Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China

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ABSTRACT

A comparative study of the heavy metal (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) concentrations in sediments collected from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China, was conducted. Compared with the maximum background values in Wuhan Province soils, Cd was the metal with the highest contamination level, especially in the mainstream, followed by Zn and Cu. In a few samples from tributaries and lakes, the Hg concentration was very high compared to background levels. The concentrations of As and Ni in all sites fluctuated close to background levels. Partitioning of speciation of each heavy metal in sediments was similar for samples taken from the mainstream, tributaries, and lakes. Compared to the other metals studied, Cd, Cu, Zn, and Pb had higher bioavailability in the three zones, which means they pose a higher ecological risk. Significant correlations among group a (Zn, Cu, and Pb, $r > 0.9$) and group b (Cr and Ni, $r = 0.978$) in the mainstream; Hg, Cu, Cd, and Pb in lakes ($r > 0.9$); and Cu and Pb ($r > 0.9$) in tributaries were observed using Cluster and correlation analysis. However, a low correlation between As and the other elements in the three zones was shown. Overall, 63.6% of samples from the mainstream, 75.0% from tributaries, and 88.9% from lakes exhibited low and moderate ecological risk of heavy metals, and the potential ecological risks in the mainstream and tributaries were higher than those in lakes.

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1. Introduction

The Yangtze River is the largest river in China and the third largest in the world. Many tributaries and lakes within the middle reaches of the mainstream of the Yangtze River form a complicated watershed within Wuhan City, which is the industrial and economic center of central China. Aquatic resources in this catchment constitute the drinking water supply for Wuhan and the downstream communities. In addition, because of south-to-north water diversion, the water quality of the Yangtze River catchment of Wuhan also affects the residents in northern China. Therefore, the Yangtze River catchment of Wuhan is a crucial resource for China; millions of inhabitants are impacted daily by water from this catchment, and it thus affects social, economic, and community health.

Unfortunately, overpopulation, local soil erosion, inadequate water use management, and intensive deforestation have severely reduced the river's water quality. Significantly, large uncontrolled contaminant inputs, including heavy metals from industrial and urban sources, have contributed to increased pollution of the mainstream, tributaries, and lakes and have accumulated in the sediments [1–3]. Heavy metals are serious pollutants because of their toxicity, persistence, and non-degradability in the environment [4–6]. When the environmental conditions of the water lying over the sediments change, heavy metals in the sediments can be released into the water, thereby deteriorating the quality of the water [7,8]. A geochemical sediment survey of heavy metals in the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan is crucial to assessing the ecological risks of heavy metals in this region.

The potential ecological risk of each heavy metal in sediments is determined by its total content and speciation [9,10]. Depending on chemical and geological conditions, heavy metals can be partitioned into different chemical forms that are associated with a variety of organic and inorganic phases [11]. Thus, speciation analysis of heavy metals might provide much useful information regarding the chemical nature or potential mobility and bioavailability of a particular element, which consequently can offer a more realistic estimate of actual environmental impact [12–14].

To date, many methodologies have been developed to assess ecological risks of heavy metals [15–17]. However, most of them are suitable only for ecological risk assessment of a single contaminant (e.g., the geoaccumulation index method) [17,18]. In reality, many kinds of heavy metals usually accumulate simultaneously and cause

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combined pollution. To address this, Hakanson [19] developed the potential ecological risk index, which introduced a toxic-response factor for a given substance and thus can be used to evaluate the combined pollution risk to an ecological system.

In this paper, comparative studies of concentration, speciation, and ecological risk of heavy metals in sediments from the mainstream, tributaries, and lakes in the Yangtze River catchment of Wuhan were systematically conducted. The results provided a comprehensive look at the current sediment contamination status of heavy metals and the potential origin of contamination in the three zones. These data can form the foundation for the protection of water quality of the Yangtze River catchment of Wuhan.

2. Materials and methods

2.1. Study area and sample collection

The Yangtze River catchment of Wuhan lies in the middle reaches of the Yangtze River. It contains many lakes and tributaries, including the Hanjiang River, which is the largest tributary of the Yangtze River. Approximately 8 million people reside in this area. Industrial activities, such as chemical, electric plating, and refining industries in the Hanyang industrial zone, are growing fast. Therefore, urban sewage and industrial wastewater could be the source of the load of pollutants transported by lakes and tributaries to the Yangtze River.

A survey of heavy metals in sediments from the mainstream (zone a), eight main tributaries (zone b), and seven representative lakes (zone c) of the Yangtze River catchment of Wuhan was conducted in 2005. A total of 36 sampling stations were selected in three zones. Of these, 11 were collected from zone a 16 from zone b and 9 from zone c. These sampling sites were located using a global positioning system. Fig. 1 shows the details of the sampling sites [20]. Approximately the top 2 cm of sediments were collected using a Van Veen grab (Eijkelamp, the Netherlands); they then were placed in a pre-cleaned aluminum box using a stainless steel spoon and freeze dried. All freeze-dried sediment samples were ground, homogenized, and stored at −20 °C prior to analysis.

2.2. Analytical methods

Metal concentrations of the samples were measured at the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences, which is certificated by the China National Accreditation Board for Laboratories (CNAL). The results met the accuracy demanded by the China State Bureau of Technical Supervision. The methods of metal extraction and analysis are established by the institute. A brief description of the methods is provided here.

