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Assessment of Heavy Metals Pollution in Sediments from Aha Lake, China

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Abstract. Assessment of the pollution for the selected six heavy metals (Pb, Cu, Zn, Fe, Mn and Ni) in ten surface sediments sampled from Aha Lake in a dry season was made in the present investigation. Principal component analysis (PCA) was used to assess the sources of the heavy metals contamination and two components were extracted. Analysis of the lake characteristics and point source pollution revealed that the discharge of industrial effluent and coal mining wastewater were the possible sources of these heavy metals contamination. Based on the speciation characteristics of heavy metals in sediments, the method ratio of secondary phase to primary phase (RSP) was applied to evaluate the loadings and the bioavailability of these heavy metals. The RSP evaluation exhibited that Pb, Zn, Fe, Mn and Ni were mainly associated with Fe-Mn oxides besides residual phase, while Cu mainly existed in organic phase and residual phase. In summary, the potential risk posed to the lake caused by the heavy metals was high and descended in the order of Mn > Ni > Zn > Pb > Cu > Fe.

Introduction

As a sink and reservoir for a wide variety of environmental contaminants, sediments provide a considerable amount of information, including natural environment of basin, human activities, and evolvement of lakes, etc. Thus, anthropic impact on lakes can be assessed by studying their sediments. Changes in environmental conditions determine the speciation transformation of heavy metals and their distribution between the solid and liquid phases [1-3]. This can cause a gradual accumulation of heavy metals in superficial sediment and their release into the water column, thereby affecting chemical composition of overlying water, and even leading to secondary pollution in lakes [4,5]. Hitherto, several methods have been developed to evaluate heavy metals contamination in sediments, such as geoaccumulation index [6], sediment enrichment factors [7], and potential ecological risk index [8]. These evaluation methods have their own characteristics and applicabilities, however they also have their own disadvantages. Since geoaccumulation index and sediment enrichment factors do not reflect the sources and bioavailability of heavy metals and potential ecological risk index does not reflect the sources of heavy metals, the method ratio of secondary phase to primary phase (RSP) is better for sediments from the same source in a small region. Principal component analysis (PCA), a multivariate statistical analysis, can reduce a raw data set consisting of many variables to a smaller set of derived variables having the statistically desirable properties of orthogonality (i.e. the derived variables are uncorrelated with each other). Loska and Wiechula applied PCA to analyze the possible origin of heavy metals in sediments from Rybnik Reservoir, and Li et al. also used this method to study heavy metals pollution around Jiaozhou Bay [9,10].

Aha Lake (E 106º37′- 106º40′, N 26º30′- 26º34′), a man-made reservoir, is located in a typical Guizhou Plateau karst area. In the catchment area of the lake, there are approximately 200 abandoned coal mines that are posing a severe threat to its water quality. A large volume of acidic mine drainage with high concentrations of heavy metals flows into the lake. In the recent years, as the government tighten regulations for drinking-water safety, 3-4 kt/year of lime has been added to Aha Lake for guaranteeing the indexes of iron and manganese. However, large quantities of mud has been produced due to the addition of lime in this lake, which has created a potential pollution threat to the water body [11]. During the recent decades, several studies have been carried out on the general pollution of heavy metals in the sediment of Aha Lake [11,12]. In the study by Qin et al. [11], chemical speciation of Pb, Cu, Zn, Fe, Mn and Ni in the surface sediments from Aha Lake in a dry season (Dec., 2008) were determined by the Tessier sequential extraction method. The results showed that the Tessier method had a better stability for heavy metals chemical speciation extraction.

The main objectives of this research were to investigate the possible sources of heavy metals with the PCA method based on the experimental data from the study by Qin et al.[11], and then the method ratio of secondary phase to primary phase (RSP) was applied to assess the loadings and bioavailability of these heavy metals, and finally to provide useful information for the lake restoration.

