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Metal Contamination in the Sediment, Pondweed, and Snails of a Stream Receiving Effluent from a Lead/Zinc Mine in Southern China

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Abstract This study assessed the potential of *Potamogeton crispus* and *Pomacea canaliculata* as biomonitors of sedimentary metal contamination. The results indicate *P. crispus* possesses several attributes of a biomonitor and its tissue concentrations of Cd, Pb and Zn may reflect the levels of sedimentary contamination by these metals. Although *P. canaliculata* can accumulate metals to high levels and serve as an indicator of metal contamination, its tissue metal concentrations did not correlate with those of the sediments or macrophytes.

Keywords *Pomacea canaliculata* · *Potamogeton crispus* · Heavy metal · Biomonitor

Metal contamination may result in reduced biodiversity. Fankou Stream received the effluent from the wetland treatment ponds of Fankou Pb/Zn Mine in southern China and this had resulted in the appearance of a few species of hydrophytes and macrobenthos (Fig. 1). However, apple snail *Pomacea canaliculata* (Lamark) and curlyleaf pondweed *Potamogeton crispus* L. were abundant. The snails are found bear broken leaves of some pondweed, indicating grazing by the snails. A previous study has shown that the wetland can remove large proportions of Cd (91%), Pb (95%) and Zn (80%) in the effluent (Lan et al. 1992). Although the effluent discharged into the stream contains low levels of Cd (2 μg/L), Pb (87 μg/L) and Zn (384 μg/L) in the water, the level of total suspended solid, a mixture of mud and mineral particles, is still quite high (46 mg/L) (Lan et al. 1992).

This study investigated Cd, Pb, Zn and Cu in the sediments, pondweed and apple snail in Faukou Stream, and assessed the potential of pondweed and apple snail as biomonitors of sedimentary metal contamination. Although a few hydrophytes (Sabti et al. 2000; Cardwell et al. 2002) and gastropods (Berger and Dallinger 1993; Flessas et al. 2000) have been proposed as biomonitors of freshwater metal contamination, such potential has not been examined in an ecosystem dominated by the pondweed and apple snails, both very common in subtropical Asia and America.

Materials and Methods

Samples were collected from Fankou Stream, which receive the wetland-treated effluent from Fankou Pb/Zn Mine (24°25′25″ N, 113°31′30″ E) (Fig. 1). The mine is located 48 km to the northeast of Shaoguan, Guangdong Province. The mean annual rainfall is 1,457 mm, and the mean annual temperature is 20°C with extreme values of −5°C in January and 40°C in July. The mine has been in operation since the 1950s, and currently generates 2.2×10^7 m^3 raw effluent per annum. To reduce metal levels, an 87,500 m^2 settling pond (P1) was constructed in 1983, with the cattail (*Typha latifolia* L.) planted in the shallow areas. New ponds (P2-P4) were subsequently constructed in 1988, 1995 and 1998 to a total area of

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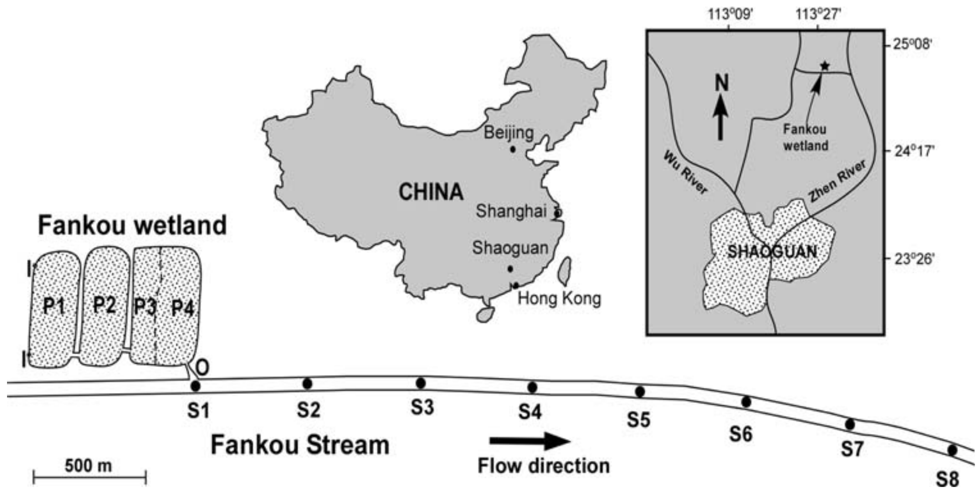

