Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 20(2008) 814–819
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Heavy metal pollution in Tianjin Bohai Bay, China

MENG Wei[1], QIN Yanwen[1,*], ZHENG Binghui[1], ZHANG Lei[1]

River and Coastal Environment Research Center, Chinese Research Academy of Environmental Sciences, Beijing 100012, China.
E-mail: mengwei@craes.org.cn

Received 18 September 2007; revised 24 October 2007; accepted 18 February 2008

Abstract

The contamination levels and distribution characters of heavy metals in coastal waters and sediments from Tianjin Bohai Bay, China were examined. Pb and Zn were found as the main heavy metal pollutants in the coastal waters of the bay. High levels of Pb and Zn appeared especially near the estuary, indicating that river discharge was the main pollution source. Moreover, atmospheric deposition resulted in Pb contamination in the middle of the embayment. Analysis of data for the period 1987–2004 indicated that Pb pollution in coastal waters of Tianjin Bohai Bay originated primarily from river discharge before 2001. Pb levels did not decrease after 2001 when annual runoff levels declined; indicating that Pb pollution by atmospheric deposition had increased due to the use of leaded petrol in motorcars. Pb, Zn, and Cd were the dominant polluting elements in surficial sediments from Tianjin Bohai Bay, with levels in excess of the corresponding upper limits of environmental background values. High concentrations of polluting elements were found in tidal sediments near water bodies such as Qihe and Dagu estuaries.

Key words: heavy metals; pollution; Tianjin Bohai Bay, China

Introduction

Pollutants entering the marine environment through rivers affect estuarine and deltaic systems in various ways. The impact of anthropogenic activities on marine environments, especially on enclosed systems such as the Bohai Sea, China, can be determined by measuring various chemical markers including nutrients, organic compounds, and toxic heavy metals in the water column, biota, and sediments (Audry *et al*., 2006; Tuncel *et al*., 2007). Of the many pollutants found in coastal and estuarine sediments, heavy metals are amongst the most persistent because they cannot be destroyed or broken down. Therefore, they are useful as markers of environmental change (Arnason and Fletcher, 2003). In coastal zones, metals can enter surface waters principally through atmospheric deposition, industrial effluent discharge, and streams. When metals enter marine environments, they are adsorbed onto the sediments of adjacent shelf regions. Marine sediments act as scavengers of trace metals and often provide an excellent record of human impact (Valette-Silver, 1992; Guevara *et al*., 2005).

The Bohai Sea is a nearly enclosed interior sea located in northeast China and consists of Liaodong Bay, Bohai Bay, Laizhou Bay, and the middle sea. The Bohai Sea is an economically and ecologically important region that covers an area of 77,000 km^2 and accounts for 1.63% of the marine belt areas in China. The abundant marine resources and special ecological conditions of this sea have played a role in the rapid economic development of the surrounding areas. However, in the last 20 years, the environmental quality of the Bohai Sea, especially that of Bohai Bay, has deteriorated, and ecosystem degeneration is becoming more serious with each passing year, a trend that has been receiving more attention from society, scholars, and government decision-makers.

Bohai Bay is located in the west of the Bohai Sea and near the city of Tianjin, the provinces of Hebei and Shandong. Accounting for about 20% of the extent of the Bohai Sea, and with a mean depth of 12.5 m, Bohai Bay is a typical semi-enclosed coastal sea and has limited water exchange with the ocean. Large quantities of wastewater are discharged into Bohai Bay each year from rivers of the Beijing-Tianjin, which are polluted with effluent and storm runoff. Pollution and environmental management of enclosed coastal seas is an important area of research, which has received a good deal of attention worldwide. Since the 1970s, the environmental quality of Bohai Bay has declined as economic development; pollution and city expansion have increased in the Bohai coastal area (Ye, 1991).

This article describes the pollution status and historical trends in heavy metal concentrations in coastal waters and sediments of Bohai Bay near the coast of the Tianjin, referred to here as Tianjin Bohai Bay. Four main estuaries are found in Tianjing Bohai Bay, namely Beitang, Dagu, Duliujian, and Qihe estuaries, through which most pollutants

* Corresponding author. E-mail: qinyw@craes.org.cn.

enter the Bohai Sea. The contamination history of heavy metals was examined, and their levels and distribution characteristics in this area were discussed, thus providing useful reference for future studies on heavy metal pollution in Tianjin Bohai Bay.

