Marine Pollution Bulletin 114 (2017) 555–563

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Baseline survey of sediments and marine organisms in Liaohe Estuary: Heavy metals, polychlorinated biphenyls and organochlorine pesticides

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ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 1 September 2016
Accepted 2 September 2016
Available online 7 October 2016

Keywords:
Liaohe Estuary
Heavy metal
Polychlorinated biphenyls
Organochlorine pesticides
Sediment
Marine organism

ABSTRACT

A geographically extensive investigation was carried out to analyze the concentrations of heavy metals, PCBs and OCPs in the sediments and marine organisms collected from the Liaohe Estuary. In order to determine the spatial distribution and potential ecological risk of heavy metals, the surface sediments were collected from 44 sites in the Liaohe Estuary. The results showed that the heavy metal contents in the sediments were observed in the following order: Cr (11.2–84.8 mg/kg) > Cu (1.7–47.9 mg/kg) > Pb (4.3–28.3 mg/kg) > As (1.61–12.77 mg/kg) > Cd (0.06–0.47 mg/kg) > Hg (0.005–0.113 mg/kg). In comparison with the concentrations of heavy metals and POPs in other regions, the concentrations of As, Pb and DDTs in the Liaohe Estuary were generally low, and other pollutant concentrations were inconsistent with those reported in other regions. The contamination factor (CF), the pollution load index (PLI), the geoaccumulation index and the potential ecological risk index were used to analyze the pollution situation, which showed that the heavy metal pollution in Liaohe Estuary is mainly dominated by Cd and Hg. The concentrations of the four heavy metals varied significantly in the three kinds of tested organisms (fish, mollusk and crustacean), indicating the different accumulative abilities of the species. The results obtained in this study provide useful information background information for further ecology investigation and management in this region.

With the rapid population growth in coastal regions, anthropogenic contaminations have resulted in the current worldwide deterioration of aquatic environment, and attracted global attention in recent years (Fu and Wang, 2011). The coastal and estuarine ecosystems are facing increasing metal pollution pressures in China. Heavy metals are being introduced to aquatic environment through a variety of natural and anthropogenic sources, including industrial and domestic discharges, mining, smelting, and e-wastes recycling (Pan and Wang, 2012). Terrestrial runoff is one of the most common way for metals entering into coastal environment. Coastal sediments always act as the final repository of various contaminants, and important sinks for metals through sedimentation (Chapman et al., 1998). Toxic metals have the tendency to accumulate by marine organisms and transfer to human via food chain, which pose a serious threat to public health. Thus, it is important to monitor their concentrations in the multiphase media for seafood safety and consumer health.

Persistent organic pollutants are subject to long-range transport, and regarded as ubiquitous contaminants in the marine environment, even present in remote and pristine areas (Klánová et al., 2008). They are of great concern for their persistent, highly accumulative nature as well as toxic biological effects. Polychlorinated biphenyls (PCBs) are introduced in the 1930s and have been used in a variety of applications as dielectric and hydraulic fluids. PCBs were banned at the end of 1970s and included in the first list of the 12 initial POPs (Xing et al., 2005). Dichlorodiphenyltrichloroethanes (DDTs) hexachlorocyclohexanes (HCHs) and are two types of popular organochlorine pesticides (OCPs). DDTs were extensively used worldwide in the 1940s and 1950s as an insecticide. It was prohibited in the 1970s and 1980s due to its negative effects on animal and human health (Turusov et al., 2002). DDTs and HCHs are still being produced and used in some developing countries because of their broad-spectrum killing characteristics. China is a large producer and user of DDTs and HCHs in the world. Technical DDTs and HCHs were widely used between 1950s and 1980s, until the production of DDTs and HCHs was officially prohibited in 1983 (Gong et al., 2007). However, measurable concentrations of DDTs and HCHs still exist in marine environment and organisms in China (Xu et al., 2013; Wang et al., 2014).

Liaohe Estuary is an important ecological and economical region in the northeast of the Bohai Sea. The Liao River watershed includes Daliao watersystem (Hun River, Taizi River, and Daliao River) and Liao River watersystem (Liao River). The Liaohe River Delta Wetland has been ranked as the largest bulrush wetland and the second largest swamp in the world. It provides important habitat for various marine wildlife,

