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Distribution and Pollution Assessment of Heavy Metals in Beidaihe Near-Shore Marine Sediments

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Abstract

The concentrations of heavy metals, Cd, Hg, Pb, Cu and As in marine sediments from 138 sites located in the Beidaihe near-shore area of Bohai bay, were analyzed to find out the distribution characteristics of these heavy metals. Potential Ecological Risk index were adopted to assess the heavy metals contamination, and the assessment results indicated that the content of heavy metals in this area is in a low to moderate level, while high values were found in the southwest and northeast region, and the value in the middle region is comparatively low. The high pollution hazard sites were close to the Renzaohe estuary and Shihe estuary and the high risk is mainly led by Hg.

1. Introduction

The study area is located at Beidaihe near-shore area of Bohai Bay, which belongs to Qinhuangdao city, Hebei Province. It is a famous holiday resorts and important Aquatic products culture zones in Bohai Bay. There are rivers running into the Bohai Bay, including Shihe, Tanghe, Daihe, Yanghe, Renzaohe, Dapuhe, etc. which bring various rich nutrients to the shore, together with pollutants emitted from land. The Beidaihe near-shore area, with shallow water depth and smooth currents, is conducive to various types of pollutants accumulation in the sediment. Due to the long time residual characteristic, easily enrichment feature and huge repairable difficulty, Heavy metals are likely to be the most important pollutants in marine sediment, which are also easily to be transferred along the food chain and proved having badly negative impact on aquatic life and human health [1]. Based on the analysis of the distribution characteristics of heavy metals in surface sediments, contamination situation of heavy metal is well assessed in order to provide basic reference data for Beidaihe near-shore marine environmental protection.

2. Sample Collection and Test

One hundred and thirty eight un-disturbing samples were collected by Julong-180 drilling rig from sediments in

Beidaihe near-shore area ranged between 119°20'E - 119°50'E and 39°40'N - 40°00'N in July, 2011 (**Figure 1**). Surface sediments were sampled in length of ten centimeter in any site as soon as profiles sediments which were collected in interval scale of half a meter vertically. Profile I, composed of drillings 2#, 3#, 4# and 5#, is located in Renzaohe estuary. Profile II, composed of drillings 11#, 25#, 24#, 29# and 27#, is located in middle position of the research area. And profile III containing drillings 17#, 16#, 19# and 15# is located in Shihe estuary. The depth of these drillings is in the rage of 3 - 5 meters. Sediment samples were stored in accordance with the relevant provisions in Part 3 of GB/T 12763.3-2007 of "Specifications for Marine Monitoring". Sample testing, with Cu, As, Pb, Hg and Cd, was completed by the Tianjin Mineral Resource Supervision Testing Center.

3. Methods

Hakanson [2] (1980) proposed Potential Ecological Risk index (i_r) of Heavy metals in sediments to assess the potential ecological risk raised by heavy metals. The index reflects the environment sensitivity to heavy metals [3] (Rubio, 2000). According to this approach, the potential ecological risk index of the heavy metal i is displayed as E_r^i. And the potential ecological risk index of a variety of heavy metals is calculated as follows (Equations (1)-(3)):

$$E_r^i = T_r^i C_f^i \tag{1}$$

$$C_f^i = C_s^i / C_n^i \tag{2}$$

$$i_r = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i C_f^i = \sum_{i=1}^{n} T_r^i C_s^i / C_n^i \tag{3}$$

where T_i^r is the toxicity coefficient of the heavy metal i, which reflects the toxic level and the biological sensitivity raised by heavy metal i; C_f^i is the enrichment factor; C_s^i is the measured concentration; C_n^i is the reference concentration.