Fig. 1 Map of the Fankou wetland showing the water inlet (I), outlet (O), interconnected treatment ponds (P1-P4), sampling sites (S1-S8), and maps showing the location of the study area in China and the region (insets left and right)

185,000 m^2 to accommodate the increased deposition of tailings. The cattail, together with hydrophytes *Phragmites communis* (L.) Trin., *Cyperus malaccensis* Lam., and *Paspalum conjugatum* Berg., occupies approximately 75% of the total pond area.

Sampling was conducted in March 2004 from the wetland outlet to 3.5 km downstream where the water was less than 1 m deep and where apple snails were mainly found on sediment and among mats of pondweed. Despite the potential risk of pollution, the stream water was used for irrigation of the paddy fields along the stream. Further downstream, the abundance of snails became rare, probably because of the lack of the pondweed for refuge and food, which did not occur in deep waters due to the lack of sunlight. Eight sampling sites were equally spaced (500 m between sites) along the section of the stream. At each site, 3 composite leaf samples of pondweed and 8 samples of several snails of similar sizes (3.0–3.6 cm shell height) were collected. Since dissection of snails showed mineral particles in the viscera, gut purging was conducted in clean water by feeding them with Chinese white cabbage (*Brassica chinensis* L.). By the end of the 4-d depuration their faeces contained no visible sediment. Snails were then dissected into head-foot and viscera. Pondweed and snail tissues were rinsed with Milli-Q water, oven-dried and homogenized. A 0.5 g sample was weighed and digested with 5 ml 70% nitric acid. A standard reference material (LUTS-1 from National Research Council, Canada) was used concurrently during tissue digestion and measurement. Recovery efficiency ranged from 83% to 96%. Data were not corrected for recovery, which in some cases would slightly underestimate actual metal concentrations. At each site, triplicates of 2 L surficial sediment were also collected. Samples were air-dried, grounded, and sieved through a 2 mm-pore mesh. 0.25 g sediment was digested with concentrated HCl and $HClO_4$ (4:1 v/v). Standard reference sediment (SRM 2710 from National Institute of Standards and Technology, USA) was used concurrently during the sediment digestion and measurement. Recovery efficiency ranged from 80% to 103%. Data were not corrected for recovery. Multielemental analyses were performed using Inductively Coupled Plasma Atomic Emission Spectrometry (Perkin–Elmer, Plasma 400). Pearson's correlation analysis was used to assess the relationship between concentrations of different metals in the snail, pondweed, and sediment. The correlation analysis was used between metal concentrations and distance from the wetland.

Results and Discussion

Figure 2 shows concentrations of Cd, Cu, Pb, and Zn in sediment samples. At each site, Cd concentration was the lowest, followed in order by Cu, Pb and Zn. There were significant negative correlations between levels of Cd, Pb and Zn and distance ($r = -0.78$ to 0.82, $p < 0.05$), showing a decreasing trend of the metals with increasing distance from the treatment wetland. At Site 3, however, the levels of the 3 metals were lower than those of the next site downstream, indicating a local decreasing effect. An examination of the sediment particle sizes showed that the sediment of this site was not much coarser than that at Sites 2 and 4, despite the presence of a small agricultural discharge point nearby. Cu concentrations, however, did not display the same attenuation trend, and varied to a lesser degree along the stream. These different distribution patterns among the metals might be caused by the higher affinity between Cu and organic matter (Fernandes 1997; Ramos 1999), which slowed down the mobilization of Cu by the agricultural discharge at this site.