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http://dx.doi.org/10.1016/j.marpolbul.2016.09.002
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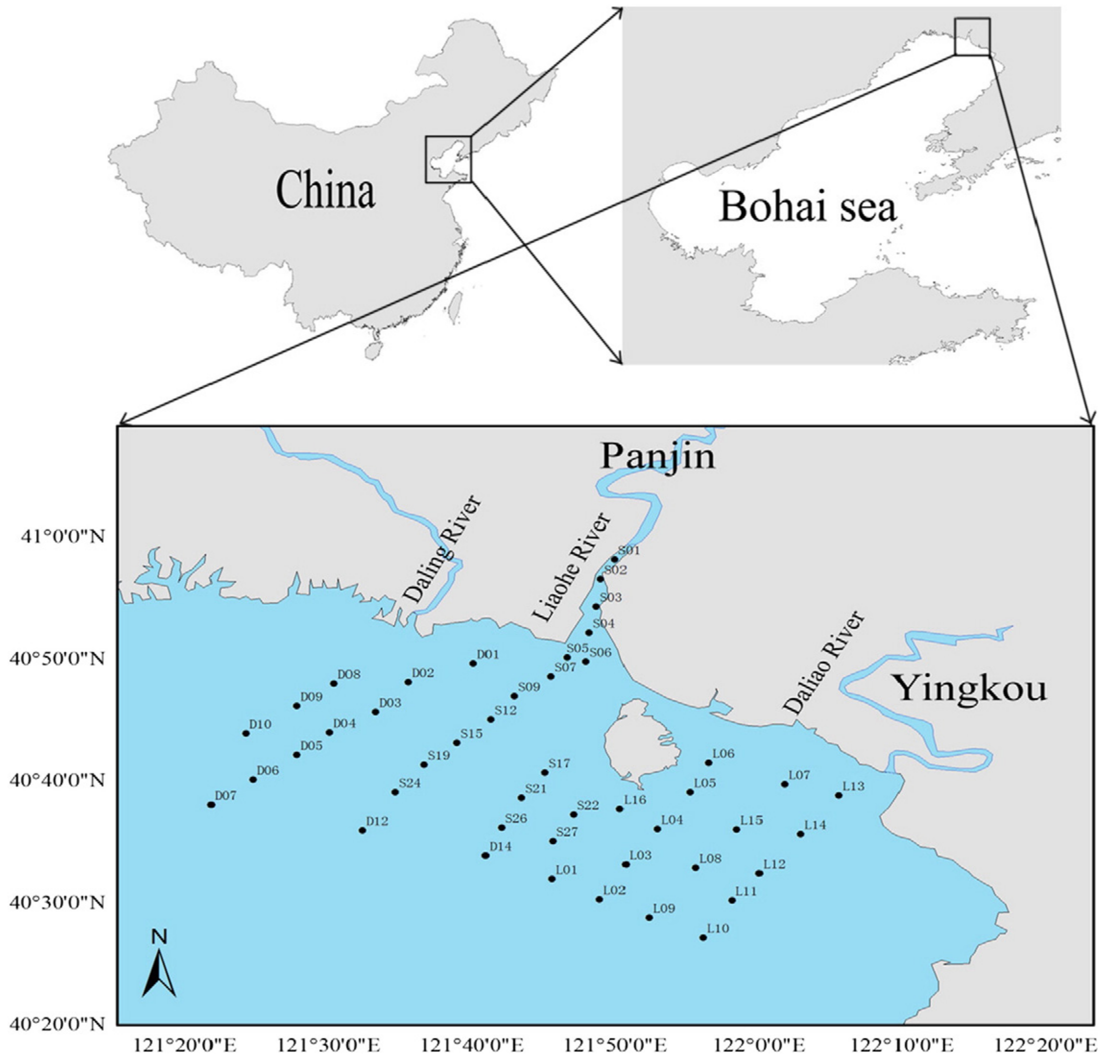

Fig. 1. Study area showing the location of sampling sites in sediment of Liaohe Estuary.

especially for some endangered species, such as spotted seal (*Phoca largha*), Saunders' Gull (*Larus saundersi*) and red-crowned cranes (*Grus japonensis*). The Liaohe River locates in the northeast of the Bohai Sea, discharges into the Liaodong Bay in Panjin City, one of the most polluted coastal areas in China. Therefore, this study aimed to discuss the following issues to benefit the sustainable development of marine ecosystem in this region: (1) to quantify and investigate the spatial distribution of heavy metals, PCBs and OCPs in surface sediments and marine organisms in the Liaohe Estuary; (2) to evaluate their potential ecological risks with ecological risk indices and sediment quality guidelines; (3) to assess their bioaccumulation differences in three kinds of marine organisms (fish, mollusk and crustacean).

Table 1
Comparison of the heavy metals concentrations (mg/kg) in the sediments from the Liaohe Estuary and other coastal areas. Abundance and guideline values of the National Standard of China (NSC, GB18668-2002) were also listed.

	Hg	As	Pb	Cu	Cd	Cr	References
Mean	0.039	6.54	12.86	14.94	0.175	49.04	This study
Range ($n = 44$)	0.005–0.113	1.61–12.77	4.3–28.3	1.7–47.9	0.06–0.47	11.2–84.8	This study
Guadiana Estuary, Spain	0.34	25.5	32.9	50.0	0.20	19.2	Delgado et al. (2010)
Gironde Estuary, France	0.16	18.7	46.8	24.5	0.48	78.4	Larrose et al. (2010)
Liaodong Bay, China	0.04	8.30	31.8	19.4	na	46.4	Hu et al. (2012)
Jiaozhou Bay, China	0.08	8.44	30.87	27.25	0.15	65.47	Wang et al. (2007)
Luoyuan Bay, China	0.06	11.6	30.1	22.9	0.16	35.2	Lin (2008)
Dingzi Bay, China	0.035	7.32	12.67	5.16	0.14	4.06	Pan et al. (2014)
Sanya Bay, China	0.06	7.10	17.5	9.5	0.13	12.4	Qiu and Yu (2011)
Masan Bay, Korea	na	na	44.0	43.4	1.24	67.1	Hyun et al. (2007)
Abundance[a]	0.025	7.7	20	15	0.06	60	Zhao and Yan (1994)
NSC Class I[b]	0.20	20.0	60	35.0	0.50	80.0	SEPA (2002)
NSC Class II[b]	0.50	65.0	130.0	100.0	1.50	150.0	SEPA (2002)

na: not available.
[a] Natural abundance of the elements.
[b] Values are the upper limit for the grades.

