Bull. Environ. Contam. Toxicol. (2006) 76:831–839

DOI: 10.1007/s00128-006-0994-y

Bulletin of Environmental Contamination and Toxicology

Spatial Distribution and Partitioning of Heavy Metals in Surface Sediments from Yangtze Estuary and Hangzhou Bay, People's Republic of China

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Received: 15 November 2005/Accepted: 10 March 2006

Yangtze estuary and Hangzhou Bay are located on the coastal zone of the East China Sea continental shelf. The total coastline is about 1,500 km in length, encompassing roughly 60,000 km^2. Two major rivers, Yangtze River, the largest river in China, and Qiantang River flow into Yangtze estuary and Hangzhou Bay, respectively. The annual average water and sediment discharges from the Yangtze River and Qiantang River are 9.24×10^{11} m^3, 4.86×10^8 ton and 3.864×10^8 m^3, 6.587×10^6 ton, respectively (Lu and Huang 2004). Due to a considerable input of riverine particulate material into the area, extensive areas of marshes and muddy or sandy tidal flats have developed which are still extending in the mouth of the Yangtze River and Hangzhou Bay. The study area is rich in natural resources (e.g. seaweeds, crustaceans and mollusks), providing crucial functions to the larger ecosystem (e.g. spawning and nursery area for invertebrates and fish) and breeding habitats for a variety of birds and reptiles. The most important areas, based on biodiversity and production, are found at the mouth of Yangtze River, on the north and south sides of Hangzhou Bay and surrounding larger islands in Zhoushan archipelago. As an essential component of marine ecosystem, marine sediments have been providing nutrients for the marine organisms living in the area. In recent years, with rapid development of Yangtze River delta and Hangzhou Bay region, increasing heavy metal pollutants discharged directly or indirectly from land-based industry, agriculture and household have caused deteriorating impacts on the quality of the marine environment (ZEPB 2001). Since marine sediments also serve as the principal sinks for heavy metals, it is necessary to understand the transport mechanisms and chemical circles of trace metals in marine environment in order to evaluate their long-term effects on the living organisms. In this study, the two neighboring areas, Yangtze estuary and Hangzhou Bay, were investigated to establish the planar distribution patterns and fractionation of heavy metals in the surface sediments.

MATERIALS AND METHODS

The study area was located between 30°10'~31°26'N and 121°2'~122°20'E. In May 2003, sediment samples were collected at 7 stations (numbered A1 to A7) from Yangtze estuary and at 6 stations (number B1 to B6) from Hangzhou Bay (Fig.1). Water depth at the sampling sites varied from 0 to 11m while salinity of

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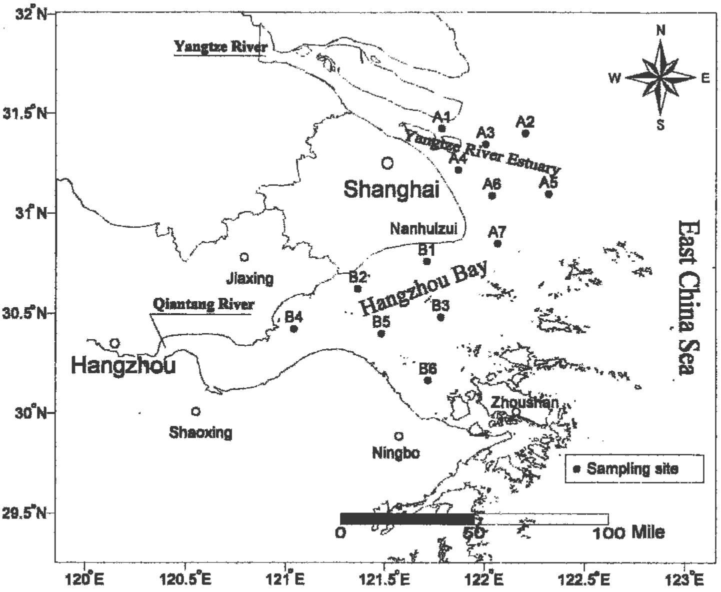

Figure 1. Locations of sampling sites in the study area.

water from <2.0 to 19.4‰. Surface sediments were taken with a Day grab, whereas the top 2 cm layer of the bottom samples was obtained with a plastic spatula. The samples were stored in pre-cleaned plastic bags at 4°C until arriving at the laboratory. Additional samples of the surface sediments were collected at each site for particle size analyses.

