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Review

Pollution status of the Bohai Sea: An overview of the environmental quality assessment related trace metals

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ABSTRACT

It is well recognized that the ecosystem of the Bohai Sea is being rapidly degraded and the Sea has basically lost its function as a fishing ground. Billions of funds have been spent in slowing down, halting and finally reversing the environmental deterioration of the Bohai Sea. Although trace metals are routinely monitored, the data with high temporal resolution for a clear understanding of biogeochemical processes in the ecosystem of the Bohai Sea are insufficient, especially in the western literature. In this review, status of trace metal contamination in the Bohai Sea is assessed based on a comprehensive review of their concentrations recorded in the waters, sediments and organisms over the past decades. Studies show that metal contamination in the Bohai Sea is closely associated with the fast economic growth in the past decades. Concentrations of trace metals are high in coastal areas especially in the estuaries. Alarmingly high metal concentrations are observed in the waters, sediments and organisms from the western Bohai Bay and the northern Liaodong Bay, especially the coasts near Huludao in the northernmost area of the Bohai Sea, which is being polluted by industrial sewage from the surrounding areas. The knowledge of the speciation and fractionation of trace metals and the influence of submarine groundwater discharge on the biogeochemistry of trace metals in the Bohai Sea is far from enough and related work needs to be done urgently to get a better understanding of the influence of trace metals on the ecosystem of the Bohai Sea. A clear understanding of the trace metal pollution status of the Bohai Sea could not be achieved presently for lack of systematic cooperation in different research fields. It is quite necessary to apply the environmental and ecological modeling to the investigation of trace metals in the Bohai Sea and then provide foundations for the protection of the environment and ecosystem of the Bohai Sea.

Contents

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1. Introduction

Large quantities of different kinds of elements and compounds are discharged into coastal seas as contaminants each year by anthropogenic activities. The coastal seas act as filters trapping both natural and anthropogenic materials transferred from the continents to the open seas. Contaminants pose a serious threat to the coastal and marine ecosystems as well as to the inhabitants, resulting in changes in structures and functions of ecosystems, eutrophication, red-tide occurrence, increased mortality of fishes and benthos and decreased fishery yields, and great economic loss.

Metals are natural components of ecosystems and many of them are essential for the organisms. Only when their contents exceed certain values could they become contaminants to the environments. Excessive amount of trace elements is a serious environmental problem in many coastal ecosystems around the world. Many environmental quality guidelines, within which elements such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) are usually used as criteria, have been developed to deal with environmental concerns as well as in response to regulatory programs (e.g., Burton, 2002).

The development of economy is always accompanied by environmental pollution, especially trace metal pollution (Pan and Wang, 2012). Since the initiation of the reform and opening-up policy in China at the end of the 1970s, the Bohai Sea has faced enormous anthropogenic stresses with the economic development in its coastal areas especially in the recent two decades. The coastal region surrounding the Bohai Sea is now one of the three most densely populated and industrialized zones in China (Fig. 1) and is called the Bohai Sea Economic Rim (BER). As a national base for manufacturing, heavy industry and chemicals, this region has gone through major changes in economy and infrastructures. The BER is rising as a northern economic powerhouse, rivaling the Pearl River Delta Economic Rim in the south and the Yangtze River Delta Economic Rim in the east. The BER is surrounded by Beijing and Tianjin, the second and the sixth largest megacity in China in terms of urban population, respectively, encompassing Hebei, Liaoning and Shandong provinces. The BER is about 5.2×10^5 km^2 in area and 230 million in population, accounting for about 5.4% and 17.5% of China's total land area and population, respectively. In 2010, its gross domestic product was about 1.6 trillion US dollars, making up about 25% of the country's total (National Bureau of Statistics of China, 2011).

While, the BER's high economic contribution rate obviously put the Bohai Sea under more environmental pollution pressure compared with other sea areas in China (Fig. 1). The Bohai Sea's semi-enclosed structure aggravates this situation. China Marine Environmental Quality Bulletin for the Year 2012 reported that the BER brought huge pressure of pollution and habitat destruction to the Bohai Sea; the ecosystem of estuaries and bays in the Bohai Sea were all in sub-healthy or unhealthy state (SOA, 2012). Many scholars have claimed that the Bohai Sea would turn into a dead sea sooner or later if no appropriate and effective measures were taken as quickly as possible.

The Chinese government did pay much attention to the Bohai Sea's environmental conditions. Based on thorough surveys, experts and officials have taken some measures. In 2001, China launched a 15-year program called 'Bohai Blue Sea Action Plan' to regulate and restore the ecosystem of the Bohai Sea with a budget of about 55.5 billion yuan, about 6.7 billion US dollars based on the exchange rate at that time. The goals of the program are that by 2005 the environmental pollution of the Bohai Sea could be controlled preliminarily and the trend of the ecological damage could get preliminary relief; by 2010 the Bohai Sea's environment could be preliminarily improved and the ecological damage could be controlled effectively; by 2015 the Bohai Sea's environment could improve markedly and its ecosystem could improve preliminarily. However, the program did not gain satisfying achievements as expected and it seems that nothing definite has been accomplished after more than 12 years since it was implemented. In 2008, another 40 billion yuan, about 5.8 billion US dollars was planned to be invested in remediating and conserving the Bohai Sea's ecology, conducting the environmental monitoring and surveillance, and building the warning and emergency systems during the 11th five-year plan of China. Besides, many other suggestions were proposed to save the ecosystem of the Bohai Sea, among which the most ambitious one was probably the one of improving the water circulation of the Bohai Sea by connecting it with the South Yellow Sea through an interbasin canal (Fig. 1; Wang, 2007).

A lot of literature has been published elaborating the situations of one to several trace metals related to environmental quality assessment of the Bohai Sea, most of which only focused on trace metals in the waters, sediments or organisms of the local/regional Bohai Sea. A comprehensive literature synthesis is necessary to have a clear understanding of the pollution situations of all the eight environmental quality assessment related trace metals – As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn – in the waters, sediments and organisms of the Bohai Sea and thus provide reference for policy and program making. To find out the deficiencies of the present research on these metals in the Bohai Sea is also an objective of this review.

2. Background information of the Bohai Sea

The Bohai Sea, also called Bohai or Bo Hai, is a semi-enclosed marginal sea of the northwestern Pacific Ocean on the northern coast of China. It is connected to the Yellow Sea on its east through the Bohai Strait (Fig. 1). The line connecting the southernmost end of the Liaodong Peninsula and the northernmost end of the Shandong Peninsula is geographically defined as the boundary between the Bohai Sea and the Yellow Sea. The Bohai Sea is often divided into three major bays, namely the Liaodong Bay in the north, the Bohai Bay in the west and the Laizhou Bay in the south, and the remaining area is called the Central Area (Fig. 1). It is approximately 7.7×10^4 km^2 in area and 1.7×10^3 km^3 in water volume. There are more than 40 rivers flowing into the Bohai Sea, among which the Yellow River, Haihe River, Luanhe River, Shuangtaizihe River and Liaohe River are the five major ones (Fig. 1). The mean depth of the Bohai Sea is $<$20 m, with the deepest region of about 70 m located near the northern coast of the Bohai Strait. In the Bohai Sea, the motion of water masses is dominated by semidiurnal and diurnal tides, which account for about 60% of the current variation and kinetic energy there (Chen et al., 2003).

The fundamental knowledge of the temporal and spatial variability of physical, chemical and biological components in the Bohai Sea is mainly gained from four comprehensive investigations across the

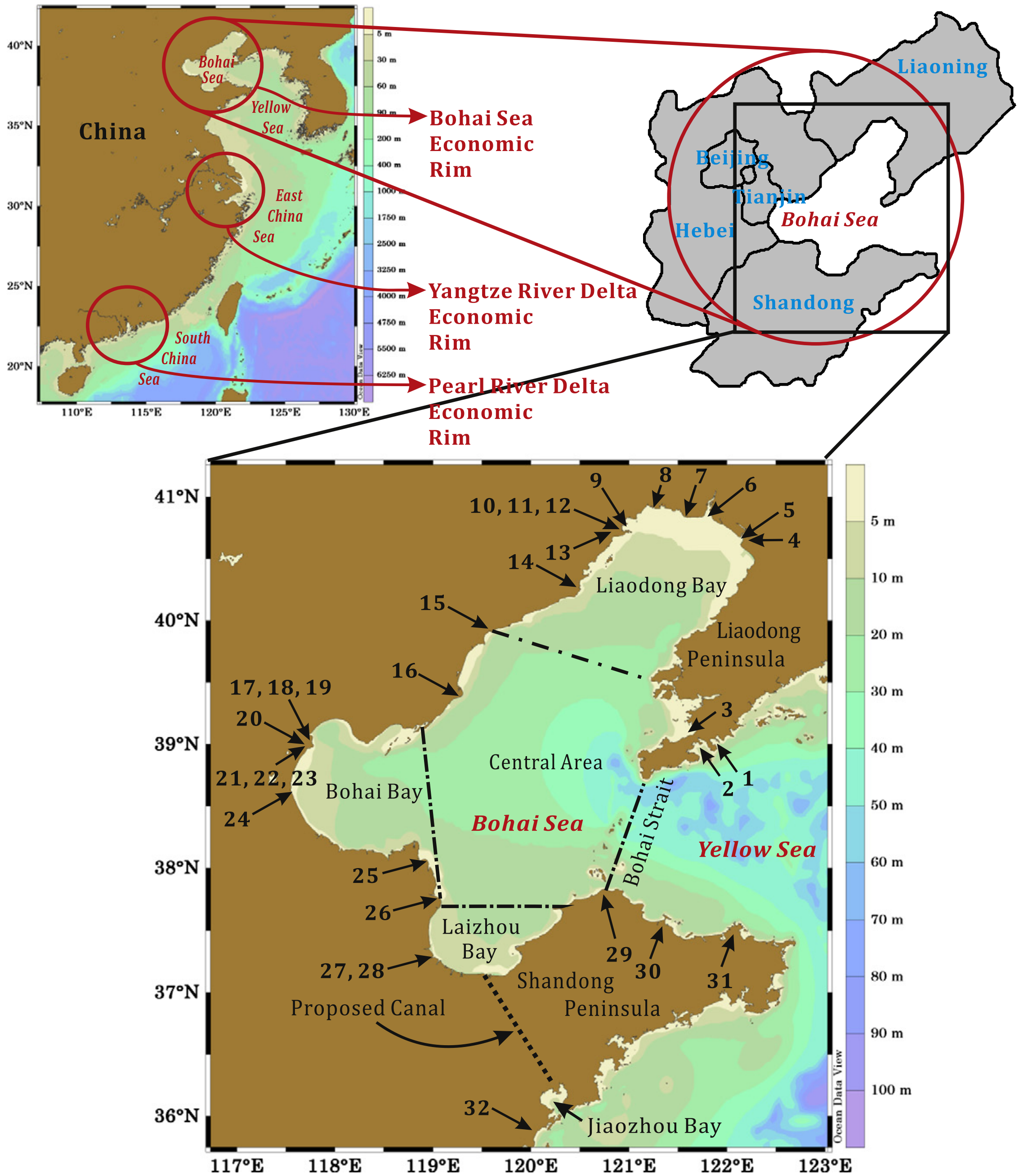

Fig. 1. Map of the Bohai Sea. The dot dash lines in the bottom panel mean the dividing line of the Bohai Sea and the Yellow Sea and the outer borders of Liaodong Bay, Bohai Bay and Laizhou Bay. The numbers in the bottom panel represent the major places along the coast of the Bohai Sea and the nearby coast of the Yellow Sea it connects with that are mentioned in the text: 1, Dayao Bay; 2, Dalian Bay; 3, Jinzhouwan Bay; 4, Yingkou; 5, Liaohe River Estuary; 6, Shuangtaizihe River Estuary; 7, Dalinghe River Estuary; 8, Xiaolinghe River Estuary; 9, Jinzhou Bay; 10, Wulihe River Estuary; 11, Cishanhe River Estuary; 12, Liangshanhe River Estuary; 13, Huludao; 14, Liuguhe River Estuary; 15, Qinhuangdao; 16, Luanhe River; 17, Dongjiang Harbor, Tianjin; 18, Yongdingxinhe River Estuary; 19, Beitanghe River Estuary; 20, Tanggu; 21, Haihe River Estuary; 22, Daguhe River Estuary; 23, Qihe River Estuary; 24, Ziyaxin River Estuary; 25, Dongying Harbor; 26, Yellow River Estuary; 27, Yangkou; 28, Xiaoqinghe River Estuary; 29, Penglai; 30, Yantai; 31, Weihai; and 32, Jiaonan.

whole area carried out monthly in 1959/1960 and 1982/1983, and seasonally in 1984/1985 and 1992/1993 (Wei et al., 2004). Two atlases and one volume of research collection have been published based on the latter three investigations (Editorial Board for Marine Atlas, 1991; Tang and Meng, 1997; Yellow Sea Fisheries Research Institute, 1991). Many important characteristics of phytoplankton such as the species composition, spatial distribution of dominant species and seasonal variation in biomass and primary production have been recognized (Cui et al., 1992; Diao, 1986; Fei, 1991; Kang, 1991; Li and Zhu, 1992; Yu and Li, 1993). The environmental factors such as sunshine duration, solar radiation, transparency, water temperature, stratification and nutrient conditions and their influences on algal growth were discussed.