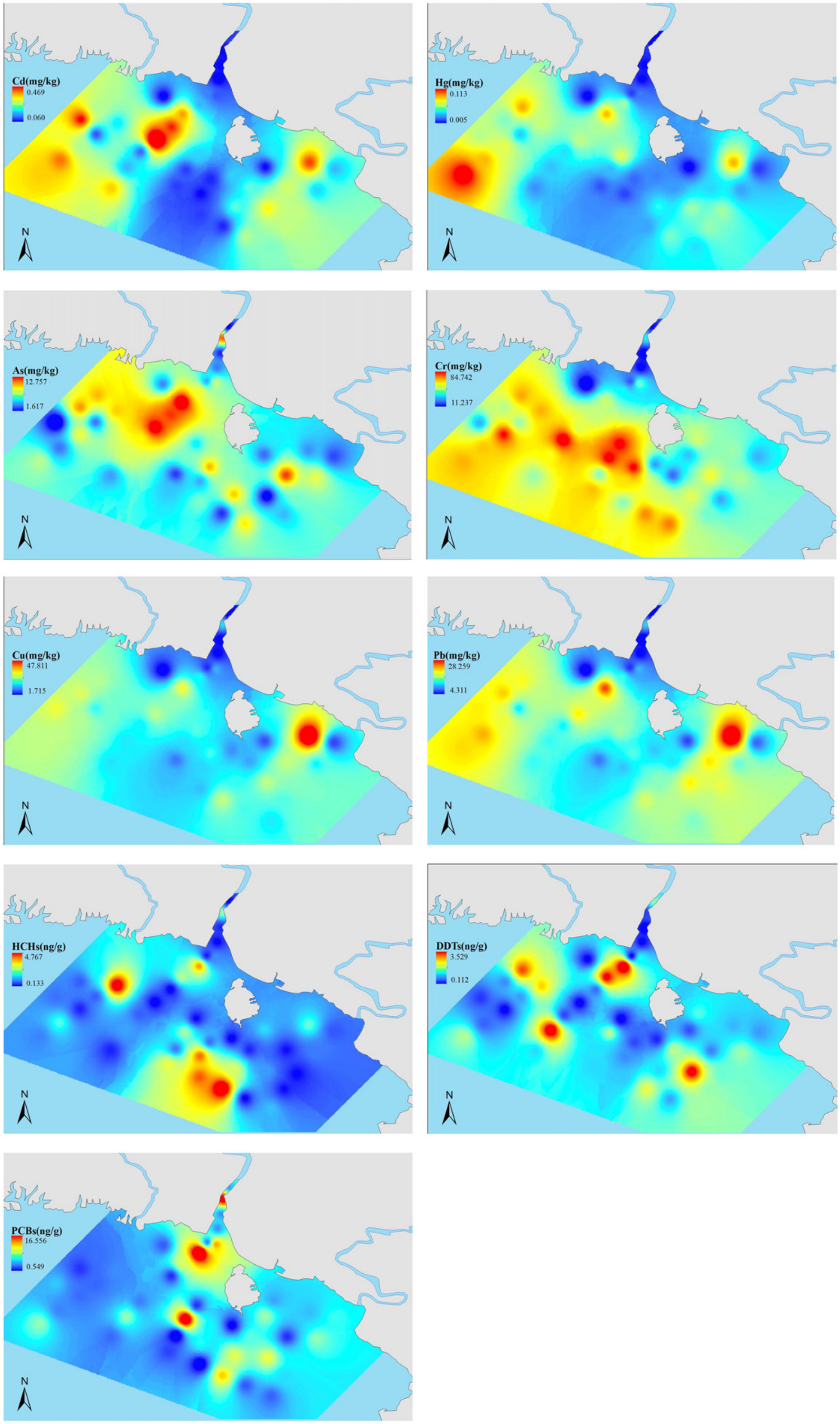

Fig. 2. The concentrations and spatial distributions of heavy metals and POPs in surface sediments throughout the study area.

Table 2
Comparison of PCBs and OCPs concentrations (ng/g) in the sediments from Liaohe Estuary and other coastal areas.

	PCBs	HCHs	DDTs	
Mean	5.162	1.209	1.069	This study
Range	0.54–16.6	0.13–4.77	0.11–3.54	This study
Shuangtaizi Estuary	1.83–36.68	0.07–7.25	0.02–0.47	Yuan et al. (2015)
East Xiamen Island	ND-23	0.18–345	75.2–2143	Chen et al. (2002)
Minjiang Estuary	ND-6.78	ND-5.07	21.5–2396	Chen et al. (2002)
Daya Bay	0.85–27.37	0.32–4.16	0.14–20.27	Zhou et al. (2001)
Caspian Sea	0.03–6.04	0.022–1.03	0.086–2.8	De Mora et al. (2004)
Bay of Bengal, India	0.02–6.6	0.17–1.56	0.04–4.8	Rajendran et al. (2005)

ND: Not detected.

Fig. 1 shows the map of the examined area and sampled sites in this study. The investigated region was mainly divided into three parts from the east to west along the Panjin and Yingkou coastline, including Daling River (sites D01 to D14), Liaohe River (sites S01 to S27) and Daliao River (L01 to L16). A total of 45 sampling sites were investigated in October 2014. Surface sediments (<5 cm) were sampled using a Van Veen grab (0.05 m^2). About 500 g of the samples was collected from each site. They were initially put in acid-washed plastic bags, stored in an icebox, and delivered to the laboratory for further analysis. All pretreatment process were referred to National Standards of China (GB 17378.5-2007). All sediment samples were oven-dried at 80–100 °C for 24 h, then the gravel and large debris were removed. The samples were ground by an agate mortar and pestle, and then sieved to obtain <96 μM fraction. These pretreated sediment samples were stored in clean plastic bags and placed in the laboratory glassware dryer.

Biota samples were obtained by bottom trawling from 12 sites as a part of fishery assessment program. Three species of fish (*Chaeturichthys stigmatias*, *Acanthogobius ommaturus*, and *Larimichthy polyactis*), one species of crustacean (*Exopalaemon carinicauda*), and two species of mollusca (*Mactra veneriformis* and *Meretrix meretrix*) were chosen to be investigated. The living samples were washed with seawater, placed in polyethylene bags and transported to the laboratory in an icebox. For the pretreatment program, the frozen samples were thawed and dissected for the muscle tissue, then some of the tissue samples were dried and eventually ground into fine powder for trace element analysis.

All trace element experiments were referred to China National Standards (GB 17378.5-2007). About 0.1 g of dried sediment was added in a 30 mL Teflon beaker, digested with HNO_3 and $HClO_4$ to near dry conditions, and deionized water was then added to dilute samples. The concentrations of Pb, Cu, Cr and Cd were determined by graphite furnace atomic absorption spectrophotometry (GFAAS), the concentration of As was analyzed by atomic fluorescence spectrometry (AFS), and the concentration of Hg was determined by cold vapor atomic absorption spectrophotometry using a direct mercury analyzer.

We used similar extraction methods for PCBs and OCPs. About 20 g freeze-dried sample was homogenized with Sodium sulfate and Soxhlet extracted with 150 mL hexane/acetone (1:1, *V*/V) for 8 h. 1 g activated copper was added to the samples for desulfurization. The extract was concentrated using a rotary evaporator to approximately 1 mL and then purified with an aluminum/silica gel column, and fractionated. The column was flushed with 30 mL of hexane and then eluted with approximately 100 mL of 70:30 (*V*/V) hexane and dichloromethane mixture. The solution was then concentrated to 100 μL. The concentrations of PCBs, DDTs and HCHs were analyzed by gas chromatography.

