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Estival Distribution of Dissolved Metal Concentrations in Liaodong Bay

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Abstact The temporal and spatial distributions of Cu, Pb, Zn, and Cd in surface water of the Liaodong Bay were studied based on samples collected at 16 sites in June and August from 2001 to 2005. The temporal distribution showed decreasing trends. The concentrations of dissolved metals in the Liaodong Bay were 4.34, 3.21, 31.54, and 0.995 μg/L for Cu, Pb, Zn, and Cd, respectively. Cu and Pb were scattered near the estuaries, and Zn and Cd were mainly found near the Wuli River. Rivers were the main metals pollution sources in the Bay.

Keywords Dissolved metals · Seawater distribution · Liaodong Bay

The Liaodong Bay located in the north of Bohai Sea has been an excellent ground for natural fishery resources. The bay is a shallow and semi-closed. It takes ~15 years to complete a water exchange cycle. The marine environment of the bay has been particularly vulnerable to pollution. A number of heavy industrial manufacturing, oilfields and fishing activities are situated along its coast and contribute to the pollution. The bay also receives a considerable portion of the contaminant from several connecting rivers including the Liao River, Shuangtaizi River, Daling River, Xiaoling River, and Wuli River. These rivers may be the most important sources of metals in the bay (Pekey 2006). Metals are serious pollutants because of their great stability, toxicity, and persistence. They are also non-degradable and biomagnified in the environment. Metals have potentially contributed to dramatic decline of biodiversity by depleting ecologically sensitive species and deteriorating or tainting fishery resources and water quality (Akhter and Al-Jowder 1997; Tuncer et al. 1998). Extensive efforts have been focused on the studies of heavy metals in the sediment of the Liaodong Bay (Zhou et al. 2004; Feng et al. 2003; Fan et al. 2002). Few studies, however, have been investigated on the dissolved metal distribution in seawater of the Liaodong Bay. The main objective of this study is to understand the status of dissolved metal contaminations in the Liaodong Bay and to provide some new insights for the planning of control strategies for marine fishery environment protection and sustainable development of marine economy.

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Materials and Methods

The study area lies in the north of the Liaodong Bay between 12°100′–12°210′ of E longitude and 40°20′–40°50′ of N latitude. Water samples were collected in June and August from 2001 to 2005 from 16 sampling sites distributed as shown in Fig. 1.

Water samples were collected using QCC10-1 Ball valve model (National Ocean Technology Center, 60 Xianyang Road, Tianjin, China) below the water surface (<10 m), and stored in pre-cleaned polythene bottles in cool boxes filled with ice packs. Water samples were filtered through nitric acid pre-cleaned sartorius cellulose acetate membrane filters (0.45 μm) and then acidified to a final pH <2 and stored in

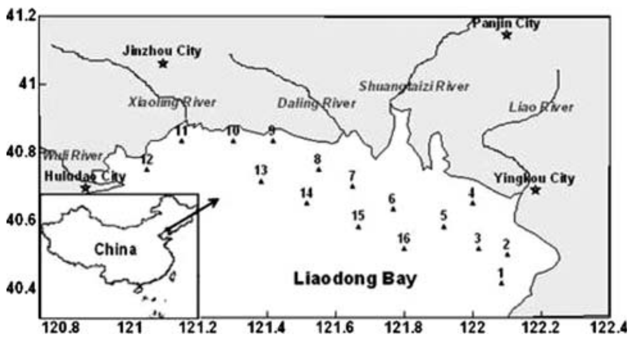

Fig. 1 Location of the study area and the sampling sites in Liaodong Bay

the dark at 4°C. Zn concentration was analyzed by flame atomic absorption spectrometry whereas the concentrations of Cu, Pb, and Cd were analyzed by flameless atomic absorption spectrometry. Collection, preservation, preparation, pretreatment and analyses of water samples were conducted according to the Monitoring Specifications of the Ocean Environment of China (SOA 1999). Precautions were taken to minimize possible metal contamination throughout all sampling and analytical procedures. Limits of detection are 3.1 μg/L for Zn, 0.03 μg/L for Pb, 0.01 μg/L for Cd, and 0.2 μg/L for Cu. The recovery values of metal analyses were between 90% and 110%.