Based on the research results from Hakanson [2] (1980), Li [4] (1994), Chen [5] (2008), Ye [6] (2008), Gan [1] (2010) and Luo [7] (2010), the toxicity coefficients of Cd, Hg, Pb, Cu and As is set up with 30, 40, 5, 5 and 10 respectively. Hakanson (1980) divided the potential ecological risk index into four levels (**Table 1**).
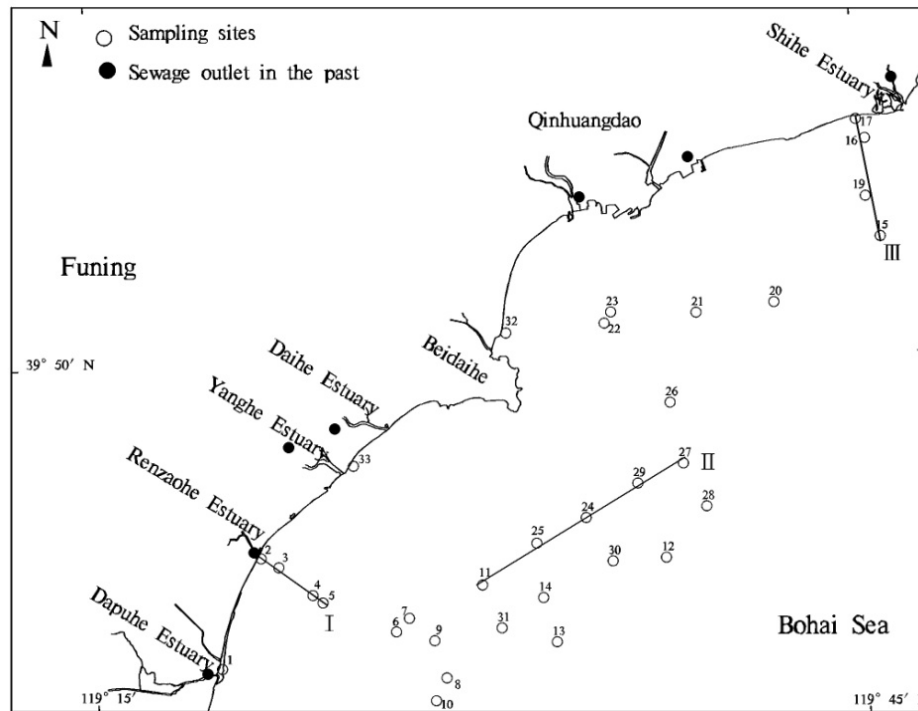

Figure 1. Location of surface sediment sampling sites in Beidaihe near-shore area.

Table 1. The classification of the potential ecological risk of heavy metals.

	Class				
	1	2	3	4	5
E_r^i	(0, 40)	[40, 80)	[80, 160)	[160, 320)	[320, +∞)
i_r	(0, 75); [75, 150)	[150, 225); [225, 300)	[300, 450); [450, 600)	[600, +∞)	
Level	Nile to very low; low	Lower-moderate; higher-moderate	High; very high	Extremely high	Ultra high

4. Analysis and Assessment

4.1. Distribution Characteristic of Heavy Metals

(1) Distribution characteristic in surface sediments

The general level of heavy metal content is low in sediments. **Table 2** clearly shows five different statistic features of heavy metal content in surface sediments, including concentration range, mean, median, root-mean-square deviation and coefficient of variation.

Cu concentration looks more apparent at 31st and 16th sites while the content of As is more heavy at 3rd and 31st sites and value of Pb is more serious at 20th, 15th and 23rd sites (**Figure 2**). Whereas the other two heavy metals pollutions, Hg and Cd, are serious at 22nd and 3rd sites, and 15th and 6th sties respectively. According to the mean value, the Hg concentration is highest while Cu concentration is the second highest among all these five heavy metals.

Concentrations of Cu, Pb, Hg and Cd, with the highest value in near-shore of Renzaohe estuary and urban in-shore area of Qinghuangdao, have a trend of higher from near-shore to sea, while As has a trend of lower (**Figure 2**).

Except that the coefficient of variation of Cu (73%) is more than 50%, other four kinds of heavy metal coefficient of variations are all smaller, indicating that there is no obvious content distribution difference throughout the study area (**Table 2**).

