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Heavy metal contamination in the marine organisms in Yantai coast, northern Yellow Sea of China

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Abstract The port city of Yantai, in Shandong province China is located on Sishili Bay in the northern Yellow Sea. Intense human activity associated with urban sewage discharge, as well as industrial and maritime activities, have stressed the Sishili Bay coastal ecosystem with anthropogenic pollution. The aim of this study was to measure the levels of heavy metal in the sediment and marine organisms of economic value from various sites within Sishili Bay, and to evaluate the data in relation to the potential health risk on human consumers. For this purpose, sediment and wild shrimps and crab were collected from three areas (a total of 13 sampling sites) of the Yantai coast and analyzed for six heavy metals (Cu, Zn, Cr, Ni, Pb, and As). For comparison, the concentrations of the same heavy metals in seven kinds of mollusks obtained from local aquaculture were also determined. The findings showed that the concentrations of heavy metals in the sediment of Yantai coast followed the order Zn $>\approx$Cr $>$ Cu $\approx$ Ni $\approx$ Pb $>$ As, and all were within the safe levels of national standard. However, the concentrations of the heavy metals varied significantly in the organism samples, indicating the different accumulative abilities of the species sampled. For the wild marine organisms, Pb concentrations in some shrimp and crab samples exceeded the standard limit of seafood safety criteria and As concentrations in all samples were over the limit. Moreover, the As levels in mollusks from aquaculture exceeded the limit of seafood standard criteria. These results indicated that the heavy metal levels in the marine organisms in the studied areas were moderate but unacceptable for As from the view of safety of seafood. Furthermore, it is very necessary and important to further study toxicological and ecological effect of As in the coast of northern Yellow sea to understand the potential for risk to human and environmental health.

Keywords Heavy metals · Pollution · Marine environment · Seafood

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Introduction

Heavy metal contamination in the marine environment has been highlighted by scientists and governments over the last decades, because their toxicity and accumulative behaviors in sediments and marine organisms can damage both marine species diversity and ecosystems (Matta et al. 1999; Roméo et al. 2005; Sivaperumal et al. 2007). Moreover, toxic heavy metals can accumulate in the body of marine organisms and transfer to human via the food chain and cause the potential health risk (Madany et al. 1996; Pourang and Dennis 2005; Firat et al. 2008). Thus, it is important to evaluate the heavy metal contents and

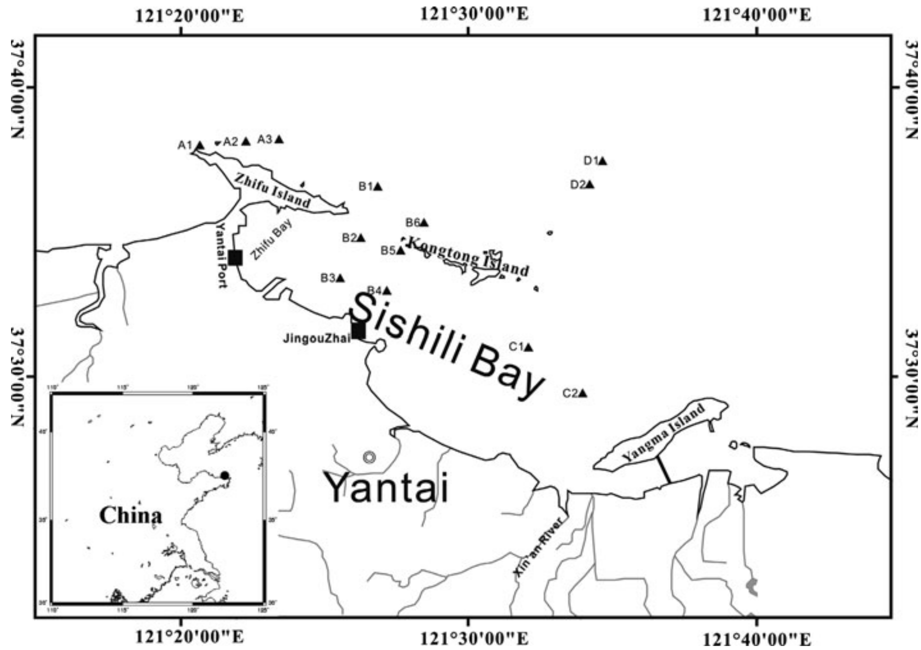

Fig. 1 The sampling sites in Yantai coast and Sishili bay for collecting surface sediment and wild marine organisms

monitor their accumulations in the marine environment and organisms for seafood safety and the health of consumers.

