130	[49]

The vertical distribution of metal concentrations in the pore water is shown in Figure 4. Dissolved Cu and Ni show similar variation trend with a maximum value at the bottom of the core, increasing slightly between 0 and 27 cm with a sudden drop at the sediment–overlying water interface. The concentration of dissolved Cd drops significantly from the bottom to 15 cm depth and then gradually increases until the surface of the core, with a sharp drop at the interface of sediment–overlying water. The concentration of dissolved Pb decreases from the bottom to a 20 cm depth and slightly increases to the top of the core, with a sharp rise at the sediment–overlying interface. The Zn concentration shows an increasing trend from the bottom to the top of the core with a sharp rise at the interface of the sediment and overlying water.

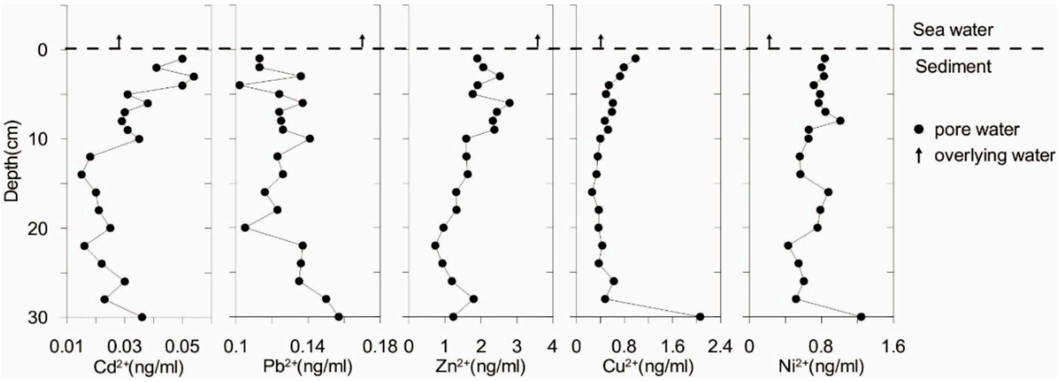

Figure 4. Vertical distribution of metal ions in the porewater.

3.4. The Distribution of Metals Fractions along the Sediment Core

The various chemical fractions of metals in the sediment profiles are plotted in Figure 5. Each geochemical partitioning is expressed as the percentage of the sum of all fractions. In the sediment, most of the Pb (49.5–72.0%) is present in the form of a residual fraction. It is consistent with the previous result in Bohai Bay [16]. The percentage of reducible fraction of Pb ranges from 16.6% to 43.7%. Previous studies showed that Pb can form stable aggregates with Fe and Mn hydroxides [50], and Fe and Mn hydrous oxides are crucial scavengers of Pb in sediments [51]. The reductive dissolution of iron oxides and subsequent release of adsorbed Pb is a potential source of Pb in porewater or overlying seawater, especially under anoxic conditions [52,53]. The oxidizable and acid-soluble fraction of Pb is 3.2–10.2% and 1.2–3.8%, respectively. Therefore, whether Pb bound to ferric or manganese oxides, organic matter would be released when environmental conditions changed. These data suggest that Pb in the sediments poses some ecological risk.