In the laboratory, the sediments were air dried, ground and screened through a 63μm nylon sieve for chemical analysis. For total metal analysis, 1-g dried aliquots were weighed into a 25mL Teflon digestion vessel to which nitric acid (2 mL), hydrofluoric acid (5 mL) and perchloric acid (5 mL) were added. The digestion of samples was carried out in a microwave digestion system MK-II (Xinke Microwave Technology Research Institute, Shanghai, China). Three stages of digestion were set with six minutes for each of the first two stages and eight minutes for the last one. The pressures in three stages were in the order of 0.5, 1.0, 1.5 MPa. After digestion, the digest was transferred to Teflon beakers and the acids were then evaporated to incipient dryness on a hot plate. After cooling, a further 2 mL of perchloric acid was added, and the contents evaporated to near dryness once more. This operation was repeated twice to remove hydrofluoric acid completely. Once cool, 18 MΩ Milli-Q water was added to the beakers and heated until remaining salts were dissolved. After cooling, the digest was diluted to 25 mL with Milli-Q water.

For metal speciation, a five-step sequential extraction procedure was adopted to distinguish five fractions representing the following chemical species: exchangeable phase, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual fraction. The sequential extraction scheme was carried out in the following order and associated reagents: (i) exchangeable phase (F1), 8 mL 1M $MgCl_2$, pH 7.0; (ii) bound to carbonates (F2), 8 mL 1M NaOAc, pH 5.0; (iii) bound to Fe-Mn oxides (F3), 20mL 0.04M $NH_2OH·HCl$ in 25% (v/v) HOAc, (iv) bound to organic matter (F4), 3 mL 0.02M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2.0 with HNO_3; 3 mL 30% H_2O_2 adjusted to pH 2.0 and then 5 mL 3.2M NH_4OAc +20% HNO_3; (v) residual fraction (F5), digestion with a concentrated mixture of HNO_3/$HCLO_4$/HF. The detailed extraction methods in this study were similar to those operation procedures described exhaustively by Tessier et al. (1979) except that the residual phrase (F5) was digested by microwave digestion method in our study. Acid washed glassware and polypropylene centrifuge tubes, analytical grade or ultrapure quality reagents and Milli-Q water were used in all procedures.

Concentrations of Fe, Mn, Zn in all solutions were determined by flame atomic absorption spectrophotometer (Varian SpectrAA220, USA). Matrix-matched standards were used to achieve quantification. Solution concentrations of Pb and Cd were determined by graphite furnace atomic absorption spectrophotometer (Unicam SOLAAR MQZ, Cambridge, UK) with Zeeman background correction. Concentrations of Cu, Ni and Cr in the extracts were determined by either FAAS or GFAAS. L'vov platform pyrolytically coated graphite tubes were used for GFAAS. NH_4NO_3+HNO_3 was used as matrix modifier for Cu, Pb and Cd determinations by GFAAS. The detection limits of GFAAS were 0.05 for copper, 0.05 for lead, 0.001 for cadmium, 0.01 for chromium, 0.08 for nickel, while those of FAAS were 1.0 for iron, 0.20 for zinc, 2.0 for manganese, 1.0 for copper, 0.5 for nickel and 1.0 for chromium ($\mu g\ g^{-1}$ in dry wt.). All data in this study were reported as dry weight.

Table 1. Analysis of certified total metal concentrations in standard reference material (nearshore marine sediment) from China.

