



Concentration and Chemical Speciation of Metals in Sediments from Upstream of the Pearl River, China

Silin Yang*, Ning Zhao***, Dawei Wang***, Liqiong Tang*, Rong Wei** and Bin Yang*†

*Faculty of Environmental Science & Engineering, Southwest Forestry University, Kunming 6500224, China

**Faculty of Environmental Science & Engineering, Kunming University of Science & Technology, Kunming 650500, China

***Faculty of Life Science, Southwest Forestry University, Kunming 650224, China

†Corresponding author: Bin Yang

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 02-09-2015

Accepted: 07-10-2015

Key Words:

Heavy metals

Sediments

Pearl river

Sediment quality standard

ABSTRACT

The concentration and chemical speciation of typical metals (Cu, Zn, Cd, Pb, Cr, As, Mn, Fe) in water and sediment were investigated from the upstream of the Pearl River. The investigated eight metals showed the total As, Cu and Pb concentrations of most sample sites in the sediment exceeded the threshold effect concentration of sediment quality guidelines, but their potential ecological risk index values were low, which posed a low risk to the local ecosystem. The speciation of Pb and Zn showed that they predominate in the reducible fractions; Cu and As were mainly held in residual fraction and reducible fraction. The order of bioavailability for the metals was Mn > Zn > Pb > As > Cu > Fe > Cr.

INTRODUCTION

Pearl River Basin (102°14'~115°53' E, 21°31'~26°49' N) is a complex basin, which comprises Xijiang, Beijiang, Dongjiang and Pearl River Delta rivers. This area covers less than 5% of the total land area in China, but its GDP accounts for 13% of the total of China. Thus, it plays a rather important role in Chinese economic development. In recent years, with the rapid industrial and agricultural development, together with the speeding up of urbanization, the eco-environment has been worsening, along with the worsening pollution in Pearl River Basin, especially heavy metal pollution, which has become an important factor in restricting the social sustainable development. Therefore, heavy metal pollution in water and sediments in the catchment has received a great deal of attention.

The previous works showed that the sediments in Guangzhou section and Estuary of the Pearl River were seriously polluted with high toxicity heavy metals (Niu et al. 2009, Qi et al. 2010). The average contents of Cu, Pb, Zn, Cd and Cr in surface sediments of the Pearl River (Guangzhou Section) were higher than background values. Especially, the average content of Cu was 21.2 times of the background value (Niu et al. 2009). The concentrations of Zn, Cu, Cd and Pb in the sediments of the Guangzhou Section of the Pear River were higher than those in the sediments

of the Pearl River estuary (Cheung et al. 2003, Wang et al. 2010). The enrichment of metals in the sediments of the Pearl River Basin was the result of anthropogenic inputs in the last few decades (Chen et al. 2012). The distribution characteristics of the metals in the sediments were similar, and the distributions were affected by a combination of both physical and chemical processes, as well as anthropogenic inputs. The sedimentation of suspended particles was a dominant factor to consider in any attempts to control the transport and distribution of metal pollutants in the river and estuarine area (Ip et al. 2007).

However, these studies about the metals in the Pearl River Basin mainly focused on the downstream areas characterized with rapid economic development, while relatively few studies were focused on metal speciation and mobility on the upstream basin. In addition, the landform of the upstream of the Pearl River, especially the Yunnan section is featured with Karst landform. A large amount of Ca could be dissolved into water, which led to a higher pH value in the upstream water than in the downstream. The current studies on what effects the higher pH value would impose on the heavy metal mobility are insufficient. Therefore, more investigation is needed to identify the source, concentration and its distribution, speciation of metal elements in the water and sediments in the upstream of the Pearl River.

This paper studied the concentration and distribution of metals (Cu, Zn, Cd, Pb, Cr, As, Mn, Fe) in the sediments in upstream of the Pearl River, China, and the sequential extraction procedure (Rauret et al. 1999, Ure et al. 1993) modified by Bureau Communautaire de Reference (BCR) was applied to study speciation distribution of the metals. This will provide useful information to understand the current metal contamination and environmental risk in upstream of the Pearl River.

MATERIALS AND METHODS

Water and Sediment Collection and Preparation

The sampling area is located at Nanpan River (25°24'~25°46'N, 103°51'~103°55'E), the upstream of the Pearl River. Twelve sites were set along the Nanpan River (A1-A12) as indicated in the previous study (Yang et al. 2013). Water and composite sediment samples were collected from twelve sites from November 12 to 13 in 2011. Water samples were collected at the surface (0-20 cm) using a water sampler, a portion of which was filtered through 0.45 millipore filters, with some filtered and unfiltered samples preserved by acidifying with ultra-pure HNO₃ to pH < 2 for dissolved and total metal analysis, and some with filtered water samples acidified to pH < 2 with ultra-pure H₂SO₄ for TOC analysis. All the water samples were stored at 4°C in polyethylene bottles. Sediment samples of 3 random points with 5 m away from water sample sites were collected and mixed as one sample. Sediment samples were collected only with a depth of 0-10 cm using a grab sampler. The collected sediment samples were put into clean polyethylene sample bags, labelled and then stored in the lab. The sediments were dried at room temperature, grilled into pieces with a wooden stick, and then filtered with a 2 mm nylon sieve. The gravels and plant residues were manually picked out. The sediments were further ground and filtered with a 0.149 mm nylon sieve for the analysis of soil pH, total organic carbon (TOC), metal total concentrations and their chemical fractions.