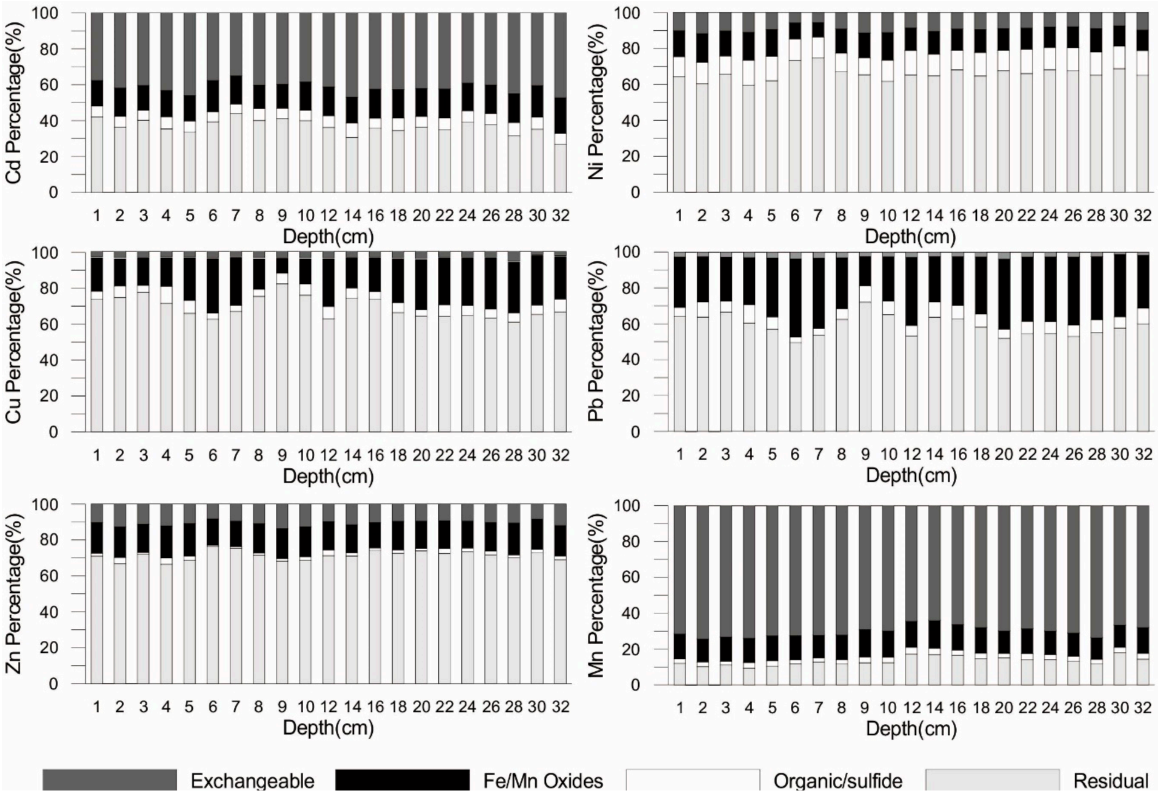

Figure 5. Vertical distribution of chemical fraction of metals in the sediments.

Similar to Pb, the predominant chemical fraction of Cu are mainly associated with residual fraction (61–82%), followed by reducible (8.3–30.5%), and oxidizable fraction (3.4–9.5%). The acid-soluble fraction of Cu is 0.8–3.5%. The high copper content in the residual fraction has been also reported in the marine sediments [54], suggesting that parent material from natural rock weathering, instead of anthropogenic activities, has an important influence on the fraction of Cu. The relatively high percentage of the reducible Cu is also consistent with a study in Bohai Bay [31]. It has been reported that Cu easily forms complexes with the organic matter due to high stability constant of organic Cu compounds [55,56]. Cu tends to accumulate mostly on the organic fraction of the marine sediment samples, especially in the sediments with high organic matter content [57,58] or in the area where direct input of organic matter from anthropogenic activities, such as sewage or mining tailing, is evident [54,59]. If the content of organic matter does not exceed 2% in soils, organic matter cannot be of the greatest importance in overall controls of trace element behavior in soils [60]. In addition, the stability of organic Cu complexes is also depending on the pH value in the environment, and the highest proportion of Cu is fixed with organic matter (i.e., humic substances) over the range of pH 4 to 7 [61]. Therefore, the low percentage of Cu in the organic fraction in our samples could be attributed to the low content of organic matter (less than 1% for most of the samples) and/or neutral pH values in the sediment from the Bohai Bay (ranging from 7 to 8.6) [62], which restricts the formation of stable complexes. Vertically, the variations of the residual and reducible fraction of Cu are similar to that of Pb, probably suggesting that the metals are controlled by the same geochemical processes or associated with similar sources.

In case of Zn, the residual fraction of Zn is dominant (66.5–76.2%), followed by reducible fraction (14.1–18.1%), acid-soluble fraction (8.2–13.8%), and oxidizable fraction (1.8–5.4%). The high percentage of Zn in the reducible form indicates that Zn can easily be absorbed or coprecipitated by iron or manganese oxides, which is consistent with the previous reports [63]. It has been reported that high stability constant occurs when Zn is combined with Fe/Mn oxides in sediments [64].

Ni might be strongly associated with low bioavailability, mobility and non-anthropogenic origin, as suggested by the highest percentage of the residual fraction of Ni (59.4–74.7%). Similar results for these metals in residual fraction have been reported by some studies [7,65–69].

