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Chemical speciation of heavy metals in the sediments of Longjiang River: after a cadmium spill

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ABSTRACT

The distribution of chemical speciation of selected elements (arsenic, iron, lead, stibium and zinc) in the stream sediments of Longjiang River (China) was studied after an environmental accident of cadmium spill. Forty samples from stream sediments of different locations of Longjiang River were selected. Sequential extraction procedures were carried out to determine the chemical forms of metals, showing that a large amount of Cd from the cadmium spill was precipitated in sediments and removed by chemical precipitation. The amount of Cd in sediments had reached an alarming level. The metals of As, Pb and Zn in the sediments might be partially converted into mobilized forms with the condition change, which should be monitored regularly. To better understand the toxicity of these pollutants and evaluate the ecological risks, principal component analysis (PCA) and Geoaccumulation Index (I_{geo}) were applied to assess the contamination levels of heavy metals in sediments. The results provide a better image in defining the contamination extent of heavy metals in sediments.

Keywords: Chemical speciation; Heavy metals; Ecological risk; Potential mobility

1. Introduction

Longjiang River is located in south of China, flowing through Guizhou and Guangxi Province and into Liujiang River [1]. Longjiang River is 358 kilometers in length. The average annual runoff is 13.2 billion m^3, and the basin area occupies 16,878 km^2 [2]. Longjiang River is mostly used for the population of coastal cities, extensive agriculture and industry. There are many mining activities around. Due to these activities, the river basin was polluted by heavy metals [3]. In 2012, pollutants containing 20 tons of toxic cadmium and other heavy metals flushed into Longjiang River, resulting in severe heavy metal contamination to river reaches of 300 km in length. The concentration of Cd contained in some parts of the reaches is 80 times more than the national water standard [4]. Therefore, the local government added an amount of aluminium polychloride into the river to clean up and precipitate heavy metals after the accident. Although most of the heavy metals were deposited and absorbed by lime and aluminium polychloride, ecological risk still remains.

The major goal of this study is to analyze the speciation of heavy metals contained in the sediments and to evaluate the ecological risk of precipitated heavy metals with emphasis on cadmium. The Tessier procedure was widely used to analyze the speciation of metals contained in sediments [5]. By gradually adding chemicals with different leaching ability, the heavy metals were separated into different phases, and five fractions were extracted in a sequence, which were represented by the following

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chemical phases: exchangeable metals, bound to carbonates, bound to iron and manganese oxides, bound to organic matter and residual fraction [6, 7].

Statistical analysis was widely used to correlate the data of the distribution of heavy metals and to discover the underlying patterns and trends [8]. Basic statistical analysis includes minimum, maximum, mean, standard deviation (SD), and standard error (SE). PCA can be applied to determine the main factors from multiple variables. Varimax normalized rotation can be used on the data-setto extract latent constructs [9, 10]. Another widely used statistic tool is Geoaccumulation Index (I_{geo}), which had been widely used to quantify the pollution degree of heavy metals in sediments and soils.

By analyzing the speciation of cadmium and other heavy metals in the sediments of Longjiang River, the potential mobility of these heavy metals will be revealed. Statistical analysis including PCA and I_{geo} will provide ecological risk information of different samples of the Longjiang River. Such information will be helpful for further ecological restoration.

2. Methodology

2.1. Samples

This survey was conducted in August, 2014. Forty sampling sites were selected along the Longjiang River from the border of Guizhou and Guangxi province to Liuzhou, Guangxi province, the beginning of Liujiang River, lasting for 307 kilometers long. For every 10 kilometers, one sampling site was picked. Other sample sites include metallurgy plant sewage outfall, "cadmium spill accident" pollutant release sites, tributaries and abouchement sites (see Fig. 1). At each site, two bottles (500 mL each) of water were collected to detect pH value, and sediments were collected to examine the contents of each fraction in same volume. The sediment samples were stored at 4°C in plastic bottles with air-dried. All samples were extracted according to the procedure of sequential exaction scheme (SES) [11].

2.2. Index of Geoaccumulation

The pollution degree of the heavy metals in sediments and soils can be categorized into seven main classes (Table 1). I_{geo} had been widely used to quantify the pollution degree. The calculation is given in Eq. (1) [12]:

$$I_{geo} = (\log_2 C_n / 1) \tag{1}$$

In this equation, C_n is the measured concentration of the heavy metals in the sediments, and B_n is geochemical background value. The coefficient 1.5 is used to account the possible variation of the background values.

The background values of heavy metals in Guangxi Province, China, have been given in Table 2.