Sishili Bay is located in the northern Yellow Sea, China, which is subject to the intense human activity from the surrounded city Yantai in Shandong province, China (Fig. 1). The increased population, urban sewage discharge and the shipment of Yantai Port have extremely stressed the coastal ecosystem (Wei et al. 2007; Yu et al. 2009). The anthropogenic inputs are considered as the important sources of heavy metals in marine environment, especially near the shoreline (Fung et al. 2004; María-Cervantes et al. 2009). However, few studies on the heavy metal contamination in marine environment and organisms have been carried out along the Yantai coastline, and the available information mainly focused on the mollusks obtained from the seafood markets (Wu et al. 2006; Wang et al. 2005). Thus, it is essential to evaluate the heavy metal contents in the marine environment and organisms along the Yantai coast for the seafood safety.

In this study, Sishili Bay, a typical marine aquaculture bay, was chosen as the study area. The variation of heavy metals in the surface sediment of the bay was studied to reflect the condition of marine environmental contamination, and the wild marine organisms were collected from the sea bottom for the analysis of the amounts of heavy metals in their tissue to understand the accumulation of heavy metal in wild marine organisms. Moreover, the main seafood from aquaculture was purchased from local seafood market to investigate the bioaccumulation of heavy metals, with a purpose of monitoring the seafood safety and comparing with the heavy metal level in the wild marine organisms.

Materials and methods

Sediments sampling and analysis

Surface sediments were collected from 13 sampling sites in the Sishili Bay, northern Yellow Sea, China (Fig. 1). For comparing with the different marine environment, sampling sites were designed in the sewage outfall area (A1, A2, and A3), Yantai port area (B1–B6), aquaculture area (C1 and C2) and less human activity area (D1 and D2 as the contrast area). Approximately, 1 kg of surface sediment was taken and put in a polyethylene bag from each sampling site. The samples were then transported to the laboratory, air-dried and sieved to 2 mm in order to remove coarse fragments. A portion of each sieved sample was ground into fine powder in a mortar. Heavy metal contents were analyzed in triplicate according to EPA method 3052 (USEPA 1996). The ground sediment (approx. 0.25 g) sample was put in a polytetrafluoroethylene digest container, 9 mL of pro-analysis 69 % HNO_3 and 3 mL of proanalysis 40 % HF were added for digestion. The container was sealed, placed into a microwave oven, heated for 5 min to reach 180 °C, then kept at this temperature for 10 min and finally allowed to be cooled down for 60 min. The obtained solution was then filtered. Heavy metals were measured using an Agilent 7500 inductively coupled plasma-mass spectrometer (ICP-MS) (Agilent Technologies Co. Ltd, USA). Accuracy of the method was also assessed using certified reference material (sediment GBW 07315(GSMS-2)). Recoveries of all elements in the reference sediment ranged from 85.2 to 110.9 %. Concentrations reported in this study were not corrected for recovery rates.

Table 1 Seven mollusk species purchased from the seafood markets of Yantai

Species	*Meretrix meretrix*	*Chiamys farrer*	*Mytilus edulis*	*Scapharca subcrenata*	*Concha Ostreae*	*Sol sricus*	*Saxidomrs purpuratus*
Abbreviation	*Mer*	*Chi*	*Myt*	*Sca*	*Con*	*Sol*	*Sax*

Marine organisms sampling and analysis

Two species of shrimps (*Oratosquilla aratoria* and *Alpheus distinguendus*) and one species crab (*Carcinoplax vestitus*) samples were collected by net hauling from three locations (A: sewage outfall area, B: port area, and D: contrast area) in the Sishili Bay. For comparison, seven kinds of mollusks from the aquaculture in the bay were purchased from the local seafood markets of Yantai. The species of mollusks are listed in Table 1. The living samples were washed with seawater, placed in polyethylene bags and transported in an icebox.