For organism samples, 0.1 g sample was accurately weighted into a beaker, and a few drops of water were added to wet the sample. 2 mL nitric acid was added to each sample and left to predigest until the foam disappeared at 40 °C. Then 0.5 mL of 30% hydrogen peroxide was added. The temperature was increased to 160–200 °C for 20 min. 2.5 mL hydrogen peroxide and 1 mL nitric acid were added gradually until 0.5 mL solution left. After cooling, the solution was diluted with deionized water in a 10 mL colorimetric tube. The detection of pollutants were similar with the sediment samples.

To evaluate the potential ecological risk of heavy metal, PCBs and OCPs in the sediments of Liaohe Estuary, ArcGIS 10.2 was used to reflect the sampling locations of heavy metals and organic pollutants across the study area. Basic descriptive statistics was accomplished using Microsoft Office 2013 and SPSS 19.0.

Table 1 shows the mean concentrations of the six trace elements in surface sediments from the studied area. The table also includes heavy metal concentrations form other coastal areas and the reference values of the Sediment Quality Guidelines (SQGs) of China (SEPA, 2002). The concentrations and spatial distributions of heavy metals and POPs in surface sediments throughout the study area are shown in Fig. 2.

Mercury can released to air and water as by-products of various industrial processes, including coal burning, fossil fuel combustion and chloroalkali production (Duan et al., 2015; Chakraborty and Babu, 2015 and Cristol et al., 2008). Mercury occurs through environmental contamination as a byproduct of mining, smelting, and industrial discharge (Duan et al., 2015). The concentrations of Hg in Panjin varied from 0.006 to 0.113 mg/kg, while the range in Yingkou was 0.005–0.082 mg/kg. The maximum and minimum levels were observed at D07 (0.113 mg/kg) and L05 (0.005 mg/kg), respectively.

Cadmium, which is a naturally occurring element and widely used in batteries, pigments, plating, and stabilizers (Boehme and Panero, 2003). Its sources include mining, industrial wastes, water pipes and electroplating plants (Newton, 2008). The highest Cd concentration was found at S15 in Panjin. The high levels were found concentrated at a few stations. The concentrations ranging from 0.06 to 0.47 mg/kg in Panjin and 0.07 to 0.34 mg/kg in Yingkou, the mean value was similar in the two areas.

The sources of Cu include domestic and industrial effluents, the atmosphere, runoff and the lithosphere (Cameron, 1992; Mulligan et al., 2001). The highest concentration of Cu (47.9 mg/kg) was observed at L07 in the Yingkou. The concentrations of Cu ranging from 1.7 to 24.4 mg/kg in Panjin and 6.2 to 47.9 mg/kg in Yingkou.

Arsenic is a naturally occurring element and is widely distributed in the natural environment (Chen et al., 2010). Its sources include mining, pesticides and power-generating plants (Newton, 2008). The concentration differences of As between the monitored sites were ranging from 1.61 to 12.77 mg/kg in Panjin and 2.36 to 10.88 mg/kg in Yingkou, while higher concentrations found at S09 (12.77 mg/kg) and S15 (12.07 mg/kg) in Panjin.

Lead occurs naturally from the decomposition of parent rocks and may accumulate from anthropogenic sources, including traffic exhaust, industrial and household lead, e.g., paints and batteries (Cameron,

Table 3
Concentrations of the heavy metals and POPs (mg/kg) in the marine organisms from Liaohe Estuary.

	Species	Pb	As	Cd	Hg	HCHs	DDTs	PCBs
	Chaeturichthys stigmatias	0.04	0.93	0.027	0.0104	0.00026	0.00213	0.0094
Fish	*Acanthogobius ommaturus*	0.06	1.19	0.028	0.0208	0.0001	0.00063	0.00522
	Larimichthy polyactis	0.04	1.05	0.015	0.0097	0.00032	0.00185	0.01316
Crustacean	*Exopalaemon carinicauda*	0.02	0.88	0.244	0.0081	0.00014	0.0001	0.0007
Mollusca	*Mactra veneriformis Reeve*	0.06	0.96	0.033	0.011	0.00008	0.00061	0.00087
	Meretrix meretrix	0.06	0.93	0.489	0.0074	0.00043	0.00054	0.00105

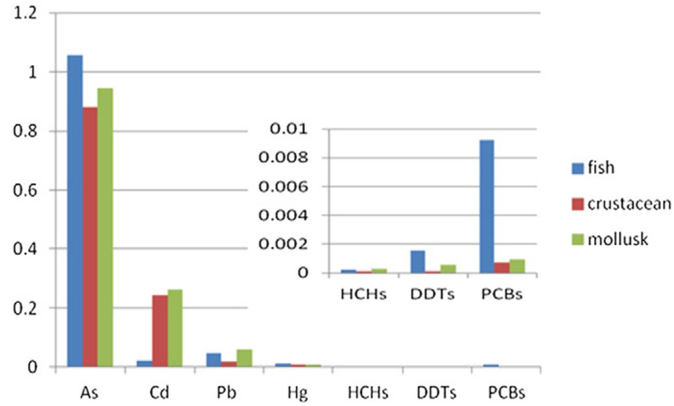

Fig. 3. Heavy metals and POPs concentrations (mg/kg dry weight) in fish, mollusks and crustacean in Liaohe Estuary.

1992). The concentrations of Pb were ranging from 4.3 to 22 mg/kg and 6.9 to 28.3 mg/kg in Panjin and Yingkou, respectively. Pb contamination was not as extensive as previously observed, which showed the mean Pb concentration was 23.936 mg/kg in the sediments of Liaodong Bay (Zhou et al., 2004). This may be attributed the phase-out of Pb in gasoline in Liaohe Estuary. The highest Pb level was observed in site L07 (28.3 mg/kg).

Cr typically originates from paint, coating, and leather industries (Lin et al., 2013). Cr was the metal with the highest mean concentrations in the present study. Its concentrations varied from 11.2 to 84.8 mg/kg in Panjin and 26 to 70.3 mg/kg in Yingkou. The highest concentration of Cr was found specifically at site S19 (84.8 mg/kg).