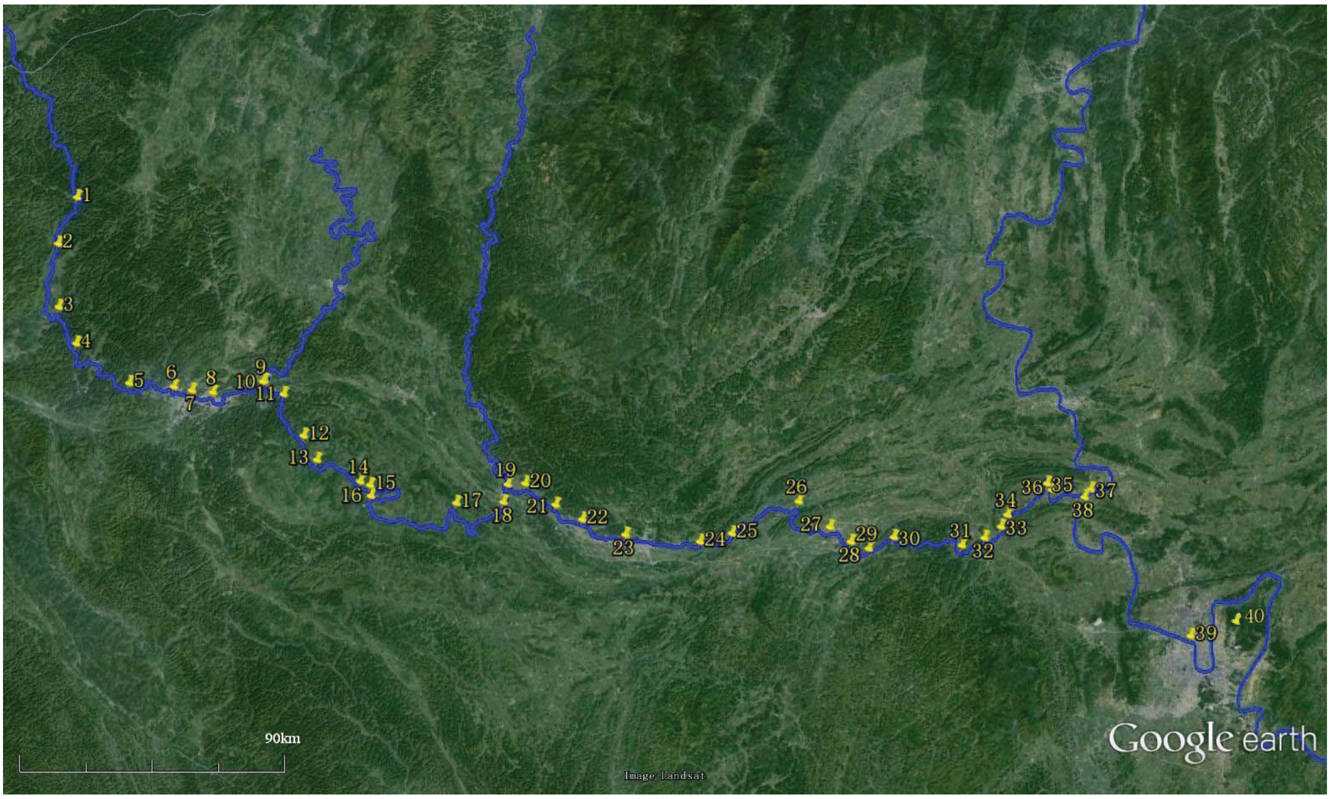

Fig. 1. Satellite map of sampling sites 414 × 256 mm (96 × 96 DPI).

Table 1
I_{geo} classes in relation to sediment quality

I_{geo}	Class	Sediment quality
<0	1	Practically uncontaminated
0–1	2	Uncontaminated to moderately contaminated
1–2	3	Moderately contaminated
2–3	4	Moderately to heavily contaminated
3–4	5	Heavily contaminated
4–5	6	Heavily to extremely contaminated
>5	7	Extremely contaminated

Table 2
Background value in Guangxi Province

Element	As	Cd	Fe	Pb	Zn
Background value (mg·kg^{-1})	20.5	0.267	38100	24	75.6

2.3. Sequential extraction scheme

The sequential extraction scheme of Tessier is widely used to determine the speciation of heavy metals. The five fractions—exchangeables, carbonates, oxides, organics, and residuals, which can be released under diffident environment conditions, are widely recognized [11, 13].

2.3.1. Step 1: Exchangeables

Metals in this phase are weakly absorbed and dissolution reaction will occur along with ion-exchange process [14]. The extraction was conducted at room temperature with 8 mL of 1 mol·L^{-1} $MgCl_2$ solution, pH 7. And 0.5 g of dried sediments was added in a 10 mL centrifuge tube with sustainable concussion for 2 h. The extract was collected and stored at 4°C. The residue was centrifuged and then washed by deionized water.