Materials and methods

The study area and analytical procedures for the determination of the chemical speciation and the total concentration of Pb, Cu, Ni, Zn, Fe, Mn and Ti in sediments were the same as the study by Qin et al. [11]. The ten sampling locations (Fig. 1) were Baiyan River, Huachong, Sha River, Ya River, Daba, Zhuchangba, Huxin, Lannigou, Caichong River and Youyu River. Generally except for residual phase (inactive species), exchangeable fraction, carbonate fraction, Fe-Mn oxides (reducible), organic material and sulfides (oxidizable) are all taken as active species and the concentrations of the heavy metals in residual fraction were determined similarly to analysis of the total concentrations in sediments.

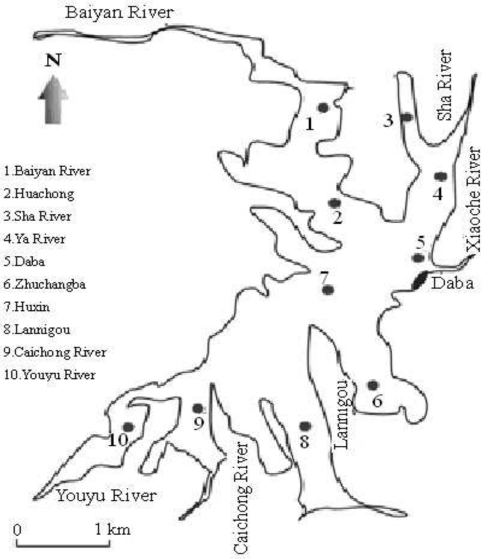

Fig. 1 Location of sampling stations [11]

Results and discussion

Results for total concentrations of heavy metals. Based on the concentrations of the six selected heavy metals (Pb, Fe, Cu, Zn, Mn and Ni) [11] in sediments from Aha Lake (Table 1), the Pearson correlation analysis was applied. As shown in Table 2, it is clear that Fe and Mn had some correlations with the other heavy metals, because Fe and Mn belong to redox-sensitive elements and their migration might influence other elements [2,3,13].

Table 1 Total concentrations of heavy metals in sediments from Aha Lake [11]

Items	Pb	Cu	Zn	Fe	Mn	Ni
Range (mg/kg)	42.7-98.6	40.3-104.0	198-305	39700-87500	1208-7964	86.3-184.0
Mean (mg/kg)	65.8	67.8	258	59276	4440	140
Variation coefficient (%)	28.8	28.3	13.6	27.8	45.9	24.2

Table 2 Pearson correlation matrix for concentrations of heavy metals in sediments from Aha Lake

	Pb	Cu	Zn	Ni	Fe	Mn
Pb	1					
Cu	-0.229	1				
Zn	0.053	0.649*	1			
Ni	-0.106	-0.241	-0.040	1		
Fe	-0.471	0.894**	0.640*	-0.062	1	
Mn	-0.181	0.151	0.308	0.791**	0.176	1

** Correlation is significant at the 0.01 level (2-tailed);
* Correlation is significant at the 0.05 level (2-tailed)

Principal component analysis of concentrations of heavy metals in sediments from Aha Lake. Previous researchers have conducted several studies on the relationship between concentrations of heavy metals in sediments and sediment grain size, showing that sediment grain size was an important factor affecting the distribution of heavy metals [14]. The content of SiO_2 in sediment of large size is high, playing a key role in the dilution of heavy metals in sediments. Therefore, when analyzing the pollution sources for Aha Lake by application of the concentrations of heavy metals, these concentrations should be normalized so as to reduce or eliminate the effect of granularity of the sediments on the distribution of heavy metals. It is well known that the geochemical property of Ti is inactive in exogenic geological processes, and its concentration is almost controlled by small terrigenous clastic silicate, consequently it is frequently used as a reference element [15]. Therefore, Ti was applied in this study to correct the concentrations of the heavy metals. The correction method is presented as follows: element correction concentration equals to the rario of element concentration in a sample to Ti concentration in the same sample. The distribution of the heavy metals in sediments, before and after being corrected by the use of Ti, is all shown in Fig. 2.