Overall, the studied heavy metals in the sediment generally showed similar distribution patterns (Fig. 2). In general, sampling sites of lower metal contents were located in the downstream regions, while the higher content sites were distributed along the entrance of the estuary. Cu and Pb exhibited similar distributions: the two elements presented elevated levels in the eastern part of the estuary near the mouth of Daliao River and in the southwestern part of the estuary near the downstream of Daling River. All metals were presented high pollution levels in L07 except Cr and As. A possible explanation for this is that these sampling sites were located near the emitting point sources and shipping channel, with frequent anthropogenic activities along the coast and domestic wastewater being discharged.

In this study, the mean values of As, Pb, Cu and Cr were within the natural abundances reported by Zhao and Yan (1994), while the mean value of Hg (0.039 mg/kg) and Cd (0.175 mg/kg) were 0.56 and 1.7 times higher than the natural abundances, respectively. More than two-thirds of Hg concentrations were higher than its natural abundance while all Cd concentrations were higher except at site S04 and D01, reflecting their considerable accumulation in this area.

The contamination levels in other metal-polluted coastal estuaries and bays from different regions were also given in Table 1 to make a comparison with the extent of metal pollutions in the studied area. Comparison of data sets reveals that levels of Hg, As, Pb and Cu in the Liaohe Estuary were lower than those observed in Jiaozhou Bay and Luoyuan Bay. The concentrations of As, Pb and Cd were similar with those in Dingzi Bay (Shandong) and Sanya Bay (Hainan). The pollution levels of the Hg, Cu and Cr were higher than the two areas. However, it was interesting that all metals pollution levels were much lower than those observed in Guadiana estuary, (Spain), Gironde Estuary (France) and Masan Bay (Korea) except Cr in Guadiana estuary. Compared with the study in Liaodong Bay in 2012, it was obvious that the concentration of Pb has decreased, and the pollution of Cu and As also experienced some improvements, while there were not much change with other metals.

Although the mean values of Hg and Cd were higher than the natural abundances, according to the SQGs of China, the metals contents at all sites were below the threshold values for Class I sediment, except Cu in L07 (47.9 mg/kg) and Cr in S17, S19, S21 and S22. Therefore, despite having suffered from severe human disturbances, the studied area was almost clean enough to be classified as Class I grade in terms of trace element contents in the sediments.

PCBs were produced as industrial chemicals that were mainly used for insulation in electrical equipments. In China, about 10,000 tons of PCBs were produced in the decade from 1965 to 1975. Their use was banned in 1980s (ref). In China, organochlorine pesticides were first used during the 1950s, reaching a maximum in the 1970s and the early 1980s. Although banned in the developed world, organochlorines such as PCBs and organochlorine insecticides including dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) are still being produced and used in many developing countries in agriculture and for the control of diseases such as malaria and typhus (Pham et al., 1996; Tkalin, 1996). The runoff of the compounds in the waterways has resulted in their accumulation in freshwater, estuarine and marine environment in China (Hong et al., 1995; Wu et al., 1999), and sediments act as an ultimate sink for POPs brought into the aquatic environment.

Table 2 shows the comparison of PCBs and OCPs concentrations in the sediments from Liaohe Estuary and other coastal areas. The levels of PCBs increased by accumulation in the sediments due to their low degradation and vaporization rates, high liposolubility, and easy

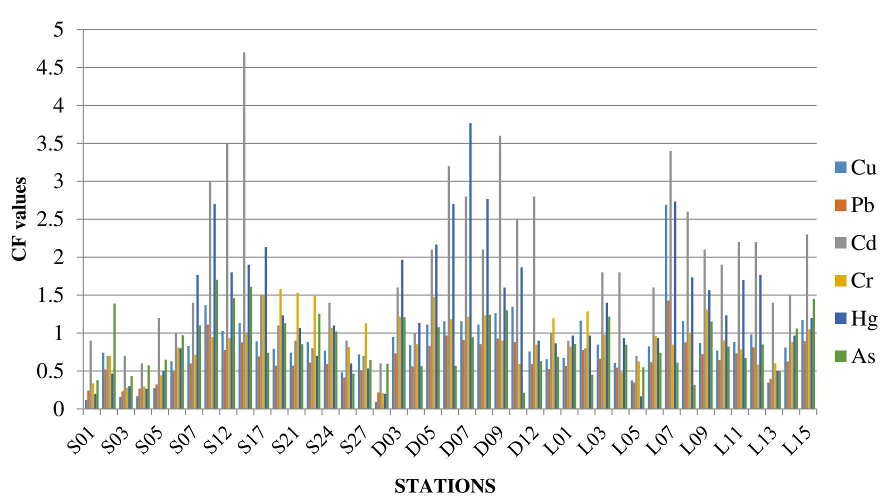

Fig. 4. The spatial variations of the contamination factor (CF) of the heavy metals in the sediments of Liaohe Estuary.

partitioning to particles with rich organic carbon (Salem et al., 2013). The concentrations of PCBs varied from 0.54 μg/kg to 16.6 μg/kg (mean 1.19 μg/kg) in the surface sediments of Panjin and from 0.75 to 9.54 μg/kg (mean 4.96 μg/kg) in those of Yingkou (Fig. 2). Generally, high concentrations of PCBs were obtained in the sites located near the mouths of the Liaohe River (S02 and S07).

HCHs and DDTs, as the most popular OCPs, were detected in most surface sediments in China. Heptachlor has been widely applied as a pesticide to control copepods in aquaculture practice in China. Approximately 11,400 t of lindane has been produced and used even since technical HCH was banned in China in 1983 (Li et al., 2001). In this study, the concentrations of HCHs revealed from 0.13 to 4.47 μg/kg with an average of 1.19 μg/kg in Panjin and revealed from 0.15 to 4.77 μg/kg (mean 1.24 μg/kg) in Yingkou. DDT concentrations varied from 0.11 to 3.54 μg/kg (mean 1.02 μg/kg) in Panjin and varied from 0.29 to 3.05 μg/kg (mean 1.16 μg/kg) in Yingkou. The highest concentration of DDTs was found at site S07 and S24 located in Panjin where the DDT levels was partly higher than those in Yingkou.

