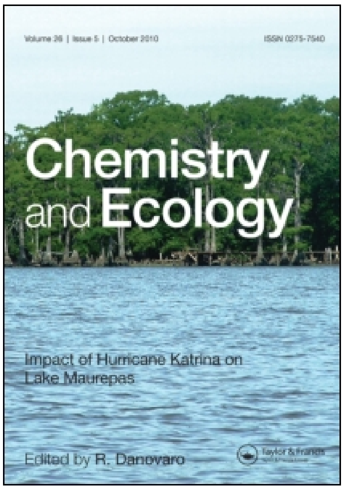

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THE ROLE OF CRABS IN THE HEAVY METAL FLOW OF THE ESTUARINE ECOSYSTEM OF YANGTZE RIVER, CHINA

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Macrobenthos play a major role in material flow of the estuarine ecosystem. As a primary consumer, they accumulate more essential elements, such as zinc and copper, than the primary producers (plants) do. However, resulting from their complex mechanisms of regulation and control on the non-essential elements, *e.g.*, lead and cadmium, they do not always accumulate more contaminates. Small sized crabs seem to accumulate more non-essential elements than the large-sized ones. In the Yangtze estuary, zinc and copper are found bio-magnified on the food chains, but there are not significant evidence of the effects on cadmium and lead. Potentially hazardous elements in the macrobenthos are harmful to the organisms at the higher trophic levels, such as waders and man.

Keywords: Heavy metals; bio-availability; *Ilyoplax deschampsi*; *Helice tridens* tientsinenses; food chain

INTRODUCTION

The Yangtze Estuary is the largest estuary in China. It was estimated that the freshwater flow to the estuary was $92.4 \times 10^9 \text{m}^{-3} \text{year}^{-1}$ (Chen *et al.*, 1995), it is a depositary estuary. Almost 0.4 billion tonnes of sediments are transported to the estuary every year, with heavy metals produced by geochemical process entering the Yangtze Estuary. It was estimated that there were almost 660 tonnes of heavy

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metals in the turbidity maximum of the estuary. There is an effect of a "physical and chemical barrier" studied at where fresh water meets sea water. The contents of heavy metals there are closely related to the physical and chemical factors, such as velocity of flow, salinity, suspension and other factors (Chen *et al.*, 1995). Influences of a biological factor were less studied, also the bio-effects of contaminates.

Like many other temperate estuaries, local species in the Yangtze Estuary was found of a high biomass with relatively low diversity (Yuan *et al.*, 1999). It is an ideal nursery for the invertebrates. Density of the benthos was 67.2 individuals m^{-2}, biomass was 123.9 g (fresh weight) m^{-2}. The Yangtze Estuary is an important stopover on the Pacific-Asia flightway for shore birds. During autumn and the next spring, there were more than one million shore birds passed by the estuary and thus feeding on invertebrates for energy (Cui *et al.*, 1985; Lu *et al.*, 1998).

Most metals in the physical environment are tightly bound to the sediments and therefore not bio-available (Hall and Pulliam, 1995). Exchangeable and easily reducible phases of the metals can release free ions when $pH > 5$, but bio-available for most organisms. In the estuarine sediments, only $1-10\%$ of the total amount is regarded as available for most organisms (Rule and Alden, 1996; Mayer *et al.*, 1996). Beside this total amount, the bio-available part is more crucial in assessing the impact of heavy metals on the estuarine ecosystem.

There were many lethal tests of heavy metals on the macro-invertebrates in the Yangtze Estuary. Less attention was paid to the ecological significance of contaminates in the organisms. The distribution of metals in the *Corbiula fluminea*, the dominant species on the mud flat of the Yangtze Estuary, was studied and found that most of the essential elements, *i.e.*, zinc and copper, in the shells, and potentially hazardous elements, *i.e.*, lead and cadmium in the soft tissues. Obviously the latter had a greater ecological significance (Ye *et al.*, 1999).

Biomagnification of heavy metals through the food chains were studied to assess the ecological risks to the wildlife. Saiki *et al.* (1995) and Pascoe *et al.* (1996) conducted experiments in the wetland ecosystem, and found that no significant evidence showing the biomagnification effect for heavy metals (zinc, copper and cadmium).

Both phases of heavy metals and their roles played in the metabolic processes do effect their fates in the ecosystems. Moreover, different species of organisms show their unique mechanism to the potentially toxic concentrations of dissolved metal in the physical environments and the food (Decho and Luoma, 1996; Rainbow, 1997).

The current research investigated the impacts (for *Ilyoplax deschampsi* and *Helice tridens* tientsiensis) on to the metal flow in the food chain. The faeces of *Helice tridens* tientsiensis were used as a marker of the regulation/control mechanism. Bio-available metals in both the sediments and faeces will be measured and used in the food chain analysis for the bio-magnification effect.