2.3.2. Step 2: Bound to carbonates

The dissolution reaction of heavy metals bound to carbonate phase will occur with the changes of ionic composition or pH [15]. Therefore, 8 mL of sodium acetate solution (adjusted to pH 5 with acetic acid) was added to the residue of Step 1. The extraction was conducted at room temperature with concussion for 5 h. The extract and wash steps were performed as described in Step 1.

2.3.3. Step 3: Bound to iron and manganese oxides

Due to their instability under reducing condition, heavy metals in this phase can be released [16]. The residue from Step 2 was incubated with 8 mL of $NH_2OH·HCl$ (0.04 mol·L^{-1}) at 96°C in a water bath with occasional concussion for 6 h. The extract and wash steps were performed as described in Step 1.

2.3.4. Step 4: Bound to organic matters

Metals bound to various organic matters in this phase can be released under oxidizing condition [17]. Thus, 3 mL of HNO_3 (0.02 mol·L^{-1}) and 5 mL of 30% (v/v) hydrogen peroxide (adjusted to pH 2) were added to the residue from Step 3. The reaction was carried out at 85°C in a water bath with occasional concussion for 4 h. Then, 2 mL of ammonium acetate (3.2 mol·L^{-1}) was added into the tube for reaction with concussion for 0.5 h. The extract and wash steps were performed as described in Step 1.

2.3.5. Step 5: Residuals

In this phase, metals are stable in the lattice mineral structure, which makes them not easily released into the water [18]. Then, 15 mL of concentrated nitric acid (HNO_3, 65% w/w), 5 mL of hydrochloride (HCl, 36.5% w/w), and 2 mL of perchloric acid ($HClO_4$, 70% w/w) were added every half an hour into a beaker (200 mL), with the residue from Step 4. The experiment was performed at 200°C with an electric furnace. After evaporated to dryness, the mixture was dissolved by 5% (w/w) HCl with a constant volume of 100 mL.

Heavy metals contained in the solution were detected by inductively coupled plasma optical emission spectrometry [19] (ICP-OES, 725-Agilent Technologies, California, USA).

2.4. Statistical analysis

Statistical analysis was applied here to figure out the possible characterization of the sediments of Longjiang River by SPSS 19.0 soft package.

3. Results and discussion

3.1. Characteristics of Longjiang River

Figs. 2 and 3 show the pH and Cd concentrations of 40 water samples. The pH of the water samples ranged from 6.8 to 8, indicating that the pH of Longjiang river water was close to neutral. This may be due to the dissolution of carbonate rock of the Karst geomorphology [20]. The water pH around sewage outfall or settlement site varied from average value, which may be due to the cadmium spill and following cleanup by chemical regents. For most water samples, the Cd concentrations were lower than 0.005 mg·L^{-1}, which can meet the national standard of surface water in China [4]. Overall, the results showed that the water quality of Longjiang River can meet the drinking water supply and aquatic organism survival standards [21, 22]. However, the potential environmental risks of heavy metals, which were precipitated in the sediments, also existed. Thus, a risk assessment should be carried out. The concentration of heavy metals in sediment samples were presented in Table 3. Fe, Zn, Pb (with mean value of 26,046; 271.11; 103.92 mg·Kg^{-1}, respectively) were the dominate metals in the sediments. Cd exhibited lower concentrations with mean values of 21.65, 5.083 mg·Kg^{-1}. Generally, the concentrations of heavy metals in sediments of Longjiang River were much higher than those in unpolluted areas, which were caused by the release of pollutants, and most notably by the cadmium pollution accident in 2012. After the occurrence of cadmium pollution spill, lime and

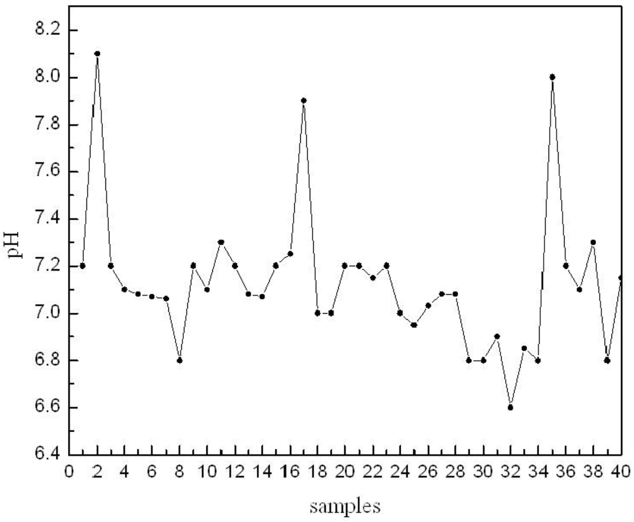

Fig. 2. pH of the water 230 × 158 mm (96 × 96 DPI).