After transported to laboratory, the marine organism samples were frozen. The animals were then dissected for the soft tissues which were homogenized in a blender, freeze-dried for 1 week, and eventually were ground into fine powder. The powder (Approx. 1 g, accurately weighted) was weighed into a polytetrafluoroethylene digestion container. Ten milliliter of concentrated nitric acid was added to each sample and left to predigest overnight at 40 °C. After cooling, 6 ml of 30 % hydrogen peroxide was added. Reagent blanks were processed simultaneously. Afterwards, the container was covered and placed in a stainless steel bomb, which was then sealed with a screw closure to avoid any acid leakage and placed in a microwave oven. The oven temperature was increased to 50 °C and kept for 1 h then increased to 160 °C for 4 h. After cooling, the solution was transferred into a 50-mL PET bottle and diluted with Milli-Q water.

Concentrations of heavy metals (Cu, Zn, Cr, Ni, Pb, and As) were measured by an ICP-MS (Agilent 7500i). All analyses were carried out in triplicate, using the external calibration method. Accuracy of the method was also assessed using Mussel 08571. Recoveries of all elements in Mussel 08571 ranged from 86.7 to 112.4 %. Concentrations reported in this study were not corrected for recovery rates.

Results and discussion

Heavy metal levels in sediment of the bay

The heavy metal contents in the sediments can indicate the contamination level of the water body related. The results of 13 sediment samples are shown in Fig. 2. Generally, the concentrations of metals in the sediments followed the decreasing order Zn $>$ $\approx$Cr $>$ Cu $\approx$ Ni $\approx$ Pb $>$ As. According to zone, the mean concentrations of metals were in order: sewage outfall area $>$ Yantai port area $>$ contrast area $>$ aquaculture area. In the sewage outfall area, the heavy metal contents of the sediment in A1 site are the highest, which are obviously higher than the other two sites. Zn, Cr, Cu, Ni, Pb, and As concentrations are 135.4, 85.7, 55.3, 41.8, 47.6, and 19.1 mg/kg d.w., respectively. In the port area, the concentrations of metals at B1 and B6 sites are relatively higher than these at B2, B3, B4, and B5 sites. The average metal concentrations from the Yantai port area are 80.8, 71.8, 25.9, 28.9, 29.2, and 11.5 mg/kg d.w. for Zn, Cr, Cu, Ni, Pb, and As, respectively. The metal levels at D1 and D2 located in the contrast area are almost the same. The mean concentrations for these metals from the contrast area are 78.1, 71.0, 23.0, 30.6, 26.9, and 11.5 mg/kg d.w., respectively. Whereas, the sediment samples from the aquaculture area showed the lowest metal contents, particularly at site C1, the Zn, Cr, Cu, Ni, Pb, and As concentrations are 63.6, 69.8, 18.4, 25.2, 26.2, and 8.6 mg/kg d.w., respectively.

The A1, A2, and A3 sampling sites are located in the sewage outfall, and site A1 is just close to the effluent outlet of the wastewater treatment plant, which may be responsible for the high metal levels in this area. The discharged effluent could diffuse from site A1 to B1, even impact the site D1and D2 with the sea current. This might be the reason that the heavy metal contents at these three sites are slightly higher than other sites except for the A1, A2, and A3. The activities of shipment may be the source of relatively higher heavy metals level in the port area. In contrast, the less industrial activities and shipment in aquaculture area showed lower levels of heavy metals.

Generally, the contamination of heavy metals in the Sishili Bay is light. According to the Chinese marine sediment quality criteria (National Standard of PR China 2002), all the metal contents in all samples are below the standard of first-class quality except for the Cu, Cr, and Ni at A1 site, which is slightly above the first-class limit and but not over the second-class standard.