1 Materials and methods

1.1 Study area

In June 2003, surficial seawater samples were collected from 20 stations in coastal areas of Tianjin Bohai Bay, between 38°20′–39°13′N and 117°35′–118°E (Fig.1). Sediment samples were collected from 11 stations in Tianjin Bohai Bay, including 3 samples collected from the tidal belt closer to terrestrial discharge outlets and 8 samples from coastal areas of Tianjin Bohai Bay (Fig.1).

Sampling sites were located to account for terrestrial discharge outlets close to shore for comparison purposes with historical data. The monitored area was about 700 km^2 or roughly 20% of Bohai Bay. Most coastal areas of Tianjin were monitored so that the environmental status of the city's coastal belt could be determined.

1.2 Sample collection

Surficial seawater samples were taken at each of the stations and then filtered through a membrane filter (0.45 μm). Aqueous samples were stored in glass bottles after acidification with 0.2 mol/L H_2SO_4.

Surficial sediment samples were collected using a grab sampler. Samples of about 2 kg were collected at each station, and all sediment samples were placed directly into pre-cleaned aluminium pots and transported to the laboratory. Samples were then dried at room temperature, sieved through a 100-mesh nylon sieve and kept at −18°C until analysis. Material retained on the sieves was not used for analysis and was discarded.

1.3 Sample analysis

The concentrations of heavy metals including Cu, Pb, Cd, and Cr in aqueous samples were analyzed by graphite furnace atomic absorption spectrometry (GFAAS) (Varian, USA), and the concentration of Zn in aqueous samples was determined by flame atomic absorption spectrometry (FAAS) (Varian, USA). Atomic fluorescence spectrometry (AFS) (Jitian Company, China) was used to determine the concentration of As in aqueous samples, and cold vapor atomic absorption spectrometry (CVAAS) (Jitian Company, China) was used to analyze the concentration of Hg in aqueous samples.

For total Cu, Pb, Zn, Cd, and As determinations in sediments, 0.5 g sediment aliquots were digested in closed Teflon beakers by ultrapure HNO_3/HF mixtures at 120°C and evaporated to dryness. The residue was then dissolved in HNO_3/H_2O_2, evaporated to dryness again, and finally dissolved in 1% HNO_3. Dissolved sediments were analyzed with a Perkin-Elmer/Sciex Elan 6100 DRC ICP-MS (Perkin-Elmer, USA).

2 Results

2.1 Metal concentrations in coastal waters

Metal concentration ranges and averages are summarized in Table 1. The National Seawater Quality Standard of China (GB3097-1997) was used to assess the levels of heavy metals in coastal waters from Tianjin Bohai Bay. The quality of seawater is plotted by four levels corresponding with the different function zones according to the standard (GB3097-1997).

The levels of most metals except Zn and Pb in surface waters of Tianjin Bohai Bay attained the first level,