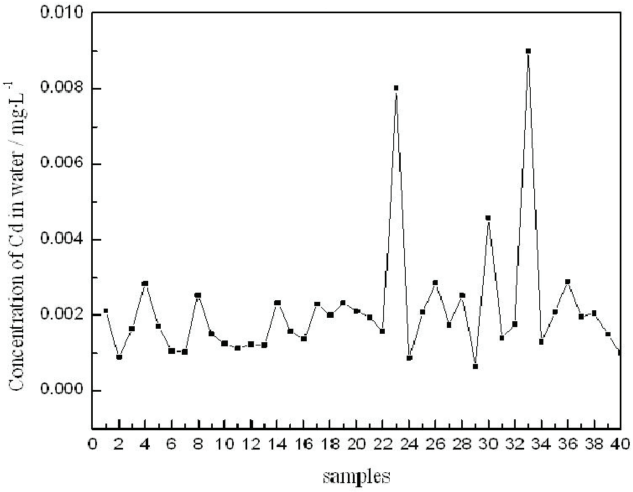

Fig. 3. The content of Cd in water 230 × 158 mm (96 × 96 DPI).

Table 3
Mean concentration (mg•kg^{-1}) of metals in sediment

	Min	Max	Mean	SD	SE
As	3.169	60.44	21.65	12.59	1.99
Cd	1.886	13.9	5.083	2.614	0.413
Fe	12456	36330	26046	5720	904.3
Pb	34.7	280.4	103.92	66.37	10.49
Zn	75.61	650.6	271.11	167.7	26.51

aluminum chloride had been used to precipitate the heavy metals, which resulted in the increase of heavy metals concentration in the sediments. It is generally recognized that in the risk assessment of soil pollution, the determination of the metal speciation can be more useful than the measurement of total heavy metals contents, as well as provide more information about the potential for bio-availability and mobility of metals. Although the heavy metals can be precipitated by lime and poly aluminum chloride [23], the mobility of such heavy metals was strongly dependent on their chemical partitioning among the different geochemical fractions, which makes sequential extraction scheme analysis necessary.

3.2. Sequential extraction scheme analysis

The different chemical speciation of As, Cd, Fe, Pb and Zn was presented in Figs. 4 to 8. The total concentrations of heavy metals in sediments were also presented, and the concentrations of different speciation were described with different color.

The concentrations of different chemical speciation of As were shown in Fig. 4, which varied greatly from different sampling sites. The total concentration of As at Site 15 was almost 20 times over that at Site 11. For As, the major fractions of most of the samples were residual forms, indicating that it would cause little effect to the environment and aquatic organisms. However, the existed fractions of As in other forms still have the potential to release into water with condition changes, and then pollute the environment. The highest content of As in unstable fractions (exchangeable, carbonates, oxides and organics) was 11.58 mg·Kg^{-1} at Site 8. As shown in the results, the concentration of As decreased by the following order: residuals > carbonates > organics > exchangeable > oxides. Only a few other sites were exceptional.

The concentrations of different chemical speciation of Cd were showed in Fig. 5. The content value of total Cd was over 2 mg·Kg^{-1} at each sampling site, and the highest reached nearly 14 mg·Kg^{-1} at Site 8 (the sewage outfall site). This was caused by the cadmium spill, where the site pollutant that contained 20 tons of toxic cadmium was flushed out and contaminated 300 kilometers of the Longjiang River. Other sites with high content of cadmium in the sediments were Sites 15, 26 and 32. These sites were the chemical reagent (lime and aluminum poly-chloride) dosing sites during the

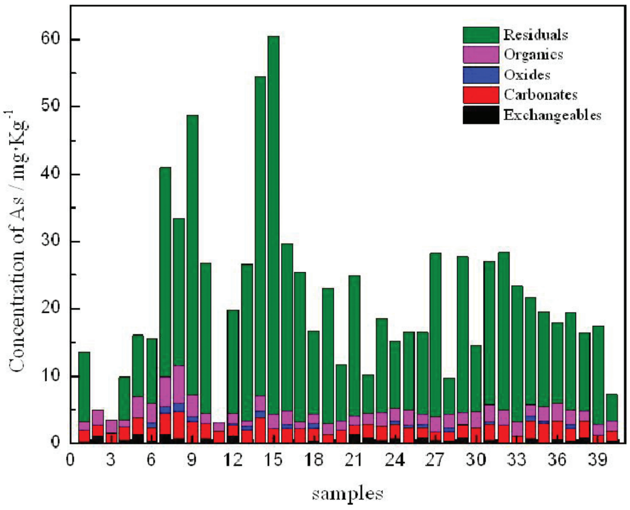

Fig. 4. The different speciation of AS 230 × 158 mm (96 × 96 DPI).

