

## Heavy metals associated with reduced sulfur in sediments from different deposition environments in the Pearl River estuary, China

Fanrong Chen<sup>1,2,4</sup>, Yongqiang Yang<sup>1,3</sup>, Derong Zhang<sup>1,3</sup> & Ling Zhang<sup>1,3</sup>

<sup>1</sup>Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 510640 Guangzhou, P.R. China

<sup>2</sup>Key Laboratory of Marginal Sea Geology, Chinese Academy of Sciences, 510640 Guangzhou, P.R. China

<sup>3</sup>Graduate School, Chinese Academy of Sciences, 100049 Beijing, P.R. China;

<sup>4</sup>Author for correspondence (tel: +86-20-85290291; fax: +86-20-85290130; e-mail: frchen@gig.ac.cn)

Received 1 February 2005; Accepted 6 February 2006

**Key words:** bioavailability, deposition environment, heavy metals, Pearl River estuary, sediment pollution

### Abstract

Distribution of acid volatile sulfur (AVS) and the simultaneously extracted metals (SEM: Cu, Pb, Zn, Cd, Ni) in sediment profiles has been studied at five sites in Pearl River estuary, China. Of the five sampling locations, Nos.1 and 2 are in the middle shoal, Nos.3 and 4 in the west shoal and No. 5 locates to the south of the estuary. The AVS content in the sediments of the middle shoal varies in a small range (0.25–4.06  $\mu\text{mol g}^{-1}$ ), while that of west shoal increases with depth from 0 to ultimately 26.09  $\mu\text{mol g}^{-1}$ . The SEM concentration in the sediment profiles at location Nos. 1, 2 and 5 is generally in the range of  $0.95 \pm 0.2 \mu\text{mol g}^{-1}$  with a slight upward increase, while that in the sediment of west shallows are much higher (1.43–2.42  $\mu\text{mol g}^{-1}$ ) with a significant upward increase, especially in the upper layer of ca. 15 cm. The observed upward increase of SEM content at all the sites implies that heavy metal contamination of sediment in the Pearl River estuary is increasing. Calculations of the excess heavy metal content which is defined by SEM-AVS molar difference suggests that the upper sediment in the Pearl River estuary, especially on the west shallows, could be a source of heavy metal contaminants and may cause toxicity to the benthos. The site-specific distribution patterns in the AVS and SEM profiles were interpreted according to the hydrogeochemistry of deposition environments.

### Introduction

Estuaries have been the focal point for a wide variety of human activities and are also important to many forms of animal life. They often form sinks for sediment, which is the most important reservoir or sink of metals and other pollutants (Salomons & Förstner 1984; Ridgway & Shimmield 2002). However, some of the sediment-bound metals may be remobilized and released back to waters with a change of environmental conditions, and impose adverse effects on living organisms. Substantial evidences have been established that acid volatile sulfide (AVS), mainly composed of the reduced sulfur in FeS, would be an important control on

heavy metal reactivity and toxicity in sediments (Di Toro *et al.* 1992; Cooper & Morse 1998; Lee *et al.* 2000; Teasdale *et al.* 2003; Machado *et al.* 2004). According to the AVS criteria, many divalent transition metals (e.g.,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ ) can replace iron cation from amorphous FeS in sediment to form very insoluble sulfide precipitates. As a result, when there is enough AVS available to bind the simultaneously extracted transition metals (i.e., SEM/AVS molar ratio is less than one), no toxic effect is expected from these metals.

In last two decades, the massive economic growth and urban development in the Pearl River delta region has led to excessive release of waste

into the estuarine and coastal environment (Huang 1995; Wen *et al.* 1995) and resulted in the increase of heavy metal content in the sediments of the Pearl River estuary (Li *et al.* 2000, 2001). Based on the analysis of AVS, SEM and reactive iron in sediment cores, this research was designed to assess the bio-availability and sulfide instability of reactive metals (Cu, Cd, Ni, Pb and Zn) in the sediments from a number of hydrogeochemical environments, and to provide clues to layout the spatial variation of heavy metal toxicity in the estuary.