Sample Analysis

Water and sediment pH and TOC: Water pH was measured by a pH meter (Leici, ZD-2), and sediment pH was

measured in a 1:2.5 (w/v) ratio of sediment to water by a pH meter. Water TOC was measured with a TOC analyser (Apollo 9000), and sediment TOC was measured using an elemental analyser (MicroCube, Elementar, Germany).

Water and sediment metals: Dissolved metal concentrations in water were determined by ICP-OES (VISFA-MPX), and total metal concentrations in water were determined by acid digestion. 15 mL of HNO₃ was added to 100 mL of water samples, and then they were heated until 1 mL. The solution was transferred into 100 mL volumetric flask and made up to the mark with distilled water. Then, the metals were detected by ICP-OES.

Total Cu, Zn, Cd, Pb, Cr, As, Mn and Fe concentrations in sediments were determined with HNO₃-HCl-HF microwave digestion followed by ICP-OES. Dried sediment samples of 0.2 g were taken into a Teflon vessel with 10 mL of HNO₃-HCl-HF (3:1:1, V/V) acid mixture solutions. Thereafter, the vessels were sealed and heated in the microwave system with the typical reaction temperature profile (digest at 180°C for 15 min, rise to 200°C in 14 min and remain at 200°C for 9 min). When the microwave program was finished, samples were removed from microwave system and cooled to room temperature; the solutions were transferred to a teflon crucible and heated on a hot plate at 110-120°C until complete evaporation of the solution. After cooling, the residues were dissolved in 10 mL of 5% HNO₃, the solutions were then transferred to the volumetric flask (50 mL) and diluted to 50 mL. Quantification of metal concentrations in these solution stands for total metal concentrations.

The optimized BCR sequential extraction procedure was also used for fractionation (weak acid soluble, oxidizable, reducible and residual fractions), and the brief procedure is given in Table 1. The concentrations of the metals in different fractions and the resultant solutions of step four were determined by ICP-OES. The analytical wavelength of Cu, Zn, Cd, Pb, Cr, As, Mn and Fe were 327.395, 213.857, 214.439, 220.353, 267.716, 188.980, 259.372 and 259.940 nm respectively.

Statistic Analysis

The correlation matrix of the total concentrations of various

Table 1: Steps in the sequential extraction procedure.

Step	Extractant	Experimental conditions	Fraction
1	0.11 mol L ⁻¹ HOAc	Shake 16 h at room temperature	Weak acid soluble fraction
2	0.5 mol L ⁻¹ NH ₂ OH·HCl (pH 1.5)	Shake 16 h at room temperature	Reducible fraction
3	30% H ₂ O ₂ (pH 2)	Digest at 85°C (water bath) for 1h with occasional shaking	Oxidizable fraction
4	1.0 mol L ⁻¹ NH ₄ Ac 2.0 (pH 2)	Shake 16 h at room temperature	
	HNO ₃ -HCl-HF	Microwave digestion	Residual fraction

Table 2: pH value and TOC contents in water and sediment.

Item	Water		Sediment	
	pH	TOC (mg·L ⁻¹)	pH (H ₂ O)	TOC (g·kg ⁻¹)
Max	8.63	62.7	8.75	35.4
Min	7.77	3.33	7.98	5.32
Mean	8.25	13.9	8.33	20.5
S. D. ^a	0.26	16.4	0.24	10.2
V. C. ^b	3.15	117	2.88	49.7

a: Standard deviation; b: Variation coefficient (%).

metals, and the relationships between the percentages of metal species and pH or TOC contents were obtained with bivariate correlation using the Pearson coefficient in a two-tailed test ($p \leq 0.05$), and Principal component analysis (PCA) and Hierarchical cluster analysis (HCA) were performed to identify relationships among metals and provide grouping of variables. All statistical analyses were performed using SPSS13.0 software. In addition, the sediment quality guidelines (SQGs) and the potential ecological risk index were employed to evaluate the sediment biological effects and potential ecological risk.

RESULTS AND DISCUSSION

Water and sediment pH and TOC: The overall pH and TOC contents of water and sediment along with the water flow of Nanpan River are summarized in Table 2. On average, the pH values were 8.25 and 8.33 for water and sediment, respectively. Generally, the water and sediment were weakly alkaline, possibly due to Karsts geographic environment, where soil and sediment were rich in calcium carbonate.