In comparison with other estuaries and bays worldwide, the level of PCBs concentration was lower in the Liaohe Estuary than Daya Bay and East Xiamen Island, but higher than that in the Minjiang Estuary. The level of HCHs was lower than East Xiamen Island, and similar with that in other coastal areas in China, and the level of DDTs was the lowest among the areas listed in the Table 2. It was obvious that all of the three pollution levels were totally higher than those observed in Caspian Sea and Bay of Bengal.

Compared with the study in Shuangtaizi Estuary in 2015 (Yuan et al., 2015), it was obvious that the concentration of PCBs and HCHs dropped, and the ratios of DDTs in some sediments was particular high, suggesting there were still fresh inputs of DDT to the sediments at some areas of the Liaohe Estuary. The study commented that DDT is officially banned for agricultural use in China, but it maybe illegally used in trace amounts recently for some agricultural practices.

It is noteworthy that the bioavailability of trace elements entering the environment through anthropogenic sources is remarkably higher than their natural counterparts. Table 3 shows the concentrations of the heavy metals and POPs in the marine organisms from Liaohe Estuary. The pollution concentrations in marine organisms presented characteristics according to organism species, due to the heavy metal sources and the different uptake and accumulation mechanism by organisms (Fig. 3). As concentrations displayed slight variations with regard to the three kinds of species. The enrichment of Cd was much lower in the fish than the other two kinds of species, while Cd concentrations didn't show significant variations between crustacean and mollusks. The enrichment of Pb and Hg displayed differences between the three kinds of organisms: mollusks > fish > crustacean for Pb, and fish > crustacean > mollusk for Hg. The POPs concentrations in crustacean were the lowest among the three kinds of species, while the highest concentrations were found in fish. These results showed that pollutants easily enriched in fish, while the minimum enrichment happened in crustacean. Although the bioaccumulation of pollutants in different types of organisms will exist significant differences, the content for the same pollutant may be varied greatly from similar species (showed in Table 3).

The contamination factor (CF) was used to evaluate the pollution of the environment by single substances in sediments, which was calculated as the ratio of the concentration of metals in sediment taken from sampling sites (Me_{sample}) to pre-industrial concentration of given metals ($Me_{baseline}$), which is defined as follows:

$$CF = Me_{sample}/Me_{baseline.}$$

Four grades are considered for the classification of sediment pollution: low degree (CF < 1), moderate degree (1 ≤ CF < 3), considerable degree (3 ≤ CF < 6) and very high degree (CF ≥ 6) (Loska et al., 1997). Thus the CF values can monitor the enrichment of metals in sediments over a period of time.

The CF values in our study (Fig. 4) indicated that S01, S03, S06, L01, 05 and D01 were the cleanest sites with CF values of all the six elements

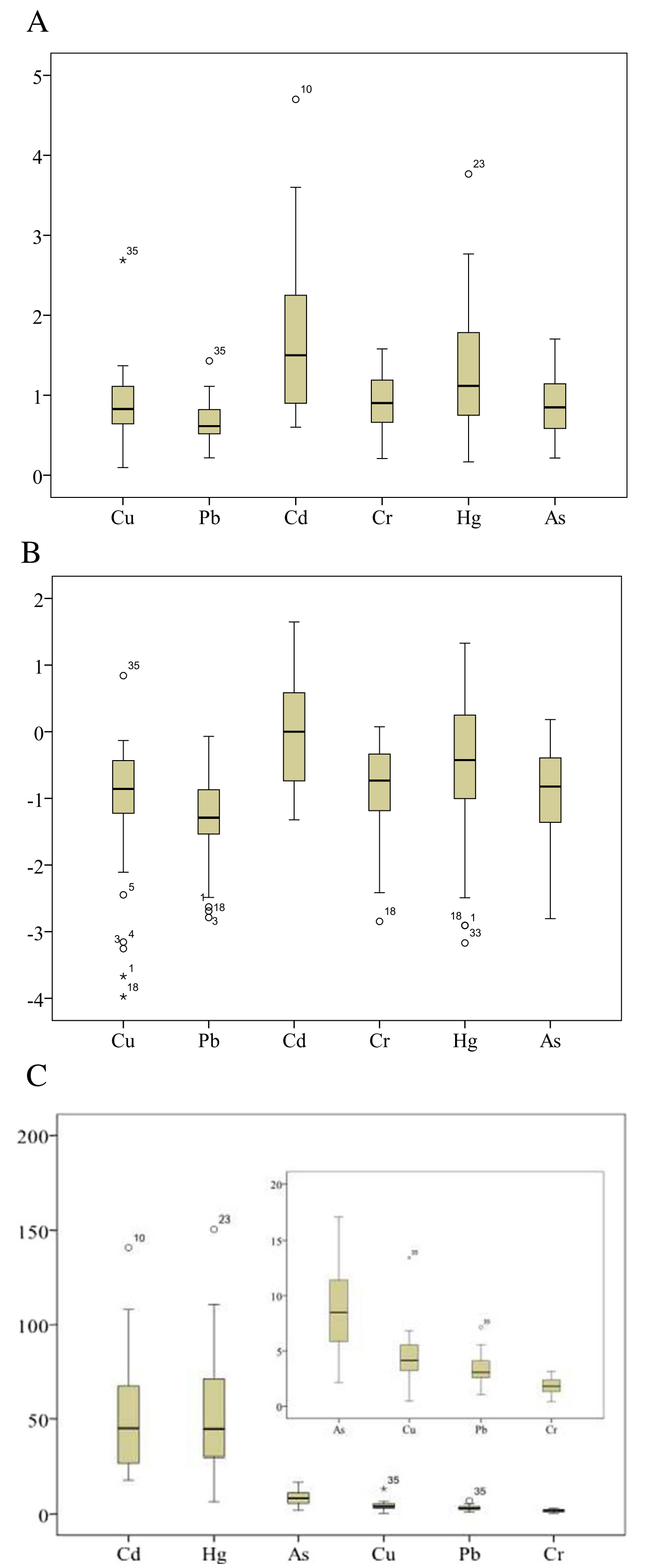

Fig. 5. Box-and-whisker plots of three indices of heavy metals in the sediment of Liaohe Estuary (A: contamination factor; B: geoaccumulation index; C: potential ecological risk index).