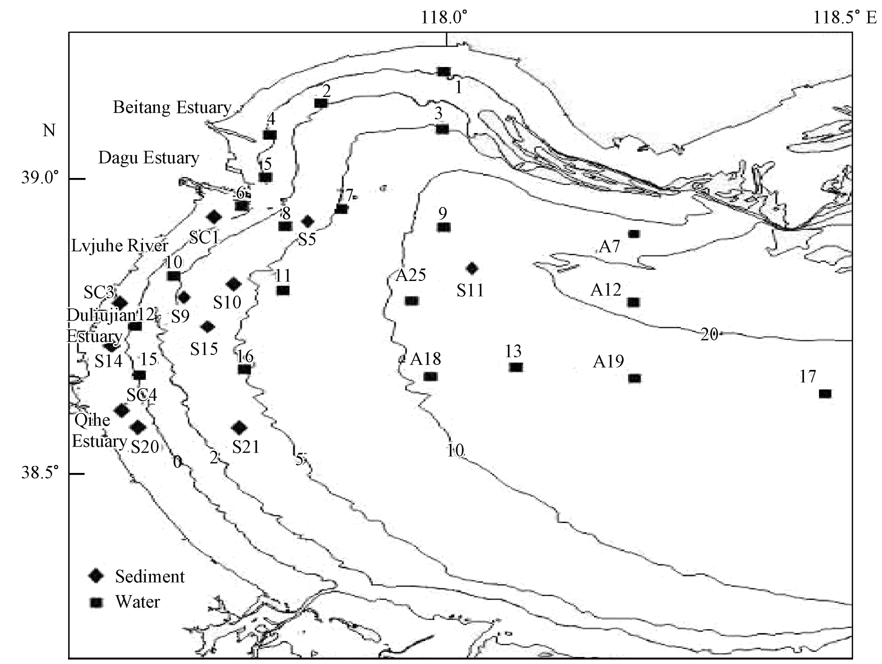

Fig. 1 Study areas and sampling locations in Tianjin Bohai Bay, China.

Table 1 Concentration ranges and average values of heavy metals in aqueous samples from various locations in the study area

Element	Concentration ranges (μg/L)	Mean (μg/L)
Cu	1.60–4.10	2.54 ± 0.77
Pb	3.63–12.65	7.18 ± 2.57
Zn	3.0–55.0	26.9 ± 14.2
Cd	0.08–0.19	0.12 ± 0.03
Cr	0.11–1.15	0.40 ± 0.26
As	0.79–2.06	1.26 ± 0.41
Hg	0.004–0.09	0.04 ± 0.02

indicating concentrations that are not out of the range of clean seawater. Consequently, Zn and Pb were the main contaminative elements in coastal waters from Tianjin Bohai Bay.

The total concentrations of Zn ranged from 3.0 to 55.0 μg/L, and the average Zn concentration in coastal waters was 26.9 μg/L. The highest Zn concentration (55.0 μg/L) was found at site 8 (Fig.2). According to the national seawater quality standard (GB3097-1997), the concentration of Zn in 70% of the sample sites attained the second level (⩽ 50 μg/L), and 10% of sites attained the third level (⩽ 100 μg/L) (Fig.2a).

The total Pb concentrations ranged from 3.63 to 12.65 μg/L, and the average in coastal waters was 7.2 μg/L. According to the standard (GB3097-1997), the concentrations of Pb in 55% of sampled sites attained the third level (⩽ 10 μg/L), 25% of sites attained the fourth level (⩽ 50 μg/L) and the remaining sites reached the second level (⩽ 5 μg/L) (Fig.2b).

2.2 Metal contents in sediments

Five areas in the coastal region of Tianjin Bohai Bay were delineated, based on hydrodynamic and sewage discharge conditions, to analyze pollution levels of metal elements in surficial sediments (Table 2). The five study regions representing the different sewage discharge conditions for Tianjin Bohai Bay were the Dagu Estuary region, the Lvjuhe River region, the Duliujian Estuary region, the Qihe Estuary region and the inner embayment region (Fig.1). Four main estuaries are distributed in the Tianjin Bohai Bay from north to south, namely Beitang, Dagu, Duliujian and Qihe estuaries and most sewage rivers, such as the south sewage river and the Beijing sewage river, discharge into these estuaries. The south sewage river and the Beijing sewage river carry a great amount of industrial and municipal sewage from the cities of Tianjin and Beijing, respectively. Consequently, all sediment samplings were attributed to the corresponding study region (Table 2). Each study region also comprised two kinds of sediment samples, that is tidal sediments and oceanic sediments.

Table 2 Compartmentalization of sampling station

Study region	Sampling station
Dagu Estuary	S5
Tidal zones of Dagu Estuary	SC1
Lvjuhe River	S9, S10
Duliujian Estuary	S14, S15
Tidal zones of Duliujian Estuary	SC3
Qihe Estuary	S20, S21
Tidal zones of Qihe Estuary	SC4
Inner region of Bohai Bay	S11

The metal element (Pb, Zn, Cu, As, Cd, and Cr) contents of sediments from the five Tianjin Bohai Bay study areas are presented in Table 3. The corresponding upper limits of environmental background values were used to determine the pollution levels of individual elements (Qin *et al*., 2006). The contamination degree of heavy metals was assessed on the basis of contamination factor C^i_f. The contamination factor is measured by the following equation (Hakanson, 1980).