Anthropogenic pollution, especially some industrial effluents, has caused notable effects on the species diversity of the phytoplankton and benthos communities in the Bohai Sea (Liu et al., 2011b; Xu, 2011). The decrease of benthos community diversity caused by the environmental pollution could further cause the decline of fishery and influence the feeding habit of benthos. The combined pollution of Cd, Hg, Pb and petroleum hydrocarbons (PHs) has been found responsible for the notable reduction of the population growth rates of common fishery species in the Bohai Sea (Xu, 2011).

Fishery species in the Bohai Sea has been declining significantly in recent decades. The mean trophic level of fishing catch exhibited a decreasing trend during 1956/2000 (Xu, 2011). The mean trophic level declined from 4.06 in 1959/1960 to 3.41 in 1998/1999, i.e. about 0.2 decade^{-1} in the Bohai Sea, higher than that of the global trend during the same period (Pauly et al., 1998; Zhang et al., 2007). Besides the fishing pressure and climate changes, the decrease of freshwater input, the decline of food organisms and reactive silicate supply, and the increase of the molar ratio of dissolved inorganic nitrogen (ammonia + nitrate + nitrite; DIN) to dissolved inorganic phosphorous (DIP) (N/P ratio) and Pb concentration were thought to be responsible for such decrease of trophic level directly or indirectly (Xu, 2011).

3. Current understanding of trace metals in the Bohai Sea

3.1. Trace metals in the seawaters

Trace metals in the seawaters of the Bohai Sea come from many sources, such as river discharge, atmospheric deposition, biodegradation, etc. Their concentration decrease can be caused by water dilution, adsorption and settlement and discharging into the Yellow Sea. According to current understanding, the trace metals in the seawaters of the Bohai Sea is mainly from river discharge, which brings high concentrations of trace metals, and other pathways influencing their concentrations have relatively little impact compared with river discharge.

3.1.1. The overall situation

Investigations of trace metals in dissolved pool covering the whole area of the Bohai Sea have not been reported much in public literature. Related works were mainly carried out in the Bohai Bay and the Liaodong Bay, especially in their nearshore areas. Related information is particularly scarce for the Laizhou Bay. Seasonal, monthly or other short-time-scale temporal variation characteristics of dissolved trace metals are not available. The dissolved Cr and Ni are reported to be much less compared with other environmental quality criteria related trace metals (Table 1). Based on the data in Table 1, the maximum concentrations of trace metals ever reported in the seawaters of the Bohai Sea are presented in Fig. 2a. It reveals that the coastal waters had the highest concentration of trace metals than other areas of the Bohai Sea. Among the three bays, the Bohai Bay seemed to be the most anthropogenically influenced considering the highest concentrations of As, Cr, Pb and Zn in the seawaters. The Liaodong Bay was next to the Bohai Bay and the maximum values of Cd and Cu were in the waters of the Jinzhou Bay and the northern Liaodong Bay, respectively. It is worth noting that the maximum concentrations of trace metals in Fig. 2 were not all recorded in the same period. The figure shows the integrated information about the extreme cases which ever occurred in the Bohai Sea in history.

The National Standard of China for Seawater Quality (SWQ) GB 3097-1997 (SEPA, 1997), classifying four levels corresponding to different function zones, has always been used as the evaluation criterion. SWQ Grade I is suitable for marine fishery, marine natural reserves and rare and endangered marine protected areas. Grade II applies to aquaculture, bathing beach, sea sports or recreation areas where people contact seawaters directly and industrial water areas that have direct relation with human consumption. Grade III is appropriate for common industrial water areas and coastal scenery tourist areas. Grade IV applies to sea port waters and the ocean development areas.

The spatial distribution of dissolved As, Cd, Cu, Hg and Pb in both surface and bottom waters of all the main parts of the Bohai Sea was reported by Wang and Wang (2007) based on a study carried out in August 2003. It showed that the dissolved Pb was the only one among the five studied elements in the Bohai Sea with the average concentration slightly higher than SWQ Grade I, which indicated that this water area was not suitable for marine fishery, marine natural reserves and rare and endangered marine organisms' protection (Table 1; SEPA, 1997). The spatial distribution pattern of Pb in the surface water was similar to those of As, Cu and Cd, and their concentration isopleths generally indicated the decreasing values from the bays to the Central Area. Only dissolved Hg showed the characteristic that the high concentrations not only appeared in the Liaodong Bay, the Bohai Bay and the Laizhou Bay, but also in the Central Area (Wang and Wang, 2007). Based on the paired samples *t*-test, Wang and Wang (2007) found that the concentrations of dissolved As, Cd, Cu and Pb in the waters of the Bohai Sea showed no significant differences between surface and bottom layers, while the concentrations of dissolved Hg were significantly different in the two layers and its average concentration was higher in bottom than in surface water which was probably owing to the benthic flux.

The terrigenous input of pollutants was thought to be the main influencing factor for the detected distribution patterns of dissolved trace metals followed by the dynamics of seawaters, benthic flux from bottom sediment and biochemical processes (Wang and Wang, 2007). The report of Wang and Wang (2007) also showed that the average concentrations of studied dissolved trace metals presented a declining trend comparing with the earlier data.

From July 2006 to October 2007, the concentrations and spatial distribution characteristics of dissolved As, Cd, Cr, Cu, Hg, Pb and Zn in surface waters were investigated in the area of 37.2°–40.3°N and 118.0°–121.7°E, which covered most areas of the Bohai Sea excluding the westernmost area of the Bohai Bay and the northernmost area of the Liaodong Bay (Fig. 1; Pan et al., 2012). The average concentrations indicated that As, Cd and Hg were the highest in summer, Cu was the highest in winter, Cr was the highest in spring and summer, and Pb and Zn were the highest in spring (Table 1). The nearshore areas around and between the Liuguhe River Estuary and Qinhuangdao (Fig. 1) had relatively high concentrations of As, Cd, Cr, Cu, Hg, Pb and Zn in summer or autumn (Pan et al., 2012).

Environmental risk assessment of dissolved Cd, Cu, Hg and Pb showed that in the Bohai Sea seawaters the major risk agents were Hg and Pb, and the localized risk agent was Cu, while the risk from Cd was at an acceptable level (Wang et al., 2010a). The coastal waters near estuaries and big cities like Tianjin and Jinzhou had higher potential risks. The Bohai Bay where the trace metal pollution was most serious had the highest environmental risks of dissolved Cu, Hg and Pb (Wang et al., 2010a).

3.1.2. The situations of the Bohai Bay

Due to the fact that the Bohai Bay is surrounded by highly industrialized areas and is semi-enclosed, the pollution status has aroused many concerns. Long-term monitoring data are available for dissolved trace metals in the seawaters of the Bohai Bay.

During 1996 to 2005, dissolved Cd, Cu, Hg, Pb and Zn in the seawaters of the Bohai Bay were investigated. Their maximum concentrations recorded were 0.89, 16.3, 0.23, 40.4 and 422 μg l^{-1}, respectively (Dai et al., 2009). The concentrations of Cd in all samples were below SWQ Grade I, while Cu, Hg, Pb and Zn, with their percentage being 2.7%, 0.4%, 30.4% and 30.0% respectively, fell in the threshold value of SWQ Grade III, suggesting that the water in this area was appropriate for general industrial use and coastal scenery tour. Cd was not the main pollutant in the seawaters of the Bohai Bay according to the study of Dai et al. (2009), and this fact could further be proved by the reports of Peng et al. (2009) and Zhang et al. (2010c).

Mao et al. (2009) got a similar result as Dai et al. (2009) did showing that the seawaters in the Bohai Bay were mainly polluted by Hg, Pb and Zn, and only slightly polluted by Cd and Cu in the period of 1996 to 2005. Their results also indicated that the concentrations of Cd, Cu, Hg, Pb and Zn did not show significant seasonal variations in the seawaters of the Bohai Bay, which was possibly influenced by the relatively stable surrounding environment in a year round, while their variation trends with time on a 10-year scale were different (Mao et al., 2009). The 10-year monitoring showed that these five kinds of trace metals in the Bohai Sea water changed significantly (Mao et al., 2009). Concentrations

Table 1
The summary of dissolved trace element concentrations (μg l^{-1} for all elements) in waters of the Bohai Sea and relevant guideline values of different criteria.

Location	Sampling date	Sampling size		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	References
Bohai Sea	Aug., 2002	52	Mean	na[a]	0.49	na	3.35	0.07	na	3.29	na	Wang et al. (2010a)
	Aug., 2003	52	Mean	na	0.35	na	3.13	0.27	na	1.16	na	Wang et al. (2010a)
	Aug., 2003	42	Mean ± SD	1.5 ± 0.3	0.31 ± 0.12	na	1.9 ± 0.8	0.03	na	1.1 ± 0.4	na	Wang and Wang (2007)
	Jul. 2006 to Oct. 2007	na	Range in spring	1.2–1.6	0.080–0.400	1.8–5.3	1.33–6.92	0.016–0.089	na	0.87–5.67	14.8–35.4	Pan et al. (2012)
		na	Mean in spring	1.3	0.160	3.5	3.22	0.047	na	2.79	18.4	
		na	Range in summer	1.0–3.4	0.052–0.466	1.9–5.4	1.29–8.24	0.029–0.140	na	1.04–6.21	11.1–34.9	
		na	Mean in summer	1.6	0.168	3.5	3.38	0.064	na	2.27	17.5	
		na	Range in autumn	0.5–2.8	0.080–0.220	2.1–4.4	1.73–4.47	0.031–0.091	na	0.88–3.41	11.9–33.9	
		na	Mean in autumn	1.0	0.150	3.2	2.99	0.046	na	1.89	17.7	
		na	Range in winter	0.7	0.057–0.226	1.2–4.6	1.23–6.77	0.017–0.056	na	1.08–6.30	11.6–30.9	
		na	Mean in winter	2.3	0.144	3.2	3.48	0.041	na	2.75	17.0	
Bohai Bay	May, Aug. & Oct., 1996–2005	22	Mean ± SD	na	0.20 ± 0.13	na	3.22 ± 2.40	0.05 ± 0.03	na	4.43 ± 4.77	43.92 ± 44.56	Mao et al. (2009)
	2000	22	Mean ± SD	na	na	na	5.69 ± 3.98	0.06 ± 0.04	na	na	73.01 ± 61.30	Dai et al. (2009)
	2004	17	Max	3.44	0.79	na	16.3	0.22	na	27.17	387	Peng et al. (2009)
			Mean ± SD	1.53 ± 0.71	0.38 ± 0.19	na	4.43 ± 2.85	0.08 ± 0.05	na	8.38 ± 6.2	79.65 ± 85.06	
Bohai Bay	June, 2003	20	Ranges	0.79–2.06	0.08–0.19	0.11–1.15	1.60–4.10	0.004–0.09	na	3.63–12.65	3.0–55.0	Meng et al. (2008)
			Mea ± SD	1.26 ± 0.41	0.12 ± 0.03	0.40 ± 0.26	2.54 ± 0.07	0.04 ± 0.02	na	7.10 ± 2.57	26.9 ± 14.2	
	Apr., 2008	20	Range	1.03–1.26	na	na	na	na	na	na	na	Duan et al. (2010)
			Mean	1.18	na	na	na	na	na	na	na	
	Apr., 2008	20	Range	na	na	na	2.22–3.12	0.035–0.068	na	1.25–2.02	na	Zhang et al. (2010b)
			Mean	na	na	na	2.68	0.048	na	1.63	na	
	Apr., 2008	20	Range	na	0.107–0.182	na	na	na	na	na	15.2–24.3	Zhang et al. (2010c)
			Mean	na	0.15	na	na	na	na	na	19.68	
Dongying Harbor	Jun., 2001	12	Max	na	na	na	na	2.59	na	na	na	Liu et al. (2003)
Northern Liaodong Bay	Jun. & Aug., 2001–2005	16	Range	na	0.016–3.48	na	1.04–25.49	na	na	nd[b]–16.76	nd–88.40	Wan et al. (2008a)
			Mean	na	0.995	na	4.34	na	na	3.21	31.54	
Coastal watersheds along the N Bohai Sea	Oct., 2008	29	Range	na	na	na	na	0.87–1.3	na	na	na	Luo et al. (2012)
			Mean	na	na	na	na	1.0 ± 0.11	na	na	na	