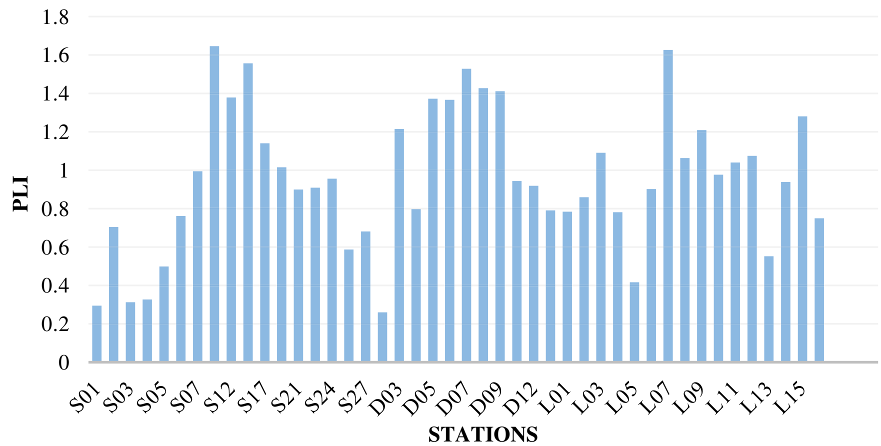

Fig. 6. The spatial variations of pollution load index (PLI) of the heavy metals in the sediments of Liaohe Estuary.

<1 (low to no pollution). In contrast, CF between 1 and 3 were observed for four elements at sites S12, S15, S19, D03, D06, D07, D09, L07, L09 and L15. What's more, the CF values of five elements at site S09, D05 and D08 were >1. The pollution of Hg and Cd were relatively serious, the sediments collected at 23 sites and 26 sites were moderately polluted by Hg and Cd, respectively. Otherwise, the D07 and even 7 sites were considerably polluted by Hg and Cd, respectively. The mean and the highest CF value of 1.75 and 4.7 respectively made Cd the most contaminated metal of all, followed by Hg, Cr, As, Cu and Pb, the values of which were 1.31, 0.91, 0.87, 0.83 and 0.65, respectively. The CF values of Pb were almost <1 except L07 and S09. As showed in Fig. 5, the contamination factor of those heavy metals were found to be in the following order: Cd > Hg > As ≈ Cr ≈ Cu > Pb.

Since heavy metals always occur in sediments as complex mixtures with great variation, therefore, the pollution load index (PLI) was applied to determine and compare the integrated pollution status at sampling sites, which is calculated using the following equation (Tomlinson et al., 1980):

$$\mathrm{PLI} = (\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \ldots \times \mathrm{CF}_n)^{1/n}$$

where CF_n is the CF value of metal n.

The values of PLI (Fig. 6) indicated that the integrated pollution status of combined metal groups were pretty serious and 18 sites were severely impacted by contamination. Especially in these three regions: S09 to S19, D03 to D09 and L07 to L12 where located at the estuary of Liaohe River, Daling River and Daliao river, respectively. The results were in accordance with that of CF values showing the most serious contamination of the studied metals (especially Cd and Hg) at S09, S15, D07 and L07.

Loska, K. proposed that geoaccumulation index could be used to determine the contamination of the examined sediment with organic and inorganic substances by comparing present concentrations with pre-industrial levels, which was applied using the following equation:

$$I_{geo} = log_2\left(\frac{C_n}{KB_n}\right)$$

where C_n is the concentration of the heavy metal and B_n is the Background values of Soil Element of China (NEPA, 1990)

The factor of 1.5 is used to minimize a possible variation in the background value due to anthropogenic influences. A seven-level classification of I_{geo} is defined in Table 4 by Müller (1969). The pollutants levels were similar with what the contamination factor showed in Fig. 5.

As showed in Fig. 7, the I_{geo} values of Pb in all the sediments are categorized as class 0, which indicates that the sediments in all sites are uncontaminated by this metal. The L07 by Cu, S17, S19, S21 by Cr and S09, S15 by As are uncontaminated to moderately contaminated, respectively. There are 15 sites and 16 sites are uncontaminated to moderately contaminated, 6 sites and one site are moderately polluted with Cd and Hg, respectively. Other regions in the Liaohe Estuary are unpolluted by Cd and Hg.

Hakanson (1980) proposed the potential ecological risk index to evaluate the characteristics and environmental behavior of heavy metal pollution in coastal sediments.

Table 4
Description of sediment quality of I_{geo} classification.

I_{geo}	Class	Quality of sediment
≤0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to strongly polluted
3–4	4	Strongly polluted
4–5	5	Strongly to extremely polluted
>5	6	Extremely polluted

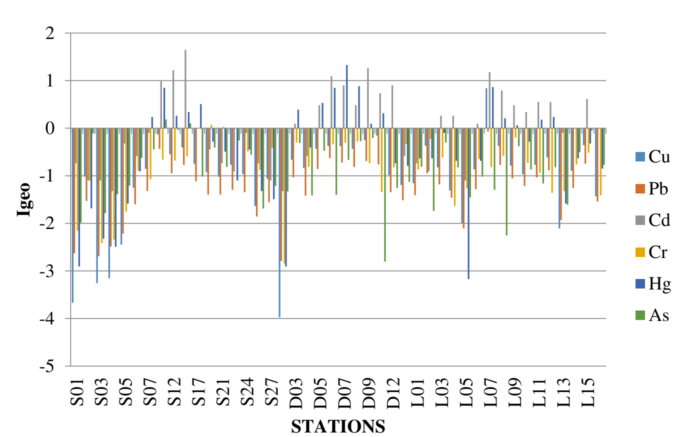

Fig. 7. The spatial variations of the geoaccumulation index of heavy metals of Liaohe Estuary.

Table 5
Risk grades indexes and grades of potential ecological risk of heavy metal pollution.