## Methodology

### Study area

The Pearl River estuary locates in southern Guangdong Province of China. The main estuary which is also called Lingdingyang, is a bell-shaped area widening to the south (Figure 1), with a N-S distance averaging about 49 km and the W-E width ranging from 4 to 58 km. The annual water

flow rate of the Pearl River is about  $11100 \text{ m}^3 \text{ s}^{-1}$ , ranking the second largest of the river flow rates in China (Wong *et al.* 1995). The whole study area is within the sub-tidal zone with strong fresh water and marine water inter-reactions and circulation currents along the west coast, while the eastern part of the estuary is significantly affected by tidal currents from the open sea (Zheng 1992; and Wong *et al.* 1995).

Two natural waterways which merge near the Humen outlet, separate the estuary into three shoals namely west shoal, middle shoal and east shoal. The west shoal is the largest one and is adjacent to the other three Pearl River outlets, namely Jiaomen, Hongqimen and Hengmen from north to south, respectively. The general sediment class in the shoals is silty clay, and that in the channels is silty sand deposited under more intensive hydrodynamic conditions (Li *et al.* 2000).

### Sampling

Sediment cores were collected in October 2003 at five sites representing different hydrogeochemical

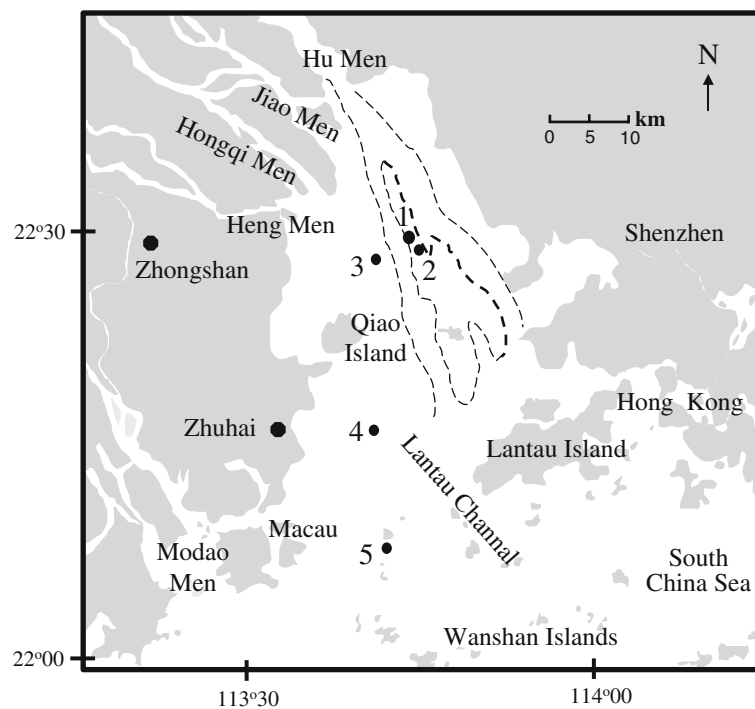


Fig. 1. Map of the Pearl River estuary showing the locations of sampling sites.

environments in the estuary (Figure 1). Site 1 and 2 are in the middle shoal, site 3 and 4 locate in the west shoal and are, respectively, adjacent to the outlets of the Pearl River and downstream a sea-farming field, and site 5 locates to the south of the estuary. The details of the sampling sites are given in Table 1.