The samples were freeze dried and then ground to a small enough size to pass a 200-mesh sieve (pore diameter: 0.074 mm). About 0.25 g of sediment was subjected to a digestion solution (5.0 mL nitric acid + 10.0 mL nitric acid + 2.0 mL perchloric acid), and the mixture then was heated on an electric heating plate at 200 °C. After being perchloric acid smoked, the mixture was heated for another 3 min then cooled to room temperature. After cooling, the residue was digested again with the digestion solution at 200 °C to dryness. The residue was treated with 8 mL aqua regia and heated until 2–3 mL of the mixture were left. The wall of the Teflon beaker containing the mixture was washed with about 10 mL deionized water and the beaker with the mixture and wash water was then slightly heated for 5–10 min to obtain a clear solution. Next, the solution was diluted with deionized water to 25 mL. One milliliter of the diluted solution was taken and further diluted with 2% nitric acid to 10 mL for analysis of Cr, Cu, Ni, Zn, Cd, and Pb using an inductively coupled plasma mass spectrometer (ICP-MS, Thermo). The mass/charge ratios of Cr, Cu, Ni, Zn, Cd, and Pb were 52, 65, 60, 66,
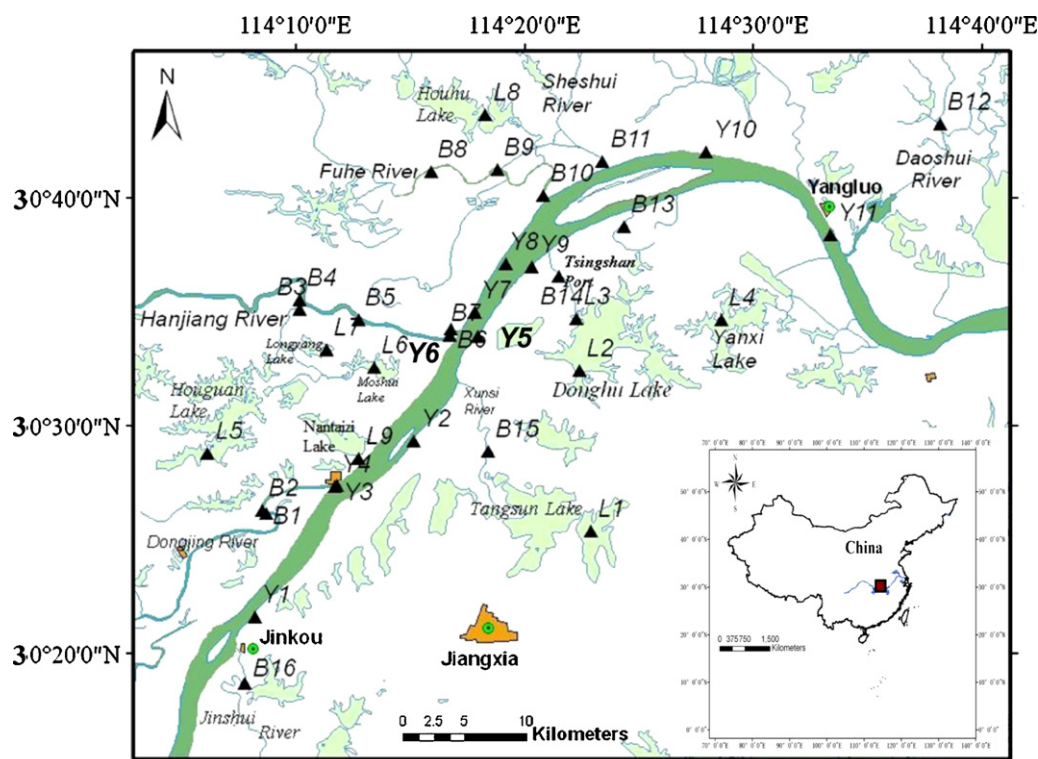

Fig. 1. Map of sediment sampling sites in the mainstream of the Yangtze River (Y), the tributaries of the Yangtze River (B), and the representative lakes (L) in the Yangtze River catchment of Wuhan.

111, and 208, respectively. Atomic fluorescence spectrometry (AFS) was used to analyze the concentrations of As and Hg; As was measured at 193.7 nm and Hg at 253.65 nm. The detection limits were 1 μg/g for As and Cu, 0.02 μg/g for Cd, 5 μg/g for Cr, 2 μg/g for Ni, Pb, and Zn, and 0.002 μg/g for Hg.

pH value was measured in the aqueous saturated soil paste before the samples were freeze dried. Particle size analysis was performed by X-ray sedigraphy using a SALD-3001 Particle Analyzer (0.269–2000 μm, R.S.D. < 3%) (Shimadzu, Japan). Total organic carbon (TOC) content of the sediments was determined using a Liqui TOC analyzer (Elementar, Germany).

Six kinds of speciation of heavy metals in sediments were obtained using the selective sequential dissolution (SSD) method of Han and Banin [21,22]. The procedures are described as follows.

2.2.1. Exchangeable fraction (EXC)

Twenty-five milliliters of 1 mol/L NH_4NO_3 solution (pH adjusted to 7.0 with NH_4OH) was added to 1.0 g of freeze-dried sediment in a 50 mL Teflon centrifuge tube and the mixture was shaken for 30 min at 25 °C. The contents then were centrifuged at 5500 rpm for 20 min and the supernatant was decanted. The residue was washed in 8 mL deionized water and centrifuged again for 20 min. The wash water was added to the supernatant. The mixture was filtered through a 0.45 μm membrane and deionized water was added to make a volume of 50 mL for measurement. The residue was retained for the next step. The same centrifugation-decantation-washing procedure was used after each of the following extraction steps.

2.2.2. Fraction bound to carbonate (CARB)

Twenty-five milliliters of 1.0 mol/L acetate buffer solution ($CH_3COOH + CH_3COONa$ at pH 5) was added to the soil residue from the previous step and the mixture was shaken for 6 h. Excess CO_2 was released by opening the tube cap during the first 2 h.

2.2.3. Fraction bound to easily reducible oxides (ERO)

Twenty-five milliliters of 0.04 mol/L $NH_2OH \cdot HCl$ in a 25% acetic acid solution was added to the soil residue from the previous step, and the mixture was shaken for 30 min.

2.2.4. Fraction bound to organic matter (OM)

Three milliliters of 0.01 mol/L HNO_3 and 5 mL of 30% H_2O_2 were added to the soil residue from the previous step. The mixture was digested in a water bath at 80 °C for 2 h. An additional 2 mL of H_2O_2 was added and the mixture was heated for 1 h. Fifteen milliliters of 0.01 M HNO_3 solution was then added and the mixture was agitated for 30 min.