Upstream regions of coastal watersheds along the N Bohai Sea	Oct., 2008	17	GM ± SD[c]	na	0.20 ± 0.031	na	na	na	na	na	7.0 ± 4.52	Luo et al. (2013)
Downstream regions of coastal watersheds along the N Bohai Sea	Oct., 2008	12	GM ± SD	na	0.37 ± 0.018	na	na	na	na	na	22 ± 10	Luo et al. (2013)
Jinzhou Bay	1987–1990	na	Range	na	0.6–5.0	na	0.18–1.30	na	na	1.36–3.14	6.16–68.6	Ma et al. (1995)
			Mean	na	1.9	na	0.40	na	na	1.92	21.1	
	Aug., 2005	30	Range	na	0.79–3.09	na	0.73–5.62	na	na	nd–1.67	4.31–53.33	Wan et al. (2008b)
			Mean ± SD	na	1.65 ± 0.69	na	1.71 ± 0.85	na	na	0.38 ± 0.52	23.14 ± 13.08	
	Jun., 2006	25	Range	na	0.94–3.01	na	0.76–13.2	na	na	0.2–2.91	10.39–101.95	Wan et al. (2008b)
			Mean ± SD	na	2.01 ± 0.68	na	3.49 ± 2.84	na	na	1.19 ± 0.78	39.16 ± 28.71	
	Aug., 2006	30	Range	na	1.33–3.08	na	0.88–4.81	na	na	nd–6.05	3.18–65.3	Wan et al. (2008b)
			Mean ± SD	na	1.94 ± 0.56	na	2.28 ± 1.06	na	na	1.13 ± 1.48	21.77 ± 13.83	
	Sep., 2009	20	Range	1.14–3.65	0.56–2.04	na	1.26–2.49	0.006–0.058	na	0.21–1.39	1.58–25.73	Wang et al. (2012)
			Mean	2.19	0.92	na	3.06	0.030	na	0.61	11.87	
Yellow River Estuary and adjacent sea	May, 2009	30	Range	0.43–1.40	0.10–3.22	na	0.10–4.46	0.004–0.028	na	0.22–1.33	12.00–81.84	Tang et al. (2010)
			Mean	0.92	0.68	na	2.65	0.013	na	0.51	37.67	
Jiaozhou Bay	1992, 1993	22	Mean	nd	1.13	na	3.48	0.028	na	22.72	48.93	Cui et al. (1997) Ling (2010)
North Yellow Sea	2007	38	Mean	nd	0.14	na	0.8	nd	na	0.35	3.8	Tian et al. (2009)
South Yellow Sea	2003	na	Mean	2.33	0.078	na	1.41	0.0036	na	0.37	6.21	He et al. (2008)
South China Sea	1998	na	Mean	nd	0.007	na	0.100	nd	na	0.058	0.086	Yu (2003)
Changjiang Estuary and Hangzhou Bay	2006	71	Mean	3.6	0.387	na	1.99	0.172	na	0.9	6.1	Sun et al. (2009)
Grade I[d]				≤20	≤1.0	≤50	≤5.0	≤0.05	≤5.0	≤1.0	≤20	SEPA (1997)
Grade II[e]				≤30	≤5	≤100	≤10	≤0.2	≤10	≤5.0	≤50	SEPA (1997)
Grade III[f]				≤50	≤10	≤200	≤50	≤0.5	≤20	≤10	≤100	SEPA (1997)

[a] na: not available.
[b] nd: not detected.
[c] GM ± SD: geometic mean ± standard deviation.
[d] Grade I: National Standard of China for Seawater Quality GB 3097-1997 Grade I.
[e] Grade II: National Standard of China for Seawater Quality GB 3097-1997 Grade II.
[f] Grade III: National Standard of China for Seawater Quality GB 3097-1997 Grade III.

of Cu and Zn showed great disparity with annual variation. While, concentrations of Cd, Hg and Pb showed relatively simple change and presented a significant increasing trend (Mao et al., 2009).

In the coastal waters of the Bohai Bay, among Cu, Pb, Zn, Cd, Cr, As and Hg, Pb and Zn were found as the main trace metal pollutants on a larger spatial scale in June 2003 (Meng et al., 2008). Before 2001, Pb in the coastal waters of the Bohai Bay originated primarily from river discharge; yet after 2001, its levels did not decrease with the declining of annual runoff, indicating that the Pb input by atmospheric deposition had increased due to the use of leaded petrol in motor cars during that period (Meng et al., 2008). Higher concentration of Zn in the Bohai Bay was the result of the terrestrial sewage discharge near the mouths of Beitang and Dagu estuaries (Meng et al., 2008).

Based on the most recent surveys reported in literature, in April 2008, among As, Cd, Cu, Hg, Pb and Zn, only the average value of Pb in the seawaters of the Bohai Bay exceeded the range of SWQ Grade I (Duan et al., 2010; Zhang et al., 2010b, 2010c). So, as to the whole Bohai Bay, the pollution situation of trace metals As, Cd, Cu, Hg and Zn in the seawaters may not be serious in recent years.

A rough historical change of trace metals in the Bohai Bay during 1996 and 2008 could be attained after comparing relevant data in Table 1. As, Cd, Cu, Hg, Pb and Zn showed a decreasing trend. This may be the result of 'Bohai Blue Sea Action Plan' program's implementation.

Concentrations of As, Cd, Cu, Hg, Pb and Zn in the inner part of the Bohai Bay, especially in the estuaries, were higher than those in the outer part, manifesting river discharge sources (Dai et al., 2009; Liu et al., 2003; Mao et al., 2009; Meng et al., 2008; Peng et al., 2009; Zhang et al., 2010c). Moreover, concentrations of Cd, Hg, Pb and Zn decreased from the south to the north in the Bohai Bay and concentrations of Cu appeared to be contrary for their different sources from different river estuaries, different industrial wastewater outfalls, different mariculture areas, different sizes of ports and so on (Mao et al., 2009). Unlike other trace metals, Hg had relatively higher concentrations which occurred not only in inshore but also in offshore areas (Dai et al., 2009; Peng et al., 2009). On a whole, transportation of pollutants from land to sea was supposed to be the main factor influencing the distribution patterns of dissolved trace metals in the Bohai Bay (Duan et al., 2010; Peng et al., 2009).

3.1.3. The situation of the Liaodong Bay

As the largest bay of the Bohai Sea, the Liaodong Bay needs 15 years to complete a water exchange cycle (Wan et al., 2008a). Major rivers discharging into it are mainly the Liaohe River, Shuangtaizihe River, Dalinghe River, Xiaolinghe River, Wulihe River and Cishanhe River (Fig. 1). These rivers were thought to be the most important sources of trace metals to the bay (Wan et al., 2008a, 2008b).

It was reported that from 2001 to 2005 the average concentrations of dissolved metals in the northern Liaodong Bay were 0.995, 4.34, 3.21, and 31.54 μg l^{-1} for Cd, Cu, Pb and Zn, respectively, with the concentrations of Pb and Zn being higher than SWQ Grade I (Table 1;

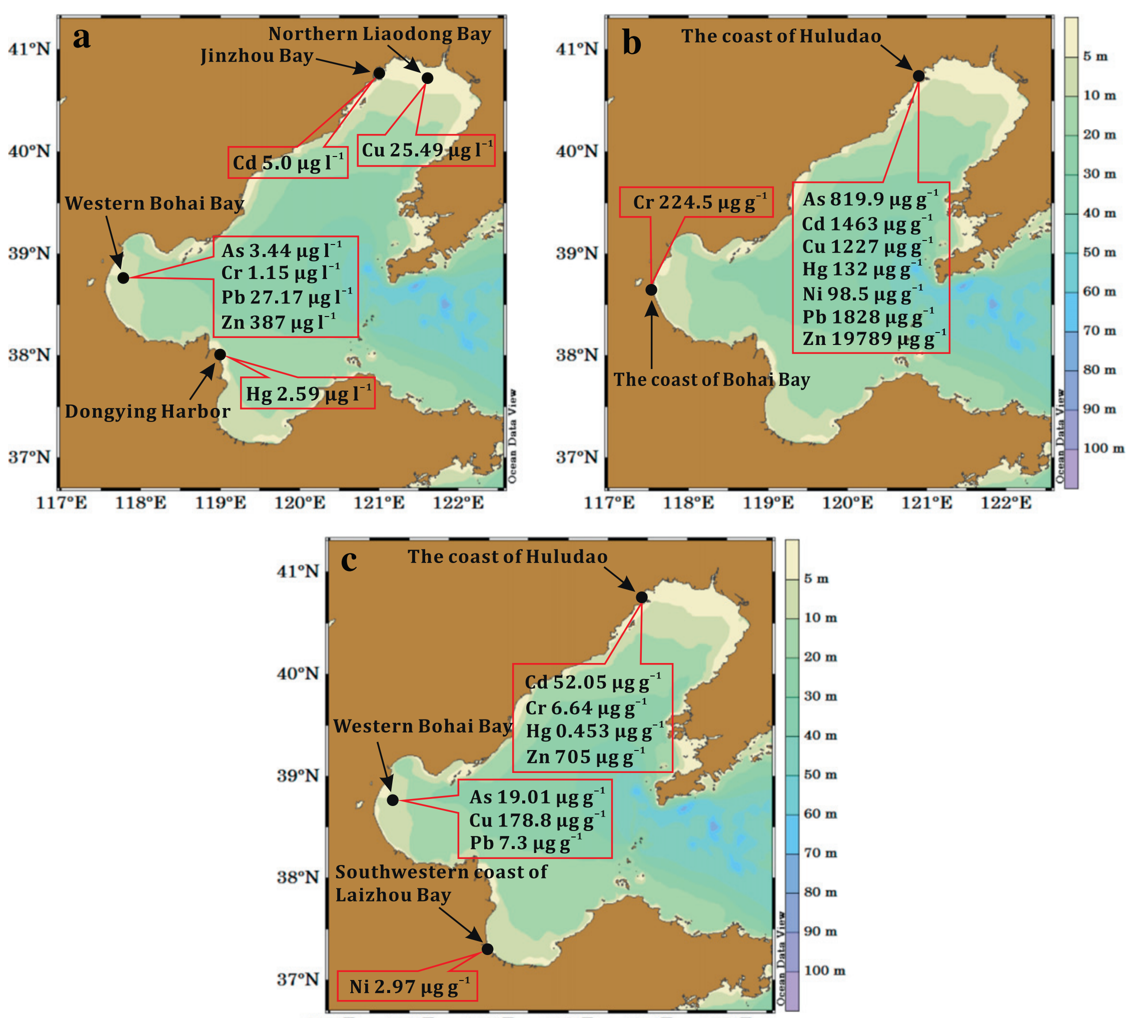

Fig. 2. Map of the distributions of the maximum levels of trace metals recorded in waters (a), sediments (b) and mollusks (c) in the Bohai Sea.

Wan et al., 2008a). Shuangtaizihe River and Dalinghe River might be the key contributors to Cu, Liaohe River might be the key contributor to Pb and Wulihe River might be the key contributor to Zn and Cd in the dissolved trace metal pool of the northern Liaodong Bay (Wan et al., 2008a). In October 2008, 67% of upstream waters of rivers in the Northern Bohai Sea and the Yellow Sea could not be used for agriculture or recreation and 53% of downstream waters of these rivers could not be used as harbors or for industrial development based on the Chinese water quality standards for Hg (Luo et al., 2012). As for Cd and Zn, their mean concentrations in downstream waters were significantly higher than those in upstream waters along the North Bohai Sea (Luo et al., 2013). Besides, most downstream waters in that area were contaminated by Zn based on the study of Luo et al. (2013).

The Jinzhou Bay is a small cove in the northwest of the Liaodong Bay. Surrounded by the industrial base along its coast, the Jinzhou Bay has been seriously contaminated by the industrial effluents of petrochemical producers/companies, chlor-alkali facilities, and non-ferrous metal smelting industries (Pan and Wang, 2012). It was reported that as early as the years 1987 and 1990 the concentrations of Cd, Cu, Pb and Zn (1.9, 0.40, 1.92, 21.1 μg l^{-1}, respectively) in the waters of the Jinzhou Bay had already exceeded the upper limit of Grade I of the National Standard of China for Seawater Quality GB 3097-82, which was executed at that time (Ma et al., 1995). The average concentrations of trace metals in 2006 in the Jinzhou Bay were 1.98, 2.89, 1.16 and 30.64 μg l^{-1} for Cd, Cu, Pb and Zn, respectively, all exceeding SWQ Grade I except for Cu (Wan et al., 2008b). But compared with the historic level of Cu in the Jinzhou Bay (0.40 μg l^{-1} during 1987/1990), its concentration is still increased about 7 times. In September 2009, the average concentrations of As, Cd, Cu, Hg, Pb and Zn in the Jinzhou Bay were 2.19, 0.92, 3.06, 0.03, 0.61 and 11.87 μg l^{-1}, respectively, and in 25% of the stations the concentrations of Cd were higher than SWQ Grade I and in all stations the concentrations of As were lower than that standard (Wang et al., 2012). From 1987 to 2009, trace metals in the Jinzhou Bay did not show much increase based on the data displayed in Table 1. The concentrations of dissolved metals in the Jinzhou Bay showed an apparent spatial pattern with the highest concentrations of Cd, Cu, Pb and Zn being found in the southwest of the bay which was near the outfalls of Huludao Zinc Plant and Bohai Ship Yard and the estuaries of Wulihe and Cishanhe rivers (Wan et al., 2008b; Wang et al., 2012).