Element	Certified	This study
Cu	31±4	29±3
Pb	25±4	24±2
Zn	87±2	86±2
Cd	0.20±0.04	0.22±0.02
Ni	34.3±4.0	32.5±2.0
Cr	86±4	84±2
MnO^*	0.096±0.004	0.094±0.001
$Fe_2O_3^*$	5.36±0.12	5.51±0.15

(means ± SD, in $\mu g\ g^{-1}$ dry wt. n=4).*w/w %

The precision of analytical procedures was assessed by duplicate analysis of sediment samples. Analytical blank and standard reference materials (GBW07314, nearshore marine sediments, China) were provided in each batch. The analytical accuracy concerning total digestions was archived by the determination of the heavy metals in the reference material and the results were within the range of certified values (Table 1). The accuracy of extraction procedures was evaluated by comparing concentrations of total digestion with the sum of the five individual species for each metal and the analytical relative deviations for all duplicate samples were within 15%. The one-way analysis of variance (ANOVA) was applied to test the differences of heavy metal concentrations between the two study areas and statistical significance was assumed when $P<0.05$.

Salinity of water in the sampling sites was determined aboard using a SCT (Model 30/25FT, YSI Incorporated, USA). Granulometric analysis of the sediments was performed using a particle-size analyzer (Model LS100, Coulter Corporation, USA). The sediments were further characterized by X-ray diffraction (Rigaku X-ray diffractometer, Model D/MAX-2550PC, Japan).

RESULTS AND DISCUSSION

The X-ray diffraction analysis showed that the mineralogical compositions of the sediments in both Yangtze River estuary and Hangzhou Bay were quite similar to each other, which was in accordance with the report of Yan and Hu (1986). The sediments were mainly formed from quartz, kaolinite, mica, feldspar, and carbonate, etc.

The particle size distributions for the sediments from the study area were illustrated in Fig.2. Surface sediments were defined as their sediment types according to the Shepard's (1954) classification scheme of ternary diagram. The sediments from the stations A5 and A7 (from Yangtze River estuary), B2 and B5 (from Hangzhou Bay) were silt type, while those of other stations clayey silt. In our study, gravel component was not found, while sand, silt and clay were dominant with different proportions. The formation of bottom sediment types and their distribution patterns were mainly under control of tidal current field (Zhu and Chang, 2000).

Concentrations of total metals at each station in the study area were shown in Fig. 3. The average values of heavy metals in sediments decreased in the order of Fe>Mn>Zn>Cr>Ni>Cu>Pb>Cd. No significant differences in the levels of heavy metals were found between Yangtze estuary and Hangzhou Bay.

The controlling effect of grain size of sediments on the concentrations of heavy metals had been demonstrated by previous studies (Zhao and Yan, 1993; Balkis and Cagatay, 2001). In our study, the concentrations of heavy metals showed significant correlations with the clay contents (grain size $< 4\mu m$), indicating that fine-grained sediments were the major carriers of the heavy metals (Table. 2). The significant positive correlations between clay content and metal concentrations were also reported by Cao (1992). The grain size of sediments was an important factor in controlling the heavy metals concentrations in the study area.

Spatial distribution patterns of metals in the study area were shown in Fig.3. In Yangtze estuary, the concentrations of heavy metals in sediments decreased from the inner reach to the river mouth of the Yangtze estuary. In Hangzhou Bay, the concentrations of heavy metals were higher in the east than in the west. High levels of heavy metals were observed in Nanhuizui. The huge input of sediment

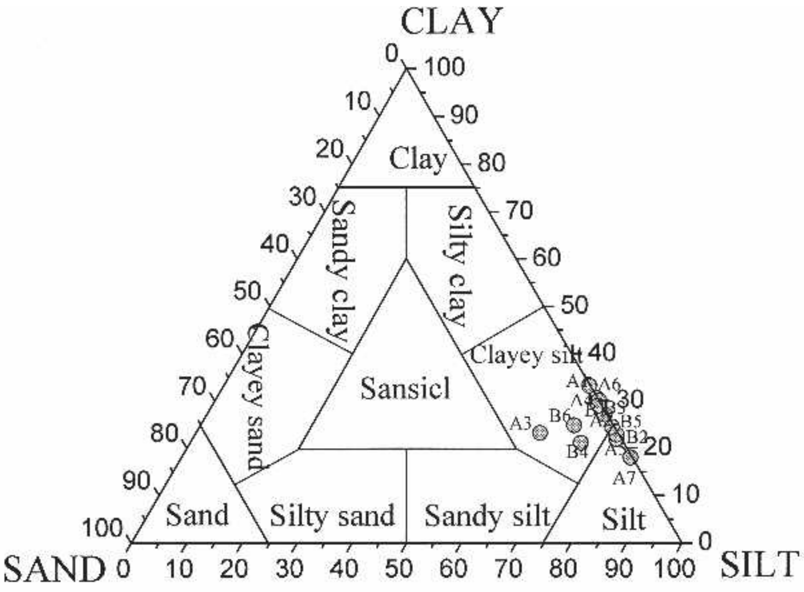

Figure 2. Ternary diagram of the surface sediments for each station.