The average TOC contents were 13.9 mg·L⁻¹ and 20.5 g·kg⁻¹ for water and sediment, respectively. The TOC of water was increasing significantly from site A12 to A1, and showed the highest content at site A1. The TOC of sediment was slightly lower than that reported by Chen et al. (26.2 g·kg⁻¹), and higher than that of other large rivers in China such as the Yangtze River (8.2 g·kg⁻¹) and the Yellow River

(1.8 g·kg⁻¹) (Chen et al. 2000). In general, the TOC content of the river sediment was not only subjected to hydrothermal conditions, but also affected by vegetation distribution and organic matter production. Because approximately 90 % of all the sediment of the Yellow river has come from the Loess Plateau with sparse vegetation (Zhang et al. 1990), thus the TOC content was very low. The higher TOC contents of Yangtze River and Pearl River basins were associated with the higher vegetation cover.

Total concentrations of metals in water and sediment:

The total and dissolved Cu, Zn, Cd, Pb, Cr and Mn concentrations of most sample sites in water were lower than the detection limits of the analysis (ICP-OES). The total and dissolved concentrations of As and Fe were also very low (Fig. 1), and total As concentrations in all the sampling sites did not exceed the As standard (0.05 mg·L⁻¹) of environmental quality for surface water in China (GB3838-2002). This result suggested that the study area had low regional background metal concentrations and low input of metals from human activities. In addition, in the alkaline water environment with relatively high pH, metals tended to remain in the sediment (Tukura et al. 2007). Therefore, the metals of the study area transported to the downstream by water were very limited.

The summarized information of the total concentrations of Cu, Zn, Cd, Pb, Cr, As, Mn and Fe for sediment are given in Table 3. Total Cd and Cr concentrations of most sample sites in sediments were lower than the detection limits of the analysis (ICP-OES). Total concentrations of Cu, Zn, Pb, As, Mn and Fe in sediments were in the wide range of 25.3-73.8, 37.9-123, 26.6-75.9, 13.7-40.7, 256-621 and 15085-41598 mg·kg⁻¹, respectively.

On the basis of a widely used sediment quality guidelines (SQGs) (Burton Jr 2002), total As concentrations of all sample sites exceeded the threshold effect concentration (TEC, 5.9 mg·kg⁻¹) for toxic biological effects, total Cu and Pb concentrations of most sample sites also exceeded the TECs (Cu, 35.7 mg·kg⁻¹; Pb, 35 mg·kg⁻¹) of SQGs, total

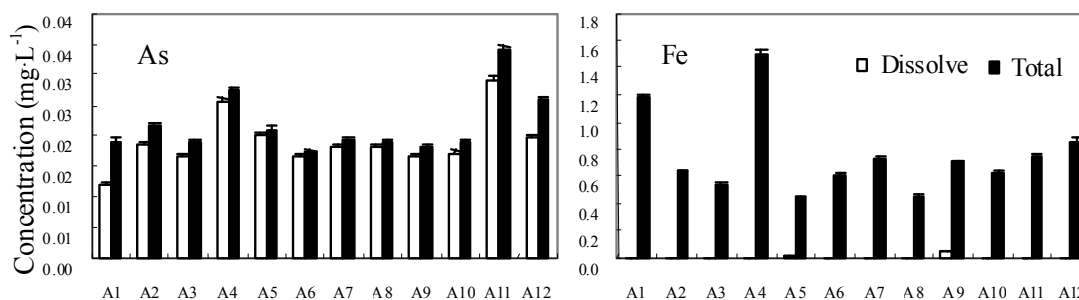


Fig. 1: Distribution and concentrations of As and Fe in water.

Table 3: Total concentrations of the metals in sediment ($\text{mg}\cdot\text{kg}^{-1}$).

Item	Cu	Zn	Cd	Pb	Cr	As	Mn	Fe
Max	73.8	123	0.54	75.9	220	40.7	621	41598
Min	25.3	37.9	-	26.6	-	13.7	256	15085
Mean	38.3	88.2	-	47.5	-	23.3	420	19572
S. D. ^a	13.5	24.5	-	16.2	-	6.25	107	7183
V. C. ^b	35.4	27.7	-	34.1	-	26.7	25.5	36.7
TEC ^c	35.7	123	0.6	35	37.3	5.9	nd	nd
Guangzhou section (2007) (Niu et al. 2007)	348	183	1.72	102	93.1	25.0		
Pearl River Estuary (1997) (Liu et al. 2002)	39.0	110	0.344	59.4	56.4	5.24		
Pearl River Estuary (2004) (Huang et al. 2006)	39.4	130	0.2	53.3	86.3	21.1		
Pearl River Estuary (2006) (Yang et al. 2009)	80.7	139.8	5.55	105.8	118	33.1		
Pearl River Estuary (2008) (Jiang et al. 2010)	63.2	261	6.7	96.7	167	38.7		

- Concentrations of most sample sites were lower than the detection limits of the analysis (ICP-OES); nd no standard; c threshold effect concentration

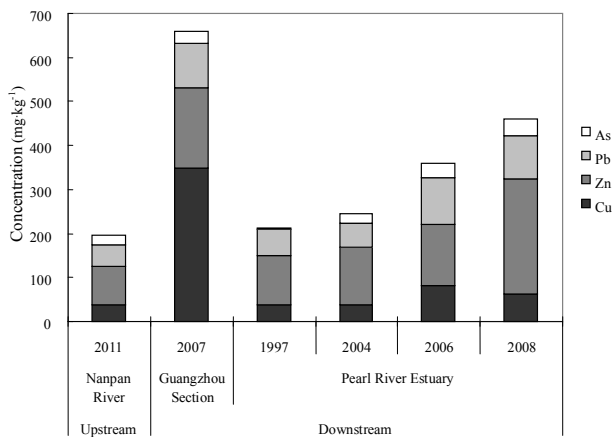


Fig. 2: Total concentrations of the metals in sediment.