3.1.4. The situation of the Yellow River Estuary and its surrounding marine areas

Although the freshwater run-off into the Bohai Sea is dominated by the Yellow River, a widely researched river home and abroad, biogeochemistry of trace metals in its estuary and adjacent marine areas is almost a blank in public literature.

A recent investigation carried out in May 2009 indicated that the concentrations of As, Cd, Cu, Hg and Pb in the seawaters of the Yellow River Estuary and its surrounding marine areas rarely exceeded the upper limit of SWQ Grade I; Zn could be regarded as a pollutant, because its average concentration exceeded the ceiling of SWQ Grade I and fell into the range of SWQ Grade II (Tang et al., 2010). Spatially, their concentrations decreased seaward from littoral sea area and the Yellow River Estuary to the sea area far from the coast, which obviously reflected the effects of human activities, Yellow River discharge and land source pollution (Tang et al., 2010).

Compared with other marine areas of China, the concentrations of As, Cd, Cu, Hg, Pb and Zn in the seawaters of the Yellow River Estuary and its surrounding marine area were lower than those of the heavily anthropogenically influenced Jiaozhou Bay, comparable with those of the Yangtze River Estuary and the Hangzhou Bay, but higher than those of some marginal seas such as the North Yellow Sea, the South Yellow Sea and the South China Sea (Cui et al., 1997; He et al., 2008; Ling, 2010; Sun et al., 2009; Tang et al., 2010; Tian et al., 2009; Yu, 2003).

3.2. Trace metals in sediments

Trace metals in sediments come from aqueous phase deposition via physical, chemical or biological ways; they can also be released through resuspension, dissolution and biodegradation. Trace metals in sediments are good indicators of historical and present environmental pollution and their concentration variations on short-time scales such as diurnal and weekly are generally smaller than in water columns, bringing extensive investigations of trace metals in the sediment phase of the Bohai Sea.

3.2.1. The overall situation

Like dissolved pools, investigations of trace metals in sediments covering the whole area of the Bohai Sea are hard to find in public literature. Related works were mainly carried out in the Bohai Bay and the Liaodong Bay, especially in their nearshore areas. Related works on the Laizhou Bay were relatively few. The elements As and Ni in sediments were reported to be less compared with other environmental quality criteria related trace metals (Table 2).

National Standard of China for Marine Sediment Quality (MSQ) GB 18668-2002 (SEPA, 2002), proposed by the State Oceanic Administration of People's Republic of China, is widely used to judge the potential risks of trace metals in marine sediments. This standard classifies the marine sediment into three classes based on the marine area's function and protection target. The Grade I marine sediment area is suitable for marine fishery, marine natural reserves, rare and endangered marine protected areas, aquaculture areas, bathing beach, sea sports or recreation areas where people contact seawaters directly and the industrial water area that has direct relation with human consumption. Grade II is appropriate for the general industrial water area and the coastal scenery tourist area. Grade III applies to the sea port waters and the ocean development area for special purposes.

Summarized from Table 2, Fig. 2b shows that the maximum data of trace metals were recorded in sediments of the Bohai Sea. Clearly, the coastal areas of Huludao were polluted most seriously considering that the concentrations of As, Cd, Cu, Hg, Ni, Pb and Zn in sediments of that area were much higher than those in the marine sediment quality guidelines (Table 2; Fig. 2b); the maximum concentration of Cr was recorded in the sediments of the coastal Bohai Bay near the Ziyaxin River estuary (Gao and Chen, 2012).

An investigation of As, Cd, Hg and Pb in the surface sediments of the whole Bohai Sea was conducted in 1998. Results showed that there was a severe contamination of Cd and Hg in the northern Liaodong Bay, an intermediate contamination of Hg in the coastal area of Qinhuangdao (Fig. 1) and a slight contamination of Hg in the southern Laizhou Bay (Chen et al., 2005). No recent literature on trace metals in sediments of the whole Bohai Sea has been found.

3.2.2. The situation of the Bohai Bay

The data of an 11-year monitoring program from 1997 to 2007 indicated that the mean concentrations of Cd, Cu, Hg, Pb and Zn in the surface sediments of the Bohai Bay were all within the range for MSQ Grade I, but all higher than the corresponding background values of sediments in this area (Table 2; Zhan et al., 2010). This indicated that these metals did increase to some extent due to the influence of human activities, although their concentrations were still within relatively satisfactory levels. An investigation in spring 2008 showed that in the Bohai Bay, the concentrations of Cd and Pb were still lower than the MSQ Grade I but the concentrations of Cu and Cr were close to or slightly higher than that guideline (Table 2; Xu et al., 2012). A comparison of these two periods showed that the concentrations of Cd, Cu and Pb increased obviously. In August 2008, a study was carried out in the southern Bohai Bay to get the knowledge of the potential contamination and environmental risks associated with heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) (Hu et al., 2013a). It showed that the concentrations of trace metals (Cd, Cr, Cu, Pb and Zn) in the sediments

Table 2
The summary of trace element concentrations (μg g^{-1} dry weight for all elements) in sediments of the Bohai Sea and relevant guideline values of different criteria.

Location	Sampling date	Sampling size		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	References
Bohai Bay	May, every other year from 1997 to 2007	15	Range	na[a]	0.04–0.84	na	7.2–44.0	0.01–0.18	na	5.9–97.0	56.3–308.5	Zhan et al. (2010)
			Mean ± SD	na	0.24 ± 0.17	na	28.1 ± 8.1	0.05 ± 0.03	na	21.2 ± 18.3	102.5 ± 33.5	
	Nov., 2003	na	Range	na	na	7.8–49	18–32	na	19.2–35.8	16.6–27.4	48–181	Qin et al. (2006a)
			Mean	na	na	25.4	25	na	26.9	22.1	88	
	Apr., 2008	27	Max	na	0.52	91.26	na	na	na	48.18	na	Xu et al. (2012)
			Mean	na	0.30	83.66	35.32	na	39.99	30.60	97.27	
Bohai Bay background value	na	na	Mean	13.0	0.112	na	25.63	0.05	na	16.55	74.61	Li and Hao (1992); Li et al. (1994)
Tianjin coastal region	May, 2000	10	Mean	16	0.19	82	32	0.15	47	29	112	Li and Li (2008)
Hebei coastal region	May, 2000	22	Mean	8	0.13	63	20	0.03	29	23	58	Li and Li (2008)
NW coast of the Bohai Bay	Jun., 2003	20	Range	6.40–16.50	0.14–1.82	18–191	11.4–27.3	0.02–0.85	na	17.5–34.9	68.7–392.8	Meng et al. (2008)
			Mean	8.22	0.63	94.25	19.36	0.33	na	22.68	131.76	
Estuary intertidal zone, W Bohai Sea	Oct., 2004	12	Range	na	0.05–0.17	na	9.82–38.99	0.010–0.16	na	0.81–4.97	5.16–137.10	Zhang et al. (2010a)
			Mean	na	0.10	na	21.26	0.12	na	2.78	62.58	
Intertidal Bohai Bay	May, 2008	15	Range	na	0.05–0.19	36.7–110	7.9–46.7	na	14.1–47.9	18.8–39.1	34.0–123	Gao and Li (2012)
			Mean	na	0.12	68.6	24.0	na	28.0	25.6	73.0	
Coastal Bohai Bay	May, 2008	42	Range	na	0.12–0.66	60.1–225	20.1–62.9	na	23.4–52.7	20.9–66.4	55.3–457	Gao and Chen (2012)
			Mean	na	0.22	101.4	38.5	na	40.7	34.7	131	
Western Bohai Bay	Jul., 2007	5	Mean ± SD	na	1.29 ± 0.12	53.1 ± 3.3	27.9 ± 1.8	na	31.4 ± 3.4	20.5 ± 1.0	83.6 ± 4.4	Feng et al. (2011)
Port of Tianjin	Jul., 2007	3	Mean ± SD	na	0.174 ± 0.049	61.5 ± 9.5	38.2 ± 16.9	na	36.1 ± 3.8	23.0 ± 2.4	109.9 ± 29.5	Feng et al. (2011)
	Sep., 2010	20	Range	2.19–5.29	0.26–2.72	na	3.32–11.95	0.13–0.78	na	2.23–50.81	na	Zhang et al. (2012)
			Mean	3.73	1.24	na	6.37	0.31	na	14.21	na	
Dagu Drainage Canal	Sep., 2010	16	Range	3.20–6.60	2.93–22.69	na	19.2–254.8	0.07–4.03	na	15.2–145.5	na	Zhang et al. (2012)
			Mean	4.87	11.25	na	69.9	0.87	na	55.9	na	
Yongdingxinhe River Estuary	Jul., 2007	2	Mean ± SD	na	0.124 ± 0.004	51.9 ± 3.5	31.4 ± 1.6	na	31.2 ± 3.1	20.4 ± 1.3	92.9 ± 2.3	Feng et al. (2011)
Haihe River Estuary	Jul., 2007	2	Mean ± SD	na	0.173 ± 0.009	57.6 ± 5.1	29.5 ± 3.5	na	33.6 ± 2.5	25.6 ± 0.7	86.0 ± 13.7	Feng et al. (2011)
Yellow River Estuary	2004–2005	27	Mean	9.0	0.1	19.7	19	0.04	na	13	31	Wu et al. (2007)
Southern Bohai Bay	Aug., 2008	119	Range	na	0.025–0.275	10.2–84	7.8–38.6	na	16.5–43.7	8.7–53.6	40.5–126	Hu et al. (2013a)
			Mean	na	0.14	33.5	22.7	na	30.5	21.7	71.7	
Dongjiang Harbor, Tianjin	Mar, 2009	11	Range	10.43–23.88	0.02–0.09	na	13.00–26.82	0.01–0.27	na	0.62–6.39	55.6–101.3	Guo et al. (2010)
			Mean	17.13	0.06	na	19.36	0.07	na	4.34	88.4	
Liaodong Bay	2009	128	Range	3.1–20.3	na	8.00–75.8	5.7–37.1	0.00–0.40	7.0–40.5	18.9–61.2	14.5–145.0	Hu et al. (2013b)
			Mean	8.3	na	46.4	19.4	0.04	22.5	31.8	71.7	
Coastal areas of the N Bohai and Yellow Seas	Oct., 2008	35	Range	5.6–13	0.05–0.83	4.2–94	0.53–35	0.02–0.18	na	9.5–49	9.8–170	Luo et al. (2010)
			Mean ± SD	8.5 ± 1.9	0.15 ± 0.14	47 ± 22	13 ± 10	0.028 ± 0.028	na	25 ± 9.2	60 ± 40	