MATERIALS AND METHODS

Sampling and Storage

Sampling was conducted during November, 1998 on the tidal flat of Chongming Island and Hengsha Island (above sea level), in Yangtze Estuary, locations of which were N.31°21′090″, E.121°44′198″ and N.31°17′625″ and E.121°51′738″. Sediment samples were collected at intervals up to 10 cm depth at 20 locations at the study site.

More than 170 individual and nearly 200 individuals of *Ilyoplax deschampsi* and *Helice tridens* tientsinensis (half male and half female) were picked out randomly to measure the width of carapace.

Fresh faeces of *Helice tridens* tientsinensis were separated from the sediments and obtained in the morning before flooding.

Sediment and Faeces

Sediment samples and faeces samples were collected by plastic spoon and kept in plastic bags at 4°C. Immediately after taken to the laboratory, samples were dried at 110°C in a muffle furnace for 8 hours. They were then ground, homogenised and kept at 4°C for further needs. A sequential extraction process (Fig. 1) was used to show the metals in exchangeable (EP), easily reducible (ERP), iron and manganese oxides (FMOP), organosulphide (OSP) and residual (RP) phases (Tessier *et al.*, 1979; Han *et al.*, 1996).

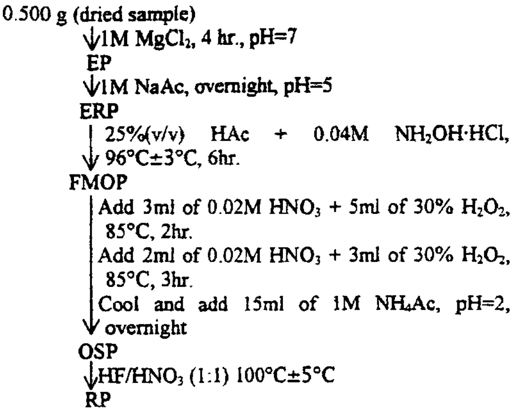

FIGURE 1 Flow chart for sequential extraction procedure.

Biota

The biological samples were rinsed rapidly by distilled water. *Helice tridens* tientsinensis with the same carapace width were divided into four groups, two for males and the other two for females. Each group contained 5 individuals. *Ilyoplax deschampsi* were divided randomly, about 85 individuals per group.

The samples were dried at 70°C for 8 hours, then weighed, ground and homogenised. About 10 kg of each group was then heated in the muffle furnace at 450°C for 24 hours. The ashes were digested with nitric acid at nearly 100°C on the heat plate. The digestates were diluted with 1% hydrochloric acid for further measurements.

Heavy Metal Determination

Concentrations of zinc, copper, lead and cadmium in the digestates were determined by Plasma 2000 Inductively Coupled Plasma-Atomic Emission Spectroscopy (Perkin-Elmer Corp., Norwalk, CT, USA).

Data Analyses

Differences between experimental groups were evaluated by *T* test for paired or unpaired, or by factorial analysis of variance (ANOVA) combined with Fisher's protected least significant different test at the 95% significance level using Statistcia 4.5 (Statsoft Inc., 1993).

RESULTS AND DISCUSSION

Bioavailability of Metals in the Sediments and Faeces

Concentrations of five phases of zinc, copper, and lead in both sediments and crab faeces are listed in Table I. All phases and total amount of cadmium in both samples were too low to detect.

Table II shows the concentrations of zinc, copper, lead and cadmium in both kinds of samples collected from Hengsha Island. Zinc

TABLE I Concentrations of zinc, copper and lead in sediments and crab faeces from Chongming Island ($\bar{x} \pm$ sd) (mg/kg, dry weight)

	EP	*ERP*	*FMOP*	*OSP*	*RP*	*Σ*
			Sediment			
Zn	8.75 ± 2.01	1.75 ± 0.35	89.5 ± 20.87	13.00 ± 2.61	16.00 ± 1.65	129.25
Cu	0.50 ± 0.00	0.50 ± 0.00	3.14 ± 0.47	1.50 ± 0.71	4.50 ± 0.68	10.39
Pb	–	–	3.67 ± 0.47	–	–	3.67
			Crab faeces			
Zn	0.75 ± 0.35	2.75 ± 0.35	11.33 ± 0.92	7.50 ± 0.44	39.5 ± 1.24	60.58
Cu	2.00 ± 0.00	1.25 ± 0.35	1.47 ± 0.28	2.00 ± 0.12	10.00 ± 0.70	16.47
Pb	–	–	2.33 ± 0.47	–	–	2.33

TABLE II Concentrations of zinc, copper, lead and cadmium in sediments and crab faeces from Hengsha Island ($\bar{x} \pm$ sd) (mg/kg, dry weight)