E_r^i	Risk grade	RI	Risk grade
<40	Low potential ecological risk	<150	Low potential ecological risk
40–80	Moderate potential ecological risk	150–300	Moderate potential ecological risk
80–160	Considerable potential ecological risk	300–600	High potential ecological risk
160–320	High potential ecological risk	≥600	Significantly high potential ecological risk
≥320	Significantly high potential ecological risk		

Table 6
Variations in the ecological risk factors (E_r^i) of 6 heavy metals in the sediment of Liaohe Estuary[a].

	Cu	Pb	Hg	Cd	Cr	As
Average	4.19	3.25	52.36	52.5	1.83	8.72
Range	0.48–13.44	1.09–7.15	6.67–150.67	18–141	0.42–3.16	2.15–17.03
40	44	44	20	17	44	44
40–80	0	0	17	19	0	0
80–160	0	0	7	8	0	0

[a] A total of 44 sample sites were investigated.

The ecological risk factor (E_r^i) and risk indices (RI) were computed to access potential ecological risks presented by the heavy metals to the ecosystem of Liaohe Estuary. The relevant equation is given as follows:

$$E_{RI} = \sum_i^m E_r^i = \sum_i^m T_r^i \cdot C_f^i$$

$$C_f^i = C_i / C_n^i$$

where C_f^i, T_r^i and E_r^i represent the contamination factor of a given metal, the toxic-response factor of metal *i*, and the potential ecological risk coefficient, respectively. C_i is the mean concentration of an individual metal examined and C_n^i is the pre-industrial concentration of the individual metal. Background values of the metals C_n^i used in this study were taken from the article Background values of Soil Element of China (NEPA, 1990).

The T_r^i values for Hg, Cd, As, Pb, Cu, and Cr being 40, 30, 10, 5, 5, and 2, respectively. Hakanson defined five categories of E_r^i, and four categories of RI, as shown in Table 5. Compared with the box-and-whisker plots of the contamination factor and the geoaccumulation index, the potential ecological risk index has a little different order as follows (Fig. 5): Cd ≈ Hg > As > Cu > Pb > Cr.

In Table 6, of the six elements listed, the E_r^i values of all elements varied widely among the 44 sample sites. The E_r^i values of Cr, Cu, As and Pb were all <40, which indicates that the risk levels for these heavy metals are relatively low. About 2/5 E_r^i Hg values were <40, at 17 stations and 7 stations, E_r^i Hg ranged 40 to 80 and 80 to 160, respectively. These results suggest that Hg contamination in most areas in Lioahe Estuary is serious. At 7 sites (D07, D09, D12, S09, S12, S15 and L07), Hg contamination reached levels of considerable ecological risk. All of these stations were close to industrial areas, which provides strong evidence to suggest that Hg contamination derived from industrial activities.

According to previous reports, Cd is the main pollutant of Liaodong Bay (Zhou et al., 2004). The Bulletin of Marine Environmental Status of China (2013) reported that Hg and Cd were the main excessive elements in Liaodong Bay. The present study (mean E_r^i Cd value 52.5) obtained similar findings. Most areas in the study region were polluted by Cd. The highest concentrations of Cd were found in 8 stations D06, D07, D09, D12, S09 S12, S15 and L07, which reached the levels of considerable ecological risk which was similar with Hg, 19 other sites exhibited moderate ecological risk.

These results indicate that contamination of Cd and Hg remains severe in the study area. Calculation of ecological risk indices (RI) of heavy metals in most stations are <300 (Fig. 8) suggests that all stations experience low and moderate ecological risk. However, it is still recommended that the local government pay more attention to this serious issue and positive measures be taken to reduce environmental risk.

In conclusion, the results of the current study provide information on the status of heavy metal in the sediments of Liaohe Estuary, Bohai Sea of China. The foregoing analysis shows that the pollution of Hg and Cd in Liaohe Estuary were relatively serious which was consistent with the China Marine Environment Bulletin. The pollution of four stations (S09, S15, D07 and L07) were more serious than others, where S09, S15 and L07 are located at the mouth of Liaohe River and Daliao River, respectively. The increased concentration of DDTs indicated that there may be a fresh DDTs input, which also need to be concerned. The concentrations of the four heavy metals varied significantly in the organism samples, indicating the different accumulative abilities of the species. From the view of seafood safety, the concentrations of almost all pollutants in six species were in the range of national seafood safety standard (National Standard of PR China, 2012), while As was an exception. The total As levels in all six species were above the seafood safety standard. To some extent, the consumption of the fish, crustacean and mollusk from this area may have a potential risk for human health. So the As pollution in marine organisms in this area could be another problem in this place. Overall, the pollution situation at Liaohe Estuary

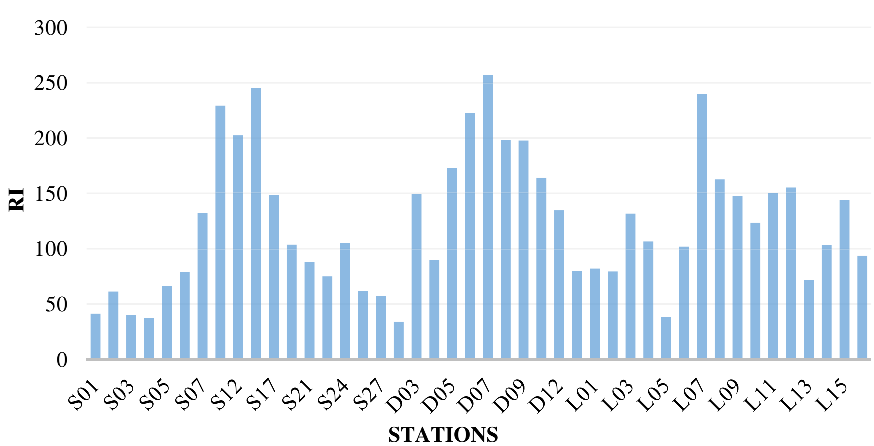

Fig. 8. Spatial variation in the ecological risk indices (RI) of heavy metals in the study area.

has some improvement, while problem still exists. The supervision and management are still needed for the government.

Acknowledgments

This study was supported by National Marine Public Welfare Research Project (201305030, 201405007), the project (GASI-03-01-05) and National Natural Science Foundation of China (31572595).

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