Coastal watersheds along the N Bohai Sea	Oct., 2008	35	Range	na	na	na	na	0.017–0.18	na	na	na	Luo et al. (2012)
			Mean ± SD	na	na	na	na	0.027 ± 0.028	na	na	na	
Upstream regions of coastal watersheds along the N Bohai Sea	Oct., 2008	17	GM ± SD[b]	na	0.13 ± 0.18	na	na	na	na	na	50 ± 39	Luo et al. (2013)
Downstream regions of coastal watersheds along the N Bohai Sea	Oct., 2008	12	GM ± SD	na	0.11 ± 0.082	na	na	na	na	na	34 ± 33	Luo et al. (2013)
Liaohe River Estuary	Before 1985	na	Mean	na	0.123	na	13.85	na	na	9.20	46.80	Zhou et al. (2004)
Liaoning coastal region	May, 2000	12	Mean	13	0.44	64	24	0.08	34	29	96	Li and Li (2008)
River mouths in the Liaodong Bay	Mar., 2003	22	Range	na	0–9.7	na	5.2–49.3	na	na	6.7–130.6	47.9–322.3	Zhou et al. (2004)
			Mean	na	1.16	na	17.6	na	na	23.9	105.3	
Shuangtaizihe River Estuary[c]	Jul., 2008	2	Range	na	0.07–0.32	26.5–65.0	9.9–27.2	na	12.3–40.8	15.1–25.9	30.3–85.0	Liu et al. (2011a)
			Mean	na	0.21	50.5	19.9	na	25.1	20.8	61.4	
Wulihe River	May, 2005	10	Range	na	1.03–30.9	na	31.3–107	0.151–15.4	na	48.7–198	144–2077	Zheng et al. (2008)
			Mean	na	7.947	na	56.63	8.668	na	80.5	525.2	
Cishanhe River	May, 2005	6	Range	na	0.374–1463	na	36.9–1072	0.344–132	na	32.7–1551	132–19,789	Zheng et al. (2008)
			Mean	na	250.3	na	217	33.07	na	454.1	5595	
Liangshanhe River	May, 2005	4	Range	na	1.25–19.4	na	29.0–106	0.22–5.39	na	59.3–164	114–508	Zheng et al. (2008)
			Mean	na	9.73	na	73.08	1.59	na	104.9	450.9	
Jinzhou Bay	na	na	Range	na	2.6–488.2	na	27–619	14.6–41.1	36.4–98.5	29.8–1650	180–10,447	Fan et al. (2006)
	Sep., 2006	14	Range	20.4–820	4.8–910	44.0–72.4	9.3–1227	na	na	21.8–1828	89.2–13,933	Zhang et al. (2008)
			Mean	396.5	248.1	60.6	417	na	na	753	6419	
	Aug., 2007	1	Max	na	64	na	400	na	na	460	na	Wang et al. (2010b)
	Oct., 2009	25	Range	na	7.91–105.31	na	24.45–327.5	na	26.29–85.99	29.17–523.5	168.1–2506	Li et al. (2012)
			Mean ± SD	na	26.81 ± 22.23	na	74.11 ± 68.54	na	43.47 ± 11.92	124.0 ± 114.7	689.4 ± 568.5	
Southern sea area of the Huludao City	na	35	Range	6.29–23.2	na	32.3–128	13.9–39.9	0.035–0.323	na	5.17–51.10	56.0–238	Wang et al. (2013)
			Mean	12.0	na	75.0	25.9	0.169	na	32.20	144	
Laizhou Bay	Aug., 2007	42	Range	9.6–17.9	0–0.025	34.0–91.1	2.9–26.4	0.02–0.115	7.6–33.9	11.6–33.1	34.3–93.4	Hu et al. (2011)
			Mean	13.1	0.081	57.1	13.3	0.053	19.4	20.2	59.4	
Yangtze River Estuary	Apr. & Aug., 2005	59	Mean	na	0.26	78.9	30.7	na	31.8	27.3	94.3	Zhang et al. (2009)
Pearl River Estuary	na	na	Mean	na	na	86.3	39.4	na	na	53.3	130.4	Huang et al. (2006)
ERL				8.2	1.2	81	34	0.15	20.9	46.7	150	Long et al. (1995)
ERM				70	9.6	370	270	0.71	51.6	218	410	Long et al. (1995)
TEL				7.24	0.68	52.3	18.7	0.13	15.9	30.2	124	MacDonald et al. (1996)
PEL				41.6	4.21	160	108	0.7	42.8	112	271	MacDonald et al. (1996)
Background value in the Bohai Sea and adjacent estuaries			Mean	10	0.069	60	19	0.050	na	11.5	57	Feng et al. (2003); Li and Liu (1994)
Grade I[d]				≤20	≤0.5	≤80	≤35	≤0.2	na	≤60	≤150	SEPA (2002)
Grade II[e]				≤65	≤1.5	≤150	≤100	≤0.5	na	≤130	≤350	SEPA (2002)

[a] na: not available.
[b] GM ± SD: geometic mean ± standard deviation.
[c] Sediment core samples.
[d] Grade I: National Standard of China for Marine Sediment Quality GB 18668-2002 Grade I.
[e] Grade II: National Standard of China for Marine Sediment Quality GB 18668-2002 Grade II.

generally met the MSQ Grade I (Table 2). The northwestern coast of the Bohai Bay was faced with the most serious threat from anthropogenic activities. Average values of Cd, Hg, Pb and Zn in that area exceeded those of the other areas of the Bohai Bay (Table 2; Meng et al., 2008). Besides, there was evidence that the surface sediments of some regions in the inintertidal Bohai Bay were contaminated by some metals (Gao and Li, 2012; Li and Li, 2008; Zhang et al., 2012). The concentrations of As, Cr, Cu and Hg exceeded the upper limit of MSQ Grade I (Table 2).

Besides comparing with the Marine Sediment Quality, other marine sediment assessment methods like Effects Range-Low (ERL) and Effects Range-Median (ERM) guidelines, enrichment factor (EF), geoaccumulation index (I_{geo}) and mean ERM quotient were also used to evaluate the Bohai Bay's situation. These assessment methods have not only their own characteristics but also the function like verifying and supplementing mutually. Gao and Chen (2012) analyzed the concentrations of Cd, Cr, Cu, Ni, Pb and Zn in 42 surface sediment samples collected from the northwestern coast of the Bohai Bay covering its nearshore zone and the major rivers it is connected with, and the Effects Range-Low (ERL) and Effects Range-Median (ERM) guidelines (Table 2; Long et al., 1995) were used to judge the potential environmental risks of these trace metals. ERL guideline values indicate the concentrations of trace metals below which adverse effects on biota are rarely observed in sediments and ERM guideline values indicate the concentrations of trace metals above which adverse effects on biota are frequently observed in sediments (Long et al., 1995). The results suggested that no sites exceeded the ERL guideline for Cd, 14% of sites were below the ERL guideline for Cr, 33% of sites were below the ERL guideline for Cu, 86% of sites were below the ERL guideline for Zn, and 95% of sites were below the ERL guideline for Pb; whereas Ni at all sites exceeded the ERL guideline and its value at one site was even slightly higher than the ERM guideline, which indicated a potential harm to benthic organisms; the Zn value at one site also exceeded the ERM guideline (Gao and Chen, 2012).

Similar to ERL and ERM, the threshold effects level (TEL) and probable effects level (PEL) of some substances with potential environmental risks were derived to aid the interpretation of sediment chemistry data (Table 2; MacDonald et al., 1996). Generally, the TELs have been used to identify relatively uncontaminated samples that pose a limited risk of toxicity; the PELs have been used to identify those samples in which chemical concentrations were sufficiently elevated to warrant further evaluation (Long et al., 1998). According to this criterion, Cd and Zn in all types of surface sediments, and Cr, Cu and Pb in the sand and silty sand surface sediments of the intertidal Bohai Bay could be regarded as relatively uncontaminated that pose only a limited risk of toxicity (Gao and Li, 2012). The surface sediment texture of the northern part of the northwestern intertidal Bohai Bay was mainly clayey silt, and that of the southern part of the northwestern intertidal Bohai Bay was mainly sand and silty sand (Gao and Li, 2012).

Among Cd, Cr, Cu, Ni, Pb and Zn, Cr was more accumulated in the surface sediments of the coastal Bohai Bay than the others, which could be reflected by their enrichment factor (EF) values; based on the criteria in Hakanson (1980), the pollution potential of Cu, Pb and Zn was negligible to low contamination for their EF values were <2 except in some riverine and several clayey silt intertidal sediments (Gao and Chen, 2012; Gao and Li, 2012). Guo et al. (2010) reported that the order of EFs of trace metals in the sediments of the Dongjiang Harbor, Tianjin was As>Zn>Cu>Hg>Pb>Cd. According to Müller's classification (Müller, 1969), the geoaccumulation index (I_{geo}) of Cd, Cr, Cu, Ni, Pb and Zn in sand and silty sand sediments of the intertidal Bohai Bay presented values falling into the unpolluted class, and the I_{geo} values of the studied metals in clayey silt sediments fell into unpolluted to moderately polluted class (Gao and Li, 2012).

The result of the mean ERM quotient (Carr et al., 1996) indicated that the combination of Cd, Cr, Cu, Ni, Pb and Zn in the riverine and nearshore surface sediments of the coastal Bohai Bay might have a 21% probability of being toxic (Gao and Chen, 2012); according to the mean PEL quotient (Long et al., 1998), the combination of Cd, Cr, Cu, Ni, Pb and Zn in the surface sediments of the intertidal Bohai Bay may also have a 21% probability of being toxic (Gao and Li, 2012).

Rivers were supposed to be the source of pollution of coastal seas, while trace metals in the sediments of some estuaries in the Bohai Bay did not show relatively higher concentrations compared with other areas of the Bohai Bay or the Bohai Sea. The contents of Cd, Cu, Hg, Pb and Zn in the intertidal surface sediments of the Yongdingxinhe River Estuary did not exceed the ambient background values and were lower than the other areas of the Bohai Sea (Zhang et al., 2010a). The contents of trace metals in the sediments from the Haihe River Estuary were comparable to their background values in the sediments of the Bohai Bay and lower than those of the sediments from the northwestern coast of the Bohai Bay (Table 2; Feng et al., 2011). Xu et al. (2012) also found that the concentrations of trace metals in the surface sediments increased and then decreased from the Haihe River Estuary to open seas. The values of trace metals in the sediments of the Yellow River Estuary were all lower than the Bohai Bay background values (Table 2; Wu et al., 2007). Besides, the Yellow River Estuary was the least polluted by trace metals compared with the Yangtze River Estuary and the Pearl River Estuary (Table 2). However, in the sediments of the areas near Daguhe River and Qihe River mouths, the contents of Cd, Pb and Zn were higher than their corresponding environmental background values (Qin et al., 2006a, 2006b). There is no doubt that river source is one of the important sources of trace metals in the Bohai Sea. The reason that concentrations of trace metals in some estuaries are lower than those of other areas of the Bohai Bay or the Bohai Sea may be the special environment of estuary, such as complex hydrodynamics, adsorption and resolution, the gradual change of chemical environment and so on.

The research of Gao and Chen (2012) and Gao et al. (2012) showed that, in the surface sediments of coastal Bohai Bay, organic matter was a key determinant of the spatial distribution of some trace metals like Cd, Pb and Zn and a large part of the terrestrial organic matter transported by the rivers that discharge into the Bohai Bay was deposited in riverine sediments before the rivers enter the sea. This may be one of the reasons that concentrations of trace metals in sediments from some areas around the estuaries of the Bohai Bay were not as high as some may have expected. Complicated hydraulic conditions in the estuary may also in part determine the distribution of trace metals in sediments of these areas.

Besides the riverine source, atmospheric deposition was thought to be another important source of trace metals in the sediments of the Bohai Bay (Meng et al., 2008), although there was a lack of supporting data. The combined effects of riverine and atmospheric sources may be responsible for higher concentrations of some trace metals in sediments occurring not only along the shoreline but also in the inner part of the Bohai Bay (Zhan et al., 2010).

The study of core sediments in the Daguhe River Estuary in September 2010 showed that from early 1950s to early 1960s, among As, Cd, Cu, Hg and Pb, Hg contributed much to the Daguhe River Estuary's ecological risk increase, while in recent 3 years, the increasing Cd and Hg contributed increasingly to its rapid increase of ecological risk (Zhang et al., 2012).

3.2.3. The situation of the Liaodong Bay

Literature reflecting the conditions of trace metals in sediments of the whole Liaodong Bay marine area is not much. A newly published literature assessed trace metals in the surface sediments of Liaodong Bay. The concentrations of As, Cr, Cu, Hg, Ni, Pb and Zn in that area generally met the MSQ Grade I (Hu et al., 2013b). Most investigations were carried out in the coastal Liaodong Bay (Liu et al., 2011a; Luo et al., 2010, 2012, 2013; Zhou et al., 2004). An investigation of 2003 indicated that the average concentrations of Cd, Cu, Pb and Zn in the estuarine surface sediments of the major rivers around the Liaodong Bay were all significantly higher than those of 1980s (Zhou et al., 2004). The reports of Li and Li (2008) and Liu et al. (2011a) also confirmed this fact after comparing their data with those of the 1980s (Table 2). Three recent publications reported the situations of As, Cd, Cr, Cu, Hg, Pb and Zn in coastal surface sediments covering the entire coastline of the Liaodong Bay and the northern coastline of the Yellow Sea in the Liaodong Peninsula based on the study in October 2008 (Luo et al., 2010, 2012, 2013). Although the concentrations of some elements exceeded the corresponding background values and apparently accumulated at certain places, none of the mean concentrations of these metals in this report exceeded the upper limit of MSQ Class I (Luo et al., 2010, 2012, 2013; Table 2). Their concentrations were unlikely to be acutely toxic, but chronic exposures could be expected to cause adverse effects on benthic invertebrates at about 1/3 of the studied sites. The degree of contamination of these elements decreased in the sequence of Pb > Cd > Zn > Cr > Cu > As > Hg (Luo et al., 2010).

The history of trace metal pollution in the sediments of the Liaodong Bay could be traced back to late 1970s, since which time the concentrations and burial fluxes of Zn, Pb, Cd, and Hg increased abruptly (Xu et al., 2009a, 2009b). The EF values of Cd, Hg, Zn and Pb in surface sediments were more than 30, 10, 7 and 3.5, respectively. Coincident with the increase of trace metal contents, the decreasing trend of $^{206}Pb/^{207}Pb$ ratio indicated that Pb in surface sediments mainly came from anthropogenic activities (Xu et al., 2009b).