$$C^i_f = C^i_{0-1}/C^i_n$$

where, C^i_{0-1} is the mean content of metals from sampling sites, and C^i_n is the pre-industrial concentration of individual metal. In this study, the background value of individual metal in sediments from Bohai Bay is applied as the pre-industrial concentration of C^i_n. The background value of individual metal is shown in Table 3. Values of the contamination factor are characterized as follows: C^i_f < 1 indicating low contamination of the sediment with the examined substance, $1 \leqslant C^i_f < 3$ moderate contamination factor, $3 \leqslant C^i_f < 6$ considerable contamination factor and $6 \leqslant C^i_f$ very high contamination factor(Loska *et al*., 1997).

C^i_f of metal elements is shown in Table 4. First, the contamination extent was set off according to the contamination factor of metal elements, Cd > Zn > Pb > Cr > Cu. Consequently, Pb, Zn, and Cd were considered the main polluting elements in surficial sediments from Tianjin Bohai Bay, and their distributions in sediments are shown in Fig.3.

Table 3 Average concentrations of metal elements in surficial sediments from Tianjin Bohai Bay and the corresponding environmental background values

Study region	Total metal (mg/kg)						
	Zn	Pb	Cd	Cu	Cr	As	Hg
Dagu Estuary	90.9	17.9	0.32	21.9	117	6.70	0.30
Tidal zones of Dagu Estuary	392.8	28.4	1.01	11.4	42	7.50	0.03
Lvjuhe River	96.6	17.5	0.25	27.3	191	7.00	0.65
Duliujian Estuary	89.9	21.5	0.20	20.9	107	6.64	0.51
Tidal zones of Duliujian Estuary	68.7	22.5	1.07	12.3	18	8.50	0.02
Qihe Estuary	91.4	17.9	0.20	22.5	110	6.49	0.85
Tidal zones of Qihe Estuary	112.9	34.9	1.82	15.6	59	16.5	0.04
Inner region of Bohai Bay	110.9	17.9	0.14	23.0	110	6.40	0.25
Background values*	75.0	16.6	0.14	25.9	60.0	13.0	0.05

* Referenced from Li *et al*. (1990, 1994).

Table 4 The contamination factor of metal elements in surficial sediments from Bohai Bay

Study region	Contamination factor C_f^i				
	Zn	Pb	Cd	Cu	Cr
Dagu Estuary	1.21	1.08	2.35	0.85	1.95
Tidal zones of Dagu Estuary	5.24	1.71	7.41	0.44	0.70
Lvjuhe Area	1.29	1.05	1.86	1.06	3.18
Duliujian Estuary	1.20	1.29	1.47	0.81	1.79
Tidal zones of Duliujian Estuary	0.92	1.35	7.90	0.47	0.29
Qihe Estuary	1.22	1.08	1.43	0.87	1.83
Tidal zones of Qihe Estuary	1.50	2.10	13.35	0.60	0.99
Inner region of Bohai Bay	1.48	1.08	1.06	0.89	1.83

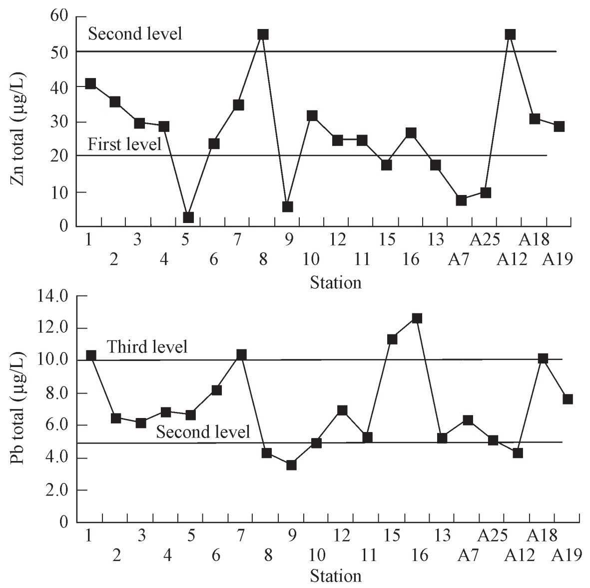

Fig. 2 Distribution of Zn and Pb in waters of Tianjin Bohai Bay on June 2003.