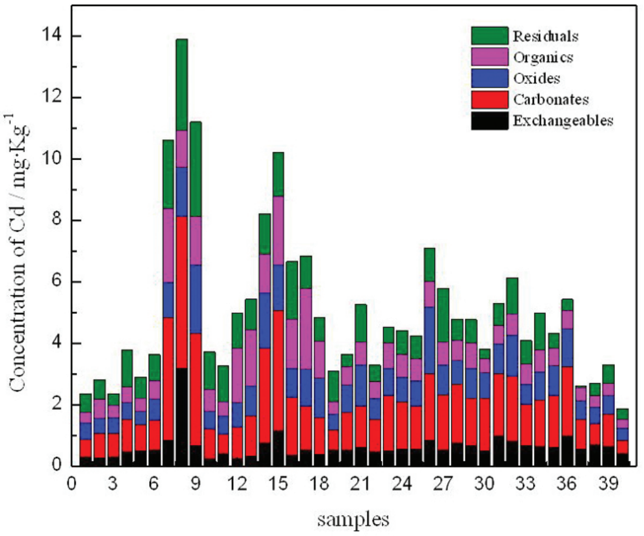

Fig. 5. The different speciation of Cd 228 × 158 mm (96 × 96 DPI).

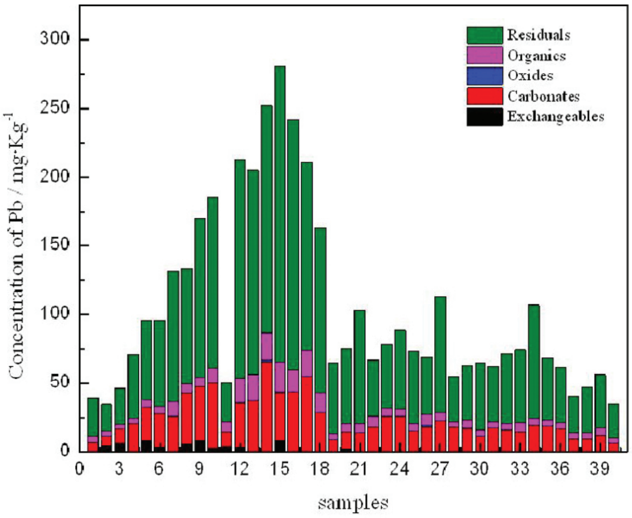

Fig. 7. The different speciation of Pb 228 × 158 mm (96 × 96 DPI).

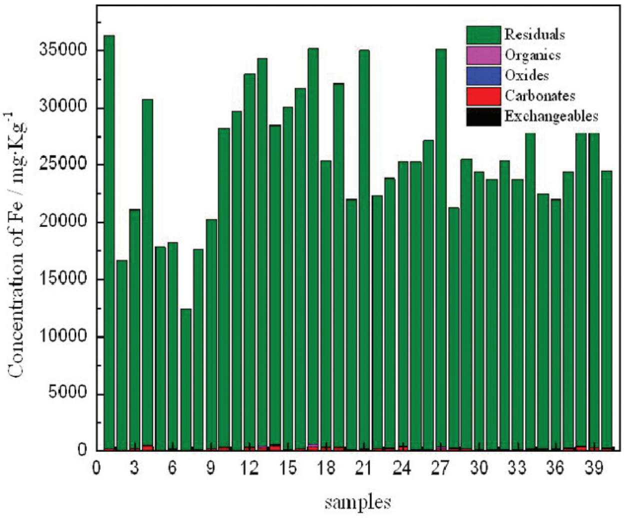

Fig. 6. The different speciation of Fe 228 × 158 mm (96 × 96 DPI).

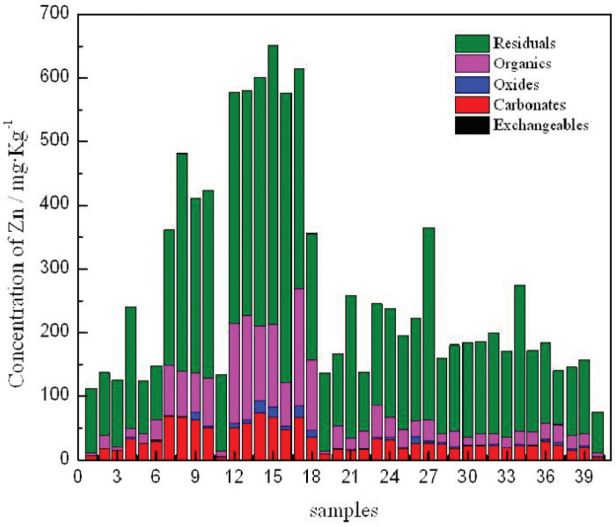

Fig. 8. The different speciation of Zn 228 × 158 mm (96 × 96 DPI).

cleanup stage. Nearly 80% of Cd existed in unstable phases, which could dissolve in water with condition changes. The concentrations of the unstable fractions followed the same trend with the total content of Cd. The average concentration of Cd was 9.72 mg·Kg^{-1}, which was almost 10 times over the Chinese guideline (1.0 mg·Kg^{-1}) [4].