(2) Distribution characteristic in profiles sediments

The concentration of Cu varies in range of 6.59 - 59.35 mg/kg, with mean value of 21.81 mg/kg, while As varies in range of 1.33 - 17.13 mg/kg with mean value of 7.30 mg/kg and the content of Pb varies in range of 6.38 - 41.32 mg/kg, with mean value of 20.62 mg/kg. At the same time, the concentration of Hg varies in range of 0.013 - 0.087 mg/kg with mean value of 0.037 when the concentration of Cd whose mean value is 0.089 varies in range of 0.041 - 0.335 mg/kg. Compared with background values, the Hg pollution is most serious while Cu pollution is the second most serious among all these five heavy metals.

In profile I (**Figure 3** and **Figure 4**), the concentration of Cu varies in range of 7.02 - 37.90 mg/kg, with mean value of 23.63 mg/kg, while As varies from 4.22 to 17.13 mg/kg with mean value of 9.11 mg/kg; The concentration of Pb varies in range of 7.52 - 38.30 mg/kg, with mean value of 23.39 mg/kg, when Hg varies in range of 0.020 - 0.072 mg/kg with mean value is 0.037 mg/kg; and the concentration of Cd whose mean value is 0.089 varies from 0.044 - 0.204 mg/kg. Samples with highest concentration of Hg and Cu are located at 4th drilling. Concentration of Hg has a trend of lower from up-section of 3rd drilling and down-section of 4th drilling to around, and Cu has an extra higher value in up-section of 5th drilling.

In profile II (**Figure 5** and **Figure 6**), the concentration of Cu varies in range of 6.59 - 34.43 mg/kg, with mean value of 15.85 mg/kg, while As varies from 1.33 to 11.10 mg/kg with mean value of 5.47 mg/kg; The concentration of Pb varies in range of 6.38 - 34.20 mg/kg, with mean value of 15.42 mg/kg, when Hg varies in range of 0.013 - 0.087 mg/kg with mean value is 0.036 mg/kg; and the concentration of Cd, mean value of 0.072, varies in range of 0.041 - 0.163 mg/kg. Samples with highest concentration of Hg and Cu are located at the bottom of 11th drilling. Concentration of Hg has a trend of lower from down-section of 11th and 24th drillings to around, and Cu has an extra higher value in the top of 29th drilling.