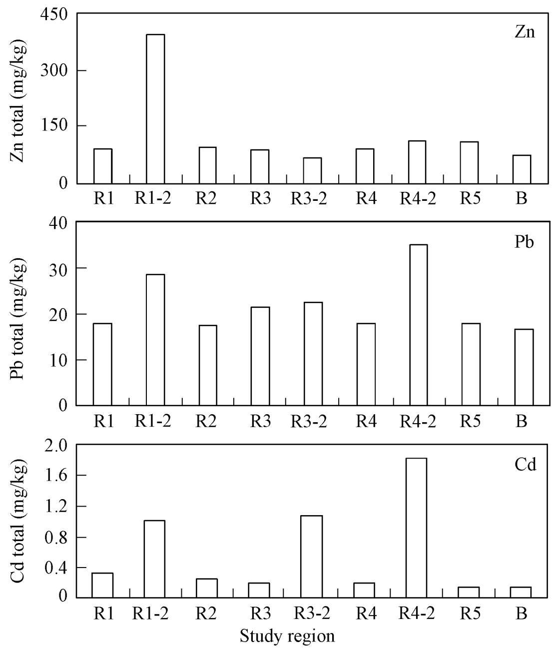

Fig. 3 Levels of metal contaminants in surficial sediments from Tianjin Bohai Bay. B: background.

The average Zn content was 131.8 mg/kg, and the highest level appeared in tidal sediments from the tidal zones of Dagu Estuary, which had levels about five times that of the environmental background value (Table 3).

The average Pb content of surficial sediments from Tianjin Bohai Bay was 22.4 mg/kg and the maximum content was found in tidal sediments from Qihe Estuary which had an average Pb content of 34.9 mg/kg and doubles the corresponding upper limit for environmental background values (Table 3).

The Cd content was higher in tidal sediments closer to the main estuary than in coastal sediments from inshore sites. The highest Cd levels appeared in tidal sediments from Qihe Estuary, which had Cd levels (1.82 mg/kg) 13 times greater than the environmental background value. In contrast, the Cd contents in sediments from the inner embayment were closer to the environmental background value and gave no sign of anthropogenic enrichment (Table 3).

3 Discussion

3.1 Distribution characteristics of the main polluting metals in surface waters

The National Seawater Quality Standard of China (GB3097-1997) was used to assess the main polluting metals in the aquatic environment of Tianjin Bohai Bay. The principal metal contaminants in coastal waters were Zn and Pb.

The distribution characteristics of heavy metal pollutants can be used to determine likely pollution sources and the physicochemical properties of elements. The distribution of Zn in surface waters exhibited a strong declining trend in concentration with distance from the estuary mouth to the outer parts of Tianjin Bohai Bay. The stations with higher Zn concentrations were located near the mouths of Beitang and Dagu estuaries, suggesting that the Zn contamination in Tianjin Bohai Bay was the result of terrestrial sewage discharge (Fig.2).

The distribution of Pb in coastal waters exhibited a different trend with that of Zn (Fig.2). First, sites with higher Pb concentrations were distributed in the inner embayment beside inshore waters. This distribution characteristic can be attributed to the pollution sources and the migratory paths of Pb (Braungardt *et al.*, 2003). Pb pollution in aqueous environments has various origins including the deposition of leaded atmospheric dust from the burning of fuels and the emission of mobile pollution sources on the sea and river discharge. The deposition of leaded atmospheric dust would result in Pb pollution in the center of the bay.

3.2 Historical changes of contaminative elements (Pb and Zn) in surface waters

Historical data of contaminative elements (Pb and Zn) in Tianjin Bohai Bay from 1987 to 2004 were collected and the trends were examined. The annual average concentrations of Pb and Zn in surface waters and the corresponding annual runoff of Tianjin Bohai Bay are shown in Fig.4.