The data shown in Fig. 2 indicated that the sediments in the study area were heavily contaminated. Metal levels at most sampling sites were similar to (Cd, Cu and Zn) or

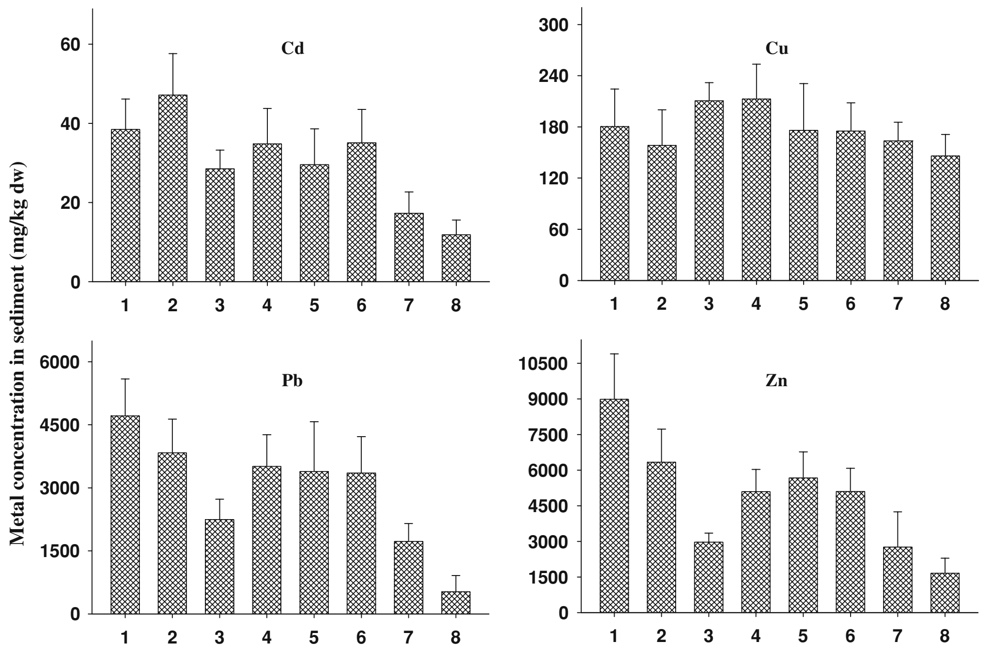

Fig. 2 Contents of metals, Cd, Cu, Pb and Zn (mean ± SD, mg/kg dw) in the sediments collected from eight sites along the Fankou Stream

about half (Pb) of the metal levels in the wetland sediments (Lan et al. 1992; Deng et al. 2004). Even at the furthest site from the constructed wetland where metal concentrations were the lowest, the level of Cd, Cu, Pb and Zn was still several folds of that of the corresponding metals in clean soils of the surrounding area. Except for Cu, the metal levels greatly exceeded the Maximum Allowable Heavy Metal Levels for agricultural soils in Austria, Poland, Canada, Japan, Germany, Great Britain (Cd 2–8 mg/kg, Cu 50–125 mg/kg, 100–500 Pb mg/kg, and Zn 250–300 mg/kg) (Kabata-Pendias and Pendias 2000). The results in this study indicate that the remaining metals discharged into the stream might still pose a threat to the aquatic flora and fauna in the studied area even although the wetland has retained a large proportion of the metals in the effluent.