Huludao City is located along the coast of the Jinzhou Bay in the northwestern coast of the Liaodong Bay (Fig. 1), and it is a region strongly affected by industrialization. Wulihe, Cishanhe and Lianshanhe Rivers flow through Huludao City.

The southern sea area of the Huludao City might be polluted by heavy metals considering its close location to the Jinzhou Bay (Wang et al., 2013). The serious contamination of trace metals in the sediments of Jinzhou Bay and the rivers it connects with has been reported by many researchers (Fan et al., 2008; Li et al., 1996; Luo et al., 2010, 2012; Ma et al., 1995; Wang et al., 2010b; Zhang et al., 2008; Zheng et al., 2008; Zhou et al., 2004). Hg was the major toxicity contributor which accounted for 53.3–93.2% and 7.9–54.9% of the total toxicity of trace metals in the sediments of Wulihe and Lianshanhe Rivers, respectively, followed by Cd; Cd was the major toxicity contributor in the sediments of Cishanhe River, accounting for 63.2–66.9% of the total toxicity of trace metals (Zheng et al., 2008). Luo et al. (2012) also found the highest concentration of Hg in coastal watersheds located along the northern Bohai Sea was in the upstream sediments of Wulihe River in Huludao. The contamination of Hg in sediments of Wulihe River originated from the chlor-alkali producing industry; the contamination of Pb, Cd, Zn and Cu was mainly derived from atmospheric deposition and small unknown pollution sources (Zheng et al., 2008). The contamination of trace metals in Cishanhe River sediments was mainly derived from the Huludao Zinc Plant, and in Lianshanhe River sediments it was primarily from the atmospheric deposition, sewage wastewater and small unknown pollution sources (Zheng et al., 2008).

After flowing through Huludao City, Wulihe, Cishanhe and Lianshanhe Rivers run into the Jinzhou Bay, making the Jinzhou Bay the most polluted marine area in the Bohai Sea since the late 1970s and early 1980s (Fan et al., 2006, 2008; Li et al., 1996; Ma et al., 1995; Wang et al., 2010b; Zhang et al., 2008). The average concentrations of As, Cd, Cu and Pb recorded in the surface sediments of the Jinzhou Bay were several times to nearly 500 times higher than the upper limit of MSQ Grade I reported in recent work (Li et al., 2012; Wang et al., 2010b; Zhang et al., 2008). With high concentrations and high proportion of bioavailable trace metals, the Jinzhou Bay's ecological risk is very high (Fan et al., 2008).

3.2.4. Trace metals in sediments of the Laizhou Bay

The Laizhou Bay is an important area for fish and shrimp spawning and nursery in China. Li et al. (1996) indicated that the Laizhou Bay was one of the least polluted major bays in the Bohai Sea before the early 1980s. In recent years, like other parts of the Bohai Sea, the Laizhou Bay has been faced with more and more pressure from anthropogenic activities. Liu et al. (2004a) reported that the trace metal contents in the upper 5–10 cm sediments increased greatly.

However, a survey in 2007 showed that all the average concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in surface sediments of the Laizhou Bay did not exceed MSQ Class I (Table 2), among which Cd, Cr, Cu, Ni and Zn were not enriched, and were mainly derived from the natural weathering of rocks (Hu et al., 2011). On the other hand, As and Pb were moderately enriched and their concentrations were influenced by both natural and anthropogenic sources. Hg was derived chiefly from the anthropogenic sources. The concentrations of As and Ni in surface sediments of the Laizhou Bay may occasionally cause adverse ecological effects as they both fell in the range between the guideline values of ERL and ERM (Hu et al., 2011). The concentrations of Cd, Cr, Cu, Hg, Pb and Zn in most parts of the Laizhou Bay were lower than their corresponding ERL guidelines, indicating that these metals may not cause adverse ecological effects. As a whole, more attention should be paid to As and Ni in the surface sediments of the Laizhou Bay.

The concentrations of trace metals in the surface sediments of the Laizhou Bay presented a certain spatial pattern. In the east–west direction, these trace metals decreased gradually from the coast toward the center of the bay; in the north of the bay the concentrations of the trace metals were generally higher than those in the south (Hu et al., 2011). The Yellow River and Xiaoqinghe River are the two major rivers running into the Laihzou Bay. The quality of surface sediments in the northwestern and outer areas of the Yellow River Estuary was relatively poor, indicating that the Yellow River may be a major pollution source of trace metals in the Laizhou Bay, while that was not the condition for the Xiaoqinghe River (Hu et al., 2011).

3.2.5. Fractionation of trace metals

The aforementioned trace metals in the sediments of the Bohai Sea are all in total concentrations. In fact, each trace metal exists in many forms like acid soluble, reducible, oxidizable and residual (Gao and Li, 2012). Different existing forms of trace metals have different environmental influence because of their different bioavailability. The concentrations of trace metals in high-bioavailability forms should be understood to know their real environmental impact.

Gao and Chen (2012) and Gao and Li (2012) applied a four-step sequential extraction procedure to study the fractionation of trace metals in surface sediments of the coastal Bohai Bay covering its intertidal and sublittoral zones and the major rivers it connects with. The same technique was also applied to assess the mobility of trace metals in sediments of other marine areas in China such as the Daya

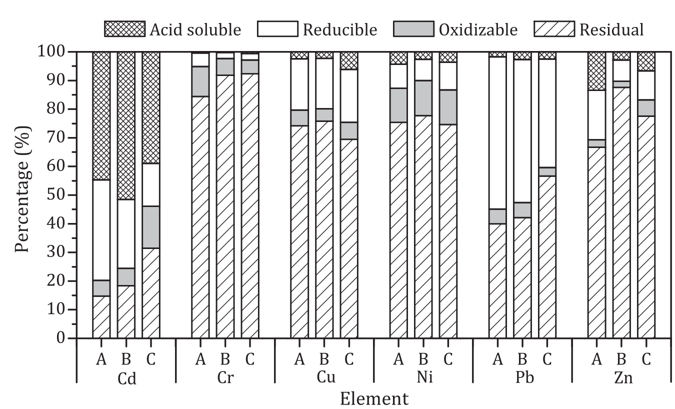

Fig. 3. The distributions of trace metals in different geochemical fractions of surface sediments from the coastal Bohai Bay based on the reports of Gao and Chen (2012) and Gao and Li (2012). A, riverine sediments; B, nearshore marine sediments; C, intertidal sediments.

Table 3
The summary of trace element concentrations (μg g^{-1} wet weight for all elements except noted) in organisms of the Bohai Sea and relevant guideline values of different criteria.

Location	Sampling date	Classification		As	Cd	Cr	Cu	Hg[a]	MeHg[b]	Ni	Pb	Zn	Reference
Bohai Sea	Jul. to Aug., 2002	Mollusks	Range	0.53–19.01	0.14–52.05	0.19–3.24	1.06–109.6	0.01–0.31	na	0.09–2.97	0.06–0.75	5.09–431.0	Wang et al. (2005a)
	Jul. to Aug., 2003	Mollusks	Range	0.63–13.99	0.13–32.18	0.13–1.36	1.08–146.85	0.01–0.10	na	0.06–1.67	0.02–1.33	5.69–550.1	Wang et al. (2005a)
	2002–2003	Mollusks	Range	na[c]	na	na	na	0.005–0.199	nd–0.033	na	na	na	Wang et al. (2005b)
		Benthic mussels	Range	0.292–12.15	0.27–6.5	na	na	0.006–0.108	na	na	0.033–0.895	na	Liu et al. (2007)
Coastal region of the Bohai and Yellow Seas	Jul. to Dec., 1990	Mollusks	Range	na	0.04–8.56	0.02–6.64	10.48–178.8	na	na	na	0.04–4.15	4.10–178.4	He (1996)
			Mean	na	1.15	0.70	5.34	na	na	na	0.36	20.2	
Coastal watersheds along the N Bohai Sea	Oct., 2008	Carp	Range	na	na	na	na	0.031–4.0	0.030–0.066	na	na	na	Luo et al. (2012)
			Mean ± SD	na	na	na	na	0.47 ± 1.2	0.44 ± 1.2	na	na	na	
		Crab	Range	na	na	na	na	0.032–3.8	0.012–3.3	na	na	na	
			Mean ± SD	na	na	na	na	0.67 ± 1.2	0.56 ± 1.0	na	na	na	
Upstream regions of coastal watersheds along the N Bohai Sea	Oct., 2008	Carp	GM ± SD[d]	na	0.0036 ± 0.042	na	na	na	na	na	na	38 ± 15	Luo et al. (2013)
Downstream regions of coastal watersheds along the N Bohai Sea	Oct., 2008	Crab	GM ± SD	na	0.020 ± 0.10	na	na	na	na	na	na	10 ± 6.7	Luo et al. (2013)
Bohai Bay	Apr. and Oct., 1981	Fish	Range	na	0.21–2.10	na	0.35–7.55	na	na	na	0.50–5.00	14.3–172	Liu et al. (1983)
			Mean	na	0.21	na	2.12	na	na	na	1.27	43.3	
		Crustacea	Range	na	0.10–0.51	na	0.59–6.47	na	na	na	0.30–3.00	20–51.8	
			Mean	na	0.18	na	2.73	na	na	na	1.82	32.5	
		Mollusks	Range	na	0.18–2.45	na	0.42–5.39	na	na	na	0.60–7.30	20.6–158.4	
			Mean	na	0.75	na	1.70	na	na	na	1.85	50.4	
		Polychaeta	Mean	na	0.18	na	0.92	na	na	na	2.90	25.3	
Yingkou	Jul. to Aug., 2002	*Rapana venosa*	Mean	na	4.71	na	33.75	0.0605	na	0.28	0.11	57.65	Liang et al. (2003, 2004)
Jinzhou Bay	1987–1990	Fish	Mean	na	na	na	na	na	na	na	na	na	Ma et al. (1995)
		Crustacea	Mean	na	0.18	na	42	0.17	na	na	0.04	127.5	
		Mollusks	Mean	na	3.16	na	2.17	0.22	na	na	0.26	53.9	
Huludao	Jul. to Aug., 2002	*Rapana venosa*	Mean	na	30.61	na	172.25	0.453	na	0.14	0.09	705	Liang et al. (2003, 2004)
Coastal Huludao	Jun., 1999	Fish	Range	0.24–2.14	0.069–0.62	na	0.8–4.70	0.00048–0.00139	na	na	0.013–0.265	12.29–30.8	Yue and Shi (2001)
		Crustacea	Range	1.71–17.21	0.595–89.28	na	4.99–44.84	0.00022–0.0173	na	na	0.038–1.427	33.73–405	
		Mollusks	Range	1.45–5.77	0.36–35.36	na	19.06–79.54	0.00002–0.00082	na	na	0.026–1.576	21.26–140	

Qinhuangdao	Jul. to Aug., 2002	*Rapana venosa*	Mean	na	4.29	na	14.08	0.0417	na	0.38	0.13	33.21	Liang et al. (2003, 2004)
	Oct. to Nov., 2005	*Argopecten irradians*	Mean	0.18	na	na	3.07	0.007	na	na	0.17	73.82	Wang et al. (2007)
	Apr. to May, 2010	*Clupanodon thrissa*	Mean	2.06	5.92[e]	12.5[e]	1.47	na	na	14.2[e]	10.0[e]	12.6	Zhang and Wang (2012)
		Cynoglossus joyneri	Mean	12.1	5.30[e]	30.2[e]	0.38	na	na	37.2[e]	72.5[e]	5.40	
		Glossogobius giuris	Mean	1.00	12.7[e]	16.2[e]	0.57	na	na	28.2[e]	12.4[e]	12.2	
		Hemirhanphus sajori	Mean	1.28	5.05[e]	17.0[e]	0.37	na	na	15.6[e]	4.58[e]	19.8	
		Lateolabrax japonicus	Mean	2.19	3.18[e]	12.1[e]	0.38	na	na	9.95[e]	3.65[e]	10.9	
		Platycephalus indicus	Mean	1.72	2.42[e]	12.2[e]	0.35	na	na	13.5[e]	2.72[e]	5.48	
		Scorpaena neglecta	Mean	1.15	15.0[e]	16.7[e]	0.36	na	na	30.8[e]	8.85[e]	6.88	
	Nov. and Dec., 2010	*Ruditapes philippinarum*	Range	0.62–0.94	0.09–0.11	0.24–0.33	2.86–5.43	0.02–0.03	na	1.18–1.75	0.09–0.10	17.47–24.04	Yang et al. (2013)
Tanggu	Jul. to Aug., 2002	*Rapana venosa*	Mean	na	3.32	na	41.57	0.0378	na	0.09	0.12	48.61	Liang et al., 2003 (2004)
Yangkou	Jul. to Aug., 2002	*Rapana venosa*	Mean	na	0.15	na	9.98	0.0591	na	0.66	0.75	8.65	Liang et al. (2003, 2004)
Laizhou Bay	Oct. to Nov., 2005	*Argopecten irradians*	Mean	0.34	na	na	3.66	0.024	na	na	0.13	51.53	Wang et al. (2007)
Penglai	Jul. to Aug., 2002	*Rapana venosa*	Mean	na	24.71	na	48.74	0.0979	na	0.47	0.23	73.75	Liang et al. (2003, 2004)
	Oct. to Nov., 2005	*Argopecten irradians*	Mean	0.42	na	na	1.92	0.015	na	na	0.07	42.51	Wang et al. (2007)
Dalian Bay	1987–1990	Mollusks	Mean	1.72	7.30	na	2.65	0.13	na	na	2.70	34.50	Ma et al. (1995)
Dayao Bay	1987–1990	Fish	Mean	0.24	0.05	na	0.24	0.06	na	na	0.03	7.5	Ma et al. (1995)
		Crustacea	Mean	na	0.08	na	10.55	0.16	na	na	0.72	20.35	
		Mollusks	Mean	2.23	0.70	0.08	0.30	0.05	na	na	0.89	27.7	
Jinzhouwan Bay	1987–1990	Mollusks	Mean	0.21	0.48	na	1.6	0.02	na	na	7.93	7.93	Ma et al. (1995)
MPL[f]		Mollusks		na	2	na	10	0.5	na	na	na	100	WHO (1982)
Hygienic standard		Fish		<0.1	<0.1	na	na	na	<1.0	na	<0.5	na	MHPR (2005)
		Other marine organisms		<0.5	na	na	na	na	<0.5	na	na	na	
Grade I[g]		Shellfish		≤1.0	≤0.2	≤0.5	≤10	≤0.05	na	na	≤0.1	≤20	SEPA (2001)
Grade II[h]		Shellfish		≤5.0	≤2.0	≤2.0	≤25	≤0.1	na	na	≤2.0	≤50	SEPA (2001)
Grade III[i]		Shellfish		≤8.0	≤5.0	≤6.0	≤50[j]	≤0.3	na	na	≤6.0	≤100[k]	SEPA (2001)