This suggests that a major fraction of these elements is strongly incorporated into minerals of the sediment matrix, and thus is unlikely to be released [70]. None of residual fraction of Ni (including acid-soluble, reducible and oxidizable fractions) is in the range within 20.3–40.6%.

On the other hand, Mn is available in a significant percentage in the first three fractions (including acid-soluble, reducible and oxidizable fraction). Mn is dominant in the acid-soluble phase (ranging from 63.9–74.2%), which is the most labile fraction. Similar results have been also observed in the study on the marine sediment [71] and on the river sediment [72]. The phase represents the portion which is associated with the carbonate or in the exchangeable form. The high proportion of Mn in this fraction is probably related to the two reasons. One reason is that Mn in the sediment could be attributed to anthropogenic sources, and is easy to be attached to the surface of sediment, causing the high percentage of Mn in the exchangeable form, as confirmed by [73]; The other reason is that Mn has a special affinity for carbonate and can be co-precipitated with its minerals [74,75]. A higher content of Mn in bound carbonate is most likely due to the similarity in ionic radii to that of calcium, which allows Mn to substitute for Ca in the carbonate phase [74,76] or due to that Mn tends to be present in less thermodynamically stable phases in the sediments, such as ion exchangeable Mn^{2+}, and Mn enclosed in carbonate minerals [72].

Cd is mainly bound to first three fractions i.e., carbonate (35.2–47.3%), reducible (13.1–19.9%) and oxidizable (5.3–8.1%) fractions. These results are similar to other works carried out previously in Bohai Bay [27,31] and Haihe River [77]. The high percentage of Cd in the acid soluble might result from the high concentration of Cl in coastal sediments, which could form the Cd–Cl complexes $CdCl^+$, $CdCl_2$ and increase the mobility and bioavailability of Cd [78]. In addition, the high percentage of Cd in the acid soluble fraction, i.e., carbonate fraction, indicates that at a slight lowering of pH in the sediment, an appreciable portion of Cd would be remobilized and become bioavailable [79].

3.5. Diffusion of Dissolved Heavy Metals in Pore Water

The dissolved heavy metal fluxes are shown in Table 2. J_{out} represents the flux across the sediment water interface, which is calculated by the Equation (2), where φ is the average porosity of the upper most interval (0–1 cm). $\Delta C/\Delta z$ is the concentration gradient at the sediment–water interface, calculated from the total dissolved metal concentrations in the overlying bottom sea water and porewaters collected from the first sediment sampling interval (i.e., 0–1 cm, thus Δz = 0.5 cm). The gradient is assumed to be linear between the overlying bottom water and the first measured porewater interval. J_{up} is the flux of metal diffusing upwardly in the sediment. J_{down} is the flux of metal diffusing downwardly in the sediment. Both J_{up} and J_{down} are calculated according to the Equation (2). Total diffusive fluxes (J) are calculated as the sum of absolute value of J_{out}, J_{up} and J_{down}.

According to the estimated total diffusive fluxes, the Zn ion is the most mobilized (2.682 $mg \cdot m^{-2}$ a^{-1}), followed by Cu (1.187 $mg \cdot m^{-2} \cdot a^{-1}$), Ni (0.789 $mg \cdot m^{-2} \cdot a^{-1}$), Pb (0.1 $mg \cdot m^{-2} \cdot a^{-1}$), and to a lesser extent Cd (0.036 $mg \cdot m^{-2} \cdot a^{-1}$). The metals transported by diffusive (upward flux) are estimated at 0.003 $mg \cdot m^{-2} \cdot a^{-1}$ for Cd, 0.432 $mg \cdot m^{-2} \cdot a^{-1}$ for Cu, 0.017 $mg \cdot m^{-2} \cdot a^{-1}$ for Pb, 0.498 $mg \cdot m^{-2} \cdot a^{-1}$ for Zn and 0.115 $mg \cdot m^{-2} \cdot a^{-1}$ for Ni. The fluxes of the expulsion of metals (J_{out}) across the sediment–water interface is -0.021 $mg \cdot m^{-2} \cdot a^{-1}$ for Cd, -0.568 $mg \cdot m^{-2} \cdot a^{-1}$ for Cu, 0.072 $mg \cdot m^{-2} \cdot a^{-1}$ for Pb, 1.595 $mg \cdot m^{-2} \cdot a^{-1}$ for Zn, and -0.551 $mg \cdot m^{-2} \cdot a^{-1}$ for Ni, respectively, suggesting that of the upwardly mobilized metals, only Cu, Cd and Ni, instead of Pb and Zn, might be released into the overlying bottom sea water from the sediment although Zn ion is the most mobilized of five metal ions.