In profile III (**Figure 7** and **Figure 8**), the concentration of Cu varies in range of 8.28 - 59.35 mg/kg, with mean value of 8.84 mg/kg, when As varies in range of 3.65 - 15.93 mg/kg with mean value of 7.26 mg/kg; The concentration of Pb varies from 7.85 - 41.32 mg/kg, with mean value of 22.48 mg/kg, while Hg varies in range
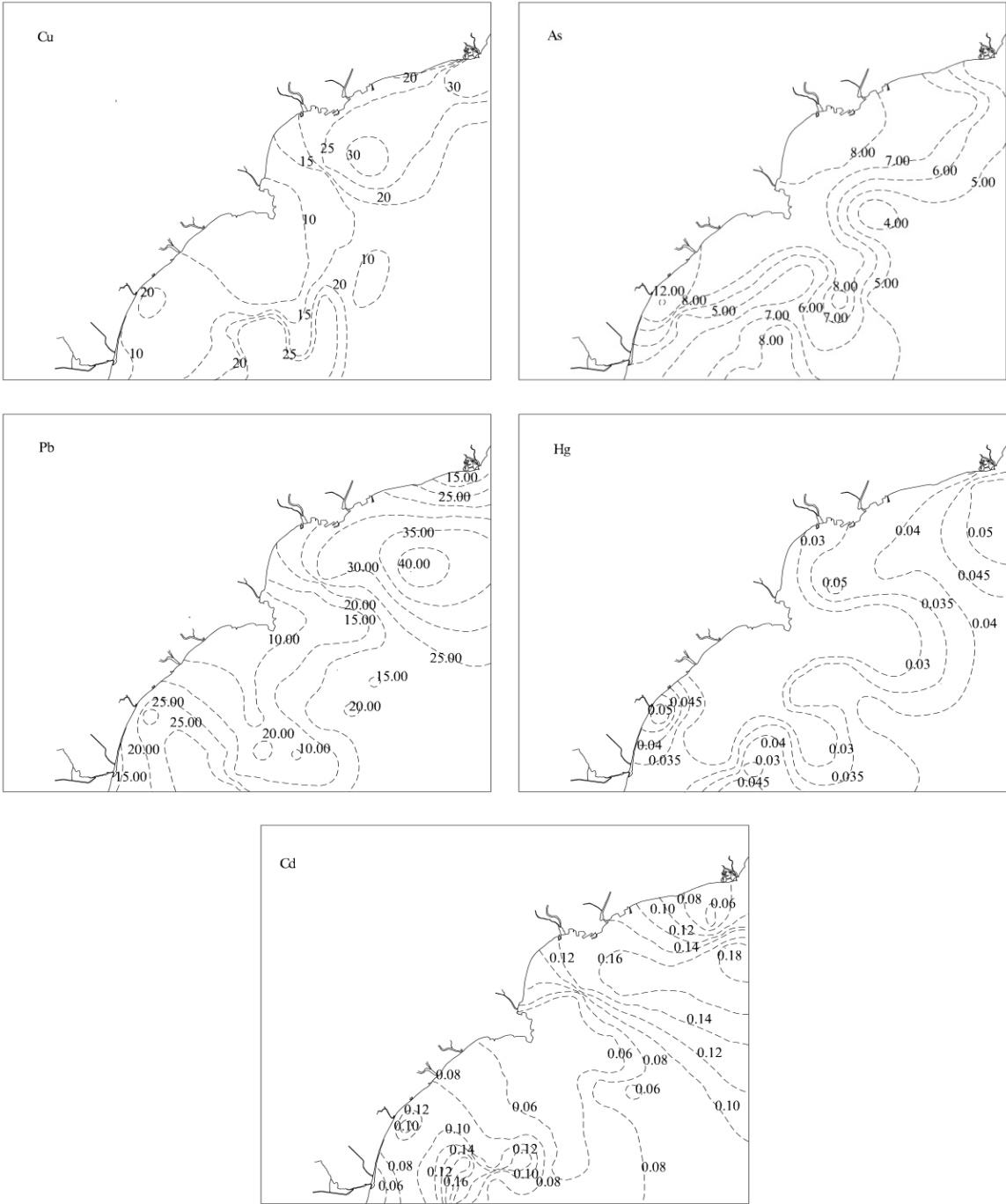
Figure 2. Distribution of the heavy medals in surface sediments [mg/kg].

Table 2. The content of the heavy metal in surface sediments [mg/kg].