[a] Total mercury.
[b] Methylmercury.
[c] na: not available.
[d] GM ± SD: geometic mean ± standard deviation.
[e] ng/g wet weight.
[f] MPL: Maximum permissible levels.
[g] Grade I: National Standard of China for Marine Biological Quality GB 18421-2001 Grade I.
[h] Grade II: National Standard of China for Marine Biological Quality GB 18421-2001 Grade II.
[i] Grade III: National Standard of China for Marine Biological Quality GB 18421-2001 Grade III.
[j] 100 for ostracean.
[k] 500 for ostracean.

Bay and the northern South China Sea (e.g. Gao et al., 2008, 2010). As shown in Fig. 3, for the Bohai Bay, on average, Cr, Cu, Ni and Zn in riverine, nearshore and intertidal surface sediments, and Pb in intertidal surface sediments were all dominated by residual fraction; Cd in riverine, nearshore and intertidal surface sediments was dominated by acid-soluble fraction; and Pb in riverine and nearshore surface sediments was dominated by reducible fraction (Gao and Chen, 2012; Gao and Li, 2012). Different existing forms of trace metals in sediment represent different sources. The residual fraction represents natural sources and the acid-soluble fraction represents mainly anthropogenic sources (Chen and Liu, 1992). The difference in the distribution of trace metals in different geochemical fractions is primarily caused by their chemical properties as well as by the physicochemical conditions of the environment and the impact of human activities.

The metals in acid-soluble fraction are considered to be the weakest bonded metals in sediments which may equilibrate with the aqueous phase and thus become more mobile and easily bioavailable (Pardo et al., 1990). The higher the proportion of metals in this fraction, the more mobile they are, and the higher the risk they could pose to the environment. So, among Cd, Cr, Cu, Ni, Pb and Zn, Cd was the most mobile one with the highest environmental risk and Cr was the least mobile one with the lowest environmental risk in surface sediments of the coastal Bohai Bay. The percentages of acid-soluble Cr/Cu/Ni/Pb in riverine, nearshore and intertidal sediments were comparable; but Zn in riverine sediment was more mobile than in nearshore and intertidal sediments (Fig. 3). The metals in the residual fraction were generally an indication of lithogenic input, while those in non-residual fractions could mainly be explained by anthropogenic inputs. Indicated by the significant correlations between Cd, Cr, Cu, Ni, Pb and Zn in the non-residual fraction and their corresponding EF values, anthropogenic inputs were probably the major contributor to their enrichment in the riverine and nearshore surface sediments of the coastal Bohai Bay; however, for Cu, Ni and Pb, the contribution of lithogenic input was as important as that of anthropogenic inputs (Gao and Chen, 2012).

A five-step sequential extraction procedure modified based on the work of Tessier et al. (1979) was applied to investigate the fractionation of Cd, Cu and Pb in sediments of the Jinzhou Bay and the results indicated that Cd was dominated by the exchangeable fraction, Cu was dominated by the residual fraction and Pb was dominated by the fraction bound to Fe/Mn oxides (Wang et al., 2010b). In the sequential extraction procedure of Tessier et al. (1979), trace metals in exchangeable and carbonate-bound fractions are considered to be with high potential environmental risks. The sum of exchangeable and carbonate-bound fractions accounted for up to 79% of Cd in total concentration, and it was 26% for Cu and 17% for Pb in sediments of the Jinzhou Bay (Wang et al., 2010b). Considering the high total concentrations of Cd, Cu or Pb in sediments of the Jinzhou Bay, which was up to 64 μg g^{-1} for Cd, 417 μg g^{-1} for Cu and 752 μg g^{-1} for Pb (Table 2), they were serious threats to the environment and ecosystem of this bay.

As one of the major chemical constituents of aquatic sediments, acid-volatile sulfide (AVS) plays an important role in controlling the activities and availability of divalent metal cations, which are mainly Cd^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+}, in the interstitial waters of sediments. AVS is operationally defined as the reactive sulfide fraction in sediment that can be volatilized with cold hydrochloric acid (usually 1 M or 6 M). The sulfide-bound metals that were extracted during this process at the same time are called “simultaneously extracted metals” (SEM). Gao et al. (2013) and Zhuang and Gao (2013) used the relationships between the molar concentrations of AVS and SEM to assess the quality of the surface sediments from the Laizhou Bay and the surrounding rivers discharging into its southwestern coast. The results indicated that SEM was present at lower concentrations than AVS for all samples except few riverine ones, which meant there was no indication of associated adverse effects of the five constituents of SEM, namely Cd, Cu, Pb, Ni and Zn, on aquatic life.

3.3. Trace metals in organisms

Marine organisms can accumulate trace metals from seawaters, suspended particles, sediments, and food chains. Bioaccumulation of metals varies strongly among different areas and species. Meanwhile, it also follows certain rules. Generally, organisms accumulate high amounts of metals when they are in the environment that has trace metals (of bioavailability) with high concentrations. So, the concentrations of metals in organisms can reflect the extent of environmental pollution and some species are good bioindicators of the pollution status of certain metals.

The concentrations of As, Cd, Hg, Cu and Pb in some organisms of the Bohai Sea exceeded relevant standards. Huludao is a hot site in the coastal zone of the Bohai Sea that showed metal pollution in marine organisms (Fig. 3C). Some species like *Rapana venosa* and *Ruditapes philippinarum* were appropriate bioindicators of metal pollution in organisms of the Bohai Sea (Liang et al., 2004; Wang et al., 2005a).

3.3.1. The situation of different metals

The background situation of metals in organisms should be mentioned for a good understanding of the pollution situation of organisms by trace metals in the Bohai Sea. Liu et al. (1983) investigated Cd, Cu, Pb and Zn in 35 species of fish, crustacean and mollusks collected from the Bohai Bay in 1981 and found that the concentrations of these trace metals were not high compared with other areas in the world (Liu et al., 1983). This is the earliest report on trace metals in marine organisms of the Bohai Sea and related values are listed in Table 3.

The situation of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn in marine organisms of the Bohai Sea in recent years is summarized as follows. National Standard of China for Marine Biological Quality (MBQ) GB 18421-2001 (SEPA, 2002) is often used to evaluate the pollution situation of trace metals in shellfish in China. This standard divides the concentration of trace metals in shellfish into three levels (Table 3). The Grade I level is applicable for marine fishing, aquaculture and natural reserve; Grade II is applicable for water supply of general industry and scenic spot; and Grade III is applicable for performance of harbor and industry development. Liu et al. (2007) studied As in 10 species of benthic mussels from 17 coastal sites of the Bohai Sea and found that the concentrations of As from all sites except one in the coastal Laizhou Bay were within the range of MBQ Grade I. Therefore, generally As was not an element with high ecological risks in the Bohai Sea and this was also in accordance with the report of Wang et al. (2007).

The concentrations of Cd in some of the nine species of mollusks collected from eight coastal sites of the Bohai Sea during 2002 and 2003 exceeded the maximum permissible level (MPL) for Cd in food product recommended by the World Health Organization (WHO) in 1982 (Table 3; Wang et al., 2005a). In some gastropods and oysters collected during July to August 2002 along the coastline of the Bohai Sea, the concentration of Cd also exceeded the MPL (Liang et al., 2004). Similarly, its concentration in different mussel species from the coastal Bohai Sea commonly exceeded the upper limit of MBQ Grade II, which is equal to its MPL value (Liu et al., 2007).

As for Cr and Ni, related reports are relatively few (Table 3). The report of Wang et al. (2005a) demonstrated that the average concentrations of Cr in different species of mollusks from the coastal Bohai Sea fluctuated around the upper limit of MBQ Class I; Ni is not an element used to judge the biological quality in the National Standard of China GB 18421-2001 and its concentrations in mollusks of the Bohai Sea varied within a range comparable to that of Cr (Liang et al., 2004; Wang et al., 2005a). The same report indicated that the concentrations of Cu in some species of mollusks exceeded its MPL value (Wang et al., 2005a). The concentrations of Cu in *Argopecten irradians* (bivalve) and *Chlamys farreri* (bivalve) collected from the mariculture areas of Qinhuangdao and the Laizhou Bay did not exceed the guideline of MBQ Grade I (Wang et al., 2007).

The concentrations of Hg in the tissue of selected mollusks in the Bohai Bay during 2002 and 2003 were relatively low and less than its MPL (0.5 μg g^{-1}) (Wang et al., 2005a, 2005b). Consistent with this, the investigation of trace metals in *A. irradians* and *C. farreri* collected from the mariculture areas of Qinhuangdao and the Laizhou Bay in 2005 indicated that the concentrations of Hg all fell in the range of MBQ Grade I (0.05 μg g^{-1}) (Wang et al., 2007). However, the study of Liu et al. (2007) showed that the concentrations of Hg in benthic mussels from some coastal sites in the Liaodong Bay and the Laizhou Bay exceeded the guideline for MBQ Class II, but were still within the range of MPL. In general, mollusks in the Bohai Sea are polluted to some extent.

Hg in organisms exists in many forms among which methylmercury (MeHg) is the most toxic. Seafood is considered to be the main source of MeHg in the human diet (Jiang et al., 2006). Though in China, aquatic foods contribute only 9.7% of Hg intake, which is less than many other countries, their consumption is still a major intake source for people around the Bohai Sea (Jiang et al., 2006). So, the determination of MeHg as well as total mercury (THg) is of great importance. The report of Liang et al. (2003) demonstrated that the mercury contamination commonly existed in gastropod and bivalve species collected from eight coastal sites along the Bohai Sea, with MeHg and THg concentration in the range of 0.005–0.168 and 0.007–0.453 μg g^{-1}, respectively, of which the maximum value of MeHg did not exceed the hygienic standard for fresh and frozen marine products of animal origin (GB2733-2005) (MHPR, 2005) but the maximum value of THg exceeded the range of MBQ Grade III. Wang et al. (2005b) got a similar result as Liang et al. (2003). Crucian carp is one of the most consumed aquatic species in China (Luo et al., 2012). The average concentrations of Hg and MeHg in carp collected along the North Bohai Sea were less than the maximum permissible level (WHO, 1982) for Hg and the hygienic standard (MHPR, 2005) for MeHg, respectively (Table 3; Luo et al., 2012). Nevertheless, carp in that area still had a potential risk to human health considering the high ratio of MeHg to THg (Luo et al., 2012). Besides, predators that eat crucian carp, like birds, would be also at risk to some extent. Crabs collected along the North Bohai Sea had a worse situation than crucian carp in that area, with the average concentrations of THg and MeHg exceeding the maximum permissible level (WHO, 1982) for Hg and the hygienic standard (MHPR, 2005) for MeHg, respectively (Table 3; Luo et al., 2012). However, the risk of crab to human health is possibly small considering its low ratio of MeHg to Hg and low cosumption compared with that of carp (Luo et al., 2012).