Almost all of the Fe in sediment samples were in the fraction of residuals, and the concentration ranged from 12,456 mg/Kg to 36,330 mg·Kg^{-1} (Fig. 6), which were lower than the background value. Because most of the Fe in the sediment samples was stable, they might not be transformed into ferric or ferrous ion and released into liquid without a big change of the condition.

The element Pb in the sediments of Longjiang River existed mainly in residuals and carbonates (Fig. 7). The concentrations of total Pb at Site 12 to Site 17 were higher than other sites. According to residuals and carbonates value, similar trends were revealed, respectively. Because these sites are river reaches, the disturbance of water flow was severe than other sites. Thus, Pb in carbonate fraction would be released into river water and contaminate the environment.

The chemical speciation of Zn in sediment samples were shown in Fig. 8. Residuals fractions of Zn accounted for the highest amount (almost 74%), indicating that Zn was stable in the sediments with other factors. Similar to Pb, the highest values were at Sites 12 to 17. These reach sites should be monitored regularly. The unstable phases of Zn mainly existed in organics and carbonates, which may cause contamination. In summary, the concentrations of heavy metals in the sediments of Longjiang River varied with sampling sites.

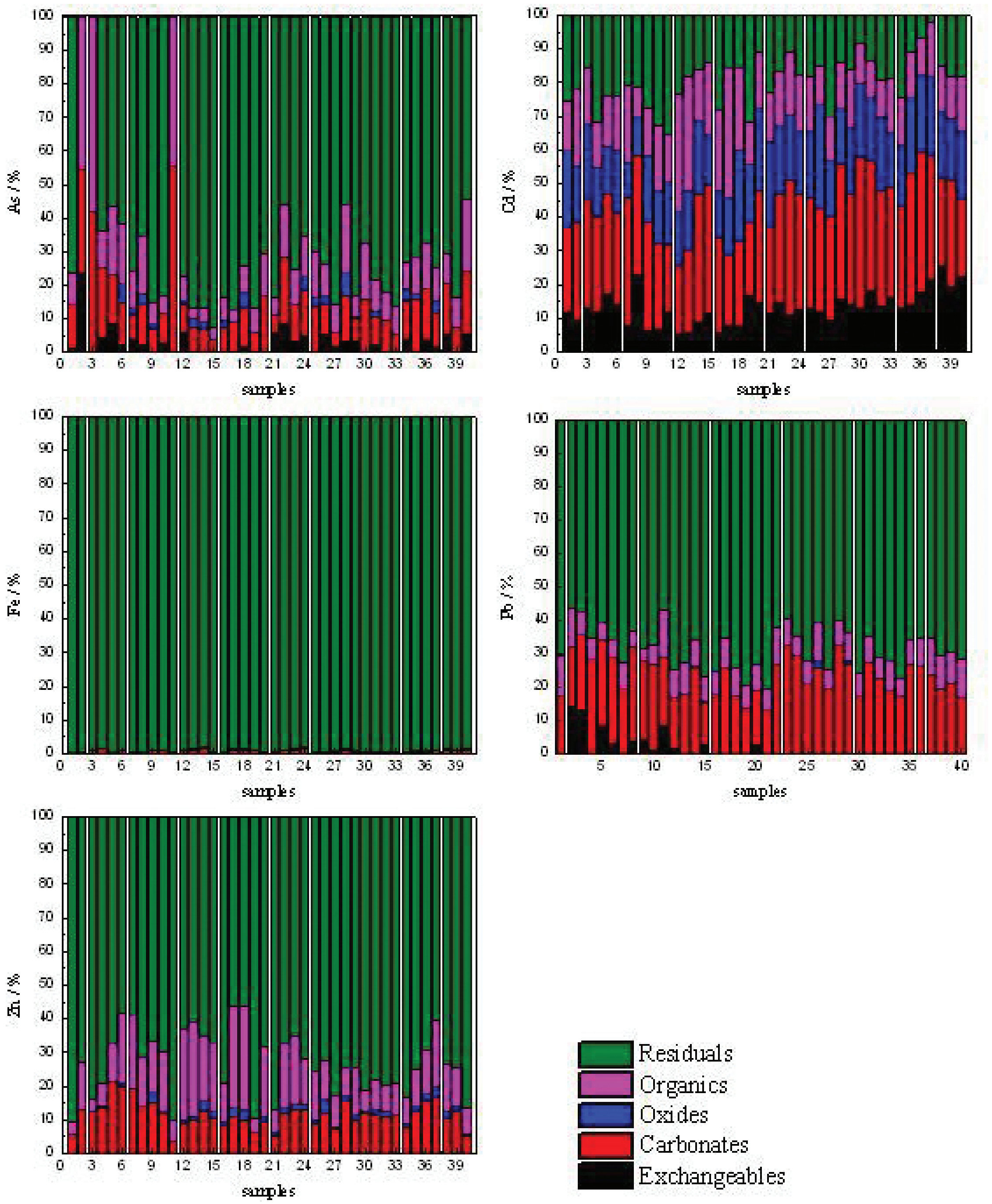

Fig. 9. Percentages of metals in different fractions 148 × 180 mm (96 × 96 DPI).

The heavy metals were mostly in the fraction of residuals, which meant the elements were stable and would not be released into liquid with minor changes of the condition. For Cd, however, it is a different story. Carbonates were the maximum content, which was unstable and would be released into liquid with a small change of pH [24]. According to the toxicity of the metals and the Chinese national guidelines, Cd and As are the most risky for environment and aquatic organisms.

3.3. Ecological risk assessment

The results (Fig. 9) showed that the amounts of heavy metals extracted from each fraction varied widely. Generally, the heavy metals mostly exist in the fraction of residuals in the sediments of Longjiang River. The average percentage of residual fraction of Fe was almost 98.95%, which meant Fe could easily complex with other matters so as to keep stable and would not change with changing condition. Although Fe had the highest concentration, its toxicity was the least.