2.2.5. Fraction bound to residual oxides (RO)

Twenty-five milliliters of 0.04 mol/L $NH_2OH \cdot HCl$ in a 25% acetic acid solution were added to the soil residue from the previous step and the mixture was digested in a water bath at 90 °C for 3 h.

2.2.6. Residual fraction (RES-R)

Twenty-five milliliters of 4 mol/L HNO_3 were added to the residue from the previous step and the mixture was transferred into a glass digestion tube. Digestion was conducted in a water bath at 80 °C for 16 h.

Quality control was assured by the analysis of duplicate samples and standard reference materials. The standard reference materials (GSS 1, GSS 8, GSD 9, GSD 10) were used for total element analysis; percentage recoveries ranged from 86% (for Cr) to 122% (for Cr). The standard reference material (GAU2a) was used to verify the accuracy of the sequential extraction method. The recovery rates for heavy metals ranged from 82% (for Pb in the EXC fraction) to 116% (for Cr in the RES-R fraction). Analytical precision, expressed as relative standard deviation, was in general better than 15%.

Table 1
Levels of heavy metals in sediments and the main characteristics of sediment from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan.

		As[a]	Cd[a]	Cr[a]	Cu[a]	Hg[a]	Ni[a]	Pb[a]	Zn[a]	TOC[a]	Clay[b] (%)	Silt[c] (%)	pH
Mainstream	Max	28.50	3.40	117.00	68.00	0.30	57.00	65.00	187.00	20.94	33.79	54.17	8.10
	Min	8.20	0.30	59.00	26.00	0.04	27.00	21.00	71.00	1.58	4.92	20.73	7.65
	Median	14.20	1.10	84.00	50.00	0.14	39.00	42.00	133.00	11.63	24.10	48.23	7.89
	Mean	15.85	1.53	87.82	51.64	0.15	40.91	45.18	140.27	12.21	21.60	42.89	7.89
	S.D.	5.98	1.00	15.68	12.54	0.07	8.73	13.30	36.45	7.03	10.52	12.13	0.13
	Skew	0.78	0.63	0.07	−0.67	0.50	0.25	−0.17	−0.42	−0.16	−0.48	−0.87	−0.36
	CV	0.38	0.65	0.18	0.24	0.50	0.21	0.29	0.26	0.58	0.49	0.28	0.02
Tributaries	Max	29.90	2.40	205.00	129.00	1.43	54.00	98.00	1142.00	89.81	51.62	63.77	8.21
	Min	7.90	0.20	57.00	27.00	0.06	26.00	20.00	74.00	2.10	2.79	24.89	6.49
	Median	14.80	0.55	112.50	49.00	0.12	46.00	42.50	164.50	14.52	34.15	52.72	7.44
	Mean	14.82	0.84	115.56	57.06	0.30	43.31	47.13	255.00	27.50	30.72	49.92	7.43
	S.D.	4.98	0.65	41.93	28.55	0.39	8.95	21.98	288.05	31.09	15.21	12.02	0.45
	Skew	1.79	1.25	0.66	1.27	2.03	−1.02	0.86	2.42	1.29	−0.89	−1.11	−0.13
	CV	0.34	0.77	0.36	0.50	1.30	0.21	0.47	1.13	1.13	0.50	0.24	0.06
Lakes	Max	22.10	1.70	296.00	343.00	1.93	55.00	142.00	682.00	84.69	49.10	61.92	7.30
	Min	9.70	0.10	59.00	21.00	0.06	20.00	26.00	49.00	9.45	25.77	50.32	6.25
	Median	15.20	0.40	91.00	41.00	0.14	42.00	44.00	121.00	25.61	37.86	58.59	6.95
	Mean	16.03	0.57	119.22	75.56	0.32	40.44	57.78	296.78	35.29	36.98	57.69	6.87
	S.D.	3.93	0.47	71.69	101.26	0.60	12.65	35.09	262.95	29.64	7.85	4.25	0.37
	Skew	0.35	1.99	2.24	2.89	2.97	(0.55	2.01	0.52	1.12	0.28	−0.98	−0.66
	CV	0.24	0.83	0.60	1.34	1.87	0.31	0.61	0.89	0.84	0.21	0.07	0.05
Others	Maximum background value of Wuhan Province soils[d]	15.00	0.20	90.00	35.00	0.15	40.00	35.00	100.00				
	TEL	7.20	0.60	42.00	36.00	0.17	16.00	35.00	123.00				
	PEL	42.00	3.50	160.00	197.00	0.49	43.00	91.00	315.00				

[a] mg kg^{-1}.

[b] Particle size < 4 μm

[c] Particle size was 4–62.5 μm.

[d] Ni et al. [26].

2.3. Descriptive analysis and multivariate analysis

Descriptive data analysis was performed, and the results included maximum, minimum, median, mean, standard deviation (S.D.), skew, and coefficient of variation (CV). Correlation and cluster analyses, as the most common multivariate statistical methods, were conducted using SPSS 13.0 (SPSS Inc., Chicago, Illinois, USA).

3. Results and discussion

3.1. Levels of heavy metals

Table 1 lists the concentration range, median, mean, S.D., skew, and CV of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan and the maximum background values of the soils in Wuhan. Two levels were considered: the threshold effect level (TEL), below which adverse biological effects are expected to occur rarely, and the probable effect level (PEL), above which adverse effects are expected to occur frequently. These concentrations were established by the Canadian Council of Ministers of the Environment (CCME). Fig. 2 shows the ratio of heavy metal concentrations in sediments with their maximum background values from Wuhan Province soils; this ration is defined as the pollution index (P_i), which generally is a quick and practical method to trace heavy metal enrichment.