Uncontaminated freshwater macrophytes typically contain concentrations of Cd $<$ 1.9 mg/kg, Cu $<$ 20 mg/kg, Pb $<$ 9.9 mg/kg, and Zn $<$ 66 mg/kg (Deng et al. 2004). Deng et al (2004) found high concentrations of Cd, Cu, Pb and Zn in both the roots and shoots of five wetland plant species, not including the pondweed, in the Fankou wetland. Compared to their study, the sampling area extended to 3.5 km downstream of the treatment wetland. The pondweed contained concentrations of Cd 0.6 to 83.9 mg/kg, Cu 10.3 to 44.9 mg/kg, Pb 111 to 2554 mg/kg, and Zn 366 to 3482 mg/kg (Fig. 3). At each site, Cd and Cu concentrations were lower than Pb and Zn concentrations. Levels of Cd, Pb and Zn decreased with the distance downstream of the wetland, and their correlations were negatively significant ($r = -0.72$ to 0.75, $p < 0.05$). Similar to the case of the sediments, Site 3 showed lower levels of the 3 metals than those of the next downstream site, indicating local attenuation. There was significant correlation between the concentrations of Pb and Zn in pondweed tissue and those of the corresponding metals in the sediment, indicating the importance of sedimentary metal-to-metal accumulation in the pondweed (Table 1). Cu concentration was the highest at Site 1 and the lowest at Site 8. However, the attenuation trend for Cu was not as obvious as for the other metals, suggesting Cu accumulation by the pondweed was less dependent on Cu level in the sediment. There is one exception, the metal levels of Cd in the pondweed at Site 8 were much higher than what would be expected from uncontaminated macrophytes (Fig. 3). The result was consistent with a previous report of high levels of heavy metals in curlyleaf pondweed collected from the polluted sites (Sabti et al. 2000).

Figure 4 shows metal concentrations in head-foot and viscera of *P. canaliculata* along the stream. Although metal levels varied greatly in snails collected from different sites, there was no consistent spatial pattern of metal distribution along the stream, except at the furthest site (Site 8) where relative low metal levels were found. Except in one case (Cd in the viscera), there was no significant correlation between metals in the snail tissue and those in the sediment, neither was there significant correlation between metal concentrations in the pondweed and those in the snail (Table 1). Overall, however, the four metals showed a consistent pattern in which much higher levels were associated with the viscera, as compared with metal contents in the head-foot. This was consistent with a previous report of higher metal levels in the viscera than in other tissues in snails (Dallinger and Wieser 1984). High metal levels in the viscera suggest that diet might contribute more than water

Fig. 3 Cd, Cu, Pb and Zn (mean ± SD, mg/kg dw) in the pondweed collected from eight sites along Fankou Stream