Zn concentrations most sample sites were found within the TEC ($123 \text{ mg}\cdot\text{kg}^{-1}$) of SQGs. This result indicated that As, Cu and Pb have potential ecological risks, and their potential ecological risk assessment is needed for extended discussion.

Total Cu, Zn, Pb and As concentrations in upstream and downstream of the Pearl River are shown in Fig. 2. The sum of total Cu, Zn, Pb and As concentrations ($197 \text{ mg}\cdot\text{kg}^{-1}$) in Nanpan River (the upstream of Pearl River) were lowest, the highest concentrations ($658 \text{ mg}\cdot\text{kg}^{-1}$) could be observed in Guangzhou Section (the downstream of Pearl River), total metal concentrations of Pearl River Estuary in 1997, 2004, 2006 and 2008 were 213, 243, 259 and $459 \text{ mg}\cdot\text{kg}^{-1}$, respectively, and total concentrations have increased with the course of time, and were higher than those of Nanpan River (the upstream of Pearl River). These phenomenon indicated that the total metal concentrations in downstream of Pearl River were higher than those in the upstream, and the enrichment of metals in the sediments of Pearl River could be attributed to local agricultural, domestic and industrial effluents (Chen et al. 2012).

Distribution of total Cu, Zn, Cd, Pb, Cr, As, Mn and Fe in sediments along with the river flow is shown in Figs. 3 and 4. As a whole the concentrations of eight metals in the sediment dispersedly distributed, there was no progressive increase from upstream to downstream of the investigated area for each type of metals, and the transfer of metal along the flow direction was not observed. The maximum values of Cu, Pb, Cr and As concentrations in sediments were all observed at site A12, with the values of 73.2 ± 6.65 , 75.9 ± 2.97 , 220 ± 23.4 and $40.7\pm 4.29 \text{ mg}\cdot\text{kg}^{-1}$, respectively. The site A12 is located at Huashan reservoir, the sediments mainly come from original soils before the reservoir impoundment, as well as the entrance of soils into the reservoir by rainfall and surface runoff, the soils may contain high concentrations of Cu, Pb, Cr and As. The highest concentrations of Zn and Cd were found at site A3, and the concentrations of the other elements in sample site A3 were also relatively high, because of site A3 relatively near to sewage outfalls from Qujing city. But the concentration of site A3 were not significantly higher than those of other sites.

Potential ecological risk assessment of metals in sediment:

The potential ecological risk index (*RI*) proposed by Hakanson (1980), was widely used to assess the contamination and ecological risk of single metal and multiple metal combination in sediments (Hakanson 1980). The equations for calculating are as follows.

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i = \sum_{i=1}^n T_r^i \times \frac{C_d^i}{C_n^i}$$

Where C_n^i is a reference value of metal. The values of Cu, Zn, Cd, Pb, Cr, As and Mn from the background values of Yunnan soil (China environment monitoring general station 1990) are 46.3, 89.7, 0.218, 40.6, 65.2, 18.4 and $626 \text{ mg}\cdot\text{kg}^{-1}$, respectively, C_d^i is the concentration of metal in the sediment, T_r^i is the biological toxic factor of an indi-

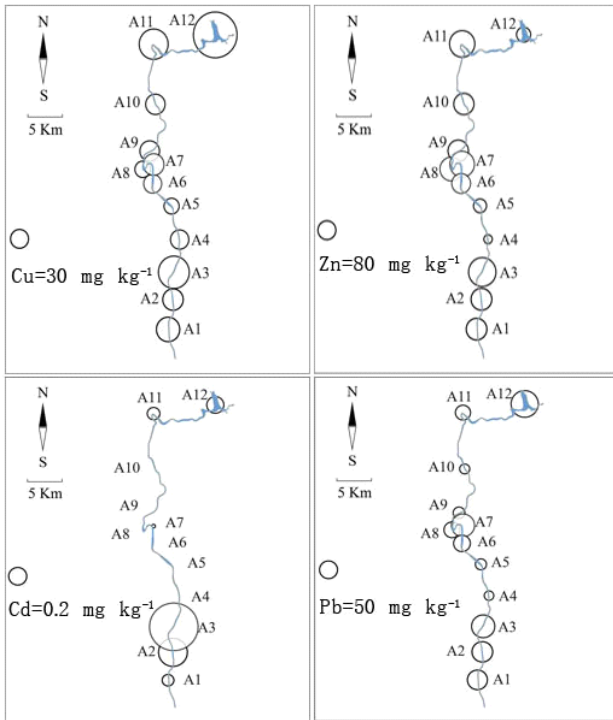


Fig. 3: Distribution of total Cu, Zn, Cd and Pb concentrations along with the water flow of Nanpan River.