	EP	*ERP*	*FMOP*	*OSP*	*RP*	*Σ*
			Sediment			
Zn	0.33 ± 0.01	5.50 ± 0.04	39.3 ± 7.07	4.80 ± 0.38	17.03 ± 2.40	99.96
Cu	0.47 ± 0.08	0.47 ± 0.19	26.50 ± 0.71	1.64 ± 0.05	12.80 ± 0.00	17.49
Pb	–	–	–	5.45 ± 6.36	10.39 ± 2.09	15.84
Cd	–	–	–	–	2.85 ± 0.55	2.85
			Crab faeces			
Zn	0.53 ± 0.01	1.13 ± 0.28	15.60 ± 1.98	5.60 ± 0.47	21.47 ± 0.01	44.32
Cu	0.33 ± 0.04	0.37 ± 0.15	22.50 ± 0.71	1.60 ± 0.00	14.32 ± 0.42	19.13
Pb	–	–	–	4.60 ± 2.83	8.40 ± 0.75	13.00
Cd	–	–	–	–	2.27 ± 0.23	2.27

and copper in the sediments of Hengsha Island had the same distribution as those in Chongming Island, that its FMOP and RP were the main phase for zinc and copper. FMOP of lead was too low to detect. Almost all the cadmium was in the residual phase.

In the sediment samples from both study sites, concentrations of iron and manganese oxides phase for zinc were the highest ones among all phases, those of the exchangeable phase were the lowest. For copper, the residual phase had the highest percentages (43.3%). Bio-available parts of zinc and copper (EP and EOP) were 8.4% and 12% of total amounts in Chongming Island, 5.8% and 4.8% in Hengsha Island. Residual phase was the dominant phase for zinc and copper in the crab faeces from both study sites.

Except for copper in the samples from Hengsha Island, concentration of a residual phase for zinc and copper were found significantly higher in the faeces than in sediments ($P < 0.01$). Comparison between bio-available zinc and copper in both sediment and faeces samples shows that the crabs have different demands for these two essential elements (Fig. 2).

Sums of concentrations of exchangeable and easily reducible zinc in sediment samples were significantly higher than in faeces samples ($P < 0.01$). That is quite a lot of bio-available zinc was taken up by the crabs, which were lower than the crabs' demand. But for copper, concentration of bio-available copper in the faeces nearly as much

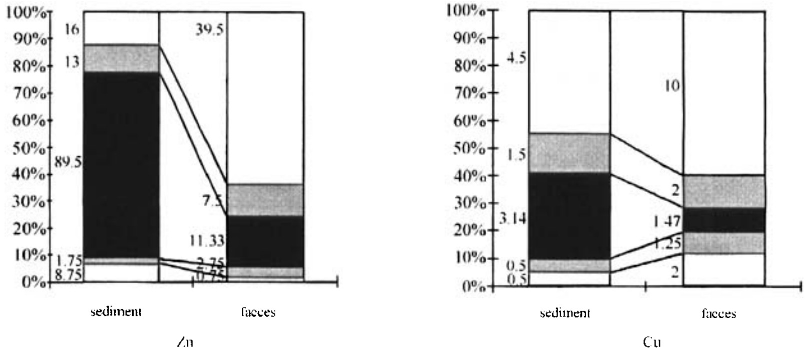

FIGURE 2 Comparison of metal phases in sediments and in crab faeces in Chongming Island (From top to ground, there are EP, ERP, FMOP, OSP and RP in turn. Numbers besides the columns are concentrations of corresponding phrases measured in mg/kg, dry weight).

as, or even a little more, than the sediments ($P > 0.9$). It is clearly that the crabs have such a mechanism of controlling the contents of copper in the body and excreting unnecessary parts.

Concentrations of iron and manganese oxides phase for zinc, copper and lead in the sediments were significantly higher than in the faeces ($P > 0.05$). Combination between metal ions and iron and manganese oxides would be weaker under the effect of pH and Eh, so that free ions of the metal would be released and available for organisms (Tessier *et al.*, 1979; Chen *et al.*, 1996). So this phase for metals can be accumulated in a certain part of the body, or used for metabolism and how they are used, needs further study.

Accumulation of Zinc, Copper, Lead and Cadmium in Crabs

Contents of heavy metals in the crabs got from Chongming Island are showed in Table III.

Because proteins and enzymes of most organisms need more zinc than copper, more zinc is taken up than copper. The result was accumulated in the crab bodies from both study sites than zinc. This result was a co-ordinate to the ones got above, that is to say, the crabs were absorbing more zinc ions and had accumulated enough copper in the bodies.