A multiple corer was used to collect the sediment cores from all sites. The corer was able to sample four separate and usually undisturbed sediment cores within an area of less than 0.3 m<sup>2</sup> each with a volume of overlying water. The plastic core tubes were 10 cm in diameter and 61 cm long, and the length of sampled sediment cores was in the range of 28 to 40 cm. One core from each site was used for analyzing AVS and SEM. After sampling, the cores with overlying water were covered using Teflon caps and placed in a water bath at the *in-situ* temperature for less than a few hours. When slicing, a sediment core was mounted vertically on a specifically designed core slicing device and the sediment was extruded upward by a plastic piston fitting into the core tube and connecting to a screw bar with a screw thread interval of 2 mm. The sediments were sectioned at an interval of 2 cm in an Ar-filled glovebag and immediately placed in polyethylene bottles filled with Ar. All the sediment samples were store at -18 °C and analyzed in a few days.

### Analysis

Grain size analysis was performed by wet sieving to separate silt and clay (<0.063 mm) and sand (>0.063 mm) fractions. For the determination of AVS and SEM a procedure was developed which is largely analogous to the one described by Allen *et al.* (1993). Briefly, the experimental set-up consists of a reaction vessel followed by two

sequentially connected trapping vessels. Initially, the reaction vessel and each of the trapping vessels contain 50 ml super-pure water and 50 ml trapping solution (0.5 M NaOH solution), respectively. After purging with water-saturated super-pure Ar for 10 min, the sediment sample (about 10 g of wet sediment) was added to the reaction vessel, and the system was purged with the super-pure Ar for another 10 min while stirring the sediment suspension in the reaction vessel to thoroughly remove oxygen from the system. After reducing the Ar flow to zero, 10 ml of 6 M hydrochloric acid was added to the reaction vessel by inserting through the silicone pipe, and the pinhole was sealed immediately. Then the Ar flow rate was slowly increased to about 40 cm<sup>3</sup> min<sup>-1</sup>, and the reaction lasted for at least 40 min while purging with Ar and stirring with polyethylene coated magnetic stirrer. The sulfide in the trapping vessel was determined using iodometric titration. The AVS recovery of the experimental procedure was checked by using sodium sulfide solution with known concentration and appeared to be larger than 95%, and the detection limit was 0.05 mg net weight of H<sub>2</sub>S. Preextractin spikes of Cu, Pb, Zn, Cd, Ni were added to a variety of sediment samples with different AVS contents, and the average recovery (4 analysis) of the spiked metals was found to be 96.9% for Cu, 92.8% for Pb, 94.8% for Zn, 89.5% for Cd, and 85.6% for Ni.

The resulting sediment suspension was centrifuged at a rate of 4800 rpm. The supernatant was volumetrically scaled to 100 ml and analyzed for Cd, Cu, Pb, Zn, Ni and Fe using ICP-AES. For duplicate analysis, the relative standard deviation of the AVS-content and SEM-content was found to be less than 10% and 3%, respectively. The results are presented as  $\mu\text{mol g}^{-1}$  dry sediment.

Table 1. Sampling site locations in the Pearl River estuary.

Sampling Location	Latitude	Longitude	Water Depth (m)
1	22°29.5' N	113°45' E	6
2	22°28.5' N	113°46.5' E	5
3	22°28' N	113°42' E	4.5
4	22°16' N	113°42' E	6
5	22°8' N	113°43' E	7.5

## Results and discussion

### Grain size distribution

Fine grained sediments (<0.063 mm) dominated all stations as expected (Figure 2). The fine grained fraction decreases upwards in the upper portion of sites 1 and 2, slightly lower in the surface sediments (0–4 cm) at sites 3 and 5, but no grain size variation with depth was found at

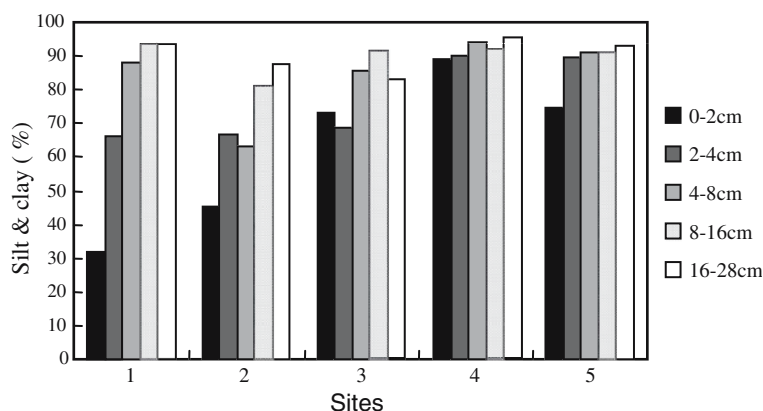


Fig. 2. Variation of grain size fraction (<0.063 mm) at the five sampling sites.