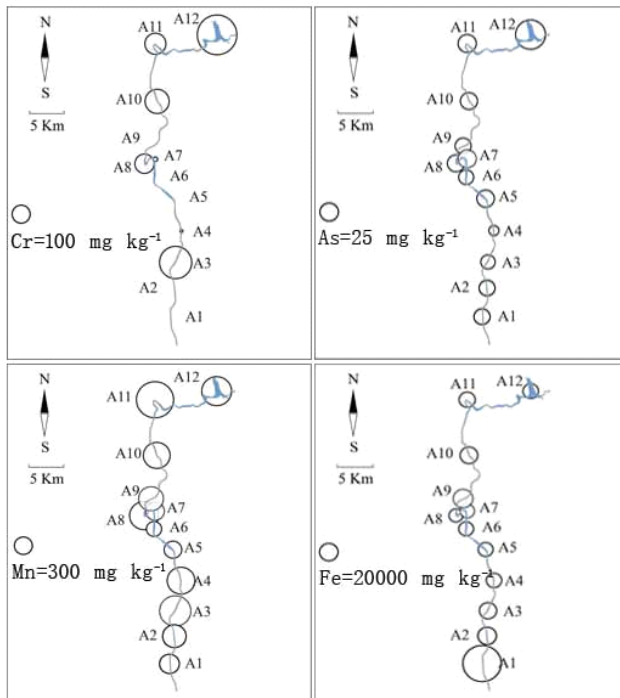


Fig. 4: Distribution of total Cr, As, Mn and Fe concentrations along with the water flow of Nanpan River.

vidual metal, the $T^i r$ values of Cu, Zn, Cd, Pb, Cr, As and Mn are 5, 1, 30, 5, 2, 10 and 1, respectively (Hakanson 1980, Xu et al. 2008). C^i_f is the single metal contamination index, $E^i r$ is the single metal potential ecological risk index, and RI is calculated as the sum of all risk indices for metals in sediments. The values of $E^i r$ and RI can be categorized into four and five classes as depicted in Table 4.

The individual metal and comprehensive potential ecological risk indices are presented in Table 5. Cd contamination at both sites (A2 and A3) posed a moderate risk, while the other metals a low risk. The RI values of eight metals ranged from 15.89 to 106.39, and were lower than 150, indicating that they posed a low risk to local ecosystem.

The correlation analysis provides valuable information about the metal concentrations and their respective pathways. Obtained correlation coefficients are given in Table 6. Significant positive correlations were found in some metal pairs such as Cu and Pb (0.690), Cu and As (0.749), Cu and Cr (0.714), Pb and Cd (0.621), As and Cr (0.582), As and Mn (0.712). High correlations between the metals reflected similar levels and common sources of contaminations, as well as their mutual dependence and identical behaviour during the transport. Zn is not significantly correlated with the other metal, and strong correlations between Fe and the other metal were also not observed, the results suggested that Zn and Fe concentrations were not controlled by a single factor, but a combination of geochemical support phases and their mixed associations. Therefore, principal component analysis (PCA) is needed for understanding the relationships.

The results of PCA for metal concentrations are given in Tables 7 and 8. The total cumulative variance of three main components was 79.28%. The metals Cu (0.915), Cd (0.691), Pb (0.751), As (0.858), Cr (0.669) and Mn (0.616) had a high positive loading in the first component (44.98% of the total variance), and that the correlation coefficient between these six metals was higher. In addition, the highest concentrations of most of these metals appeared in Huashan Reservoir with less human activities, and that near city sewage outfall, which also had a higher concentration. These results suggested that these metals may originate from both pedogenic and anthropogenic contributions.

Fe (0.707) had a high positive loading in the second component (18.56% of the total variance), indicating that Fe may originate from pedogenic contribution. The positive loadings of Zn in the first, second and third components were 0.391, 0.538, and 0.483, respectively. This result suggested that Zn could be contributed to pedogenic, anthropogenic and unknown factors.

In addition, HCA was used to identify relationships

Table 4: Standards of the potential ecological risk for and RI .

Item	Grade of the potential ecological risk				
	Low	Moderate	Considerable	High	Very high
E_r^i	<40	40-80	80-160	160-320	≥ 320
RI	<150	150-300	300-600	-	≥ 600

The potential ecological risk index; RI : The potential ecological risk index

Table 5: Potential ecological risk factors and risk indices of heavy metals in surface sediment.

