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Spatial and Temporal Variations of Heavy Metals in Surface Sediments in Bohai Bay, North China

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Abstract Characteristics of the spatial and temporal distributions of selected heavy metals (Cu, Zn, Cd, Pb and Hg) in Bohai Bay, north China was examined. Surface sediment samples from 15 sites were collected and analyzed for the selected metals with atomic absorption spectrometry (AAS) from the year of 1997–2007. Mean concentrations of metals in the 11-year period showed that Hg and Zn concentrations slightly fluctuated, while Cu, Cd and Pb concentrations in sediments varied with time. High levels of heavy metals occurred not only along the shoreline but also at some site in the inner part of the bay, suggesting the contamination sources of heavy metals from both terrestrial inputs and the atmospheric deposition. Compared with the environmental background values of selected heavy metals it indicated that anthropogenic activities influenced the sediment quality. The contamination factor C_f^i, which is used to evaluate the pollution of the environment, showed that the contamination by selected heavy metals was moderate. Cd, Zn and Pb were the main polluting elements in this area.

Keywords Heavy metals · Bohai Bay · Marine sediment quality · Assessment

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Heavy metals pollution in the aquatic environment is of great concern around the world due to their toxicity, persistence and bioaccumulation characteristics (Pekey 2006; Osher et al. 2006; Lafabrie et al. 2007). These chemicals pose potential threats to ecosystems and human health because of their certain properties such as being not decomposable naturally, being enriched by organisms and sometimes being converted to more toxic organic complexes (Liu et al. 2009). The distribution and pollution levels of heavy metals in the rivers, estuaries, coastal, bay and sea environments have been extensively investigated around the world (Pempkowiak et al. 2000; Tang et al. 2002; Sweeney and Sañudo-Wilhelmy 2004; Gavriil and Angelidis 2005; Meng et al. 2008; Unlu et al. 2008). Heavy metals in sediments are essential to the functioning of aquatic ecosystems, and concentration variations in sediments are generally smaller than in the water columns, resulting in the extensively investigation of heavy metals in sediment phase. After being introduced into the aquatic environment, metals in aqueous phase will eventually deposit to sediment via physical, chemical or biological ways. Sediment-associated metals are extremely important to the food webs and their eventual transfer back to human, therefore sediments are commonly used as environmental indicators to reflect the prevailing quality of aquatic systems (Unlu et al. 2008).

Surrounded by big cities and highly industrialized areas, Bohai Bay in north China is facing severe pollution problems. The bay is a typical semi-enclosed coastal area, making it difficult for the exchange of bay water with the open ocean. Large quantities (approximately 1 billion tons of wastewater each year) of contaminants are discharged into the bay, causing great risk to the marine ecology, which has attracted considerable attention of both scientific and regulatory communities. Heavy metals contamination of Bohai Bay in the past few years have been investigated (Zhang et al. 2002; Hua et al. 2005; Wang et al. 2005; Wang and Li 2006; Wang and Wang 2007; Liu et al. 2007; Meng et al. 2008), however, no comparison was available to show the spatial and temporal distribution of heavy metals in the bay sediments in an 11-year duration. This study is to address this concern. Heavy metals including Cu, Zn, Pb, Cd and Hg were measured in Bohai Bay sediment samples from 15 sites from the year of 1997 to 2007, to investigate the spatial and temporal variations of heavy metals in this area. The sediment data will provide essential information for the ecological risk assessment and evaluating ambient environmental quality conditions.