Cadmium in the sediment was hardly detected, but the contents of cadmium in the bodies were markedly higher than in the sediments ($P < 0.01$). However, concentrations of lead were too low to detect in the bodies, but higher in both faeces and sediments. Cadmium and

TABLE III Contents of heavy metals in the crabs of Chongming Island ($\bar{x} \pm \mathrm{sd}$) (mg/kg, ash weight)

	Zn	*Cu*	*Pb**	*Cd*
H. tridens tientsinensis (♂)	86.688 ± 6.577	171.198 ± 27.773	< 1.444	0.758 ± 0.192
H. tridens tientsinensis (♀)	94.830 ± 13.003	227.88 ± 43.566	< 1.058	0.878 ± 0.131
*I. deschampsi***	97.765 ± 7.184	180.635 ± 21.221	< 1.330	3.77 ± 0.608

*Analytical results of lead were below the measurement detection limit, a value of one-half the detection limit was regarded as the minimum limit.

** Unit: mg/kg, dry weight.

TABLE IV Heavy metals in the components of the simplified food chain in wetland ecosystem on Chongming Island (mg/kg, ash weight)

	Sediment		*Saltmarsh grass**		*Reed**		*H. tridens tientsinensis*		*I. des-champsi*	*Crab faeces*		*rufous-necked stint***
	BA	*RP*	*AG*	*UG*	*AG*	*UG*	♂$^{\#}$	♀$^{\#}$		*BA*	*RP*	
Zn	113	16	7.19	17.42	22.47	45.12	94.83	86.69	97.77	22.33	39.5	850.8
Cu	5.64	4.5	18.67	13.37	12.58	37.69	227.88	171.20	180.64	6.72	10	521.13
Pb	3.67		1.66	4.37	0.69	2.28	< 1.058	< 1.44	< 1.33	2.33		23.86
Cd	–		0.33	0.78	0.20	0.717	0.88	0.76	7.54	< 0.14		4.34

BA: Bio-available phases; RP: Residual phase; AG: Above ground part; UG: Under ground part; *Data from Lu and Tang, 1998; **Data from He and Lu, 1999; $^{\#}$ Unit: mg/kg, dry weight.

lead are both potentially hazardous to health. Crabs showed strong abilities of accumulating cadmium and excreting lead.

Ilyoplax deschampsi accumulated much more cadmium than *Helice tridens* ($P < 0.5$), reasons for which are: (1) they are smaller than *Helice tridens* tientsinensis, and have a relatively large surface area. Average carapace width of *Ilyoplax deschampsi* is 6 mm, and that of *Helice tridens* tientsinensis is 27 mm (female) and 33 mm (male). (2) *Ilyoplax deschampsi* may have a stronger ability of accumulating cadmium, which needs more study.

Partly because smaller size, female *Helice tridens* tientsinensis accumulated more elements than male ones did ($P < 0.05$) and it seems that they need more copper than males do.

Bio-magnification Effect

Contents of zinc, copper, lead and cadmium in the primary producers (salt marsh grass and reed) and secondary consumers (rufous-necked stint) were measured respectively (Lu and Tang, 1998; He and Lu, 1999). Small sized crabs are preyed frequently by waders such as rufous necked stint, especially *Ilyoplax deschampsi* (Cui *et al.*, 1986). So the crabs can be regarded as the primary consumers. Not all elements were bio-magnified along the food chain (Tab. IV).

Comparison of the contents of elements in the primary producers and secondary consumers shows bio-magnification effect of the food chain clearly. Birds have greater metabolism than the crabs, resulting more zinc and copper than the latter ones. The preying frequency of rufous necked stints in autumn and winter is higher than usual, for they need to gather energy for wintering. So the contents of metals in the body rise at that time. However, resulting from the regulation mechanism of excreting hazardous lead, concentrations of lead in the primary consumer are much lower than in the primary producers, especially *Ilyoplax deschampsi.* Concentration of cadmium in the bivalves collected from the same study site is also significantly higher than in sediments and primary producers (Ye *et al.*, 1999). Cadmium is removed from the physical environment largely by the macrobenthos, which will be potentially dangerous to their predators, such as waders and man. All together, cadmium can be graded as a more hazardous contaminant than lead.

CONCLUSIONS

1. Iron and manganese and residual phases of metals in both sediments and crab species; bio-available phases of exchangeable percentages and easily reducible ones in the Yangtze Estuary.
2. Crabs show regulation/accumulation mechanisms for both essential elements and non-essential ones, which enable them to excrete unnecessary copper ions and the hazardous element of lead, but accumulate much cadmium in the bodies.
3. Zinc and copper are bio-magnified along the food chain in the study sites. Less lead was found in the primary consumers than in the primary producers.
4. Macrobenthos have a strong ability of accumulating cadmium in the body, which will be potentially hazardous to the organisms at the higher trophic levels.

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