Table 2. The correlation coefficients between heavy metals in surface sediments (<63μm) and clay content.

	Cu	Pb	Cd	Cr	Ni	Zn	Fe	Mn	Clay(%)
Cu	1								
Pb	0.984^{**}	1							
Cd	0.669^{**}	0.600^{**}	1						
Cr	0.861^{**}	0.790^{**}	0.745^{**}	1					
Ni	0.984^{**}	0.986^{**}	0.591^{*}	0.822^{**}	1				
Zn	0.994^{**}	0.985^{**}	0.634^{*}	0.839^{**}	0.990^{**}	1			
Fe	0.700^{**}	0.693^{**}	0.530^{NS}	0.465^{NS}	0.649^{*}	0.694^{**}	1		
Mn	0.973^{**}	0.957^{**}	0.659^{*}	0.847^{**}	0.978^{**}	0.981^{**}	0.666^{*}	1	
Clay(%)	0.752^{**}	0.697^{**}	0.783^{**}	0.783^{**}	0.662^{*}	0.727^{*}	0.692^{**}	0.653^{*}	1

$^{*}P<0.05$; ** $P<0.01$; NS: not significant. ($n=13$).

from the Yangtze estuary is seaward dispersed and comes directly to Hangzhou Bay by way of the coastal waters along Nanhuizui (Chen et al. 1985; Su and Wang 1989; Wang et al. 2004). Che et al. (2003) reported that fine-grained sediments, as the main carriers of heavy metals, increased gradually and reached 80% in Nanhuizui and the variations of metals in the suspended substance and sediments were mainly due to the particle size compositions in the study area.

As can be seen in Table 2, there were significant positive correlations among all metal concentrations with the exception of Fe-Cr and Fe-Cd, while Cu and Pb were highly correlated with other metals ($p<0.01$). These close inter-element relationships would imply a similar terrigenous source or a result of similar mechanisms of transport and accumulation within the sediments (Kiratli and