In order to explore factors affecting the distribution of heavy metals in Aha Lake, PCA was used to study the normalized values of their concentrations in sediments. Prior to the PCA, the normalized data should be standardized (i.e. by adding 1 to the value for the logarithm to base 10 of a nomalized concentration) in order to remove the influences resulting from different order of magnitude among variables. Barlett sphericity test was carried out as well. The results showed that the accompanied probability was 0.000, which was less than a significant level of 0.05, and correlation coefficients were not likely to be a unit matrix, indicating that there were correlations between variables. Therefore, the results presented above suggested that this set of data was suitable for a factor analysis. The results of the PCA (Table 3) demonstrated that there were two principal components which could explain 81.20% of the total variance, indicating that both components were able to reflect the most information of the original data. In order to more intuitively present the discrete degree of the normalized values of heavy metals in the PCA and reflect the characteristics of factors affecting the distribution of heavy metals in sediments from Aha Lake, a loading plot of the heavy metals in the space defined by two components were shown in Fig. 3.

It could be found from the PCA results that the six heavy metals presented high positive loading scores to component I. By the analysis of the surrounding environment of Aha Lake, it could be inferred that the heavy metals in sediments from Aha Lake were mainly from acidic effluent discharged by abandoned mines. It is thus implied that the factual significance of component I

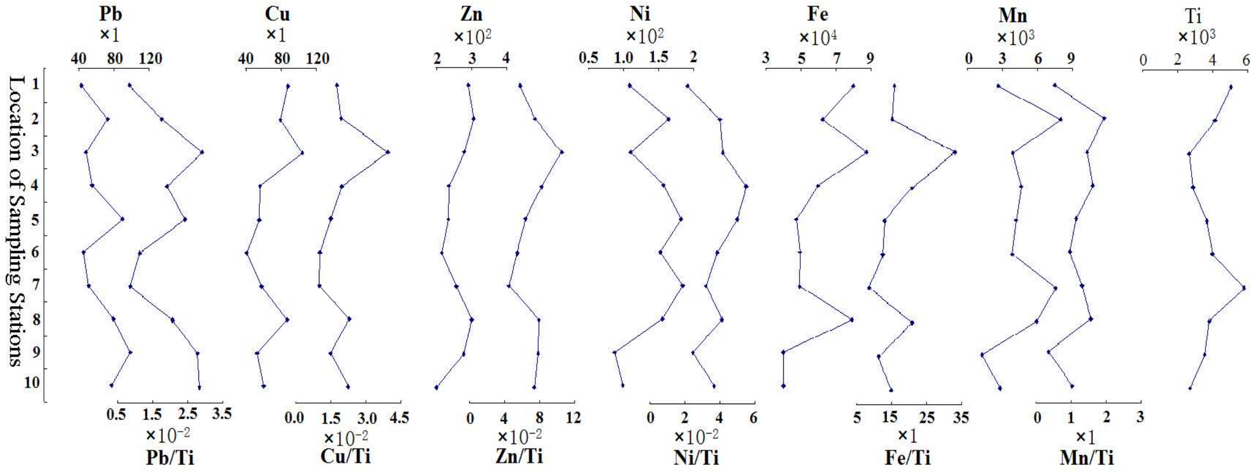

Fig. 2 Variation of the heavy metals concentration and thei corresponding concentration normalized by the concentration of element Ti in sediments from Aha Lake

might be associated with the impact of the mining effluent on the heavy metals distribution. However, Mn and Ni presented high positive loading scores to component II. It is known that there are large quantities of pollution to the lake discharged from e.g., Caijiaguan Town, Mawangmiao Town, the tyre company etc. According to the analysis, agricultural non-point sources and industrial pollution were also the important sources of pollution. Therefore, component II could be considered as the influence of industrial wastewater and farmland runoff on the distribution of heavy metals. As a result, the distributions of Pb, Cu, Zn and Fe were mainly affected by the mining drainage, while both Mn and Ni distributions were influenced by the mining drainage, industrial effluent and urban sewage.