For coastal waters in Tianjin Bohai Bay before 2001,

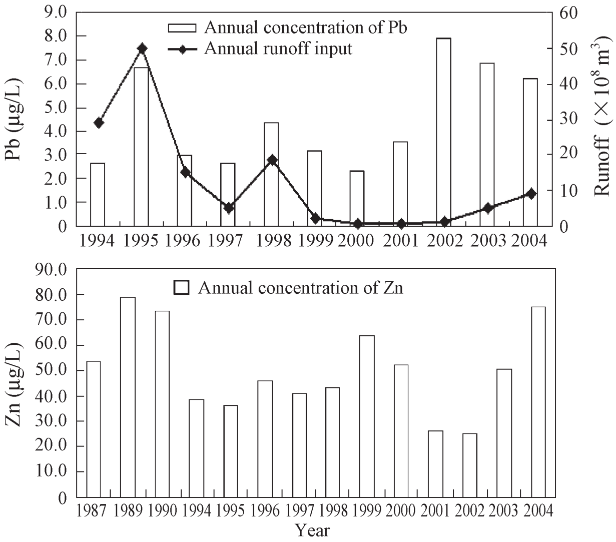

Fig. 4 Annual average concentrations of Pb and Zn in surface waters and the corresponding annual runoff into Tianjin Bohai Bay.

the annual average concentration of Pb was well correlated with annual river runoff (r^2 = 0.77), indicating that Pb pollution in these waters originated primarily from river discharge during this period. However, the levels of Pb did not decrease after 2001, when annual runoff levels declined; indicating that Pb pollution by atmospheric deposition had increased because of the use of leaded petrol in motorcars.

According to the standard (GB3097-1997), the concentrations of Pb in coastal waters of Tianjin Bohai Bay have exceeded the first level since 1994. Moreover, the Pb levels in coastal waters have attained the third level since 2001, despite the continued decrease in annual runoff. As a whole, Pb concentrations increased from 2.6 μg/L in 1994 to 6.2 μg/L in 2004, with a sharp rise occurring after 2001, probably due to the use of leaded petrol. Annual runoff declined continually before 2001 owing to the construction of reservoirs upstream on input rivers and the continually decreasing rainfall in the drainage basin of North China.

Zn concentrations in Tianjin Bohai Bay coastal waters exhibited three climax phases from 1987 to 2004. The first climax was from 1989 to 1990 and the average concentrations of Zn were 68.6 μg/L. The second climax appeared in 1999, with concentrations of 63.7 μg/L, and the third appeared in 2004 with concentrations of 74.9 μg/L, within the range of the third level ($\leqslant$ 100 μg/L). However, the annual concentrations of Zn showed little correlation with annual runoff input, suggesting that Zn contamination had various origins: river discharge, atmospheric deposition, salt-water advection from the ocean and industrial discharge.

3.3 Anthropogenic enrichment of polluting metals in sediments

The upper limit of environmental background values for sediments was used to estimate the main anthropogenic enrichment metals in sediments of Tianjin Bohai Bay. The main anthropogenic enrichment metals in sediments were Zn, Pb, and Cd.

The distribution of Zn in surficial sediments was similar to that of Zn in water, and higher Zn contents centered on the tidal sediments near Dagu Estuary. However, the distribution of Pb in sediments showed a declining trend from the coastal zones to the inner parts of the embayment, and the highest levels of Pb appeared in tidal sediments near Qihe Estuary. The finer grain size and faint hydrodynamics and dilution conditions in this estuary likely resulted in the enrichment of Pb in these sediments. Relative to Zn and Pb, Cd is prone to accumulating in sediments. Although the Cd concentration in coastal waters was very low, obvious anthropogenic enrichment of Cd in coastal sediments was observed, indicating that the sediments were major repositories for Cd.

The largest quantity of wastewater and pollutants entering the Bohai Sea were discharged from estuaries, followed by municipal sewerage outlets. Most pollutants (including heavy metals) are prone to adhere to finer grains and accumulate in regions far from the Dagu sewage mouth. Thus, the contents of most elements analyzed (Cu, Cd, Pb, Ni, and Cr) were higher in the Qihe Estuary because of the finer grain size, faint hydrodynamics, and less dilution by seawater. Grain size analysis has shown that sediments from Tianjin Bohai Bay become finer from north to south (Qin *et al.*, 2006), and Qihe Estuary is situated at the most inland extent of Tianjin Bohai Bay, where the hydrodynamics and dilution by seawater are faint, allowing contaminants to easily accumulate there.

However, the spatial distribution of Zn showed an opposite trend, with the highest concentrations in tidal sediments near Dagu Estuary. The reason for this distribution is not clear, but suggests that a new source of zinc contamination may occur near Dagu Estuary.