Heavy metal levels in wild marine organisms

Heavy metal contents in the shrimp and crab which were collected from three zones by net hauling were analyzed

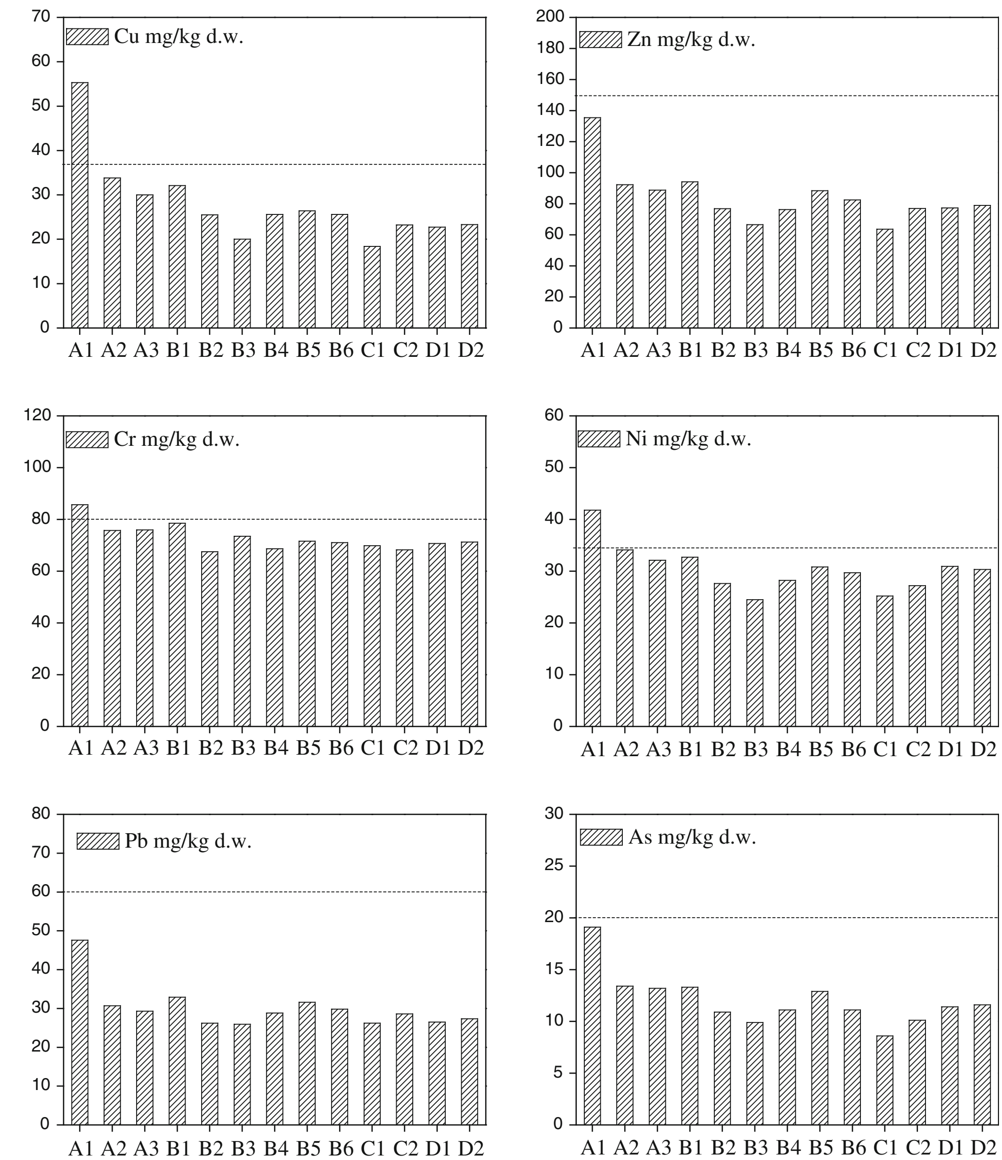

Fig. 2 Heavy metal contents in sediment samples of the Sishili Bay (Unit: milligrams per kilogram dry weight, *dash lines* using to compare the national criteria of good marine sediment quality)