Sample sites	E_r^i							RI
	Cu	Zn	Cd	Pb	Cr	As	Mn	
A1	4.23	1.03	17.89	6.83	-	12.05	0.53	42.56
A2	3.71	1.04	44.04*	7.08	-	11.98	0.63	68.47
A3	5.60	1.37	74.31*	7.95	5.50	10.82	0.84	106.39
A4	3.34	0.42	-	3.28	0.51	7.60	0.74	15.89
A5	2.73	0.65	-	3.86	-	13.19	0.47	20.90
A6	3.27	0.94	-	5.73	-	11.25	0.41	21.60
A7	3.75	1.22	5.50	7.99	0.78	13.73	0.50	33.49
A8	2.85	1.13	-	5.53	3.30	12.92	0.78	26.51
A9	3.54	1.02	-	4.03	-	12.06	0.66	21.32
A10	3.52	1.01	-	3.44	4.14	12.92	0.71	25.75
A11	5.22	1.26	19.27	5.20	3.60	13.73	0.99	49.28
A12	7.90	0.71	26.15	9.35	6.78	22.50	0.80	74.18

* Middle contamination; - No valid data; E_r^i : The potential ecological risk index; RI : The potential ecological risk index

Table 6: Correlation matrix for total metal concentrations in sediments.

	Cu	Zn	Cd	Pb	As	Cr	Mn	Fe
Cu	1							
Zn	0.100	1						
Cd	0.556	0.452	1					
Pb	0.690*	0.369	0.621*	1				
As	0.749**	0.235	0.435	0.407	1			
Cr	0.714**	-0.020	0.070	0.570	0.582*	1		
Mn	0.516	0.246	0.376	0.041	0.712**	0.176	1	
Fe	0.045	0.104	0.116	0.117	-0.264	-0.104	-0.203	1

* Significance at the 0.05 probability level; ** Significance at the 0.01 probability level

among metals. The derived dendrogram is shown in Fig. 5. In this dendrogram, eight metals are grouped into two clusters. Cluster 1 consisted of Cu, Pb, Cr, Cd, Zn, As and Mn, Cluster 2 only included Fe. This result coincides with the conclusion of the correlation and PAC analysis. This may be due to the sediments receiving large amount of red soils with high concentration of Fe.

Metals speciation: Although results of potential ecological risk assessment for the metals were low ecologic risk, the bioavailability and mobility of metals depended not only on their concentrations, but also on their chemical speciation

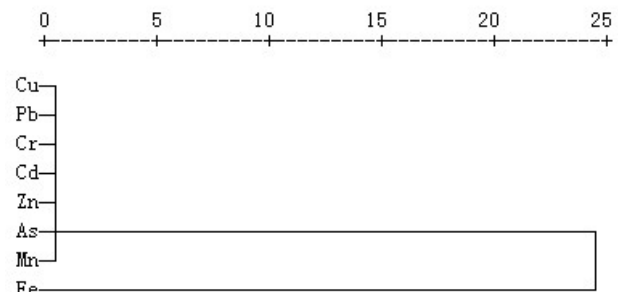


Fig. 5: Dendrogram of the metals in sediments.

and surrounding conditions such as pH and organic matter (Whitehouse 2000).

The percentages of metals from each extraction step are shown in Fig. 6. The percentages of residual fraction for Cr were close to 100%, and the percentages of residual fraction for Fe were more than 70%, indicating that Fe and Cr were mainly held in residual fraction bound in mineral lattice, which is generally regarded as relatively stable or inert under normal conditions, thus, minerals in this fraction are less likely to harm the environment.

The speciation of Pb and Zn showed that they predominate in the reducible fractions. Appreciable amounts also