Table 1 Dissolved metal concentration in water of Liaodong Bay from 2001 to 2005 (μg/L)

Site	*n*	Cu			Pb			Zn			Cd		
		Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
1	10	1.27	7.65	3.68 ab*	nd	8.68	2.95 ab	5.03	88.40	34.25 ab	0.290	1.130	0.754 ab
2	10	1.04	8.97	4.07 ab	nd	16.76	5.75 b	7.10	50.79	23.88 ab	0.200	2.450	0.842 ab
3	10	1.65	12.27	5.10 ab	0.61	9.86	4.52 ab	8.28	79.10	31.28 ab	0.300	1.370	0.752 ab
4	10	1.92	10.95	4.55 ab	0.68	8.39	3.72 ab	nd	62.70	21.59 a	0.310	1.180	0.654 ab
5	10	1.65	10.29	4.45 ab	nd	13.22	4.75 b	6.66	68.72	25.51 ab	0.320	1.220	0.755 ab
6	10	1.92	6.99	4.27 ab	nd	9.67	4.64 ab	8.06	60.70	30.96 ab	0.310	2.440	0.912 ab
7	10	1.92	25.49	6.67 b	nd	11.97	3.49 ab	9.90	57.51	28.93 ab	0.410	3.480	1.084 bc
8	10	2.26	8.31	4.15 ab	nd	15.19	3.92 ab	9.90	55.64	23.57 a	0.470	1.710	1.107 bc
9	10	2.31	6.33	4.01 ab	nd	6.54	2.02 a	6.66	56.02	30.45 ab	0.662	1.736	1.097 bc
10	10	2.26	7.65	4.11 ab	nd	6.51	2.25 a	9.00	60.50	33.15 ab	0.990	2.210	1.490 cd
11	10	2.18	13.60	4.77 ab	nd	4.74	1.84 a	9.90	54.84	32.85 ab	1.000	2.680	1.500 cd
12	10	1.65	9.63	4.69 ab	nd	4.49	2.77 ab	8.28	63.49	39.30 b	0.849	2.580	1.692 d
13	10	1.92	8.31	3.99 ab	nd	3.93	1.79 a	8.28	65.73	33.85 ab	0.016	1.920	0.969 ab
14	10	1.54	5.67	3.02 a	nd	5.73	1.86 a	8.28	66.13	34.51 ab	0.450	1.478	0.907 ab
15	10	1.92	14.92	4.17 ab	nd	16.17	3.67 ab	8.71	78.43	28.52 ab	0.410	1.200	0.817 ab
16	10	1.65	10.95	3.79 ab	nd	4.54	1.38 a	5.03	64.98	27.87 ab	0.020	1.010	0.585 a
Total	160	1.04	25.49	4.34	nd	16.76	3.21	nd	88.40	31.54	0.016	3.480	0.995

nd, not detected

a, least significant differences

* mean values sharing the same letter(s) in a column do not differ significantly according to Duncan's multiple range test ($p = 0.05$ for Cu, Pb and Cd; $p = 0.20$ for Zn)

Table 2 Comparison of dissolved metal concentrations (μg/L) with other field data

Area	Cu	Pb	Zn	Cd	Reference
Liaodong Bay (China)	4.34	3.21	31.54	0.995	This study
Pearl River Estuary (China)	6.53	2.22	48.3	0.16	Wang et al. (2004)
Xinghua Bay (China)	0.8	0.5	16.9	0.08	Ruan et al. (2000)
Dapeng Bay (China)	4.16	0.34	9.03	0.08	Huang et al. (2005)
Intertidaliteof Tianjin (China)	7.99	7.06	8.5	–[a]	Cao et al. (2006)
Shuangtai Estuary (China)	6.73	2.79	16.9	0.24	Feng et al. (2003)
Hangzhou Bay (China)	2.32	1.74	–	0.12	Jin and Shao (2003)
Red Sea	1.45–9.75	0.14–2.58	3.52–23.3	nd–1.13	Hamed and El-Moselhy (2000)
Arabian Gulf (UAE)	2.95	1	9.96	0.26	Banat et al. (1998)
Tyrrhenian coast (Italy)	2.76	0.26	9.32	0.13	Manfra and Accornero (2005)
coastal waters (Australia)	7.46	3.7	10.69	0.170	Diaz et al. (1990)