and the results are illustrated in Fig. 3. The heavy metal levels in the shrimp and crab samples were in order: Cu > Zn > As > Ni > Cr > ≈Pb and the contents ranged from 73.13 to 163.84, 74.6 to 97.09, 14.11 to 23.65, 5.77 to 23.13, 1.55 to 5.24, and 1.82 to 4.95 mg/kg d.w., respectively. This suggested that the metal accumulative ability of the marine organism samples varied significantly, depending on the metal species. The metal accumulative abilities of the shrimp and crab followed the order Cu > Zn > As > Ni > Cr > ≈Pb. For the same heavy metal, its concentrations in different organism species did not vary significantly. For examples, Zn contents in the *Oratosquilla aratoria*, *Alpheus distinguendus*, and *Carcinoplax vestitus* from sewage outfall area were 94.45, 79.28, and 86.09 mg/kg d.w., respectively; Pb contents in these three species from the port area were 2.09, 2.25, and 2.88 mg/kg d.w., respectively. These data indicate that similar organism species have similar accumulative abilities towards the same heavy metal. For the view of the zone, the metal contents in the shrimp and crab samples collected from sewage outfall area are slightly higher than those from port area and contrast area. This is positively correlated with the results of metal contents from the surface sediment, to some extent, although the zone difference was not so significant as we expected.

Through the Cu and Zn concentrations in the organisms were high; they are in the range of national seafood safety standard (National Standard of PR China 2005). The Cr