site 4. Pearl River delta is one of the most prosperous economic regions in China. As a result of rapid reclamation, the northwestern coastline has moved seaward at a rate of  $156 \text{ m a}^{-1}$  (Liu *et al.* 1998), which may account for the vertical variation of sediment grain size at relevant sites.

#### AVS profiles

All the AVS profiles within the estuary (sites 1–4) show an increasing trend in AVS levels with depth (Figure 3a–d), which agrees with the general recognition that sulfides in sediments are produced by biogeochemical reduction of  $\text{SO}_4$  under anoxic conditions (Urban *et al.* 1994; Morse & Luther 1999), and with many AVS distribution patterns observed in sediment cores from other places (e.g., Van den Hoop *et al.* 1997). However, AVS concentration range and vertical variation pattern in sediment cores are controlled by sediment source, deposition environment and diagenetic reactions, and can be quite different from location to location (Correia & Costa 2000; Morse & Luther 1999;

Van den Berg *et al.* 2001). The AVS content in the sediments of the middle shoal varies in a small range ( $0.25\text{--}4.06 \mu\text{mol g}^{-1}$ ), while that in the anoxic sediments of the west shoal is much higher with a maximum value of  $26.09 \mu\text{mol g}^{-1}$ . The nearly continuous increase in AVS content with depth in the profile at site 4 (Figure 3d) is indicative of steady-state deposition (Van den Berg *et al.* 2001). Whereas, the AVS content in the sediment of upper approximately 8 cm below the sediment-water interface (SWI) at site 3 is close to detection limit, suggesting that the surface sediment should be aerated to prevent the reduction of  $\text{SO}_4$ , presumably due to the sediment suspension caused by the currents from the Pearl River tributaries. The elevated sediment AVS content in the west shoal may result from the enhanced deposition flux of organic matter from the Pearl River and/or the upstream sea-farming field.

By contrast, the sediment core at site 5 is characterized by a peak in the AVS profile a few cm below SWI, with the AVS level in the surface sediment similar to that in the deeper sediment (Figure 2e). This type of AVS profile pattern is

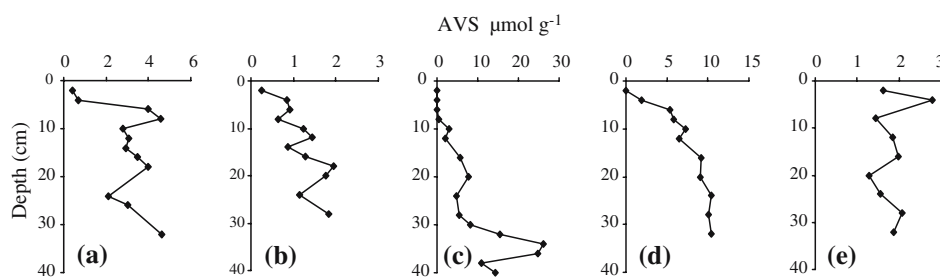


Fig. 3. AVS profiles of the sediment at different sites.

most probably to form in a non-steady state deposition environment where occasional re-suspension and settling of anoxic sediment would elevate the AVS content in surface sediments (Matisoff & Holdren 1995; Van den Berg *et al.* 2001).