Obviously, the highest contamination metal is Cd. P_i values for Cd at most sites were >1, except for sites B4, B5, and L5, and the
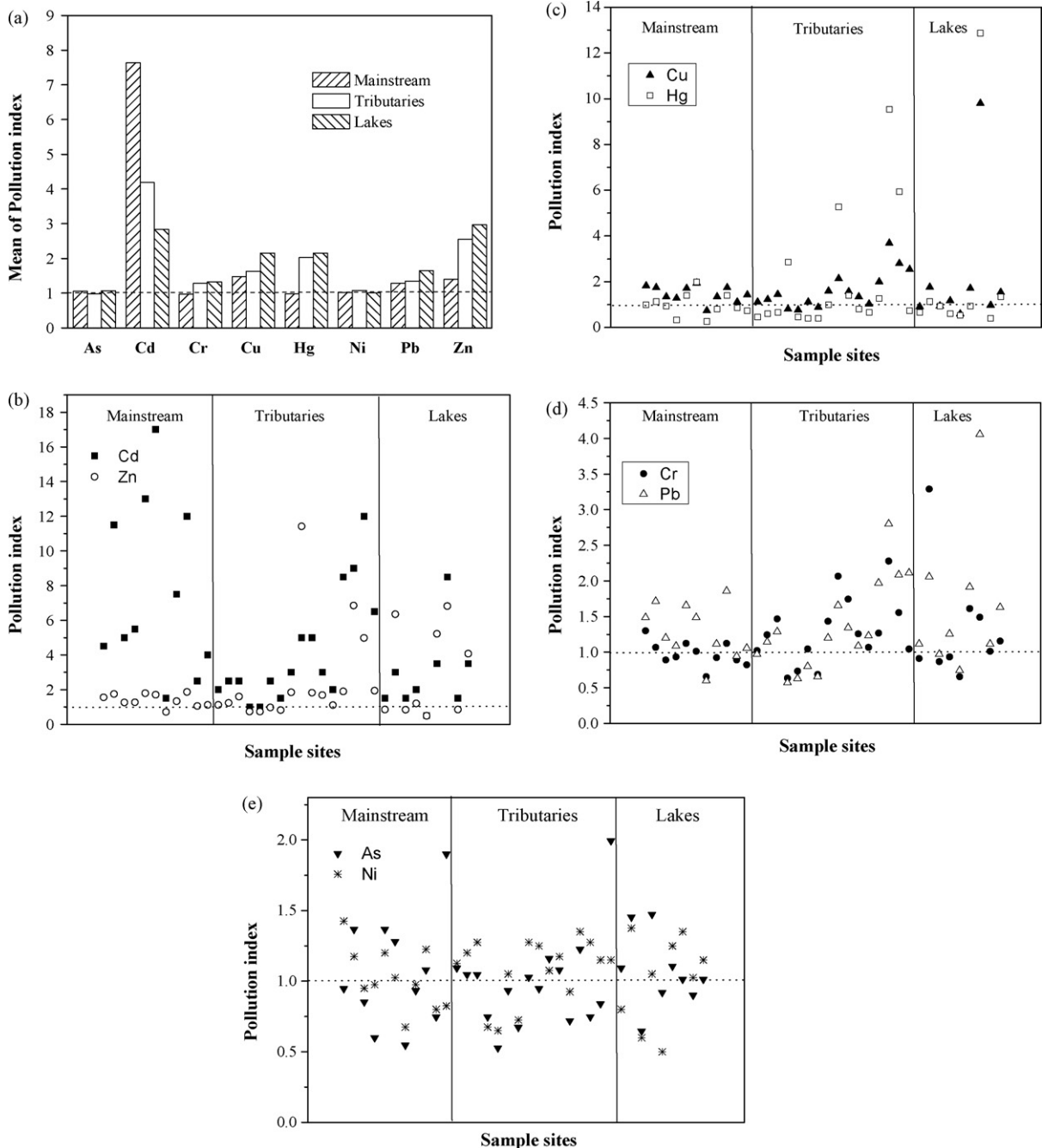

Fig. 2. (a) Comparison of the mean pollution index of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan; (b–e) pollution index values of heavy metals in every sampling sites.

mean P_i reached as high as 7.64, 4.19, and 2.83 in the mainstream, tributaries, and lakes, respectively. Accumulation of Cd was most serious in the mainstream. In more than 64% of samples, P_i values for Cu, Pb, Zn, and Cr were >1. Higher mean P_is were observed for Cd, Zn, Hg, and Cu compared to the other metals. These results suggest that the accumulation of Zn and Cu were relatively serious. P_i values for Hg at most sites (61% of samples) were <1, but in some sites (L7, B14, B15, and B9) they were >5. P_i values for As and Ni at all sites fluctuated around 1, and values did not differ obviously among the three zones. Cr, Cu, Hg, Pb, and Zn exhibited similar distributions among zones (i.e., mean P_i in lakes > mean P_i in tributaries > mean P_i in the mainstream; Fig. 2(a)).

Generally, toxicity rarely occurs below the TEL and frequently occurs above the PEL [23]. Fig. 3 shows the average metal levels of Cd, Zn, and Hg in the three zones compared with the TEL.

The concentrations of Cd in sediments in 82% of samples from the mainstream, 38% from tributaries, and 33% from lakes of the Yangtze River catchment of Wuhan were higher than the TEL. The mean concentration of 1.53 mg kg^{-1} for Cd in the mainstream was higher than that from tributaries and lakes (Table 1 and Fig. 3). These results indicated that heavier contamination of Cd occurred in the mainstream. The highest Cd concentration – about 5.6 times as high as the TEL – occurred at site Y6, which is located downstream from the confluence of the Yangtze and Hanjiang Rivers. The high Cd concentration at Y6 might be due to the deposition of more small suspended particles at this site, where a low flow rate occurs because of the nearby Wuhan Port. In the tributaries, higher Cd concentration were observed in sediments of the Wuchang region (B14 and B15) and at sites B13 and B16. In the lakes, the sediments of Longyanghu Lake, which lies in the Hanyang industrial zone (site L7), were most contaminated with Cd (1.7 mg kg^{-1}). In nature, Cd is usually associated with Pb–Zn ore and Cu–Pb–Zn ore, so Cd in three zones mainly originated from mining and smelting [24]. The increasing industrial discharge from electric plating, paint manufacturing, and refining likely was responsible for the introduction of large quantities of Cd (such as at sites B14, B15, B13). A small quantity of Cd, which exists in coal and crude oil, also might be released into the air during fuel combustion and subsequently be deposited into sediments. The input of phosphate fertilizer, which contains some Cd, is yet another source for the accumulation of Cd in sediments, such as seen in the Jinshui River (site B16) [25].