Pb concentration in mollusks of the Bohai Sea was very low during 2002 and 2003 according to the study of Wang et al. (2005a). However, because Pb and its salts were capable of causing hematosis and damaging the nervous system and kidneys of the human body, even low concentrations of Pb in food could not be ignored (Chuang et al., 2004; Wang et al., 2005a). The concentrations of Pb in *A. irradians* and *C. farreri* collected from mariculture areas of Qinhuangdao and the Laizhou Bay in 2005 did not exceed the range of MBQ Grade I (Wang et al., 2007), while in the study of Liu et al. (2007), the concentrations of Pb in some samples of benthic mussels from the Liaodong Bay and the Laizhou Bay exceeded the standard. The concentrations of Zn in some mollusks collected along the coastline of the Bohai Sea during 2002 and 2003 exceeded the MPL, indicating that Zn may have potential ecological risk to the environment of that area (Liang et al., 2004; Wang et al., 2005a).

He (1996) studied Cd, Cr, Cu, Pb and Zn in the main economic mollusks collected from the coastal region of the Bohai Sea and the Yellow Sea in 1990 and found that only the average concentration of Cu did not exceed the MBQ Grade I. This showed that the economic mollusks were polluted to some extent. Hazard quotients of As, Cd, Cr, Cu, Ni, Pb and Zn in fish species and bivavel *R. philippinarum* collected from Qinhuangdao were all less than 1, manifesting there was no obvious health risk from the intake of these marine organisms (Yang et al., 2013; Zhang and Wang, 2012). A survey made a historical comparison of concentrations in marine organisms and demonstrated that the concentrations of As, Cd, Hg and Pb in most benthic mussel samples collected from the Bohai Sea showed a decreasing trend or remained steady (Liu et al., 2011c).

3.3.2. The situation of different areas

The Jinzhou Bay and Huludao are widely known for their suffering from metal pollution. Among the Dayao Bay, Dalian Bay, Jinzhouwan Bay and Jinzhou Bay (Fig. 1), the four seriously anthropogenically influenced marine areas along the coast of Liaoning Province, the Jinzhou Bay had the highest concentrations of Hg and Cu in marine organisms (Ma et al., 1995). *R. venosa* is a species of large predatory sea snail, a marine gastropod mollusk or whelk, in the family Muricidae, the rock shells. This species is native to the marine and estuarine waters of the Bohai Sea. *R. venosa* from Huludao exhibited the highest values of Cd (30.61 mg kg^{-1}), Cu (172.25 mg kg^{-1}) and Zn (705 mg kg^{-1}) among the sampling sites surrounding the Bohai Sea. While those collected from Penglai took the second place (Liang et al., 2004). The rank of Hg concentrations in mollusks among these sites was similar to that of Cd, Cu and Zn (Liang et al., 2003). Wang et al. (2005a) also reported that Cd in mollusks from Huludao had the highest contents compared with the other sampling sites surrounding the Bohai Sea.

The Laizhou Bay is also an area presenting high concentrations of trace metals in marine organisms. Liu et al. (2007) pointed out that As, Cd, Hg and Pb in benthic mussels from the area of the southwestern Laizhou Bay displayed higher average concentrations compared with other areas of the Bohai Sea (Liu et al., 2007). The reason for this might be that the area is close to the mouth of Xiaoqinghe River which discharges about 30% of the whole pollutants that run into the Laizhou Bay (Liu et al., 2004).

The Bohai Sea is one of the most polluted areas in terms of metal pollution in organisms compared with other coastal areas in China. Wang et al. (2005a) compared the trace metal contents in soft tissues of *Mytilus edulis* (bivalve) in their study with those from other sites along the Chinese coastline and found that Penglai and Huludao were the most seriously polluted cities by trace metals. Penglai's pollution came from the local paper mills and the indigenous method of smelting gold. The largest zinc industry in Asia is located in Huludao and it is the major pollution source for the city. Another publication reported that among the seven mariculture areas in the northern China seas including the Dalian Bay, Qinhuangdao, the Laizhou Bay, Yantai, Weihai, the Jiaozhou Bay and Jiaonan, the concentration of Hg (0.024 μg g^{-1}) in *A. irradians* of the Laizhou Bay was the highest and the concentration of As (0.34 μg g^{-1}) in this bivalve species from the Laizhou Bay ranked the second highest among these areas (Wang et al., 2007). Qinhuangdao was the only site in the Bohai Bay that was studied by Zhang and Wang (2012). Cd in fish species from Qinhuangdao had higher concentrations than that from Huilai, the Pearl River Estuary, Zhejiang and Haikou (Zhang and Wang, 2012). Yang et al. (2013) also showed that along the coast of China, Qinhuangdao was one of the hotspots for the trace element contamination in bivalve *R. philippinarum*.

3.3.3. The situation of different species

Different organism species in the Bohai Sea have different abilities in accumulating trace metals. Ma et al. (1995) compared the concentrations of trace metals in organisms of the Jinzhou Bay and other bays of Liaoning Province and found that metal concentration in the organisms had a relationship with not only the marine environment but also species, years and features. Two recent studies explained part of these phenomena from their species and characteristics. There are dominantly three species of clams (White, Liangdao Red and Zebra) along the coast of the Bohai Sea (Liu et al., 2011d, 2011e). When the adductor muscle was used as the target organ, White clams could be a preferable bioindicator of the pollution monitoring for dissolved mercury compared with the other two clam species, i.e. Liangdao Red and Zebra (Liu et al., 2011d); while, when digestive gland tissue was used as the target organ, Liangdao Red clams exhibited more sensitive disturbances to the mercury exposure (Liu et al., 2011e).

Significant differences in accumulating different metals were found among different species collected from the sea area near Huludao (Yue and Shi, 2001). Fish, crustacean and mollusks had a low ability in accumulating Hg and Pb but a high ability in accumulating As, Cu, Cd and Zn. The latter two groups of marine organisms accumulated trace metals with higher concentrations than the former one (Ma et al., 1995; Yue and Shi, 2001). Species that have special ability in accumulating certain metals can act as a biomonitor. Wang et al. (2005a) studied the accumulation of trace metals of nine kinds of mollusks (*R. venosa*, *Neverita didyma*, *Scapharca subcrenata*, *M. edulis*, *Amusium*, *Crassostrea talienwhanensis*, *Meretix meretrix*, *R. philippinarum*, and *Mactra veneriformis*) in the Bohai Sea. Gastropods (*R. venosa* and *N. didyma*) were loaded with higher As and Hg than bivalves, *R. venosa*, *Amusium*, *S. subcrenata*, and *M. veneriformis* presented higher Cd levels than others, and *M. meretrix* and *R. philippinarum* had larger enrichment of Ni than others manifesting the fact that they can act as bioindicators of corresponding metals (Wang et al., 2005a). The study of Liang et al. (2004) also demonstrated that *R. venosa* and *R. philippinarum* were hopeful bioindicators of monitoring Cd and Ni pollution, similar to the report of Wang et al. (2005a).

Few studies focused on trace metals in marine fish and crabs from the Bohai Sea. Fish and crabs are the major seafood for humans. Knowing the situation of trace metals in them is of great importance. Zhang and Wang (2012) conducted a large scale investigation of twelve trace element levels in twenty-nine marine fish species collected from Chinese coastal waters. Qinhuangdao was the only studied site located in the Bohai Sea. *Cynoglossus joyneri* showed the highest concentrations of As, Cr, Ni and Pb and *Hemirhamphus sajori* had the highest concentration of Zn compared with other different fish species collected from Qinhuangdao (Zhang and Wang, 2012). Luo et al. (2013) studied Cd and Zn in carps and crabs from the upstream and downstream regions of coastal watersheds along the Northern Bohai Sea. Concentration of Cd in these two species was obviously low compared with that of other species listed in Table 3. While this was not the situation for Zn in carps and crabs (Table 3).

3.4. The relations between trace metals in the seawaters, sediments and organisms

As shown in Fig. 2, the pollution status was the worst in the western Bohai Bay and the northern Liaodong Bay, especially in the coast of Huludao. By comparing with SWQ, MSQ and MBQ, the degree of sediment pollution by trace metals was much greater than that of seawaters and marine biological pollution (Tables 1, 2 and 3; Fig. 2). The Bohai Sea should be seen as a whole system to get a good understanding of the information of trace metals for there is a close relationship among the concentrations of trace metals in the seawaters, sediments and organisms. Based on the summarized data of trace metals in the waters, sediments and organisms of the Bohai Sea, we found that trace metals in these three media all had relatively higher concentrations in the Jinzhou Bay and Huludao compared with other areas in the Bohai Sea (Tables 1, 2 and 3). This obviously explained that trace metals in these three media influenced mutually.

Unfortunately, until now not much literature has ever linked trace metals in these three media together. Ma et al. (1995) compared the pollution status of trace metals in the sea waters, sediments and organisms in bays of Liaoning Province based on the content in these three media, which may not be correct, and concluded that considering the concentrations of Cu and Zn sediments were most polluted, followed by organisms, and seawaters were the least polluted. The comparison of sediments, seawaters and organisms is beneficial to the conduction of research on relations among them which then can help select the more representative medium and simplify the sampling.

There is a close connection between trace metals in waters and sediments. Zhang et al. (2010a) reported that in the intertidal zone of the Yongdingxinhe River mouth in the western Bohai Bay, the order of the average trace metal contents in sediments was the same as that in seawaters, Zn > Cu > Pb > Hg > Cd, which indicated that trace metals in sediments and seawaters were in an equilibrium state. Meng et al. (2008) also demonstrated that Pb and Zn were found as the main trace metal pollutants in both waters and surface sediments of the Bohai Bay. So, if other conditions such as hydraulics, winds and salinity are similar, it is likely to predict the environmental situation of trace metals in one medium based on another medium.

Trace metals in seawaters may affect marine organisms directly. Based on this, some researchers evaluated the water condition of the Bohai Sea or determined trace metal biomonitors for the water condition. Zhang et al. (2010b, 2010c) used a widely maricultured bivalve species, *C. farreri*, in China to study its physiological change under the trace metal concentration levels equivalent to those in the seawaters of the Bohai Bay and determined the potential harmful elements. The results indicated that among Cd, Cu, Hg, Pb and Zn, the concentrations of Cd and Pb might have reached a level with potential risks to organisms.

Besides, the dietary exposure is another important way for trace metals to affect marine organisms. Organisms of low trophic level like phytoplankton can absorb certain trace metals in waters. Organisms of higher trophic level can accumulate trace metals by eating organisms of lower trophic level. When humans eat those organisms which accumulate high concentrations of trace metals, they may get pathological lesions. For example, minamata is caused by eating fish that has MeHg of high concentrations. In the study of Luo et al. (2013), the relationships among Cd and Zn concentrations in waters, sediments and biota were studied. Results showed that Cd and Zn in crabs were primarily derived from sediment exposure. This was due to the fact that crabs are bottom dwellers and they take up Cd and Zn indirectly by eating sediment-dwelling invertebrates (Luo et al., 2013).

4. Concluding remarks and perspectives

The Bohai Sea has been considered as one of the most polluted marine areas in China. Metals from various sources have put much pressure on its ecosystems. The structure of the phytoplankton community has changed, causing the decline of fish species in the Bohai Sea. Besides, fish and other marine products are no longer as safe as before because they accumulate trace metals which may do harm to human health when they reach a certain concentration. River discharge, sediments release, industrial waste drainage and atmospheric sedimentation are the major sources of the pollutants in the Bohai Sea. The whole situation of the Bohai Sea does not seem to be that serious in terms of trace metals. However, it is particularly worrisome that relatively high concentrations of trace metals occur in estuaries and bays in the Bohai Sea. Based on the rough historical change summarized from Tables 1, 2 and 3, we found that trace metals in the Bohai Sea did not increase much and even declined to some extent in recent years. This demonstrated that the 'Bohai Blue Sea Action Plan' and other pollution control programs may have certain effects. So we suggest further implementing these pollution control programs.

There is a lack of systematic cooperation in the studies on trace metals in the Bohai Sea which is the same situation as other sea areas in China. Too much attention has been paid to a few local/regional coastal areas and little attention has been paid to the rest of the Bohai Sea. Systematic cooperation in studies is in urgent need for the effective protection of the Bohai Sea. There are many methods applicable for the determination of benchmarks of heavy metals in marine environment, their environmental/ecological risks and so on, which makes it difficult to compare the results of different researchers' studies and draw satisfying conclusions. So a system of targeted standard methods should be established to handle these issues. Just knowing the pollution status is far from enough. The knowledge of the sources, sinks and fluxes of trace metals can make us understand more clearly the environmental status of the Bohai Sea. More investigations of trace metals for their sink and source modeling should be conducted. The knowledge of the speciation and fractionation of trace metals in the Bohai Sea and the influence of submarine groundwater discharges on the biogeochemistry of trace metals is almost blank and related work needs to be carried out urgently.

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