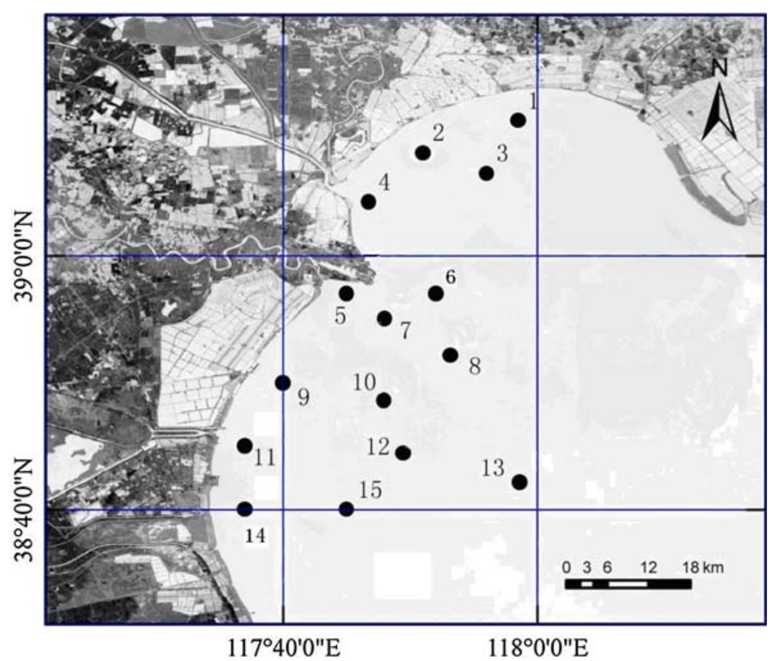
Materials and Methods

Figure 1 shows the sampling sites in Bohai Bay along the shoreline of Tianjin, China. Sampling campaigns were carried out in May every other year from 1997 to 2007. The sampling sites were selected considering the functioning regions such as estuarine area, natural reserve area, harbor area, landscape area, oil drilling area, etc. Surface sediments (top 10 cm) were grab sampled with a stainless steel container. Samples were transported to the laboratory, freeze dried and ground with a mortar and pestle then passed through a sieve with 1 mm opening.

One gram of dried sediment sample was placed in a 250 mL Pyrex flask. A total of 9 mL of concentrated HNO_3 and 3 mL of concentrated $HClO_4$ were added to the flask and the flask was then placed on a heating plate for digestion. A small amount of nitric acid was added intermittently to digest the sediment completely until the supernatant became clear and a brownish-colored fume was no longer generated. After the sample became nearly dried, it was taken up in 1% HNO_3, and the solution was filtered through a 0.45 μm membrane filter and ready for analysis.

Cu, Pb, Cd and Zn were determined with Flame Atomic Absorption Spectrometry, and Hg was determined with Cold Vapor Atomic Absorption Spectrometry. The limits of detection of Cu, Zn, Pb, Cd and Hg were 0.20, 3.10, 0.03, 0.01 and 0.001 μg/L, respectively. The organic carbon (OC) content of the sediments was determined by the potassium dichromate-sulfuric acid oxidation method. All samples were analyzed in triplicate, and data shown below were average values of the triplicates. In order to evaluate the precision and recovery of the extraction procedure, a stream sediment reference material (GBW07310) was used following the course of extraction. Results showed that the extraction procedure is repeatable and reliable, with recoveries for all heavy metals ranging from 92.8 to 108.5%. All glassware used in this study was previously soaked in 15% HNO_3 (v/v) and rinsed with de-ionized water. For statistical analysis, two-tailed *t* test was used to compare the average concentrations between samples in the present study.

Fig. 1 The sampling sites in the study area



Results and Discussion

Average concentrations of Cu, Zn, Pb, Cd and Hg at 15 sites in Bohai Bay during 1997–2007 were shown in Fig. 2. Different metals undertook their own temporal variations in the 11-year period in Bohai Bay. Average concentrations of all sampling sites showed that for Hg and Zn, their concentrations fluctuated slightly from 1997 to 2007. Cu concentrations in 1999 were the highest, with mean values greater than 35 mg/kg for all sites. In 2001, it reached the lowest levels, and increased afterward. For Cd, high sediment concentrations were found in 2001 and 2005. From 1997 to 2003, Pb levels decreased slowly, and began to increase from 2003. Spatial variations showed that high levels of heavy metals occurred along the shoreline at sites 2, 4, 5, 9, 11, and 14, while at the inner part of the bay their concentrations were relatively low. This trend was quite similar to our previous findings that the dissolved concentrations of the above metals in sea water samples descended from the coastline to the central areas of the bay (Dai et al. 2009). It was assumed that terrestrial inputs may be the important source for the heavy metals contamination. An exception, Site 12, which was at the inner part of the bay, was burdened with high metal concentrations, suggesting some other input ways may exist for this area. Atmospheric deposition was considered by some