Table 3 PCA results of heavy metals in sediments from Aha Lake

Heavy metals	Components	
	1[#] (57.13%)*	2[#] (24.07%)*
Pb	0.596	—
Cu	0.897	—
Zn	0.919	—
Ni	0.618	0.692
Fe	0.885	—
Mn	0.507	0.818

Note: *The percentage of the total variance

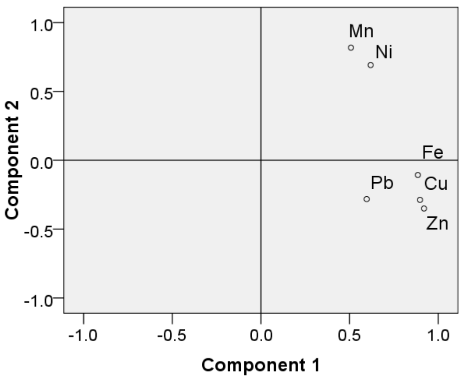

Fig. 3 Loading plots of heavy metals in the space defined by two components

Assessment of heavy metals pollution by RSP method. In this investigation, the RSP method was applied to assess the pollution and bioavailability of the six heavy metals for Aha Lake. Different forms of heavy metals possess different environmental behavior and bioavailability. The form of a heavy metal in sediment is defined as a certain combination or state between the heavy metal and other compositions in sediment (also known as geochemical phase). Based on the traditional geochemical concepts, Chen et al. proposed that primary minerals in these particles are defined as primary geochemical phase (primary phase), whereas weathering products (such as carbonate and manganese oxides, etc.) derived from primary mineral and external secondary substances (organic matter) are both defined as secondary geochemical phase (secondary phase) [16]. The ratio of the total percentage of a heavy metal in secondary phase to that in primary phase reflects its pollution source and level. The equation for the RSP method is Eq. 1:

$$K_{RSP} = M_{sec}/M_{prim} \tag{1}$$

where K_{RSP} stands for the distribution ratio (enrichment coefficient) of a heavy metal between the two phases of a sediment sample; M_{sec} for the concentration of this heavy metal in secondary phase of the same sediments sample; M_{prim} for the concentration of the heavy metal in primary phase of the same sediment sample.

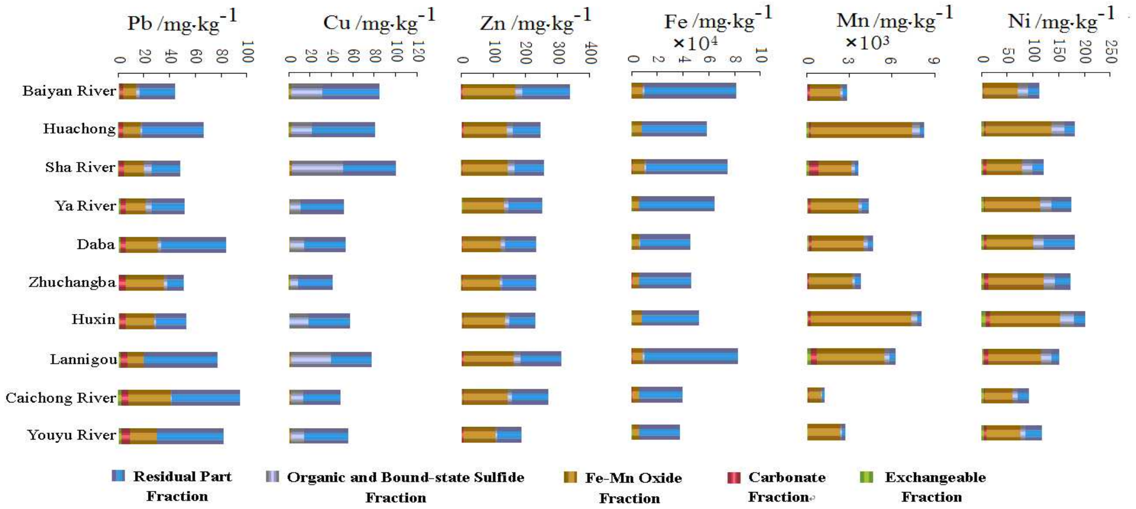

Fig. 4 Chemical forms of heavy metals in sediments from Aha Lake

The larger the ratio, the higher the pollution level. The result concerning the chemical speciation of Pb, Cu, Zn, Fe, Mn and Ni in the surface sediments from Aha Lake (illustrated in Fig. 4) were based on the study by Qin et. al. [11]. The ratios between concentrations of the six heavy metals in the two phases (K_{RSP}) of ten sediments from Aha Lake are shown in Fig. 5.