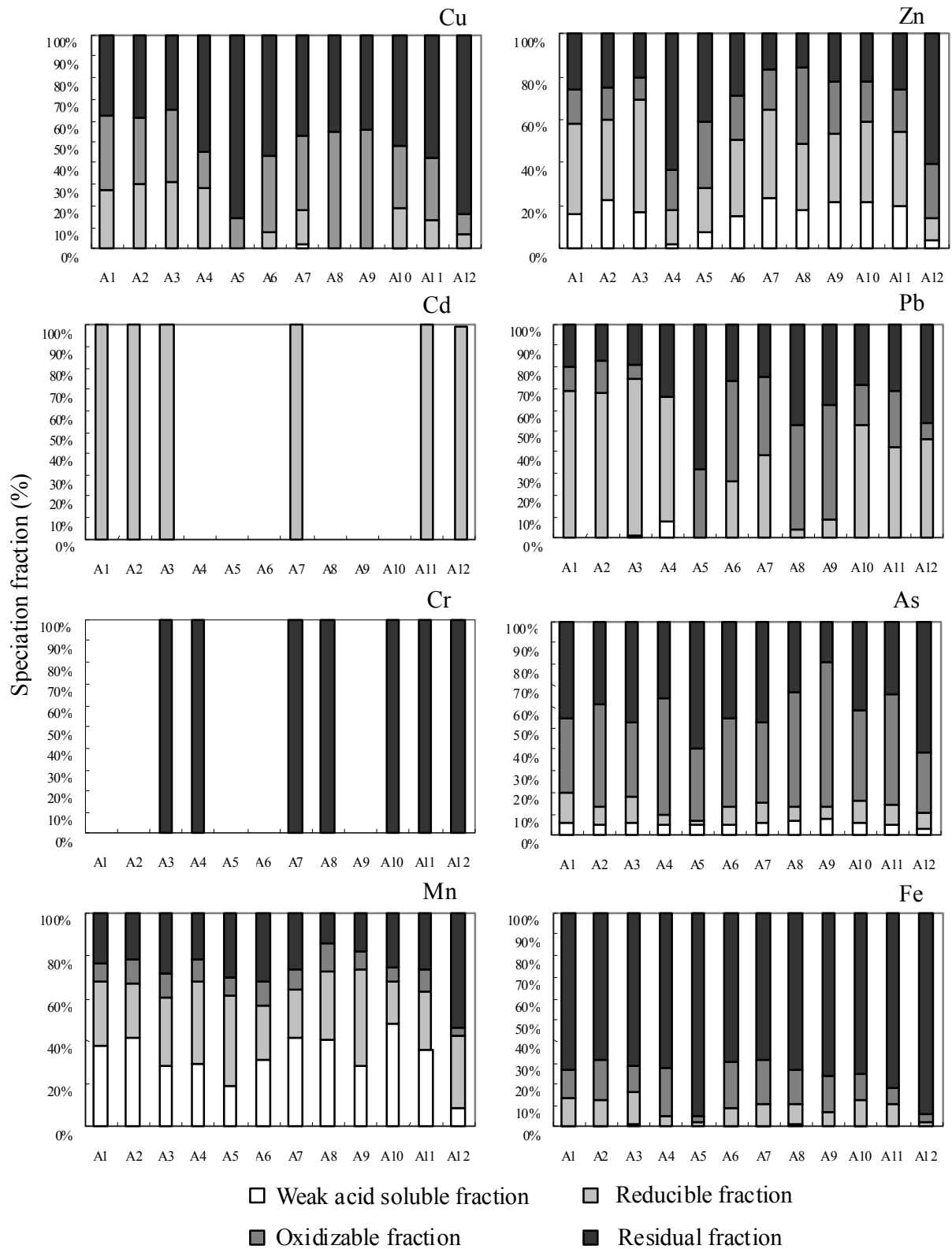


Fig. 6: Speciation distributions of the heavy metals in sediments.

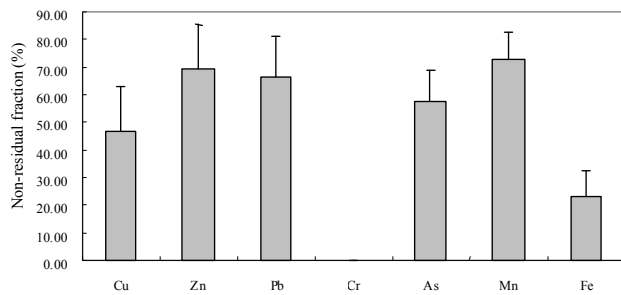


Fig. 7: The bioavailability of heavy metal in sediments.

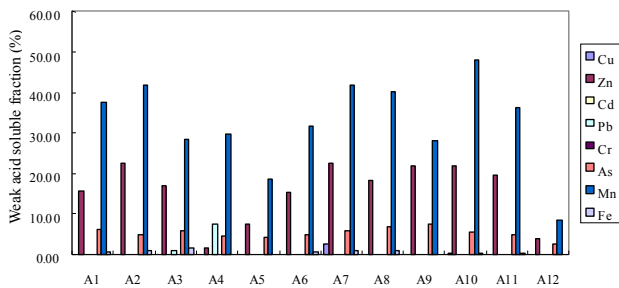


Fig. 8: The mobility factors of heavy metal in sediment.

occurred in other fractions, the order of percentages for each fraction of Pb and Zn was as follow: reducible > residual > oxidizable > weak acid soluble.

The reducible fraction of Pb was higher than those of the other metals, which were in accordance with the researches of Yu (Yu et al. 2010), Liu (Liu et al. 2010) and Huang (Huang et al. 2013). Fe and Mn oxides contained in this fraction can easily adsorb trace metals, especially Pb, which are recognized as efficient scavengers (Ianni et al. 2010). Under reducing conditions, the Fe-Mn oxides can be decomposed into the aquatic system (Boughriet et al. 2007), which Pb of reducible fraction becomes unstable and has the potential to be transferred to available forms if the redox potential changes (Guvén & Akinci 2008).

Cu and As were mainly held in residual fraction and oxidizable fraction; the percentages of weak acid soluble for Mn were the highest. Generally, residual metals reflect background geochemical conditions, while anthropogenically sourced metals preferentially partition to the non-residual fraction (Liu et al. 2011). Percentages of residual fraction for most of the metals were the highest at site A12, and their lowest values were observed at site A3, indicating that the metals at site A12 had a natural origin, while that at site A3 come mainly from anthropogenic source. In addition, non-residual fraction of metal was more bioavailable than the residual of metal (Ma & Rao 1997), the order of bioavailability for the metals was Mn > Zn > Pb > As > Cu > Fe > Cr (Fig. 7).