[a] There are no corresponding data

nd, not detected

Results and Discussion

The ranges of dissolved metal concentrations at 16 sites were listed in Tables 1 and 2. Results showed that the seawater of Liaodong Bay were contaminated with different levels of dissolved metals according to the Class I of Sea Water Quality Standard in China (5 μg/L for Cu, 1 μg/L for Pb, 20 μg/L for Zn, and 1 μg/L for Cd). Pb (3.21 μg/L) and Zn (31.54 μg/L) were the main pollution factors because their concentrations exceeded the Class I Sea Water Quality Standard in China. The results also indicated that the concentrations of Cu and Zn at some sites, such as sites 3–6, 11, 15, 16, and sites 7, 9 exceeded the maximum permissible levels of 10 μg/L for Cu and 100 μg/L for Zn according to Water Quality Standard for Fisheries (GB11607-89) in China. The overall ranges of mental concentrations in the seawater of the Liaodong Bay were from 1.04 to 25.49 μg/L for Cu, from nd to 16.76 μg/L for Pb, from nd to 88.40 μg/L for Zn and from 0.016 to 3.48 μg/L for Cd, respectively.

In order to compare the level of dissolved metal concentrations at 16 sites, Duncan's multiple range test was conducted. The results revealed that the high value of Cu was found at site 7, Pb at sites 2 and 5, Zn and Cd at site 12. They also told that the source of Cu was mainly from the Shuangtaizi River and Daliang River, Pb from the Liao River, while Zn and Cd from the Wuli River (nearest to Huludao Zinc Plant). Zn concentration was higher than Class I of Sea Water Quality Standard for all sample sites. There were no significant differences ($p = 0.05$) between them because of the hydrodynamic force. Meanwhile, it showed decreasing trends from the inshore to the offshore except for Zn. It also suggested that the Wuli River was main metal pollution source in the Liaodong Bay.

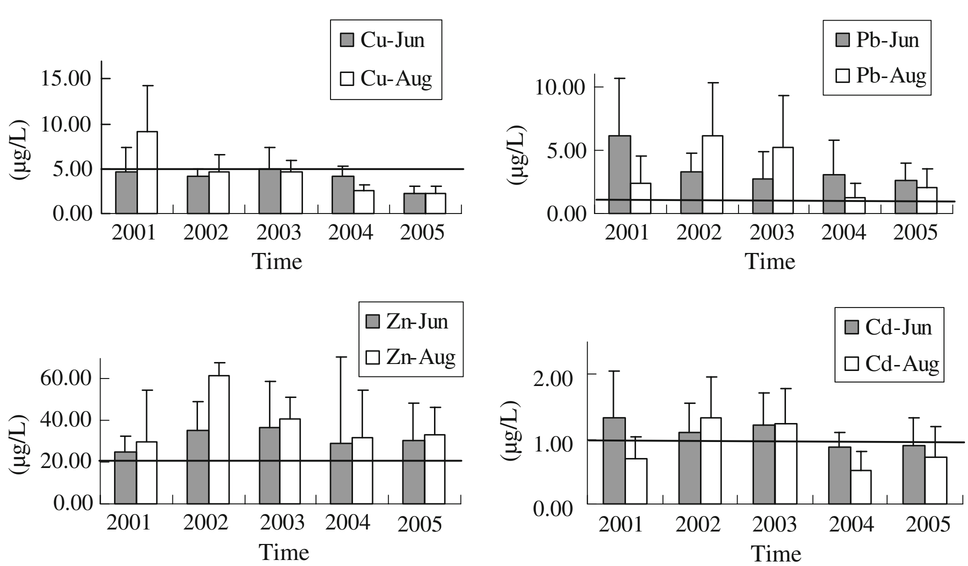

Fig. 2 Dissolved metal concentrations variations between June and August in Bay

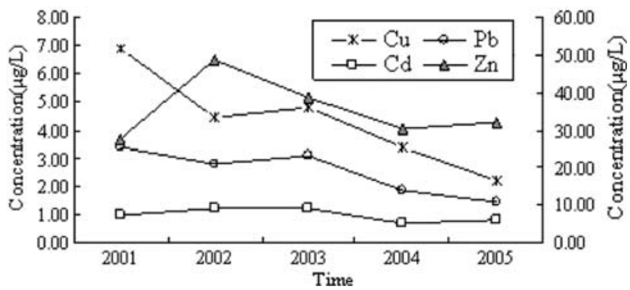

Fig. 3 Temporal trend of dissolved metal concentrations from 2001 to 2005 in Bay

Temporal variation in June and August from 2001 to 2005 was given in Fig. 2. Results showed Zn concentration in August was higher than that in June while Cd concentration was the opposite and the variations of Cu and Pb concentrations were random between June and August. Only Cu concentration in August 2001 exceeded the Class I sea water quality standard in China whereas Cu concentration in others times remained relatively low and below the Class I standard. Both Zn and Pb concentrations went above the Class I standard. Cd concentrations in June 2001 and June and August 2002 and 2003 exceeded the Class I standard and others were below.