*SEM distribution*

Depth distributions of simultaneously extracted Cu, Pb, Zn, Ni, Cd and total SEM are shown in Figure 4. In general, the sediment cores from the middle shoal and outside the estuary have low

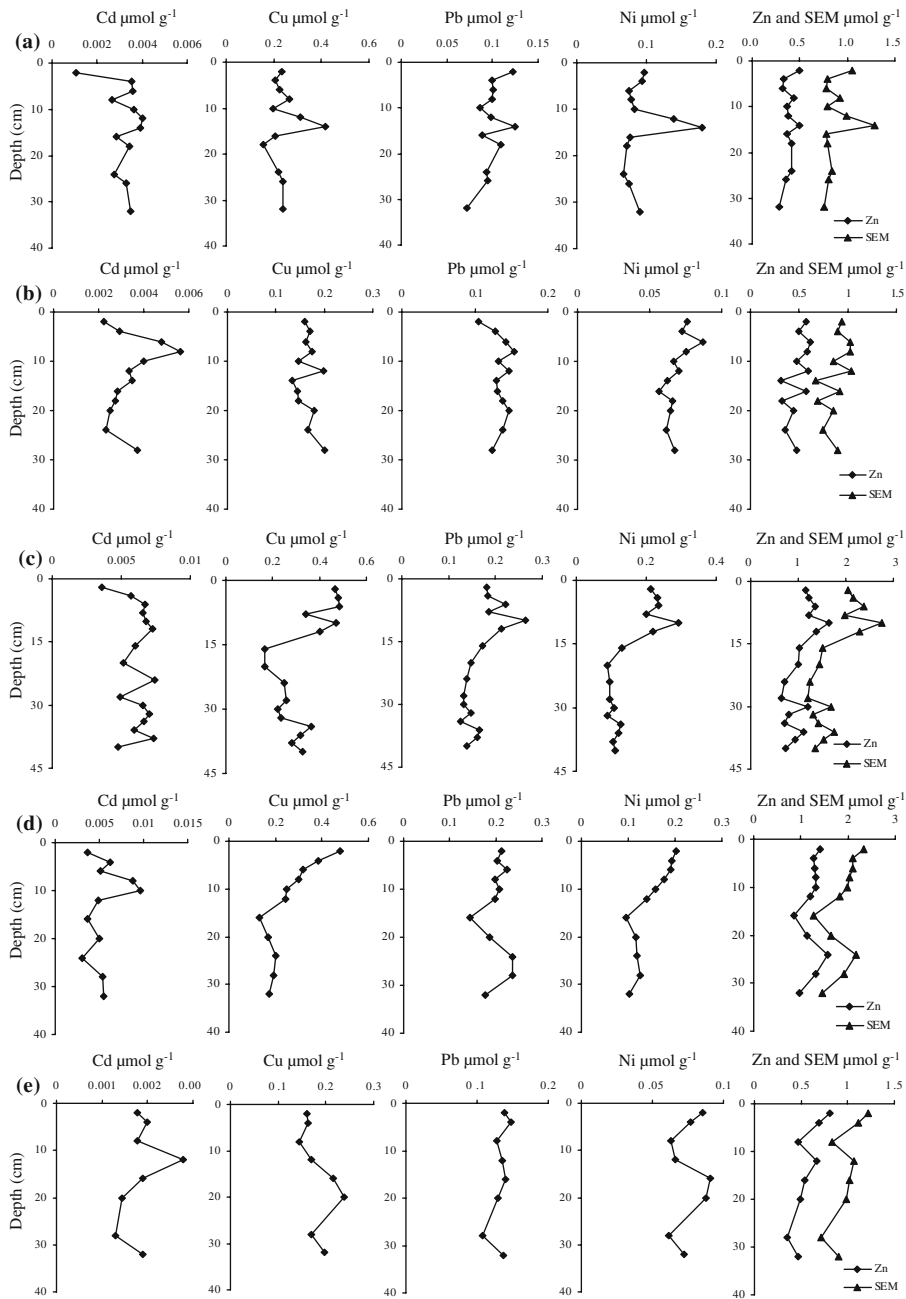


Fig. 4. Distribution patterns of selected heavy metals and SEM in the sediment profiles.

and relatively constant SEM contents ranging from 0.75 to 1.15  $\mu\text{mol g}^{-1}$  with a slight upward increase, whereas the SEM contents of the sediment cores from the west shoal are much higher (1.43–2.42  $\mu\text{mol g}^{-1}$ ) with a significant upward increase, especially in the upper layer of ca. 15 cm below SWI.