Metals speciation reveals not only their bioavailability, but also reflects their mobility. The mobility factor (MF) had been calculated in many researches to evaluate metal mobility in soil and sediment (Dhanakumar & Mohanraj 2013, Venugopal et al. 2009). Metals bound to the weak acid soluble fraction are readily and potentially mobile, therefore the fraction of weak acid soluble metal divided by the sum of all fractions can be taken as an equivalent index of metal mobility (Pueyo et al. 2003). The MFs of Cu, Zn, Cd, Pb, Cr, As, Mn and Fe are shown in Fig. 8. The MFs of Mn, Zn and As were higher than that of other metals in sediments, and the order was Mn > Zn > As, suggesting that the mobility of Mn was the strongest among the eight metals. The MFs of Cu, Cd, Pb, Cr and Fe were almost zero, suggesting their low mobility.

Organic matter in sediment is an important factor controlling the sorption of trace metals and organic compounds (Gundersen & Steinnes 2003, Rubio et al. 2000). Table 9 presents correlation coefficients for percentages of metal fractions and TOC contents in the sediment. The percentages of oxidizable fractions of all metals, except Cd and Cr, correlated positively with the TOC contents, and the contents of TOC were significantly positively correlated with the percentages of oxidizable fractions of the six metals, but not with the percentages of weak acid soluble fraction, reducible fraction and residual fraction. This phenomenon indicates that these metals can easily complex with organic matters, especially Cu, due to such as humic compounds with negatively charged sites on carboxyl and phenol groups (Mouvet & Bourg 1983, Stevenson 1994). The TOC content is a more important factor than grain size in controlling the distribution of trace metals in the sediments (Wang & Chen 2000). Accordingly, organic matter can act as an agent to trap the important scavengers for metals in river sediments (Jones 1974, Veeh 1968).

CONCLUSIONS

From this study, the total and dissolved Cu, Zn, Cd, Pb, Cr and Mn concentrations of most sample sites in water were lower than the detection limits of the analysis (ICP-OES). The total and dissolved concentrations of As and Fe were also very low, this result suggested that a very limited portion of metals in the study area were transported to the downstream. Although total As concentrations of all sample sites and Cu and Pb concentrations of most sample sites in sediment exceeded the threshold effect concentration of sediment quality guidelines, the potential ecological risk index values of eight metals were low, which they posed a low risk to local ecosystem. In addition, as a whole, the concentrations of eight metals in the sediment dispersedly distrib-

Table 7: Eigen values and variance of Principal component analysis for the metals in sediments.

Initial eigenvalues	Component							
	1	2	3	4	5	6	7	8
Total	3.59	1.48	1.25	0.76	0.56	0.15	0.10	0.06
Variance (%)	44.98	18.56	15.73	9.58	7.03	1.98	1.27	0.84
Cumulative (%)	44.98	63.54	79.28	88.86	95.89	97.88	99.15	100.0

Table 8: Loading for first three principal components for the metals in sediments.

	Cu	Zn	Cd	Pb	As	Cr	Mn	Fe
PC1	0.915	0.391	0.691	0.751	0.858	0.669	0.616	-0.066
PC2	-0.076	0.538	0.465	0.388	-0.349	-0.302	-0.333	0.707
PC3	-0.243	0.483	0.27	-0.364	0.161	-0.579	0.571	-0.27

Table 9: Correlation between speciation percentages of heavy metal and pH, TOC contents in sediment.

Speciation	Item	Cu	Zn	Cd	Pb	Cr	As	Mn	Fe
Weak acid soluble fraction	pH	-0.298	-0.861**	-	0.483	-	-0.617*	-0.580*	-0.699*
	TOC	0.484	0.784**	-	-0.486	-	0.707*	0.511	0.211
Reducible fraction	pH	-0.213	-0.896**	-0.470	-0.230	-	-0.621*	0.509	-0.826**
	TOC	-0.434	0.457	-0.047	-0.472	-	-0.012	-0.221	0.291
Oxidizable fraction	pH	-0.615*	0.434	-	-0.255	-	-0.125	-0.286	-0.212
	TOC	0.730**	0.190	-	0.814**	-	0.448	0.225	0.274
Residual fraction	pH	0.698*	0.868**	-	0.638*	-	0.362	0.321	0.567
	TOC	-0.328	-0.772**	-	-0.104	-	-0.516	-0.457	-0.340

- No effect data; * Significance at the 0.05 probability level; ** Significance at the 0.01 probability level.

uted, there was no progressive increase from upstream to downstream of the investigation area for each type of metals, and the transfer of metal along the flow direction was not observed. The speciation of Pb and Zn showed that they predominate in the reducible fractions; Cu and As were mainly held in residual fraction and reducible fraction; the percentages of weak acid soluble for Mn were the highest. The order of bioavailability for the metals was Mn > Zn > Pb > As > Cu > Fe > Cr. The mobility factors of Mn, Zn and As were higher than the other metals in the sediment, and the order was Mn > Zn > As.

ACKNOWLEDGMENTS

This study was supported by the National Scientific Foundation of China (41173124 and 41222025), Educational Commission of Yunnan Province of China (2013Y119), the Key Scientific Research Foundation of Southwest Forestry University (111417).

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