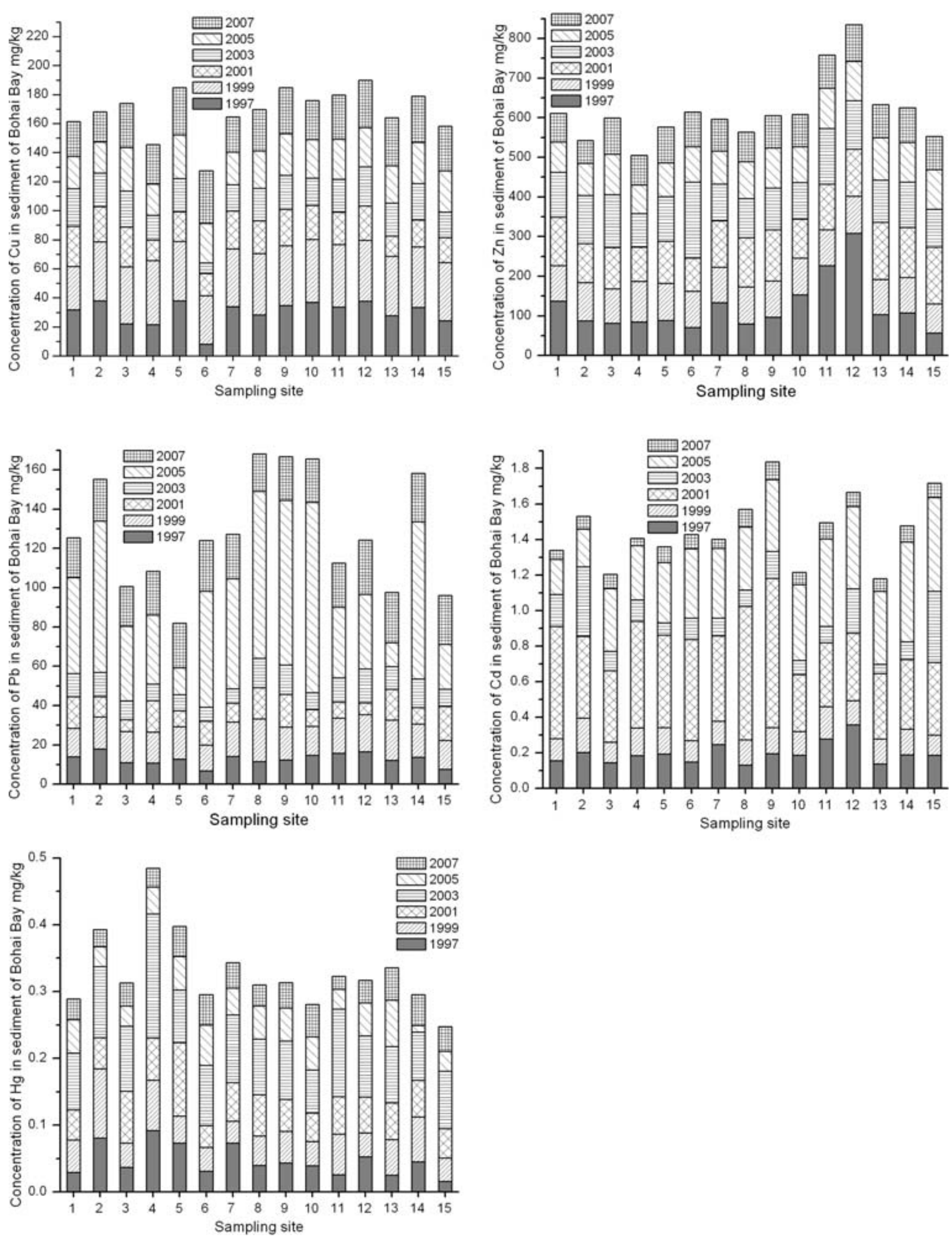


Fig. 2 The average concentrations of selected heavy metals in surface sediments from different sites of Bohai Bay in 1997–2007