Though operationally defined, SEM is predominated by sulfide-bounded and adsorbed heavy metals. Sulfide is formed by anaerobic degradation of organic matter, and fine-grained particles (clay minerals and amorphous iron oxyhydroxide) are major sorbents of heavy metals. It is known that sediment characteristics, such as organic matter and metal concentrations are dependent upon <0.063 mm grain size fraction (Mucha *et al.* 2004; Hu *et al.* 2006). Thus, the upward increase of SEM in the upper part of sites 1 and 2 would have been abated by the lower content of fine-grained fraction of the sediment (Figure 2). A detailed examination of the single element and SEM profiles reveals that there is no significant concentration difference among the profiles for Cu, Pb, Cd and Ni, with Zn

dominating the SEM in all the sediment cores. As a result, the SEM distribution patterns are largely determined by Zn distribution. The observed upward increasing trend of SEM content at all the locations may imply that heavy metal contamination of the sediment in the Pearl River estuary is increasing. Elevated heavy metal content in the sediment of west shoal was also observed by Li *et al.* (2000) and was proposed to reflect the direct inputs from the Pearl River tributaries. Further, the apparent coherent increase of Zn, Cu and Ni content in the upper 15 cm of the sediment cores from the west shoal (Figure 4c, d) indicate that the anthropogenic source of these metals could be most probably related to sewage sludge (Halcrow *et al.* 1973; Alloway 1990). By contrast, the low and relatively constant content of lead may imply its distinctiveness of the source or biogeochemical behavior in diagenetic processes.

#### AVS and SEM relationship

In order to assess the reactivity and bioavailability of the heavy metals of concern, the relationship

Table 2. Concentrations of AVS and reactive iron and related ratios in the sediment of 0–10 cm below SWI.

Locations	Depth (cm)	AVS ( $\mu\text{mol g}^{-1}$ )	Fe ( $\mu\text{mol g}^{-1}$ )	AVS/SEM	FeS/Fe
1	0–2	0.41	130.94	0.39	0
	2–4	0.69	140.37	0.88	0
	4–6	4.00	162.11	5.16	0.020
	6–8	4.60	171.34	4.97	0.021
	8–10	2.81	176.40	3.54	0.011
2	0–2	0.25	107.05	0.27	0
	2–4	0.84	121.94	0.94	0
	4–6	0.91	136.26	0.88	0
	6–8	0.64	126.88	0.62	0
	8–10	1.24	125.36	1.45	0.003
3	0–2	UD	161.37	0	0
	2–4	UD	159.42	0	0
	4–6	UD	170.76	0	0
	6–8	0.56	169.70	0.28	0
	8–10	2.91	228.07	1.05	0.001
4	0–2	UD	172.92	0	0
	2–4	1.88	180.53	0.9	0
	4–6	5.39	195.42	2.57	0.017
	6–8	5.81	191.91	2.85	0.020
	8–10	7.26	184.62	3.65	0.029
5	0–2	1.63	145.00	1.33	0.003
	2–4	2.79	141.74	2.51	0.012
	6–8	1.45	141.65	1.74	0.004
	8–10	1.84	154.75	1.72	0.002

The FeS content is assumed to be equal to the excess AVS (EAVS: AVS-SEM molar difference) when the EAVS is positive and is set to zero when EAVS is negative;  
UD = under detection limit.