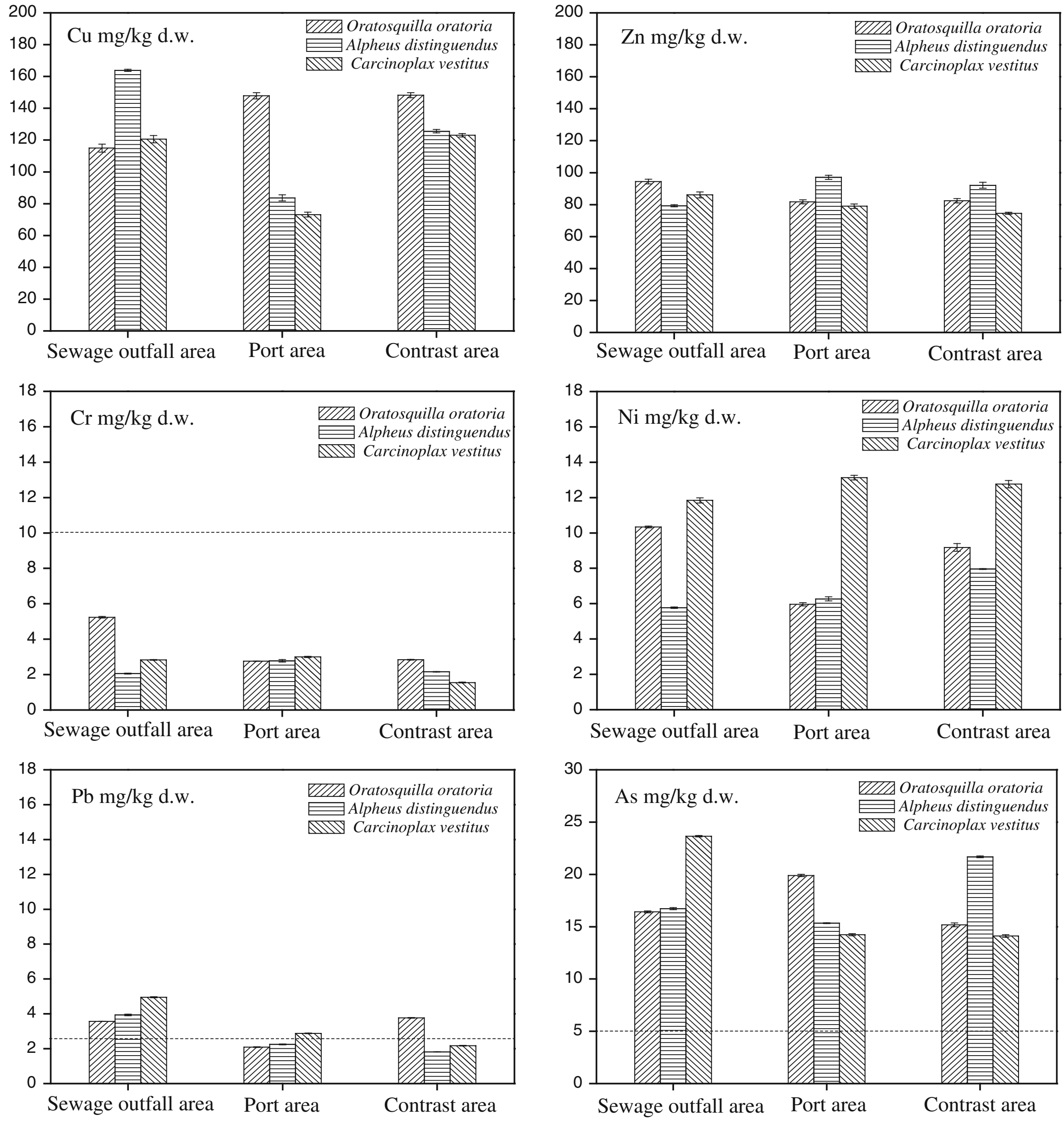

Fig. 3 Heavy metal contents in shrimp and crab samples collected from three sampling sites in the Sishili Bay (Unit: milligrams perkilogram dry weight, *dash lines* represent the national criteria of marine seafood safety for heavy metals)

levels in all samples are low as well meeting the safety criteria. Pb contents in some samples were a little high and exceeded slightly safety criteria. The As contents in the shrimp and crab are in the range of 14.11–23.65 mg/kg d.w., which exceeded the seafood safety standard. As for Ni, its levels in the shrimp and crab samples are relatively high and should be noted, although no related limit standard is given by national seafood safety.

Heavy metal levels in the mollusks from aquaculture

Concentrations of six metals (Cu, Zn, Cr, Ni, Pb, and As) in the mollusks collected from the Sishili Bay are demonstrated in Fig. 4. Obviously, the Zn contents in the mollusks were the highest (66.6–494.4 mg/kg d.w.); Particularly in the *Con* and *Chi (F)*, the Zn contents reached to 494.4 and 445.5 mg/kg d.w., respectively, which indicate that the mollusks could have the high accumulative ability to the Zn element. The Cu contents in the organisms were not significant except for the species *Con.* with a value of 211.68 mg/kg d.w. which was much higher than the other species. The As concentrations were relatively higher than other metals with a range of 7.72–30.35 mg/kg d.w. The Pb and Ni concentrations were relatively lower, they ranged from 1.49 to 18.48 and 0.72 to 12.28 mg/kg d.w., respectively. The Cr contents in the