The average percentages of residual form of Zn, Pb and As were 73.16%, 68.11% and 69.41%, respectively, indicating that the proportion of Zn, Pb and As in sediments were mostly stable, but part of them still may be released from oxides if conditions became acidic. The most unstable element in the river sediments samples was Cd. The biggest proportion of Cd (31.24%) was in the fraction of carbonate, and the least proportion (13.15%) was in the fraction of exchangeable. The concentrations of Cd in the fraction of oxide, organic, residual fraction were 19.18%, 17.15% and 19.27%, respectively, indicating that Cd might be released into water body once the environment changed. The potential mobility (the phase except residual) was presented as follows: Cd-80.73% > Pb-31.89% > As-30.59% > Zn-26.84% > Fe-1.05%.

3.4. Statistical analysis

According to the Spearman correlation analysis, there were significant relationships between As, Cd, Pb and Zn (Table 4). The significant correlation indicated that the heavy metals had common sources and similar behaviors during transport.

Table 5 showed loadings of metals on the principal components with the cumulative percentages in each case. These two factors/components accounted for approximately 88.9% of the total variance. These two factors contributed in the largest difference to the overall variance, 65.21% for the first factor and 23.69% for the second. In terms of five kinds of metal concentrations, the factor scores for all sediments samples were presented. The cumulative values were over 85%. Factor 1 was heavily dominated by Pb and Zn, then by Cd and Fe, and As to a lesser extent. All the elements measured had a positive loading on Factor 1. Fe contributed the most

Table 4
Correlation between heavy metals concentrations in sediment

	As	Cd	Fe	Pb	Zn
As	1	***0.762***	0.204	***0.677***	***0.733***
Cd		1	0.088	***0.71***	***0.856***
Fe			1	0.24	0.327
Pb				1	***0.866***
Zn					1

Bold italic values are significant at $p < 0.1$.

Table 5
PCA result of the unstable phases

Metals	Principal component		Communalities
	1	2	
Pb	0.93	0.171	0.894
Zn	0.948	0.178	0.93
Cd	0.812	–0.463	0.874
Fe	0.238	0.933	0.927
As	0.884	–0.196	0.82
Eigenvalue	3.261	1.185	
Cumulative %	65.21	88.9	