Table 2. Concentrations of metals in the porewater and overlying water samples, and diffusive fluxes of metals (concentrations in $\mu g \cdot L^{-1}$ and fluxes in $mg \cdot m^{-2} \cdot a^{-1}$).

Metal	Interstitial Water	Uppermost Pore Water	Overlying Water	Diffusive			Total Flux
				J_{out}	J_{up}	J_{down}	J
Cd	0.031 ± 0.011 [a]	0.05	0.028	−0.021	−0.003	0.012	0.036
Cu	0.59 ± 0.39	0.984	0.406	−0.568	−0.432	0.187	1.187
Pb	0.13 ± 0.014	0.113	0.17	0.072	−0.017	0.011	0.1
Zn	1.72 ± 0.58	1.899	3.576	1.595	−0.498	0.589	2.682
Ni	0.74 ± 0.19	0.836	0.22	−0.551	−0.115	0.123	0.789

[a] Mean concentration ±1 standard error; J_{up} = flux directed upwards; J_{down} = flux directed downwards; negative fluxes are directed upwards; J_{out} = flux across the sediment-water interface, negative fluxes are from sediments to the overlying water.

4. Discussion

4.1. Statistical Analysis

Correlation analysis has been performed for sediment properties and metals to better understand the effects of sediment properties on metal concentration (Table 3). Fe, Al, Mn and clay have significant correlations with the Cu, Ni, Zn and Pb. Al and Fe are mostly found in fine-grained sediments and detrital minerals, without being influenced significantly by the authigenic and biologic processes [80]. Petrogenetic element Al, together with Fe, was the major component of silica minerals that are the products of rock and soil weathering on land [81], and the dominant signals for terrestrial inputs [82,83]. Therefore, good correlations of Al with Fe, Cu, Ni, Pb and Zn suggest mainly terrestrial sources of these elements, which is in agreement with the results that Ni, Cu, Pb and Zn are dominated by the detrital residual fraction (Figure 5). Since fine-grained aluminosilicates minerals and Fe/Mn oxides are very effective scavengers and/or geochemical carriers in sediments [84,85], while high correlation coefficients among Fe, Mn, Al, clay and trace metals might also suggest that the trace metals could be adsorbed on fine-grained aluminosilicates minerals and Fe–Mn oxides, as reported by the literature [86]. TOC and AVS are significantly negatively correlated with the total concentrations of these metals except for Cd and Al. The TIC is significantly positively correlated with Mn, Fe, Cu, Ni, Pb and Zn. The metals Cu, Pb, Zn and Ni are significantly correlated with each other, suggesting they are controlled by similar geochemical processes and/or come from the same sources. Cd is only significantly positively correlated with Pb at the 0.1 probability level and not significantly correlated with other metals or sediment properties such as grain size, TOC and AVS at the 0.05 probability level, suggesting a different source or controlling process from other metals except for Pb.

Table 3. Pearson correlation coefficients for the relationship among the metal concentrations, grain size, acid-volatile sulfide (AVS), total inorganic carbon (TIC) and total organic carbon (TOC) ($N = 21$).