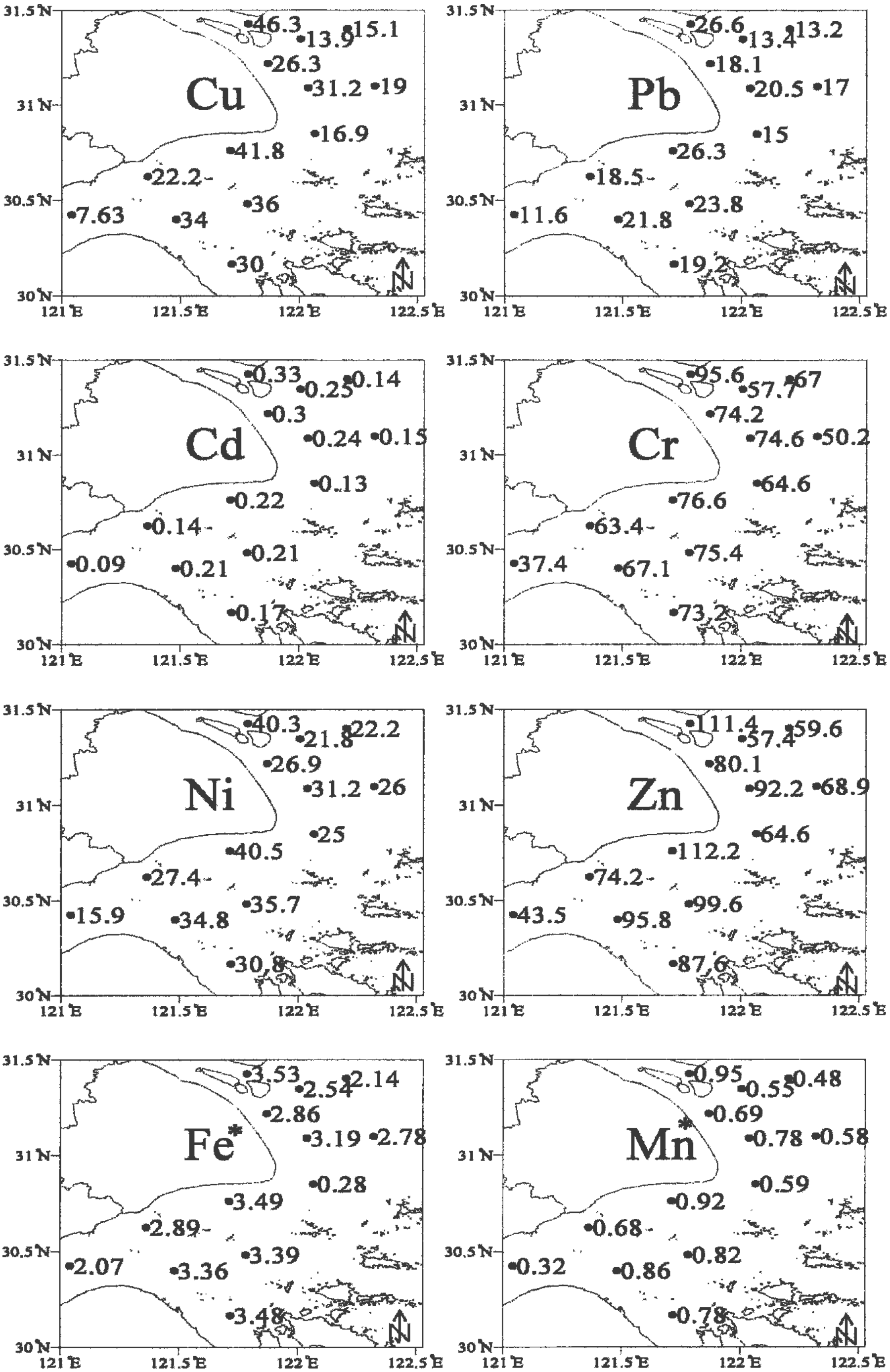

Figure 3. Spatial distributions of heavy metals in surface sediments (<63μm) from the study area. (unit: μg g^{-1}; * w/w %)

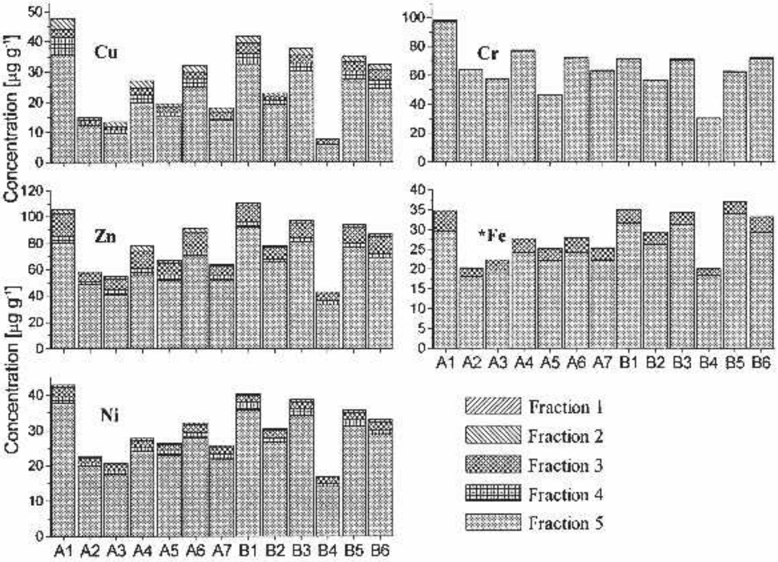

Figure 4. Distributions of Cu, Cr, Zn, Fe and Ni in the surface sediments from Yangtze estuary and Hangzhou Bay. *unit mg g^{-1}.