Table 6
The assessed results of PCA and I_{geo} index

Sample	PCA	I_{geo}				
		As	Cd	Fe	Pb	Zn
1	–0.19	–1.17	2.56	–0.65	0.12	–0.02
2	–1.16	–2.62	2.81	–1.77	–0.05	0.27
3	–0.97	–3.09	2.56	–1.44	0.36	0.15
4	–0.14	–1.65	3.24	–0.89	0.98	1.08
5	–0.76	–0.94	2.87	–1.68	1.41	0.13
6	–0.69	–0.99	3.18	–1.65	1.42	0.39
7	0.02	0.42	4.73	–2.2	1.87	1.67
8	0.45	0.12	5.12	–1.7	1.89	2.09
9	0.71	0.67	4.81	–1.5	2.24	1.86
10	0.66	–0.2	3.22	–1.02	2.37	1.9
11	–0.52	–3.28	3.03	–0.95	0.49	0.23
12	1.17	–0.63	3.64	–0.79	2.56	2.35
13	1.3	–0.21	3.76	–0.74	2.51	2.36
14	1.66	0.82	4.36	–1	2.81	2.41
15	2.05	0.97	4.67	–0.93	2.96	2.52
16	1.39	–0.05	4.06	–0.85	2.75	2.35
17	1.44	–0.27	4.1	–0.7	2.55	2.44
18	0.25	–0.89	3.59	–1.17	2.18	1.65
19	–0.11	–0.42	2.94	–0.83	0.84	0.27
20	–0.61	–1.39	3.19	–1.38	1.07	0.55
21	0.44	–0.3	3.72	–0.71	1.52	1.18
22	–0.71	–1.6	3.04	–1.36	0.89	0.27
23	–0.29	–0.73	3.5	–1.26	1.11	1.11
24	–0.24	–1.01	3.47	–1.17	1.29	1.07
25	–0.35	–0.89	3.41	–1.18	1.02	0.78
26	–0.15	–0.9	4.15	–1.07	0.94	0.97
27	0.7	–0.12	3.85	–0.7	1.65	1.68
28	–0.73	–1.65	3.58	–1.43	0.61	0.49
29	–0.25	–0.15	3.58	–1.16	0.8	0.67
30	–0.48	–1.09	3.25	–1.23	0.84	0.69
31	–0.31	–0.18	3.72	–1.26	0.8	0.71
32	–0.15	–0.11	3.94	–1.17	0.99	0.82
33	–0.37	–0.39	3.35	–1.26	1.05	0.59
34	0.2	–0.5	3.64	–0.93	1.57	1.28
35	–0.49	–0.65	3.43	–1.34	0.92	0.6
36	–0.51	–0.77	3.76	–1.37	0.78	0.7
37	–0.61	–0.66	2.7	–1.23	0.17	0.3
38	–0.33	–0.9	2.75	–0.91	0.38	0.37
39	–0.36	–0.81	3.05	–1.03	0.63	0.47
40	–0.9	–2.07	2.24	–1.22	–0.05	–0.58

for Factor 2 in positive influence. Meanwhile, As had less than Fe in negative loading, Cd, Zn, and Pb did less and less in absolute value.

The values of these two principal components, Z_1 and Z_2, could be presented by the concentrations of heavy metals in sediments (Eqs. (2) and (3)). A weighed sum of the value of Z_1 and Z_2 can be calculated with the eigenvalue of each metal so as to get the comprehensive contamination score of each metal (Eq. (4)).

$$Z_1 = 0.271C_{As} + 0.249C_{Cd} + 0.073C_{Fe} + 0.285C_{Pb} + 0.291C_{Zn} \tag{2}$$

$$Z_2 = -0.165C_{As} - 0.391C_{Cd} + 0.788C_{Fe} + 0.144C_{Pb} + 0.150C_{Zn} \tag{3}$$

$$\text{PCA} = Z_1 \times 3.261 / (3.261 + 1.185) + Z_2 \times 1.185 / (3.261 + 1.185) \tag{4}$$

where Z_1 and Z_2 are the values of first two principal components, and Ci, $i \in$ (As, Cd, Fe, Pb, Zn) are the contents of heavy metals in the sediments.

The assessment results of PCA and I_{geo} index are shown in Table 6. According to the values of I_{geo} index, Cd was the most contaminated element in the sediments samples of Longjiang River, with 40 sampling sites I_{geo} ranging from 2.24 to 5.12. The distribution of contamination levels of Fe was different from other metals in study sediments. Forty sampling sites were below value 0 for Fe, which indicated no pollution in sediments samples were found with Fe element. The results of PCA provided the comprehensive information of pollution levels of heavy metals. The highest value of PCA occurred in sample Site 15, which was the closest addition place of lime and aluminum chloride to the cadmium spill source.

4. Conclusion

The accident of cadmium spill had a serious impact on the distribution of chemical speciation of selected elements in the sediments. The heavy metals were precipitated by lime and poly aluminum chloride in unstable phases, which should be monitored regularly.

Chemical speciation showed the mobility of different elements. The most amounts of Fe were stable in residual fraction. The existing forms of parts of As, Pb and Zn would be converted with condition changes, which should also be monitored regularly. Large amounts of Cd, which were precipitated in the sediments caused by the cadmium spill and the following cleanup by chemical precipitation, had reached the alarming value with high potential hazardousness.

The method of PCA concerned itself with the concentration distribution of all elements in sediments, while I_{geo} was mainly determined by the high content in sediments. Combination of PCA and I_{geo} can determine both the comprehensive and single factor pollution levels of different elements, which is important for defining the extent of heavy metal pollution in the sediments.

Acknowledgments

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