Variable	Mn	Al	Fe	Cd	Cu	Ni	Pb	Zn	Sand	Silt	Clay	TOC	TIC	AVS
Mn	1.00													
Al	0.17	1.00												
Fe	0.66 *	0.62 *	1.00											
Cd	−0.08	0.34	0.30	1.00										
Cu	0.54 *	0.49 *	0.75 *	0.21	1.00									
Ni	0.65 *	0.58 *	0.99 *	0.31	0.76 *	1.00								
Pb	0.69 *	0.49 *	0.96 *	0.38 **	0.71 *	0.96 *	1.00							
Zn	0.66 *	0.63 *	0.99 *	0.31	0.82 *	0.97 *	0.94 *	1.00						
Sand	−0.24	−0.36	−0.53 *	−0.02	−0.52 *	−0.55 *	−0.47 *	−0.52 *	1.00					
Silt	0.29	0.08	0.40 **	−0.05	0.42 **	0.43 **	0.37	0.37	−0.89 *	1.00				
Clay	0.18	0.50 *	0.56 *	0.06	0.52 *	0.56 *	0.47 *	0.56 *	−0.95 *	0.72 *	1.00			
TOC	−0.47 *	−0.36	−0.61 *	0.15	−0.62 *	−0.62 *	−0.53 *	−0.63 *	0.74 *	−0.60 *	−0.74 *	1.00		
TIC	0.72 *	−0.13	0.44 **	−0.13	0.60 *	0.48 *	0.49 *	0.48 *	−0.29	0.36	0.21	−0.55 *	1.00	
AVS	−0.89 *	−0.18	−0.60 *	0.13	−0.53 *	−0.60 *	−0.57 *	−0.61 *	0.22	−0.28	−0.15	0.38 **	−0.64 *	1.00

* Significant at 0.05 probability level. ** Significant at 0.1 probability level.

4.2. Risk Assessment and Contamination of Metals in Sediment

4.2.1. Geo-Accumulation Index (I_{geo})

The geoaccumulation index (I_{geo}) proposed by the literature [87] has also been adopted as the index to assess the pollution degree of metals. It is recommended the use of pre-industrial or pre-civilization values via sedimentary core analysis to establish the background values for the evaluation of heavy metal contamination [88,89]. Therefore, the background values of heavy metals in the Bohai Sea from sediment cores, the bottom layer of which could be dated to pre-industrial time (i.e., ca. 200 year) [1], are used as the regional background values to calculate their I_{geo} values (Table 1), except for Mn using the soil background values in Tianjin [90]. The average I_{geo} values of the metals follow the order: Pb > Cd> Mn > Cu > Zn > Ni. The I_{geo} values for Pb range from 0.67 to 1.02 (with an average of 0.89) (Figure 6), indicating a condition from unpolluted to moderately polluted. Pb could be affected by both natural processes and anthropogenic influences based on its statistically significant coefficient with Al ($R = 0.41$, $p < 0.05$). The I_{geo} values for Cd are more than 0, suggesting an anthropogenic input of Cd in these years. The very low correlation coefficient between Cd and Al ($R = -0.01$, $p < 0.05$) is not statistically significant, reinforcing this presumption. The enrichment or pollution of Cd in coastal sediments from the Bohai Sea has been widely reported in some previous literature [1,23,91,92]. The I_{geo} values for Mn range from 0.23 to 1.04 (with an average of 0.69). Combined with a low correlation coefficient of Mn with Al ($R = 0.17$, $p < 0.05$), it is more probable that Mn originates mainly from anthropogenic sources. The I_{geo} values for Cu and Zn in all of the samples are more than 0 but less than 1, suggesting an evident anthropogenic influence. Ni is in an unpolluted level since their I_{geo} values are all less than 0 throughout the core.

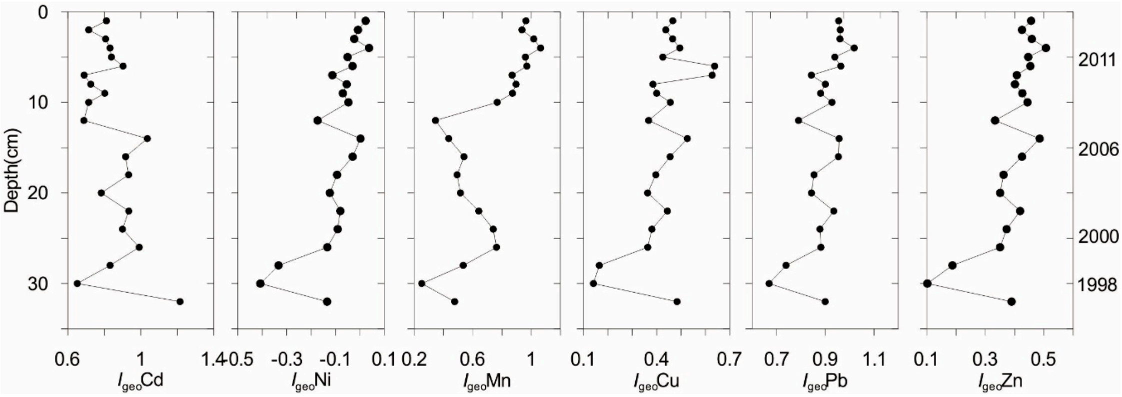

Figure 6. The vertical variation of the geoaccumulation index (I_{geo}) of the metals in the sediments.