The concentrations of Zn in sediments in 73% of samples from the mainstream, 63% from tributaries, and 44% from lakes of the Yangtze River catchment of Wuhan were higher than the TEL; however, the mean concentration of Zn in lakes was the highest among the three zones. These results suggest that the accumulation of Zn was relatively serious in the mainstream, although the concentration of Zn in some samples from lakes and tributaries also was very high. The concentration of Zn in the sediments of Donghu Lake (L2), Longyanghu Lake (L6), and Moshuihu Lake (L7) ranged from 521.5 mg kg^{-1} to 682.1 mg kg^{-1}, which was 4.2–5.5 times higher than the TEL and also higher than the background values of Wuhan Province soils. This result was close to that reported by Ni et al. [26]. Additionally, higher concentrations of Zn were observed at site B9 (1142 mg kg^{-1}), B14 (685 mg kg^{-1}), and B15 (499 mg kg^{-1}). This distribution pattern might be related to nearby industrial and residential activities. A large amount of urban sewage and industrial wastewater is discharged into river, which might explain the high level of Zn accumulation in sediments.

The concentrations of Hg in sediments in 27% of samples from the mainstream, 38% from tributaries, and 22% from lakes of the Yangtze River catchment of Wuhan were higher than the TEL. Thus, most samples in the three zones were not polluted with Hg. However, the accumulation of Hg in some samples from tributaries and lakes were serious. Maximum levels of Hg in sediments were found at sites L7 (1.93 mg kg^{-1}) and B14 (1.43 mg kg^{-1}), which were sig-
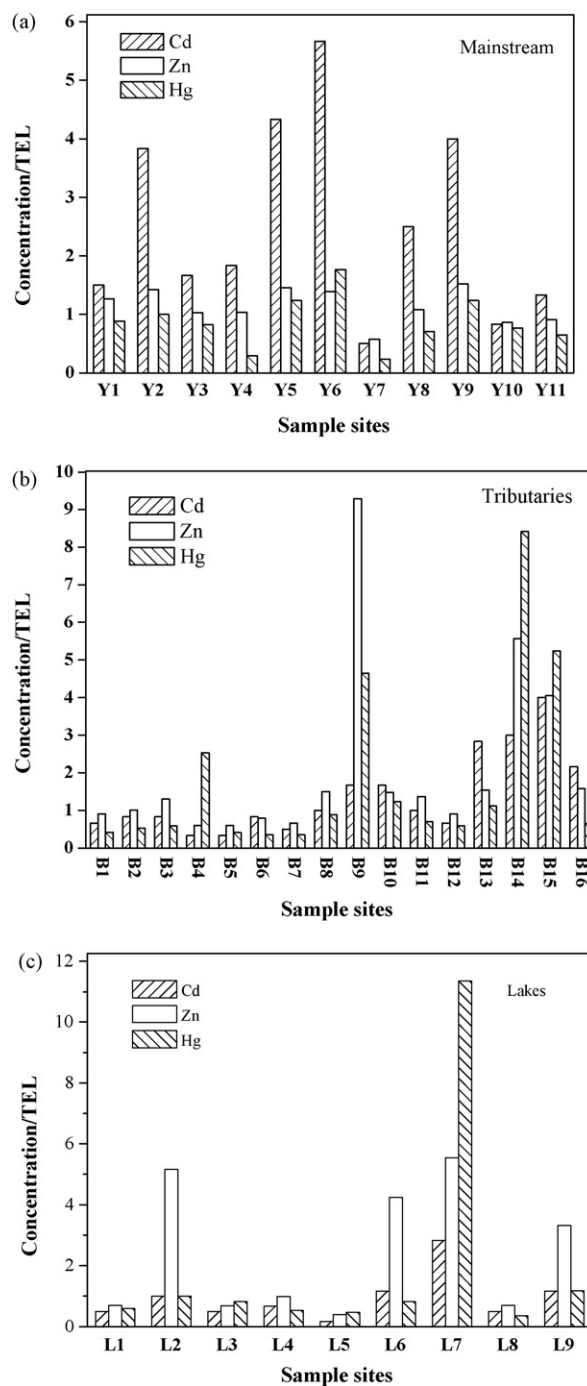

Fig. 3. Ratios of heavy metal levels (Cd, Hg, and Zn) with TEL in sediments from the (a) mainstream, (b) tributaries, and (c) lakes of the Yangtze River catchment of Wuhan.

nificantly higher than the TEL and the background value of Wuhan Province soils. According to other researchers, the most important input of Hg contamination is fuel and coal combustion [25].