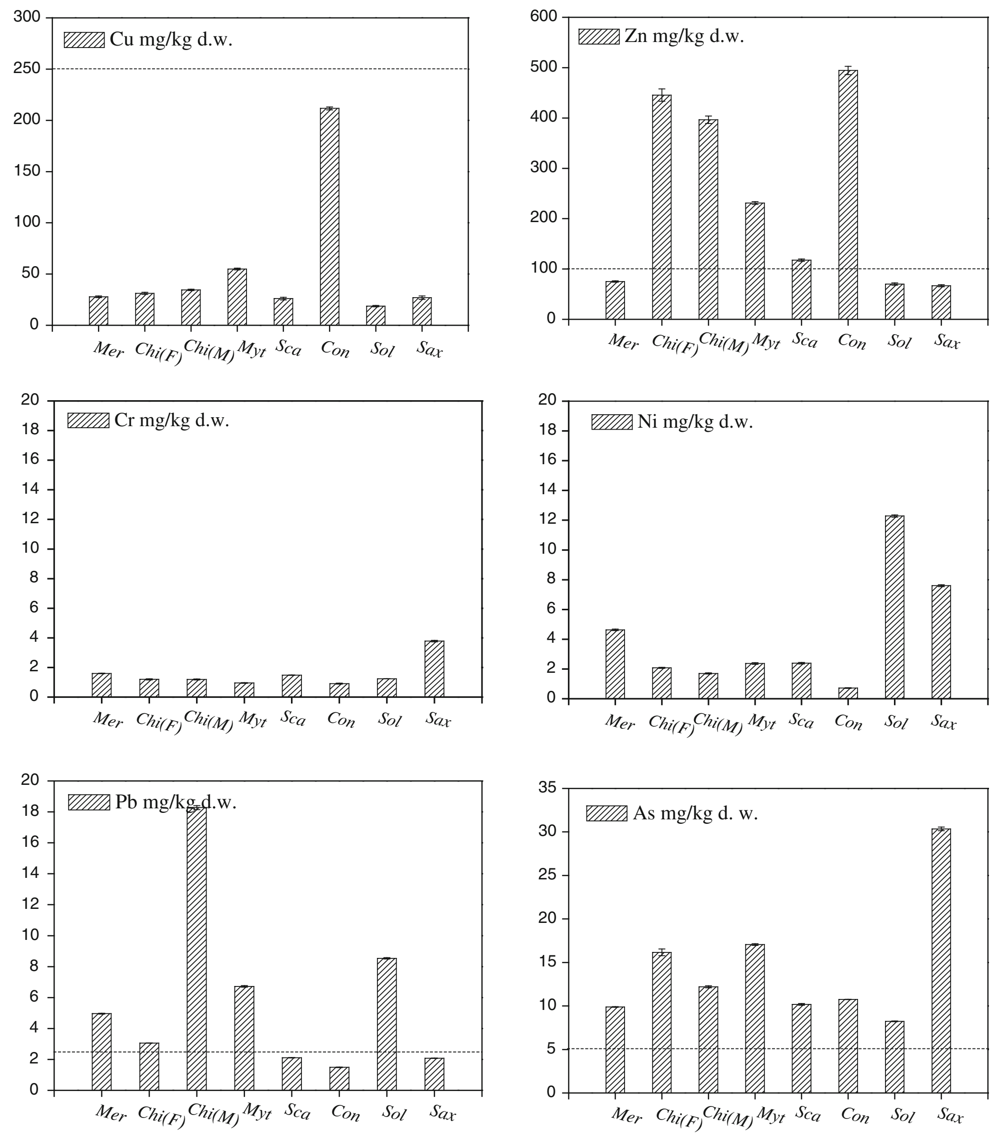

Fig. 4 Heavy metal contents in mollusks collected from seafood market of Yantai coast (Unit: milligrams perkilogram dry weight, *F* (female) and *M* (male) represent and the sex of mollusks, *Dash lines* represent the national criteria of marine seafood safety for heavy metals)

mollusks were the lowest, only in the range of 0.91–3.78 mg/kg d.w. Thus, the general order of heavy metal concentrations in the mollusks was Zn > Cu > As > Ni > ≈ Pb > Cr.

For the same heavy metal, its content in mollusks varied greatly from species to species. For example, Cu level in *Sol* was the lowest (18.8 mg/kg d.w.), while in *Con.* was the highest (211.7 mg/kg d.w.). Moreover, the same mollusk species displayed different metal accumulative ability. The *Con.* had a high accumulative ability towards Zn (494.4 mg/kg d.w.), whereas it had a very low accumulative ability to Cr (0.91 mg/kg d.w). Additionally, the Cu, Zn, Cr, Ni, and As contents in *Chi(F)* were higher or equal to those in *Chi(M).* Interestingly, the Pb content in the *Chi(M)* was significantly higher than that in the *Chi(F)*. This indicates that the *Chi(M)* could have very high accumulative ability towards the Pb.

To assess the current situation of metal contamination in marine organisms from Yantai coastal area, we compared the heavy metal contents in *Con* and *Myt* in this study with other reports from the northern Yellow Sea (Table 2). We found the metal concentrations in the *Con* in this study did not differ greatly from those reported by Liang et al. (2004). In the case of *Myt* collected from different sampling area and time (Table 3), the metal contents varied markedly. In general, the metal levels in the *Con* and *Myt* from the Yantai coastal area were not very high and the contamination was moderate.