4.2.2. Risk Assessment Code (RAC) of Metals

The result of speciation studies could also be used to assess the mobility and bioavailability connected with the presence of metals in an aquatic environment [93]. The mobility and availability of heavy metals were assessed using the Risk Assessment Code (RAC). This index is based on individual metal mobility and it does not account for the metal toxicity [94]. The assessment of the RAC is important since the exchangeable and bound to carbonate fractions of metals, which are associated with the anthropogenic activities, are loosely bonded metals that could equilibrate with the aqueous phase and thus become more rapidly bioavailable [74].

The RAC is calculated based on the percentage of metals associated with exchangeable and carbonate fractions (equivalent to the acid soluble fraction obtained in the BCR procedure). The RAC of heavy metal and its criteria [95] are shown in Table 4. Based on the code, Mn poses a very high risk to the local environment due to its significant percentage of exchangeable fraction. Cd could pose a high risk to the local ecosystem with their high exchangeable fraction (35.2–47.3%). Ni and Zn pose a low to medium risk to the local environment, with their exchangeable fraction ranging from 5.6–11.7%

and 8.2–13.8%, respectively. Cu (1.78–5.36%) and Pb (1.2–3.78%) in their exchangeable form have a low risk to the environment.

Table 4. Risk assessment code (RAC) of metal and its classification.

Metal	**Percentage in the Exchangeable Fraction**			**Risk**
	Mean	**Max.**	**Min.**	
Cu	3.28	5.36	1.78	Low
Pb	2.66	3.78	1.2	Low
Ni	9.23	11.71	5.60	Low to Medium
Zn	10.62	13.75	8.24	Low to Medium
Cd	41.4	47.3	35.1	High
Mn	69.9	74.2	63.9	Very high
Risk	Metal in carbonate and exchangeable fractions (%)			
No	<1			
Low	1–10			
Medium	11–30			
High	31–50			
Very high	>50			

4.3. Source Identification of Metals

As one of the most populated and industrialized regions in China, the Bohai Sea watershed received a large amount of the input and discharge of toxic chemicals through the atmosphere, runoff, and surrounding rivers over the past few decades, and nearly 60% of Cu, Zn and Cd are discharged into the Bohai Sea through riverine discharge [96]. Along the Western coastal zone of Bohai Bay, there are three major estuaries including the Yongdingxin River, Haihe River, and Duliujian River (Figure 1). The Yongdingxin River receives a great deal of industrial effluents from Tianjin and industrial and municipal sewage from Beijing without any treatment or with primary treatment only, via small streams or sewers, including heavy metals such as Cu, Zn, Mn and Ni (Beitang Drainage River, for example) [30,97]. It has been reported that sediment in the Yongdingxin River estuary has been contaminated by Cu with its concentration as high as 38.99 mg·kg^{-1} [22]. In our study, the Ni, Pb, Zn and Cu concentrations in sediment have exhibited a similarly increasing trend since 1998 (Figure 3). The study area is located in the Tianjin Binhai New Area (TBNA), a new coastal developmental zone with the top three growth rates in China. Therefore, some heavy metals such as Ni, Pb, Zn and Cu might be associated with the local industrial processes such as the electroplating and leather manufacturing in the TBNA, as proposed by [62]. In addition, although the industrial source of wastewater of Tianjin has not changed in general over the last two decades, domestic sewage discharge of Tianjin shows an increasing trend with time, which coincides with the vertical change of Cu, Pb, Zn and Ni in our samples [98], suggesting that domestic sewage might have had an important influence on the source of heavy metals (except for Cd and Mn) by river runoff since 1998.