Statistic feature	Cu	As	Pb	Hg	Cd
Range	5.03 - 66.26	2.42 - 13.52	7.85 - 45.17	0.016 - 0.06	0.047 - 0.186
Mean	18.90	6.70	19.93	0.04	0.09
Median	13.69	6.50	18.88	0.04	0.07
Root-mean-square deviation	13.76	2.15	9.35	0.01	0.04
Coefficientof variation	0.73	0.32	0.47	0.32	0.48
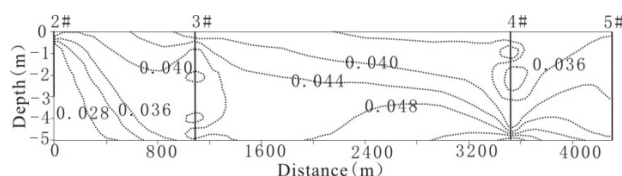
Figure 3. Distribution of the Hg in I-profile sediments [mg/kg].
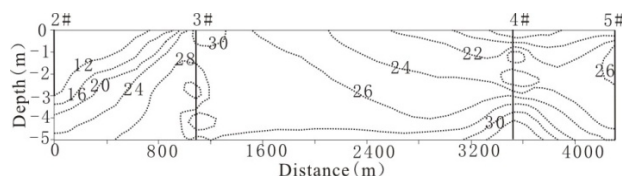
Figure 4. Distribution of the Cu in I-profile sediments [mg/kg].
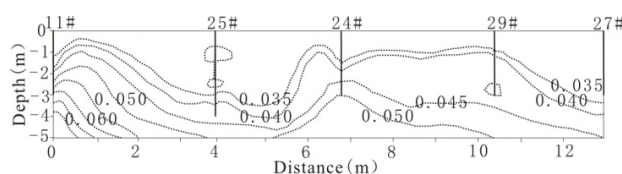
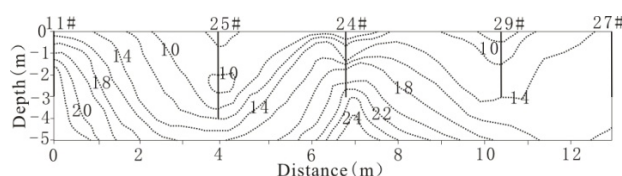**Figure 5.** Distribution of the Hg in II-profile sediments [mg/kg].

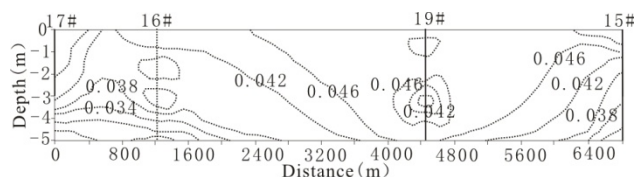**Figure 6.** Distribution of the Cu in II-profile sediments [mg/kg].

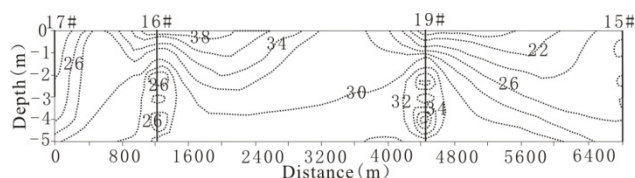**Figure 7.** Distribution of the Hg in III-profile sediments [mg/kg].

Figure 8. Distribution of the Cu in III-profile sediments [mg/kg].

of 0.021 - 0.083 mg/kg with mean value of 0.039 mg/kg; and the concentration of Cd whose mean value is 0.104 varies in range of 0.053 - 0.335 mg/kg. Samples with highest concentration of Hg and Cu are located at the top and middle of 16th drilling. Concentration of Hg has a trend of lower from up-section of 16th drilling and middle-section of 19th drilling to around as soon as Cu.

4.2. Pollution Assessment of Heavy Metals

(1) Assessment result in surface sediments

In the view of all the sample sites(**Figure 1**, **Figure 9**), the indexes of potential ecological risk (E_r^i) of heavy metals are generally less than 40 except the risk index of Cd in sites 3rd, 6th, 15th, 20th, 21st, 23rd and 31st and the data of Hg at all sites are above 40. It indicates that the potential ecological risk of heavy metals, Cd, As, Cu and Pb, is comparatively low. However, the risk of Hg is at the moderate level in this region, therefore Hg is undoubtedly the main potential ecological risk pollutant.

The potential ecological risk (i_r) of each site in the study area is below 250, which is at the range of low to moderate potential ecological risk level. The sites near to the Renzaohe estuary, Shihe estuary and Qinhuangdao City inshore area are with comparatively high risk. The 3rd site at the south area has the highest potential risk with the index 240.60. Combined with the characteristic of heavy metal distribution in this site, the high risk is led by Hg.