3.2. Speciation of heavy metals

The potential environmental risk of heavy metals in sediments is associated with both their total content and their speciation. Fig. 4 shows the partitioning of the speciation of heavy metals in the sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan. Similar chemical fractionation distribution for each heavy metal was observed in the three zones.
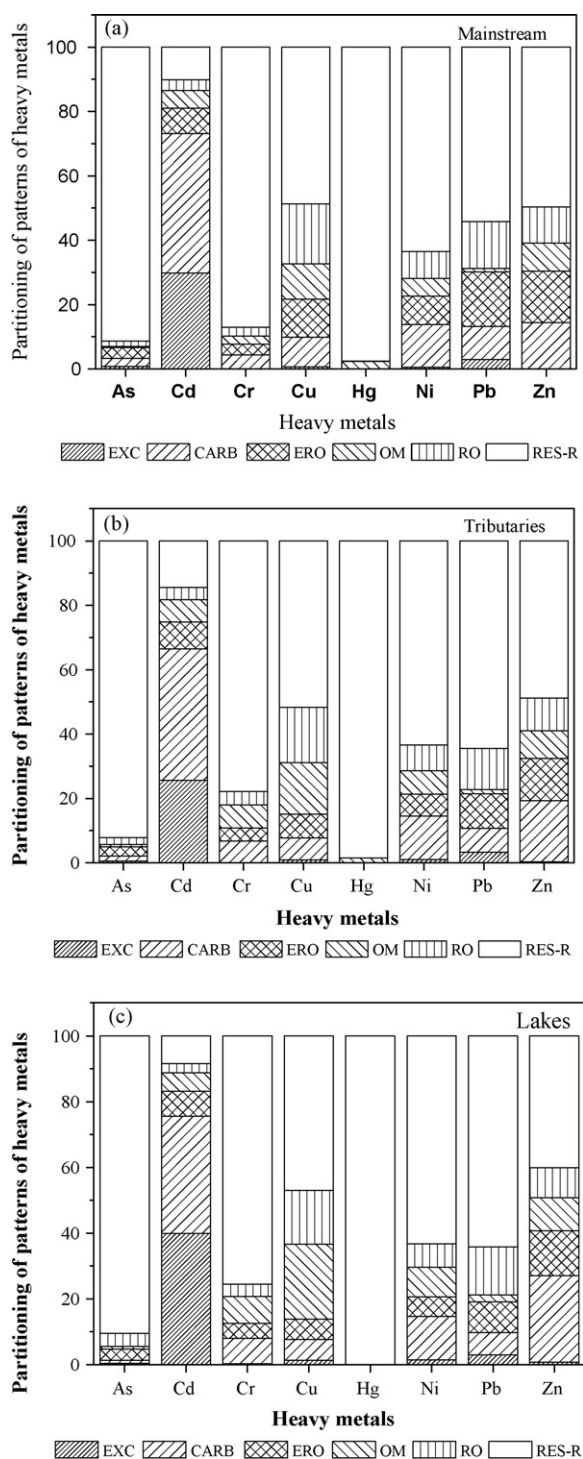
Fig. 4. Partitioning of speciation of heavy metals in sediments from the (a) mainstream, (b) tributaries, and (c) lakes of the Yangtze River catchment of Wuhan.

Compared with other heavy metals, Cd possessed the highest CARB and EXC fractions in sediments from the three zones. The percentages of CARB-Cd accounted for 43.37%, 40.68%, and 35.63% for the mainstream, tributaries, and lakes, respectively, which resulted from the high concentration of HCO_3^- in the sediments. $CdCO_3$ is easily formed in the neutral pH condition, thus this fraction was sensitive to environmental conditions such as pH. When pH decreases, Cd bound to carbonate is released into the water, thus causing pollution [27]. High percentages of EXC-Cd (29.86%, 25.69%, and 39.95% for the mainstream, tributaries, and lakes, respec-

tively), also were observed; these values were associated with the higher capacity of principal polarization (an ion cause other ions nearby polarized in the effect of electric field itself, i.e., principal polarization), resulting in strong adsorption of Cd onto colloids in the sediments. Generally, the EXC fraction had the greatest tendency toward remobilization from the sediment phase to the more bioavailable pore water phase [28]. Overall, the speciation of Cd in the sediments from the three zones exhibited high bioavailability and consequently this element posed a high ecological risk.

Cu and Zn exhibited similar chemical partitioning in the three zones: for both, the percentage of the RES-R fraction accounted for about 50%. The EXC fraction (0.72–1.30% for EXC-Cu and 0.13–0.69% for EXC-Zn) were low. The percentages of RO-Cu and OM-Cu were 16.33–18.71% and 10.95–22.75%, respectively, which were higher than those of Zn. The RO-Cu likely was bound to ferric oxides, which would be released when environmental condition changed. The percentages of CARB-Zn and ERO-Zn were 14.29–26.33% and 13.14–16.02%, respectively, which were greater than those of Cu. These data suggest that Cu and Zn in the sediments from the three zones posed some ecological risk.

In the three zones, the RES-Pb fraction was 54.19–64.51%. The fractions bound to residual oxides and easily reducible oxides were similar at about 12.75–14.57% and 9.44–16.97%, respectively; these values were related with Fe and Mn dioxide and crystal ferric oxides [29], respectively. When the environmental conditions changed, both fractions were easily released from the sediment phase into the water. Additionally, EXC-Pb, which had the highest mobility, reached 2.97–3.23%. As a kind of environmental hormone, Pb can affect the procreation ability of a biological system. Therefore, once Pb is transferred from the sediment to the water, it poses a higher ecological risk.

The predominant chemical partitioning of As and Hg in the three zones was into the RES-R fraction (>90%). The levels of the other fractions of both metals were all <5%. This As result agreed with that obtained from the sediments of Guanting Reservoir, but the Hg results differed [30]. The RES-Cr fraction in the sediments of the three zones was >75%, whereas the EXC-Cr fraction was only 0.11–0.24%. Additionally, CARB-Cr and OM-Cr levels were not high (4.30–7.79% and 2.62–8.21%, respectively). This result was consistent with the distribution of Cr in the sediments of Taihu Lake [31]. Ni was predominantly associated with RES-R and CARB fractions in the three zones. The percentages of ERO-Ni, OM-Ni, and RO-Ni ranged from 5.55% to 8.00%, which agrees with results reported by Wei et al. [32]. Based on these data, As, Hg, Cr, and Ni exhibited lower bioavailability compared to Cd, Cu, Pb, and Zn in this region.