From the view of seafood safety, the Cu levels in the mollusks were acceptable. The Zn levels in the *Chi*, *Myt*,

Table 2 Comparison of heavy metal contents in *Concha Ostreae* from other areas of the Northern Yellow Sea

Sampling time	Sampling site	Ni	Pb	Zn	Cu	Ref.
2009.07	Sishili Bay[a]	0.14	0.30	98.88	42.34	Present study
2002.07–08	Weihai	0.11	0.21	135.40[a]	27.31[a]	Liang et al. (2004)
2002.07–08	Penglai	0.44	0.46	115.95[a]	60.75[a]	Liang et al. (2004)
2002.07–08	Qinhuangdao	0.30	0.30	142.35[a]	109.60[a]	Liang et al. (2004)
2002.07–08	Tanggu	0.18	0.22	181.40[a]	25.24[a]	Liang et al. (2004)
2002.07–08	Dalin	0.22	0.62	379.55[a]	31.32[a]	Liang et al. (2004)

[a] The values have been converted to wet weight contents (calculated as 80 % water content)

Table 3 Comparison of heavy metal contents in *Mytilus edulis* from other areas of the Northern Yellow Sea

Sampling time	Sampling site	Cr	Ni	Pb	Zn	Cu	As	Ref.
2009.7	Sishili Bay[a]	0.19	0.474	1.34	46.22	10.98	3.41	Present study
1990	Bohai Sea			0.05	7.20	0.48		He (1996)
1990	Yellow Sea			0.81	89.8	2.30		He (1996)
1994	Dalian Bay[a]		0.18	0.59	50.60	4.54		Liu et al. (1995)
1994	Xinghai Bay[a]			0.64	49.60	2.32		Liu et al. (1995)
2001.9–10	Dalian		1.50	0.51	76.89	1.83	12.7	Fung et al. (2004)
2001.9–10	Qingdao	2.18	3.31	0.90	104.9	22.08	9	Fung et al. (2004)
2002.07–08	Weihai	10.93	0.25	0.22	16.49	2.52	13.5	Liang et al. (2004)
2002.07–08	Penglai		0.23	0.60	22.42	2.07	0	Liang et al. (2004)
2002.07–08	Qinhuangdao		0.25	0.25	13.65	1.19	12.9	Liang et al. (2004)
2002.07–08	Yingkou		0.19	0.22	12.69	1.16	3	Liang et al. (2004)
2002.07–08	Dalin		0.18	0.16	11.87	1.14		Liang et al. (2004)
2002.07–08	Bohai Sea		0.18–0.25	0.16–2.52	11.87–22.42	1.16–2.52		Liang et al. (2004)

[a] The values have been converted to wet weight contents (calculated as 80 % water content)

and Con exceeded greatly the criteria of safety standard and *Sca* was slightly over the criteria. The Pb levels in the *Mer*, *Chi*, *Myt and Sol* exceeded obviously the criteria. The total As levels in all seven mollusk species were above the seafood safety standard. In fact, the same phenomenon was observed in the wild shrimp and crab samples collected by net hauling. Our results indicate that As pollution in marine organisms in this area could be a problem in future if the pollution can not be controlled well, in spite that its concentrations in the sediment were not high during our survey. Thus, to some extent, the consumption of the shrimp, crab and mollusk from this area may have a potential risk for human health. However, the toxicity of organic arsenic is greatly lower than the inorganic and some literature reported that most of the As occurred as organic species in the marine organisms (Schaeffer et al. 2005; Borak and Hosgood 2007). Therefore, the determination of As species in the above organisms should be made in the further study.

Conclusions

The contamination of heavy metal in sediment in the Sishili Bay is not serious. The heavy metal concentrations in the sediment samples collected from the sewage outfall area were relatively higher. Sewage discharge may be the main cause for the higher concentrations.

The metal contents in shrimp and crab samples collected from three areas did not differ greatly, a little higher at sewage outfall area. Pb concentrations in some shrimp and crab samples exceeded the limit of seafood safety. In the case of As, all samples were over the limit. The levels of heavy metals in the mollusks purchased from the seafood market of Yantai varied greatly, depending on the metal species and organism species. The mollusks had high accumulative abilities towards the Zn and As. The concentrations of Zn and As were much above the limit of seafood standard. To some extent, the consumption of the shrimp, crab and mollusk from this area may have a potential risk for human health. However, the determination of As species in the above organisms should be made in the further study.

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