(2) Assessment result in profiles sediments

From the result of the single element (**Figures 10-12**), the index of Cu varies in range of 2.48 - 22.35, with mean value of 8.24, while As varies in range of 1.82 - 23.43 with mean value of 10.02 mg/kg and index of Pb
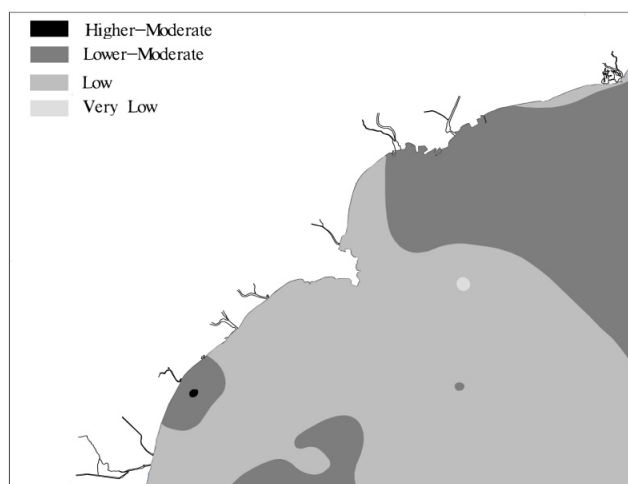

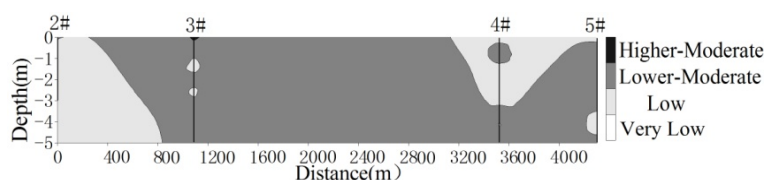**Figure 9.** Assessment result based on i_r in surface sediments.

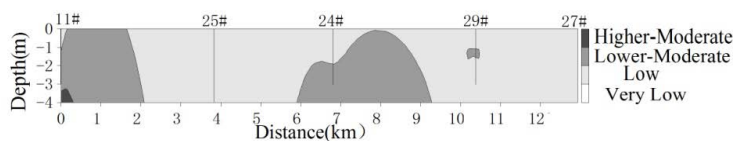**Figure 10.** Assessment result based on i_r in I-profile sediments.

Figure 11. Assessment result based on i_r in II-profile sediments.
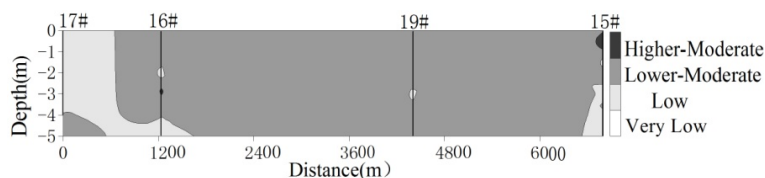

Figure 12. Assessment result based on i_r in III-profile sediments.

ranged from 1.63 to 10.57, with mean value of 5.27. Whereas the other two heavy metals pollutions, Hg and Cd, are in range of 33.10 - 221.51 (mean of 94.74) and 13.67 - 111.67 (mean of 29.72) respectively. Incontrovertibly, Hg pollution is most serious among these five heavy metals.

The indexes of potential ecological risk in profiles, with mean value of 147.99 and highest value of 288.40, indicate the heavy metals risk is in a low to higher-moderate level.

The i_r of profile I and profile III indicate that the heavy metals risks, in majority of samples, are in low-moderate levels (**Figure 10**, **Figure 12**). According to the low value of i_r, the risk level in profile II is demonstrated low except the contamination in bottom of left-section is at high-moderate level (**Figure 11**).

5. Conclusions

Results show that the contents of these five heavy metals are lower at the inshore area of Beidaihe and increase along the coastal lines. The distribution of As is different from others whose peak value lied at the inshore area, which is probably caused by the dissimilar sources. The average contents of Hg and Cu are comparatively higher than other metals.

Based on the assessment result of Potential Ecological Risk, pollution of heavy metals is in a low to moderate level in this area. Those sites nearing to Renzaohe estuary, Shihe estuary and central urban inshore zone are with higher risk comparatively.

Acknowledgements

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