Temporal distribution from 2001 to 2005 was given in Fig. 3. It appeared that overall dissolved metal concentrations showed decreasing trends from 2001 to 2005. There were two styles of temporal trends. Cd and Zn had the same trend: pollution was most severe in 2002, increased between 2001 and 2002, decreased between 2002 and 2004, slightly increased again between 2004 and 2005, whilst Cu and Pb also had the same trend: pollution was most severe in 2001, decreased between 2001 and 2002, increased between 2002 and 2003, decreased again between 2004 and 2005.

In comparison with the data from other sea areas (Table 2), Cu concentration in the present study was lower than those reported from Tianjin, Australia, Pearlriver and Shuangtaizi Estuary. Pb concentration was lower than those found in the intertidal zone of Tianjin (China) and coastal waters (Australia). Only the level of Zn was comparable to previous reports for the Pearl River Estuary. Cd concentration was the highest than those found in other sea areas. Cu and Cd were slightly below the Class I water quality standard. Pb and Zn were substantially higher than the Class I water quality standard .The differences outlined above were probably due to the fact that sampling was different in each case. Some data had originated from programs designed specifically to sample “hot spots” where anthropogenic influence was considerable (Tianjing and Pearl river Estuary).

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References

Akhter MS, Al-Jowder O (1997) Heavy metal concentrations in sediments from the coast of Bahrain. Int J Environ Health Res 7:85–93

Banat IE, Hassan ES, EI-Shahawi ES, Abu-Hilal AH (1998) Post-gulf-war assessment of nutriments, heavy metal irons, hydrocarbons, and bacterial pollution levels in the United Arab Emirates coastal waters. Environ Int 24(1–2):109–116

Cao HY, Liang T, Wang LJ, Ding SM, Ding LQ, Yan X (2006) Contents and distribution haracteristics of heavy metals in water and sediment of intertidalite (in Chinese). Environ Sci 27(1):126–131

Diaz C, Galindo L, Montelongo FG, Larrechi MS, Rius FX (1990) Metals in coastal waters of Santa Cruz de Tenerife, Canary Islands. Mar Pollut Bull 21(2):91–95

Fan WH, Wang WX, Chen JS, Li XD, Yen YF (2002) Cu, Ni, and Pb speciation in surface sediments from a contaminated bay of northern China. Mar Pollut Bull 44:820–826

Feng MH, Long JP, Yu L, Li JJ (2003) Ecological risk evaluation of heavy metals of marine sediment in liaodong bays shallow waters. Mar Sci 27(3):52–56

Hamed MA, El-Moselhy KM (2000) Levels of some metals in coastal water and sediments of the Red Sea. Egypt JAMSE 61(1,2):43– 58

Huang XY, Zhang SZ, Huo ZH (2005) Heavy metal distribution in seawater in Dapeng Bay of Shenzhen and the Pearl River estuary (in Chinese). Trans Oceanol Limnol 4:38–44

Jin HW, Shao XW (2003) Analysis of Water Quality off Zhejiang (in Chinese). J Zhejiang Ocean Univ (Nat Sci) 22(4):327–331

Manfra L, Accornero A (2005) Trace metal concentrations in coastal marine waters of the central Mediterranean. Mar Pollut Bull 50:686–692

Pekey H (2006) The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. Mar Pollut Bull 52:1197–1208

Ruan JS, Xu CY, Luo DL (2000) Assessment of heavy metals in sea water, surface sediments and fishery organisms at Xinghua Bay, Fujian Province (in Chinese). Tropic Oceanol 19(1):52–57

State Oceanic Administration of People’s Republic of China East China Sea Branch (1999) The specification for the marine monitoring. Standards Press of China, Beijing, China

Tuncer G, Karakas T, Balkas T, Gökcay C, Aygün S, Yurteri C, Tuncel G (1998) Land-based sources of pollution along the Black Sea coast of Turkey: concentrations and annual loads to the Black Sea. Mar Pollut Bull 36:409–423

Wang ZH, Liu Q, Li CH, Huang HH, Yang ML, Gan JL, Cai WG (2004) Variation features and ecological assessment of heavy metals from Pearl River estuary (in Chinese). J Fish Sci China 11(3):214–219

Zhou XY, Wang ED, Zhu EJ (2004) Evaluation on heavy metal pollution in the sediments at the river mouths around liaodong bay (in Chinese). Environ Chem 23(3):321–325