3.3. Cluster and correlation analyses

Cluster analysis was used to quantitatively identify specific areas of contamination. Fig. 5 shows three dendrograms summarizing samples from the mainstream, tributaries, and lakes. Two major clusters are noted. Clusters Y_a (Y2, Y5, Y9, Y6, and Y1), L_{b2} (L7), and B_b (B9) represent highly contaminated sites where ecotoxicological damage might be occurring; these clusters all were located below major suspected pollution sources (i.e., large quantities of discharge of urban sewage and industrial wastewater). Accordingly, these sites should be given first priority in initial remediation efforts. The other clusters represented sites of moderate (Y_{b1}, L_{b1}, and B_{a2}) and lower (Y_{b2}, L_a, and B_{a1}) heavy metal levels in the sediments.

Correlation analysis was conducted on heavy metal concentrations at each site to assess possible co-contamination from similar sources among the data set. Table 2 shows intensively significant correlations among group a (Zn, Cu, and Pb, $r > 0.9$) and group b (Cr and Ni, $r = 0.978$) in the mainstream (these are metals commonly seen in industrial activities); among Hg, Cu, Cd, and Pb in lakes ($r > 0.9$) (these metals commonly occur in mining, smelting, and fuel

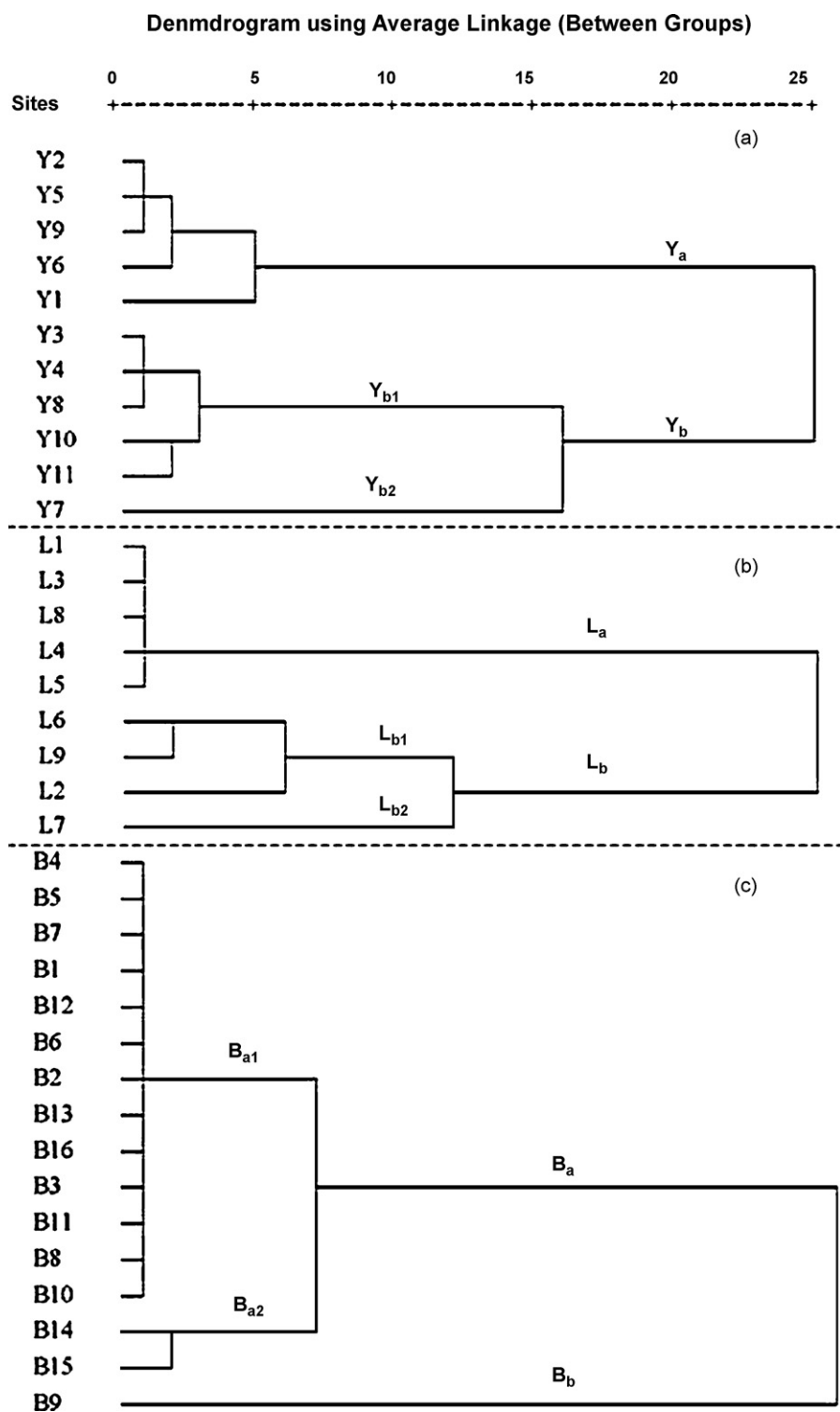**Denmdrogram using Average Linkage (Between Groups)**

Fig. 5. Cluster analysis dendrogram indicating relatedness of sites with heavy metal contamination in sediments: (a) sites in the mainstream are divided into cluster Y_a, sub-clusters Y_{b1} and Y_{b2}; (b) sites in lakes are divided into cluster L_a, sub-clusters L_{b1} and L_{b2}; (c) sites in tributaries are divided into cluster L_a, sub-clusters L_{b1} and L_{b2}.

and coal combustion); and among Cu and Pb in tributaries ($r > 0.9$) (these metals commonly are observed in industrial and residential activities). No correlations were noted between As and other metals in the three zones, suggesting that As contamination might be from a different source than the other metals or that it might have different sediment deposition characteristics. From a management perspective, this analysis suggests that remediation efforts should focus on reducing the discharge of urban sewage and industrial

wastewater (such as that produced by mining and smelting); such efforts likely would have the broadest benefit to the whole river system, especially for Hg, Zn, Cd, Cu, and Pb.