Table 3. Concentrations of simultaneously extracted Pb, Zn and Cu and excess SEM in the surface (0–2 cm) sediments from different sites.

Sampling stations	Cu ( $\mu\text{mol g}^{-1}$ )	Pb ( $\mu\text{mol g}^{-1}$ )	Zn ( $\mu\text{mol g}^{-1}$ )	SEM-AVS ( $\mu\text{mol g}^{-1}$ )
1	0.21	0.10	0.34	0.40
2	0.16	0.11	0.57	0.71
3	0.47	0.18	1.15	2.01
4	0.48	0.21	1.41	2.42
5	0.16	0.14	0.81	<0
Background values*	0.47	0.12	1.26	

\*Background values in Chinese coastal areas (Zheng *et al.* 1992).

among AVS, SEM and reactive iron has been examined in the sediment profiles. As can be seen in Table 2, the surface sediments within the Pearl River estuary have AVS/SEM molar ratios of less than one, indicating that the SEM is only partially immobilized by metal sulfides. The simultaneously extracted Cu, Pb, Zn and excess heavy metal contents in the surface sediments are significant as compared with the background metal content values in the sediments of Chinese coastal areas (Table 3), and the excess heavy metal content in the surface sediment from the west shoal is close to or even higher than the background values. Thus, the surface sediment in the Pearl River estuary, especially on the west shoal, could be a source of heavy metal contaminants and may cause toxicity to the benthos. The AVS/SEM molar ratios in the sediment core from site 5 are higher than one, thus, toxic effects are not expected to result from these metals.

Moreover, the sulfide-associated heavy metals could be remobilized during sulfide oxidation caused by, for example, sediment resuspension and bioturbation (Morse 1994; Cooper & Morse 1996). Previous research has indicated that when above 20% reactive Fe is bound to AVS, there is enough sulfide to effectively trap trace metals, and temporal variations in AVS and pyrite do not necessarily result in temporal variations in diagenetically-available concentrations of such metals within anoxic coastal sediments (Cooper & Morse 1998). In the studied area, the reactive Fe bounded to AVS in the sampled sediment cores is less than 3% in the upper 10 cm (Table 2) and less than 5%

in the upper 20 cm, indicating very low system stability with respect to sulfide-associated metals.

### Acknowledgements

This research was financially supported by Chinese Academy of Sciences (Grant ZKCX2-SW-212, 2000 (254)) and Guangzhou Institute of Geochemistry (Grant GIGCX-03-07).

### References

- Allen HE, Fu G, Deng B. 1993 Analysis of acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ Toxicol Chem* **12**, 1441–1453.
- Alloway BJ. 1990 *Heavy Metals in Soils*. London: Blackie.
- Correia AD, Costa MH. 2000 Effects of sediment geochemical properties on the toxicity of copper-spiked sediments to the marine amphipod *Gammarus locusta*. *Science Total Environ* **247**, 99–106.
- Cooper DC, Morse JW. 1996 The chemistry of Offatts Bayou, Texas: A seasonally highly sulphidic basin. *Estuaries* **19**, 595–611.
- Cooper DC, Morse JW. 1998 Biogeochemical controls on trace metal cycling in anoxic marine sediments. *Environ Sci Technol* **32**, 327–330.
- Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Carlson AR, Ankley GT. 1992 Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environ Sci Technol* **26**, 96–101.
- Halcrow W, Mackay DW, Thornton I. 1973 The distribution of trace metals and fauna in the Firth Clyde in relation to disposal of sewage sludge. *J Mar Biol Assoc UK* **53**, 721–739.
- Hu JF, Peng PA, Jia GD, Mai BX, Zhang G. 2006 Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. *Marine Chemistry* **98**, 274–285.
- Huang XP. 1995 Application of the receptor model to research on heavy metal pollution of sediments in Lingdingyang estuary. *Trop Oceanol* **14**, 1–6 (in Chinese).
- Lee JS, Lee BG, Luoma SN, Choi HJ, Koh CH, Brown CL. 2000 Influence of acid volatile sulfides and metal concentrations on metal partitioning in contaminated sediments. *Environ Sci Technol* **34**, 4511–4516.
- Li XD, Wai OWH, Li YS, Coles BJ, Ramsey MH, Thornton I. 2000 Heavy metal distribution in sediment profiles of the Pearl River estuary, China. *Appl Geochem* **15**, 567–581.
- Li XD, Shen ZG, Wai OWH, Li YS. 2001 Chemical forms of Pb, Zn and Cu in the sediment of Pearl River estuary. *Mar Poll Bull* **42**, 215–223.
- Liu Y, Han M, Wu L, Nobuo M. 1998 Recent evolution of outlets in Zhujiang River delta and the prospect for land reclamation. *Acta Geogr Sin* **53**, 492–500 in Chinese with English abstract.