Ergin, 1996).

The concentrations of eight heavy metals in surface sediments determined at each sequential extraction step were presented in Figs. 4-5. The distribution patterns of eight metals were divided into two groups according to the degree of their association with the residual phrase (F5). Cu, Cr, Zn, Fe and Ni were assigned to a group that were mainly found in the residual fraction (more than 70% of the total concentrations), while Cd, Pb and Mn were in a group with their residual fraction less than 50% of the total levels. The percent (%) of Cu, Cr, Zn, Fe and Ni in the residue fraction were 71.7-83.8%, 98.8-99.1%, 72.8-84.3%, 84.7-91.5% and 82.7-88.9%, respectively (Fig.4). The results that Cr was mostly retained in the residual fraction were reported by Martin et al. (1998) and Yuan et al (2004). The levels of exchangeable Cr, Fe, Ni and Zn were lower than their respective detection limits and low proportion of Cu averaged 0.1%. The percentages of five fractions for Cu, Fe, Ni and Zn in the sediments followed the same order as residual > Fe-Mn oxides > organic > carbonate > exchangeable, while those of Cr followed the order as residual > organic > Fe-Mn oxides > carbonate > exchangeable.

The results of Cd, Pb and Mn were illustrated in Fig.5. A considerable proportion of Cd and Mn were found in all of the five fractions, while Pb was not detected in the exchangeable fraction. The average percentages of Cd, Pb and Mn in the residual fraction were 17.5%, 45.2% and 27.5%, respectively. In the non-residual fraction, Cd was mainly presented in exchangeable, carbonate fraction and Fe-Mn oxides while Pb was mainly retained in Fe-Mn oxides fraction. Mn was mainly dominated in carbonate and Fe-Mn oxides, as observed by other researchers

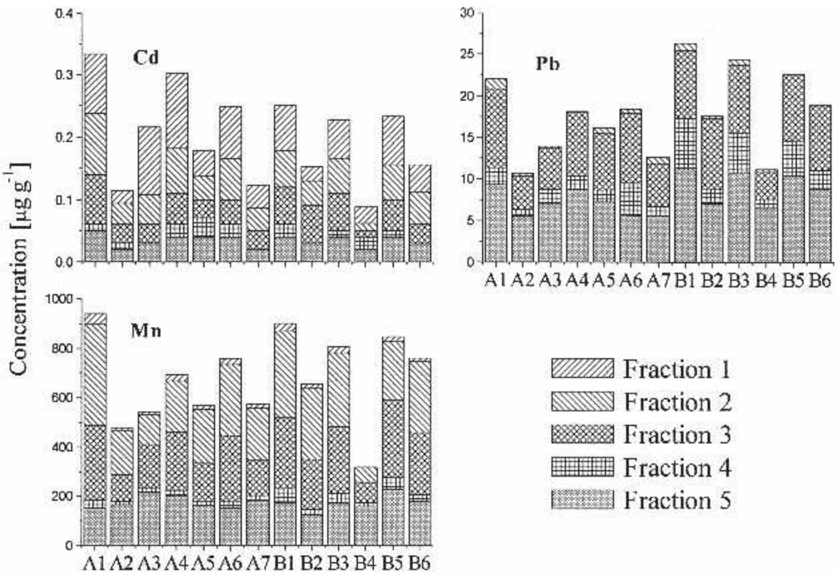

Figure 5. Distribution of Cd, Pb and Mn in the surface sediments from Yangtze estuary and Hangzhou Bay.

(Navas and Lindhorfer 2003). Among the five fractions, the heavy metals in exchangeable (F1) and carbonate fractions (F2) can be easily remobilized by changes in environmental conditions such as pH, salinity, etc (Thomas et al. 1994). In our case, the sum of F1 and F2 for Cd, Mn and Pb averaged 54.7%, 37.5% and 2.7%, indicating that the study area had Cd and Mn pollution risks.

Acknowledgments We thank the crew on R/V Zhehaihuanjian and the technical personnel in Zhoushan Marine Ecological Environmental Monitoring Station for participating in field sampling and pretreatment of the surface sediments in this study.

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