3.4. Comparative ecological impact assessment

To assess the effect of multiple metal pollution in the sediments from the mainstream, tributaries, and lakes of the Yangtze

Table 2
Correlation analysis of heavy metals among all sampling sites.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mainstream								
As	1.000							
Cd	0.432	1.000						
Cr	0.221	0.505	1.000					
Cu	0.564	0.785[**]	0.848[**]	1.000				
Hg	0.472	0.872[**]	0.576	0.826[**]	1.000			
Ni	0.213	0.503	0.978[**]	0.830[**]	0.516	1.000		
Pb	0.447	0.784[**]	0.844[**]	0.903[**]	0.753[**]	0.857[**]	1.000	
Zn	0.420	0.855[**]	0.843[**]	0.925[**]	0.796[**]	0.846[**]	0.982[**]	1.000
Lakes								
As	1.000							
Cd	0.102	1.000						
Cr	0.566	0.320	1.000					
Cu	−0.007	0.950[**]	0.181	1.000				
Hg	−0.071	0.924[**]	0.115	0.995[**]	1.000			
Ni	0.574	0.705[*]	0.701[*]	0.514	.433	1.000		
Pb	0.178	0.986[**]	0.428	0.951[**]	0.920[**]	0.732[*]	1.000	
Zn	0.358	0.814[**]	0.752[*]	0.654	0.594	0.860[**]	0.847[**]	1.000
Tributaries								
As	1.000							
Cd	0.268	1.000						
Cr	0.076	0.608[*]	1.000					
Cu	0.298	0.885[**]	0.762[**]	1.000				
Hg	−0.237	0.669[**]	0.715[**]	0.799[**]	1.000			
Ni	0.503	0.549[*]	0.716[**]	0.612[*]	0.265	1.000		
Pb	0.371	0.884[**]	0.738[**]	0.968[**]	0.702[**]	0.667[**]	1.000	
Zn	−0.053	0.520[*]	0.783[**]	0.659[**]	0.775[**]	0.421	0.592[*]	1.000

r denotes the correlation coefficient.
[*] $p < 0.05$.
[**] $p < 0.01$.

River catchment of Wuhan, the quantitative approach developed by Hakanson [19] was used. According to this methodology, the potential ecological risk index (*RI*) is defined as

$$RI = \sum_{i=1}^{n} \left(T_i \times \frac{C_i}{C_0} \right) \tag{1}$$

where T_i is the toxic-response factor for a given substance (e.g., Hg = 40, Cd = 30, As = 10, Pb = Cu = Ni = 5, Cr = 2, Zn = 1); C_i represents metal content in the sediments; and C_0 is the regional background value of heavy metals in the sediments. In this study, the heavy metal content of soils in Wuhan (Table 1) was used as the regional background value.

The *RI* of sediment samples from the three zones are compared in Fig. 6. *RI* values for most sampling sites (63.6% of samples from the mainstream, 75.0% from tributaries, and 88.9% from lakes) were
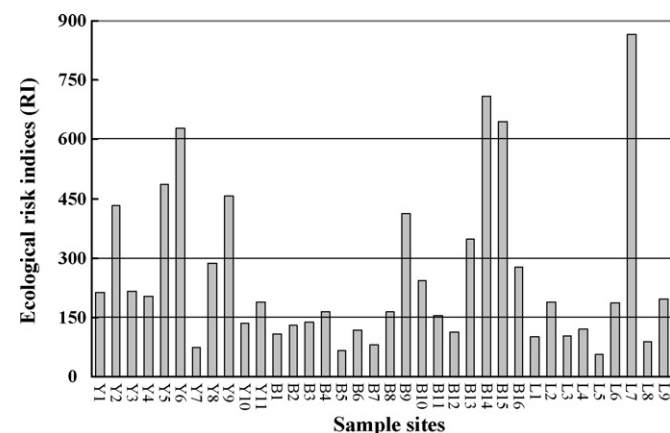
lower than 300, suggesting that more sediment samples from the Yangtze River catchment of Wuhan exhibited low and moderate ecological risk of heavy metals [19]. However, 27.3% and 12.5% of sediment samples from the mainstream and tributaries, respectively, had *RI* values ranging from 300 to 600, which indicates high ecological risk of heavy metals [19]. *RI* values of residual sediment samples (L7, B14, B15, and Y6) were higher than 600, which means high ecological risk of heavy metals [19]. Thus, the mainstream and tributaries had higher potential ecological risk than lakes. However, the highest *RI* value was observed at site L7 (Longyang Lake), which is located in the Hanyang industrial zone; this result likely was caused by high levels of industrial discharge.

4. Conclusions

The comparative assessment of heavy metal concentrations (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China, indicated that Cd is the highest contaminating metal, especially in the mainstream. The accumulation of Zn and Cu was the second most serious problem. In some samples from tributaries and lakes, the concentration of Hg was very high compared to background levels; however, such accumulation was not observed in most samples. The concentrations of As and Ni at all sites fluctuated around the background level.

The speciation of Cd, Cu, Zn, and Pb in the sediments from the mainstream, tributaries, and lakes of showed higher bioavailability compared to the other metals studied, and consequently they posed greater ecological risk. Lower ecological risk was observed for As, Hg, Cr, and Ni in the three zones because residual fraction dominated. Significant correlations among group a (Zn, Cu, and Pb, $r > 0.9$) and group b (Cr and Ni, $r = 0.978$) in the mainstream; Hg, Cu, Cd, and Pb in lakes ($r > 0.9$); and Cu and Pb ($r > 0.9$) in tributaries were observed. A low correlation between As and the other elements in the three zones suggests that As may originate from

Fig. 6. Potential ecological risk indices (*RI*) of heavy metals in surface sediments from the Yangtze River catchment of Wuhan.

different sources. The discharge of urban sewage and industrial wastewater has been identified as a major pollutant source, thus these sources should addressed first in remediation efforts.

In view of multiple heavy metal contamination, 63.6% of samples from the mainstream, 75.0% from tributaries, and 88.9% from lakes exhibited low and moderate ecological risk of heavy metals. The residual samples were exposed to high ecological risk. Moreover, the potential ecological risks of the heavy metals in the mainstream and tributaries were higher than that in lakes.

Acknowledgements

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