Except for river runoff, atmospheric deposition is also an important source for some heavy metals such as Pb and Ni. The lowest Pb concentration in the sediment was consistent with the low concentration of Pb in coastal waters in Tianjin Bohai Bay in 1999, which corresponded to the very low annual runoff into Tianjin Bohai Bay at that time [9], suggesting that the Pb in sediment was mainly associated with river discharge in 1999. However, the contents of Pb in sediment then increased significantly until 2001, when annual runoff into Tianjin Bohai Bay was still at a very low level [23], and the use of leaded petrol began to be banned completely in China in 2001. This suggests that Pb input into the sediment from leaded petrol was also an important source for Pb before 2001. In addition, the atmospheric deposition of aerosols or coal burning and some industrial activities might be other sources of Pb in the sediment after 2001, as confirmed by [99] and [100] in other estuary systems. It has been estimated that atmospheric deposition dominated the input of Pb for the entire Bohai Sea [96]. As for Ni, there is a very high Ni emission intensity (> 3.0 kg·km^{-2}) in the Beijing-Tianjin-Hebei

Region around the Bohai Bay, which are highly industrialized and densely populated areas, and these Ni emissions are mainly affected by the volume of fossil fuels consumption, except for industrial process such as metals smelting [101]. The research area of this study is located in one of the most industrialized zones in China. It is reasonable to presume that industrial processes and atmospheric deposition (mainly fossil fuels consumption) are the main sources for Ni in the sediment except for natural source.

In the case of Mn, there were few reports on the Mn concentration in sediment from the coastal zone in Tianjin Bohai Bay. Higher Mn concentration of the sediments might be associated with the anthropogenic source, as confirmed by low correlation coefficient between Mn and Al ($R = 0.17$, $p < 0.05$), and Mn and clay ($R = 0.18$, $p < 0.05$), as well as its relatively high I_{geo} value (ranging from 0.23 to 1.04, with an average of 0.69) and/or significantly higher percentage in the most mobile fraction.

In our study, Cd is not significantly correlated with other metals including Cu, Zn, Co, Ni, Al, and Fe. In the Bohai Sea, the pollution of Cd in the sediment has been widely reported although its concentration is relatively low in the sea [92,102]. Pathways for Cd to enter the Bohai Sea might be complicated, possibly including riverine input (mainly the Yellow River and Haihe River), atmospheric deposition (the combustion of fossil fuels such as coal and petroleum), direct discharge, and biological processes [103,104]. In Bohai Bay, the anthropogenic source of Cd might include additives used by local factories for manufacturing synthetic rubber and PVC materials [65], the electroplating industry including aeronautics and astronautics, electronic components, and equipment manufacturing in Tianjin [18], and agricultural non-point source pollution. The industrial effluent and agricultural runoff containing Cd could be discharged into the Bohai Bay via some small rivers (e.g., the Yongdinghe and Daguhe) around Bohai Bay.

Therefore, the high mobility of Cd, anthropogenic input sources and pathways (via riverine input, such as the Yellow and Hai River, atmospheric deposition and agricultural non-point source pollution) may explain the different distribution of Cd with respect to other metals in sediments.

5. Conclusions

According to the estimated total diffusive fluxes, the Zn ion is the most mobilized of five metals. However, the upwardly mobilized metals, only Cu, Cd and Ni might be released into the overlying bottom sea water from the sediment.

Results of speciation of metals indicate that Cu, Pb, Zn and Ni are mainly derived from natural rock weathering and relatively stable with lower bioavailability. The low percentage of Cu in the organic fraction in our samples could be attributed to the low content of organic matter in the sediment (less than 1% for most of the samples) and/or the neutral pH in the sediment, which restricts the formation of stable organic complexes.

Correlation analysis shows that Ni, Cu, Pb and Zn perhaps have a mixed source (natural and anthropogenic). Organic matter and AVS have no significant influence on the distribution of these metals in the sediment.

Results of I_{geo} values reveal that metal Ni is of unpolluted level, and Cu, Pb and Zn are in a level from unpolluted to moderately polluted throughout the core. Mn and Cd have an obvious anthropogenic influence. The low correlation coefficient among Cd, Mn and Al reinforces this presumption. Based on the RAC, Cd and Mn pose a high to very high risk to the local environment due to the significant percentage of exchangeable fraction.

Different metals in sediments might have different sources or input pathways. Generally, river runoff is an important source for heavy metals, especially for Cu, Zn, and Ni. Domestic sewage discharge has a significant influence on the source of heavy metals (except for Cd and Mn) since 1998. Atmospheric deposition dominated the input of some metals such as Pb. The high mobility of Cd, anthropogenic input sources and transportation pathways may explain the reason that the distribution of Cd is different from those of other metals in the sediments.

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