- Mucha AP, Teresa M, Vasconcelos SD, Bordalo AA. 2004 Vertical distribution of the macrobenthic community and its relationship to trace metals and natural sediment characteristics in the lower Douro estuary, Portugal. *Estuar Coast Shelf Sci* **59**, 663–673.
- Machado M, Carvalho MF, Santelli RE, Maddock JEL. 2004 Reactive sulfides relationship with metals in sediments from a eutrophicated estuary in Southeast Brazil. *Mar Pollut Bull* **49**, 89–92.
- Matisoff G, Holdren GR Jr. 1995 A model for sulfur accumulation in soft water lake sediments. *Water Resour Res* **31**, 1751–1760.
- Morse JW. 1994 Interaction of trace-metals with authigenic sulfide minerals – Implications for their bioavailability. *Mar Chem* **46**, 1–6.
- Morse JW, Luther GWIII. 1999 Chemical influence on trace metal-sulfide interactions in anoxic sediments. *Geochim Cosmochim Acta* **63**, 3373–3378.
- Ridgway J, Shimmield G. 2002 Estuaries as repositories of historical contamination and their impact on shelf seas. *Estuar Coast Shelf Sci* **55**, 903–928.
- Salomons W, Förstner U. 1984 *Metals in the Hydrocycle*. Berlin: Springer.
- Teasdale PR, Apte SC, Ford PW, Batley GE, Koehnken L. 2003 Geochemical cycling and speciation of copper in waters and sediments of Macquarie harbour Western Tasmania Estuarine. *Coast Shelf Sci* **57**, 475–487.
- Urban NR, Brezonik PL, Baker LA, Sherman LA. 1994 Sulfide reduction and diffusion in sediments of little Rock, Wisconsin. *Limnol Oceanogr* **39**, 797–815.
- Van den Berg GA, Buykx SEJ, Van den Hoop MAGT. 2001 Vertical profile of trace metals and acid volatile sulphide in a dynamic sedimentary environment: Lake Ketel, The Netherlands. *Appl Geochem* **16**, 781–791.
- Van den Hoop MAGT, Den Hollander HA, Kerdijk HN. 1997 Spatial and seasonal variations of acid volatile sulphide (AVS) and simultaneously extracted metals (SEM) in Dutch marine and freshwater sediments. *Chemosphere* **35**, 2307–2316.
- Wen WY, Zhang GX, Du WC 1995 A study on water pollution in the Zhujiang estuary. In Wong CK et al. (ed.) *Environmental Research in Pearl River and Coastal Areas*. Guangzhou China: Guangdong Higher Education Press, pp. 99–108 (in Chinese).
- Wong CK, Chu KH, Chen QC, Ma XL. 1995 *Environmental Research in Pearl River and Coastal Areas*, Guangzhou, China: Guangdong Higher Education Press.
- Zheng JL. 1992 The study of heavy metals in the Pearl River estuary. In Chen JS, Zhou JY, eds, *Heavy Metal Research in the Aquatic Environment of China*. Environmental Science Press of China, pp. 369–387 (in Chinese).