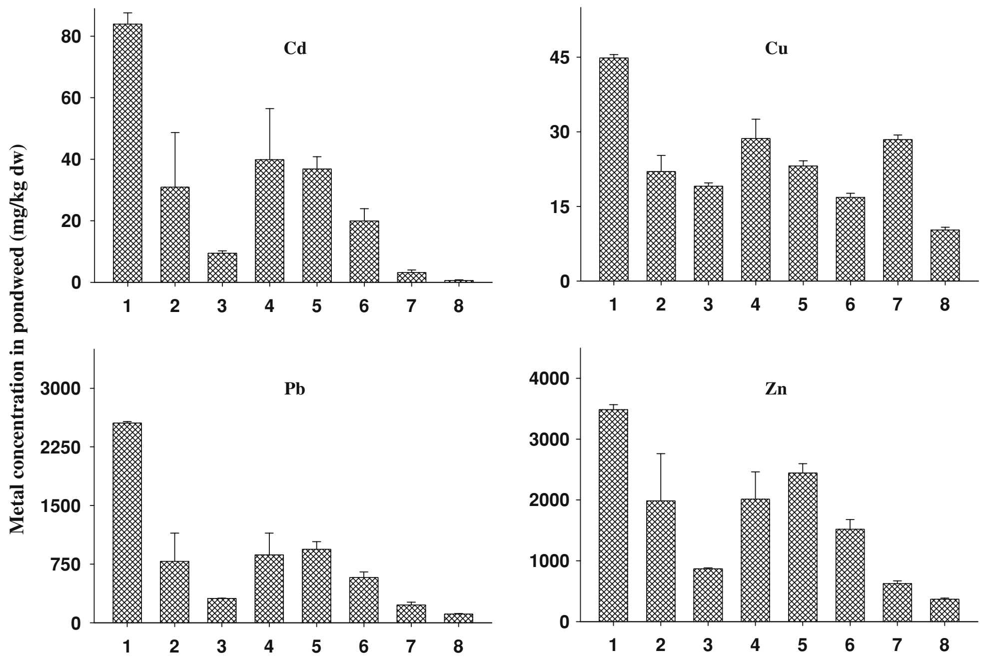

Table 1 Correlation between metal concentrations between the samples of sediment, pondweed, head-foot and viscera

	Sediment	Pondweed	Head-foot	Viscera
Cd				
Sediment	–			
Pondweed	0.64	–		
Head-foot	0.48	0.15	–	
Cu				
Viscera	0.71*	0.40	0.88*	–
Sediment	–			
Pondweed	0.29	–		
Head-foot	0.29	0.50	–	
Viscera	0.08	0.15	0.19	–
Pb				
Sediment	–			
Pondweed	0.81*	–		
Head-foot	0.31	0.14	–	
Viscera	0.53	0.52	0.89**	–
Zn				
Sediment	–			
Pondweed	0.97**	–		
Head-foot	0.14	0.15	–	
Viscera	0.32	0.29	0.31	–

Note: * and ** indicate statistically significance at $p < 0.05$ and 0.01, respectively

to the overall body burden of metals, whereas relatively low metal concentrations in the head-foot indicate the snails have developed some mechanisms to regulate translocation of metals from head-foot to the viscera. The metal concentrations in the head-foot, although lower than those in the viscera, still greatly exceeded the Maximum Level of Metals in Fisheries Products in China (Cd 0.1 mg/kg, GB15201-94; Cu 10 mg/kg, GB15199-94; Pb 0.5 mg/kg, GB14935-94; Zn 50 mg/kg, GB13106-91) (MPH and CSA 1991–1994). The highly contaminated snails might thus provide a source of metal accumulation for animals of high trophic levels, such as several species of fish, which have been reported in the Fankou Wetland (Lan et al. 1992) and were likely to feed on apple snails (Cowie 2002).

The data of the present study did not show that the metal contents in the snails and hydrophytes were correlated. Positive correlation of metal levels in the snails and in the sediment was found only in one case, i.e. between Cd in the viscera and sedimentary Cd. Such a lack of correlation might be related to the snail's feeding habit. In addition to the pondweed, the snail might feed on the epibiota on the streambed, and thus accidentally ingest sediments. Future studies to quantify metal accumulation in this snail with a general feeding habit should thus consider the contribution from different uptake pathways.

In conclusion, our results showed that the section of the stream investigated was still heavily contaminated by heavy metals at the time of sampling. However, there was a trend of attenuation in the levels of Cd, Pb and Zn in the sediment and the pondweed with increasing distance from the wetland treatment ponds. The sediment, curlyleaf pondweed, and apple snail all contain high levels of the metals. The pondweed possesses several attributes of a biomonitor (Phillips 1990): abundant throughout Eurasia, Africa, Australia and North America, tolerant to high levels of metal contamination, and occurring in metal contaminated area as a dominant