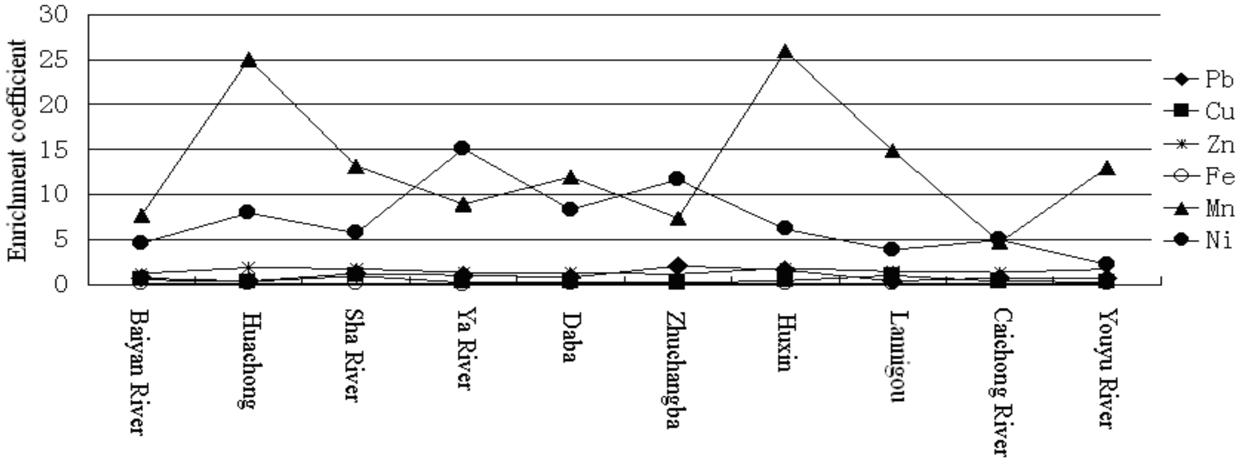

Fig. 5 Assessment of Pb, Cu, Zn, Fe, Mn and Ni with RSP method

It was found that the enrichment coefficient of Mn and Ni were the highest, indicating that both heavy metals pollution resulting from human activities were the most serious. This is consistent with the PCA results. Pb and Zn were mainly distributed in secondary phase, which indicated that there was some anthropic pollution for these two metals. The K_{RSP} of Cu and Fe changed slightly, with the most K_{RSP} values being less than 1.0, suggesting that the pollution of these elements resulting from anthropic activities was relatively low. The distribution ratio of the heavy metals (K_{RSP}) on average descended in the order of Mn > Ni > Zn > Pb > Cu > Fe. The high enrichment coefficients of Mn and Ni should be casused by heavy metal loadings from the abandoned coal mines. In addition, Mn exhibited a strong migration in contrast to some other elements. Hence, with a fresh runoff, Mn deposited largely in the area where there existed a slow water flow. These might be the reason why the enrichment coefficient of Mn was high in some regions of the lake. According to the distribution ratios for the ten different sampling locations, most contaminated sites were Huachong and Huxin, while areas with a lighter pollution degree were Baiyan River and Caichong River.

Conclusions

In principal component analysis (PCA), two components were extracted, accounting for more than 80% of the total variance. Analysis of the lake characteristics and point source pollution revealed that the discharge of industrial effluent and coal mining drainage were the possible sources of the heavy metals contamination. In addition, the results from the RSP assessment showed that the enrichment coefficients of Mn and Ni were the largest, and both heavy metals pollution resulting from anthropic activities were the most serious. The enrichment coefficients (K_{RSP})of the six heavy metals on average descended in the order of Mn > Ni > Zn > Pb > Cu > Fe.

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