Table 1 Marine sediment quality standard of China for selected heavy metals, $\times 10^{-6}$

Element	Grade-I	Grade-II	Grade-III
Cu	35.0	100.0	200.0
Zn	150.0	350.0	600.0
Pb	60.0	130.0	250.0
Cd	0.50	1.50	5.00
Hg	0.20	0.50	1.00
OC	2.0	3.0	4.0

researchers to contribute the heavy metals contamination to the sediments in the central bay (Cao et al. 2006; Meng et al. 2008).

The sediment quality was assessed by comparing detected metal concentrations with the marine sediment quality standard of China (GB18668-2002; MSQSC), which was shown in Table 1. Calculation results showed that of the five metals and OC content, concentrations greater than MSQSC-I happened for Cu, Zn, Pb, Cd and OC at some sampling sites in some certain years. Cu had the highest percentage exceeding MSQSC-I, which was up to 19.57%. The exceeding MSQSC-I percentages for Zn, Pb, Cd, and Hg were 4.35%, 5.43%, 8.70% and 0%, respectively.

Compared with the environmental background values of selected heavy metals (shown in Table 2) it could be found that average concentrations of Cu, Zn, Pb and Cd were greater than their individual background values, indicating the anthropogenic influences on the sediment quality, while Hg levels were almost equivalent to its background value. The contamination factor, C_f^i, is often used to evaluate the pollution of the environment by single substances (Loska et al. 1997), which is measured by the following equation (Hakanson 1980):

$$C_f^i = C_{0-1}^i / C_n^i$$

where C_{0-1}^i is the mean content of metals in the bottom sediment, and C_n^i is the pre-industrial concentration of each metal. Contamination level is categorized as follows: $C_f^i < 1$, low contamination of the sediment with the examined substance; $1 \leq C_f^i < 3$, moderate contamination factor; $3 \leq C_f^i < 6$, considerable contamination factor; and $6 \leq C_f^i$, very high contamination factor (Loska et al. 1997). In the present study, the environmental background values were used as pre-industrial concentrations for each metal. The calculation results were shown in Table 3. It can be seen that most C_f^i values were between 1 and 2, showing that the contamination of this area by selected heavy metals was moderate. For Cu, concentrations from examined sites were basically at its background value level, suggesting its low contamination. Although the highest C_f^i values were found for Cd at Site 9 (2.19) and Site 15 (2.04), they still posed moderate contamination burden to the environment. From the average C_f^i data of 11 years (1997–2007) it could be concluded that the contamination extent of each metal was Cd > Zn > Pb > Hg > Cu. This order was in agreement with the result by Meng et al. (2008). They analyzed the surface sediment samples from Bohai Bay in June 2003, and found Cd, Zn and Pb were the main polluting elements in this area.

Table 2 gives some literature data for heavy metals from tidal zone and estuarine areas in Bohai Bay. Comparison result showed the average concentrations of Cu, Zn and Cd in the Bay area were higher than in tidal zones, while Pb and Hg had higher concentrations in tidal zones. Compared with the estuarine sediments, Cu, Zn and Pb levels were higher, while Cd and Hg were lower in the Bay sediments. To examine the possible correlation among different metals, the concentration data of metals in the sediments were subjected to the Pearson correlation analysis. Correlation coefficients among different metals and OC were shown in Table 4. Results showed that negative correlations were found between metal combinations including Cu-Cd, Cu-Hg, and Pb-Hg, while Zn-Cd and Pb-Cd were highly