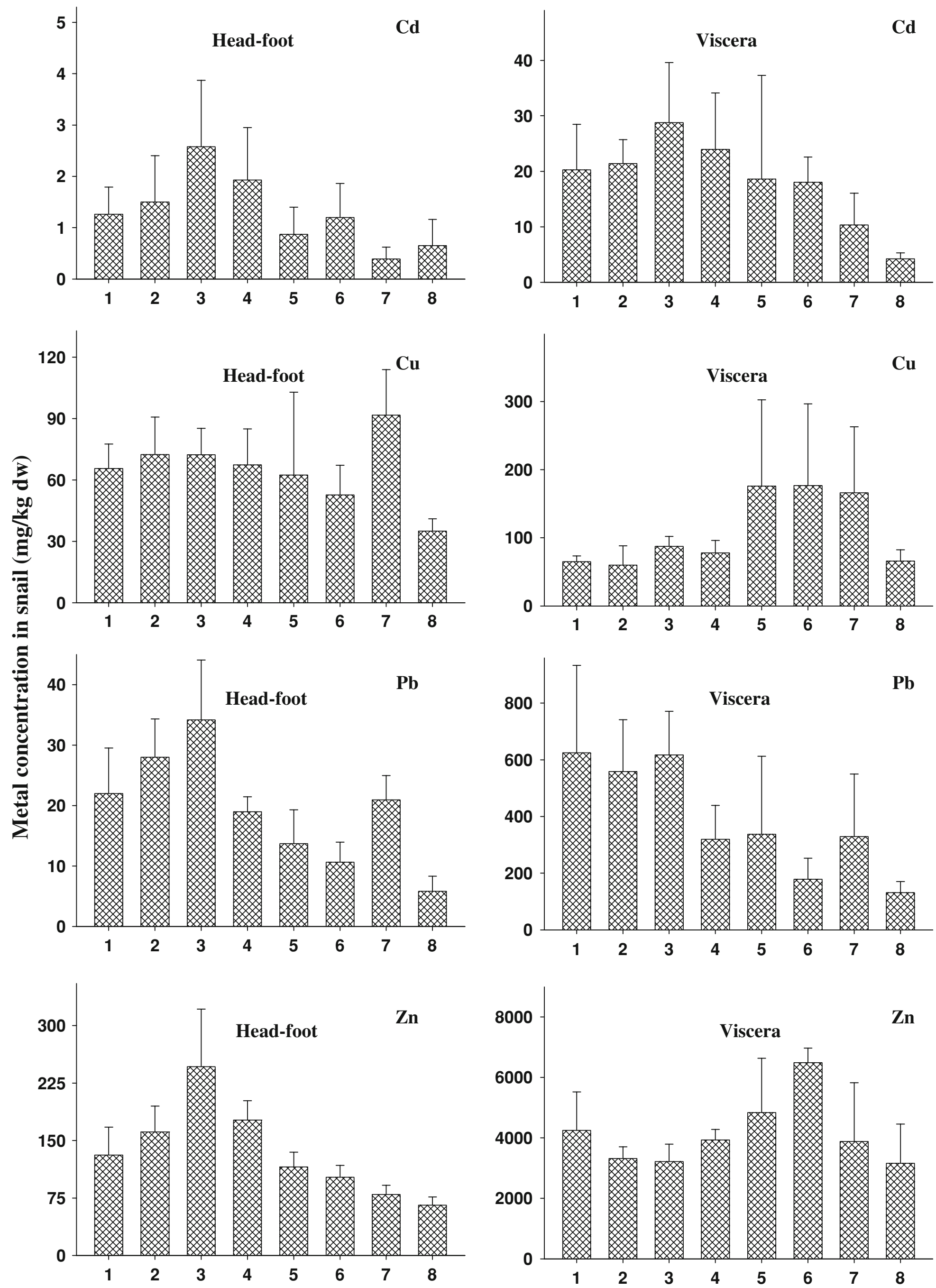

Fig. 4 Cd, Cu, Pb and Zn (mean ± SD, mg/kg dw) in snails collected from the eight sites along the Fankou Stream

hydrophyte. Our data indicate that its tissue concentrations of Cd, Pb and Zn may reflect the levels of sedimentary contamination by these metals. However, the pondweed is not available for sampling during the summer in many places when the upper ground tissues died off. The apple snail, although common in South America and Asia, tolerant of metal pollution, available year round, relatively sedentary and being an important link in the wetland food chain, can only serve as an indicator of metal contamination, because its tissue metal concentrations did not correlate with those of the sediments or macrophytes in this study.

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