4 Conclusions

The main contaminative elements of coastal waters, according to the corresponding National Seawater Quality Standards, were Zn and Pb. The coastal stations with higher Zn values in water samples were located near the mouths of Beitang and Dagu estuaries, indicating that the sources of Zn contamination in Tianjin Bohai Bay were terrestrial sewage discharges. The distribution of Pb in coastal waters exhibited a different trend than that of Zn. Sample sites with higher Pb concentrations were distributed in the inner embayment along inshore waters, indicating that Pb may reach coastal waters through atmospheric deposition, industrial effluent discharge and stream flow.

Historical levels (1987–2004) of contaminative elements (Pb and Zn) in Tianjin Bohai Bay indicated that before 2000, annual Pb levels in coastal waters of Tianjin Bohai Bay were strongly correlated with annual river runoff, showing that Pb pollution in the coastal waters of Tianjin Bohai Bay mainly originated from river discharge during this period. However, Pb levels did not decrease after 2000, when annual runoff declined; indicating that Pb pollution by atmospheric deposition had increased, likely as a result of the use of leaded petrol in motorcars.

Zn contamination began in the late 1980s. From 1987 to 2004, three Zn climax phases were detected. The first climax was from 1989 to 1990, with an average Zn concentration of 68.6 μg/L. The second climax appeared in 1999 (63.7 μg/L) and the third occurred in 2004, with concentrations of Zn (74.9 μg/L) meeting the demands of the third level (⩽100 μg/L).

The contaminative levels and distribution characters of heavy metals in coastal sediments in Tianjin Bohai Bay were also studied. Pb, Zn, and Cd were the primary polluting elements in surficial sediments from Tianjin Bohai Bay based on comparison with corresponding upper limits of environmental background values. Higher concentrations of these contaminants occurred in the tidal sediments near bodies of water such as Qihe and Dagu estuaries. Qihe Estuary lies at the most inland extent of Tianjin Bohai Bay, where hydrodynamics and dilution by seawater are faint, thus leading to the accumulation of contaminants.

Acknowledgements

This work was supported by the National Basic Research Programme (973) of China (No. 2007CB407306).

References

Arnason J G, Fletcher B A, 2003. A 40-year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA. *Environmental Pollution*, 123(3): 383–391.

Audry S, Blanc G, Schafer J, Chaillou G, Robert S, 2006. Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, and V) in the freshwater reaches of a macrotidal estuary. *Geochimica et Cosmochimica Acta*, 70(9): 2264–2268.

Braungardt C B, Achterberg E P, Elbaz-Poulichet F, Morley N H, 2003. Metal biogeochemistry in a mine-polluted system in Spain. *Applied Geochemistry*, 18(11): 1757–1771.

Guevara R, Rizzo A, Sanchez R, 2005. Heavy metal inputs in Northern Patagonia lakes from short sediment core analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 265(3): 481–493.

GB3097-1997, National Seawater Quality Standard of China.

Hakanson L, 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Research*, 14: 975–1001.

Li S Y, Liu G X, Du R Z, 1990. The contaminative history of heavy metals in Bohai Bay I. The environmental background contents of Zn and Cd. *Marine Environmental Science*, 9(3): 6–16.

Li S Y, Liu G X, Miao F M, 1994. The distribution and environmental background values of the heavy metals in sediment of the Bohai Sea. *China Environmental Science*, 14(5): 370–376.

Qin Y W, Meng W, Zheng B H, Su Y B, 2006. Heavy metal pollution in tidal zones of Bohai Bay using the dated sediment cores. *Journal of Environmental Sciences*, 18(3): 610–615.

Tuncel S G, Tugrul S, Topal T, 2007. A case study on trace metals in surface sediments and dissolved inorganic nutrients in surface water of Ölüdeniz Lagoon-Mediterranean, Turkey. *Water Research*, 41(2): 365–372.

Valette-Silver N J, 1992. Historical reconstruction of contamination using sediment cores: a review. NOAA Technical Memorandum NOS/ORCA, 65: 1–40.

Ye C M, 1991. Pollution and protection of Bohai Bay. *Marine Pollution Bulletin*, 23: 15–18.