Table 2 Statistical results of heavy metal data in Bohai Bay sediments

Element	Range (mg/kg)	Average (mg/kg)	Percentage exceeding MSQSC-I (%)	Background value,[a] (mg/kg)	Tidal zone value,[b] (mg/kg)	Estuarine zone value[c], (mg/kg)
Cu	7.2–44.0	28.1 ± 8.1	19.57	25.63	25.3 ± 4.6	20.9–27.3
Zn	56.3–308.5	102.5 ± 33.5	4.35	74.61	87.7 ± 38.2	89.9–91.4
Pb	5.9–97.0	21.2 ± 18.3	5.43	16.55	22.1 ± 2.8	17.9–21.5
Cd	0.04–0.84	0.24 ± 0.17	8.70	0.112	0.06 ± 0.03	0.2–0.32
Hg	0.01–0.18	0.05 ± 0.03	0	0.05	0.13 ± 0.07	0.30–0.85
OC	0.01–0.84	0.41 ± 0.13	–	–	–	

[a] Referenced from Li and Hao (1992)

[b] Referenced from Cao et al. (2006)

[c] Referenced from Meng et al. (2008)

Table 3 Contamination factor of heavy metals in surface sediments from Bohai Bay

Site	Contamination factor, C_f^i				
	Cu	Zn	Pb	Cd	Hg
1	1.04	1.36	1.26	1.59	0.96
2	1.08	1.21	1.56	1.82	1.31
3	1.12	1.33	1.01	1.43	1.04
4	0.94	1.12	1.09	1.67	1.62
5	1.19	1.28	0.82	1.62	1.32
6	0.82	1.37	1.24	1.70	0.99
7	1.06	1.33	1.28	1.67	1.14
8	1.09	1.25	1.69	1.87	1.03
9	1.19	1.35	1.67	2.19	1.05
10	1.13	1.35	1.66	1.45	0.93
11	1.16	1.69	1.13	1.78	1.07
12	1.22	1.86	1.25	1.98	1.06
13	1.06	1.41	0.98	1.40	1.12
14	1.15	1.39	1.59	1.76	0.98
15	1.02	1.23	0.96	2.04	0.83
Average	1.08	1.37	1.28	1.73	1.10

Table 4 Correlation analysis of elements in the surface sediments from Bohai Bay

	Cu	Zn	Pb	Cd	Hg	OC
Cu	1					
Zn	−0.015	1				
Pb	0.031	−0.160	1			
Cd	−0.271**	0.235*	0.209*	1		
Hg	−0.237*	0.163	−0.276**	−0.029	1	
OC	0.131	−0.003	0.202	0.526**	−0.214	1

* $p = 0.05$, ** $p = 0.01$

positive-correlated. High correlation coefficient between different metals means their common sources, mutual dependence and identical behavior during transport. The absence of strong correlation among other metals suggests that the concentrations of these metals are not controlled by a single factor, but a combination of geochemical support phases and their mixed associations (Jain et al. 2005). The results in the present study indicated that most examined metals don't have common sources, that is, they may originate from various sources, and their behavior during the transport may be varied. The positive inter-element relationship of Zn-Cd and Pb-Cd suggested a similar terrigenous source or a result of similar mechanisms of transport and accumulation within the sediments. It was notable that highest correlation coefficient (0.526) was found between Cd and OC. Generally, high correlation existed for organic contaminants with OC in sediments (Xu et al. 2007). Heavy metal levels in sediments were reported to be mainly influenced by particle size and composition of sediments (Krumlgalz 1989; Jain et al. 2005), and OC was not a good predictor of the concentration of elements. The reason for the high correlation between OC and Cd here may be due to the same origin of OC and Cd in Bohai Bay. It was considered that atmospheric dust (Tianjin EPA 2000; Nankai U 2008) and agricultural non-point pollution (Wei et al. 2004; Zhang and Shan 2008) that consisted of high content of Cd and OC contributed to the Cd and OC accumulation in Bohai Bay.

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